



The Interaction between Surfactants and Montmorillonite and its Influence on the Properties of Organo-Montmorillonite in Oil-Based Drilling Fluids

Guanzheng Zhuang, Zepeng Zhang, Shanmao Peng, Jiahua Gao, Francisco Pereira, Maguy Jaber

► To cite this version:

Guanzheng Zhuang, Zepeng Zhang, Shanmao Peng, Jiahua Gao, Francisco Pereira, et al.. The Interaction between Surfactants and Montmorillonite and its Influence on the Properties of Organo-Montmorillonite in Oil-Based Drilling Fluids. *Clays and Clay Minerals*, 2019, 67 (3), pp.190-208. 10.1007/s42860-019-00017-0 . hal-02308616

HAL Id: hal-02308616

<https://hal.sorbonne-universite.fr/hal-02308616>

Submitted on 8 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

INTERACTION BETWEEN SURFACTANTS AND MONTMORILLONITE AND ITS INFLUENCE ON THE PROPERTIES OF ORGANO-MONTMORILLONITE IN OIL-BASED DRILLING FLUIDS

Guanzheng Zhuang¹, Zepeng Zhang^{1,*}, Shanmao Peng¹, Jiahua Gao¹, Francisco A.
R. Pereira^{2,3}, and Maguy Jaber^{2,*}.

¹ Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid
Wastes, National Laboratory of Mineral Materials, School of Materials Science and
Technology, China University of Geosciences, No. 29, Xueyuan Road, Haidian
District, Beijing 100083, PR China

² Sorbonne Université, Laboratoire d'Archéologie Moléculaire et Structurale (LAMS),
CNRS UMR8220, case courrier 225, UPMC 4 Pl. Jussieu, 75005 PARIS CEDEX 05,
France

³ Chemistry Department, Science and Technology Center, Universidade Estadual da
Paraíba, Campina Grande, Paraíba, Brazil.

Corresponding Author:

Zepeng Zhang

Address: School of materials science and technology, China University of
Geosciences, Beijing, China.

Tel: +86-010-8232-1845

Fax: +86-10-8232-2974

23 Email: unite508@163.com

24

25

26 Maguy Jaber

27 Address: Sorbonne Université, Laboratoire d'Archéologie Moléculaire et Structurale

28 (LAMS), CNRS UMR8220, case courrier 225, UPMC 4 Pl. Jussieu, 75005 PARIS

29 CEDEX 05, France

30 Tel: +33-(0)1-4427-6289

31 Fax: +33-(0)1-4427-8298

32 Email: maguy.jaber@upmc.fr

33

34 Received 13 May 2018; revised 6 February 2019; accepted 11 February 2019; Ms

35 1289

36

37

38

39

40

41

42

43

44

45

46 Abstract

47 The increasing demands of oil and gas and associated difficult drilling operations
48 require oil-based drilling fluids that possess excellent rheological properties and
49 thermal stability. The objective of the present work was to investigate the rheological
50 properties and thermal stability of organo-montmorillonite (OMnt) modified with
51 different surfactants and different loading levels in oil-based drilling fluids, as
52 revealed by the interaction between organic surfactants and montmorillonite. The
53 influence of the structural arrangement of surfactants on the thermal stability of
54 organo-montmorillonite (OMnt) in oil-based drilling fluids was also addressed. OMnt
55 samples were prepared in aqueous solution using surfactants possessing either a single
56 long alkyl chain and or two long alkyl chains. OMnt samples were characterized by
57 X-ray diffraction, high-resolution transmission electron microscopy, thermal analysis,
58 and X-ray photoelectron spectroscopy. Organic surfactants interacted with
59 montmorillonite by electrostatic attraction. The arrangements of organic surfactants
60 depended on the number of long alkyl chains and geometrical shape of organic
61 cations. In addition to the thermal stability of surfactants, intermolecular interaction
62 also improved the thermal stability of OMnt/oil fluids. A tight paraffin-type bilayer
63 arrangement contributed to the excellent rheological properties and thermal stability
64 of OMnt/oil fluids. The deterioration of rheological properties of OMnt/oil fluids at
65 temperatures up to 200°C was due mainly to the release of interlayer surfactants into
66 the oil.

Keywords: Arrangement, Oil-Based Muds, Organo-Clay, Rheological Properties, Thermal Behavior.

INTRODUCTION

Montmorillonite (Mnt) belongs to the general family of phyllosilicates. An ideal Mnt layer is composed of two continuous $[\text{SiO}_4]$ tetrahedral sheets (T) and an $[\text{AlO}_6]$ octahedral sheet (O). Thus, the structure of Mnt is described as a TOT type (Bergaya *et al.*, 2012). Due to isomorphic substitution, Mnt layers are often negatively charged. A negatively charged layer arises from the substitution of Mg^{2+} and other smaller charge cations for Al^{3+} in octahedral sites (Brigatti *et al.*, 2013; Jaber *et al.*, 2014). Consequently, cations such as Na^+ and Ca^{2+} present in the interlayer space counterbalance the deficit of positive charges. Significantly, these cations are exchangeable (Lagaly, 1981) with organic cations such as quaternary ammonium salts and quaternary phosphonium salts.

The preparation of organo-montmorillonite (OMnt) with cationic surfactants (Paiva *et al.*, 2008; He *et al.*, 2010; Lagaly *et al.*, 2013), non-ionic surfactants (Shen, 2001; Bertuoli *et al.*, 2014; Guégan *et al.*, 2015), anionic surfactants (Sarier *et al.*, 2010; Zhang *et al.*, 2010), and a mixture of different kinds of surfactants (Chen *et al.*, 2008; Gunawan *et al.*, 2010; Zhang *et al.*, 2013; Wu *et al.*, 2014) is reported commonly. OMnt prepared with cationic surfactants (often quaternary ammonium salts) are used widely in industrial and scientific applications. A substantial industry has been established for years to develop the utilization of OMnt in paint, adsorbents, greases, cosmetics, and nanocomposites, *etc.* (Jaber *et al.*, 2002; Paiva *et al.*, 2008; He

et al., 2010; Lee and Tiwari, 2012).

An important use of OMnt is as a rheological additive in oil-based drilling fluids (Caenn and Chillingar, 1996; Caenn *et al.*, 2011). Quaternary ammonium salts in which the alkyl chain has 12–22 carbon atoms are usually used to prepare OMnt for oil-based drilling fluids (Dino and Thompson, 2002; Frantz, 2014); for example, cetyl trimethyl ammonium (Zhuang *et al.*, 2016; Ratkievicius *et al.*, 2017), octadecyl trimethyl ammonium chloride (Zhuang *et al.*, 2017a), octadecyl benzyl dimethyl ammonium (Hermoso *et al.*, 2014, 2017), and dimethyl dioctadecyl ammonium chloride (Hermoso *et al.*, 2014, 2017). With the increasing demands of the oil and gas industry, drilling operations have been undertaken in many difficult wells, such as high-temperature, high-pressure, high-angle, and offshore wells. Oil-based drilling fluids are more popular due to their excellent lubricity, high rate of penetration, shale inhibition, wellbore stability, and good thermal stability (Caenn and Chillingar, 1996; Khodja *et al.*, 2010).

Previous studies identified that the rheological properties of oil-based drilling fluids are affected by the concentration and nature of OMnt (Hermoso *et al.*, 2014, 2015; Zhuang *et al.*, 2016, 2017a). The lipophilicity of surfactants contributes to the compatibility between oil and OMnt. Furthermore, for the same surfactant, more surfactant usually results in a larger basal spacing and further improves the swelling ability or even exfoliation. Exfoliation of OMnt in oil improves the rheological properties (Zhuang *et al.* 2017a,c). The dissolution of organic surfactants into oil might be a crucial reason for the deterioration of rheological properties at high

temperature. Such previous studies mostly reported the relationship between the structure and properties of OMnt and the properties of oil-based drilling fluids.

Some problems, however, are still unsettled: (i) how do organic surfactants remain stable on the exfoliated OMnt layers? (ii) what is the reason for the deterioration of rheological properties at high temperatures? and (iii) the influence of the arrangements of interlayer surfactants on the properties of oil-based drilling fluids is unresolved. The purpose of the present study was to try to resolve these problems, using two typical organic surfactants to modify Mnt, by determining the rheological properties and thermal stability of different OMnt samples in oil-based drilling fluids, thus revealing the interaction between organic surfactants and Mnt, and to measure the attendant structural changes in OMnt at the molecular scale.

MATERIALS AND METHODS

Materials

Mnt was obtained from the Kazuo Shuanglong Mining Co., Ltd, Liaoning Province, China. The mass percentage of montmorillonite included in the Mnt sample was calculated from X-ray diffraction (XRD) patterns (Chinese standard SY/T 5163-2010: Analysis method for clay minerals and ordinary non-clay minerals in sedimentary rocks by X-ray diffraction). This method was explained in a previous study (Zhuang *et al.*, 2018). The calculation follows the formula: $X_i = \left[\frac{I_i}{K_i} / \left(\sum \frac{I_i}{K_i} \right) \right] \times 100\%$, where X_i is the mass percent of phase i ; K_i is the intensity ratio of phase i to corundum with the mass ratio $i/\text{corundum} = 1:1$. For the current work, the K values of

minerals are listed in Table 1. The XRD pattern of Mnt (Figure 1) indicated the presence of montmorillonite (88%), quartz (7%), calcite (2%), albite (2%), and pyrite (1%) (Table 2). The cation exchange capacity (CEC) of the Mnt was 120 cmol₍₊₎/kg. Cationic surfactant octadecyl trimethyl ammonium chloride (C18) and dimethyldioctadecyl ammonium chloride (DC18) were purchased from Anhui Super Chemical Technology Co., Ltd, Hefei, Anhui, China. The ideal structures of these two organic cations (Figure 2) were optimized by ChemBio 3D using the molecular mechanics (MM2) minimization program (Bowen *et al.*, 1987). The purity of the surfactants was 99%. The base oil, No. 5 white oil, was obtained from the China National Petroleum Corporation.

Preparation of OMnt

OMnts were prepared in aqueous solution as reported previously (Zhuang *et al.*, 2017a): 100 g of Mnt was added to 1 L of deionized water and stirred for 0.5 h; surfactant was then added to the previous dispersion and the resulting dispersion stirred for 1 h. Finally, after centrifugation, drying at 60°C for 24 h, and milling and sieving with a 200-mesh sieve, OMnt was obtained. C18-modified OMnts were named C18-Mnt-1.0 and C18-Mnt-2.0, where 1.0 and 2.0 indicated that the amounts of C18 were equivalent to 1.0 CEC or 2.0 CEC of Mnt, respectively. Correspondingly, OMnts prepared with DC18 (0.5 CEC and 1.0 CEC of Mnt) were marked as DC18-Mnt-0.5 and DC18-Mnt-1.0.

Preparation of oil-based fluids

Twelve grams of OMnt was added to 400 mL white oil (concentration of 30 kg/m³) and blended for 20 min at 8000 rpm. A drilling fluid should be aged at different temperatures to model the real drilling operation. The blended fluids were placed in a rotary oven heated to 66°C, 150°C, 180°C, and 200°C in which they were aged for 16 h. All the operations followed the standards of the American Petroleum Institute (API), *i.e.* API SPEC 13A (Specification for Drilling Fluid Materials, 2010) and API RP 13B-2 (Recommended practice for field testing oil-based drilling fluids, 2014). The oil-based fluids were named following the template of OMnt/oil-temperature. For example, C18-Mnt-1.0/oil-66 was prepared by C18-Mnt-1.0 and white oil aged at 66°C.

Characterization

The XRD analysis was conducted using a Bruker D8 Advance X-ray powder diffractometer (Germany), using Cu K α radiation at 40 kV and 40 mA and a scan speed of 0.05 s per step (step size of 0.02°). The XRD data points covered the range 1.5° to 70°2 θ . The transmission electron microscope (TEM) analysis was conducted using Tecnai G2 F20 TEM equipment (Hillsboro, Oregon, USA) and operated under the voltage of 200 kV. Thermogravimetry (TG) analysis was tested on a NETZSCH STA 449 F3 type DTA-TG instrument (Selb, Bavaria, Germany) from room temperature to 900°C in air, with a heating rate of 10°C/min. The X-ray photoelectron spectroscopy (XPS) analysis was carried out using a Thermo escalab 250Xi instrument (Waltham, Massachusetts, USA). Bombardment of the surface with X-rays (monochromated Al K α radiation, 1486.6 eV) resulted in the emission of

photoelectrons with element-specific binding energies (BE). Firstly, a survey scan in the energy range of 1350–0 eV was recorded at a resolution of 1 eV. Then, high-resolution O 1s, Si 2p, Al 2p, C 1s, and N 1s scans were obtained. The rheological properties (apparent viscosity (AV), plastic viscosity (PV), and yield point (YP)) of aged oil-based drilling fluids were determined at 20°C, using a FANN 35A viscometer (Qingdao HaiTongDa Special Purpose Instrument Co., Ltd., China). $AV = 1/2\theta_{600}$ (θ_{600} is the dial reading at 600 rpm, corresponding to a shear rate of 1021.8 s^{-1}). $PV = \theta_{600} - \theta_{300}$ and $YP = 1/2(\theta_{300} - PV)$. The dynamic rheological behavior of oil-based fluids was measured using a Thermo Scientific HAAKE Roto Visco 1 rotational viscometer (USA). The programmed measurement regime was: the shear rate increased linearly from 0 s^{-1} to 100 s^{-1} in 5 min (up step), and then decreased linearly from 100 s^{-1} to 0 s^{-1} in 5 min (down step).

RESULTS AND DISCUSSION

XRD of OMnt powders

The basal reflection of Mnt occurred at $7.05^\circ 2\theta$, corresponding to $d_{001} = 1.25 \text{ nm}$ (Figure 1). After organic modification, the basal spacing of OMnt increased (Figure 3), giving d_{001} values for C18-Mnt-1.0, C18-Mnt-2.0, DC18-Mnt-0.5, and DC18-Mnt-1.0 of 2.12 nm, 4.06 nm, 3.51 nm, and 3.68 nm, respectively. The d_{001} of C18-Mnt-2.0 is almost double the d_{001} of C18-Mnt-1.0. In the case of DC18-modified OMnt, however, the d_{001} of DC18-Mnt-1.0 increased by ~5% over DC18-Mnt-0.5. This phenomenon indicated that C18 and DC18 occupied very different structural arrangements in OMnt.

The (002) and (003) reflections emerged in the XRD patterns of C18-Mnt-2.0, DC18-Mnt-0.5, and DC18-Mnt-1.0, whereas no peaks can be referred to (002) and (003) reflections in the XRD pattern of C18-Mnt-1.0. The basal reflection intensity showed the sequence of DC18-Mnt-1.0 > C18-Mnt-2.0 > DC18-Mnt-0.5 > C18-Mnt-1.0. Thus, the order of the degree of layer stacking (along the *c* axis) follows DC18-Mnt-1.0 > C18-Mnt-2.0 > DC18-Mnt-0.5 > C18-Mnt-1.0. DC18 likely was arranged in a more ordered manner in the interlayer space than C18.

TEM analysis

High-resolution TEM images (Figure 4) gave information about the basal spacing and the thickness of platelets. The TEM images of raw Mnt showed tightly stacked aluminosilicate layers. The thickness of the platelets of raw Mnt was >50 nm and the lamellae contained >50 layers. The lamellae of OMnt were thicker than those of raw Mnt and contained fewer layers. For both C18- and DC18-modified OMnt, more surfactant led to thicker lamellae. The thickness of C18-Mnt-1.0 lamellae was a little larger than that of DC18-Mnt-0.5 lamellae, and the thicknesses of C18-Mnt-2.0 and DC18-Mnt-1.0 lamellae were similar. This fact indicates that 1.0 CEC DC18 and 2.0 CEC C18 resulted in similar effects on the thickness of OMnt lamellae.

The TEM images also revealed the basal spacing directly. The layers in C18-Mnt-1.0 were not arranged neatly and the basal spacing ranged from 1.44 to 1.79 nm. Ordered stacking of layers was observed in the TEM images of C18-Mnt-2.0, DC18-Mnt-0.5, and DC18-Mnt-1.0. DC18-modified OMnt samples were more likely

to exhibit an ordered arrangement of layers. More surfactant also led to ordered layer stacking. The basal spacing derived from the TEM images, however, was smaller than the results derived from XRD (Table 3). This phenomenon might be caused by the radiation damage from the high voltage (200 kV). The lattices of clay minerals are easily damaged by high voltage in high-resolution TEM (Kogure, 2013). Surfactants would degrade under high voltage, resulting in the decrease of basal spacing. Δd_{001} indicated the change of arrangement of the interlayer surfactants. C18-Mnt-2.0 exhibited the largest Δd_{001} value, demonstrating the dramatic re-organization of interlayer surfactants under high voltage. The similar Δd_{001} values of DC18-Mnt-0.5 and DC18-Mnt-1.0 suggested similar arrangements of interlayer surfactants in these two OMnt samples.

Thermal analysis

Mnt showed two steps of mass loss (Figure 5). The first step ($<150^{\circ}\text{C}$), corresponding to a mass loss of 6.8%, was attributed to the loss of the water molecules on the surface and in the interlayer space of Mnt (He *et al.*, 2005; Zhuang *et al.*, 2015). The second mass loss step ($500\text{--}745^{\circ}\text{C}$, mass loss of 6.3%) represented the dehydration of hydroxyl groups coordinated by the structural cations in tetrahedral and octahedral sites (Greene-Kelly, 1957; Hedley *et al.*, 2007). The organic surfactants completely decompose above 500°C . The onset temperatures (T_{onset}) corresponding to the thermal decomposition of C18 and DC18 were 202°C and 145°C , respectively, indicating that C18 is more thermally stable than DC18.

In summary, dehydration of adsorbed water (below 150°C), oxidation of organic surfactants (150°C to 430°C), continuous oxidation of organic surfactants (430°C to 650°C), and dehydration of hydroxyl groups (650°C to 800°C) can be observed in the TG and DTG curves of OMnt. The percentage water loss from C18-Mnt-1.0, C18-Mnt-2.0, DC18-Mnt-0.5, and DC18-Mnt-1.0 was 2.2%, 1.8%, 0.8%, and 0.0%, respectively. OMnt samples contained less water than Mnt. In addition, C18-modified OMnt samples contained more adsorbed water than DC18-modified OMnt samples. The main factors affecting the interlayer hydration of montmorillonite include: (i) hydration energy of the interlayer cations, (ii) polarization of the water molecules by interlayer cations, (iii) variation of the electrostatic surface potentials because of differences in layer charge locations, (iv) activity of water, and (v) size and morphology of the clay particles (Brigatti *et al.*, 2013). Although C18 and DC18 cations had the same positive charges with Na⁺ cations, the organic cations showed a larger size and lower polarity due to the alkyl chains. In addition, the hydrophobicity of organic cations could prevent the adsorption of water. DC18 cations exhibited a larger size and better hydrophobicity than C18 cations, resulting in less interlayer water in the DC18-modified OMnt.

The T_{onset} corresponding to the thermal decomposition of organic surfactants in OMnt samples revealed the thermal stability of the samples. The T_{onset} values of C18, C18-Mnt-1.0, and C18-Mnt-2.0 were 202°C, 185°C, and 175°C, respectively. The T_{onset} values of DC18, DC18-Mnt-0.5, and DC18-Mnt-1.0 were 145°C, 180°C, and 159°C, respectively. C18-modified OMnt, therefore, showed better thermal stability

than DC18-modified OMnt. For C18-modified OMnt, the T_{onset} value was lower than that of C18 because organic surfactants not only intercalated into the interlayer space, but also occupied the outer surface (He *et al.*, 2005; Hedley *et al.*, 2007; Zhu *et al.*, 2011). The interlayer surfactants were protected by the Mnt layers. However, the surfactants exposed on the external surface were more susceptible to thermal degradation without the protection of the Mnt interlayers. Evidently, surfactants were mostly intercalated in the interlayer space when the surfactant loading level was <1.0 CEC of Mnt. When more surfactant was used, more should have adsorbed on the external surface, resulting in the decrease of T_{onset} (Zhuang *et al.*, 2016). For DC18-modified OMnt, most of the surfactant was intercalated into the interlayer space due to the smaller amount of surfactant (≤ 1.0 CEC). Accordingly, DC18-Mnt exhibited better thermal stability than the pure surfactant.

XPS analysis

The XPS survey scans of Mnt (Figure 6) showed the presence of O, Si, Al, Mg, Fe, Na, and C in Mnt. The presence of C in Mnt was assigned to calcite. After surfactant modification, the signals of N and Cl emerged in the spectra of OMnt samples. In addition, the intensity of the C 1s signal in OMnt was much greater than that in Mnt, demonstrating the adsorption and intercalation of organic surfactants. The signals of Cl 2s and Cl 2p in C18-Mnt-2.0 were more intense than those in other OMnt samples. This phenomenon indicated that more Cl^- ions are included in C18-Mnt-2.0, because the excess surfactant (more than 1.0 CEC of Mnt) cannot

intercalate into the interlayer space *via* cation exchange but remains neutral as an ion pair with Cl^- (He *et al.*, 2007).

Oxygen is the element most exposed on the surface of Mnt and TOT layers. Interaction between Mnt and surfactants should, therefore, first affect the binding energy of O. The binding energy of O 1s in Mnt was 532.5 eV (Figure 7), representing oxygen in Si-O(H) and Al(Mg, Fe)-O(H) groups. Compared with Mnt, the binding energy of O 1s in OMnt samples was smaller, indicating greater electron density around O atoms in OMnt. The high-resolution XPS scans of Si 2p (Figure 8) and Al 2p (Figure 9) also showed a decrease in binding energy, suggesting that the $[\text{SiO}_4]$ tetrahedra and $[\text{Al}(\text{Mg, Fe})\text{O}_6]$ octahedra, as a whole, exhibited higher electron densities after organic modification.

The C 1s spectra (Figure 10) of surfactants can be distinguished as two parts: C-C groups corresponding to a binding energy of 284.8 eV and C-N groups corresponding to 285.9 eV (C18) and 286.0 eV (DC18) (He *et al.*, 2007; Schampera *et al.*, 2015).

The binding energy of C 1s involving C-C groups maintained a constant value of 284.8 eV after organic modification, indicating no interaction involving the long alkyl chains. The binding energy of C 1s spectra involving C-N groups, however, shifted to larger values, demonstrating the decline of electron density around C atoms connecting with N. From the high-resolution XPS spectra of N 1s (Figure 11) in organic surfactants, the binding energy of N 1s was 402.1 eV. However, the binding energy of N 1s in OMnt increased slightly, demonstrating a decrease of electron density around N. The decrease of binding energies of N 1s and C 1s in the C-N

groups proved that the reduction of electron density occurs only in the polar heads of surfactants, without the long alkyl chains.

From the high-resolution XPS spectra, the interaction between Mnt and organic surfactants occurred between the TOT layers of Mnt and polar heads of surfactants. TOT layers were electron acceptors and the polar heads of organic surfactants were electron donors. The shift of the binding energy (ΔBE) (Table 4) value of O 1s was in the range of -1.2 to -1.0 eV. The ΔBE value of C 1s (C-N) was between 0.3 and 0.5 eV and that of N 1s was in the range 0.1 – 0.3 eV. Two conclusions can be drawn from the XPS results: (i) no new signals emerged in the XPS spectra, except for small changes in binding energy; (ii) compared with Mnt and surfactants, the binding energy of Mnt elements (O 1s, Si 2p and Al 2p) in OMnt decreased while the surfactant elements (C 1s and N 1s) in OMnt increased. Considering the negatively charged Mnt layers and organic cations, the XPS results demonstrate electrostatic attraction between the TOT layers and the polar heads of surfactants, without chemical bonds. The binding energy of O 1s in C18-Mnt-2.0 showed the smallest shift because extra surfactants intercalate into the interlayer space in the form of ion pairs (Cl^- anions and C18 cations). DC18-modified OMnt samples showed smaller ΔBE values than C18-modified OMnt samples, due to the conjugated effect of two long alkyl chains.

Arrangements and interactions of interlayer surfactants

Electrostatic attraction between Mnt and the polar heads of surfactants is affected

only by the quantity of electricity. Thus, electrostatic attraction is irrelevant to the molecular size or conformation. Previous reports revealed that OMnt modified with different surfactants exhibited different properties and thermal stability. Hence, the interaction between organic surfactants should be considered. C18 cations, having a single long alkyl chain, can be considered as having a 'linear shape' and DC18 cations can be regarded as being 'V-shaped' due to its two long alkyl chains (Figure 1). Interlayer surfactants arrange themselves as lateral-monolayer, lateral-bilayer, pseudo-trimolecular layer, paraffin-type monolayer. or paraffin-type bilayer (Vaia *et al.*, 1994; Lagaly *et al.*, 2013). The arrangements of interlayer surfactants are influenced by the loading level, conformation of surfactants, the length of the alkyl chain, and even the charge of Mnt. Short-chain alkylammonium cations are arranged in monolayers and longer chain alkylammonium ions in bilayers with the alkyl chain axes parallel to the silicate layers (Lagaly *et al.*, 2013); a pseudo-trimolecular arrangement is often observed with highly charged smectites and/or long surfactant cations. The periodicity along the *c* axis of Mnt (without cations and water) is 0.96 nm (Brigatti *et al.*, 2013). Considering the size of the C18 cation (Figure 1), C18-modified OMnts ideally exhibit a basal spacing of 1.33 nm with a monolayer arrangement, 1.73 nm with a bilayer arrangement, and 2.19 nm with a pseudo-trimolecular arrangement. Lagaly *et al.* (2013) concluded that the monolayer arrangement had a basal spacing of 1.4 nm, the bilayer 1.8 nm, and the pseudo-trimolecular arrangement 2.2 nm. Thus, the basal spacing (2.12 nm) of C18-Mnt-1.0 suggests that C18 molecules were arranged as a pseudo-trimolecular

layer (Figure 12). The positive heads of C18 were attached on the silicate layers, whereas the alkyl chains assumed a trimolecular arrangement by the formation of kinks. The pseudo-trimolecular arrangement of C18 cannot result in ordered arrangements of C18 cations in the interlayer space. In addition, the octadecyl chains could kink by formation of gauche bonds at different C atoms (Lagaly, 1976). Hence, the arrangement of C18 molecules was not sufficiently homogeneous to form very ordered stacks of layers. Only the low-intensity (001) reflection, therefore, emerged in the XRD patterns of C18-Mnt-1.0; the TEM image also testified to the non-uniform basal spacing. With the increase of loading level or alkyl chain length, organic cations tended to be arranged as a paraffin-type in a tilted to vertical arrangement (Lagaly, 1986). Based on the basal spacing of 4.06 nm, C18-Mnt-2.0 nm is proposed to be arranged as a tilted paraffin-type bilayer (Figure 12). The tilting angle, θ , is correlated positively with the amount of intercalated organic surfactants. In the case of C18-Mnt-2.0, θ is 52°. 1.0 CEC organic cations were assumed to exchange all the inorganic cations and occupy all the negative sites. The extra 1.0 CEC surfactants cannot intercalate into the interlayers completely because all of the exchangeable sites had been occupied. They should be adsorbed in the form of ion pairs (with anions). More surfactant molecules resulted in a tight arrangement, which made every single surfactant molecule hard to move. Consequently, C18-Mnt-2.0 showed a more ordered structure and displayed (002) and (003) reflections.

Quaternary alkylammonium ions with two or more long alkyl chains often form paraffin-type arrangements in the interlayer space of smectites (Lagaly *et al.*, 2013).

DC18 has two long octadecyl chains. Considering the size of the DC18 and the basal spacing of OMnt, DC18 molecules in the interlayer space of DC18-Mnt-0.5 and DC18-Mnt-1.0 must arrange themselves in the form of a paraffin-type bilayer (Figure 12). The angle between the two octadecyl chains varied with the loading level. The most stable conformation of DC18 corresponded to an angle of $\sim 118.9^\circ$. This angle, however, must gradually reduce in order to accommodate more DC18 cations, *i.e.* $\alpha > \varphi > \gamma$. Finally, an almost parallel orientation of the chains was attained by formation of gauche bonds near the ammonium group. The conformation of DC18 cations allowed a denser packing of these surfactants in mono- and bimolecular films (Favre and Lagaly, 1991). This intensive arrangement with a strong interaction between DC18 cations bound individual cations together.

Rheological properties of OMnt in oil

Drilling fluids are often evaluated using the Bingham plastic flow model and are often required to work in high-temperature conditions with low viscosity. Generally, AV is used as the effective viscosity to evaluate the viscosity of drilling fluids. PV is not expected to be too high, because extremely high PV would make starting to drill difficult. The rheological properties of OMnt/oil drilling fluids (AV, PV, and YP) vary with different temperatures of ageing (Table 5). A commercial OMnt (DG-Mnt), as used by Mud Service Company, Bohai Drilling Engineering Co. Ltd, was used as a reference. DG-Mnt/oil, C18-Mnt-1.0/oil, and DC18-Mnt-0.5/oil fluids all showed quite low viscosities and yield points. Their yield points were zero or very close to

397 zero, indicating these OMnt/oil fluids possessed no gel strength. Although the values
398 of AV, PV, and YP were stable, the thermal stabilities of DG-Mnt/oil, C18-Mnt-1.0/oil,
399 and DC18-Mnt-0.5/oil fluids were meaningless because of their poor rheological
400 properties. Compared to the rheological properties of DG-Mnt/oil, C18-Mnt-1.0/oil,
401 and DC18-Mnt-0.5/oil fluids, the rheological properties of C18-Mnt-2.0/oil and
402 DC18-Mnt-1.0/oil fluids were dramatically increased. This result demonstrates that
403 more surfactants lead to better rheological properties. C18-Mnt-2.0 showed bigger
404 d_{001} than DC18-Mnt-1.0; however, DC18-Mnt-1.0/oil fluids presented better
405 rheological properties than C18-Mnt-2.0/oil fluids. This phenomenon testifies that a
406 bigger basal spacing does not necessarily result in better rheological properties. The
407 rheological properties of OMnt in oil-based drilling fluids should not be influenced
408 only by surfactant loading level and basal spacing, but also by the arrangements of
409 interlayer surfactants. The AV and YP of both C18-Mnt-2.0/oil and DC18-Mnt-1.0/oil
410 fluids firstly increased and finally decreased with rising temperature. For example, the
411 viscosity of C18-Mnt-2.0/oil fluid increased from 16.5 mPa s at 66°C to 31.0 mPa·s at
412 150°C, then decreased to 26.5 mPa s at 180°C and 24.0 mPa s at 200°C. The AV of
413 DC18-Mnt-1.0/oil fluid and the YP of C18-Mnt-2.0/oil and DC18-Mnt-1.0/oil fluids
414 are affected similarly. Viscosity and gel strength improved with increasing
415 temperature because higher temperatures promote the swelling and even exfoliation of
416 OMnt in oil (Zhuang *et al.*, 2017a, 2017c). Temperature increase above 180°C,
417 however, was harmful for rheological properties. Focusing on the rheological
418 properties of OMnt/oil fluids aged at 150 to 200°C, DC18-Mnt-1.0/oil fluid was more

stable than C18-Mnt-2.0/oil fluid. The AV of DC18-Mnt-1.0/oil fluid decreased from 47.0 mPa s to 40.0 mPa s and the YP decreased from 18.0 Pa to 15.0 Pa. But the AV of C18-Mnt-2.0/oil fluid decreased from 31.0 mPa s to 24.0 mPa s and the YP decreased from 15.0 Pa to 3.0 Pa.

The dynamic rheological curves of OMnt/oil fluids (Figure 13) revealed rheological behavior and thixotropy. The DG-Mnt/oil, C18-Mnt-1.0/oil, and DC18-Mnt-0.5/oil fluids showed non-linear curves and presented low shear stress, in agreement with the results in Table 5. The rheological curves of DG-Mnt/oil, C18-Mnt-1.0/oil, and DC18-Mnt-0.5/oil can be divided into two parts: (i) the Bingham plastic model (a line which does not cross the zero point) in the range of 20–100 s⁻¹; (ii) deviation from the Bingham plastic model to the zero point. DC18-Mnt-1.0/oil fluid exhibited greater shear stress than C18-Mnt-2.0/oil fluid. The shear stress of C18-Mnt-2.0/oil decreased dramatically from 150°C to 200°C. However, the rheological curve of DC18-Mnt-1.0/oil aged at 180°C nearly coincided with that of DC18-Mnt-1.0/oil aged at 150°C. When the temperature increased to 200°C, the shear stress decreased a little.

Thixotropy is another important rheological property. It is a reversible isothermal transformation of a colloidal sol to a gel. In drilling practice, low resistance (low viscosity) is expected for the bit to ensure a rapid drilling rate, while high viscosity is needed for carrying cuttings. Excellent thixotropy is, thus, a necessary property of an oil-based drilling fluid. The areas of thixotropic loops (Figure 13) were applied to evaluate thixotropy of OMnt/oil fluids. The areas were calculated by integration

(Table 6). Similarly with the viscosity results, DG-Mnt/oil, C18-Mnt-1.0/oil, and DC18-Mnt-0.5/oil fluids showed very small areas, indicating nearly no thixotropy of these fluids. The area of C18-Mnt-2.0/oil aged at 66°C is 2.61 Pa s⁻¹. It increased to 193.43 Pa s⁻¹ at 150°C, then decreased to 27.50 Pa s⁻¹ at 200°C, declining by 86% from the area at 150°C. The area of DC18-Mnt-1.0/oil aged at 66°C was 26.21 Pa s⁻¹ and then increased to 424.68 Pa s⁻¹, indicating that high temperature below 150°C promotes thixotropy. With the temperature rising to 200°C, the area decreased to 324.85 Pa s⁻¹ at 200°C, down by 19% from that at 150°C. This result demonstrated that the thixotropy of DC18-Mnt-1.0/oil fluid was more stable than that of C18-Mnt-2.0/oil fluid.

In conclusion, the rheological properties and thermal stability followed the order of DC18-Mnt-1.0/oil > C18-Mnt-2.0/oil > DC18-Mnt-0.5/oil ≈ C18-Mnt-2.0/oil. Two possible reasons for decrease of rheological properties at high temperatures can be proposed: (i) thermal decomposition of surfactants and (ii) dissolution of interlayer surfactants into oil. Based on the thermal analysis results, DC18-Mnt-1.0 started to decompose below 180°C (in air). But DC18-Mnt-1.0/oil fluid showed very stable rheological properties at 200°C, indicating the thermal stability of OMnt in oil was improved due to the lack of oxygen. Thus, the decline of other OMnt/oil fluids below 200°C was not caused by thermal decomposition. The only possibility is the dissolution of interlayer surfactants into oil at high temperature. The HLB values of C18 and DC18 are 14.9 and 6.8. DC18 showed more lipophilicity than C18. DC18-Mnt-1.0, however, led to more stable rheological properties than C18-Mnt-2.0,

indicating that the paraffin-type bilayer of DC18 in OMnt can resist high temperatures better than the paraffin-type bilayer of C18.

XRD of OMnt/oil gels

To reveal the relationship between the thermal stability of OMnt/oil fluids and the arrangement of surfactants in the interlayer space of OMnt, the structure of OMnt in oil must be known. The structural change of OMnt in oil can be determined by XRD of OMnt/oil gel (Figure 14). All the samples showed a wide and low-intensity reflection at $17^{\circ}2\theta$, which is assigned to the oil (Zhuang *et al.*, 2017b). Two reflections, corresponding to d values of 2.05–2.06 nm and 1.38–1.43 nm, emerged in the C18-Mnt-1.0/oil aged at 66°C, 150°C, and 180°C. The d values of these two reflections were smaller than the basal spacing of C18-Mnt-1.0 (2.12 nm), suggesting that the d_{001} of C18-Mnt-1.0 in oil was reduced. Thermal analysis results proved that C18-Mnt-1.0 was stable up to 180°C. Therefore, the decrease of basal spacing must be due to the surfactants dissolving in oil. These two reflections cannot be attributed to (001) and (002) reflections, because the d value of the second reflection is not half that of the first. The two reflections, therefore, represented different basal spacings, indicating that the interlayer surfactants dissolved into oil gradually. The surfactants on the surfaces and edges dissolved first, then the internal surfactants dissolved, resulting in two reflections. Finally, aged at 200°C, most of the surfactants in the interlayer space were lost, leading to one reflection with d value of 1.36 nm. This phenomenon also demonstrated that high temperature promoted the dissolution of

interlayer surfactants, possibly because high temperature facilitated the thermal motion of oil molecules and surfactant molecules. A similar phenomenon happened to DC18-Mnt-0.5/oil fluid. The shrinkage of basal spacings of C18-Mnt-1.0 and DC18-Mnt-0.5 in oil demonstrated that loose arrangements resulted in the easy loss of interlayer surfactants. The basal spacing of C18-Mnt-2.0 increased gradually as the temperature increased to 180°C. The basal spacing of C18-Mnt-2.0 in oil reached a maximum value of 4.33 nm when aged at 150°C, corresponding to the best rheological properties of C18-Mnt-2.0/oil fluid. Aged at 200°C, the basal spacing of C18-Mnt-2.0 in oil declined to 1.39 nm. Although C18 cations and molecules are arranged tightly, the interlayer C18 was still lost at high temperature because no strong interaction force exists among the surfactants.

DC18-Mnt-1.0/oil-66 showed a similar reflection to DC18-Mnt-1.0 powder, indicating that no swelling happened, and no surfactants were lost. Because of the tight arrangement of DC18 in OMnt, no extra space was available to accept oil molecules. Below $15^{\circ}2\theta$, no reflection is observed in the XRD patterns of DC18-Mnt/oil gels aged at high temperatures, while the (100) reflection remained. Thus, DC18-Mnt-1.0 was exfoliated in oil at high temperatures because of thermal motion and interaction among surfactants. Surfactants in the interlayer space were protected by silicate layers, resulting in stabilization. DC18 cations could still remain stably on the surface of exfoliated layers because the strong interaction between DC18 cations fixed them tightly on the nanolayers. Hence, tight arrangement and strong interaction are necessary for the stability of OMnt in oil based-drilling

507 fluids.

508

509 CONCLUSION

510 Based on the results and discussions above, several conclusions can be drawn.
511 Organic surfactants occupy the surface and interlayer space of Mnt by electrostatic
512 attraction. Interaction happens between the Mnt layers and polar heads of surfactants
513 only. Interaction between organic cations has a critical influence on the stability of
514 OMnt in oil. The style of arrangement of a surfactant with a single long alkyl chain
515 changed from a pseudo-trimolecular layer to a paraffin-type bilayer with the increase
516 of the surfactant's loading level. Surfactants with two long alkyl chains arranged as a
517 paraffin-type. Paraffin-type arrangements were more ordered than
518 pseudo-trimolecular layers. A paraffin-type bilayer arrangement of DC18 resulted in
519 more ordered layer stacking than the same arrangement of C18. Tight paraffin-type
520 bilayer arrangements generally led to excellent rheological properties and thermal
521 stability. Loose paraffin-type, pseudo-trimolecular layer and tilted bilayer
522 arrangements resulted in easy dissolution of interlayer organic cations into oil at high
523 temperature. A tight paraffin-type bilayer arrangement of DC18 led to exfoliation of
524 OMnt in oil at high temperatures, improving rheological properties. Organic cations
525 can remain stable in the interlayer space or even on the exfoliated Mnt layers because
526 of the strong interaction force among cations, in addition to the electrostatic attraction.
527 In conclusion, to improve the rheological properties and thermal stability of OMnt in
528 oil-based drilling fluids, more than 1.0 CEC surfactants with two or three long alkyl

529 chains are advised.

530

531 Acknowledgments

532 This work was supported financially by the Fundamental Research Funds for
533 Central Universities (China). The support provided by the China Scholarship Council
534 (CSC) during the visit of Guanzheng Zhuang (No. 201706400010) to Sorbonne
535 Université is acknowledged.

536

537 REFERENCES

538 Bergaya, F., Jaber, M., and Lambert, J.F. (2012) *Clays and clay minerals as layered*
539 *nanofillers for (bio)polymers*. Pp. 41-75. Springer London.

540 Bertuoli, P.T., Piazza, D., Scienza, L.C., and Zattera, A.J. (2014) Preparation and
541 characterization of montmorillonite modified with
542 3-aminopropyltriethoxysilane. *Applied Clay Science*, **87**, 46-51.

543 Bowen, J. P., Pathiaseril, A., Profeta Jr, S., and Allinger, N. L. (1987) New molecular
544 mechanics (MM2) parameters for ketones and aldehydes. *The Journal of*
545 *Organic Chemistry*, **52**(23), 5162-5166.

546 Brigatti, M.F., Galan, E., and Theng, B.K.G. (2013) Chapter 2 structures and
547 mineralogy of clay minerals. Pp. 21-81. In F. Bergaya, and G. Lagaly, Eds.
548 *Developments in clay science*, 5, Elsevier, Netherland.

549 Caenn, R. and Chillingar, G.V. (1996) Drilling fluids: State of the art. *Journal of*
550 *Petroleum Science and Engineering*, **14**, 221-230.

- 551 Caenn, R., Darley, H.C., and Gray, G.R. (2011) *Composition and properties of drilling*
 552 *and completion fluids*. Gulf professional publishing, Houston.
- 553 Chen, D., Zhu, J.X., Yuan, P., and Yang, S.J. (2008) Preparation and characterization of
 554 anion-cation surfactants modified montmorillonite. *Journal of Thermal*
 555 *Analysis and Calorimetry*, **94**, 841-848.
- 556
- 557 Dino, D. and Thompson, J. (2002). U.S. Patent No. 6,462,096. Washington, DC: U.S.
 558 Patent and Trademark Office.
- 559 Favre, H. and Lagaly, G. (1991) Organo-bentonites with quaternary alkylammonium
 560 ions. *Clay Minerals*, **26**, 19-32.
- 561 Frantz, E. B. (2014). U.S. Patent No. 0,011,712. Washington, DC: U.S. Patent and
 562 Trademark Office.
- 563 Greene-Kelly R. (1957) The montmorillonite minerals. In: Mackenzie RC, Editor. *The*
 564 *differential thermal investigation of clays*. London: Mineral Society, p 140-164.
- 565 Guégan, R., Giovanela, M., Warmont, F., and Motelica-Heino, M. (2015) Nonionic
 566 organoclay: A ‘swiss army knife’ for the adsorption of organic micro-pollutants?
 567 *Journal of Colloid and Interface Science*, **437**, 71-79.
- 568 Gunawan, N.S., Indraswati, N., Ju, Y.H., Soetaredjo, F.E., Ayucitra, A., and Ismadji, S.
 569 (2010) Bentonites modified with anionic and cationic surfactants for bleaching
 570 of crude palm oil. *Applied Clay Science*, **47**, 462-464.
- 571 He, H., Ding, Z., Zhu, J., Yuan, P., Xi, Y., Yang, D., and Frost, R.L. (2005) Thermal
 572 characterization of surfactant-modified montmorillonites. *Clays and Clay*

573 *Minerals*, **53**, s319.

574 He, H., Ma, Y., Zhu, J., Yuan, P., and Qing, Y. (2010) Organoclays prepared from
 575 montmorillonites with different cation exchange capacity and surfactant
 576 configuration. *Applied Clay Science*, **48**, 67-72.

577 He, H., Zhou, Q., Frost, R.L., Wood, B.J., Duong, L.V., and Klopogge, J.T. (2007) A
 578 x-ray photoelectron spectroscopy study of hdtmab distribution within
 579 organoclays. *Spectrochimica Acta Part A Molecular and Biomolecular*
 580 *Spectroscopy*, **66**, 1180-1188.

581 Hedley, C.B., Yuan, G., and Theng, B.K.G. (2007) Thermal analysis of
 582 montmorillonites modified with quaternary phosphonium and ammonium
 583 surfactants. *Applied Clay Science*, **35**, 180-188.

584 Hermoso, J., Martinez-Boza, F., and Gallegos, C. (2014) Influence of viscosity
 585 modifier nature and concentration on the viscous flow behavior of oil-based
 586 drilling fluids at high pressure. *Applied Clay Science*, **87**, 14-21.

587 Hermoso, J., Martinez-Boza, F., and Gallegos, C. (2015) Influence of aqueous phase
 588 volume fraction, organoclay concentration and pressure on invert-emulsion oil
 589 muds rheology. *Journal of Industrial and Engineering Chemistry*, **22**, 341-349.

590 Hermoso, J., Martínez-Boza, F. J., and Gallegos, C. (2017). Organoclay influence on
 591 high pressure-high temperature volumetric properties of oil-based drilling
 592 fluids. *Journal of Petroleum Science and Engineering*, **151**, 13-23.

593 Jaber, M., Georgelin, T., Bazzi, H., Costatorro, F., and Clodic, G. (2014) Selectivities in
 594 adsorption and peptidic condensation in the (arginine and glutamic

acid)/montmorillonite clay system. *Journal of Physical Chemistry C*, **118**,
25447-25455.

Jaber, M., Miehé-Brendle, J., and Dred, R.L. (2002) Mercaptopropyl al-mg
phyllosilicate: Synthesis and characterization by xrd, ir, and nmr. *Chemistry
Letters*, **80**, 954-955.

Khodja, M., Canselier, J.P., Bergaya, F., Fourar, K., Khodja, M., Cohaut, N., and
Benmounah, A. (2010) Shale problems and water-based drilling fluid
optimisation in the hassi messaoud algerian oil field. *Applied Clay Science*, **49**,
383-393.

Kogure, T. (2013) Chapter 2.9 - electron microscopy. Pp. 275-317. In F. Bergaya, and G.
Lagaly, Eds. *Developments in clay science*, 5, Elsevier, Netherlands.

Lagaly, G. (1976) Kink-block and gauche-block structures of bimolecular films.
Angewandte Chemie International Edition, **15**, 575-586.

Lagaly, G. (1981) Characterization of clays by organic compounds. *Clay minerals*,
16(1), 1-21.

Lagaly, G. (1986) Interaction of alkylamines with different types of layered compounds.
Solid State Ionics, **22**, 43-51.

Lagaly, G., Ogawa, M., and Dékány, I. (2013) Chapter 10.3 clay mineral–organic
interactions. Pp. 435-505. In F. Bergaya, G.B.K. Theng, and G. Lagaly, Eds.
Developments in clay science, 5, Elsevier.

Lee, S.M. and Tiwari, D. (2012) Organo and inorgano-organo-modified clays in the
remediation of aqueous solutions: An overview. *Applied Clay Science*, **s 59–60**,

617 84–102.

618 Paiva, L.B.D., Morales, A.R., and Díaz, F.R.V. (2008) Organoclays: Properties,
619 preparation and applications. *Applied Clay Science*, **42**, 8-24.

620 Ratkievicius, L. A., Da Cunha Filho, F. J. V., Neto, E. L. D. B., Santanna, V. C. (2017).
621 Modification of bentonite clay by a cationic surfactant to be used as a viscosity
622 enhancer in vegetable-oil-based drilling fluid. *Applied Clay Science*, **135**,
623 307-312.

624 Sarier, N., Onder, E., and Ersoy, S. (2010) The modification of na-montmorillonite by
625 salts of fatty acids: An easy intercalation process. *Colloids and Surfaces A
626 Physicochemical and Engineering Aspects*, **371**, 40-49.

627 Schampera, Solc, B., Woche, R., Mikutta, S.K., Dultz, R., Guggenberger, S., Tunega,
628 G., and D. (2015) Surface structure of organoclays as examined by x-ray
629 photoelectron spectroscopy and molecular dynamics simulations. *Clay
630 Minerals*, **50**, 353-367.

631 Shen, Y. H. (2001) Preparations of organobentonite using nonionic surfactants.
632 *Chemosphere*, **44**, 989-995.

633 Vaia, R.A., Teukolsky, R. K., and Giannelis, E.P. (1994) Interlayer structure and
634 molecular environment of alkylammonium layered silicates. *Chemistry of
635 Materials*, **6**, 1017-1022.

636 Wu, S., Zhang, Z., Wang, Y., Liao, L., and Zhang, J. (2014) Influence of
637 montmorillonites exchange capacity on the basal spacing of cation–anion
638 organo-montmorillonites. *Materials Research Bulletin*, **59**, 59–64.

639 Zhang, Z., Liao, L., and Xia, Z. (2010) Ultrasound-assisted preparation and
640 characterization of anionic surfactant modified montmorillonites. *Applied Clay*
641 *Science*, **50**, 576-581.

642 Zhang, Z., Zhang, J., Liao, L., and Xia, Z. (2013) Synergistic effect of cationic and
643 anionic surfactants for the modification of ca-montmorillonite. *Materials*
644 *Research Bulletin*, **48**, 1811-1816.

645 Zhu, J., Qing, Y., Wang, T., Zhu, R., Wei, J., Tao, Q., Yuan, P., and He, H. (2011)
646 Preparation and characterization of zwitterionic surfactant-modified
647 montmorillonites. *Journal of Colloid and Interface Science*, **360**, 386-392.

648 Zhuang, G., Gao, J., Chen, H., and Zhang, Z. (2018) A new one-step method for
649 physical purification and organic modification of sepiolite. *Applied Clay*
650 *Science*, **153**, 1-8.

651 Zhuang, G., Zhang, H., Wu, H., Zhang, Z., and Liao, L. (2017a) Influence of the
652 surfactants' nature on the structure and rheology of organo-montmorillonite in
653 oil-based drilling fluids. *Applied Clay Science*, **135**, 244-252.

654 Zhuang, G., Zhang, Z., Gao, J., Zhang, X., and Liao, L. (2017b) Influences of
655 surfactants on the structures and properties of organo-palygorskite in oil-based
656 drilling fluids. *Microporous and Mesoporous Materials*, **244**, 37-46.

657 Zhuang, G., Zhang, Z., Guo, J., Liao, L., and Zhao, J. (2015) A new ball milling method
658 to produce organo-montmorillonite from anionic and nonionic surfactants.
659 *Applied Clay Science*, **104**, 18-26.

660 Zhuang, G., Zhang, Z., Jaber, M., Gao, J., and Peng, S. (2017c) Comparative study on

661 the structures and properties of organo-montmorillonite and
 662 organo-palygorskite in oil-based drilling fluids. *Journal of Industrial and*
 663 *Engineering Chemistry*, **56**, 248-257.

664 Zhuang, G., Zhang, Z., Sun, J., and Liao, L. (2016) The structure and rheology of
 665 organo-montmorillonite in oil-based system aged under different temperatures.
 666 *Applied Clay Science*, **124**, 21-30.

667

668 FIGURE CAPTIONS:

669 Figure 1. XRD pattern of Mnt with the JCPDS cards of montmorillonite, quartz,
 670 calcite, albite, and pyrite.

671 Figure 2. Structural diagrams of organic cations with optimized geometrical shapes
 672 and molecular sizes.

673 Figure 3. XRD patterns of OMnt samples.

674 Figure 4. TEM images of Mnt and OMnt samples.

675 Figure 5. TG and corresponding DTG curves of Mnt, organic surfactants, and OMnt
 676 samples.

677 Figure 6. XPS survey scans of Mnt and OMnt samples.

678 Figure 7. O 1s high-resolution XPS spectra of Mnt and OMnt samples.

679 Figure 8. Si 2p high-resolution XPS spectra of Mnt and OMnt samples.

680 Figure 9. Al 2p high-resolution XPS spectra of Mnt and OMnt samples.

681 Figure 10. C 1s high-resolution XPS spectra of surfactants and OMnt samples.

682 Figure 11. N 1s high-resolution XPS spectra of surfactants and OMnt samples.

Figure 12. Schematic diagram of the different arrangements of surfactants in the interlayer space of OMnt.

Figure 13. Dynamic rheological curves of OMnt/oil fluids aged at 66°C, 150°C, 180°C, and 200°C.

Figure 14. XRD results for OMnt/oil gels aged at 66°C, 150°C, 180°C, and 200°C.

Tables:

Table 1. K-values of selected minerals.

Mineral	(<i>hkl</i>)	°2 θ	<i>d</i> value (nm)	K-value
Corundum	(104)	35.16	0.2550	1.00
Montmorillonite	(020)	19.80	0.4880	0.50
Quartz	(101)	26.65	0.3343	4.32
Calcite	(104)	29.42	0.3034	2.80
Albite	(002)	27.92	0.3193	1.80
Pyrite	(200)	33.00	0.2712	2.06

Table 2. A summary of the components in the Mnt sample.

Component	Montmorillonite	Quartz	Calcite	Albite	Pyrite
Mass (%)	88%	7%	2%	2%	1%

696 Table 3. Summary of basal spacings derived from XRD and TEM.

Sample	d_{001} (XRD)/nm	d_{001} (TEM)/nm	Δd_{001} /nm
C18-Mnt-1.0	2.12	1.44–1.79	0.33–0.68
C18-Mnt-2.0	4.06	1.87	2.19
DC18-Mnt-0.5	3.51	2.42	1.09
DC18-Mnt-1.0	3.68	2.53	1.15

697 Note: $\Delta d_{001} = d_{001} \text{ (XRD)} - d_{001} \text{ (TEM)}$

698

699 Table 4. Summary of Δ BE values.

Sample	Δ BE (eV)		
	O 1s	C 1s (C-N)	N 1s
C18-Mnt-1.0	- 1.2	0.5	0.3
C18-Mnt-2.0	- 1.0	0.4	0.3
DC18-Mnt-0.5	- 1.1	0.5	0.2
DC18-Mnt-1.0	- 1.2	0.3	0.1

700 Note: Δ BE (O 1s) = BE (O 1s, OMnt) – BE (O 1s, Mnt); Δ BE (C 1s) = BE (C 1s,

701 OMnt) – BE (C 1s, surfactant); and Δ BE (N 1s) = BE (N 1s, OMnt) – BE (N 1s,

702 surfactant).

703

704 Table 5. Rheological properties of OMnt/oil fluids aged at different temperatures.

Sample	AV (mPa·s)	PV (mPa·s)	YP (Pa)
--------	------------	------------	---------

	66°C	150°C	180°C	200°C	66°C	150°C	180°C	200°C	66°C	150°C	180°C	200°C
DG-Mnt	16.0	17.0	15.5	15.0	16.0	16.0	15.0	15.0	0.0	1.0	0.5	0.0
C18-Mnt-1.0/oil	14.5	15.0	15.0	14.0	14.5	14.5	14.5	14.0	0.0	0.5	0.5	0.0
C18-Mnt-2.0/oil	16.5	31.0	26.5	24.0	16.0	16.0	21.0	21.0	0.5	15.0	5.5	3.0
DC18-Mnt-0.5/oil	15.0	15.0	16.0	15.0	15.0	14.5	16.0	14.5	0.0	0.5	0.0	0.5
DC18-Mnt-1.0/oil	24.5	47.0	43.0	40.0	21.0	29.0	26.0	25.0	3.5	18.0	17.0	15.0

705

706

707 Table 6. Areas of thixotropic loops derived from Figure 13.

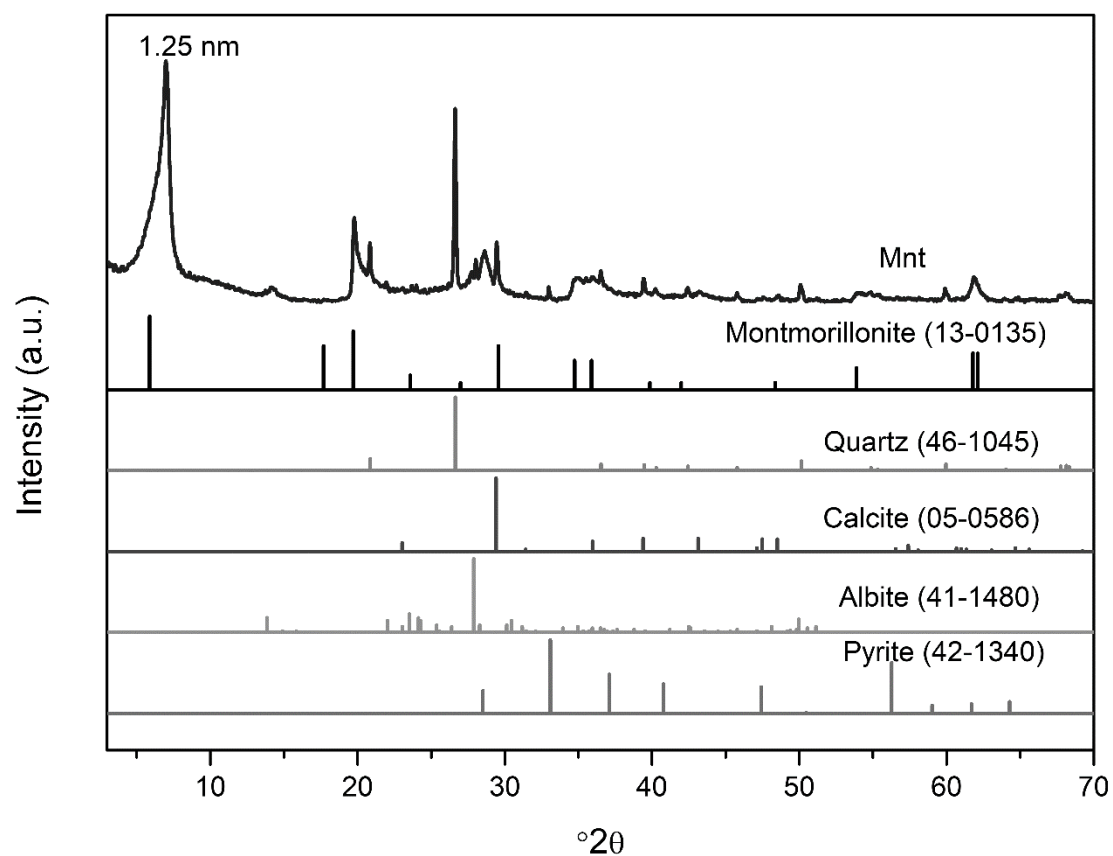
Sample	Areas of thixotropic loops (Pa·s ⁻¹)			
	66°C	150°C	180°C	200°C
DG-Mnt/oil	4.25	3.65	3.07	4.45
C18-Mnt-1.0/oil	1.62	1.64	1.52	1.45
C18-Mnt-2.0/oil	2.61	193.43	75.50	27.50
DC18-Mnt-0.5/oil	3.40	3.84	1.65	1.43
DC18-Mnt-1.0/oil	26.21	424.68	394.94	342.85

708

709

710 FIGURES:

711



712

713 Figure 1 XRD pattern of Mnt with the JCPDS cards of montmorillonite, quartz,

714 calcite, albite and pyrite.

715

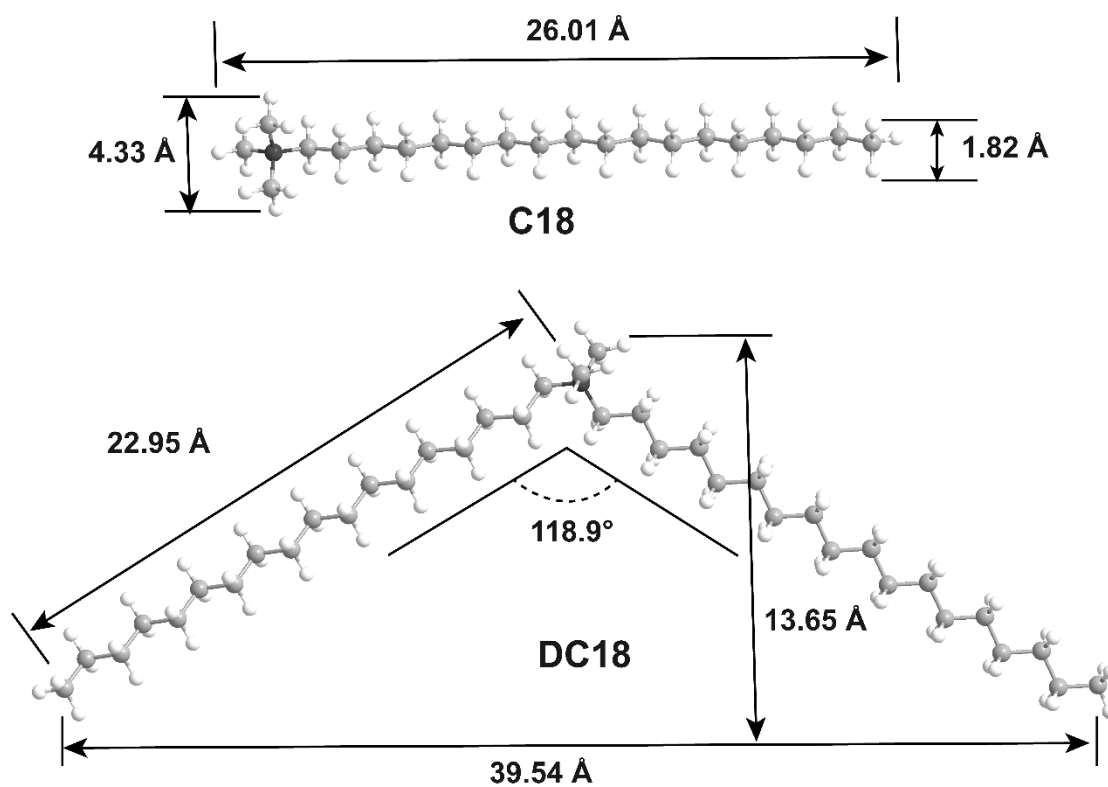


Figure 2 Structural diagrams of organic cations with the optimized geometrical shapes and molecular sizes.

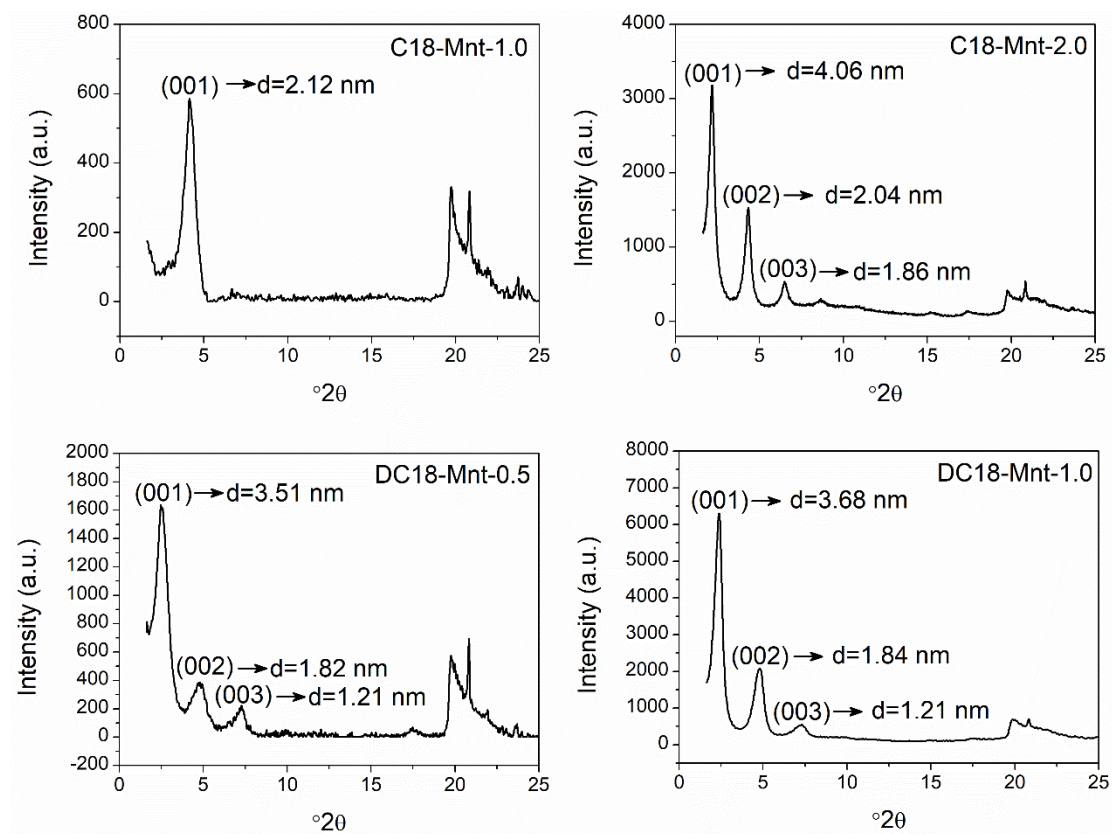


Figure 3 XRD patterns and OMnt samples.

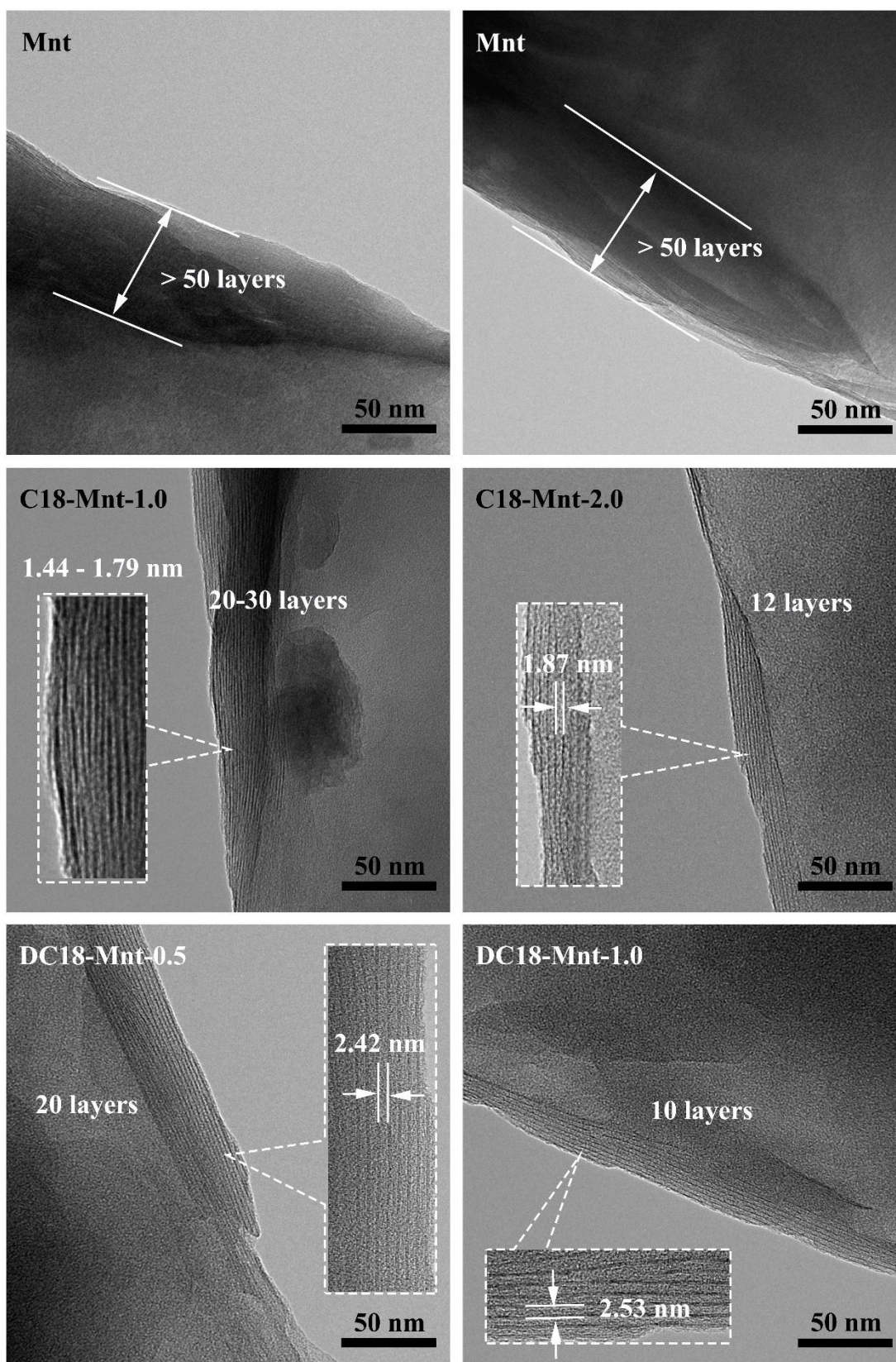


Figure 4 TEM images of Mnt and OMnt samples.

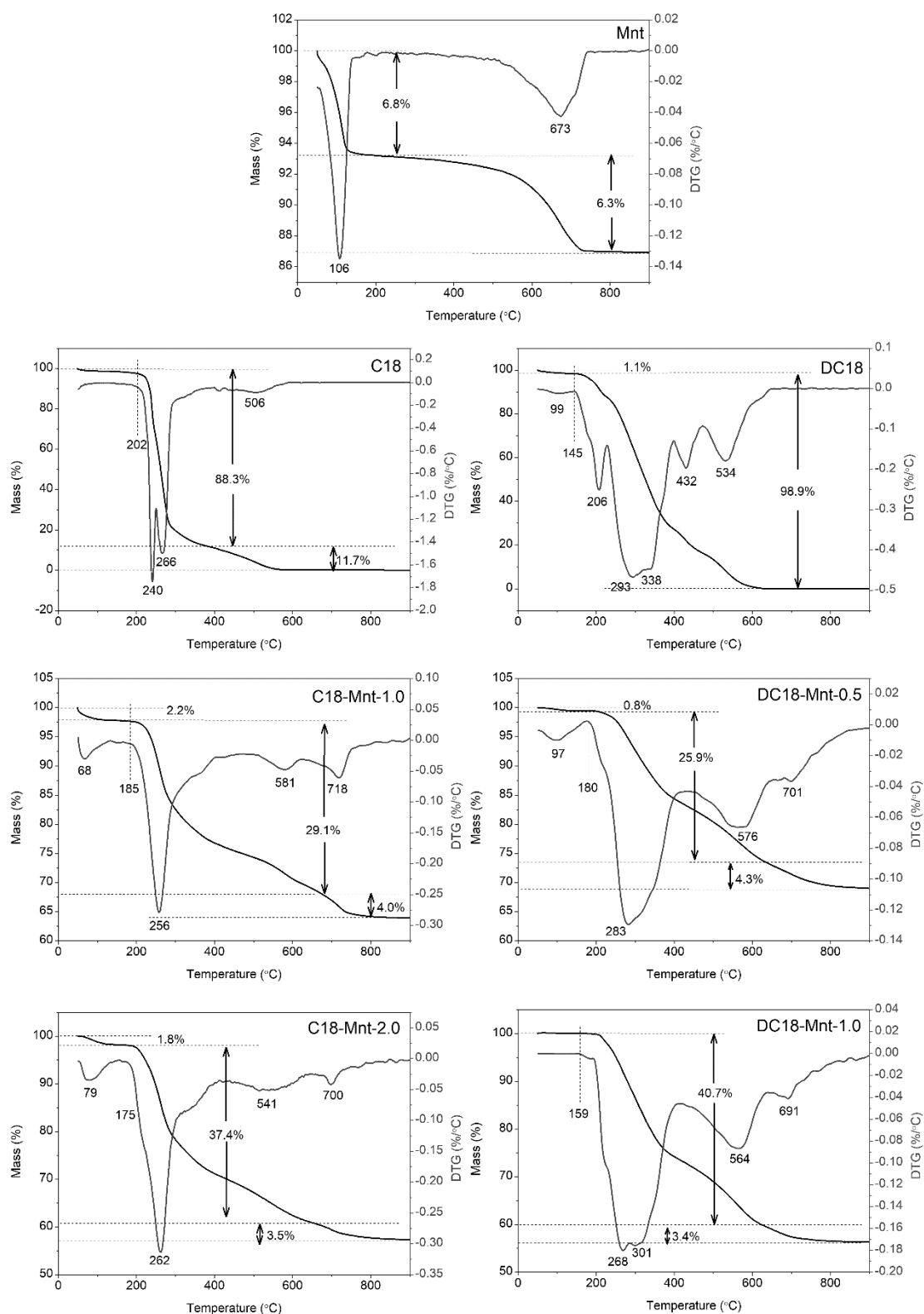


Figure 5 The TG and corresponding DTG curves of Mnt, organic surfactants, and OMnt samples.

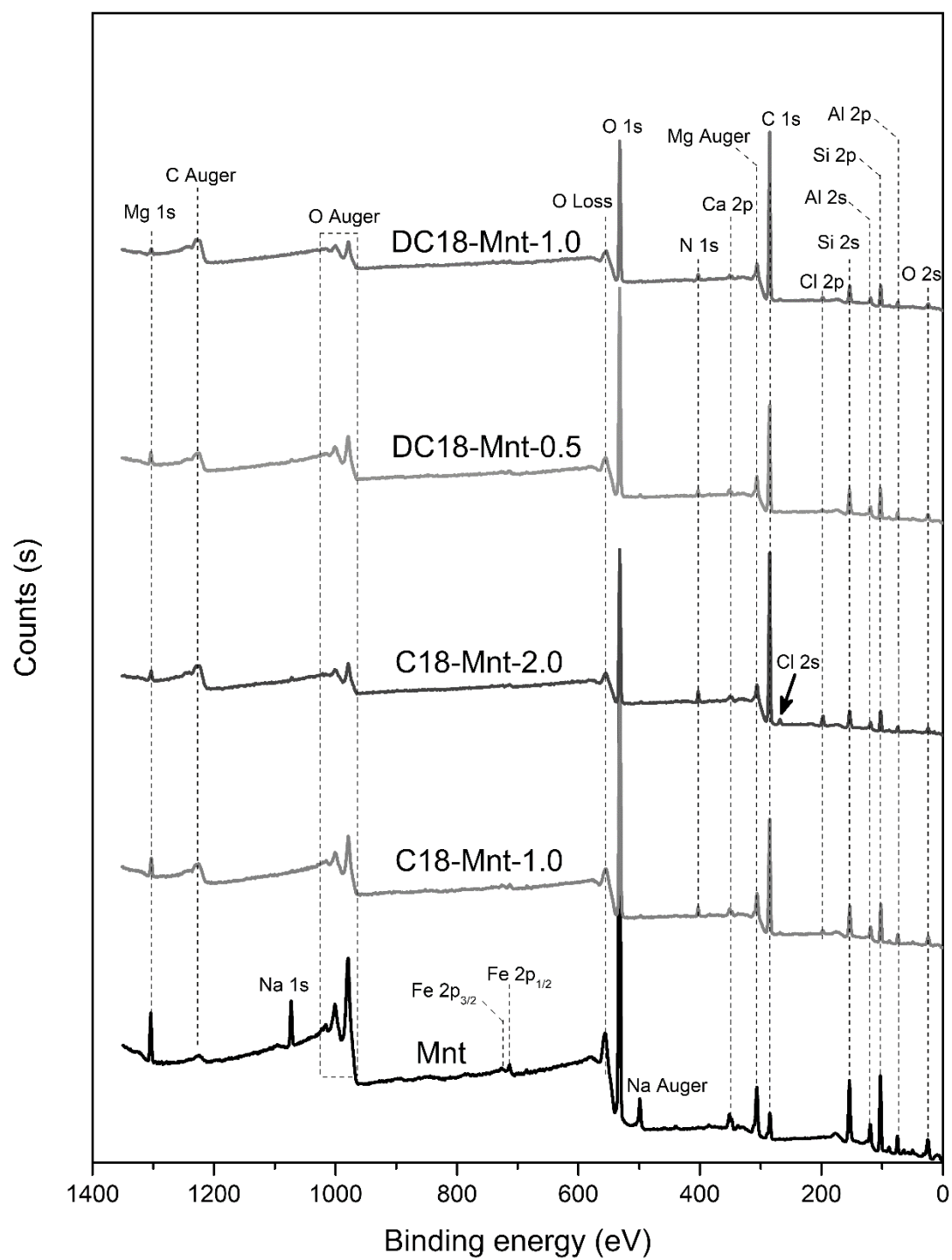


Figure 6 Survey scans of Mnt and OMnt samples.

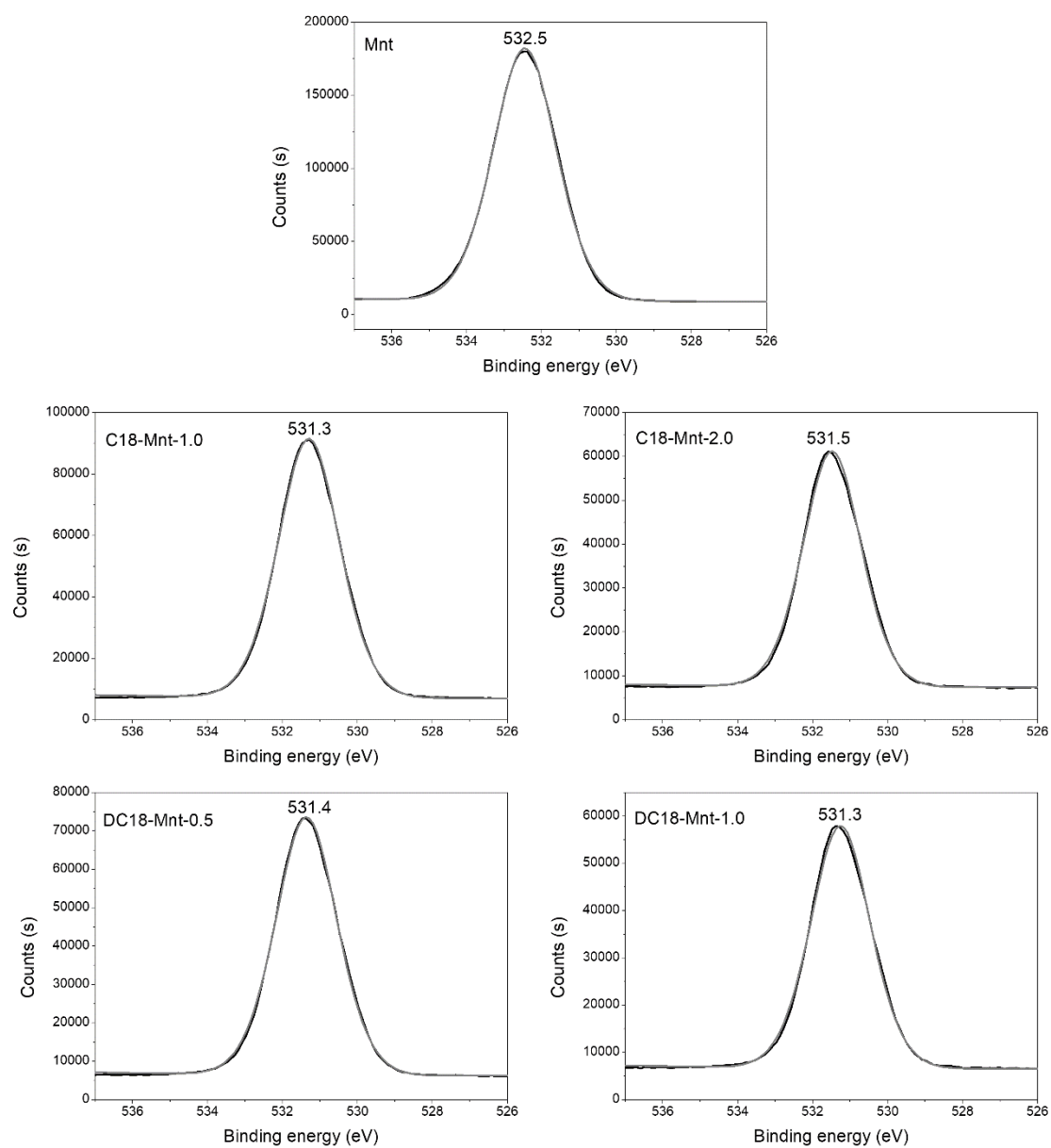


Figure 7 O 1s high-resolution XPS spectra of Mnt and OMnt samples.

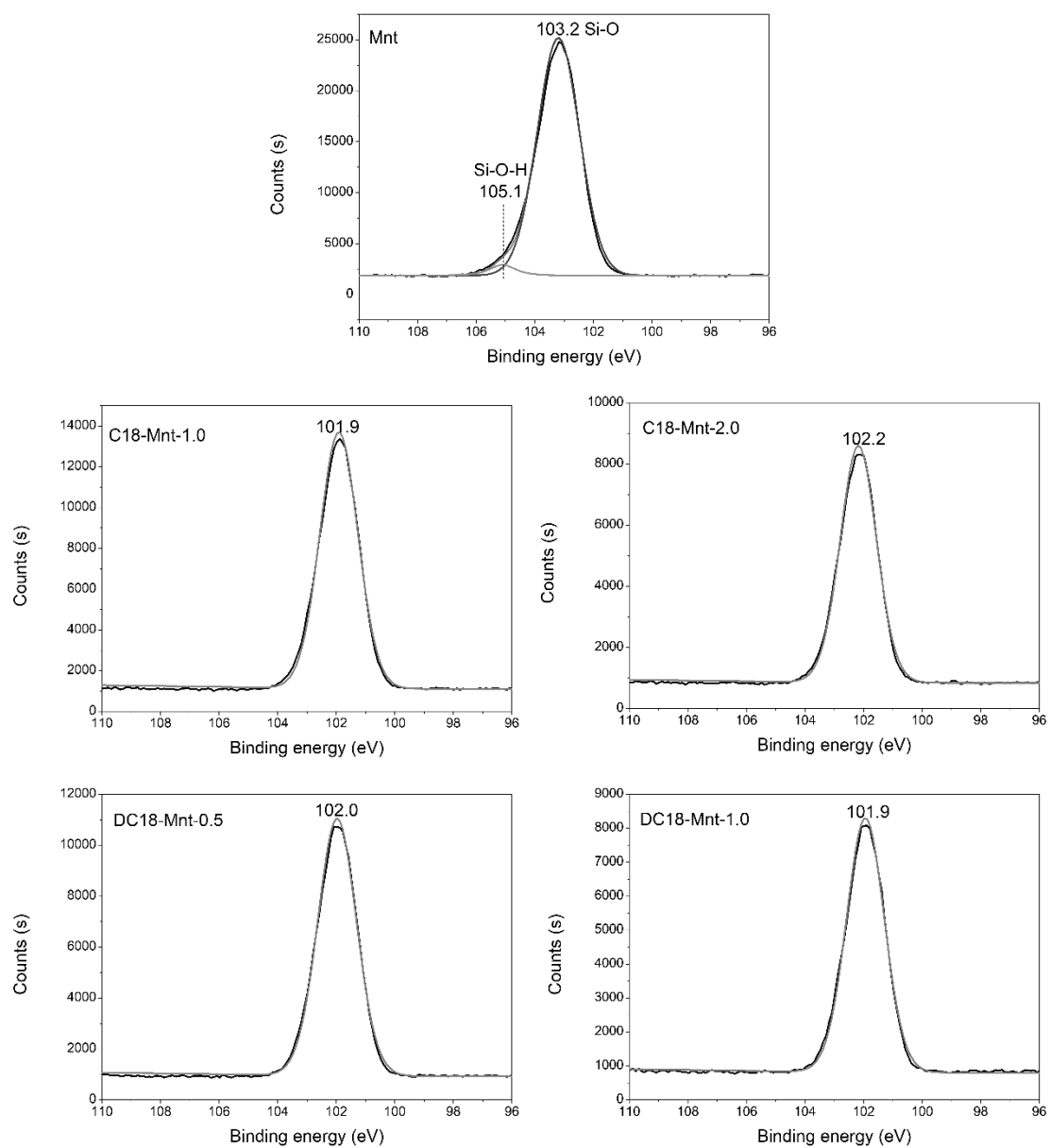


Fig. 8 Si 2p high-resolution XPS spectra of Mnt and OMnt samples.

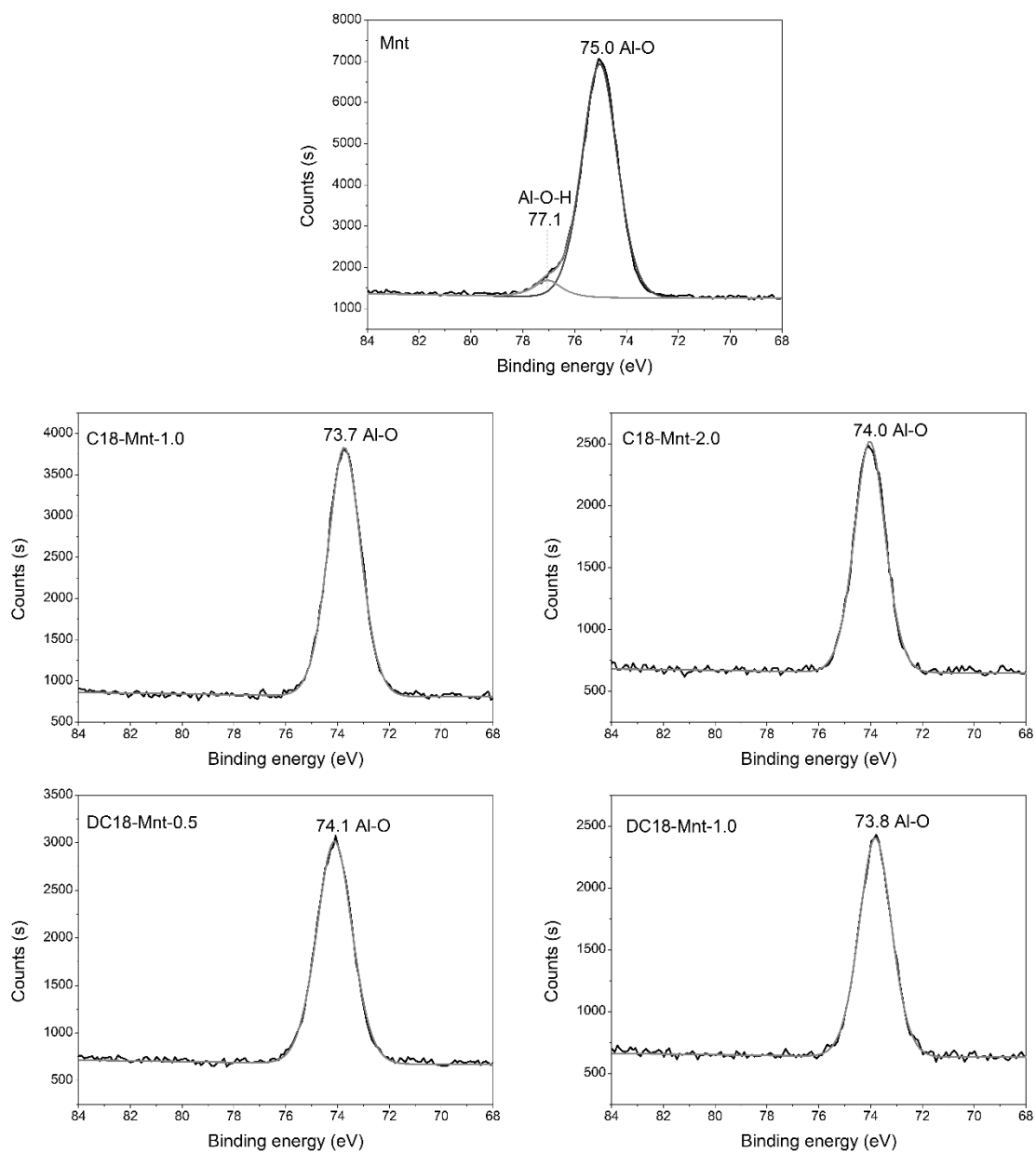


Fig. 9 Al 2p high-resolution XPS spectra of Mnt and OMnt samples.

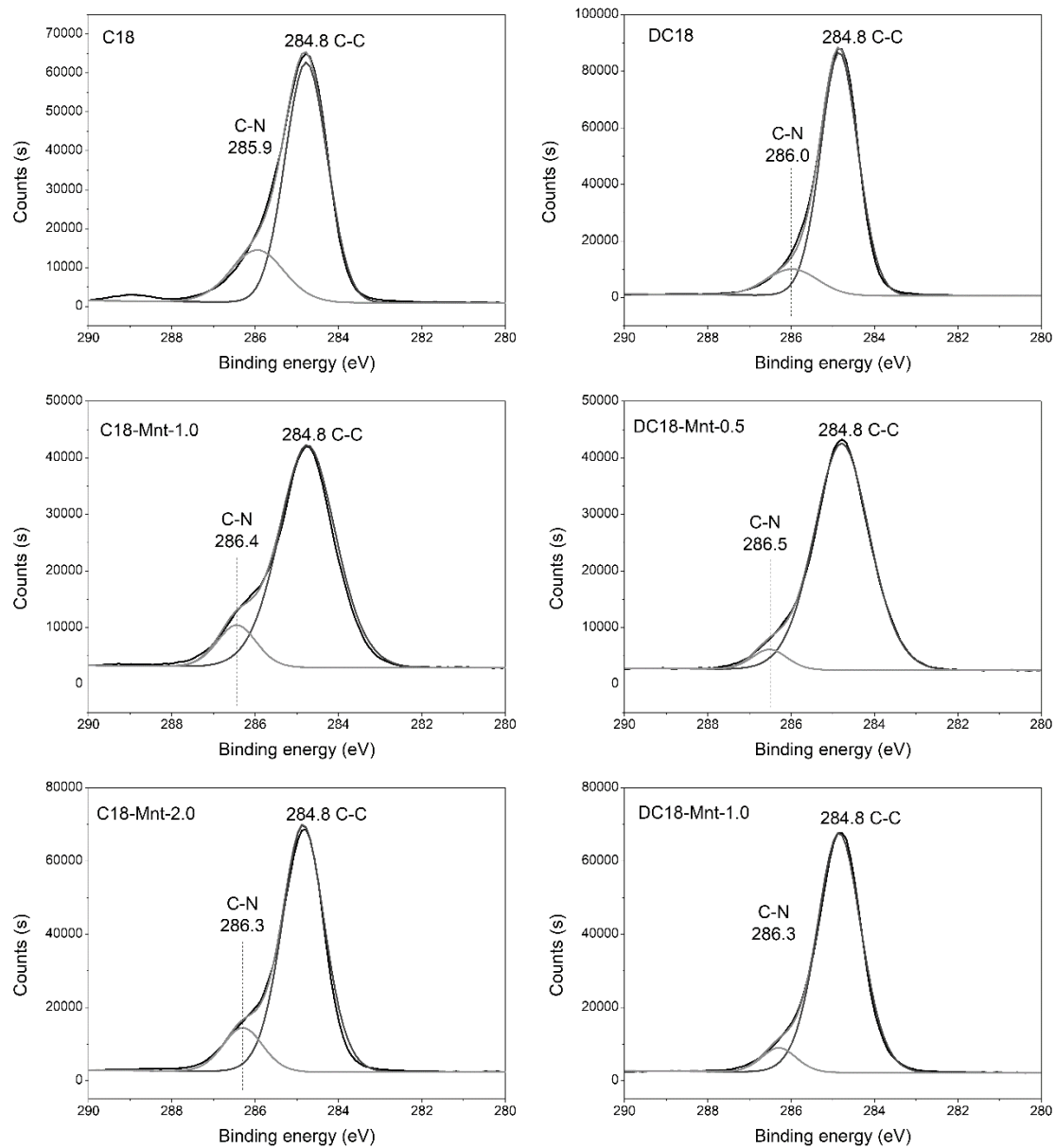


Figure 10 C 1s high-resolution XPS spectra of surfactants and OMnt samples.

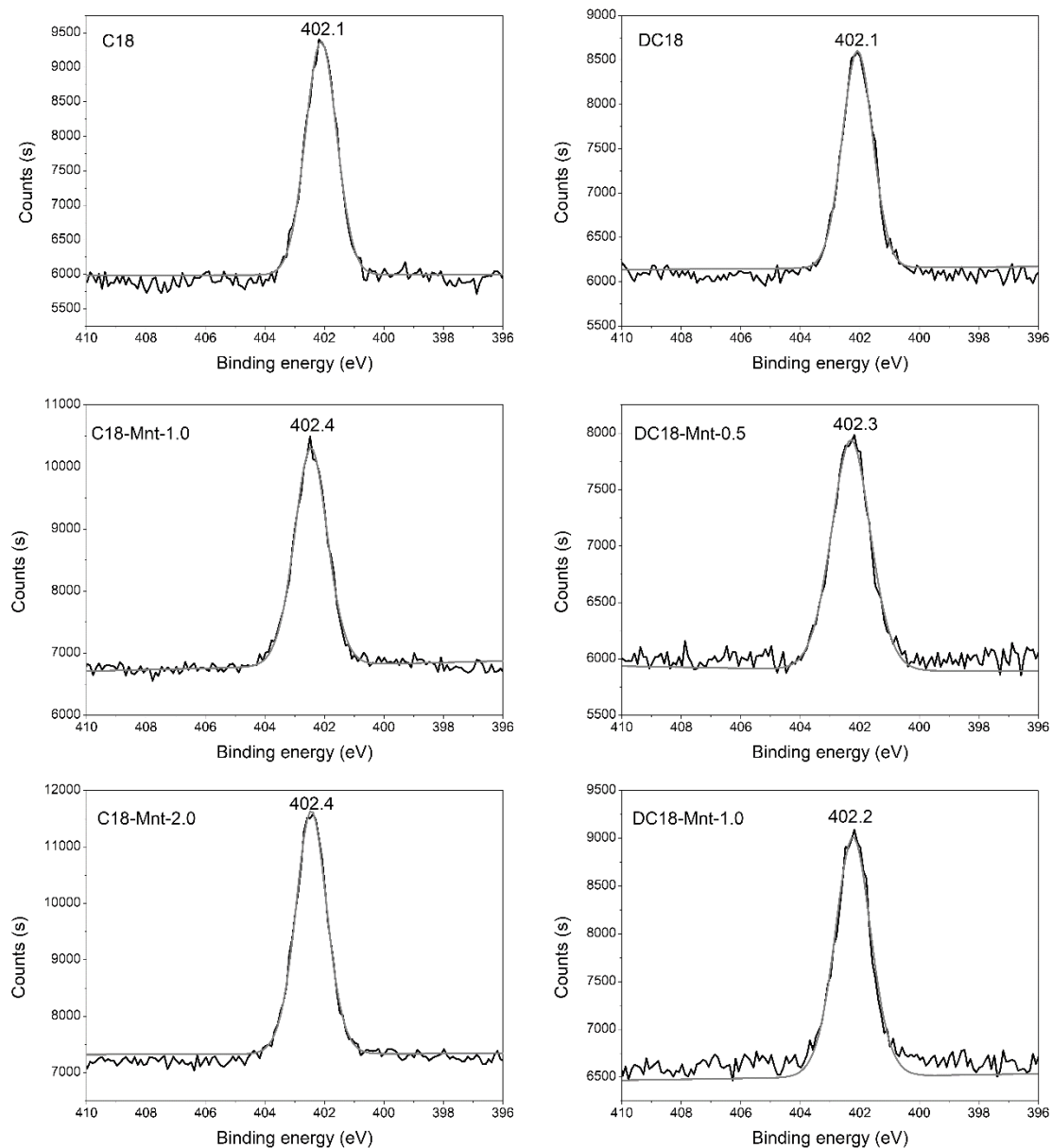


Figure 11 N 1s high-resolution XPS spectra of surfactants and OMnt samples.

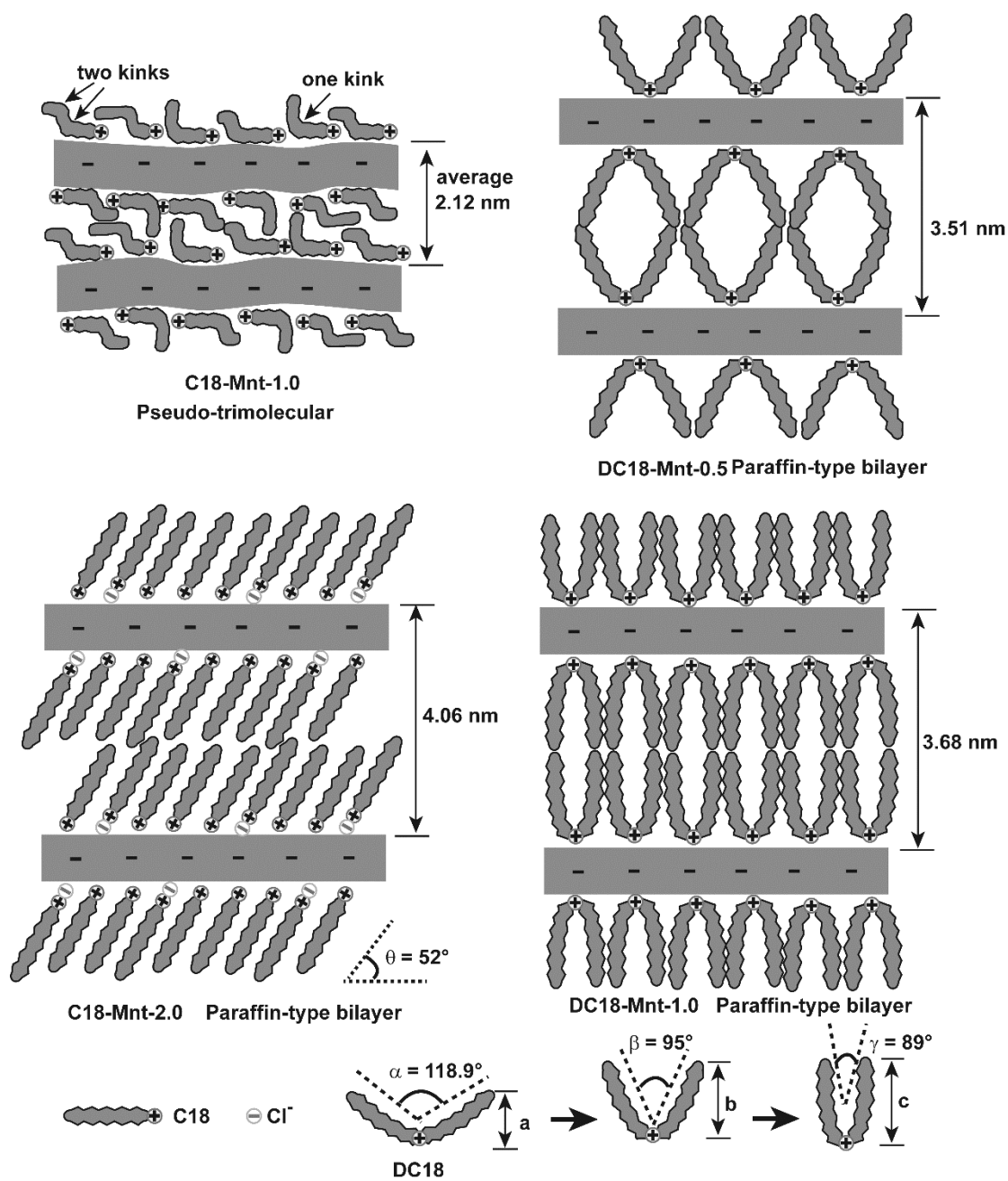


Figure 12 Schematically interpretive diagram of arrangements of surfactants in the interlayer space of OMnt.

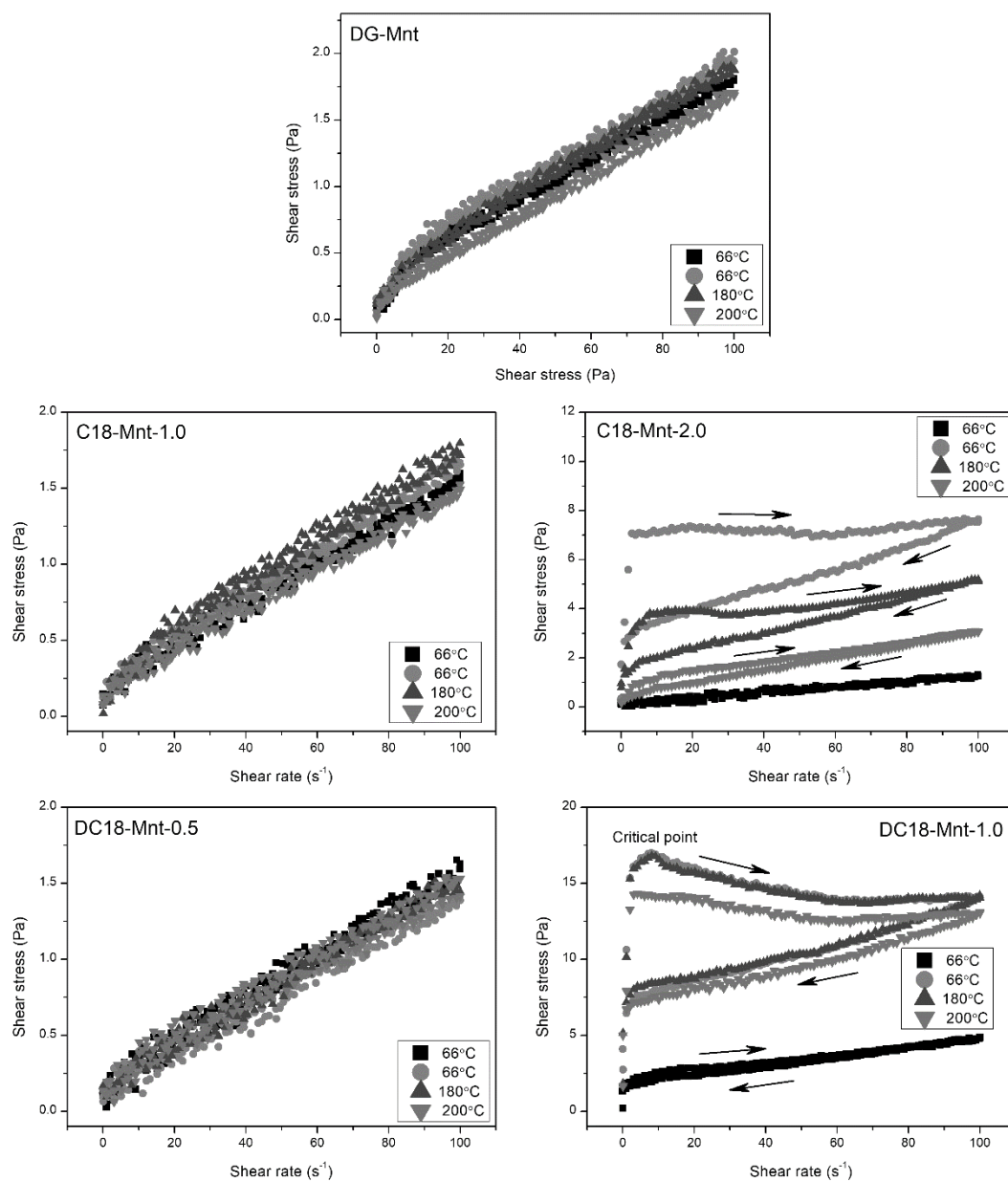


Figure 13 Dynamic rheological curves of OMnt/oil fluids aged at 66°C, 150°C, 180°C and 200°C.

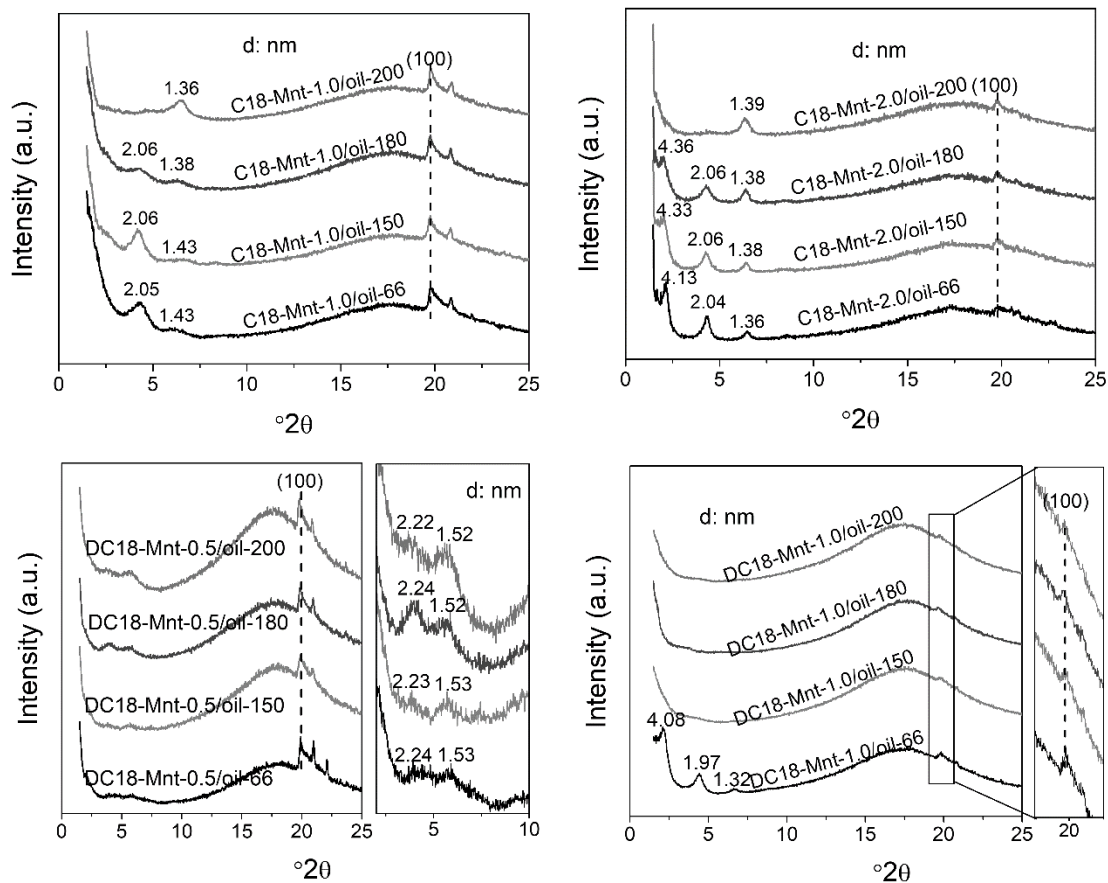


Figure 14 XRD results of OMnt/oil gels aged at 66°C, 150°C, 180°C and 200°C.