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Characterization of organic phases in the interlayer of montmorillonite using FTIR and ^{13}C NMR

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Abstract

The molecular conformation and mobility of the intercalated surfactant molecules, cetyltrimethylammonium bromide (CTMAB), have been studied using Fourier transform IR spectroscopy (FTIR) and high-resolution single-pulse ^{13}C magic-angle-spinning nuclear-magnetic-resonance (^{13}C SP MAS NMR) spectroscopy. Conformation and mobility of alkyl chains was found to be a function of the surfactant concentration. The splitting of the methylene scissoring mode at 1473-1463 cm^{-1} and the rocking mode at 730-720 cm^{-1} in FTIR is considered to be diagnostic of the packing density increase of the intercalated surfactants within the clay gallery. Compare with the ^{13}C SP MAS NMR spectrum of CTMAB in the bulk state, 1~ 3 ppm upfield chemical shifts for end-methyl (δC_{16}) and methylene (δC_{15}, δC_{2-14}) of the intercalated surfactant molecules in the hybrids indicate the more free conformational situation. For these hybrids, the conformational freedom decrease with the increase of surfactant concentration. In addition, ~2 ppm downfield shift for the C_1 carbon atom in the hybrids with higher surfactant content suggests a special local environment. This study demonstrates the different mobility of carbon atoms in the intercalated alkyl chain.

Keywords: Montmorillonite; Alkylammonium; Organic phase; FTIR; NMR

1. Introduction

In the past twenty years, much interest has been focused on the behavior and properties of the

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surfactant/clay hybrids. These hybrids are synthesized through intercalating surfactant molecules into the phyllosilicate interlayers. Among these phyllosilicates, montmorillonite has been extensively investigated as host due to its excellent properties such as cationic exchangeability, swelling behavior, sorption properties, and large surface area. Montmorillonite has a kind of "sandwiched" structure and the clay layer was negatively charged, which is counterbalanced by exchangeable cations in the galleries between layers. The surfactant cations intercalated into interlayer though exchange reaction formed the "ultrathin film" or "organic phase" within the gallery. The behavior and properties of the hybrids strongly depend on the structure and molecular environment of the intercalated surfactant cations [1].

The most widely used technique to characterize the surfactant/clay hybrids is X-ray diffraction (XRD), which gives the basal d spacing of the hybrids. However, XRD does not provide the detailed information about the local conformation and phase state of the intercalated surfactants. This information is critical for understanding the effectiveness of the surface treatment and the role in the formation of organoclays based nanocomposites [2]. The detailed information about the interlayer structure and phase state of alkylammonium in silicate interlayer was firstly obtained by using FTIR [3]. Their results revealed that the frequency shift of the CH_2 stretching and scissoring vibrations was a function of interlayer packing density, chain length, and temperature. In addition, a wide range of molecular environments varying from solidlike to liquidlike was found for the first time. Recently, the conformation of alkylammonium confined in clay interlayer space was extensively studied by techniques of differential scanning calorimetry [1], Raman [4] and NMR [5, 6]. These results suggest that the conformation ordering of the intercalated surfactants strongly depends on the loading amount of amine and their orientation. The ordered (all-trans) conformation would be predominant when amine chains radiate away from the clay surface with the increase of amine concentration [7-9]. More recently, molecular modeling provided some critical information about the structure of organic clay and interaction of surfactant-clay and surfactant-surfactant [10], which was not elucidated by previous experimental results.

MAS NMR has been proved to be a powerful technique to probe the local environments of atoms in materials. However, previous reports paid the most attention on backbone of alkyl chain (C_{2-14}) to elucidate the conformation of the intercalated surfactants [7,8,11] because of their strong and distinct resonance peak, and no attention was paid on the end-group, C_1, C_{15} and C_{16}, which are critical to the conformation and mobility of the intercalated surfactants.

In this study, ^{13}C SP/MAS NMR study, combining with FTIR, is performed on all carbon atoms in the

alkyl chain, to probe their local environment and mobility. Our present study provides some new insights about the conformation and dynamic properties of the intercalated alkylammonium ions and their conformation and phase state of organic surfactant in montmorillonite interlayer. It is of high importance to understanding the microstructure of surfactant/clay hybrids.

2. Materials and methods

2.1 Materials

Montmorillonite (HM) was obtained from Hebei province, China. The sample was purified by sedimentation and the <2 μm fraction was collected and dried at 90 °C. The sample was ground to 200 mesh and sealed in a glass tube for use. The cation exchange capacity (CEC) was 57.9 meq/100g. Its structural formula is $[Na_{0.05}Ca_{0.18}][Al_{1.58}Fe_{0.03}Mg_{0.49}][Si_{3.77}Al_{0.23}]O_{10}(OH)_2 \cdot nH_2O$.The surfactant used in this study is cetyltrimethylammonium bromide (CTMAB) with a purity of 99%. Na_2CO_3, C.P..

2.2 Preparation of CTMAB-montmorillonites

Before the synthesis of surfactant/montmorillonite, the montmorillonite was made into sodium montmorillonite (Na-Mont). The preparation of Na-Mont was carried out by the following procedure: 10g amount of a mixture of montmorillonite and Na_2CO_3 in the ratio 94: 6 was added to 100 ml of deionized water and stirred at 80 °C for 3 h. Na-Mont was collected by centrifugation and washed with deionized water until the pH of the solution was 7. The Na-Mont was dried at 90°C, ground to 200 mesh and kept in a sealed bottle.

The syntheses of CTMAB–montmorillonite hybrids were performed by the following procedure: 2.5 g amount of Na-Mont was first dispersed in about 300 ml of deionized water and then a desired amount of CTMAB was slowly added. The concentration of CTMAB varied from 0.2 to 5.0 of the CEC of montmorillonite. The reaction mixtures were stirred for 10 h at 80 °C. All products were washed free of bromide anions, dried at 90 °C and ground in an agate mortar to pass through a 200 mesh sieve. The CTMAB–montmorillonite hybrid prepared at a concentration of 0.2 CEC was denoted HM0.2CEC and the others were denoted in the same way.

2.3   Characterization methods

IR spectra were recorded as KBr pellets in the spectral range 4000-300cm^{-1} on a Perkin-Elmer1725X FT-IR spectrometer in air at room temperature. ^{13}C MAS NMR experiment was carried out with a Varian Infinity-Plus 400 NMR spectrometer with a 7.5 mm ZrO_2 rotator at room temperature. Spectra were collected using a single-pulse (SP) excitation Blochdecay method with a 4.5 ms (90º) ^{13}C pulse and a repetition delay of 70 s. Rotors were spun in air at 4.5 kHz. The ^{13}C chemical shifts were referenced to tetramethylsilane at 0ppm.

3. Results and discussion

In our previous work [6,12], we used X-ray diffraction and ^{13}C MAS NMR spectroscopy to investigate the arrangement model and conformation of the intercalated surfactant molecules within montmorillonite interlayer with different surfactant loading level. The XRD patterns indicate that the thickness of organic phase (gallery heights) changed from 0.52 to 3.07nm with the increase of surfactant packing density. The arrangement of the intercalated surfactants in the interlayer will vary from lateral-monolayer, to lateral-bilayer, then to paraffin-type monolayer and finally to paraffin-type bilayer. The small energy difference between the trans and the gauche conformers of the alkyl chains allows a great degree of conformational freedom for the alkyl chain tail of the surfactant, restricted only by the gallery dimensions. ^{13}C MAS NMR spectra display two main ^{13}C NMR resonance peaks at ca. 30 and 33 ppm, corresponding to disordered and ordered conformers, respectively. Furthermore, the ^{13}C MAS NMR demonstrates the coexistence of ordered and disordered conformers in the hybrids and the quantity of trans conformer of surfactant molecules increases with the increase of surfactant loading level. According to the literature [13], the interlayer organic phases were consist of domains of all trans chains and domains of disordered chains and have a liquid-like population of trans and gauche conformations. Therefore, it is reasonable to assume that there were several different organic phase states in the interlayer. Vibrational spectroscopies provide a powerful and quantitative local probe of the structure and dynamics in the alkylammonium chains [14], this will be help of us a molecular level understanding the microcosmic environment in the confined organic phase.

3.1 FTIR Spectroscopic Studies

The FTIR spectra of CTMAB and surfactant-intercalated montmorillonites are shown in Figures 1 and 2. Figure 1 displays the C-H stretching vibration of the infrared spectrum (3300-2700 cm^{-1}) of the CTMAB/Montmorillonite hybrids with different surfactant loading levels. The bands at ~2920 cm^{-1} and ~2850 cm^{-1} correspond to CH_2 asymmetric stretching mode ($v_{as}(CH_2)$) and symmetric stretching mode ($v_s(CH_2)$), respectively [8,15]. With the increase of the surfactant loading level and interlayer packing density, $v_{as}(CH_2)$ shifts from 2926 to 2919 cm^{-1} and $v_s(CH_2)$ shift from 2854 to 2850 cm^{-1} for the specimen from HM0.2CEC to HM5.0CEC (Table 1). The band shift from lower frequency to higher frequency means that the number of highly ordered (all-trans) conformers of alkyl chain decreases whereas guache conformers increases. This reflects that, with the increase of surfactant packing density, the "liquid-like" molecular environment of the intercalated surfactants change to solid-like environment [3].

Infrared spectra in the frequency region of 1480-1450 cm^{-1} and 740-710 cm^{-1} are shown in Figure 2(a, b). The methylene scissoring mode at 1480-1450 cm^{-1} and the rocking mode at 740-710 cm^{-1} are diagnostic of packing arrangements in alkyl chain assemblies [16, 17]. As shown in Figures 2 a and b, the FTIR spectra of HM0.2-1.0CEC display singlets at ca. 1470 and 720 cm^{-1}, with a bandwidth of ca. 10cm^{-1}. These broad singlets relate with either a liquidlike molecular environment and/or disordered hexagonal subcell packing, where the alkyl chain rotates freely around its long axis. However, these two singlets split into two peaks gradually with the increase of the intercalated surfactant packing density. This should be attributed to the interaction between contiguous CH_2 groups of neighboring chains in an orthorhombic arrangement of alkyl chains [18], indicating the prominent change of the surfactant local environment. This is accordance with our previous XRD patterns [12]. Our XRD patterns demonstrated that the intercalated surfactants adopted a parallel arrangement in HM0.2-0.7CEC whereas a paraffin arrangement was adopted in HM1.0-5.0CEC.

3.2 ^{13}C SP MAS NMR

Detailed information regarding the structure and dynamics of surfactant molecules in the confined interlayer spaces of the hybrids has been obtained using ^{13}C MAS NMR methods. The behavior of surfactant on the series sample of CTMAB-montmorillonites was compared with pure crystalline CTMAB

and surfactant solution. Figure 3 shows the solid single-pluse ^{13}C MAS NMR spectra of crystalline CTMAB, CTMAB/montmorillonite hybrids and ^{13}C NMR spectrum of CTMAB in solution. The liquid NMR spectrum of CTMAB was cited from literature [19], which was recorded in $CDCl_3$ with a 0.1M concentration of CTMAB at 25 °C. The chemical shift δ (ppm) and their assignment are shown in Table 2. The numbering of the carbons, along with their assignments, is shown in Figure 3. The assignment is based on the previous report for crystalline CTMAB [20].

For crystalline CTMAB, five carbon resonances, C_{16} (16.8 ppm), C_{15} (24.9 ppm), C_{2-14} (32.9 ppm)(mixture of multi-peaks), C_1 (64.5 ppm) and C_N (55.1 ppm), were observed at the range of 0 and 80 ppm.

Normally, alkyl chains adopt all-trans conformation in the bulk state and gauche conformation in solution. For the ^{13}C MAS NMR spectra of surfactant/montmorillonoite hybrids, the signals at 30-33 ppm, corresponding to the resonance of the methylene carbon atoms (C_{2-14}) have been discussed in our previous article[6]. The ordering conformation of surfactant molecules within the gallery of montmorillonite strongly depends on their orientation and packing density. When alkyl chains oriented parallel to the silicate layers, the amount of all-trans conformer decreases with the increase of amine concentration. However, the amount of all-trans conformer increases with increase of amine concentration when amine chains radiate from the silicate layers.

Besides the C_{2-14} resonance, we find that the resonance of C_1, C_{15} and C_{16} also provide useful information about the ordering conformation and their local environment of the intercalated surfactants. In ^{13}C SP MAS NMR spectra (Figure 3), the signal of C_1 locates at 64.5ppm for the crystalline CTMAB and at 66.9ppm for CTMAB in solution. However, the signal corresponding to C_1 is indiscernible in the hybrids prepared at lower surfactant concentration whereas it is distinguished (66.2ppm) in HM2.0-5.0CEC. Its chemical shift is different from that of the crystalline CTMAB (64.5ppm), but similar to that of the CTMAB in solution (66.9 ppm), indicating that the local environment of the intercalated surfactants is similar to "liquid-like". The resonances of other two carbon atoms, C_{15} and C_{16}, shift downfield gradually with the increase of surfactant packing density, from 23.2 ppm to 24.5 ppm for C_{15} and from 14.7 ppm to 15.7 ppm for C_{16} (see Table 2), respectively. Compared with the corresponding resonance peak of crystalline CTMAB, we can find that the chemical shifts of C_{15} and C_{16} become much closer to that of crystalline CTMAB with the increase of the packing density. The chemical shift variation of C_{15} ($\Delta\delta C_{15}$) between HM5.0CEC and crystalline CTMAB is 0.4 ppm while $\Delta\delta C_{16}$ is 1.1 ppm. This

reflects that, even in the sample HM5.0CEC with the most ordered conformation and highest surfactant loading level, the local molecular environment is different from that of the crystalline. Meanwhile, we can find that $\Delta\delta C_{16}$ is bigger than $\Delta\delta C_{15}$, indicating that there is much mobility for C_{16} than that for C_{15}. This provides the supporting evidence for the proposal that the tail of alkyl chain is movable even in higher packing density of the intercalated surfactants [4]. This was consisted with the result of FTIR that there was a special phase state between solid and liquid in the interlayer even the highest concentration sample. But the mobility information about C_1, C_{15} and C_{16} was absence in FTIR. Because of the little content of end-head carbon atoms in the totals carbon, and the FTIR provide an average estimate of asymmetric and symmetric of CH_2 at range of 2920-2850cm^{-1}, the special changes caused by C_1, C_{15} and C_{16} cannot been distinguished from total information.

The chemical shift of C_{2-14} from ~30 to ~33ppm is attributed to the change of gauche conformation to all-trans conformation [2, 20, 21]. However, there is little explanation about the chemical shift of C_1, C_{15} and C_{16}. Comparison of chemical shift of C_1 of crystalline CTMAB ($\delta C_{1(crystalline)}$=64.5 ppm) with that of the hybrids with higher surfactant packing density (δC_1=66.2ppm) indicates that, contrary to the upfield shift for C_{15} and C_{16}, the C_1 adopts a downfield shift, indicating a "liquid-like" phase ($\delta C_{1(solution)}$=66.9ppm). This may be attributed the following reasons. The angle between the axes of alky chain and head of alkylammonium cation ($-N^+-(CH_3)_3$) is different from that for CTMAB in the bulk state. Previous studies have demonstrated that the arrangement of the intercalated surfactants strongly depends on the loading level of surfactants. In hybrids with higher surfactant packing density, the arrangement of paraffin model is formed by the head group anchoring on the silicate surface and the long alkyl chain radiate away from it. Two opposite interactions, attractive force to head of alkylammonium cation and repulsive force to alkyl chain from the silicate surface, and interaction between alkyl chains distort the surfactant molecule. This made the carbon atom C_1, the "pivot" between the long alkyl chain and positive head ($-N(CH_3)_3^+$), located into a special molecular environment. The other possibility is that the local molecular environment of C_1 is greatly affected by the loss of Br$^-$, which is left in the solution during the ion exchange reaction.

4. Conclusion

Cetyltrimethylammonium bromide has been intercalated into the gallery of montmorillonite by

ion-exchange. The local environment of the intercalated CTMAB is different from those of CTMAB in bulk state and in solution. FTIR spectra demonstrate that CH_2 stretching (3000-2800 cm^{-1}), scissoring (1480-1450 cm^{-1}) and rocking (740-710 cm^{-1}) modes are diagnostic for the conformation of intercalated surfactants within the gallery. With the increase of stacking density, the singlets at 1480-1450 cm^{-1} (scissoring mode) and at 740-710 cm^{-1} (rocking mode) split into doublets while the bands corresponding to CH_2 asymmetric and symmetric stretching modes shift to ~2920 cm^{-1} and ~2850 cm^{-1}, respectively. FTIR spectra demonstrate that the mobility of the intercalated surfactants even in higher surfactant packing density.

Our ^{13}C SP MAS NMR spectra provide detailed information about the local molecular environment and dynamic properties of the intercalated surfactants. Compared with that of crystalline CTMAB, the bigger variation of C_{16} chemical shift than that of C_{15} indicates the different mobility for the carbon atoms in the intercalated alkyl chain. This provides the supporting evidence for the proposal, concluded from FTIR, that the tail of alkyl chain is movable even in higher surfactant packing density. Contrary to the upfield shift for C_{15} and C_{16} with the increase of the surfactant packing density, C_1 displays a downfield shift and its chemical shift is similar to that of CTMAB in solution, indicating a "liquid-like" phase. This reflects that there is no complete "solid-like" state for the intercalated surfactants. This study firstly demonstrates the different mobility of carbon atoms in the intercalated alkyl chain. It is of high importance to understanding the local molecular environment and dynamic properties of the surfactant modified clays.

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Table 1

Observed FTIR frequencies and their assignments of the CTMAB and CTMAB-Montmorillonite

Sample	Wavenumber(cm^{-1})	
	$\nu_{as}(CH_2)$	$\nu_s(CH_2)$
HM0.2CEC	2926	2854
HM0.5CEC	2922	2852
HM0.7CEC	2921	2851
HM1.0CEC	2920	2851
HM1.2CEC	2919	2851
HM1.5CEC	2919	2851
HM1.7CEC	2919	2850
HM1.9CEC	2919	2850
HM2.0CEC	2919	2850
HM2.2CEC	2919	2850
HM3.0CEC	2919	2850
HM5.0CEC	2919	2850
CTMAB	2918	2850

Table 2

^{13}C δ (ppm) of surfactant in Bulk , Solution and CTMAB-Montmorillonite

| Sample	Chemical shift of different carbon atom δ(ppm)				
	C_N	C_1	C_{2-14}	C_{15}	C_{16}
CTMAB (solution)	53.3	66.8	23.3~31.9[*]	22.7	14.1
HM0.2CEC	55.1	-	33.0/30.2	23.2	14.7
HM0.6CEC	55.1	-	33.3/30.6	23.6	14.7
HM0.7CEC	55.1	-	33.7/30.1	23.0	14.6
HM1.0CEC	55.1	-	33.1/30.5	23.5	15.0
HM1.5CEC	55.1	-	33.0/30.6	23.4	15.0
HM1.7CEC	55.1	-	33.0/30.5	23.5	14.7
HM2.0CEC	55.1	-	33.3/30.9	24.2	15.4
HM2.2CEC	55.1	66.2	33.2/31.1	24.3	15.5
HM3.0CEC	55.1	66.2	33.3/31.3	24.6	15.6
HM5.0CEC	55.1	66.2	33.3/31.3	24.5	15.7
CTMAB (Solid)	55.1	64.5	32.9	24.9	16.8

* multi peak
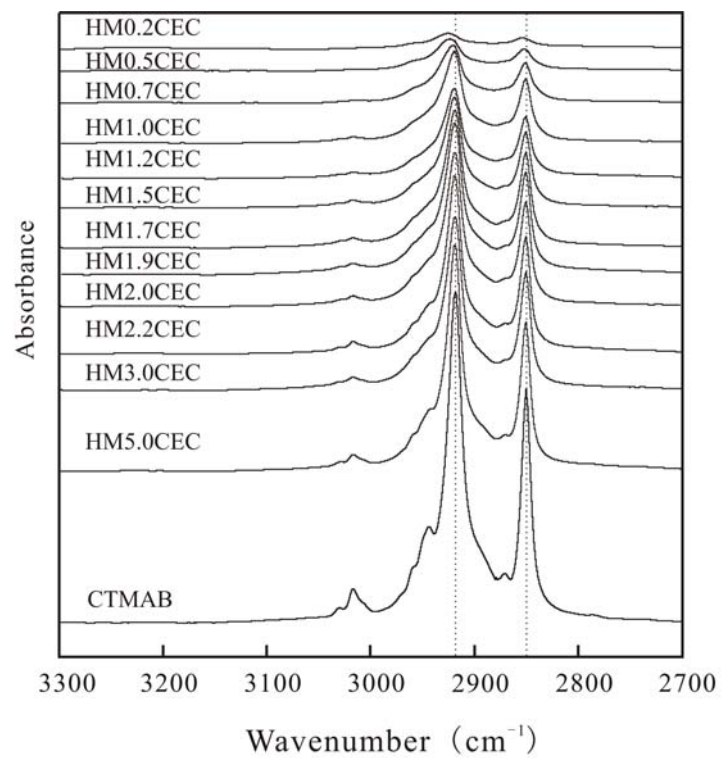
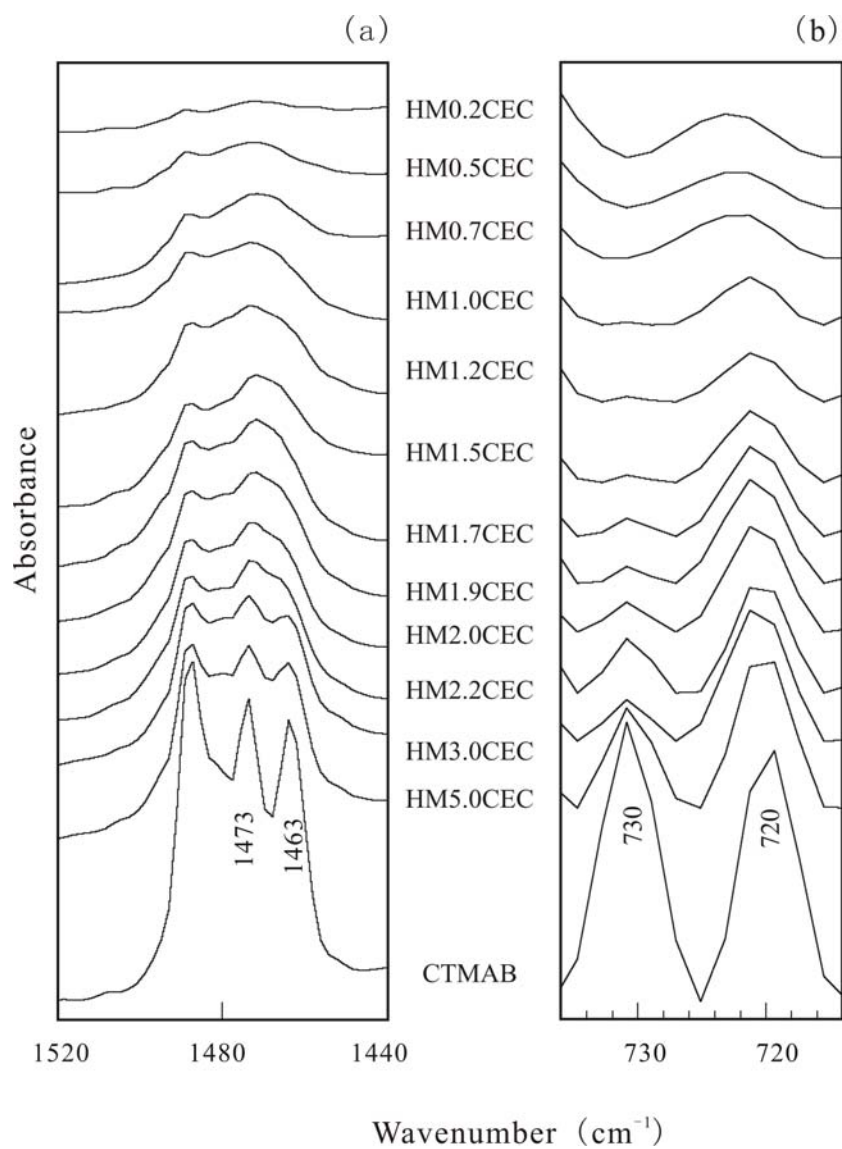Fig. 1. FTIR spectra of CTMAB and CTMAB-Montmorillonite at region of 3300-2700cm^{-1}

Fig. 2. FTIR spectra in the C-H stretching region of the CTMAB-Montmorillonite hybrids recorded at different surfactant loading level: (a) 1480-1450cm^{-1} range; (b) 740-710cm^{-1} range.
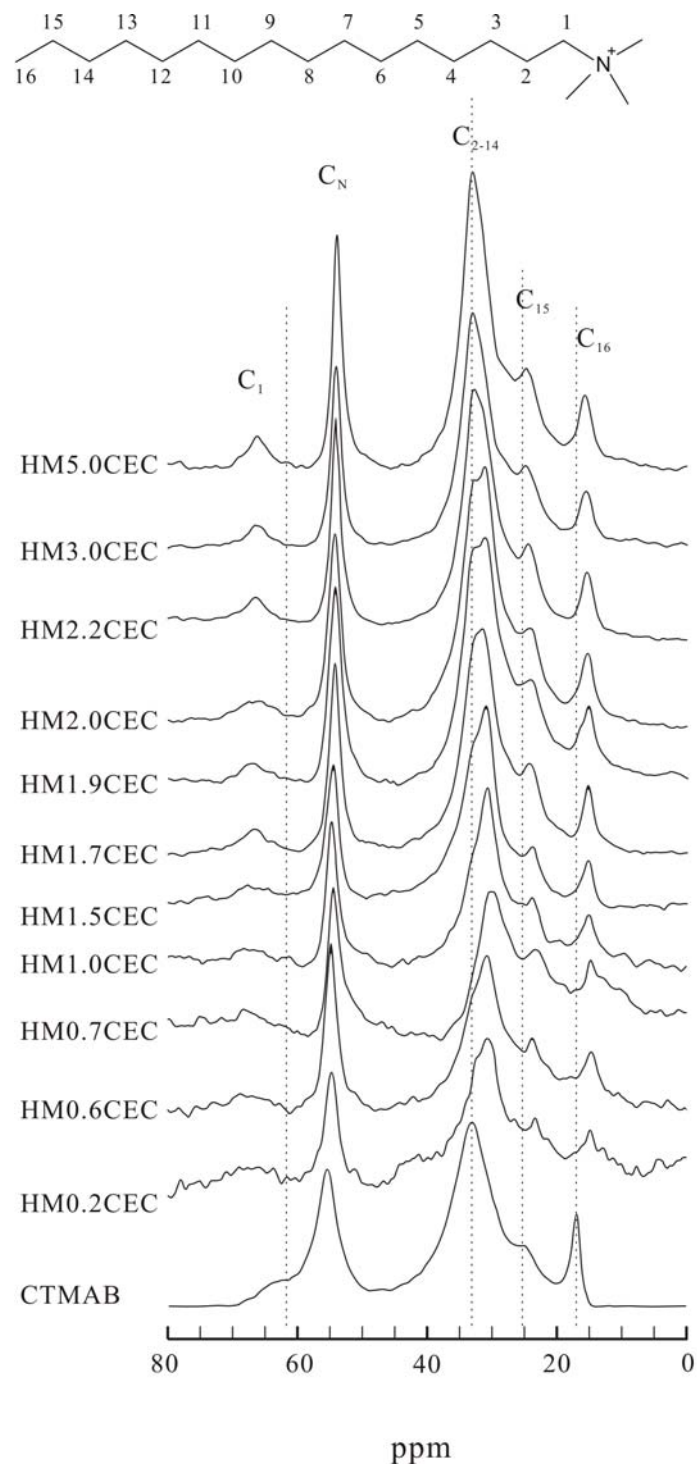
Fig. 3. ^{13}C SP MAS NMR spectra of crystalline CTMAB and the CTMAB-Montmorillonite. The assignments along with the numbering of the carbon atoms are shown. The dotted lines are simply a guide for the eye.