

## Effect of organoclay purity and degradation on nanocomposite performance, Part 1: Surfactant degradation

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### ABSTRACT

The alkylammonium surfactants used to form commercial organoclays are known to begin to degrade at temperatures below the typical melt processing temperatures of some polymers. In this study, the thermal stability and degradation of various surfactants and their corresponding organoclays were investigated. Several factors, such as surfactant type and excess surfactant in the organoclay, that affect the thermal stability of surfactants on organoclays are explored. Nuclear magnetic resonance (NMR) spectroscopy was used to analyze the decomposition products. Thermogravimetric analysis (TGA) was used as the primary method to characterize the thermal stability of these surfactants and organoclays; the neat surfactants lose mass more rapidly, at a given temperature, than the corresponding organoclay. Washing the organoclay with methanol proved to be an effective way to remove the excess surfactant from the clay galleries. Such purification generally improves the thermal stability of the as-received organoclays. Depending on the availability of residual halide anions in the organoclay, the organoclays decompose via either S<sub>N</sub>2 nucleophilic substitution or Hoffmann elimination pathways.

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### 1. Introduction

Polymer nanocomposites comprising nanometric-sized aluminosilicate platelets can exhibit remarkably improved performance, such as increased strength and heat resistance [1–5], decreased gas permeability [6–10] and flammability [11–13], and increased biodegradability of biodegradable polymers [14] at very low concentrations (2–5 vol%) of inorganic filler. In principle, these improvements can be realized without significantly increasing the density of the polymer or changing its optical properties. To take advantage of the high aspect ratio and high surface area of the clay platelets, the key is to exfoliate the individual platelets in the polymer matrix. Generally, the hydrophilic silicate surface of sodium montmorillonite can be converted to a more organophilic one by ion-exchange reactions with cationic surfactants, such as tertiary or quaternary alkylammonium salts, which makes effective dispersion in some polymers possible.

Montmorillonite, MMT, is thermally stable at temperatures up to several hundreds of degree Celsius, while the surfactants used to form organoclays may begin to undergo degradation reactions at temperatures below the typical melt processing temperatures for

the polymers of interest [15–17]. Thus, organoclay degradation becomes an issue that must be considered when forming polymer nanocomposites by melt processing. This paper (Part 1) reports a detailed characterization of the thermal degradation of several commercial and experimental organoclays often used to form polymer nanocomposites and how their degradation processes are altered by simple purification schemes. A companion paper (Part 2) compares the structure and properties of nanocomposites formed from selected purified and unpurified organoclays [18].

Thermogravimetric analysis (TGA) was the primary method used to characterize the thermal degradation behavior of the organoclays. In addition to the generally used temperature sweep mode of analysis, isothermal TGA runs were used to compare the thermal stability of the surfactants and the organoclays formed from them; the isothermal method provides a more relevant way to evaluate the extent of degradation during the melt blending with polymers, since this is essentially an isothermal procedure. Nuclear magnetic resonance (NMR) spectroscopy was used to provide additional support and insight about the decomposition processes.

Surfactant type is a main focus of this study. For example, the number of long alkyl tails on the surfactant cations may play an important role in the degradation process as do other functional groups that may be present. We also explore the role of excess surfactant in the organoclay. Washing with solvent to remove the unbound surfactant from the organoclay provides a unique way of exploring this.

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## 2. Experimental

### 2.1. Materials

Organically modified clays, formed by ion-exchange reaction between sodium montmorillonite (Na-MMT) and ammonium surfactants, were generously donated by Southern Clay Products, Inc. The selected organoclays are listed in Table 1. A similar nomenclature system as used in prior papers [5,19–21] is adopted to describe the chemical structure of the ammonium cations in a concise manner. The letters M, B and (HE) represent methyl, benzyl, and 2-hydroxyethyl substituents, respectively. The letter T represents tallow, derived from natural products, which is predominantly

**Table 1**  
Organoclays and surfactants used in this study

Organoclay commercial designation <sup>a</sup>	Surfactant used to make the organoclay	Molecular weight of surfactants <sup>b</sup> (anion included)	Organic loading in the organoclay <sup>c</sup> , MER (mequiv./100 g of clay)
SCPX 3056	$\begin{array}{c} M_1(HT)_3 \\   \\ M \\   \\ HT-N^+-HT \\   \\ HT \end{array} \quad Cl^-$	949	95
Cloisite 20A Cloisite 15A Cloisite 6A	$\begin{array}{c} M_2(HT)_2 \\   \\ M \\   \\ M-N^+-HT \\   \\ HT \end{array} \quad Cl^-$	570	95 125 140
SCPX 1137	$\begin{array}{c} M_3(HT)_1 \\   \\ M \\   \\ M-N^+-M \\   \\ HT \end{array} \quad Cl^-$	340	95
SCPX 2730	$\begin{array}{c} M_3(C16)_1 \\   \\ M \\   \\ M-N^+-M \\   \\ C16 \end{array} \quad Cl^-$	319.45	100
Experimental	$\begin{array}{c} M_2(HT)_2 \\   \\ M \\   \\ M-N^+-HT \\   \\ HT \end{array} \quad MeSO_4^-$	645	95 140
Cloisite 30B	$\begin{array}{c} (HE)_2M_1T_1 \\   \\ CH_2CH_2OH \\   \\ M-N^+-T \\   \\ CH_2CH_2OH \end{array} \quad Cl^-$	394	90
Cloisite 10A	$\begin{array}{c} M_2(HT)_1B_1 \\   \\ M \\   \\ M-N^+-CH_2-C_6H_5 \\   \\ HT \end{array} \quad Cl^-$	422	125

<sup>a</sup> All the organoclays used in this study are generously donated by Southern Clay Products, Inc.

<sup>b</sup> The molecular weights of the surfactants are obtained from Akzo Nobel.

<sup>c</sup> The organic loadings shown here are values reported by Southern Clay Products, Inc.

composed of chains with 18 carbons (~65%); while HT denotes the tallow-based product in which the majority of the double bonds in these materials have been hydrogenated. The organoclays were carefully chosen to explore the possible factors that may influence their thermal stability. The neat surfactants used in this study were supplied by Akzo Nobel to Southern Clay Products, Inc. It should be noted that the ammonium surfactants are typically added in stoichiometric proportion to that of the cation exchange capacity (CEC) of the clay. In some cases, excess amounts of ammonium surfactant are added to over-saturate the montmorillonite galleries. The level of the surfactants added to the clay is designated by the milliequivalent ratio (MER) defined as the milliequivalents of surfactant per 100 g of clay [5]. When the ion exchange is in ideally perfect stoichiometry, the MER should ideally be equal to the intrinsic cation exchange capacity, CEC, of the clay. However, the fact that the measured MER is close to or equal to the CEC does not assure that the ion-exchange process is complete since any unbound surfactant will be included in the MER measurement.

### 2.2. Organoclay purification

The as-received organoclays selected for this study were purified using methanol as solvent to remove the excess free surfactant that may exist. Two methods of purification were adopted to make a head-to-head comparison of their effectiveness. The first was to subject the as-received organoclay in powder form to Soxhlet extraction in methanol for 1–5 days [22–24]. The other method involved suspending the organoclay in methanol, while magnetically stirring at room temperature for 1 h, letting the mixture set without stirring until the suspension stratified, and then decanting the top clear solution. Fresh methanol was added and the entire procedure was repeated several times. The as-received organoclays were subjected to 1–3 washings of this type.

For both methods, the resulting white precipitate was washed with methanol and distilled water while being filtered. The final product was dried at room temperature and then under vacuum at 80 °C overnight. The hard white cake formed was ground into a fine powder again prior to any further usage.

### 2.3. Determination of organic content of organoclay

The amount of organic component in the as-received and purified organoclays was calculated from the experimentally determined ash content following burning the pre-dried organoclays in a furnace for over 45 min at 900 °C.

$$MMT\% = \frac{MMT_{ash}\%}{0.935} \quad (1)$$

$$ORG\% = 100\% - MMT\% \quad (2)$$

The factor of 0.935 in this calculation corrects for loss of water during structural rearrangement of the pristine montmorillonite during the analysis; oxidative heating of the clay has been previously shown to result in a 6.5% mass loss [25–27]. The milliequivalent ratio (MER), the milliequivalents of surfactant per 100 g of MMT, is a commonly used way to represent the surfactant loadings of organoclays. The MER values can be calculated from the ashing results by using the following equation:

$$MER = \frac{(ORG\%/molecular\ weight\ of\ surfactant) \times 10^3}{MMT\%} \times 100 \quad (3)$$

## 2.4. Analysis of the degradation process via NMR spectroscopy

### 2.4.1. Neat surfactants

A 2 dram vial (Vial #1) was charged with either  $M_2(HT)_1B_1^+Cl^-$ ,  $M_2(HT)_2^+Cl^-$ ,  $M_3(HT)_1^+Cl^-$ , or  $(HE)_2M_1T_1^+Cl^-$  (~50 mg) and then sealed with a septum. Vial #1 was then connected via a cannula to another 2 dram vial (Vial #2) containing  $CDCl_3$  (2 mL) and sealed with a septum. A slight pressure of nitrogen gas was applied to Vial #1 (connected via a metal gas-hose adapter) and a relief valve was connected to Vial #2 in such a way that enabled excess pressure to be carefully purged from the system. Vial #1 was then heated to 250 °C (internal temperature) using a sand bath as the heat source; Vial #2 remained at ambient temperature. Periodically, the relief valve on Vial #2 was opened for 5 s to help facilitate transfer of the volatile decomposition products from Vial #1 into the Vial #2 containing  $CDCl_3$  as well as to release excess pressure. After 5 min of repeating this procedure, Vial #1 was cooled to ambient temperature and purged with excess nitrogen; the residual material was then dissolved in  $CDCl_3$ . The contents of both vials were subsequently analyzed by  $^1H$  NMR spectroscopy.

### 2.4.2. Purified organoclays

Samples of purified Cloisite 10A, Cloisite 20A, SCPX 1137, and Cloisite 30B (~100 mg) were independently subjected to similar conditions as described above for the decomposition studies of the neat surfactants. Likewise, collected volatile by-products were analyzed by  $^1H$  NMR spectroscopy ( $CDCl_3$ ); the residual solids were first triturated with  $CDCl_3$  and then filtered to obtain clear solutions which were also analyzed by  $^1H$  NMR spectroscopy.

## 2.5. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted on organoclays and neat surfactants using a Perkin–Elmer TGA 7 under nitrogen atmosphere at a gas flow rate of 20 mL/min. All organoclays and neat surfactants were kept in a vacuum oven overnight at 80 °C prior to thermal analysis to remove most of the moisture and volatiles that existed in the as-received samples. Before performing the TGA tests, all the samples were held at 110 °C until their weight stabilized. Two thermal protocols were used: (1) heating isothermally at various temperatures and (2) heating at the constant rate of 20 °C/min from 110 °C to 750 °C.

## 2.6. WAXS

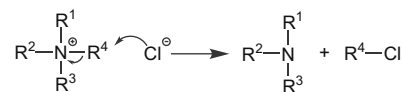
WAXS scans were obtained using a Scintag XDS 2000 diffractometer in reflection mode with an incident X-ray wavelength of 1.542 Å at a scan rate of 1.0°/min. X-ray analysis was performed on organoclays in powder form. The interlayer spacing,  $d_{001}$ , was determined from the peak position in the XRD spectrum via Bragg's law:

$$d_{001} = \lambda / (2 \sin \theta) \quad (4)$$

## 3. Results and discussion

### 3.1. Degradation mechanism

The primary degradation pathways of ammonium chloride based surfactants (in bulk form and contained within organoclays) are generally believed to follow either substitution or elimination-type reactions [17,28,29]. In the former, nucleophilic attack of the  $R_4N^+$  moiety by a chloride ion would lead to the formation of  $RCl$  and  $R_3N$ , which is essentially the reverse reaction of most



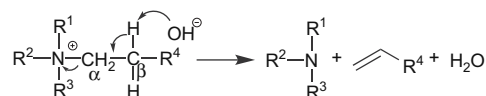
**Scheme 1.** Nucleophilic substitution leading to the decomposition of an ammonium surfactant.

quaternary ammonium syntheses (see Scheme 1 for a representative example). In the cases where the quaternary ammonium features different alkyl substituents, the least sterically hindered (i.e., methyl) and/or other electrophilic alkyl groups (i.e., benzyl) are generally the most susceptible to nucleophilic attack. The Hoffmann elimination reaction, on the other hand, is a process where a quaternary ammonium salt is decomposed into an olefin and a tertiary amine via exposure to basic conditions (e.g., silver oxide and water) (see Scheme 2 for a representative example). The mechanism of this reaction is believed to be a bimolecular elimination-type reaction, where a base, such as hydroxide, abstracts a hydrogen atom from the  $\beta$ -carbon of the quaternary ammonium salt.

To gain insight into whether either of these mechanisms were operative during decomposition of the surfactants and organoclays explored in this study and, if so, which one dominated, the volatile by-products and residues of these materials were analyzed using NMR spectroscopy. These experiments were performed by heating the material to 250 °C for 5 min with continuous trapping of the by-products into  $CDCl_3$  that was subsequently analyzed; the residual solids were dissolved in  $CDCl_3$  and analyzed as well.

The  $CDCl_3$  solutions of the volatile by-products from the thermally induced decomposition of  $M_2(HT)_2^+Cl^-$ ,  $M_3(HT)_1^+Cl^-$ ,  $M_2(HT)_1B_1^+Cl^-$ , or  $(HE)_2M_1T_1^+Cl^-$  showed the presence of significant amounts of (>99%) chloromethane ( $ClCH_3$ ), as evidenced by the signal found at  $\delta = 3.00$  ppm in  $^1H$  NMR spectrum. The identity of this compound was corroborated using GC–MS, which showed the presence of two signals corresponding to 50 Da and 52 Da, with intensities in accord with the relative isotopic abundance of  $^{35}ClCH_3$  and  $^{37}ClCH_3$ , respectively. Decomposition of  $M_2(HT)_1B_1^+Cl^-$  leads to the formation of a 2:1 molar ratio of benzyl chloride ( $\delta = 4.58$  ppm, benzylic  $-CH_2-$ ) and chloromethane ( $\delta = 3.00$  ppm) as the volatile decomposition by-products. Note that although the ratio of by-products did not correspond to the relative reactivity rates of these two groups in  $S_N2$  reactions (i.e., benzyl is 4× more reactive via  $S_N2$  than methyl), the discrepancy may be due to the high volatility of  $ClCH_3$  [30]. The non-volatile residues remaining after thermal decomposition were found to be the respective demethylated and/or debenzylated neutral amines of the aforementioned surfactants. These assignments were based upon the relatively upfield chemical shift (i.e.,  $\delta \sim 2.2$  ppm) exhibited by the remaining methyl groups on the surfactant as well as integration of the remaining alkyl groups which indicated that a single methyl or benzyl group had been lost. In all cases, the total olefin content, as determined by integrating the 4–6 ppm region of the aforementioned  $^1H$  NMR spectra and comparing that value with that of the entire spectrum, was found to be less than 0.1%.

Thermal decomposition of purified Cloisite 20A, SCPX 1137, Cloisite 10A, and Cloisite 30B (i.e., organoclays containing the surfactants mentioned above) afforded chloromethane (as well as benzyl chloride for Cloisite 10A) and water ( $\delta = 1.55$  ppm) as the

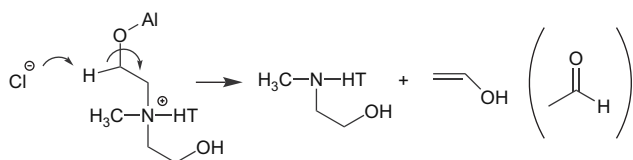


**Scheme 2.** Representative example of a Hoffmann-type elimination reaction.

major volatile by-products. In contrast with results obtained for the neat surfactant, up to 5% of olefin ( $\delta = 5.45\text{--}5.20$  ppm) was found in the non-volatile residues, in addition to the expected neutral amines. Notably, a significant amount ( $\sim 15\%$  total, as determined by comparing the signal intensities of these compounds versus total signal in the sample) of 2-chloroethanol ( $\delta = 3.87$  ppm and 3.65 ppm) and acetaldehyde ( $\delta = 9.77$  ppm,  $\text{CH}_3\text{CHO}$ ; 2.20 ppm,  $\text{CH}_3\text{CHO}$ ) were observed upon decomposition of Cloisite 30B. Since these latter decomposition products were not detected in the respective neat surfactant  $(\text{HE})_2\text{M}_1\text{T}_1^+\text{Cl}^-$ , alternative decomposition mechanisms may be operational for the organoclays. For example, the presence of Lewis basic Si and Al sites may activate the material toward elimination, as illustrated in Scheme 3.

Based on the aforementioned results, the predominant pathway of decomposition for the neat surfactants is  $\text{S}_{\text{N}}2$  attack by the chloride on an available methyl leading to the formation of the respective free amine and chloromethane (and/or benzyl chloride for  $\text{M}_2(\text{HT})_1\text{B}_1^+\text{Cl}^-$ ); all of which were observed as volatile by-products. Notably, at  $250^\circ\text{C}$ , all of the surfactants under investigation are effectively ionic liquids which, due to their high polarities, facilitate  $\text{S}_{\text{N}}2$  reactions [31,32]. The organoclays appeared to have primarily decomposed via similar processes; however, the non-volatile residues of these materials did contain relatively large amounts of terminal olefin (up to  $\sim 5\%$ ) which suggested that other (elimination-type) decomposition mechanisms are involved. These observations were corroborated by results reported by Xie et al. [17], who analyzed the degradation products of organoclays and various surfactants using FTIR and mass spectroscopy and found higher quantities of olefins in decomposed organoclays when compared with decomposed surfactants.

The presence of chlorine in the decomposition products of organoclays indicates that these materials contain chloride ions even after purification by a methanol wash. The likely source of chloride is from the cation exchange reaction by-product, NaCl, not removed by methanol washing. To further explore this issue, organoclays were first washed by methanol to remove excess surfactant and then extracted using a Soxhlet apparatus for 48 h in water in an attempt to remove any remaining NaCl. The residual chloride contents in these as-received and various versions of purified organoclays were determined by titration with mercuric nitrate solution. The results showed a clear trend of decreasing chloride content as the organoclays were subjected to more exhaustive purification protocols. The decomposition products of both the organoclay washed once with methanol and that subjected to further water Soxhlet extraction were characterized by NMR spectroscopy. Experiments were run on 100 mg of each organoclay. For the single methanol washed organoclay, about  $7\ \mu\text{mol}$  of  $\text{ClCH}_3$  and  $0.21\ \mu\text{mol}$  of olefin were detected; for the organoclay subjected to further purification by water Soxhlet extraction, approximately  $4.3\ \mu\text{mol}$  of  $\text{ClCH}_3$  and  $3.6\ \mu\text{mol}$  of olefin were detected. In other words, the amount of  $\text{ClCH}_3$  produced decreased by 38.5%, while the production of olefin increased by nearly 17 times, after the single methanol washed organoclay was further purified by water Soxhlet extraction. This result leads us to believe that if the chloride anions could be completely removed, the degradation pathway via Hoffmann elimination would dominate.



**Scheme 3.** Activation of a hydroxyethyl group with an Al site in an organoclay may facilitate a Hoffmann-type elimination reaction.

Additional support for this supposition stems from a report by Davis et al. who also found that organoclays purified using exhaustive extraction methods degraded mainly via elimination-type processes [29]. The relatively enhanced elimination pathways may be caused by: (1) the presence of Lewis basic aluminates and silicates present in the clay that facilitate Hoffman-type eliminations, (2) the physical structure of the clay which is capable of trapping volatile chloromethane upon production and thus maintaining an equilibrium between chloromethane and the starting material until a non-reversible Hoffman elimination occurs, (3) smaller amounts of chloride present in the clay (compared with neat surfactant) as a result of partially successful purification which ultimately leads to increased chances of elimination, or (4) any combination thereof. Regardless, in all cases, the rate of degradation in the surfactants was found to be much faster in the bulk form than when incorporated into an organoclay (see below).

### 3.2. Effect of temperature on isothermal TGA results

The degradation of the surfactants, in the neat state and on the organoclay, was monitored in all cases by thermogravimetric analysis, TGA, using isothermal runs. It is important to recognize some of the assumptions implicit in interpreting weight loss data as a measure of the extent of reaction in the isothermal mode. The degradation reaction can be written in the following general form:



where we assume there is a volatile by-product whose escape from the sample is a true measure of the extent of reaction. For surfactants, some of these by-products may be rather large molecules or molecular fragments having 18 or more carbon atoms; thus, the volatility of these by-products is an important consideration. Furthermore, loss of these rather large by-products from the galleries of the organoclay may experience some mass transfer resistance. In what follows, we will assume that the mass loss is a reliable indicator of the extent of the reaction. However, it is important to remember that the situation may be more complex. We further assume that the effect of temperature on the reaction and the extent of reaction are separable functions, i.e.,

$$\text{Rate of mass loss} = g(T) \times f(\text{extent of reaction}) \quad (6)$$

where the rate parameter  $g(T)$  is described by an Arrhenius form,

$$g(T) \sim e^{-E/RT} \quad (7)$$

where  $E$  is an activation energy.

Fig. 1 shows weight loss curves versus time for temperatures ranging from  $150^\circ\text{C}$  to  $240^\circ\text{C}$  for two types of as-received organoclays, Cloisite 20A and SCPX 1137. The signals from the TGA have been scaled to represent the weight percent of surfactant originally on the organoclay that remains after time  $t$ ; thus, this is not the mass of the original organoclay remaining. As expected, temperature has a very strong effect on the rate of mass loss or extent of degradation.

Based on Eq. (6), we can take the mass loss at a given time as proportional to the rate parameter,  $g(T)$ , since the extent of reaction is small ( $\sim 16\%$  at most and usually much less) as seen in Fig. 1. If the rate of mass loss follows the same mechanism at all temperatures, simple considerations of reaction kinetics suggest that the activation energy should be constant, i.e., a plot of mass loss for a fixed time versus temperature should be a straight line on Arrhenius coordinates. Fig. 2 shows such plots for percent surfactant mass loss in 10 min as a function of temperature. The data points for both organoclays interestingly fall along relatively straight lines over the temperature from  $190^\circ\text{C}$  to  $240^\circ\text{C}$ , indicating that within this



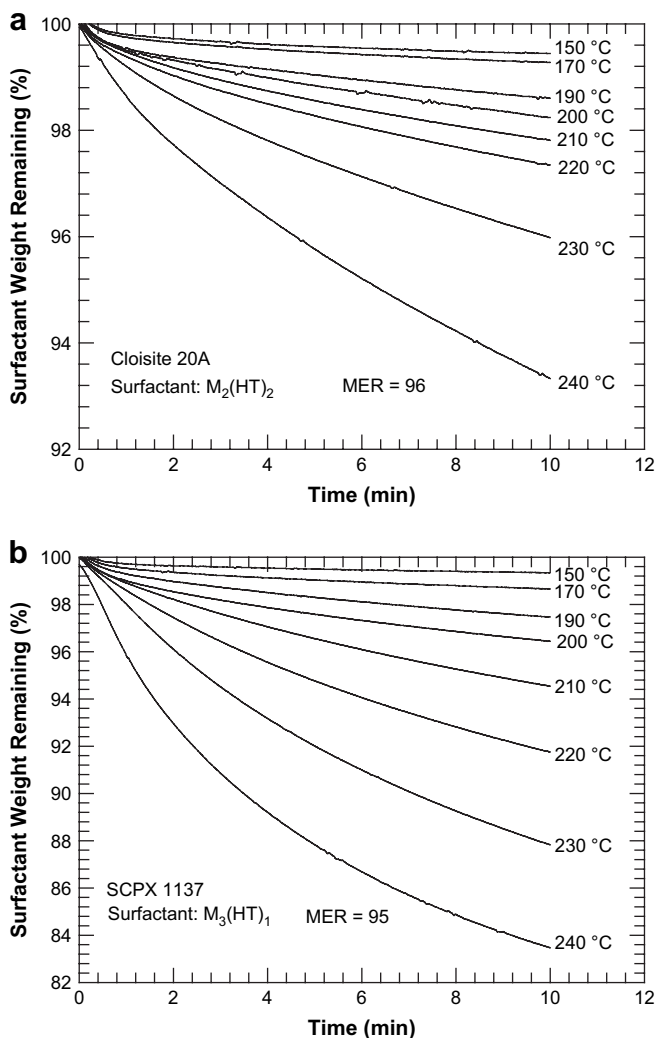


Fig. 1. TGA isothermal tests at various temperatures on organoclays: (a)  $M_2(HT)_2$  and (b)  $M_3(HT)_1$ .

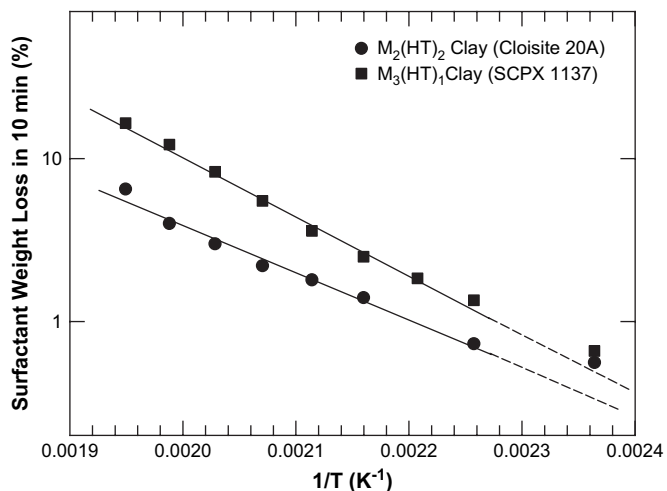


Fig. 2. Relationship between surfactant weight loss in 10 min and temperature of isothermal TGA experiment on Arrhenius coordinates.

temperature range, the organoclay degradation (or mass loss) follows the same mechanism. These results are consistent with the aforementioned NMR studies where thermally induced

decomposition of surfactants and related organoclays were found to afford similar by-products. On the other hand, at temperatures lower than about 170 °C, there appears to be some non-linearity. A number of factors, other than a change in mechanism, may be responsible for this. At these low temperatures, the very small mass losses may be subjected to a relatively large percentage error owing to instrument sensitivity. Although all samples were held at 110 °C until their weight stabilized before the initial zero weight was read, we should note that the volatiles can be extremely difficult to completely remove. Small amounts of residual volatiles would have a much more significant effect at low reaction rates. At these low temperatures, the volatility of the by-products may be inadequate to use mass loss as an accurate indicator of the reaction rate. With the exception of the lowest temperatures, where the data may be compromised for the reasons suggested, the data do follow the simple Arrhenius form surprisingly well. Simple calculations of the activation energies for the degradation reactions from the slope of the linear regression curves show activation energies of 56 kJ/mol for Cloisite 20A and 70 kJ/mol for SCPX 1137.

### 3.3. Effect of organoclay purification method on degradation rate

Selected as-received organoclays were purified by using methanol as the solvent to remove any excess surfactant that may exist in them. The organoclays were purified by both Soxhlet extraction and the washing methods described earlier. The SCPX 1137 organoclay made from  $M_3(HT)_1^+Cl^-$  surfactant was taken as an example to compare the effect of organoclay purification method on degradation rate; other organoclays, such as Cloisite 20A and SCPX 2730, show similar trends. TGA results for purified and as-received SCPX 1137 organoclays are compared in Fig. 3. The first day of Soxhlet extraction or the first methanol wash appears to have substantial effects on the extent of mass loss at 240 °C; however, subsequent washes or longer periods of Soxhlet extraction lead to only slightly different results. Comparing the two purification methods, Soxhlet extraction tends to lead to slightly more thermally stable organoclay, but the differences are not significant. The washing method is more efficient for producing larger amounts of purified organoclay, and since the difference between the two methods of purification is not significant, a single wash with methanol was adopted as the purification method for subsequent studies.

### 3.4. Location of excess surfactant in organoclay

Since some part of the surfactant associated with the as-received organoclay can be removed by solvent washes, it is clear that this excess surfactant is not bound in any way, e.g., ionically to the clay. Hence, where does this excess surfactant reside? Is it inside the clay galleries physically mixed with the bound surfactant, or does it reside external of the galleries, e.g., around the edges of the platelet stacks? To answer this question, several as-received and their corresponding purified organoclays were studied in detail. Based on the ash measurements for each organoclay, the mass ratio of the organic to inorganic components was calculated. X-ray scans were performed on these purified and as-received organoclays to determine the characteristic  $d$ -spacing which represents the sum of the MMT platelet thickness and the gallery height. The  $d$ -spacings obtained from X-ray tests for each organoclay are plotted versus the experimentally determined mass of organic/mass of MMT ratios in Fig. 4, as suggested in prior publications from this laboratory [5,33]. The organoclays with lower organic loadings tend to have lower  $d$ -spacings, and the data points fall onto a single straight line with a  $d$ -spacing intercept of 0.96 nm as the organic content goes to zero; this is the  $d$ -spacing of native dry sodium montmorillonite platelets. Assuming the organic surfactants have similar density, this

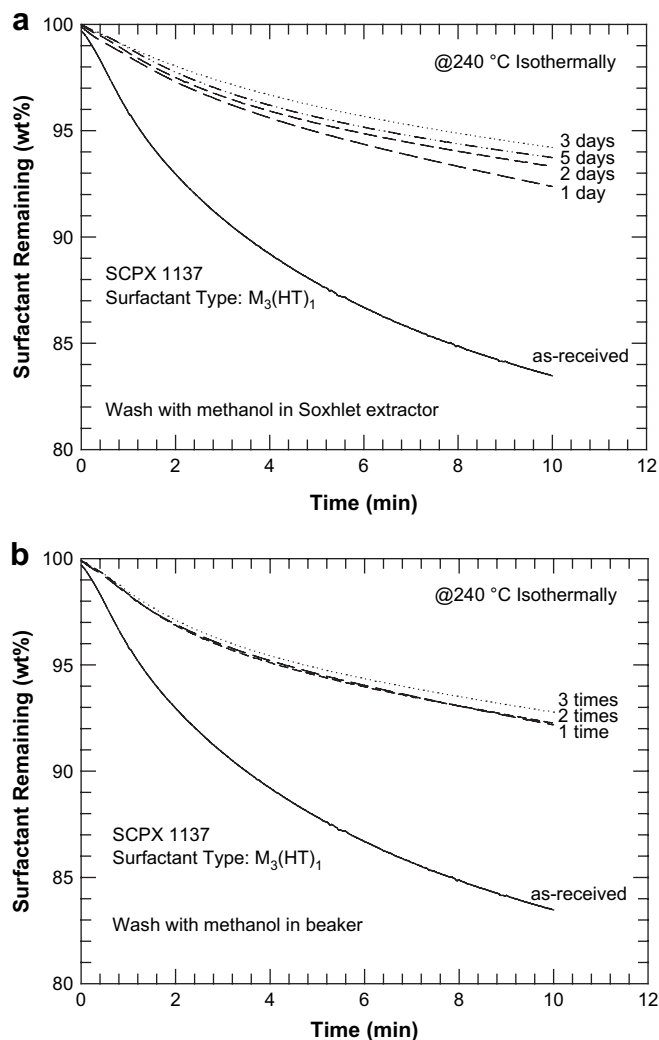


Fig. 3. TGA isothermal tests at 240 °C on as-received and purified  $M_3(\text{HT})_1$  organoclays (SCPX 1137) by (a) Soxhlet extraction and (b) washed in beaker.

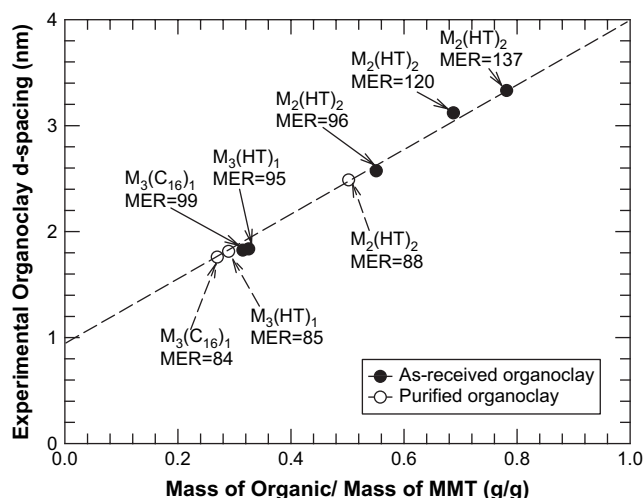


Fig. 4. Relationship between experimentally determined  $d$ -spacing and surfactant loading of organoclays.

result indicates that the unbound surfactant resides in the clay galleries. The rationale behind this type of analysis and plotting of the data has been described previously [5,33].

### 3.5. Effect of MER loading

Commercially available  $M_2(\text{HT})_2$  organoclays, modified by  $M_2(\text{HT})_2\text{Cl}^-$  surfactant, such as Cloisite 20A, Cloisite 15A, and Cloisite 6A, were selected to explore the effect of MER loading on organoclay's thermal stability. For comparison, purified Cloisite 20A and pure  $M_2(\text{HT})_2\text{Cl}^-$  surfactant are also included in this study. The MER of the purified and as-received organoclays were determined experimentally using the ashing method with the results shown in Table 2.

First, it is useful to summarize some facts and assumptions before discussing the data: (1) As-received organoclays include both ionically bound surfactants and unbound free surfactants. The excess surfactant, by necessity, carries with it the counter anion which in the present case is a chloride ion. (2) Purified Cloisite 20A only has ionically bound surfactant. (3) The bound surfactant in as-received organoclays behaves like those in purified Cloisite 20A, while any unbound surfactant in as-received organoclays behaves like the neat surfactant.

Fig. 5(a) shows data from a temperature sweep at a rate of 20 °C/min. Comparing pure surfactant,  $M_2(\text{HT})_2\text{Cl}^-$ , used to form the organoclays with purified Cloisite 20A (MER = 88 mequiv./100 g of clay), we see a large elevation of the decomposition onset temperature for purified Cloisite 20A sample, which suggests that ionically bound surfactants are much more thermally stable than neat surfactant with its associated chloride anions. The as-received organoclays with MER = 96, 120, 137 mequiv./100 g of clay show intermediate behavior.

Isothermal tests at 240 °C are shown in Fig. 5(b). The data are again expressed as the weight percent of the original surfactant in the organoclay remaining rather than that of the total sample weight. Neat surfactant and purified Cloisite 20A define the two extremes of thermal stability, with the purified Cloisite 20A having the least weight loss while the neat surfactant,  $M_2(\text{HT})_2\text{Cl}^-$ , shows the highest extent of mass loss. The rate of surfactant mass loss for the as-received organoclays falls in-between these limits in a sequence of increased MER. Some simple calculations, based on the assumptions described previously, using the following equation, will be helpful to understand why MER becomes a factor in the rate of surfactant mass loss for unpurified organoclays.

$$f(t) = \left(\frac{88}{\text{MER}}\right)f_{\text{poc}}(t) + \left(\frac{\text{MER} - 88}{\text{MER}}\right)f_{\text{surf}}(t) \quad (8)$$

where  $f(t)$  = wt% surfactant remaining at time  $t$  for as-received organoclay,  $f_{\text{poc}}(t)$  = wt% surfactant remaining at time  $t$  for the purified organoclay, and  $f_{\text{surf}}(t)$  = wt% surfactant remaining at time  $t$  for neat surfactant. In this equation, the factor of 88 represents the organic loading of the purified Cloisite 20A, which is assumed to have only ionically attached surfactant cations. The results are shown in Table 2. It is clear that the calculated weight losses of the as-received organoclays in 10 min are fairly close to the experimental data, except at higher initial surfactant loadings, i.e., high MER. It is possible that some unknown impurities in the

Table 2

Comparison of experimental and calculated surfactant remaining after 10 min heating at 240 °C

Organoclay	MER (mequiv./100 g of clay)	Surfactant weight remaining at 10 min (%)		
		Experimental	Calculated	$\Delta$ (cal. – exp.)
Purified Cloisite 20A	88	96.59	–	–
Cloisite 20A	96	93.45	94.91	1.46
Cloisite 15A	120	89.61	91.20	1.59
Cloisite 6A	137	85.72	89.37	3.65
$M_2(\text{HT})_2\text{Cl}^-$ surfactant	–	76.39	–	–

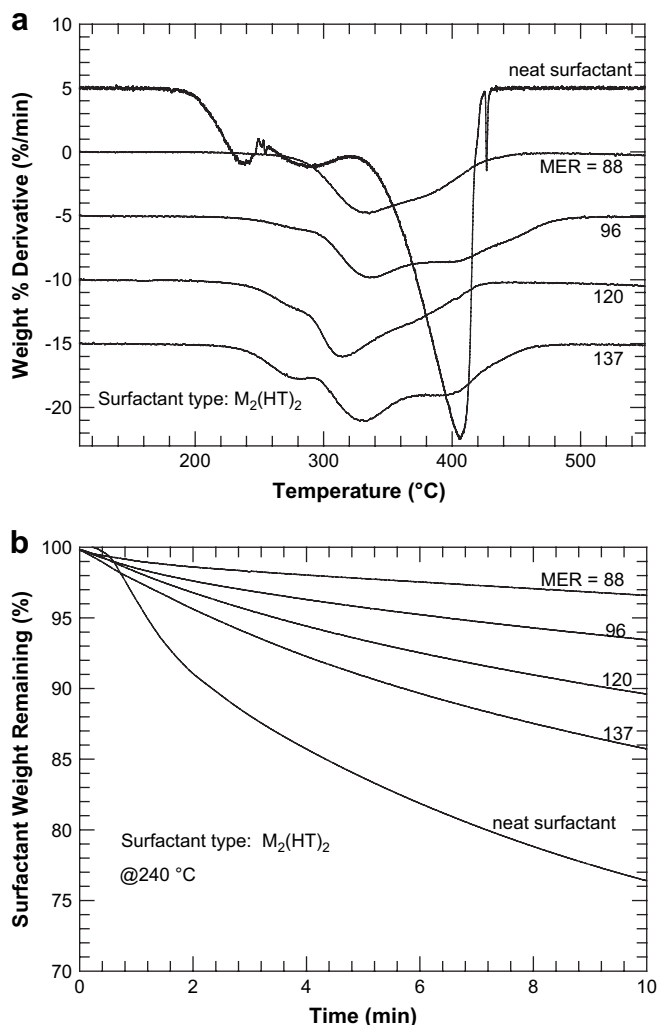


Fig. 5. TGA tests on organoclays (MER = 88, 97, 120, 137 mequiv./100 g of clay) and neat surfactant: (a) temperature sweeps (derivative) and (b) isothermally at 240 °C.

as-received organoclay also facilitate the decomposition of the surfactant.

### 3.6. Effect of various counter ions

It has been reported that the counter anion can often influence the thermal stability of the surfactant; halide salts are often thermally less stable than other anions [34,35]. To examine the effect of various anions, the following experiments were conducted using  $M_2(HT)_2 Cl^-$  and  $M_2(HT)_2 MeSO_4^-$  as the neat surfactants.

TGA tests, both temperature sweeps and isothermal runs, were performed on the two neat surfactants with the results shown in Fig. 6. The differences in thermal stability are quite remarkable. The only difference between the two surfactants is that they have different anions associated with the  $M_2(HT)_2^+$  ammonium cations. Fig. 6(a) shows that the  $MeSO_4^-$  salt is far more stable than the  $Cl^-$  salt. The  $M_2(HT)_2 MeSO_4^-$  surfactant begins to decompose at 300 °C; whereas at this temperature, the  $M_2(HT)_2 Cl^-$  surfactant has already lost about 25% of its weight. Fig. 6(b) offers another obvious proof of their dramatically different thermal behavior. After 30 min at 240 °C,  $M_2(HT)_2 MeSO_4^-$  still retains more than 95% of its initial mass; while the  $M_2(HT)_2 Cl^-$  surfactant has lost more than 30% in weight. These results may be explained by the fact that  $MeSO_4^-$  is a weaker nucleophile than  $Cl^-$ ; the aforementioned NMR studies

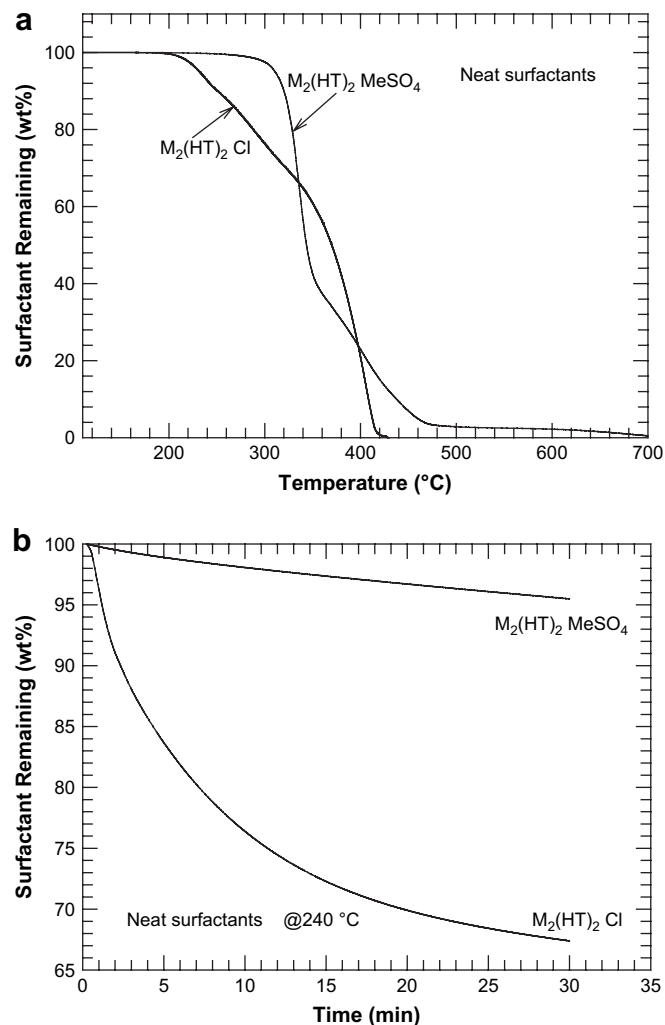


Fig. 6. Comparison of thermal stability of  $M_2(HT)_2 Cl^-$  and  $M_2(HT)_2 MeSO_4^-$  surfactants by TGA: (a) temperature sweeps and (b) isothermally at 240 °C.

revealed that surfactants of this type thermally decompose primarily via nucleophilic substitution.

Considering the dramatic difference in thermal behavior of these two surfactants, it is logical to ask if this difference will translate to organoclays made from these two surfactants. Fig. 7 answers this question in a direct way; organoclays with various surfactant loadings and purification levels are compared. As-received organoclay made from  $M_2(HT)_2 MeSO_4^-$  is more stable than the as-received organoclay made from  $M_2(HT)_2 Cl^-$  if the surfactant loading, or MER, is the same, and the differences between them tend to diminish as their surfactant loading decreases. After the ion exchange to form the organoclay, the original surfactant anions are mostly, but not completely, removed and replaced by the negative charges of the clay platelets. Ideally, so long as the cations of the surfactant are the same, there should not be a difference in the organoclays formed. However, unbound surfactant and the associated chloride anion in the as-received organoclay cause the differences seen in Fig. 7. After removal of the free surfactant and the associated anion, either  $Cl^-$  or  $MeSO_4^-$ , the two organoclays have exactly the same thermal behavior, as shown in Fig. 7. Clearly, the  $M_2(HT)_2 MeSO_4^-$  surfactant is more thermally stable than the  $M_2(HT)_2 Cl^-$  surfactant; while the organoclays formed from the two surfactants have similar thermal behavior once the excess surfactant and the associated anion are removed. There is a dramatic increase in the thermal stability of the surfactant in the organoclay

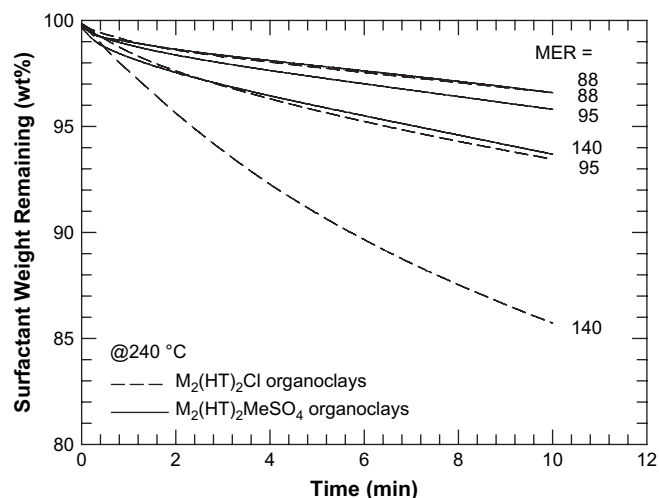


Fig. 7. Comparison of isothermal mass loss for  $M_2(\text{HT})_2\text{Cl}^-$  and  $M_2(\text{HT})_2\text{MeSO}_4^-$  organoclays at 240 °C. Note that the organoclays with MER of 88 mequiv./100 g of clay are the purified version of the corresponding organoclays.

as compared to the chloride salts; the halide anion is a good nucleophile favoring the  $\text{S}_{\text{N}}2$  decomposition of the surfactant. On the other hand, it seems that there is no significant change in thermal stability of the surfactant in the organoclay as compared to the methyl sulfate salt; this can be attributed to the weak nucleophilicity of methyl sulfate anion. The larger weight loss in  $M_2(\text{HT})_2\text{MeSO}_4^-$  organoclay with higher MER is possibly due to the impurities in the as-received organoclay facilitating the decomposition of the surfactant.

### 3.7. Effect of number of long alkyl tails

The thermal stability of three surfactants with different number of alkyl tails and their corresponding organoclays is compared here. Considering that the counter anion can be an important factor that greatly influences the thermal stability as shown above, surfactants with the same anion, i.e., chloride  $\text{Cl}^-$ , were chosen.

Samples were subjected to temperature sweeps as shown in Fig. 8(a). It is very interesting to note that the three surfactants begin to degrade at roughly similar temperatures, while the more the number of alkyl tails on the surfactant, the higher the temperature for the most substantial weight loss. This result is consistent with the mechanism study discussed earlier; all the surfactants decompose mainly via the  $\text{S}_{\text{N}}2$  pathway, and the different volatilities of the various alkyl amine residues explain the differences in the temperature at which their most substantial weight losses occur. Table 3 compares the boiling points of these possible degradation products.

Fig. 8(b) shows isothermal TGA data at 240 °C for the three surfactants studied. Surfactants with fewer alkyl tails tend to lose larger percents of their masses, in the same period of time, compared to surfactants with more alkyl tails. Isothermal plots for the corresponding organoclays, see Fig. 8(c), show similar large differences in mass loss as the neat surfactants, see Fig. 8(b), but on a much smaller scale because of the improved thermal stability of the ionically bound surfactant.

It is worth noting that there is a significant difference in the molecular weight of the three surfactants with various number of alkyl tails as shown in Table 1. Because of this, it is helpful to look at the isothermal mass loss data in other ways. If we only look at the results on a percentage weight loss basis, losing the same mass from a two tail surfactant versus from a one tail surfactant results in nearly half the percent mass change for the two tail surfactant than

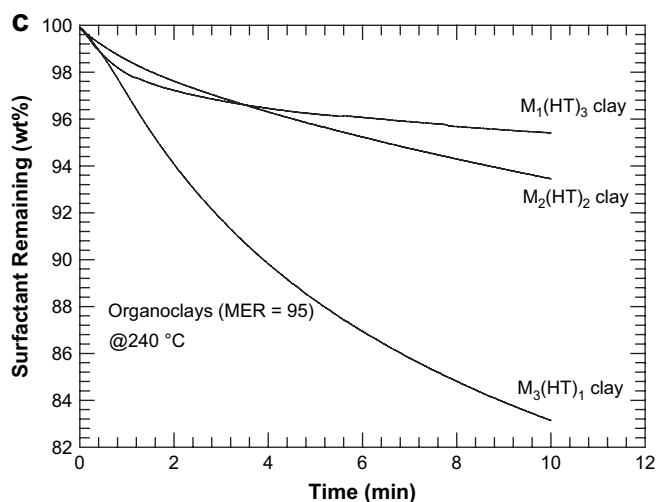
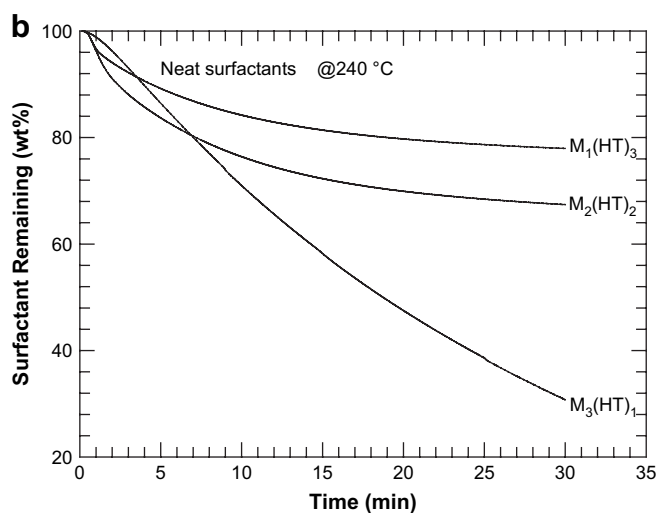
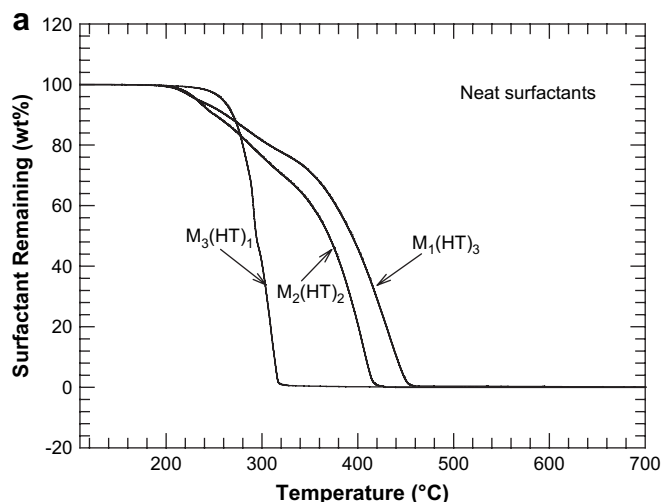


Fig. 8. Comparison of thermal stability by TGA of the three surfactants,  $M_1(\text{HT})_3\text{Cl}^-$ ,  $M_2(\text{HT})_2\text{Cl}^-$ , and  $M_3(\text{HT})_1\text{Cl}^-$ , and corresponding organoclays: (a) temperature sweeps on surfactants, (b) isothermally at 240 °C for surfactants, and (c) isothermally at 240 °C for organoclays.

for the one tail surfactant. As shown in Fig. 8(b) and (c), comparing these surfactants on the weight percentage mass loss basis, there are indeed huge differences among the surfactants. However, if these results are expressed as mass loss per mole of surfactant as



**Table 3**  
Boiling points of degradation products

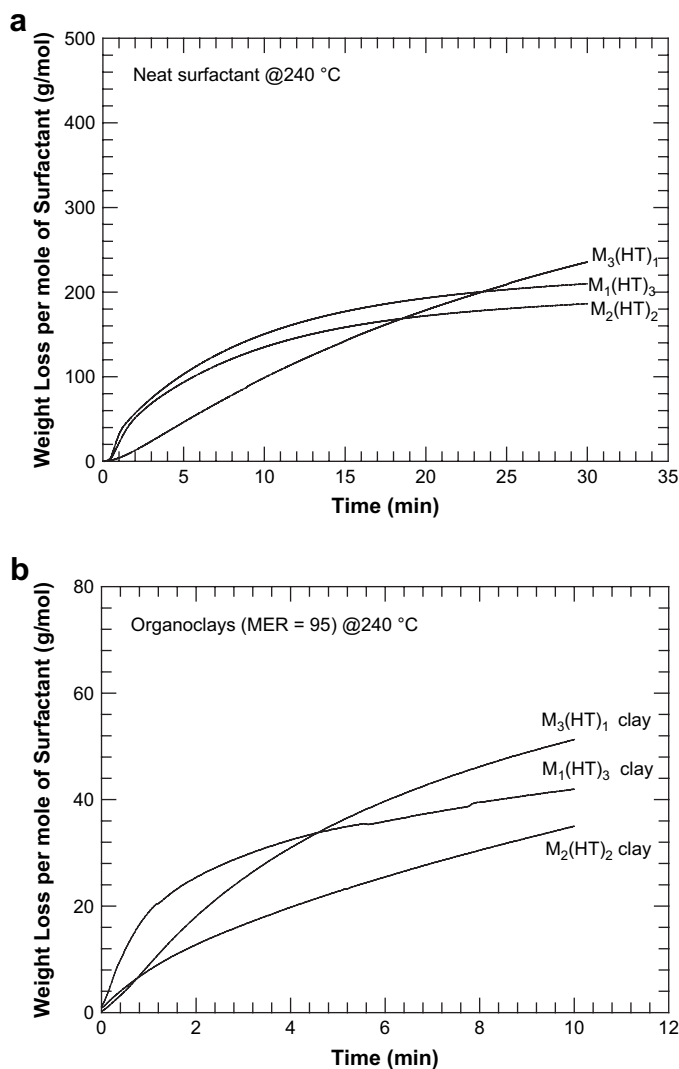
Substance	Boiling point (°C)
CH <sub>3</sub> Cl	-24.2 (at 1 atm)
(CH <sub>3</sub> ) <sub>2</sub> N(C <sub>18</sub> H <sub>37</sub> )	347 (at 1 atm)
(CH <sub>3</sub> )N(C <sub>18</sub> H <sub>37</sub> ) <sub>2</sub>	252 (at 0.05 mmHg)
N(C <sub>18</sub> H <sub>37</sub> ) <sub>3</sub>	-

shown in Fig. 9, the differences become much smaller. When viewed in this way, it appears that the surfactants with different number of alkyl tails have similar thermal stabilities; analogous results are observed for their corresponding organoclays.

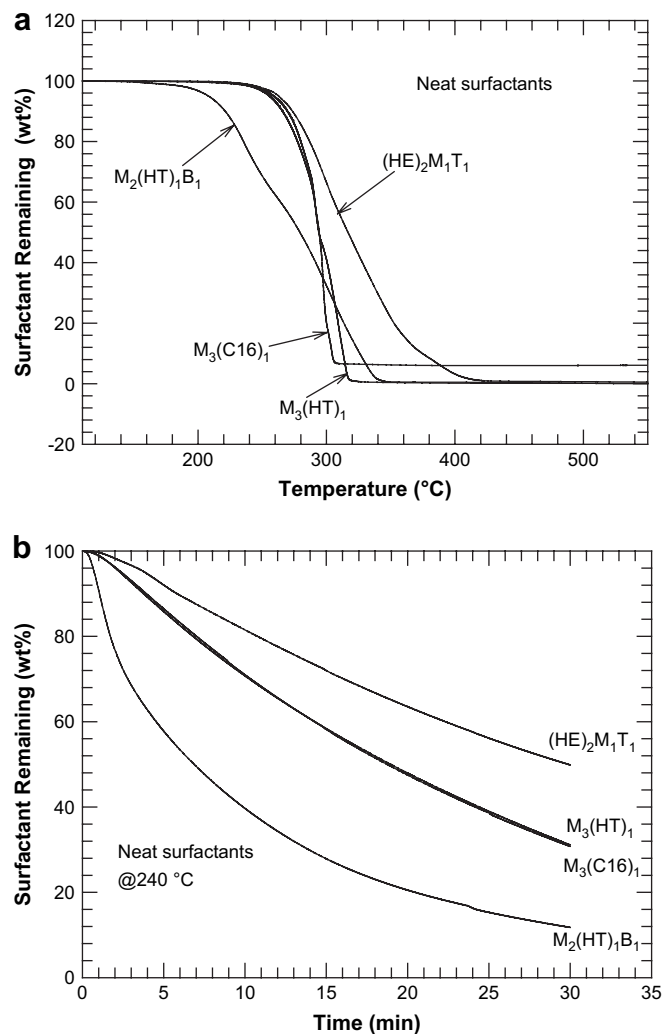
### 3.8. Comparison of organoclays with one long alkyl tail

Here we compare a series of surfactants having a single long alkyl tail: M<sub>3</sub>(HT)<sub>1</sub><sup>+</sup>Cl<sup>-</sup>, M<sub>3</sub>(C16)<sub>1</sub><sup>+</sup>Cl<sup>-</sup>, (HE)<sub>2</sub>M<sub>1</sub>T<sub>1</sub><sup>+</sup>Cl<sup>-</sup>, and M<sub>2</sub>(HT)<sub>1</sub>B<sub>1</sub><sup>+</sup>Cl<sup>-</sup>. Their TGA results are compared in Fig. 10.

The surfactants, M<sub>3</sub>(HT)<sub>1</sub><sup>+</sup>Cl<sup>-</sup> and M<sub>3</sub>(C16)<sub>1</sub><sup>+</sup>Cl<sup>-</sup>, both have one long alkyl tail. The hydrogenated tallow (HT) tail consists of a mixture of primarily of C18 alkyls (65%) and some shorter alkyls,



**Fig. 9.** Comparison of isothermal mass loss of the three surfactants, M<sub>1</sub>(HT)<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, M<sub>2</sub>(HT)<sub>2</sub><sup>+</sup>Cl<sup>-</sup>, and M<sub>3</sub>(HT)<sub>1</sub><sup>+</sup>Cl<sup>-</sup>, and corresponding organoclays on a molar basis: (a) surfactants and (b) organoclays.



**Fig. 10.** Comparison of thermal stability by TGA of various surfactants (M<sub>3</sub>(HT)<sub>1</sub><sup>+</sup>Cl<sup>-</sup>, M<sub>2</sub>(HT)<sub>1</sub>B<sub>1</sub><sup>+</sup>Cl<sup>-</sup>, (HE)<sub>2</sub>M<sub>1</sub>T<sub>1</sub><sup>+</sup>Cl<sup>-</sup>, and M<sub>3</sub>(C16)<sub>1</sub><sup>+</sup>Cl<sup>-</sup>): (a) temperature sweeps and (b) isothermally at 240 °C.

such as C16 and C14, while M<sub>3</sub>(C16)<sub>1</sub><sup>+</sup>Cl<sup>-</sup> contains only C16 alkyls. These two surfactants show quite similar results in both temperature sweep and isothermal tests. Fig. 10 compares M<sub>3</sub>(HT)<sub>1</sub><sup>+</sup>Cl<sup>-</sup> and (HE)<sub>2</sub>M<sub>1</sub>T<sub>1</sub><sup>+</sup>Cl<sup>-</sup> surfactants. Since these tests were run under an atmosphere of nitrogen, the difference between T and HT, saturated and unsaturated, should be negligible since oxidation is not possible. The relevant difference in the structure of these two surfactants is the hydroxyethyl (HE) substituents versus the methyl (M) groups. We see better thermal stability for the (HE)<sub>2</sub>M<sub>1</sub>T<sub>1</sub><sup>+</sup>Cl<sup>-</sup> surfactant than that shown by M<sub>3</sub>(HT)<sub>1</sub><sup>+</sup>Cl<sup>-</sup>. This can be explained by the fewer available methyl groups in the former and the steric hindrance provided by the hydroxyethyl (HE) substituents which protects pendant methyl groups from nucleophilic attack. The M<sub>2</sub>(HT)<sub>1</sub>B<sub>1</sub><sup>+</sup>Cl<sup>-</sup> surfactant is far less thermally stable than the other surfactants. Similar behavior was also reported in the literature [28]; this can be attributed to the presence of the electrophilic benzyl group, which can be easily attacked by the chloride anion. As noted in the NMR studies described above, benzyl chloride was observed in the volatile by-products of thermally degraded, bulk M<sub>2</sub>(HT)<sub>1</sub>B<sub>1</sub><sup>+</sup>Cl<sup>-</sup>.

Results for organoclays formed from these surfactants are shown in Figs. 11 and 12. The isothermal results in Fig. 11 for the four as-received organoclays show similar trends to that of the

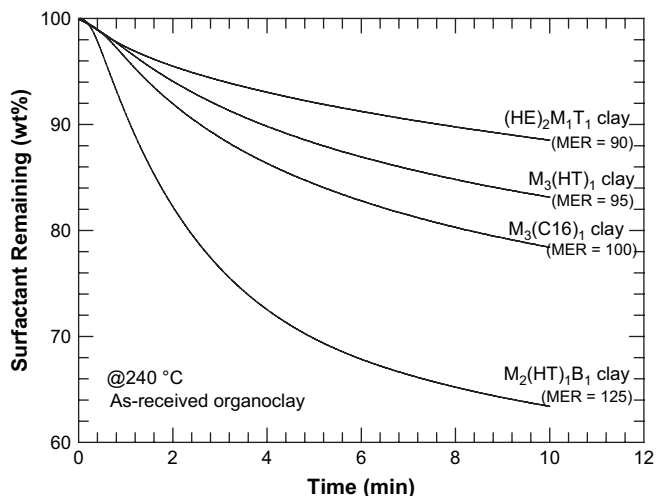


Fig. 11. Comparison of isothermal mass loss of various as-received organoclays ( $M_3(\text{HT})_1$ ,  $M_2(\text{HT})_1\text{B}_1$ ,  $(\text{HE})_2\text{M}_1\text{T}_1$ ,  $M_3(\text{C16})_1$ ) at 240 °C.

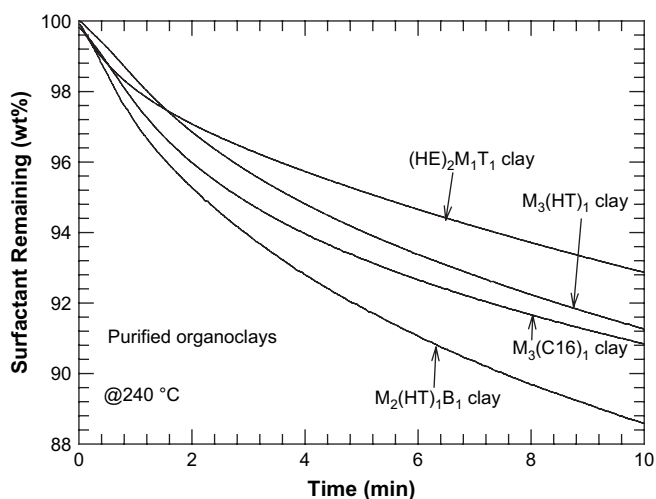


Fig. 12. Comparison of isothermal mass loss of various purified organoclays ( $M_3(\text{HT})_1$ ,  $M_2(\text{HT})_1\text{B}_1$ ,  $(\text{HE})_2\text{M}_1\text{T}_1$ ,  $M_3(\text{C16})_1$ ) at 240 °C.

corresponding surfactants, only on a much smaller scale of mass loss. However, there are some small inconsistencies that, for the most part, can be attributed to the different MERs of the as-received organoclays: the  $M_3(\text{C16})_1$  organoclay had an MER of 100 mequiv./100 g of clay, the  $M_2(\text{HT})_1\text{B}_1$  organoclay had an MER of 125 mequiv./100 g of clay, the MER of the  $(\text{HE})_2\text{M}_1\text{T}_1$  clay was 90, and that of the  $M_3(\text{HT})_1$  clay was 95 mequiv./100 g of clay. Since the free surfactant with its associated  $\text{Cl}^-$  anion is less stable than the surfactant ionically bound to the clay surface, the  $M_3(\text{C16})_1$  and  $M_2(\text{HT})_1\text{B}_1$  organoclays show more unstable behavior than expected based on the trends shown by the neat surfactants. It is helpful to remove the excess surfactant in the as-received organoclays by washing with methanol solvent to simplify the problem. The purified organoclays are compared in Fig. 12; these results show analogous trends as the corresponding neat surfactants, but the extent of degradation is less for the organoclays than for the neat surfactants.

#### 4. Conclusions

The thermal degradation of organoclays made from various surfactants was studied by NMR spectroscopy and

thermogravimetric analysis. The NMR data suggests that these surfactants and organoclays decompose primarily via nucleophilic attack of chloride anions; however, if the residual chloride anions could be completely removed from the organoclay, we believe the primary degradation pathway would switch to an elimination-type mechanism. Furthermore, a simple Arrhenius analysis of isothermal degradation results suggested to us that the degradation mechanism is the same as temperature is varied from 240 °C to 170 °C and possibly lower. Most as-received organoclays contain excess surfactant, as well as the ionically attached surfactants, which resides in the clay galleries. Washing the organoclay with methanol proved to be an effective way to remove the excess surfactant from the clay galleries, but not the by-product NaCl of the ion-exchange process. Such purification generally improves the thermal stability of the as-received organoclays. Ionically bound surfactants are more thermally stable than the neat surfactant associated with  $\text{Cl}^-$  anion. The free surfactants in the organoclay degrade at rates similar to the neat surfactants used to form the corresponding organoclay. The anions associated with the ammonium cations play a significant role in the thermal stability of the surfactant salts and the surfactants in organoclay; anions which are weaker nucleophiles (i.e.,  $\text{MeSO}_4^-$ ) can result in a much more thermally stable surfactant. Surfactants and organoclays with various number of alkyl tails have similar thermal stabilities. It is worth noting that caution needs to be exercised when interpreting isothermal percentage mass loss data of samples with significant different molecular weights; a similar extent of degradation may lead to much smaller in percentage mass loss for the sample with significantly higher molecular weight. Finally, the substituents on the ammonium cations may also influence the thermal stability of neat surfactants as well as organoclays which contain them. In general, our results suggest that methyl and benzyl groups in these materials are susceptible to nucleophilic attack at elevated temperatures by the halide anions. Depending on the availability of residual halide anions in the organoclay, the organoclays decompose via either  $\text{S}_{\text{N}}2$  nucleophilic substitution or Hoffmann elimination.

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