2003

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Acosta, Erick J.; Deng, Youjun; White, G. Norman; Dixon, Joe B.; McInnes, Kevin J.; Senseman, Scott A.; Frantzen, Alyx S.; and Simanek, Eric E., "Dendritic Surfactants Show Evidence for Frustrated Intercalation: A New Organoclay Morphology" (2003). *Faculty Publications*. 33.  
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Dendritic Surfactants Show Evidence for Frustrated Intercalation: A New Organoclay Morphology

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Received February 19, 2003. Revised Manuscript Received May 9, 2003

Mixing a smectite clay with some dendritic surfactants shows that despite the large size of some of these molecules, a property that frustrates complete intercalation into the gallery of the clay, organoclay materials are obtained. X-ray powder diffraction (XPD) reveals no significant increases in lattice spacing as these surfactants are added. Infrared (IR) spectroscopy and thermal gravimetric analysis (TGA) show that interlayer water is preserved. Consistent with an undisturbed interlayer, the amount of organic material in organoclay derived from frustrated surfactants does not exceed 15% of the cationic exchange capacity (CEC) of the composite. Smaller dendritic surfactants do not display frustrated intercalation and instead readily enter into the gallery of the smectic clay yielding traditional organoclay materials. A range of organic compositions (5–50% w/w) that exceed the CEC of the materials are observed. The organic content is corroborated by UV spectroscopy and TGA. XPD reveals increasing lattice spacings with increasing organic content. IR spectroscopy and TGA support an increasingly hydrophobic interlayer. A linear isomer of a frustrated surfactant can intercalate into the gallery (5–33% w/w) yielding morphologies that depend on the amount of surfactant added. These results support the hypothesis that shape, and not only size, is important for producing frustrated intercalation.

Introduction

The structure of the organic component has a profound effect on the morphology of the resulting organoclay material. Ordered monolayers and bilayers have been observed in organoclay derived from aliphatic alcohols and amines.1 Polymers show evidence for serpentine intercalation of the linear polymer chain, leading to extended or collapsed structures that transist the interlayer.2,3 Formation of these organoclay composites is facilitated through attractive interactions between the clay (or its absorbed cations) and the organic additive. The paradigm for interactions between small molecules and clay is the exchange of alkylammonium ions with clay presumably is mediated through the cation or other polar functional groups (i.e., alcohols) are also obtained, although the anchoring interaction with the clay presumably is mediated through the cation or available water molecules. Polymer–day interactions depend on the nature of the polymer. Polar, linear polymers including poly(ethylene oxide)4,5 or nylon6 can provide polar groups to interact with the cation. To incorporate hydrophobic polymers based on styrene and its derivatives7,8 or poly(dimethylsiloxane)9 into the gallery of the clays, the clays are treated first with a hydrophobic surfactant to facilitate interactions with the day through the surfactant molecule. These surfactants can play an additional role, that of a curing agent.10

Branched surfactants including dendrimers11–13 (or constituents thereof) offer an interesting energetic challenge to the formation of organoclay composites. A dendritic surfactant bearing a cationic anchor could favorably participate in cation exchange, but the inability of dendrimers to pack together in ordered arrays facilitates through attractive interactions between the clay and its derivatives,7,8 or poly(dimethylsiloxane)9 into the gallery of the clays, the clays are treated first with a hydrophobic surfactant to facilitate interactions with the clay through the surfactant molecule. These surfactants can play an additional role, that of a curing agent.10

Branched surfactants including dendrimers11–13 (or constituents thereof) offer an interesting energetic challenge to the formation of organoclay composites. A dendritic surfactant bearing a cationic anchor could favorably participate in cation exchange, but the inability of dendrimers to pack together in ordered arrays facilitate interactions with the clay through the surfactant molecule.

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Published on Web 07/08/2003

10.1021/cm0302328 CCC: $25.00 © 2003 American Chemical Society
infinite interlayer spacings (ILSs; exfoliation), a finding that globular polymers show a global minimum favoring interactions with clay while multi-armed polymers show a local minimum corresponding to an idealized structure. When the interaction between the star and clay is unfavorable, linear polymers show a local minimum corresponding to an idealized structure. Instead, an energetic compromise could be reached wherein the cationic group anchors the dendron to the clay surface and the gallery of the clay is left unmodified. We describe such a morphology as frustrated intercalation (Scheme 1). This morphology should be characterized by (i) a reduced organic content in the organodendrimer (in comparison to small-molecule surfactants), (ii) a reasonably hydrophilic interlayer, and (iii) a small interlayer spacing.

Dendrimer–clay interactions have attracted only limited experimental and computational attention. Månson and coworkers mixed three generations of dendrimers based on bis(hydroxymethyl)propanoic acid (BHP; Perstorp, Sweden) with sodium montmorillonite (Scheme 1). This study describes the exploration of four dendritic surfactants based on triazines interconnected with diamines (Chart 1). These surfactants differ in size from generation one, G1, to generation three, G3, with molecular weights ranging from 526 to 2282 g/mol. Two second-generation surfactants, a dendritic G2 and a linear G2L, are isomers with identical molecular weights (1112 g/mol) to allow us to evaluate size and shape effects. These molecules are slightly different than those reported by Månson or Balazs in that they are neither star polymers nor dendrimers. Additionally, these molecules presumably interact with the clay differently. That is, the surfactants described here can participate in a single cationic exchange reaction while the BHP dendrimers are limited to the potential for multivalent interactions between the polar hydroxyl groups and the clay surface.

**Experimental Section**

**Clay Preparation.** The smectite clay is a bentonite powder obtained from Southern Clay Products, Gonzalez, TX (CEC = 81.2 mequiv/100 g of clay). The clay is treated with dithionite–bicarbonate to remove iron oxides, with hydrogen peroxide to eliminate residual organic material, and then with sodium acetate to remove the carbonate minerals. Procedure: 25 g of clay powder is transferred to a 250 mL Nalgene centrifuge tube and mixed with 100 mL of a 1 M sodium acetate solution. The mixtures are heated to 90 °C in a water bath and occasionally stirred. After 1 h, the sample is centrifuged at 2000 rpm for 5 min and the supernatant is decanted. This treatment is repeated twice to make sure the sample is free from carbonate minerals. The sediment in the centrifuge tube is washed once with 1 M sodium chloride and subsequently washed several times with a solution of 0.15 g/L of pH 10 sodium carbonate to remove the excess sodium acetate. Then, the sample is passed through a 325 mesh sieve to separate the sand fraction (> 50 μm). The remaining clay and silt mixture is transferred to a 250 mL centrifuge tube and the height of the suspension adjusted to 10 cm with the

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**Scheme 1. Morphologies of Organoclay Composites**

<table>
<thead>
<tr>
<th>Ordered Monolayer</th>
<th>Ordered Bilayer</th>
<th>Serpentinite Penetration</th>
<th>Frustrated Intercalation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="https://example.com/scheme1.png" alt="Image" /></td>
<td><img src="https://example.com/scheme1.png" alt="Image" /></td>
<td><img src="https://example.com/scheme1.png" alt="Image" /></td>
<td><img src="https://example.com/scheme1.png" alt="Image" /></td>
</tr>
</tbody>
</table>

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A New Organoclay Morphology

**Organoclay Preparation.** A series of organoclay composites containing different weight percents of dendritic surfactant were prepared for each dendrimer generation. First, clay suspensions were prepared by adding 20 mL of distilled water to 500 mg of Ca²⁺-saturated clay. To these suspensions was added dropwise 5 mL of a surfactant solution. For the G₁ dendrimer—day materials, solutions containing 25, 50, 100, 150, 200, 250, and 500 mg of the dendrimer in acetone were used to prepare seven different formulations. For the G₂ and G₃ dendrimer—day materials, six formulations of each were prepared by adding 25, 50, 100, 150, 200, and 250 mg of the dendrimer in acetone to be used to prepare seven different formulations. For the G₂, G₂L, and G₃ dendrimer—day materials, six formulations of each were prepared by adding 25, 50, 100, 150, 200, and 250 mg of the dendrimers dissolved in tetrahydrofuran (THF) to the day suspensions. Both organic solvents are completely miscible with water. The organoclay suspensions are incubated, while shaking, for at least 16 h. The organoclay composite is separated by centrifugation and rinsed with water twice to remove any excess of surfactant. The solid materials are vacuum-dried and ground for IR or XPD analysis.

**Dendritic Surfactants.** The three generations (G₁–G₃) of dendritic surfactants explored compromise hydrophobic tert-octyl groups, triazine rings, and a primary amine to anchor the surfactant to the clay. Scheme 2 shows the synthesis of the melamine-based dendritic surfactants using the convergent method. Surfactant G₁ is prepared in two steps in 76% overall yield. Surfactants G₂ and G₃ are available in four and six steps in 47% and 23% overall yield, respectively. The linear analogue of G₂, G₂L, is prepared in four steps in 30% overall yield. Synthesis and characterization data for G₁, G₂, G₂L, G₃, and 1–6 are described in the following paragraphs.
Intermediate 1. Cyanuric chloride (20 g, 109 mmol) is dissolved in 200 mL of THF and cooled to 0 °C. tert-Octylamine (100 mL, 620 mmol) in THF is added dropwise over 30 min. The reaction is stirred for 4 h at 25 °C. The precipitate is removed by filtration. The filtrate is concentrated, and the resulting material is precipitated with cold methanol. The pure product is of 48.0% and 49.8% organic content when analyzed by TGA analysis in the fifth section. Attempts to calculate the amount of organic surfactant that was removed from the aqueous phase by the clay was measured (by subtraction) using UV–vis spectroscopy and a calibration curve. After washing and drying of the organoclay composite, the amount of organic material was measured using thermal gravimetric analysis (TGA). Both techniques were in excellent agreement (vida infra). The ILS was calculated by X-ray diffraction using a powder diffractometer [Bruker D8, 6°/min, Mo Kα source (0.71 Å)]. IR spectra (4021 Galaxy Series FT-IR) were recorded using KBr pellets after grinding of the sample.

Results and Discussion

The discussion of the organoclay derived from these four surfactants is divided into seven sections. First, our nomenclature for these materials is introduced. Second, a comparison of the X-ray diffraction data derived from the G1 surfactant, a molecule that behaves like a typical alkylammonium ion, is made with the data derived from the G2 and G3 surfactants that show that these dendritic surfactants do not appreciably change the ILS. In the third section, organoclays comprising G2L are introduced to dissect the role of size and shape. Fourth, the analysis of these materials by infrared spectroscopy is presented, which shows that interlayer water is retained for G2 and G3 materials but is absent in G1 and G2L organoclays. This observation is corroborated by TGA analysis in the fifth section. Attempts to characterize these materials by transmission electron microscopy (TEM) are described in the sixth section. In the final section, we introduce a model to explain the intercalation behavior of the four surfactants.

Surfactant-Dependent Relative Compositions

The organoclay composite derived from the respective surfactants are named for the relative amount of organic material in the composite. Table 1 identifies these composites and shows the amount of surfactant as determined by both UV–vis spectroscopy and TGA. For example, when 100 mg of G1 is mixed with 100 mg of clay, the resulting composite name G1-50 appears to be of 48.0% and 49.8% organic content when analyzed by TGA and UV–vis analysis (Subtractive).

Table 1. Percentage of Organic Material in Organoclay Composites from the G1 Surfactant from TGA and UV–Vis Analysis (Subtractive) of the Solution from Which the Composites Are Prepared

<table>
<thead>
<tr>
<th>Name</th>
<th>TGA analysis (% organic)</th>
<th>UV–vis analysis (% organic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1-5</td>
<td>5.3</td>
<td>4.6</td>
</tr>
<tr>
<td>G1-10</td>
<td>9.2</td>
<td>9.0</td>
</tr>
<tr>
<td>G1-17</td>
<td>15.7</td>
<td>16.6</td>
</tr>
<tr>
<td>G1-23</td>
<td>20.2</td>
<td>22.6</td>
</tr>
<tr>
<td>G1-29</td>
<td>28.6</td>
<td>28.3</td>
</tr>
<tr>
<td>G1-33</td>
<td>31.2</td>
<td>32.7</td>
</tr>
<tr>
<td>G1-50</td>
<td>48.0</td>
<td>49.8</td>
</tr>
</tbody>
</table>
Evidence for Frustrated Intercalation from the ILS. X-ray powder diffraction (XPD) confirms that, as \(G_1\) is added to the clay, the ILS increases (Figure 1), as is expected in traditional small organic surfactants. The ILS of the untreated calcium-smectite clay is 1.47 nm. Upon addition of \(G_1\), the ILS increases to 1.57 nm. At medium concentrations (23–33%) of \(G_1\), the ILS increases to 3.00 nm. This concentration of organic material corresponds to the CEC of the clay. At high concentrations (50%) of \(G_1\), the ILS shifts again to 3.64 nm.

In contrast to \(G_1\) surfactants that appear to form a range of morphologies, the XPD traces of materials derived from \(G_2\) and \(G_3\) show only a nominal increase in ILS to 1.57 nm, consistent with reduced loadings of these surfactants (Figure 2). It is unlikely that these large but conformationally flexible \(G_2\) and \(G_3\) molecules could penetrate the interlayer and remain in an extended, flat conformation, but this cannot be proven from XPD data. Instead, we favor frustrated intercalation wherein these molecules are confined to the surface of these materials.

The Role of Shape. To better evaluate the role of shape in these composites, a linear isomer of \(G_2\), \(G_2L\), was prepared and evaluated. As with \(G_1\), \(G_2L\) shows a linear correlation between the amount of surfactant added (5–33%) to a solution of clay and the amount of surfactant incorporated as determined by TGA. These values differ greatly from the dendritic molecule \(G_2\): organoclay loads are limited to 12% organic content. XPD traces are consistent with the appearance of a new morphology at high loadings of \(G_2L\) when the organic content exceeds 17% (w/w). While the predominant morphology appears to be monolayer adsorption showing an ILS of 1.5 nm over the entire range, at higher loadings of surfactant, an intermediate ILS of 2.3 nm and a final (but poorly resolved because of limitations of the instrument) ILS of 4.6–5.2 nm are observed for \(G_2L-33\). This distance corresponds to the fully extended dimensions of the linear surfactant calculated to be \(\sim 3.6\) nm.

Evidence for Frustrated Intercalation from Interlayer Water: IR Spectroscopy. At ambient temperature and humidity, water is present in the interlayer of the clay. Bare clay shows two characteristic water bands (Figure 3): tightly bound interlayer water appears at \(\sim 1635\) cm\(^{-1}\) in the bare clay, and a broader O–H absorption band appears around 3300 cm\(^{-1}\). Water loss can occur when cationic surfactants displace the exchangeable inorganic cations and their associated water molecules. The surfactant shows two characteristic aromatic stretches at 1514 and 1574 cm\(^{-1}\) as well as in the aliphatic C–H region at \(\sim 2950\) cm\(^{-1}\). These stretches appear in the organoclays as well. IR features at both 1635 and 3300 cm\(^{-1}\) are notably reduced in \(G_1-33\) and \(G_2L-33\) as the organic molecules displace molecules of water from the interlayer. For molecules displaying frustrated intercalation, the interlayer water should be preserved. Indeed, the stretch for tightly bound water at 1635 cm\(^{-1}\) for \(G_2L-12\) appears to be more

![Figure 1. XPD of the \(G_1\) organoclay composites.](image1)

![Figure 2. XPD of the \(G_2\), \(G_3\), and \(G_2L\) organoclay composites.](image2)
dominant than the aromatic stretches. This band also appears as a significant shoulder for G3-20.

Evidence for Frustrated Intercalation from Interlayer Water: TGA. TGA confirms the data from IR spectroscopy. Across the entire range of organoclay morphologies derived from G1, TGA reveals that, as the amount of surfactant is increased, the amount of water present in the interlayer (as revealed by the thermal transitions below 150 °C) is greatly reduced (Figure 4). A similar trend is observed for G2L. On the contrary, molecules showing frustrated intercalation do not show appreciable water loss.

Microscopy Is Inconclusive. We attempted to characterize the ILS that resulted from the addition of G1 surfactant by TEM, but such investigations proved unsatisfying beyond establishing the integrity of the composite. Fringes were observed in these samples, suggesting that the clay retains its flexibility, but these fringes did not provide a spacing that was consistent with the XPD data (3.6 nm): the TEM image from G1-33 shows fringes ranging from 1 to 2 nm. We cannot distinguish between heterogeneity in the sample or localized destruction of the morphology during the course of the experiment. TGA reveals that the surfactant is lost sharply over a temperature range of 175-200 °C, values consistent with estimations of the local temperature due to electron bombardment.

Our Conceptual Model. Based on the data from XPD, TGA, and IR and the dimensions of the surfactants, our conceptual model for intercalation is shown in Scheme 3. As increasing amounts of G1 are added, the clay interlayer separates to form three different morphologies: (i) surfactant lying flat on the surface of the clay or extending from the interlayer; (ii) a semi-ordered mono- or bilayer in which the hydrophobic groups aggregate away from the hydrophilic clay surface; (iii) a more ordered layered structure resulting from a fully extended surfactant. The surfactant is approximately 2.4 nm when fully extended. These values are consistent with those of the proposed model. For G2 and G3, however, the predominant morphology, frustrated intercalation, is shown in part iv with the dendritic portion extending into the solvent. A model similar to G1 can be applied to G2L (v). These models are now the focus of computational investigations that will be reported in due course.

Conclusions

The organoclay architectures reported here are notably different than the traditional monolayer, bilayer, and paraffinlike structures first described beginning more than 50 years ago.1 The data presented here—small lattice spacings, a hydrophilic gallery, linear versus branched isomer comparison—is consistent for a new morphology of organoclay composites in which a large branching group attached to a linear anchor precludes complete intercalation of the organic component into the interlayer gallery. We describe this morphology as “frustrated intercalation”.

Interestingly, a morphology similar to this one has been hypothesized in a linear polycation wherein complete penetration is precluded enthalpically. As the polycation reptates into the interlayer, increasing numbers of clay–polycation interactions increasingly retard penetration to the limit where much of the polycation remains accumulated at the surface, with portions of the molecule freely interacting with solution. In these systems surface coverage rarely exceeds 50%.20 Frus-

Trated intercalation may produce similar effects but by a different mechanism. In frustrated intercalation, failure to completely intercalate in this gallery is the result of shape and not the result of multivalent anchoring of the surfactant to the clay surface. The role of steric and shape in these architectures is further supported by the preparation and examination of the linear analogue G2L, a molecule that enters the interlayer, increases lattice spacing, and decreases the amount of bound water. In both morphologies, the organic component remains on the surface of the clay particle.

Definitively establishing morphologies for organoclay composites not only is challenging but relies on the accumulation of inference from a variety of systems.

Additional studies will be required to evaluate whether this type of morphology is general and whether our conceptual model is accurate. Computational and experimental studies are currently underway. We find these architectures intriguing: they should allow for the surface of a clay particle to be selectively tailored without sacrificing surfactant to the interlayer.

**Acknowledgment.** This work was supported by the Welch Foundation (A-1430) and the USDA-CSREES 2002-35102-12504.

CM0302328