A Small-Angle Neutron Scattering Study of a Commercial Organoclay Dispersion

H. J. M. Hanley and C. D. Muzny*

Physical and Chemical Properties Division, National Institute of Standards and Technology, Boulder, Colorado 80305

D. L. Ho and C. J. Glinka

NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899

Received August 1, 2002. In Final Form: April 4, 2003

The paper explores the capacity of small angle neutron scattering (SANS) to characterize the dispersion of an exchanged clay in an organic solvent. As an illustration, results are reported for 1% and 2% by mass suspensions of a representative commercial complex, known as Cloisite, C15A in toluene. C15A is prepared from montmorillonite and the cation ditallow (a naturally occurring variant of dimethyldioctadecylammonium). For this particular example, the SANS scattered intensity data suggest that the complex is well dispersed into clusters which consist of a stack of between three and six ditallow-coated montmorillonite platelets. The size of the clusters, the amount of ditallow adsorbed on a montmorillonite platelet, and an estimate of the thickness of the adsorbed layer are evaluated. General comments on the fitting of SANS data obtained from a cluster composed of stacked, coated disks are given.

Introduction

A typical polymer/clay nanocomposite encapsulates an organoclay in a polymerized medium.1 In most cases, the organoclays are complexes prepared by exchanging the metal cations on the platelet surface of a base clay mineral with an organic cationic surfactant, and it is well-known that the mechanical and thermal characteristics of the polymerized nanocomposite are optimal when this cation exchange took place over the largest possible clay surface area. Ideally, then, the clay mineral should be separated into its constituent platelets in the nanocomposite precursor state. The object of this paper is to investigate how well the technique of small-angle neutron scattering (SANS) can probe this separation.

For a case study, we selected the commercial complex known as Cloisite (designated C15A) as a typical exchanged clay. Cloisite is formed from montmorillonite and the cation ditallow, a natural variant of dimethyldioctadecylammonium. Toluene was selected as a typical precursor medium. The SANS procedure discussed here, in conjunction with dynamic light scattering and wide-angle X-ray experiments, follows the pattern Hanley et al. introduced to investigate clay complexes in aqueous solvents2 and the very recent work of Ho et al. who have investigated solution extracted C15A in various organic solvents.3 We note in passing that while several authors2,4–6 have applied SANS to investigate clay complexes in aqueous solvents, SANS investigations on exchanged clays and their subsequent polymerization into organic-based systems are very scarce.

Experimental Section

Materials. The clay materials used in this work were C15A and the sodium montmorillonite base, here designated CNa+. Materials C15A and CNa+ are commercial products provided to us as powders by Southern Clay Products, Inc. (Commercial names are used to identify the materials so that the experiments can be repeated if necessary. Their endorsement by NIST is not implied.) The supplier synthesized C15A by exchanging the sodium ions of CNa+ with 125 mequiv/100 g of the ditallow. The ditallow itself is a mixture of dimethylammonium surfactants with various carbon chain lengths: C14 (65%), C16 (30%), and C18 (5%). Since the cation exchange capacity (CEC) of CNa+ is estimated to be 92 mequiv/100 g, the surface of C15A is covered to about 130% of one CEC layer.

A nominal 1% by mass suspension of CNa+ was made up by adding the commercial powder to distilled water and stirring vigorously for 3 h, sonicating for 20 min, and lightly centrifuging for 5 min. This suspension was then diluted to give two other samples of nominal 0.5% and 0.1% by mass.

Mass suspensions (1% and 2%) of C15A in toluene were prepared following the simple procedure recommended by the supplier. For the 2% suspension: 1 g of C15A was added to 57.7 mL of toluene, and the solution stirred for 30 min in a flask. At this point a small amount of methanol, equivalent to 30% by mass of the clay content (i.e., 0.379 mL), and 0.2 mL of water were added. The mixture was then stirred vigorously with a magnetic stir bar for 45 min, followed by centrifugation for 15 min at 13,000 rpm. For the 1% suspension: 0.5 g of C15A was added to 11.5 mL of toluene; the mixture was then stirred vigorously with a magnetic stir bar for 45 min, followed by centrifugation for 15 min at 13,000 rpm. In both cases, the supernatant was decanted into a 10 mL graduated glass vial.

10.1021/la026342v This article is not subject to U.S. Copyright. Published 2003 by the American Chemical Society.

* To whom all correspondence should be addressed. E-mail: chris.muzny@nist.gov.
were added. The mixture was stirred for an additional 30 min, centrifuged, and sonicated briefly. The final sample was viscous and clear and stable for several weeks with no significant settling. The 1% suspension was made up by direct weighing in a similar manner. In addition, as will be discussed, contrast matching SANS experiments were carried out with the C15A samples prepared as described above, but in deuterated/protonated (d/h)-toluene.

**Neutron Scattering.** Neutron scattering intensities from the CN1+ clay and the C15A complex suspensions were extracted from the appropriate samples loaded in 1 mm gap thickness quartz cells at room temperature. The cells were placed in the beam of the 30 m N7.5 SANS instrument at the National Institute of Standards and Technology Center for Neutron Research. N7.5 was bilaterally fitted with an incident neutron wavelength \( \lambda = 0.6 \) nm and sample–detector distances of 1.2, 5.0, and 15.3 m to give a scattering wavevector range 0.02 < q nm\(^{-1} \) < 1.2. Here q = |q| and q = 4\( \pi \) sin(\( \theta /2 \))/\( \lambda \), with \( \lambda \) the incident neutron wavelength and \( \theta \) the scattering angle. Scattered neutrons were detected on the instruments 2D position sensitive detector. Because all measured scattering patterns were isotropic, the measured counts were azimuthally averaged. These averaged data were corrected for empty cell and solvent scattering and were placed on an absolute scale by normalizing to the intensity obtained from a water standard.\(^7\)

**Other.** Standard autocorrelation spectroscopy dynamic light scattering (DLS) measurements\(^8\) were carried out with an He–Ne laser (\( \lambda = 632.8 \) nm) at multiple scattering angles from 20° to 130°. Samples were loaded into 25 mm diameter light scattering vials and thermostated to 25 °C. Log–time autocorrelated data were analyzed by the CONTIN routine.\(^9\)

Wide-angle X-ray (WAX) scattering measurements were performed at room temperature on both dry samples and suspensions over a range 0.71 < q nm\(^{-1} \) < 10.65 using Ni-filtered Cu K\( \alpha \) X-rays of wavelength \( \lambda = 0.154 \) nm.

Selected dry samples of C15A were investigated with atomic force microscopy (AFM). These samples were spun from the appropriate dispersion onto cleaned 2.5 cm silicon wafers of thickness ~0.02 cm and imaged with a Digital Instrument, Dimension 3100 AFM. The microscope operated in tapping mode with commercial silicon microcantilever probes. Topographic and phase images were obtained simultaneously using a resonance frequency of approximately 300 Hz for the probe oscillation and a free-oscillation amplitude of 60 ± 5 nm, with a set-point ratio between 0.65 and 0.75.

**SANS Equations.**

The coherent contribution to the scattered intensity I(q) from a noninteracting monodisperse suspension of N particles of volume \( V_p \) occupying volume V can be written\(^11\)

\[
I(q) = A \phi V_p (\rho - \rho_m)^2 P(q)
\]

where A is an apparatus constant and \( \phi = (N/V) V_p \) is the volume fraction. The scattering length density \( \rho = \rho_{mol} \sum_{j} N_j \) (where \( \rho_{mol} \) is the molecular density, \( b_j \) is the neutron scattering length of nucleus \( j \), and \( N_j \) is the number of nuclei of type \( j \)) in a particle. Experimentally, the scattering from a species is measured with respect to the scattering length density of the medium, \( \rho_m \), assuming that this scattering length density difference is independent of particle position. In eq 1, P(q) is the square of the orientationally averaged form factor written in dimensionless form. Here we will assume that the clay platelets can be approximated by disks and, for a disk of radius R and height 2H, we have\(^11\)

\[
P(q) = F(q)^2 = 4 \int_0^{\pi/2} f^2(q, \beta) \sin \beta \, d\beta
\]

where

\[
f^2(q, \beta) = \left( \frac{\sin^2(q \cos \beta)}{(qH)^2 \cos^2 \beta} \right) \left( \frac{R \sin \beta}{(qR)^2 \sin^2 \beta} \right)
\]

Here \( j \) is the first integer-order Bessel function and \( \beta \) is the angle between \( q \) and the major axis of the disk. Equation 2 simplifies considerably if \( qH \ll 1 \)

\[
P(q) = \frac{2}{(qR)^2} \left( 1 - \frac{J_1(2qR)}{qR} \right)
\]

and if \( 2qR \ll H \), one gets

\[
P(q) = \frac{2}{(qR)^2} \exp(-qH^2/3)
\]

Hence a plot of log(I) versus log(q) from a system of noninteracting thin disks will have a slope of ~2 over a wide range of qR.

In this work, the scatterers are clay platelets for which the surface sodium ions have been replaced by an organic interface; hence the organoclay complex can be considered to be made up of a central core and a surface coating. If this core has a characteristic scattering length density, \( \rho_c \), and the surface has a characteristic scattering length density, \( \rho_s \), the scattered intensity from a system of isolated coated particles is of the form\(^2\)

\[
I(q) \sim ((\rho_2 - \rho_m) [V_1 F_T(q) - V_1 F_1(q)]) + (\rho_1 - \rho_m) [V_1 F_1(q)]^2
\]

where \( V_1 \) is the volume of the core and \( V_T \) the total volume of the particle; similarly, \( F_T(q) \) and \( F_1(q) \) are the form factors for the core and total particle.

Equation 5 is too simplistic if the particles, although isolated as a whole, consist of stacked layers to form a cluster. In this work, therefore, we will assume that the nearest neighbor distance between the platelets obeys a Gaussian distribution and consider an internal structure factor, \( S_s(q) \), first proposed by Kratky and Porod in 1949\(^12\)

\[
S_s(q) = 1 + \frac{2}{N} \sum_{i=1}^{N} (N - k) \cos(kDq \cos \beta) \exp[-(k \cos \beta)^2 \sigma_D^2/2]
\]

Here, \( N \) corresponds to the number of stacked platelets, and \( D \) and \( \sigma_D \) represent the next neighbor center-to-center distance and its Gaussian standard deviation, respectively.

Having eq 6, the intensity for the cluster is thus represented by the expression

\[
I(q) \sim \int_0^{\pi/2} ((\rho_2 - \rho_m) [V_1 F_T(q, \beta) - V_1 F_1(q, \beta)]) + (\rho_1 - \rho_m) [V_1 F_1(q, \beta)]^2 S_s(q) \sin \beta \, d\beta
\]

where the subscripts are for the core and total particle, as defined in eq 5.

---


Results and Discussion

**Montmorillonite, CNa⁺.** Figure 1 displays the SANS intensities, $I(q)$, taken at the three detector positions from an 0.5% suspension of CNa⁺ in water. The result is consistent with the SANS and X-ray scattering from montmorillonite previously observed by several authors.\(^{13}\) The power law exponent of the curve is $-2.2$, close to the predictions of eqs 3-4 given that the sample is estimated by the manufacturer to be 20–30% polydisperse.

In principle, the radius ($R$) and half-height ($H_0$) of the disks could be estimated from SANS data using the low-$q$ Guinier limit of eq 2, $I(q) \propto \exp(-q^2 R_g^2/3)$ with $R_g$ the radius of gyration of a disk, and the higher-$q$ relation, eq 4. The data here, however, do not show a Guinier region at low-$q$ and are scattered at the higher $q$. Accordingly, we calculated the half-height from WAX data on the dry powder as discussed in ref 3. WAX gave $H_0 = 0.99$ nm, the anticipated result for montmorillonite. The radius $R$ was estimated from dynamic light scattering to be $R \sim 0.13 \mu$m, but see next section.

**Cloisite C15A.** Inspection of eq 7 indicates that if the scattering length density of the medium is the same as that for the surfactant species 2, the SANS scattered intensity will be from the clay core. Similarly, if $\rho = \rho_m$, the scattering power of the system is controlled by the surfactant surface. Scattering lengths and scattering length densities, together with the molecular mass and the mass density of the components of the suspensions, are listed in Table 1. The parameters for CNa⁺ are those for a clay mineral layer with the formula $[\text{Si}_4\text{Mg}_{0.33}\text{Al}_{1.67}\text{H}_2\text{O}_{12}]\text{Na}_{0.33}^+$. The parameters for the ditallow assume the carbon chain breakdown discussed above, namely, $C_{18}$ (65%), $C_{16}$ (30%), and $C_{14}$ (5%).

The first set of C15A SANS data was obtained with the cloisite suspended in toluene. Scattering from the ditallow is not quite contrasted out in this solvent but is minor compared to that from the CNa⁺ core. The second set were obtained from a 50/50 d/h-toluene suspension. Here the scattering length density of the solvent is close to that of the clay, so the scattered intensity is predominately that from the surfactant layer alone. Curves for the 1% suspensions are shown in Figure 2, and those for the 2% C15A suspension are shown in Figure 3.


<table>
<thead>
<tr>
<th>Molecular mass, g</th>
<th>Mass density, g cm$^{-3}$</th>
<th>Scattering length, $10^{-12}$ cm</th>
<th>Scattering length density, $10^{10}$ cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNa⁺</td>
<td>359.4</td>
<td>2.66</td>
<td>8.647</td>
</tr>
<tr>
<td>ditallow⁺</td>
<td>545.6</td>
<td>0.9</td>
<td>$-3.58$</td>
</tr>
<tr>
<td>ditallow Cl</td>
<td>581.1</td>
<td>0.9</td>
<td>$-2.62$</td>
</tr>
<tr>
<td>toluene</td>
<td>92.0</td>
<td>0.867</td>
<td>1.658</td>
</tr>
<tr>
<td>d-toluene</td>
<td>100.0</td>
<td>0.943</td>
<td>9.991</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>18.0</td>
<td>1.0</td>
<td>$-0.168$</td>
</tr>
</tbody>
</table>

Figure 1. SANS intensities, $I(q)$, as a function of wavevector, $q$, from a 0.5% suspension of montmorillonite CNa⁺ in water. Some error bars are smaller than the plotting symbols.

Figure 2. SANS intensities from 1% suspensions of Cloisite C15A in h- and d/h-toluene. Some error bars are smaller than the plotting symbols.

Figure 3. SANS intensities from 2% suspensions of Cloisite C15A in h- and d/h-toluene. Some error bars are smaller than the plotting symbols.
Clusters. Let us compare the scattered intensities from the C15A suspensions in toluene with those from the unmodified clay, CNa\textsuperscript{+} in water, Figure 1. In Figures 2 and 3, power law behavior is seen over a range of $q$, as observed in Figure 1, but the exponents are slightly more negative at about $-3.0$. We consider this exponent to be slightly outside the limit expected from a thin disk, even given a fair degree of polydispersity. In addition, the intensities from C15A in toluene suggest a peak at $q \sim 1.3$ nm\textsuperscript{-1}, absent in the corresponding curve for CNa\textsuperscript{+}, and thus indicate a repeat characteristic length in the system of about 5 nm. In our opinion, this length represents the spacing between stacked C15A coated platelets in a cluster.

Wide-angle X-ray scattering experiments\textsuperscript{3} substantiated that the C15A aggregates form clusters, and also gave an estimate of the half-height, $H$, of the C15A platelet. The complex C15A was investigated in 2% toluene, Figure 4. The curve in Figure 4 indicates three orders of primary spacing of about 5.0 nm. Since the $d$ spacing of dry CNa\textsuperscript{+} was measured to be $\sim 1.0$ nm, 5.0 nm corresponds to a single ditallow layer thickness of about 2.0 nm.

In Figure 5, we have plotted the form factor of a coated disk, eq 5 at $\beta = 0$ with parameters $R = 300$ nm and $2H = 4.9$ nm and a core thickness of 1.0 nm. Also shown are two curves of the Kratky Porod structure factor $S_s(q)$, eq 6, with parameters $N = 2$ and 10, also at $\beta = 0$. It can easily be shown that the first deep minimum in $P(Q)$ for $\beta = 0$ is preserved in the full orientational average. The first peak in $S_s(q)$ moves to larger $q$ continuously as beta increases from zero. In general, and specifically for the suspensions in d/h toluene, the scattered intensities have to be modeled by the angle averaged product of eqs 5 and 6 as shown for example in our previous work.\textsuperscript{3} Overall, the model indicates a peak around $0.01 < q \text{ nm}\textsuperscript{-1} < 0.02$. As a matter of interest, the calculations actually indicate the rather unexpected result that a peak at $q \sim 1.3$ nm\textsuperscript{-1} could decline as the number of platelets in a cluster increased. This has been observed and reported in ref 3.

For the system in toluene, however, the form factor plays a minor role since, as noted, the surfactant coating of C15A is almost contrasted out by the toluene medium. Hence, the form factor is effectively that of an uncoated disk, eq 2, which is a slowly decreasing monotonic function.

![Figure 4](image1.png)

**Figure 4.** WAXS intensities from 2% suspensions of Cloisite C15A in h-toluene.

![Figure 5](image2.png)

**Figure 5.** The form factor, $P(q)$, of a coated disk, eq 5, with parameters $R = 300$ nm and $2H = 4.9$ nm and a core thickness of 1.0 nm. Also shown are two curves of the Kratky Porod structure factor $S_s(q)$, eq 6 with parameters $N = 2$ and 10.
Comparisons are shown in Figures 6 and 7. For the 2% dispersions were fitted to eq 7, using eq 6, and the values that are within the supplier’s estimate.

Attempts to estimate a radius of the complex in the C15A suspensions by performing DLS were inconclusive, observed before with other systems. Given the parameters listed in Table 1, our curves for the 2% dispersions were fitted to eq 7, using eq 6, and the comparisons are shown in Figures 6 and 7. For the h-toluene system the best fit was obtained with D = 5.0 nm (corresponding to a layer thickness of 1.95 nm) and \( \sigma_0 = 0.443 \) nm to give N = 6, the number of plates in a cluster; for d/toluene, D = 5.0 nm and \( \sigma_0 = 0.226 \) nm lead to N = 3.

The discrepancy between the values of N occurs largely because the power law exponents of the h-toluene and d/toluene data, Figures 2 and 3, are different: about −3.0 and −2.6, respectively. Unfortunately, we do not have a convincing reason that theseh and d/toluene should not be parallel. We do, however, recall that the results reported here were obtained from the commercial samples with excess surfactant present, and the amount of excess is dependent on the preparation history of the dispersion. There is also some ambiguity on the amount of surface coverage that will be mentioned in the next section. Overall, however, the difference between the two estimates for N is not significant given that the clusters are very likely polydisperse in thickness.

As a matter of interest, a very simplistic calculation can account for the relatively high negative power-law exponents at low q (with respect to −2.2 for the uncoated CNa+ observed in Figures 2 and 3 for C15A. If we assume that the Kratky and Porod \( S(q) \) is constant for q < 1.3 nm\(^{-1} \) and that the complexes are noninteracting, a complex can be approximated by a uniform disk of finite thickness.

If we further arbitrarily assume that the complex suspensions are 20–30% polydisperse in the half-height, we calculate using eq 2 that slopes of −3.0 would be generated from a disk for which the height is about 15% of the radius R. If, as DLS indicates, 2R for CNa+ is about 0.26 \( \mu \)m, the thickness of the C15A complex is approximately 19 nm. Given the X-ray data for the repeat spacing of a coated platelet, the calculation thus indicates that the C15A clusters consist of stacks of around four coated platelets. The corresponding calculation using the AFM estimate of 2R would give stacks of between 4 and 16 platelets. This simplistic calculation can, of course, only be considered a guideline and specifically ignores the q dependence of the internal structure factor.

Surface Coverage. A method, introduced by Hanley et al., that requires no assumptions on the surface morphology, gives an estimate of surface coverage. A shift in the forward scattering for a sample in various solvents is proportional to the number of moles displaced by the scatterers. The scattering power, \( \Delta_{ab} \), of 1 mol of scatterer a that displaces \( x_{ab} \) mol of solvent b is

\[
\Delta_{ab} = \sum_{ib} \left( b_i - x_{ab} \sum_{lb} b_l \right)^2
\]  

(8)

Supposing 1 mol of scatterer a now has \( x_i \) moles of a surface compound c attached to it, and species c displaces \( x_{cb} \) mol of solvent b. The scattering power then becomes

\[
\Delta_{abc} = \sum_{ib} \left( x_i + \sum_{lc} b_l - x_{ab} \right) - \sum_{ib} b_l (x_{ab} + x_{cb})^2
\]  

(9)

In our case, the unknown quantity is \( x_i \), the number of moles of ditallow that form the surface layer of 1 mol of CNa+. But this can be estimated from the ratio of the scattering power of C15A in the two solvents, toluene and d/toluene, provided the scattering from any unattached surfactant is negligible and that there is no interaction between clusters on the length scale of interest. If the surface layer is one CEC equivalent of ditallow, eq 9 predicts a ratio between the scattered intensities from the sample in toluene and the 50% d/toluene mixture of approximately 25. If, however, we realize that the surface layer contains some ditallow molecules (i.e., with Cl), the ratio calculated from eq 9 increases substantially.

Specifically, for 0.1 mol of ditallow in excess (based on the suppliers estimate that the surface of dry C15A is covered to about 130% of one CEC layer) the ratio is about 250.

For the 1% suspensions (Figure 2), the ratio at low q is ~60, a ratio that corresponds to an excess surface coverage of about 15%. We thus speculate that the toluene solvents are washing some of the excess ditallow from the immediate clay surface of the complexes. However, the experimental ratio for the 2% suspension is around 25 (Figure 1). This value is very low. We have verified that the scattering from dispersions in toluene solvents is consistent with the amount of clay in suspension. Thus, why there appears to be far less excess surfactant on the clusters of the 2% dispersion, with respect to the 1% dispersion, is not clear.

**Conclusion**

In this paper we have attempted to address two, related, problems. To what extent can SANS data help characterize a surfactant-modified clay in suspension, particularly can the data be resolved to determine the degree of dispersion or exfoliation of the clay into its constituent platelets? How well is a commercial modified clay, in this case the ditallow montmorillonite complex known as Cloisite C15A, prepared under commercial conditions, dispersed in a simple organic solvent?

We have shown that the SANS data give significant information. Scattered intensity plots of C15A in toluene suspension obey a power law over a range of low-q and indicate a peak at a value of q (q ~ 1.3 nm$^{-1}$) that corresponds to a characteristic length in the system of 5 nm. The data suggest that C15A aggregates in toluene to form clusters of about three to six ditallow coated clay platelets. SANS confirmed that the C15A complex has a disklike morphology which is preserved in the clusters. In addition, the powerful contrast matching feature of neutron scattering allows one to evaluate the approximate ditallow coverage on the base montmorillonite clay platelet.

The analysis of the SANS results depended strongly on corresponding WAX data to resolve the peak at q ~ 1.3 nm$^{-1}$, and the experiments discussed here illustrate the importance of combining information from SANS and WAX. For example, in general, the absence of a WAX peak in an intensity plot from a modified clay is a necessary but not sufficient indication that the exchanged clay platelets are properly, and randomly, dispersed. Conversely, of course, a peak in the WAX plot—as observed—must indicate order at high q, so the exchanged clay platelets must aggregate to form clusters. The behavior, however, of the SANS intensities at lower q would indicate if the system was ordered over a longer length scale, which it is not.

With respect to the second question. We conclude that the commercial exchanged clay Cloisite C15A can be dispersed in toluene suspensions; although there is some aggregation or clustering, the aggregates are made up of only a few of its constituent clay platelets. The aggregate has a disk shape with a very high aspect ratio, so that a large amount of the exchanged surface area is available. Whether or not, the suspensions can be prepared so that the clay is even better dispersed is a commercial decision that depends on its ultimate applications.

Finally, it would be interesting to investigate more fully the relationship between various preparation techniques and the SANS, DLS, and WAX characterization of the subsequent suspensions. We also need to understand better the relation between the organic layer of the exchanged clay and its dispersion in a given solvent.

**Acknowledgment.** The SANS data were taken on the NG7 30 m instrument at the NIST Center for Neutron Research. We thank the staff there for their encouragement and support. Part of the work was carried out at the Lucas Heights site of the Australian Nuclear Science and Technology Organization, and at the Research School of Chemistry, Australian National University, Canberra. LA026342V