Articles

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

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　　The paper explores the capacity of small angle neutron 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 dimethydioctodecylammonium). 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 organoclay is a complex 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 dimethydioctodecylammonium. 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 solvents[2] 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 authors[2,4−6] 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: C_{18} (65%), C_{16} (30%), and C_{14} (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

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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 CNa+ 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 NG7 SANS instrument at the National Institute of Standards and Technology Center for Neutron Research. NG7 was configured 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 $q = |\mathbf{q}|$ and $q = 4\pi \sin(\theta/2)/\lambda$, with λ the incident neutron wavelength and θ 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° $< \theta < 130°$. Samples were loaded into 25 mm diameter light scattering vials and thermostated to 25 °C. Log−time auto-correlated 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 Kα 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 2.54 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 probe tips. 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]

$$I(q) = A\phi V_p(\rho - \rho_m)^2 P(q) \tag{1}$$

where A is an apparatus constant and $\phi = (N/V)V_p$ is the volume fraction. The scattering length density is $\rho = \rho_{mol}\sum b_j N(j)$, where ρ_{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, ρ_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 dimen-

sionless 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]

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

where

$$f^2(q,\beta) = \left(\frac{\sin^2(qH\cos \beta)}{(qH)^2 \cos^2 \beta}\right)\frac{J_1^2(qR\sin \beta)}{(qR)^2 \sin^2 \beta}$$

Here J_1 is the first integer-order Bessel function and β is the angle between $\mathbf{q}$ and the major axis of the disk. Equation 2 simplifies considerably if $qH \ll 1$

$$P(q) = \frac{2}{(qR)^2}\left[1 - \frac{J_1(2qR)}{qR}\right] \tag{3}$$

and if $2 < qR < R/H$, one gets

$$P(q) = \frac{2}{(qR)^2} \exp[-(qH)^2/3] \tag{4}$$

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, ρ_1, and the surface has a characteristic scattering length density, ρ_2, the scattered intensity from a system of isolated coated particles is of the form[2]

$$I(q) \sim \{(\rho_2 - \rho_m)[V_T F_T(q) - V_1 F_1(q)] + \\ (\rho_1 - \rho_m)V_1 F_1(q)\}^2 \tag{5}$$

where V_1 is the volume of the core and V_T the total volume of the particle; similarly, $F_1(q)$ and $F_T(q)$ 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]

$$S_s(q) = 1 + \frac{2}{N}\sum_{k=1}^{N} (N - k) \cos(kDq \cos \beta) \\ \exp[-k(q\cos \beta)^2\sigma_D^2/2] \tag{6}$$

Here, N corresponds to the number of stacked platelets, and D and σ_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

$$I(q) \sim \int_0^{\pi/2} \{(\rho_2 - \rho_m)[V_T f_T(q,\beta) - V_1 f_1(q,\beta)] + \\ (\rho_1 - \rho_m)V_1 f_1(q,\beta)\}^2 S_s(q) \sin \beta \, d\beta \tag{7}$$

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

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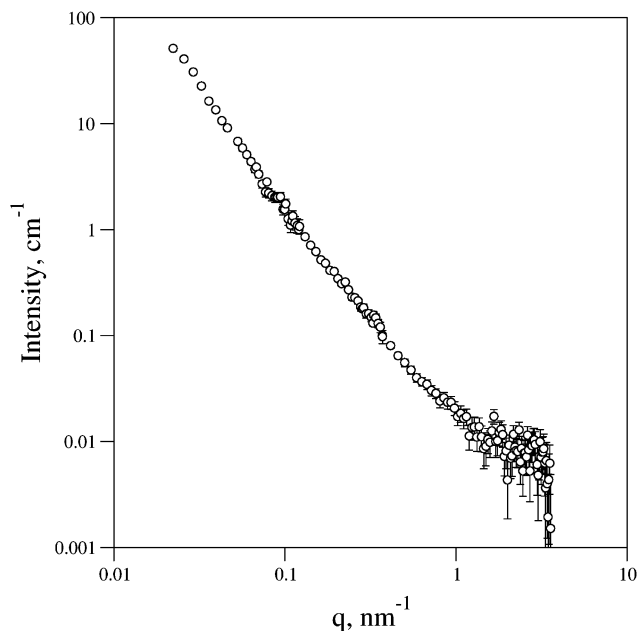(12) Kratky, O.; Porod, G. *J. Colloid Sci.* **1949**, *4*, 35.

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.

Table 1. Parameters for the CNa+ and C15A Systems

	molecular mass, g	mass density, g cm^{-3}	scattering length, 10^{-12} cm	scattering length density, 10^{10} cm^{-2}
CNa+	359.4	2.66	8.647	3.86
ditallow+	545.6	0.9	−3.58	−0.35
ditallow Cl	581.1	0.9	−2.62	−0.24
toluene	92.0	0.867	1.665	0.90
d-toluene	100.0	0.943	9.991	5.68
H$_2$O	18.0	1.0	−0.168	−0.56

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) 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 $2H = 0.99$ nm, the anticipated result for montmorillonite. The radius R was estimated from dynamic light scattering to be $R \sim$ 0.13 μm, 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 surface 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
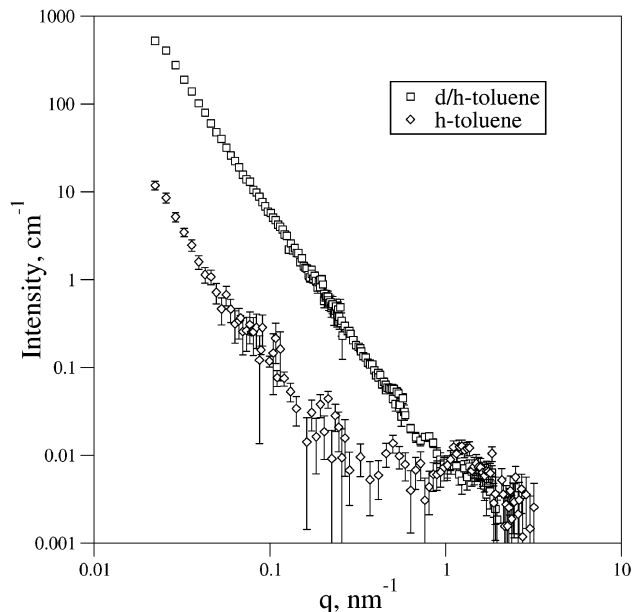
(13) For example: Morvan, M.; Espinat, D.; Lambard, J.; Zemb, T. *Colloids Surf., A* **1994**, *82*, 193. Bongiovanni, R.; Ottewill, R. H.; Rennie, A. R. *Prog. Colloid Polym. Sci.* **1991**, *84*, 299.

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.
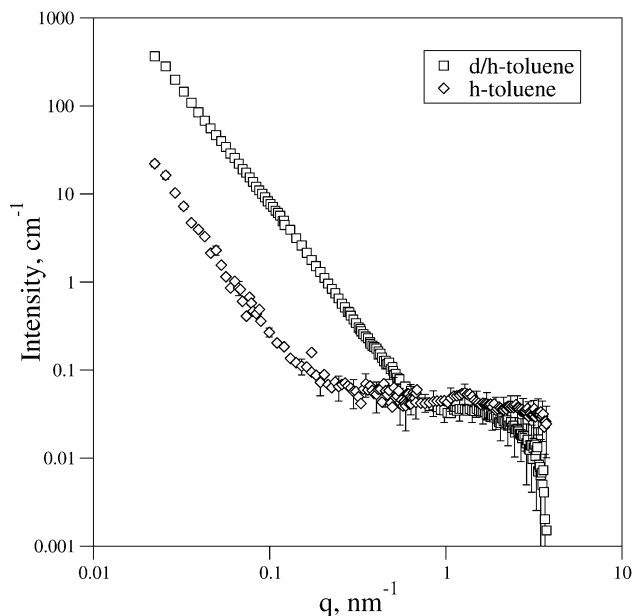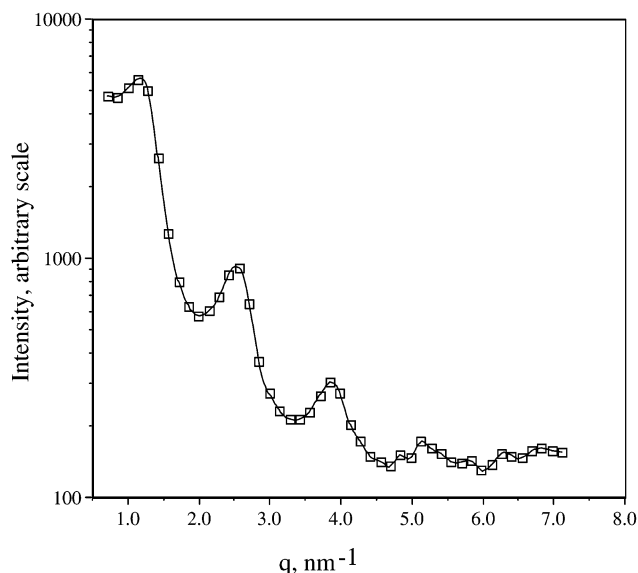

Figure 3. SANS intensities from 2% suspensions of Cloisite C15A in h- and d/h-toluene. Some error bars are smaller than the plotting symbols.

the components of the suspensions, are listed in Table 1. The parameters for CNa+ are those for a clay mineral layer with the formula [Si$_4$Mg$_{0.33}$Al$_{1.67}$H$_2$O$_{12}$]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.

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

Clusters. Let us compare the scattered intensities from the C15A suspensions in toluene with those from the unmodified clay, CNa+ 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^{-1}, absent in the corresponding curve for CNa+, 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[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+ was measured to be ~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.[3] Overall, the model indicates a peak around $0.01 < q$ nm$^{-1} < 0.02$. As a matter of interest, the calculations actually indicate the rather unexpected result that a peak at $q \sim 1.3$ nm^{-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
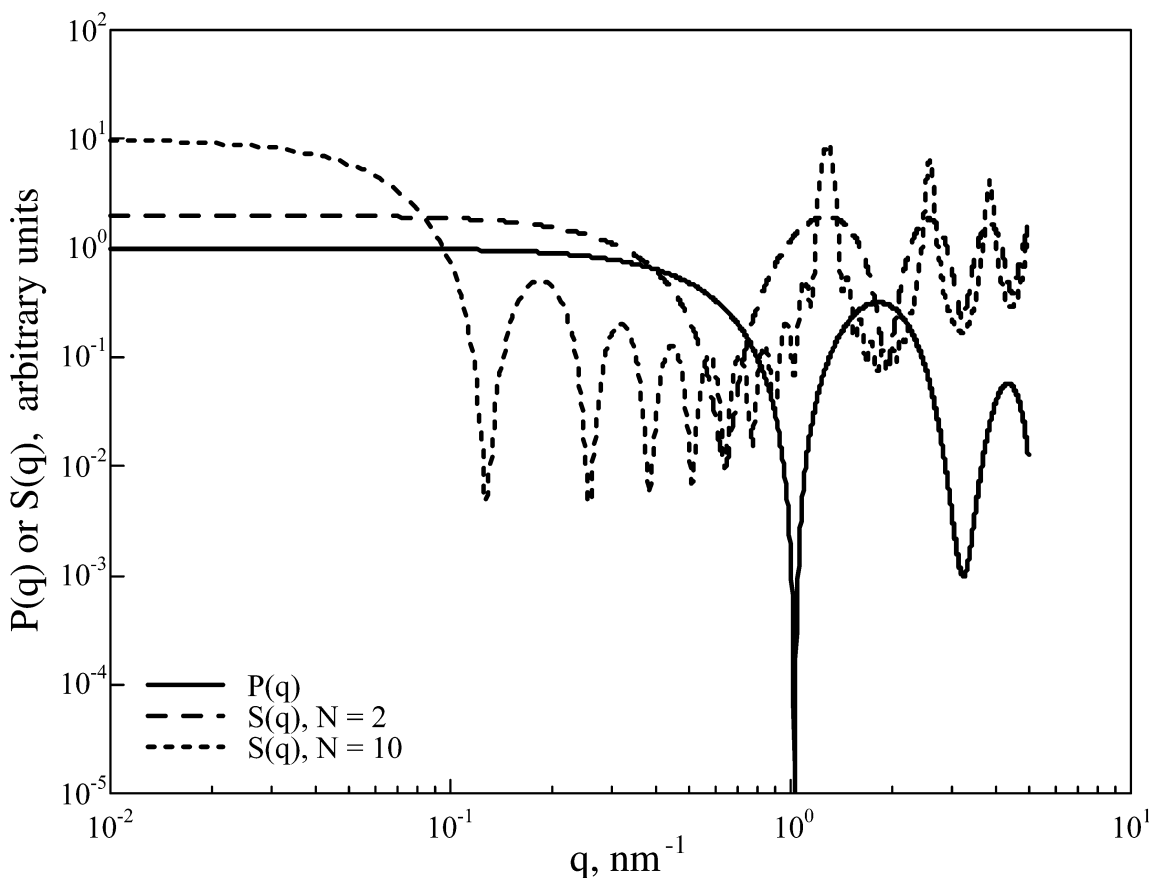

Figure 5. The form factor, P(*q*), of a coated disk, eq 5, with parameters $R = 300$ nm and $2H = 4.9$ nm and a core thickness of 1.0 nm. Also shown are two curves of the Kratky Porod structure factor $S_s(q)$, eq 6 with parameters $N = 2$ and 10.
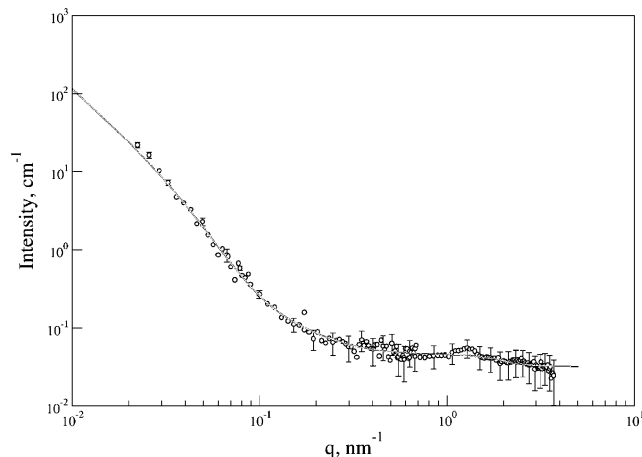
Figure 6. Fit (curve) of the SANS data (circles) for the 2% dispersion in *h*-toluene using eqs 6 and 7 corresponding to N = 6, the number of plates in a cluster. To ease comparison of the fit to the data, error bars have been included on only every fifth point.
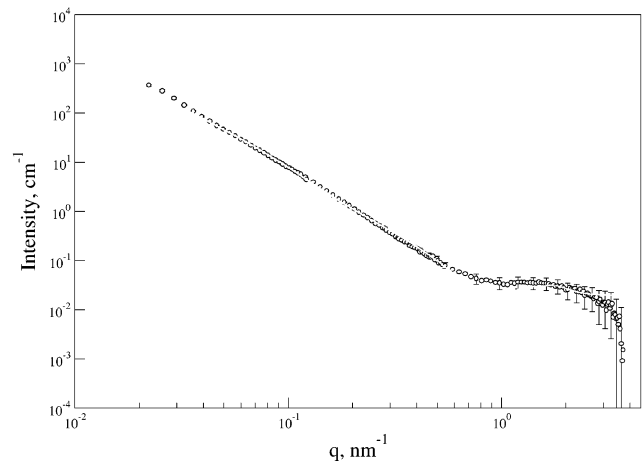

Figure 7. Fit (curve) of the SANS data (circles) for the 2% dispersion in *d/h*-toluene leading to to N = 3. Compare with Figure 6. To ease comparison of the fit to the data, error bars have been included on only every fifth point.

of q in the q-range of interest. In this case, the peak is modeled by the behavior of $S_s(q)$ alone.

Attempts to estimate a radius of the complex in the C15A suspensions by performing DLS were inconclusive, no doubt because the system was strongly interacting.[2] Consequently, the 1% suspension was diluted to 0.02% and DLS was repeated to yield an effective hydrodynamic diameter of 0.32 μm—slightly greater than the diameter obtained from the unmodified CNa+. We should point out, however, that AFM measurements on the dry C15A yielded an approximate diameter of between ~0.4 and ~1 μm. The discrepancy between the AFM and the DLS estimates is acceptable, and similar differences have been observed before with other systems,[14] and both techniques gave values that are within the supplier's estimate.

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 σ_D = 0.443 nm to give N = 6, the number of plates in a

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cluster; for *d/h* toluene, D = 5.0 nm and σ_D = 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/h*-toluene data, Figures 2 and 3, are different: about -3.0 and -2.6, respectively. Unfortunately, we do not have a convincing reason that these *h*- and *d/h*- sets 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 $S_s(q)$ 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 ~0.26 μm, 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 simple 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, Δ_{ab}, of 1 mol of scatterer a that displaces x_{ab} mol of solvent b is

$$\Delta_{ab} = [\sum_{ia} b_i - x_{ab}\sum_{ib} b_i]^2 \qquad (8)$$

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

$$\Delta_{acb} = [(\sum_{ia} b_i - x_c\sum_{ic} b_i) - \sum_{ib} b_i(x_{ab} + x_{cb})]^2 \qquad (9)$$

In our case, the unknown quantity is x_c, 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/h*-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/h*-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 ($q \sim 1.3$ 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 $q \sim 1.3$ 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.