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Three-Phase Coexistence in Colloidal Rod−Plate Mixtures

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S *Supporting Information*

ABSTRACT: Aqueous suspensions of clay particles, such as montmorillonite (MMT) platelets and sepiolite (Sep) rods, tend to form gels at concentrations around 1 vol %. For Sep rods, adsorbing sodium polyacrylate to the surface allows for an isotropic−nematic phase separation to be seen instead. Here, MMT is added to such Sep suspensions, resulting in a complex phase behavior. Across a range of clay concentrations, separation into three phases is observed: a lower, nematic phase dominated by Sep rods, a MMT-rich middle layer, which is weakly birefringent and probably a gel, and a dilute top phase. Analysis of phase volumes suggests that the middle layer may contain as much as 6 vol % MMT.
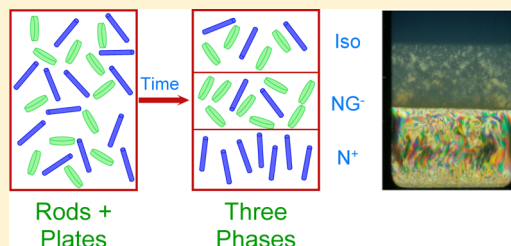
INTRODUCTION

Suspensions of anisometric (rod or plate-like) colloidal particles with hard interactions can spontaneously form liquid crystalline phases as the concentration is increased. Onsager demonstrated how formation of an ordered (nematic) phase can maximize entropy for suspensions of rod-like particles,[1] and the same is true for suspensions of colloidal plates.[2] Several experimental systems have been found to display such an isotropic−nematic transition; for reviews, see refs [3] and [4]. For clay mineral particles in water, such as montmorillonite (MMT) plates or sepiolite (Sep) rods, however, charges contribute to the particle interactions and liquid crystalline phases are not observed as a rule; instead, gels are found at modest clay concentrations slightly above 1 vol % for MMT[5] and Sep.[6] The gelation also depends upon salt concentrations, with the highest gel point for MMT being around 10^{-3} M NaCl. Here, the behavior of Sep is modified by polymer adsorption, giving rise to isotropic−nematic phase separation. Adding MMT to such suspensions is found to result in three-phase coexistence at low MMT concentrations, with a middle MMT gel layer sandwiched between a dilute isotropic phase and a Sep-dominated nematic phase. At higher MMT concentrations, more gels are obtained.

For mixtures of hard rods and plates, the possibility of a biaxial phase arises,[7] competing with a phase separation into rod-like (N+) and plate-like (N−) phases. Experimentally, gibbsite plates and boehmite rod particles dispersed in toluene were individually shown to form nematic phases.[8,9] However, mixtures of these two types of particles showed a very complex phase diagram[10] and even samples that appeared to break the Gibbs phase rule. Initially, this was ascribed to particle size polydispersity, but later work by Wensink and Lekkerkerker showed that gravity can have a noticeable effect on dispersion phase behavior over length scales as small as a centimeter.[11] Despite the rich phase behavior observed, the aligned particles always demixed into separate phases and a biaxial phase was not observed, in accordance with computer simulations.[12]

The behavior of aqueous clay suspensions, such as MMT plates or Sep rods, is rather different from these results obtained on hard repulsive particles, as a result of the charge distribution around these particles. As a rule, such suspensions are not found to form a nematic phase but instead form gels upon the increase of the concentration (as an aside, we note there are exceptions in the form of suspensions of plate-like minerals with isomorphous substitutions in the tetrahedral layer, as opposed to the octahedral layer for MMT;[13] a nematic phase was reported in recent years for nontronite[14] and beidellite[15]).

As a result, clay particles tend to find application as thickeners. Clay particles are in common use in applications, such as food,[16] paints, cosmetics, lubricants,[17] oil extraction,[18] and the production of composite materials.[19]

The behavior of MMT platelets mixed with other inorganic particles was reviewed recently.[20] The behavior depends upon a range of factors: shape, size, and charge of the second species as well as pH, ionic strength, and concentration of the sample. The addition of anionic, rod-like particles of Sep was explored previously,[21] and the similar mineral palygorskite (Pal) was also studied.[18,22] These studies investigated the rheology of mixtures, and in all cases, the pure mineral without any additional stabilizer was used. Gelation is generally observed; Chemeda et al. mixed Sep from Spain with Wyoming MMT, similar to the materials used in this paper, and it was found that, for samples with 5 wt % solids, addition of a small amount of MMT (0−10% of the solids) gave little change in the viscosity but, for higher levels of MMT, the viscosity increased across a range of shear rates. Adding around 10 wt % MMT to Pal was found to enhance the gel strength.[22] Bailey et al.[23] added like charged spheres to MMT samples below the overlap concentration, and the resulting drop in viscosity was attributed

to the formation of MMT tactoids. The reduction of the viscosity did not enable any phase separation in these samples, and upon an increase of the concentration above the overlap concentration, the existing gel network was strengthened.

Recently, we demonstrated that Sep can be stabilized in water by adsorbing a polyelectrolyte (sodium polyacrylate), giving rise to isotropic−nematic phase separation.[6] Similarly, it is possible to modify interactions between MMT platelets by adsorbing surfactants. While this was found to increase the concentration at which a gel was formed, a nematic MMT phase remains elusive.[24] Here, we report on the addition of MMT platelets to polymer-stabilized Sep suspensions. At low MMT concentrations, separation into three phases results: a nematic phase dominated by Sep, a gel phase containing a high concentration of MMT as well as Sep, and a dilute top phase. Particle concentrations were deduced from a novel analysis of the phase volumes.

■ EXPERIMENTAL SECTION

A total of 9 g of Sep (Tolsa, S9) was dispersed in 200 mL of deionized water (Millipore Milli-Q), which was then dialyzed against 1 M NaCl for 1 week, replacing the water 5 times to ensure all counterions on the clay were sodium. The sample was then dialyzed against deionized water until a stable reading below 5 μS cm^{-1} was achieved. The mixture was then diluted to roughly 1 wt % and allowed to settle for 10 days, with the supernatant being retained. The same procedure of dialysing against NaCl and then sedimentation of the large clusters was also performed on 9 g of MMT (Wyoming, SWy2, Clay Minerals Repository) in 200 mL of deionized water. A total of 1.1 g of poly(acrylic acid) sodium salt (NaPAA; M_w = 5100 g/mol; Sigma-Aldrich, used as received) was added to the Sep sample, shaken for 5 min, and then agitated using a roller mixer (SRT6, Stuart) for 1 h. Centrifugation at 11000g for 1 h (Sorvall Legend T, SS-34 rotor) was used twice on the Sep sample to remove excess NaPAA stabilizer, redispersing the sediment each time with deionized water. The final sediment was diluted to roughly 9.5 wt %. The MMT sample was concentrated to roughly 5 wt % using a rotary evaporator, making sure that it did not dry out, producing a highly viscous gel. From these two stock samples, various mixtures were made at different concentrations in 10 mm wide, 1 mm path length optical glass cells (Starna 8G), with dilutions made with deionized water where necessary. Cells were filled to a height of roughly 30 mm. The samples were left undisturbed for a number of days, with the phase behavior being recorded over time. Images were taken using a Nikon D40 camera (18−55 mm Nikon lens) of samples placed between crossed polarizing filters (200 × 200 mm, <0.004 transmission crossed, Edmund Optics) and backlit by a fluorescent light panel (MedaLight LP-20). Time lapse videos were made by combining a number of photos taken at a set interval. For the determination of the gelation of the samples, they were tilted ~30°, and if the samples did not flow, they were considered gelled. Micrographs were taken on samples in 1 mm cells using a 4× lens (Olympus), and transmission electron microscopy (TEM) images (JEOL JEM 1200 EX) were taken on a dried 0.01 wt % sample on a carbon-coated copper grid. To gauge the clay content in the isotropic phase, the transmission of light (632.8 nm) through the isotropic phase was measured using a setup described previously.[25] The transmission was compared to a blank cell filled with deionized water, and the transmissions of known concentrations of pure clays were measured to create a Beer−Lambert plot (Supporting Information).

■ RESULTS

Pure suspensions of polymer-stabilized Sep displayed an isotropic−nematic phase separation (Figure 1a). The behavior reproduced the findings previously reported,[6] and the nematic volume as a function of the Sep concentration is shown in Figure 2. It has previously been shown that it is possible to
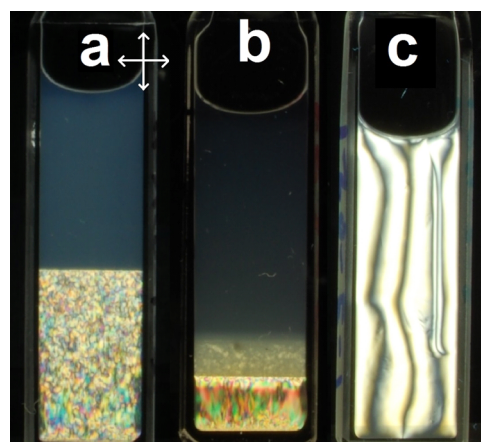
Figure 1. Illustrative examples of behavior: (a) pure Sep (ϕ_{Sep} = 2.3%), (b) three phases (ϕ_{Sep} = 1.5%, and ϕ_{MMT} = 0.6%), and (c) gel (ϕ_{Sep} = 0.9%, and ϕ_{MMT} = 0.9%). Arrows denote polarizer orientations.
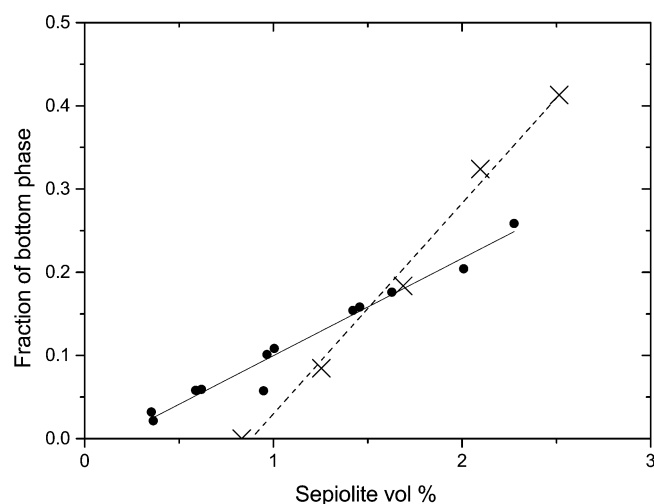

Figure 2. Fraction of sample that is nematic as a function of the Sep concentration. Crosses are pure Sep samples, and filled circles are samples with 0.2−0.9 vol % MMT added. Trend lines are linear fits.

obtain a fully nematic sample using stabilized Sep, but in this report, samples were not concentrated enough to achieve a sample with over half the volume nematic. To assist further analysis of the phase behavior below, all concentrations are expressed in terms of volume fractions ϕ of the clay minerals dispersed in water (wat), calculated from the weight percent w of the particles following eq 1 and using mass densities ρ_{Sep} = 2.1 g cm^{-3}[26] and ρ_{MMT} = 2.7 g cm^{-3}.[27]

$$\phi_{Sep} = \frac{w_{Sep}/\rho_{Sep}}{w_{Sep}/\rho_{Sep} + w_{MMT}/\rho_{MMT} + w_{wat}/\rho_{wat}} \quad (1)$$

An equivalent expression was used to calculate ϕ_{MMT}. Aqueous dispersions of MMT did not show any phase separation but remained liquid below 3 wt %, as reported by Cui;[24] above this concentration, a space-filling gel was formed.

We now turn to the behavior of suspensions containing both MMT and Sep. The range of sample compositions is shown in Figure 3. The maximum concentrations achievable were limited, as samples were prepared by mixing stock suspensions of MMT and Sep (that individually needed to be sufficiently
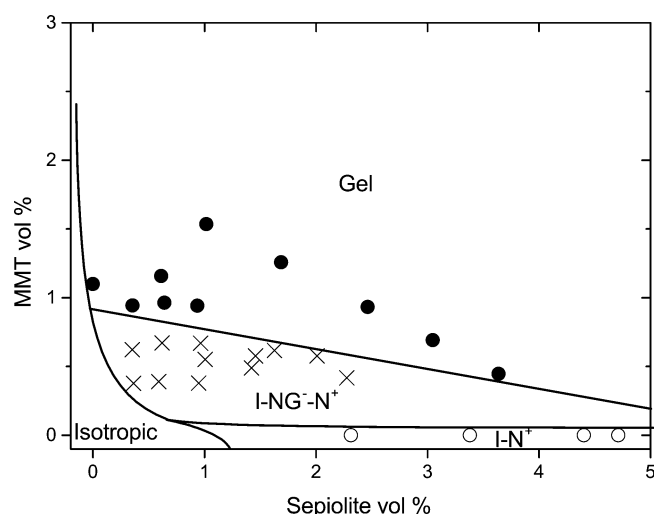
Figure 3. Phase diagram of the mixtures of Sep and MMT. Closed circles show gelled samples; crosses show samples with three phases; and open circles show samples with one nematic phase. The solid lines separating regions are to guide the eye.

fluid). The pure Sep suspensions formed a nematic layer, as discussed above. For samples to which MMT was added, broadly speaking, two types of behavior were observed. At a low MMT concentration (in any case below 0.9 vol %), samples separated into three phases (see Figure 1b for an example). These samples had an isotropic top phase, a weakly birefringent middle layer, and a highly birefringent lower phase. The lower phase apperance was similar to the nematic layer observed in pure Sep suspensions, and indeed, we argue below that this phase was nematic and dominated by Sep (N^+ phase). The composition of the middle layer is discussed further below, but we will refer to it as NG^-, meaning a birefringent (nematic) gel dominated by platelets. Finally, samples with a higher MMT concentration formed moderately birefringent, space-filling gels (Figure 1c) (in the Supporting Information, there are video clips of the time evolution of some of these samples and also details on the relative phase volumes).

To characterize the phase behavior in more detail, information is needed on the composition of the three phases formed. To illustrate the composition of the three-phase samples, TEM images were taken on a small amount of each phase of a sample with $\phi_{Sep} = 1.0\%$ and $\phi_{MMT} = 0.7\%$ (Figure 4). This confirmed that the lower phase predominantly contains rod particles (Figure 4c), and the texture observed closely matches the texture seen for aqueous nematic Sep (see also ref 6). The middle phase has more plates present (Figure 4b). While this provides an indication of the relative numbers of platelets and rods in each layer, making this analysis

quantitative was not possible in the present work as a result of the high polydispersity of both particle species. Also, this analysis does not provide any information on the concentrations of the phases.

Ideally, one would determine both Sep and MMT concentrations in each phase or at least the overall mass concentration in each layer. Note that, because the samples were so small, measurements of the concentrations of the separated phases through drying were not consistent and gave too large an error to be useful. Because the particle species are both clay minerals, in principle, it should be possible to characterize the content as a function of the height in the sample non-invasively using X-ray attenuation,[28] and small-angle X-ray scattering could perhaps reveal more detail on the structure of the middle layer.[29] These approaches have not been attempted here. Instead, the analysis that follows is based entirely around observations of the phase volumes, made 24 days after the samples were mixed up (this also has the benefit of being non-invasive).

To make a more quantitative analysis, in Figure 2, the volume fraction of the lower nematic phase is plotted against the overall Sep concentration. As for the pure Sep suspensions, the amount of nematic phase increases with the Sep concentration, and it is now already possible to observe some nematic phase at a very low concentration of Sep. Also, if one were to extrapolate the phase volumes in the figure, this would suggest that, in the presence of MMT, the concentration of the Sep phase would be distinctly more concentrated than that seen in the pure Sep suspensions.

If a sample containing two solutes separates into three phases of known compositions, in general, this dictates what the relative phase volumes have to be, to allow for overall mass balance. Furthermore, we assume that, for all three-phase samples, the composition of each phase is constant across different samples (note that, for polydisperse samples, such as these, a more detailed analysis is likely to reveal some variation of phase compositions as one traverses the three-phase triangle.[9,30]) We used an iterative procedure, choosing three coexisting phase compositions such that optimum agreement with the experimental phase volumes was obtained. Details of this procedure and the resulting phase volumes is given in the Supporting Information.

The final estimates for the three-phase compositions are shown in Table 1, and this three-phase triangle is overlaid on the phase diagram in Figure 5. All samples that were experimentally found to give rise to separation into three phases are indeed inside this three-phase triangle, at the dilute end. A small increase in the MMT concentration gave rise to space-filling, birefringent gels. The compositions of the three phases are in line with the qualitative observations presented above. The lower phase is dominated by Sep, and the
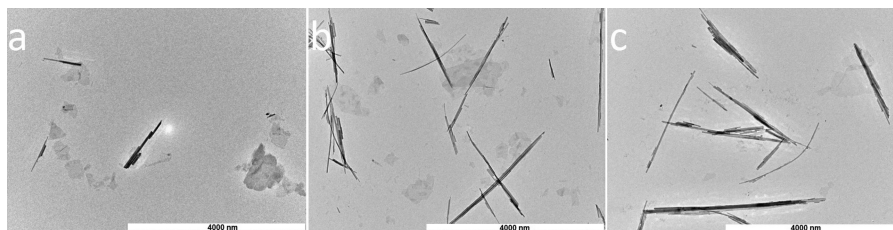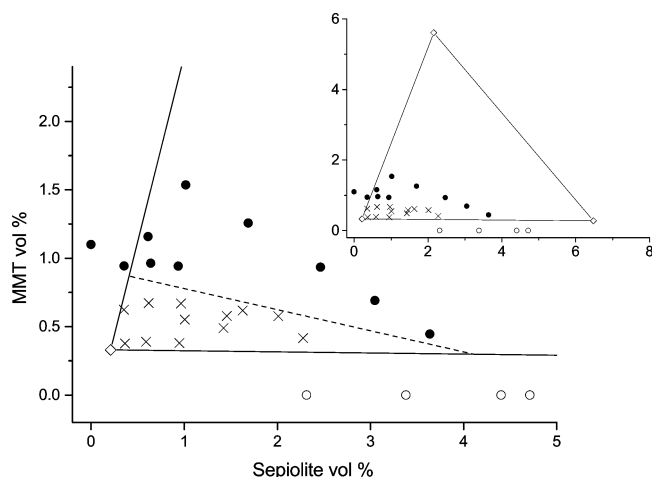

Figure 4. TEM images taken from fractions of the three phases for a sample with $\phi_{Sep} = 1.0\%$ and $\phi_{MMT} = 0.7\%$: (a) top phase, (b) middle phase, and (c) bottom phase. Scale bars represent 4000 nm.

Table 1. Particle Volume Fractions (in Percent) and Mass Densities of the Three Coexisting Phases

phase	Sep	MMT	density (g/mL)
isotropic	0.21 ± 0.03	0.33 ± 0.04	1.008 ± 0.001
NG⁻	2.2 ± 0.5	5.6 ± 0.6	1.12 ± 0.02
N⁺	6.5 ± 0.2	0.3 ± 0.2	1.08 ± 0.01

Figure 5. Calculated composition triangle for the three phases in a multiphase system with the experimental samples as labeled in Figure 3. The dashed line is a guide for the eye to separate the liquid and gelled samples, and the inset shows the full calculated phase triangle.

Figure 6. Time lapse video stills from a sample that had been left to separate into three phases and then tilted to observe the flow properties of the phases present ($\phi_{Sep} = 1.0\%$, and $\phi_{MMT} = 0.7\%$).

concentration of rods in this phase (around 7 vol %) is higher than that in pure Sep suspensions (around 5 vol % obtained by extrapolating the results in Figure 2). The middle phase mainly contains MMT but also some Sep.

The comparison between the calculated and measured relative phase volumes for the samples can be seen in the Supporting Information. In many cases, the middle phase was larger in the experiment than predicted and the lower phase was smaller. We should add that the analysis presented here is based around the total volume of the two lower phases. We found that, in some cases, distinguishing the boundary between the lower two phases was not straightforward. Attempts to repeat the analysis, taking into account the experimental individual lower phase volumes, also did not produce a satisfactory result. This is discussed in more detail below.

The middle phase is quite concentrated in MMT as well as weakly birefringent. The MMT phase had a dramatically different flow behavior to that displayed by the nematic Sep phase, which can be seen in Figure 6 (the full video is in the Supporting Information). The phase resisted flow initially and then, after a certain time, began to flow more freely. We therefore consider this phase to be a birefringent gel phase. Such phases have been reported for pure MMT suspensions previously.[31] The interface between top and middle phases does not appear well-defined, consistent with the middle phase being a gel.

■ DISCUSSION

The suspensions of MMT and polyacrylate-stabilized Sep clay studied here have been characterized individually previously but not when mixed together. The wide range of samples displaying three phases, observed here, suggests that the two particle species do not display significant mutual attractions, as that
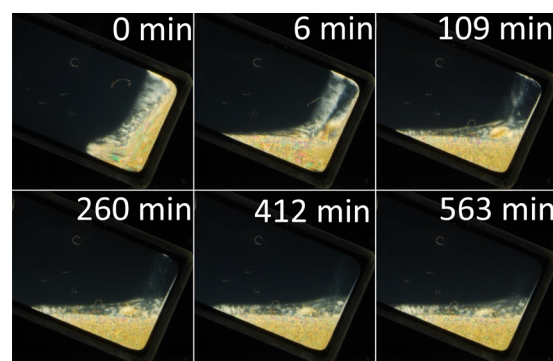
would be expected to result in gels forming throughout. For the Sep samples, excess stabilizer had been removed in the sample preparation. The addition of MMT did not appear to disrupt the PAA stabilization of Sep (through competitive adsorption for instance).

The pure Sep undergoes an isotropic−nematic transition, and upon adding MMT, the width of this transition was found to widen, as discussed above (Figure 2). A similar broadening of the isotropic−nematic coexistence region was predicted for colloidal rod−polymer mixtures using computer simulations by Bolhuis and Frenkel[32] and theoretically by Matsuyama and Kato.[33] This is the result of effective (depletion) attractions between the rods, induced by adding the second species, leading to extensive immiscibility at a high polymer concentration.[34] Experimentally, such a broadening was also observed by van Bruggen and Lekkerkerker[35] in mixtures of boehmite rods and polydimethylsiloxane (PDMS).

The phase compositions in Table 1 show a very high estimated MMT content for the middle phase, which exceeds what could be achieved in a pure sample. The table also shows the mass densities of the three phases, and the MMT-rich phase is calculated to have the highest density, closely followed by the Sep-rich phase. In practice, the MMT phase is usually the middle phase, but the densities of the two lower phases are close, taking into account the error bars. Moreover, in some of the samples, the interface between the two layers became less well-defined over time or even multiple layers were found (see the Supporting Information), consistent with both layers having a similar density. Such an ABA phase stacking sequence was predicted (but not yet observed) for colloidal sphere−plate mixtures,[36] and more generally, a wide range of different sequences can arise for binary colloidal mixtures at sedimentation equilibrium, as shown recently by de las Heras and Schmidt.[37] To make the estimates of the phase compositions more accurate, it would have been useful to analyze the phase behavior of samples with a higher MMT content, but it was found that samples above 0.9 vol % of MMT gelled very quickly and did not evolve over time (Figure 5).

From inspection of the sample videos (1 and 2) closely, a dense layer forms rapidly in all samples and is essentially established within 1 day. Subsequently, this layer develops over about 2 days into two clearly defined phases. One possible explanation is that, initially, dense droplets containing both rods and plates are formed and that, only in a second step, domains with the final phase compositions are formed. Such a two-step phase separation scenario was observed previously in

another example of entropy-driven phase separation involving colloid−polymer mixtures.[38] Alternatively, droplets of the rod- and plate-rich domains form right at the start but take time to rearrange themselves into two distinct layers. It would be of interest for future work to investigate such mixtures using (confocal) microscopy to distinguish which mechanism applies.

As reported previously,[6] the aqueous Sep suspensions have a tendency to form gels as time progresses (weeks to months), and therefore, we have concentrated here on the sample behavior in the first few weeks after preparation. As a result, samples had not reached sedimentation equilibrium; the fact that the phase behavior could successfully be analyzed using a decomposition into three phases of fixed compositions also suggests that the behavior reported here is not affected significantly by gravity.

A striking feature of the middle phase was the birefringence displayed between crossed polarizers, which would suggest alignment of the rods in the lower phase against the interface (Figure 7).
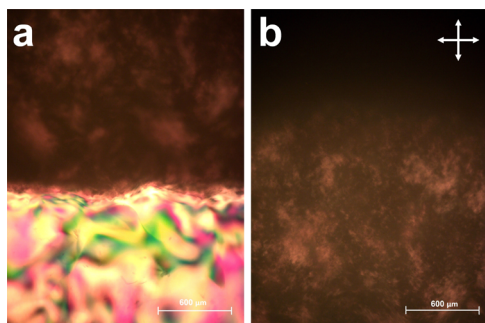
Figure 7. Polarizing microscope images of interfaces for a sample with ϕ_{Sep} = 2.0% and ϕ_{MMT} = 0.6% between (a) lower and middle and (b) middle and top phases.

The high concentration of MMT in the middle phase is a bit surprising, because when suspensions of MMT in water are made, it is hard to achieve concentrations above 2 vol %. As a further, non-invasive method to support our analysis, we have measured the light transmission through the top layer in the three-phase samples (see the Supporting Information). Because concentrations of both Sep and MMT should be low in this phase (and because it is not thought that the two species strongly interact), the Beer−Lambert law can be used to predict the absorbance as a sum of individual contributions. On the basis of calibration plots for the individual species, the composition of the top phase (Table 1) would correspond to an absorbance A = 0.08. In practice, values ranged from 0.01 to 0.10, with an average of 0.07. These measurements therefore suggest that the MMT concentration in the top layer is not underestimated, and if anything, this top layer may in some cases be more dilute instead. Because the middle phase is in all likelihood a gel, this would also help to explain why in some cases the experimental volume of the middle phase was found to be larger than predicted on the basis of the phase volume analysis; perhaps some of the nematic lower phase had become trapped in the middle gel phase. In some cases, the middle phase appeared to separate out from the bottom phase as time progressed (see Videos 1 and 2 in the Supporting Information), and it may be helpful to consider this as an example of viscoelastic phase separation.[39]

The behavior of the middle phase can be compared to the work by Bailey et al.,[23] where spherical particles were added to MMT samples. They found that the samples became less viscous below the overlap concentration of plates (2.5 wt %) but formed a stronger gel above this concentration, which is consistent with the samples presented in this work. For the samples below the overlap concentration, they proposed that the plates formed tactoids surrounded by the spheres, resulting in a precipitation of the tactoid layer. Here, the presence of the nematic Sep phase appears to drive the MMT tactoids together into a concentrated MMT-rich phase, which is more concentrated than what can be obtained without adding Sep.

The appearance of the middle phase was shown to be sensitive to details of the sample preparation. In a second series of samples, separation into three phases still occurred, and the compositions of the three phases were similar to those reported above; however, the middle phase showed less birefringence (see the Supporting Information).

■ CONCLUSION

Aqueous MMT suspensions tend to gel at concentrations around 1 vol %. The addition of polymer-stabilized Sep to such samples still results in space-filling gels. At lower MMT concentrations, however, across a range of Sep concentrations, samples were found to separate into three phases, with a concentrated and probably gelled layer dominated by MMT (around 6 vol %) sandwiched between an isotropic phase and a nematic phase rich in Sep. While the middle layer is not thought to reach equilibrium, a consistent analysis of the isotropic phase volumes in terms of three coexisting phases was demonstrated.

The ability to strengthen or weaken a gel phase by adding moderate amounts of another material can give greater flexibility to formulations, and this work has shown it is possible to dramatically alter the behavior of a mixture of particles from a rigid gel to a three-phase system, in which one of the phases is a highly dense compressed gel. The evolution of the samples, which did phase separate, also provided interesting behavior. Initially, the samples formed one dense, highly birefringent phase and an isotropic phase, but over time, the birefringent phase separated into two distinct phases. Furthermore, in some cases, the interface between these lower two phases became less well-defined over time, and in some instances, the two phases changed position. It would be of interest to characterize the structure of these lower phases in more detail, for instance, using small-angle X-ray scattering.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b02224.

> Supporting data, movie clips, and details on the analysis of phase volumes (PDF)
> Video 1 (AVI)
> Video 2 (AVI)
> Video 3 (AVI)

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Notes

The authors declare no competing financial interest.

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