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Three-phase coexistence in colloidal rod-plate mixtures

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Abstract

Aqueous suspensions of clay particles such as montmorillonite (MMT) platelets and sepiolite (Sep) rods tend to form gels at concentrations around one percent by volume. For Sep rods, adsorbing sodium polyacrylate to the surface allows an isotropic - nematic phase separation to be seen instead. Here MMT is added to such Sep suspensions resulting in a complex phase behaviour. 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 volume% MMT.

Introduction

Suspensions of anisometric (rod-like or plate-like) colloidal particles with hard interactions can spontaneously form liquid crystalline phases as concentration is increased. Onsager demonstrated how formation of an ordered (nematic) phase can maximise 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. 3,4 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 con-
centrations slightly above 1 % volume for MMT5 and sepiolite.6 The gelation also depends
on salt concentrations, with the highest gel point for MMT being around 10^{-3} M NaCl. Here
the behaviour 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 coex-
istence 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,
once 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 particle showed a very
complex phase diagram10 and even samples which 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 affect on dispersion phase behaviour
over length scales as small as a centimetre.11 Despite the rich phase behaviour observed, the
aligned particles always demixed into separate phases and a biaxial phase was not observed,
in accordance with computer simulations.12

The behaviour 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 on increase of 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 behaviour of MMT platelets mixed with other inorganic particles was reviewed recently.\(^{20}\) The behaviour depends on a range of factors: shape, size and charge of the second species, as well as pH, ionic strength and concentration of the sample. 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 stabiliser was used. Gelation is generally observed; Chemeda \textit{et al.} mixed sepiolite 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 \textit{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 on increase of the concentration above the overlap concentration the existing gel network was strengthened.

Recently we demonstrated that Sep can be stabilised 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. Whilst 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 stabilised Sep suspensions. At low MMT concentrations, separation into three phases results: a nematic phase dominated by sepiolite, 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**

9 g of sepiolite (Tolsa, S9) was dispersed in 200 ml of deionised water (Millipore MilliQ), which was then dialysed against 1 M NaCl for a week replacing the water 5 times to ensure all counter ions on the clay were sodium. The sample was then dialysed against deionised water until a stable reading below 5 $\mu$S 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 montmorillonite (Wyoming, SWy2, Clay Minerals Repository) in 200 ml of deionised water. 1.1 g of polyacrylic acid sodium salt, NaPAA ($M_w = 5,100$ g/mol, Sigma Aldrich, used as received) was added to the sepiolite sample, shaken for 5 min then agitated using a roller mixer (SRT6, Stuart) for an hour. Centrifugation at 11,000 g for 1 hr (Sorvall Legend T, SS-34 rotor) was used twice on the sepiolite sample to remove excess NaPAA stabiliser, redispersing the sediment each time with deionised 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 deionised 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 behaviour being recorded over time. Images were taken using a Nikon D40 camera (18-55 mm Nikon lens) of samples placed between crossed polarising filters ($200 \times 200$ 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 $\sim 30^\circ$ and if the samples did
Results

Pure suspensions of polymer-stabilised sepiolite displayed an isotropic - nematic phase separation (Fig. 1a). The behaviour reproduced the findings previously reported and the nematic volume as a function of sepiolite concentration is shown in Fig. 2. It has previously been shown that it is possible to obtain a fully nematic sample using stabilised sepiolite 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 behaviour below, all concentrations are expressed in terms of volume fractions $\phi$ of the clay minerals dispersed in water (wat), calculated from the weight% $w$ of the particles following Eq. 1 and using mass densities $\rho_{\text{Sep}} = 2.1 \text{ g cm}^{-3}$ and $\rho_{\text{MMT}} = 2.7 \text{ g cm}^{-3}$.

$$\phi_{\text{Sep}} = \frac{w_{\text{Sep}}/\rho_{\text{Sep}}}{w_{\text{Sep}}/\rho_{\text{Sep}} + w_{\text{MMT}}/\rho_{\text{MMT}} + w_{\text{wat}}/\rho_{\text{wat}}}.$$  

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

We now turn to the behaviour of suspensions containing both MMT and Sep. The range of sample compositions is shown in Fig. 3. The maximum concentrations achievable were limited, as samples were prepared by mixing stock suspensions of MMT and Sep (that
Figure 1: Illustrative examples of behaviour. a) Pure sepiolite ($\phi_{\text{Sep}} = 2.3\%$), b) Three phases ($\phi_{\text{Sep}} = 1.5\%, \phi_{\text{MMT}} = 0.6\%$) and c) Gel ($\phi_{\text{Sep}} = 0.9\%, \phi_{\text{MMT}} = 0.9\%$). Arrows denote polariser orientations.

Figure 2: Fraction of sample which is nematic as a function of sepiolite concentration. Crosses are pure sepiolite samples and filled circles are samples with 0.2 - 0.9 vol % MMT added. Trend lines are linear fits.
individually needed to be sufficiently fluid). The pure Sep suspensions formed a nematic layer, as discussed above. For samples to which MMT was added, broadly speaking two types of behaviour were observed. At low MMT concentration (in any case below 0.9 vol%), samples separated into three phases (see Fig. 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 appearance 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 \(\text{NG}^-\), meaning a birefringent (nematic) gel dominated by platelets. Finally, samples with higher MMT concentration formed moderately birefringent, space filling gels (Fig. 1c). (In the Supplementary Information, there are video clips of the time evolution of some of these samples, and also details on the relative phase volumes).

![Figure 3: Phase diagram of the mixtures of sepiolite and MMT. Closed circles show gelled samples, crosses samples with 3 phases and open circles samples with one nematic phase. The solid lines separating regions are to guide the eye.](image)

In order to characterise the phase behaviour 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
φ_{Sep} = 1.0\% and φ_{MMT} = 0.7\% (Fig. 4). This confirmed that the lower phase predominantly contains rod particles (Fig. 4c) and the texture observed closely matches the texture seen for aqueous nematic sepiolite (see also Ref. 6). The middle phase has more plates present (Fig. 4b). Whilst 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 due to 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 as 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. As the particle species are both clay minerals, in principle it should be possible to characterise the content as function of height in the sample non-invasively using X-ray attenuation, and small-angle X-ray scattering could perhaps reveal more detail on the structure of the middle layer. 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).

![Figure 4: TEM images taken from fractions of the 3 phases for a sample with φ_{Sep} = 1.0\% and φ_{MMT} = 0.7\%. a) Top phase, b) middle phase and c) bottom phase. Scale bars represent 4000 nm.](image)

To make a more quantitative analysis, in Fig. 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 Sep concentration, and it is now already possible to observe some nematic phase at very low concentration of Sep. Also, if one were to extrapolate the phase volumes in the figure, this would suggest that in 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, in order to allow 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.\textsuperscript{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 Supplementary 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 Fig. 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 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 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 Fig. 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 Supplementary Information. In many cases the middle phase was larger in experiment than predicted, and the lower phase 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.

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

Table 1: Particle volume fractions (in per cent) and mass densities of the three coexisting phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Sep</th>
<th>MMT</th>
<th>Density (g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic</td>
<td>0.21 ± 0.03</td>
<td>0.33 ± 0.04</td>
<td>1.008 ± 0.001</td>
</tr>
<tr>
<td>NG−</td>
<td>2.2 ± 0.5</td>
<td>5.6 ± 0.6</td>
<td>1.12 ± 0.02</td>
</tr>
<tr>
<td>N+</td>
<td>6.5 ± 0.2</td>
<td>0.3 ± 0.2</td>
<td>1.08 ± 0.01</td>
</tr>
</tbody>
</table>

The middle phase is quite concentrated in MMT, as well as weakly birefringent. The MMT phase had a dramatically different flow behaviour to that displayed by the nematic sepiolite phase which can be seen in Fig. 6 (the full video is in Supplementary Information). The phase resisted flow initially, 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.\textsuperscript{31} The interface between top and middle phases does not appear well defined, consistent with the middle phase being a gel.

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

**Discussion**

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

The pure Sep undergoes an isotropic-nematic transition, and on adding MMT the width of this transition was found to widen as discussed above (Fig. 2). A similar broadening of the isotropic - nematic coexistence region was predicted for colloidal rod - polymer mixtures using computer simulations by Bolhuis and Frenkel,\textsuperscript{32} and theoretically by Matsuyama and Kato.\textsuperscript{33} This is the result of effective (depletion) attractions between the rods, induced by
adding the second species leading to extensive immiscibility at high polymer concentration.\textsuperscript{34} Experimentally such a broadening was also observed by van Bruggen and Lekkerkerker\textsuperscript{35} in mixtures of boehmite rods and 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 Supplementary 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\textsuperscript{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.\textsuperscript{37} To make the estimates of the phase compositions more accurate it would have been useful to analyse the phase behaviour 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 (Fig. 5).

Inspecting the sample videos (1 and 2) closely, a dense layer forms rapidly in all samples and is essentially established within a 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.\textsuperscript{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 in order to distinguish which mechanism applies.
As reported previously,\textsuperscript{6} the aqueous sepiolite suspensions have a tendency to form gels as time progresses (weeks to months) and therefore we have concentrated here on the sample behaviour in the first few weeks after preparation. As a result samples had not reached sedimentation equilibrium; the fact that the phase behaviour could successfully be analysed using a decomposition into three phases of fixed compositions also suggests that the behaviour reported here is not affected significantly by gravity.

A striking feature of the middle phase was the birefringence displayed between crossed polarisers, which would suggest alignment of the rods in the lower phase against the interface (Fig. 7).

![Figure 7: Polarising microscope images of interfaces for a sample with $\phi_{\text{Sep}} = 2.0\%$ and $\phi_{\text{MMT}} = 0.6\%$. between (a) lower and middle and (b) middle and top phases.](image)

The high concentration of MMT in the middle phase is a bit surprising, as when suspensions of MMT in water are made, it is hard to achieve concentrations above 2 volume %. 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 Supplementary Information). As 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 Lambert-Beer law can be used to predict the absorbance as a sum of individual contributions. Based on 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. As 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.\textsuperscript{39}

The behaviour of the middle phase can be compared to the work by Bailey et al.\textsuperscript{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 sepiolite 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 the 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 phase still occurred, and the compositions of the three phases were similar to those reported above, but the middle phase showed less birefringence (see SI).
Conclusions

Aqueous MMT suspensions tend to gel at concentrations around 1 volume%. Addition of polymer-stabilised 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 volume%) sandwiched between an isotropic phase and a nematic phase rich in Sep. Whilst 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 behaviour 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 behaviour. 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 phase became less well-defined over time, and in some instances the two phases changed position. It would be of interest to characterise the structure of these lower phases in more detail, for instance using small-angle X-ray scattering.

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Supporting Information Available

Supporting data, movie clips, and details on the analysis of phase volumes.

This material is available free of charge via the Internet at http://pubs.acs.org/.

References


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