Mixtures of these two types of particles showed a very complex phase behavior over length scales as small as a centimeter.\(^1\) 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\(^1,3\) a nematic phase was reported in recent years for nontronite\(^1,4\) 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. 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. Here, we report on the addition of concentration at which a gel was formed, a nematic MMT adsorbing surfactants. While this was found to increase the possible to modify interactions between MMT platelets by the phase volumes.

**EXPERIMENTAL SECTION**

A total of 9 g of Sep (Tolsa, S9) was dispersed in 200 mL of deionized water (Millipore Mili-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, SW2, Clay Minerals Repository) in 200 mL of deionized water. A total of 1.1 g of poly(acrylic acid) sodium salt (NaPAA; Mw = 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. The transmission was compared to a blank cell filled with deionized water, and the transmissions of known concentrations of pure clay 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, 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 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 ω of the particles following eq 1 and using mass densities ρ = 2.1 g cm⁻³ and ρ = 2.7 g cm⁻³.

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

An equivalent expression was used to calculate ϕ. 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 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...
of platelets and rods in each layer, making this analysis 4b). While this provides an indication of the relative numbers phase of a sample with samples, TEM images were taken on a small amount of each formed. To illustrate the composition of the three-phase information is needed on the composition of the three phases (Figure 4). This con

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 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 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 \( \phi_{\text{Sep}} = 1.0\% \) and \( \phi_{\text{MMT}} = 0.7\% \) (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.

Idealyle, 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, 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).

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. 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 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.

Figure 4. TEM images taken from fractions of the three phases for a sample with \( \phi_{\text{Sep}} = 1.0\% \) and \( \phi_{\text{MMT}} = 0.7\% \): (a) top phase, (b) middle phase, and (c) bottom phase. Scale bars represent 4000 nm.
**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 and theoretically by Matsuyama and Kato. 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. Experimentally, such a broadening was also observed by van Bruggen and Lekkerkerker 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, 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. 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

| 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 ($\phi_{\text{sep}} = 1.0\%$, and $\phi_{\text{MMT}} = 0.7\%$).
another example of entropy-driven phase separation involving colloid–polymer mixtures. Alternatively, droplets of the rod–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, 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 \( \phi_{\text{Sep}} = 2.0\% \) and \( \phi_{\text{MMT}} = 0.6\% \) between (a) lower and middle and (b) middle and top phases.](image)

The behavior of the middle phase can be compared to the work by Bailey et al., 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.
ACKNOWLEDGMENTS

Phillip Woolston was supported by a Ph.D. scholarship [Engineering and Physical Sciences Research Council (EPSRC), EP/J500379/1]. The authors acknowledge J. Jones (Electron and Scanning Probe Microscopy Facility) for training and access to the electron microscope and D. Davis for carrying out the elemental analysis measurements. Sep was a gift from Dr. M. Perez (Tolsa). The authors thank Michael Ziegler for preliminary experiments and Professor Henk Lekkerkerker for enlightening discussions about the composition of the phases. Original images can be accessed at (DOI: 10.5523/bris.11er895thp6414g6e92i4898a).

REFERENCES

(1) Onsager, L. The Effects of Shape on the Interaction of Colloidal Particles. Ann. N. Y. Acad. Sci. 1949, 51, 627–659.
(2) Allen, M. P.; Evans, G. T.; Frenkel, D.; Mulder, B. M. Hard Convex Body Fluids. Adv. Chem. Phys. 1993, 86, 1–166.
(3) Davidson, P.; Gabriel, J.-C. P. Mineral liquid crystals. Curr. Opin. Colloid Interface Sci. 2005, 9, 377–383.
(4) Vroege, G. J.; Lekkerkerker, H. N. W. Phase transitions in lyotropic colloidal and polymer liquid crystals. Rep. Prog. Phys. 1992, 55, 1241–1309.
(5) Abend, S.; Ziegler, M. Sol-gel transitions of sodium montmorillonite dispersions. Appl. Clay Sci. 2000, 16, 201.
(6) Woolston, P.; van Duijneveldt, J. S. Isotropic-nematic phase transition in aqueous sepiolite suspensions. J. Colloid Interface Sci. 2015, 477, 65–70.
(7) van Rooij, R.; Mulder, B. Demixing in a hard rod-polymer mixture. J. Phys. II 1994, 4, 1763–1769.
(8) Lekkerkerker, H. N. W.; van der Kooij, F. M.; Kassapoglou, K. Liquid crystal phase transitions in suspensions of polydisperse plate-like particles. Nature 2000, 406, 868–871.
(9) Binning, P. A.; Lekkerkerker, H. N. W. Isotropic-Nematic Phase Separation of a Dispersion of a Dispersion of Organophilic Boehmite Rods. J. Phys. Chem. 1993, 97, 11510–11516.
(10) van der Kooij, F. M.; Lekkerkerker, H. N. W. Liquid-crystalline phase behavior of a colloidal rod-polymer mixture. Phys. Rev. Lett. 2000, 84, 781–784.
(11) Wensink, H. H.; Lekkerkerker, H. N. W. Sedimentation and multi-phase equilibria in mixtures of platelets and ideal polymer. Europhys. Lett. 2004, 66, 125–131.
(12) Wensink, H. H.; Vroege, G. J.; Lekkerkerker, H. N. W. Isotropic-nematic phase separation in asymmetric rod-polymer mixtures. J. Chem. Phys. 2001, 115, 7319–7329.
(13) Grandjean, J.; Laszlo, P. Octahedral or tetrahedral isomorphous substitution: How it affects water and acetonitrile interaction with a clay as seen by NMR. Clays Clay Miner. 1994, 42, 652–654.
(14) Michot, L. J.; Bihanic, I.; Maddi, S.; Baravian, C.; Levitz, P.; Davidson, P. Sol-gel and isotropic/nematic transitions in aqueous suspensions of natural nontronite clay. Influence of particle anisotropy. 1. Features of the I/N transition. Langmuir 2008, 24, 3127–39.
(15) Paineau, E.; Antonova, K.; Baravian, C.; Bihanic, I.; Davidson, P.; Dozov, I.; Impeor-Clerc, M.; Levitz, P.; Madsen, A.; Meneau, F.; Michot, L. J. Liquid-crystalline nematic phase in aqueous suspensions of a disk-shaped natural beidellite clay. J. Phys. Chem. B 2009, 113, 15858–15869.
(16) Dickinson, E. Stabilising emulsion-based colloidal structures with mixed food ingredients. J. Sci. Food Agric. 2013, 93, 710–721.
(17) Odom, I. E. Smectite clay Minerals: Properties and Uses. Philos. Trans. R. Soc. A 1984, 311, 391–409.
(18) Abdo, J.; Haneef, M. D. Clay nanoparticles modified drilling fluids for drilling of deep hydrocarbon wells. Appl. Clay Sci. 2013, 86, 76–82.
(19) Bledle, A. K.; Gassan, J. Composites reinforced with cellulose based fibres. Prog. Polym. Sci. 1999, 24, 221–274.
(20) Bailey, L.; Lekkerkerker, H. N. W.; Maitland, G. C. Smectite clay-inorganic nanoparticle mixed suspensions: phase behaviour and rheology. Soft Matter 2015, 11, 222–236.
(21) Chemedy, Y. C.; Christidis, G. E.; Khan, N. M. T.; Koutroulou, E.; Hatzistamou, V.; Kessaidi, V. Rheological properties of palygorskite-bentonite and sepiolite-bentonite mixed clay suspensions. Appl. Clay Sci. 2014, 90, 165–174.
(22) Neaman, A.; Singer, A. Rheology of Mixed Palygorskite-Montmorillonite Suspensions. Clays Clay Miner. 2000, 48, 713–715.
(23) Bailey, L.; Lekkerkerker, H. N. W.; Maitland, G. C. Rheology modification of montmorillonite dispersions by colloidal silica. Rheol. Acta 2014, 53, 373–384.
(24) Cui, Y.; Pizze, C. L.; van Duijneveldt, J. S. Modifying the structure and flow behaviour of aqueous montmorillonite suspensions with surfactant. Philos. Trans. R. Soc. A 2013, 371, 20120262.
(25) Ganley, W. J.; van Duijneveldt, J. S. Controlling Clusters of Colloidal Platelets: Effects of Edge and Face Surface Chemistry on the Behavior of Montmorillonite Suspensions. Langmuir 2015, 31, 4377–4385.
(26) Yasarawan, N.; van Duijneveldt, J. S. Dickrom in dye-doped colloidal liquid crystals. Langmuir 2008, 24, 7184–7192.
(27) Wada, S.-I.; Wada, K. Density and Structure of Allophane. Clay Miner. 1977, 12, 289–298.
(28) Davis, K. E.; Russel, W. B.; Glantschnig, W. J. Settling Suspensions of Colloidal Silica: Observations and X-Ray Measurements. J. Chem. Phys. 1991, 87, 411–424.
(29) Petukhov, A. V.; Thijssen, J. H. J.; ’t Hart, D. C.; Imhof, A.; van Blaaderen, A.; Bolinya, I. P.; Snigirev, I.; Mousaid, A.; Snigireva, I. Microradian X-ray diffraction in colloidal photonics. J. Appl. Crystallogr. 2006, 39, 137–144.
(30) Zhang, Z. X.; van Duijneveldt, J. S. Isotropic-nematic phase transition of nonaqueous suspensions of natural clay rods. J. Chem. Phys. 2006, 124, 154910.
(31) Michot, L. J.; Baravian, C.; Bihanic, I.; Maddi, S.; Mayne, C.; Duval, J. F. L.; Levitz, P.; Davidson, P. Sol-Gel and Isotropic/Nematic Transitions in Aqueous Suspensions of Natural Nontronite Clay. Influence of Particle Anisotropy. 2. Gel Structure and Mechanical Properties. Langmuir 2009, 25, 127–139.
(32) Bolhuis, P.; Stroobants, A.; Frenkel, D.; Lekkerkerker, H. N. W. Numerical study of the phase behavior of rodlike colloids with attractive interactions. J. Chem. Phys. 1997, 107, 1551–1564.
(33) Matsuyama, A.; Kato, T. Orientation-dependent depletion interaction in rodlike colloid-polymer mixtures. Eur. Phys. J. E: Soft Matter Biol. Phys. 2001, 6, 15–24.
(34) Lekkerkerker, H. N. W.; Tuinier, R. Colloids and the Depletion Interaction; Springer: Dordrecht, Netherlands, 2011.
(35) van Bruggen, M. P. B.; Lekkerkerker, H. N. W. Tunable Attractions Directing Nonequilibrium States in Dispersions of Hard Rods. Macromolecules 2000, 33, 5532–5535.
(36) de las Heras, D.; Doshi, N.; Cosgrove, T.; Phipps, J.; Gittins, D. L.; van Duijneveldt, J. S.; Schmidt, M. Floating nematic phase in colloidal platelet-sphere mixtures. Sci. Rep. 2012, 2, 789.
(37) de las Heras, D.; Schmidt, M. Sedimentation stacking diagram of binary colloidal mixtures and bulk phases in the plane of chemical potentials. J. Phys.: Condens. Matter 2015, 27, 194115.
(38) Zhou, J.; van Duijneveldt, J. S.; Vincent, B. Two-stage phase separation in ternary colloid-polymer mixtures. Phys. Chem. Chem. Phys. 2011, 13, 110–113.
(39) Tanaka, H.; Koyama, T.; Araki, T. Network formation in viscoelastic phase separation. J. Phys.: Condens. Matter 2003, 15, S387–S393.
(40) Bledzki, A. K.; Gassan, J. Composites reinforced with cellulose based fibres. Prog. Polym. Sci. 1999, 24, 221–274.