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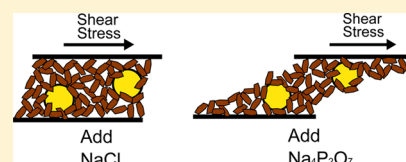
Controlling the Rheology of Montmorillonite Stabilized Oil-in-Water Emulsions

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Supporting Information

ABSTRACT: The rheology of hexadecane-in-water emulsions stabilized by montmorillonite platelets was investigated. In these systems excess particles form a network in the continuous phase which strongly dictates their rheological behavior. The emulsions were modified by the addition of NaCl and Na₄P₂O₇ to the continuous phase at varying concentrations. Remarkably, changes of up to 3 orders of magnitude in elastic modulus and yield stress of the emulsions were achieved. The droplets retained long-term coalescence stability after the addition of NaCl or Na₄P₂O₇ and even after the removal of the continuous phase network. The latter finding shows that the droplets are primarily stabilized by the formation of a solid barrier at the interface. These emulsions are therefore highly versatile formulation materials with an exceptional degree of stability and tunability.



INTRODUCTION

The stabilization of emulsions by solid particles (known as Pickering stabilization) has received much interest over recent decades as the formation of a mechanical barrier at the interface can lead to much higher coalescence stability than that observed in traditional surfactant stabilized emulsions. First reported over a century ago,^{1,2} the design rules for formulating these systems are now well established.^{3,4} These include methods for controlling particle wettability,⁵ the effects of particle shape,^{6–8} and also the impact of preparation methods.^{9,10}

Many different types of soft materials can be prepared using Pickering stabilization including simple emulsions,³ high internal phase emulsions,¹¹ arrested bicontinuous systems,¹² and droplet embedded gels.¹³ These droplet embedded gels (herein referred to as emulsion gels) arise due to an excess of stabilizing particles remaining in the continuous phase after emulsification which form a gel due to competing attractive and repulsive interactions. This excess can be by either design or a result of processing conditions, but the nature of the continuous phase network dictates the rheology of emulsion gels and this will be the focus of the work presented here. Montmorillonite clay particles are studied as they are well reported to form gels in suspension at particularly low weight fractions^{14–17} and to stabilize emulsions.^{6,13,18}

Contributions to Pickering emulsion gel rheology can be separated into bulk and interfacial effects. When the droplets are closely packed, the mechanical response is due to interfacial deformation as a result of either Laplace pressure¹⁹ or the viscoelasticity of the particle barrier formed at the interface.²⁰ For lower droplet concentrations, but under conditions where a network forms in the continuous phase, the rheological response is typically characteristic of the continuous phase network.^{21–23} Similar rheological results have been reported for protein stabilized emulsion gels, and the droplets are

interpreted as network fillers which can either be active, where the coated droplets interact attractively with the continuous phase network and enhance the mechanical properties, or passive, where the droplets do not interact with the network and behave as voids, thereby weakening the gel.²⁴

Figure 1 depicts the rheological response of active and passive

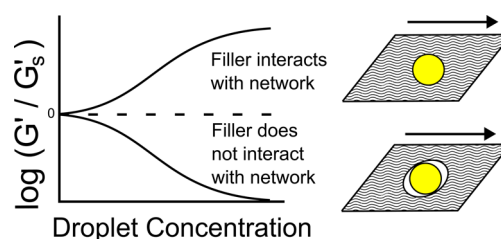


Figure 1. Depiction of rheological behavior of actively and passively filled gels. Adapted from ref 24.

fillers where the vertical axis shows the ratio of emulsion and continuous phase elastic moduli. Active fillers increase the elastic modulus of the emulsion relative to that of the continuous phase when the droplet concentration is increased and passive fillers decrease it. Many reports of Pickering emulsions gel rheology show an increase in elastic modulus with droplet concentration.^{13,21,23,25–27} They can therefore be interpreted as actively filled, likely due to adsorbed particles interacting attractively with the continuous phase network.

An aspect of these systems that has received significantly less attention is the modification of emulsion rheology by modifying the continuous phase network. Previous work has shown that emulsion gel strength can be increased by tuning the ionic

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strength^{21–23} and solvent conditions;²⁸ however, little attention has been given to the adsorption of molecules known to weaken the rheological properties of montmorillonite suspension gels, such as multivalent anions,^{29–32} to allow formulation rheology to be tuned from any starting to point to any desired end point.

In this work we expand the current understanding of the rheological behavior of particle stabilized emulsion gels by taking an emulsion that has previously been reported to be stable (40 wt % hexadecane with 3 wt % montmorillonite and 0.01 M NaCl in the continuous phase^{6,10}) and increasing NaCl concentration or adding Na₄P₂O₇. These modifications result in changes of elastic modulus and yield stress by up to 3 orders of magnitude and steady shear viscosity of up to 2 orders of magnitude. These significant rheological modifications can be achieved with no loss of coalescence stability, and furthermore we show that the emulsions are stable to coalescence in the absence of a network in the continuous phase.

MATERIALS AND METHODS

Wyoming montmorillonite (SWy-2) was purchased from the Clay Minerals Society source clays repository at Purdue University. The composition of SWy-2 is (Si_{7.94}Al_{0.06})(Al_{2.88}Fe_{0.5}Mg_{0.62})O₂₀(OH)₄Na_{0.68}¹⁶ and it has a cation exchange capacity of 84 mequiv/100 g.³³ Berol R648 is an alkyl polyglycol ether ammonium methyl chloride and was kindly donated by Akzo Nobel. Reagent grade NaCl was purchased from Fischer; *n*-hexadecane (99%) and reagent grade Na₄P₂O₇·10H₂O were purchased from Sigma-Aldrich.

Montmorillonite dispersions were prepared as previously reported.³² 45 g L⁻¹ powdered clay was added to deionized water and stirred for 24 h. The suspension was then dialyzed against aqueous NaCl (1 M) for 1 week, changing the solution every day to remove unwanted ions such as Ca²⁺, and then dialyzed against deionized water, changing water every day, until the conductivity of the dialysate was below 5 μS cm⁻¹. The dialyzed suspension was then diluted to 1 wt % and left for 24 h for large impurities such as sand and quartz to settle out. The supernatant was concentrated by evaporation and used as stock.

The emulsions were prepared by first diluting stock montmorillonite suspension with appropriate NaCl and Berol R648 solutions. NaCl concentration was initially fixed at 0.01 M and Berol R648 added at 25 mg g⁻¹ montmorillonite. Previous work has shown that the use of montmorillonite platelets treated with Berol R648 results in improved emulsion stability and lower polydispersity in droplet size distributions compared to montmorillonite alone.⁶ Rheological measurements were carried out on montmorillonite suspensions without Berol R648, and it was found that the only impact is a slight increase in elastic modulus at high NaCl concentration. These measurements can be found in the [Supporting Information](#). Hexadecane was then added to the suspensions, hand-shaken to pre-emulsify, and finally mixed under high shear using an Ultra Turrax IKA T18 with a S18-10G dispersing element at 22 000 rpm for 5 min. Total sample masses were 10 g.

The emulsions were then separated into samples (1 g), and solutions of NaCl and Na₄P₂O₇ (0.05 g, various concentrations) were added and the samples left to stand overnight before commencing rheological measurements. For all experiments the diluted sample at 0.01 M NaCl was used as a reference state as this was previously found to produce very stable emulsions.⁶ NaCl concentrations between 0.01 and 0.1 M and Na₄P₂O₇ concentrations between 0 and 40 μmol g⁻¹ montmorillonite were investigated. Na₄P₂O₇ is known to quantitatively adsorb to the surface of montmorillonite particles;³² therefore, concentrations were expressed in μmol g⁻¹ montmorillonite. Above 0.1 M NaCl extensive aggregation of the particles and coalescence of the droplets was observed (as has been reported previously³⁴), and Na₄P₂O₇ concentrations above 20 μmol g⁻¹ have previously been shown to have minimal further measurable effect.³²

Previous work on montmorillonite stabilized oil-in-water emulsions has shown that emulsions can be prepared at particle concentrations in the continuous phase as low as 0.5 wt %; however, the minimization of droplet size¹⁰ and formation of a gel^{15,32} require higher concentrations. The montmorillonite concentration in the continuous phase was therefore fixed at 3 wt % for the main part of the study.

During initial experiments NaCl and Na₄P₂O₇ were added to the montmorillonite suspensions prior to emulsification; however, the resulting change in viscosity made it difficult to achieve the same mixing conditions across different samples. To mitigate this, the salt solutions were instead added after the emulsions has been prepared.

Emulsions were imaged using an Olympus BX51 optical microscope and Pixelink PL-B62CU color CCD camera using differential interference contrast optics. Average droplet size was measured by counting a minimum of 100 droplets from each sample using Linear Intercept software (TU Darmstadt). The surface-weighted droplet diameter D_{32} is used throughout.

Rheological measurements were carried out using a Malvern Kinexus Pro rheometer with 20 mm parallel plates at a 1 mm gap and temperature of 20 ± 0.1 °C. Samples were preconditioned by resting for 10 min after loading. Oscillatory amplitude sweeps were carried out in controlled strain mode at 0.1 Hz at strains (γ) from 0.1 to 50% followed immediately by viscometry measurements shearing at 10 s⁻¹ for 90 s. The plateau elastic moduli (G_0') of the emulsions were measured by extrapolating the amplitude sweeps to zero strain and the yield stress (σ_y) by taking maxima in the elastic stress component ($G'\gamma$). Droplet sizes of a subset of samples were checked by microscopy before and after measurements, and no evidence for droplet coalescence was found.

RESULTS

The following section shows coalescence stability and rheological measurements of montmorillonite stabilized emulsions and their corresponding continuous phase dispersions where NaCl and Na₄P₂O₇ solutions are added after emulsification. The droplet size measurements investigate the dominant stability mechanism. The rheological measurements investigate the interactions between particle stabilized droplets and the particulate network formed in the continuous phase as well as the effects of modifying interactions between particles in the continuous phase network on the emulsion plateau elastic modulus, yield stress, and steady shear viscosity.

Coalescence Stability. Network forming colloidal particles can stabilize emulsions in two different ways. The first is the formation of a mechanical barrier at the interface which prevents extensive thinning of the continuous phase film between droplets,^{3,35,36} and the second is the immobilization of the droplets within the continuous phase network which prevents them from moving into contact.^{13,21,23,25–27} Emulsions with different concentrations of NaCl or Na₄P₂O₇ were prepared, and droplet sizes were monitored over time to identify the dominant stabilization mechanism.

An emulsion with 40 wt % hexadecane and 3 wt % montmorillonite in the aqueous phase was prepared as detailed above. This was split into three and either NaCl or Na₄P₂O₇ solution added (increasing the total mass by 5%), resulting in samples with NaCl concentrations of 0.01 and 0.1 M NaCl and a Na₄P₂O₇ concentration of 40 μmol g⁻¹ montmorillonite. Note that the Na₄P₂O₇ treated sample additionally contained 0.0095 M NaCl from the parent emulsion. A second emulsion was then prepared, and excess particles in the aqueous phase were removed by dilution to allow creaming, removal of the aqueous serum, and gentle redispersion of the cream into NaCl solution (0.01 M). The mass of particles remaining in the serum was measured by drying the suspension under vacuum, and no more than 10% of the initial particle mass remained in

the emulsions which is well below the gelation concentration.^{15,32} This was split into three, NaCl and Na₄P₂O₇ were added as above, and the D_{32} was recorded over a similar period of time.

Figure 2 shows that D_{32} does not change significantly over 30 days even after the addition of NaCl or Na₄P₂O₇. Additionally,

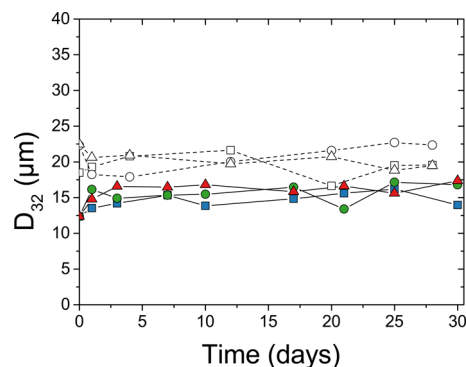


Figure 2. D_{32} of emulsions either with no additive (squares), $40 \mu\text{mol g}^{-1}$ Na₄P₂O₇ (triangles), or 0.1 M NaCl (circles) and either with particles in the continuous phase (closed symbols) or without (open symbols).

apart from a rapid initial increase in D_{32} which was too fast to be recorded (see discussion below), the samples without excess particles in the continuous phase did not show any significant change in droplet size over the course of the experiment.

Figure 3 shows micrographs of the emulsions with particles in the continuous phase after 30 days using differential interference contrast and polarizing optics. The 0.01 M NaCl sample is used as a reference state as this was previously reported to produce very stable emulsions.⁶ The reference state was used as a benchmark with which the Na₄P₂O₇ treated and higher concentration NaCl samples were compared. The droplets for all three sets of conditions show birefringence at the edges when viewed through crossed polarizers which was previously reported to indicate the adsorption of particles parallel to the interface.^{6,10} This suggests that modification of particle interactions after emulsification does not significantly alter the configuration of the particles at the interface.

Rheological Properties of Montmorillonite Stabilized Emulsions. The interaction between platelet-coated droplets and the platelet network formed in the continuous phase was probed using oscillatory rheology. Emulsions were prepared at 40 wt % hexadecane and diluted with montmorillonite suspension to give a series of emulsions with identical droplet size distributions but different dispersed phase weight fractions. Montmorillonite concentrations of 2.5 and 3 wt % in the aqueous phase were investigated. The plateau elastic moduli (G'_0) of these suspensions were then measured by performing amplitude sweeps at a constant frequency of 0.1 Hz and extrapolating the elastic modulus to zero strain. Figure 4 shows G'_0 for each emulsion relative to that of the continuous phase alone (G'_s) for the two different weight fractions of particles in the continuous phase. An enhancement in the elastic modulus is observed for increasing dispersed phase weight fraction of 10-fold for the weaker continuous phase gel (2.5 wt % montmorillonite) and 3-fold for the stronger gel (3 wt % montmorillonite) which would be expected for an actively filled gel.²⁴ The platelet-coated droplets therefore interact with the continuous phase network as an active filler.

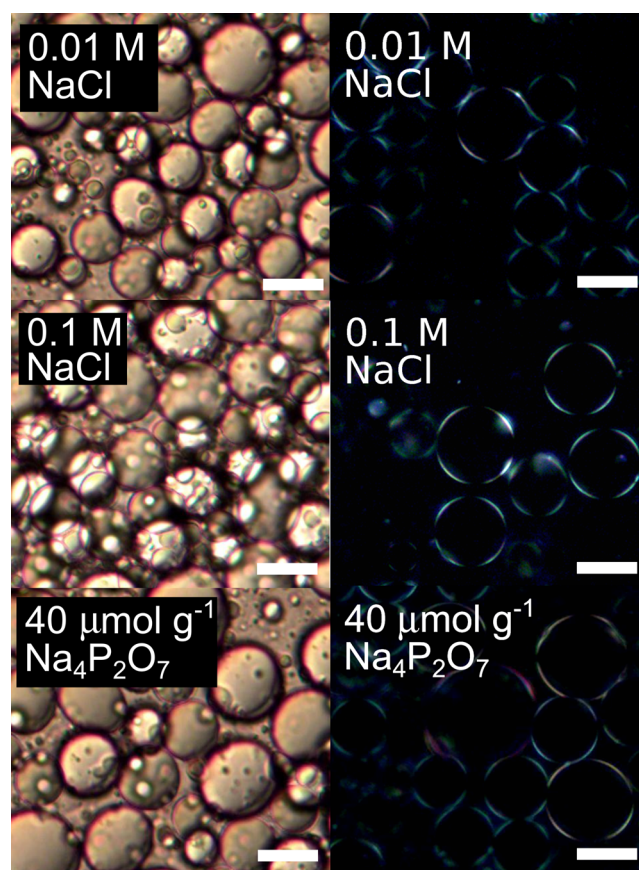


Figure 3. Differential interference contrast microscopy (left) and polarizing optical microscopy (right) images of montmorillonite stabilized emulsions after 30 days (40 wt % hexadecane, 3 wt % montmorillonite). Scale bars represent $20 \mu\text{m}$. Contrast of right-hand images has been enhanced for clarity.

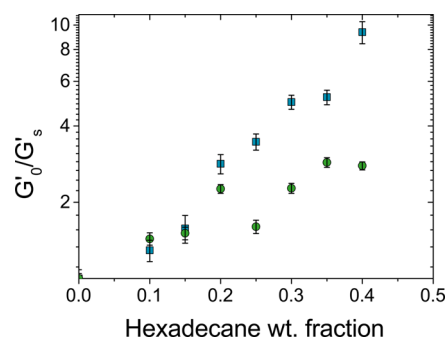


Figure 4. Plateau elastic moduli of emulsions at fixed montmorillonite (wt %) in the continuous phase (circles: 3 wt %; squares: 2.5 wt %) and different concentrations of dispersed phase.

Modification of Rheological Properties. The previous two sections have shown that the rheological properties of montmorillonite stabilized emulsions with an excess of particles in the continuous phase can be understood as actively filled gels and that treatment of such emulsions with NaCl or Na₄P₂O₇ does not hinder coalescence stability. This section shows how these additives can be used to dramatically alter the rheological behavior of montmorillonite stabilized emulsion gels.

Figures 5 and 6 show G'_0 and σ_y of emulsions and suspensions as a function of NaCl and Na₄P₂O₇ concentration. It should be noted that the emulsion containing 0.01 M NaCl

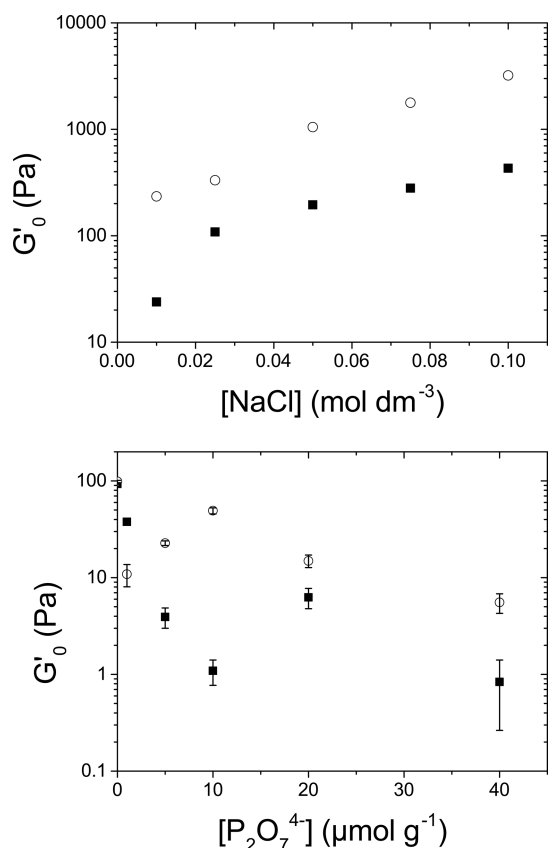


Figure 5. Plateau elastic moduli of 40 wt % hexadecane-in-water emulsions with 3 wt % montmorillonite in the continuous phase (circles) and continuous phases consisting of 3 wt % montmorillonite (squares) as a function of NaCl concentration (top) and $\text{Na}_4\text{P}_2\text{O}_7$ concentration (bottom). $\text{Na}_4\text{P}_2\text{O}_7$ samples all contained 0.0095 M NaCl.

was used as a reference state for both series and therefore corresponds to the leftmost points of the plots in Figures 5 and 6. Also, the samples with added $\text{Na}_4\text{P}_2\text{O}_7$ all contain 0.0095 M NaCl from the parent emulsion. The NaCl concentration was probed from 0.01 M, which was found to be appropriate to form stable emulsions,⁶ to 0.1 M above which extensive coalescence was observed. $\text{Na}_4\text{P}_2\text{O}_7$ concentrations from 0 to 40 $\mu\text{mol g}^{-1}$ montmorillonite were investigated. Previous work has found that concentrations above 20 $\mu\text{mol g}^{-1}$ have a minimal effect on montmorillonite suspension rheology and that small initial increases in $\text{Na}_4\text{P}_2\text{O}_7$ concentration result in dramatic reductions in rheological parameters.³² This may amplify the experimental error in sample preparation at small $\text{Na}_4\text{P}_2\text{O}_7$ concentrations resulting in the observed scatter in G'_0 and σ_y in this region.

At fixed dispersed phase weight fraction G'_0 and σ_y of the emulsions increase by over an order of magnitude upon addition of NaCl and decrease by over an order of magnitude upon addition of $\text{Na}_4\text{P}_2\text{O}_7$. The trend is mirrored in the rheology of the continuous phases alone (closed symbols in Figures 5 and 6), showing that the modifications to the emulsion rheology are due to the strengthening or weakening of the continuous phase network in the linear viscoelastic regime.

For both NaCl and $\text{Na}_4\text{P}_2\text{O}_7$ the emulsions have higher absolute values of G'_0 than the suspensions, but the general trend with additive concentration is common across each

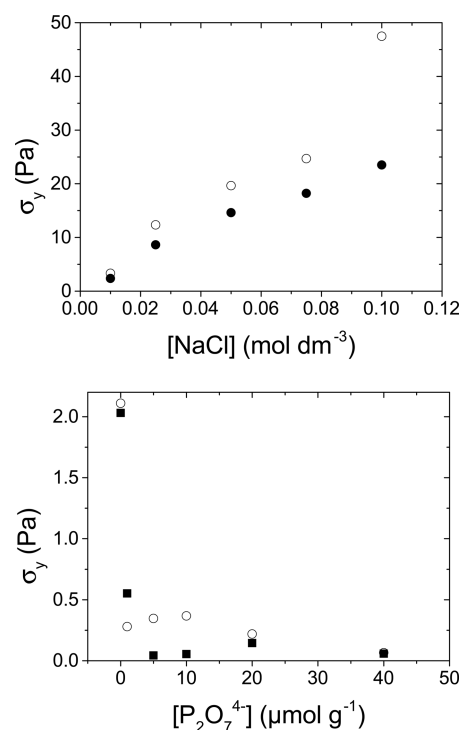


Figure 6. Yield stresses of 40 wt % hexadecane-in-water emulsions with 3 wt % montmorillonite in the continuous phase (circles) and continuous phases consisting of 3 wt % montmorillonite (squares) as a function of NaCl concentration (top) and $\text{Na}_4\text{P}_2\text{O}_7$ concentration (bottom). $\text{Na}_4\text{P}_2\text{O}_7$ samples all contained 0.0095 M NaCl.

emulsion and its corresponding continuous phase suspension. The relative increases from suspension to emulsion are of order 1 for both NaCl treated samples and range from 1 to 50 for the $\text{Na}_4\text{P}_2\text{O}_7$ treated samples, which is consistent with observations in Figure 4. The droplets behave as active fillers, and trends in emulsion elasticity are characteristic of the behavior of the continuous phase. Similar behavior was previously reported for silica stabilized emulsions at different NaCl concentrations.^{21–23}

A similar effect is seen under continuous shear where the steady state viscosity followed as a function of NaCl and $\text{Na}_4\text{P}_2\text{O}_7$ concentration. The Figure 7 shows an order of magnitude increase or decrease in viscosity upon addition of NaCl and $\text{Na}_4\text{P}_2\text{O}_7$ respectively at fixed dispersed phase weight fraction for both the 40 wt % hexadecane-in-water emulsions and the corresponding aqueous phases (open and closed symbols in Figure 7, respectively).

This section has demonstrated that the rheological behavior of montmorillonite stabilized Pickering emulsions is dictated by the continuous phase network and incorporation of the droplets reinforces the mechanical properties. Modification of particle interactions, and hence the strength of the continuous phase network, can therefore be used as a method to predictably control rheological parameters of emulsions by up to 3 orders of magnitude based on an understanding of the continuous phase network alone. This was achieved by increasing ionic strength by the addition of NaCl and increasing the electrostatic repulsion between particles by the adsorption of polyvalent pyrophosphate anions. In the following section we discuss these results mechanistically with the aim of developing a framework within which these emulsions can be understood.

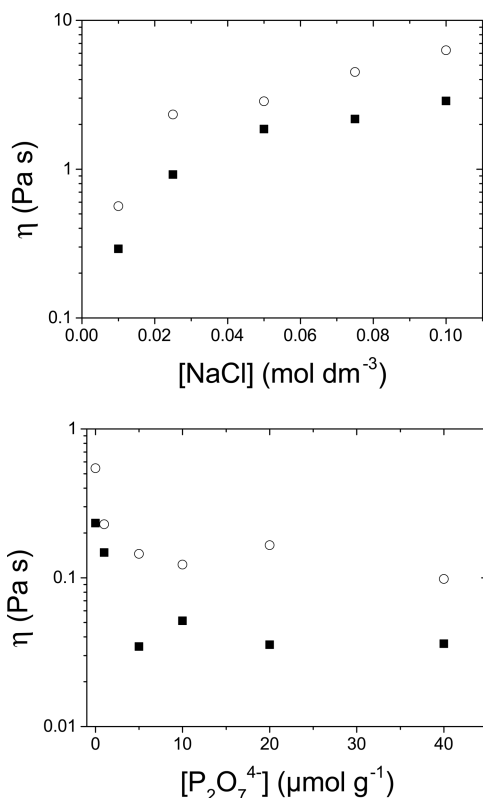


Figure 7. Viscosity of 40 wt % hexadecane-in-water emulsions with 3 wt % montmorillonite in the continuous phase (circles) and continuous phases consisting of 3 wt % montmorillonite (squares) as a function of NaCl concentration (top) and $\text{Na}_4\text{P}_2\text{O}_7$ concentration (bottom). $\text{Na}_4\text{P}_2\text{O}_7$ samples all contained 0.0095 M NaCl.

DISCUSSION

There are two often quoted mechanisms for the stabilization of emulsions by clay particles highlighted by the studies of Lagaly and co-workers.^{13,37} The first is the adsorption of particles forming a barrier at the interface, and the second is the immobilization of the droplets in a network of particles preventing them from moving into contact and coalescing. These mechanisms are depicted in Figure 8. Both could occur in this system as montmorillonite platelets are well-known to

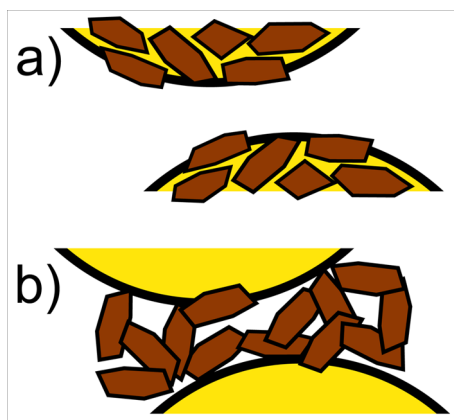


Figure 8. Stabilization mechanisms of emulsions by platelet particles. Adsorption of particles to the interface forming a solid barrier (a) and incorporation of droplets into the continuous phase network (b). Adapted from ref 37.

form gels in aqueous suspension,^{15,32} and previous work has estimated the adsorption energy of a single platelet at a hydrocarbon–oil interface to be of order $10^5 k_B T$.¹⁰

Figure 2 shows that emulsions both with and without excess particles in the continuous phase do not show any appreciable change in D_{32} over time. In the absence of a continuous phase network D_{32} is slightly higher, and this is attributed to some initial coalescence occurring too rapidly to be recorded. It should be noted that the process of extracting the excess particles involves concentrating the droplets and manipulating the concentrated cream. This is not representative of normal storage conditions and may have led to the initial rise in D_{32} . Once the droplets are rediluted and allowed to cream and stand, there is no evidence of further coalescence. The continuous phase network and the barrier of adsorbed particles at the interface therefore both contribute to coalescence stability, but the formation of a barrier at the interface is the more significant effect. After removal of the continuous phase network and for all surface chemistries tested the adsorbed layer of particles is sufficient to maintain stability over a long period of time despite a local concentration increase due to creaming. This is partly at odds with previous studies of emulsions stabilized by the slightly smaller Laponite platelet particles. Ashby and Binks first reported the stabilization of oil-in-water emulsions by Laponite platelet particles and warned that the addition of polyvalent anions known to adsorb to the particle edge would hinder coalescence stability by inducing repulsive interactions between the adsorbed particles.³⁸ Here we do not find this to be the case; however, the larger aspect ratio (and therefore smaller edge surface area proportional to face surface area) of montmorillonite particles may reduce the impact of particle edge surface chemistry. More recently, Dinkgreve and co-workers reported that high internal phase emulsions stabilized by Laponite particle gels are very unstable to shear, and this is attributed to the major stabilization mechanism being immobilization of the droplets in a Laponite gel.³⁹ They find that the gel re-forms slowly after being broken down by the shear field which allows the droplets to come into close proximity and coalesce. Figure 2 shows that the droplets are stable to coalescence even in the absence of a network in the continuous phase; therefore, the formation of a barrier at the interface is the dominant stabilization mechanism. The difference in particle size, droplet concentration, or surface chemistry (here we optimize the wettability of the platelets by adsorbing the hydrotrope Berol R648⁶) may be the cause of this discrepancy. An interesting further study would be to test the limits of stability of these emulsions under controlled shear as we have recently shown that particles desorb during high shear mixing.¹⁰

The rheological data presented in the previous section show that NaCl can enhance rheological properties of montmorillonite emulsion gels, $\text{Na}_4\text{P}_2\text{O}_7$ can reduce rheological parameters, and the presence of droplets provides an enhancement to the rheology of the continuous phase gel. To understand these effects, we need to establish the mechanisms by which the droplets enhance the rheology of the continuous phase gels and those by which the additives modify the continuous phase resulting in the observed 3 orders of magnitude change in rheological parameters.

The response of aqueous montmorillonite gels to NaCl and $\text{Na}_4\text{P}_2\text{O}_7$ is already well reported. Montmorillonite platelets are high aspect ratio (300:1) and have complex charge anisotropy resulting in competing attractive electrostatic and dispersion

and repulsive electrostatic interactions.^{15,29,40} These competing interactions result in the formation of a network state when the attractive interactions begin to dominate over the repulsive interactions and the particle concentration exceeds a critical level. It is well-known that ionic strength can be used to reduce the relative contribution of repulsive interactions and therefore enhance gel strength.¹⁵

Conversely, the addition of polyvalent anions (such as $\text{P}_2\text{O}_4^{4-}$) to suspensions of montmorillonite and related clay minerals is well reported to weaken and eventually break up the particulate gels.^{29–32} We have recently utilized rheology, light scattering, and electrophoretic mobility experiments to show that the weakening of the gels is consistent with a change in structure due to the adsorption of the phosphate anions to the edges of the montmorillonite particles.³² Similar trends in suspension viscosity are expected as resistance to flow results from a competition between breakup and re-formation of gel fragments under continuous shear. We build upon this understanding of aqueous clay mineral gels by combining these two handles on the balance of interactions results here in the 3 orders of magnitude change in rheological parameters observed in Figures 5, 6, and 7.

It has already been established that particle armored droplets interact actively with the continuous phase network and the stress bearing properties of the droplets enhance rheological parameters,^{13,25–27} and this is true across a range of NaCl^{12,22,23} and particle concentrations (see Figure 4). We show that this is a more general phenomenon that also occurs when the gel strength is weakened by the adsorption of $\text{Na}_4\text{P}_2\text{O}_7$ to the particle edges as shown in Figures 5 and 6.

The ability of the dispersed droplets to bear stress transmitted through the gel results in the observed rheological enhancement. The mechanisms for this can be different depending on whether the droplets deform significantly under shear. The capillary number compares viscous and interfacial forces and indicates whether a droplet will deform in a given flow field. The capillary number is defined as

$$Ca = \frac{\eta_s \dot{\gamma} a}{\Gamma} \quad (1)$$

where η_s is the viscosity of the suspending medium, $\dot{\gamma}$ is the shear rate, a is the droplet radius, and Γ is the interfacial tension. Using the measured viscosities of the continuous phases at $\dot{\gamma} = 10 \text{ s}^{-1}$ (see Figure 7), droplets of order $10 \mu\text{m}$, and interfacial tension 50 mN m^{-1} , Ca is much less than unity. This indicates that interfacial forces dominate; therefore, the droplets do not deform significantly during shearing and act as hard objects. The contribution of nondeforming fluid objects to suspension viscosity is reported to be similar to that of hard spheres where redirection of the flow field around the objects causes an increase in the stress required to achieve a given flow rate and hence the viscosity increases. The models of Taylor⁴¹ and Pal⁴² describe this (see ref 43 for a summary of relevant models). The system of attractive platelet particles and nondeforming droplets under flow investigated here is much more complex than the two-component dispersions considered by these models. However, they do provide the basic prediction that the viscosity should increase relative to that of the continuous phase alone matching what is observed in Figure 7.

Under oscillation in the linear viscoelastic regime the deformation of the emulsion gels is slightly different. Here the gel does not break up but is deformed, which moves the particles away from their lowest energy separations and results

in the observed elastic response. Where there are also droplets bound within the network droplet deformation, droplet–droplet and droplet–network interactions may also contribute to the elastic response. The dimensionless elastocapillary stress is analogous to Ca for this mode of deformation and can be used to identify the extent of droplet deformation given the stress transmitted through the network. It is defined as^{27,44}

$$\sigma_{Ca} = \frac{aG'_0}{\Gamma} \quad (2)$$

For the systems tested here σ_{Ca} is of order or less than unity which shows that the stress transmitted through the network does not cause any significant droplet deformation. Droplet–droplet interactions are unlikely as this would require adsorbed particles to be bridged between two droplets. Because of the 1 nm thickness of the platelets, bridging would require droplet to come into very close proximity. It is likely that this separation is below the critical film thickness for coalescence; therefore, such droplet–droplet interactions are unlikely.^{45,46} Droplet–network interactions resulting from stress transmitted through the network acting on adsorbed particles are therefore the likely contributors to emulsion elasticity. This stress will be opposed by the adsorption energy holding the particles at the interface, inherent attractive interactions between interfacial particles, and possibly capillary attractions between the particles as a result of any small local deformation of the interface. These factors contribute to the enhancement in G'_0 which is observed in Figure 5, but also mean that a higher stress is required to break the network down resulting in the increase in σ_y observed in Figure 6. Interestingly, due to an elastic mismatch between the network and the droplets, fractures in the network may form along the matrix–filler interface as adsorbed particles are pulled out of contact with those in the network. This causes the emulsion gels to be more brittle (have a lower breaking strain than the continuous phase gel alone), and this is seen in the raw oscillatory strain sweeps shown in the Supporting Information.

It has therefore been shown that the rheological response of montmorillonite stabilized hexadecane-in-water emulsions, where the droplets are bound to the continuous phase network, is defined by the behavior of the continuous phase network and enhanced by the stress bearing capabilities of the bound droplets. This agrees with previous studies on similar systems.^{21–23} We also expand this to show that different types of additive, in this case $\text{Na}_4\text{P}_2\text{O}_7$, result in modifications in rheological properties mirroring those observed in the continuous phase network alone with an enhancement from the presence of the droplets.

CONCLUSIONS

This study has investigated the rheological modification and coalescence stability of particle stabilized emulsions in which excess stabilizer particles form a network in the continuous phase. Montmorillonite stabilized hexadecane-in-water emulsions exhibited no change in average droplet size over a period of 30 days whether the droplets were immobilized by a continuous phase network or allowed to cream showing that the formation of a solid barrier at the interface contributed most significantly to coalescence stability.

The rheological behavior of the emulsions was found to be dominated by the behavior of the continuous phase network and enhanced by the presence of the droplets through redirection of the shear field and matrix–filler type interactions.

The emulsion rheology was controlled by altering the rheological properties of the continuous phase network. Increasing the NaCl concentration of the emulsion resulted in more than an order of magnitude increase in plateau elastic modulus, yield stress, and viscosity, and the addition of $\text{Na}_4\text{P}_2\text{O}_7$ resulted in an order of magnitude decrease in these parameters.

This work shows that the rheological parameters of montmorillonite stabilized hexadecane-in-water emulsions can be modified over multiple orders of magnitude by the addition of salt solutions, the emulsions are stabilized primarily by the formation of a mechanical barrier at the interface, and the rheological modifications occur with no loss of coalescence stability. Such systems therefore provide a versatile class of materials upon which to base fluid formulations with a wide range of flow properties and a high level of stability.

■ ASSOCIATED CONTENT

● Supporting Information

Raw rheological data and micrographs used to measure droplet sizes in Figure 2 can be found in a data repository DOI: 10.5523/bris.d2tt5g35buds1d4j3f3mj9dc9 (<https://data.bris.ac.uk/data/dataset/d2tt5g35buds1d4j3f3mj9dc9>). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b04161.

Photographs of emulsions at the end of stability experiments detailed in Figure 2 and rheological amplitude sweeps used to calculate yield stresses and plateau elastic moduli in Figures 4–7 and control experiments of montmorillonite suspensions without Berol R648 (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Ramsden, W. Separation of Solids in the Surface-Layers of Solutions and 'Suspensions' (Observations on Surface-Membranes, Bubbles, Emulsions, and Mechanical Coagulation). - Preliminary Account. *Proc. R. Soc. London* **1903**, *72*, 156–164.
- (2) Pickering, S. U. Emulsions. *J. Chem. Soc., Trans.* **1907**, *91*, 2001–2021.
- (3) Aveyard, R.; Binks, B. P.; Clint, J. H. Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.* **2003**, *100–102*, 503–546.
- (4) Chevalier, Y.; Bolzinger, M. A. Emulsions stabilized with solid nanoparticles: Pickering emulsions. *Colloids Surf., A* **2013**, *439*, 23–34.
- (5) Binks, B. P.; Clint, J. H. Solid Wettability from Surface Energy Components: Relevance to Pickering Emulsions. *Langmuir* **2002**, *18*, 1270–1273.

- (6) Cui, Y.; Threlfall, M.; van Duijneveldt, J. S. Optimizing organoclay stabilized Pickering emulsions. *J. Colloid Interface Sci.* **2011**, *356*, 665–671.

- (7) Kalashnikova, I.; Bizot, H.; Bertoncini, P.; Cathala, B.; Capron, I. Cellulosic nanorods of various aspect ratios for oil in water Pickering emulsions. *Soft Matter* **2013**, *9*, 952–959.

- (8) de Folter, J. W. J.; Hutter, E. M.; Castillo, S. I. R.; Klop, K. E.; Philipse, A. P.; Kegel, W. K. Particle Shape Anisotropy in Pickering Emulsions: Cubes and Peanuts. *Langmuir* **2014**, *30*, 955–964.

- (9) Yuan, Q.; Cayre, O. J.; Manga, M.; Williams, R. A.; Biggs, S. Preparation of particle-stabilized emulsions using membrane emulsification. *Soft Matter* **2010**, *6*, 1580–1588.

- (10) Ganley, W. J.; van Duijneveldt, J. S. Steady-state droplet size in montmorillonite stabilised emulsions. *Soft Matter* **2016**, *12*, 6481–6489.

- (11) Menner, A.; Ikem, V.; Salgueiro, M.; Shaffer, M. S. P.; Bismarck, A. High internal phase emulsion templates solely stabilised by functionalised titania nanoparticles. *Chem. Commun.* **2007**, 4274–4276.

- (12) Herzig, E. M.; White, K. A.; Schofield, A. B.; Poon, W. C. K.; Clegg, P. S. Bicontinuous emulsions stabilized solely by colloidal particles. *Nat. Mater.* **2007**, *6*, 966–971.

- (13) Lagaly, G.; Reese, M.; Abend, S. Smectites as colloidal stabilizers of emulsions: II. Rheological properties of smectite-laden emulsions. *Appl. Clay Sci.* **1999**, *14*, 279–298.

- (14) Luckham, P. F.; Rossi, S. The colloidal and rheological properties of bentonite suspensions. *Adv. Colloid Interface Sci.* **1999**, *82*, 43–92.

- (15) Abend, S.; Lagaly, G. Sol-gel transitions of sodium montmorillonite dispersions. *Appl. Clay Sci.* **2000**, *16*, 201–227.

- (16) Michot, L. J.; Bihannic, I.; Porsch, K.; Maddi, S.; Baravian, C.; Mougel, J.; Levitz, P. Phase Diagrams of Wyoming Na-Montmorillonite Clay. Influence of Particle Anisotropy. *Langmuir* **2004**, *20*, 10829–10837.

- (17) Paineau, E.; Michot, L. J.; Bihannic, I.; Baravian, C. Aqueous Suspensions of Natural Swelling Clay Minerals. 2. Rheological Characterization. *Langmuir* **2011**, *27*, 7806–7819.

- (18) Tsugita, A.; Takemoto, S.; Mori, K. Studies on OW emulsions stabilized with insoluble montmorillonite-organic complexes. *J. Colloid Interface Sci.* **1983**, *95*, 551–560.

- (19) Ferri, J. K.; Carl, P.; Gorevski, N.; Russell, T. P.; Wang, Q.; Böker, A.; Fery, A. Separating membrane and surface tension contributions in Pickering droplet deformation. *Soft Matter* **2008**, *4*, 2259–2266.

- (20) Arditty, S.; Schmitt, V.; Giermanska-Kahn, J.; Leal-Calderon, F. Materials based on solid-stabilized emulsions. *J. Colloid Interface Sci.* **2004**, *275*, 659–664.

- (21) Horozov, T. S.; Binks, B. P.; Gottschalk-Gaudig, T. Effect of electrolyte in silicone oil-in-water emulsions stabilised by fumed silica particles. *Phys. Chem. Chem. Phys.* **2007**, *9*, 6398–6404.

- (22) Kpogbemabou, D.; Lecomte-Nana, G.; Aimable, A.; Bienia, M.; Niknam, V.; Carrion, C. Oil-in-water Pickering emulsions stabilized by phyllosilicates at high solid content. *Colloids Surf., A* **2014**, *463*, 85–92.

- (23) Fuma, T.; Kawaguchi, M. Rheological responses of Pickering emulsions prepared using colloidal hydrophilic silica particles in the presence of NaCl. *Colloids Surf., A* **2015**, *465*, 168–174.

- (24) Dickinson, E. Emulsion gels: The structuring of soft solids with protein-stabilized oil droplets. *Food Hydrocolloids* **2012**, *28*, 224–241.

- (25) Simon, S.; Theiler, S.; Knudsen, A.; Øye, G.; Theiler, S.; Knudsen, A.; Øye, G.; Sjo, J. Rheological Properties of Particle-Stabilized Emulsions. *J. Dispersion Sci. Technol.* **2010**, *31*, 632–640.

- (26) Torres, L.; Iturbe, R.; Snowden, M.; Chowdhry, B.; Leharne, S. Preparation of o/w emulsions stabilized by solid particles and their characterization by oscillatory rheology. *Colloids Surf., A* **2007**, *302*, 439–448.

- (27) Katepalli, H.; John, V. T.; Tripathi, A.; Bose, A. Microstructure and rheology of particle stabilized emulsions: Effects of particle shape and inter-particle interactions. *J. Colloid Interface Sci.* **2017**, *485*, 11–17.

(28) Binks, B. P.; Clint, J. H.; Whitby, C. P. Rheological behavior of water-in-oil emulsions stabilized by hydrophobic bentonite particles. *Langmuir* **2005**, *21*, 5307–5316.

(29) Van Olphen, H. *An Introduction to Clay Colloid Chemistry: For Clay Technologists, Geologists, and Soil Scientists*; Krieger Publishing Company: 1991.

(30) Penner, D.; Lagaly, G. Influence of anions on the rheological properties of clay mineral dispersions. *Appl. Clay Sci.* **2001**, *19*, 131–142.

(31) Mongondry, P.; Nicolai, T.; Tassin, J.-F. Influence of pyrophosphate or polyethylene oxide on the aggregation and gelation of aqueous laponite dispersions. *J. Colloid Interface Sci.* **2004**, *275*, 191–196.

(32) Ganley, W. J.; van Duijneveldt, J. S. Controlling clusters of colloidal platelets: effects of edge and face surface chemistries on the behavior of montmorillonite suspensions. *Langmuir* **2015**, *31*, 4377–4385.

(33) Cui, Y.; van Duijneveldt, J. S. Adsorption of Polyetheramines on Montmorillonite at High pH. *Langmuir* **2010**, *26*, 17210–17217.

(34) Whitby, C. P.; Khairul Anwar, H.; Hughes, J. Destabilising Pickering emulsions by drop flocculation and adhesion. *J. Colloid Interface Sci.* **2016**, *465*, 158–164.

(35) Tambe, D. E.; Sharma, M. M. Factors controlling the stability of colloid stabilised emulsions: an experimental investigation. *J. Colloid Interface Sci.* **1993**, *157*, 244–253.

(36) Binks, B. P.; Lumsdon, S. O. Stability of oil-in-water emulsions stabilised by silica particles. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3007–3016.

(37) Lagaly, G.; Reese, M.; Abend, S. Smectites as colloidal stabilizers of emulsions: I. Preparation and properties of emulsions with smectites and nonionic surfactants. *Appl. Clay Sci.* **1999**, *14*, 83–103.

(38) Ashby, N.; Binks, B. Pickering emulsions stabilised by Laponite clay particles. *Phys. Chem. Chem. Phys.* **2000**, *2*, 5640–5646.

(39) Dinkgreve, M.; Velikov, K. P.; Bonn, D. Stability of LAPONITE® stabilized high internal phase Pickering emulsions under shear. *Phys. Chem. Chem. Phys.* **2016**, *18*, 22973–22977.

(40) Shalkevich, A.; Stradner, A.; Bhat, S. K.; Muller, F.; Schurtenberger, P. Cluster, Glass, and Gel Formation and Viscoelastic Phase Separation in Aqueous Clay Suspensions. *Langmuir* **2007**, *23*, 3570–3580.

(41) Taylor, G. The Viscosity of a Fluid Containing Small Drops of Another Fluid. *Proc. R. Soc. London, Ser. A* **1932**, *138*, 41–48.

(42) Pal, R. Rheology of polymer-thickened emulsions. *J. Rheol.* **1992**, *36*, 1245–1259.

(43) Larson, R. *The Structure and Rheology of Complex Fluids*; Oxford University Press: 1999.

(44) Van Hooghten, R.; Imperiali, L.; Boeckx, V.; Sharma, R.; Vermant, J. Rough nanoparticles at the oil-water interface their structure, rheology and applications. *Soft Matter* **2013**, *9*, 10791–10798.

(45) Stancik, E. J.; Kouhkan, M.; Fuller, G. G. Coalescence of Particle-Laden Fluid Interfaces. *Langmuir* **2004**, *20*, 90–94.

(46) Denkov, N.; Ivanov, I.; Kralchevsky, P. A.; Wasan, D. T. A possible mechanism of stabilization of emulsions by solid particles. *J. Colloid Interface Sci.* **1992**, *150*, 589–593.