

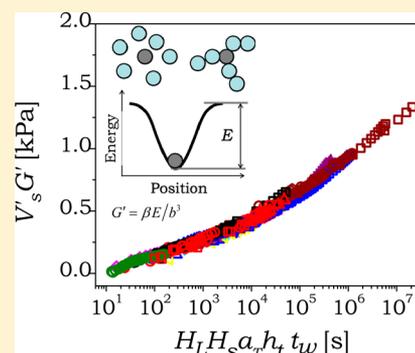
Physicochemical Effects in Aging Aqueous Laponite Suspensions

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Supporting Information

ABSTRACT: We study aging behavior of an aqueous suspension of Laponite as a function of concentration of Laponite, concentration of salt, time elapsed since preparation of suspension (idle time), and temperature by carrying extensive rheological and conductivity experiments. We observe that temporal evolution of elastic moduli, which describes structural build-up and aging, shifts to low times for experiments carried out for higher concentration of Laponite, higher concentration of salt, greater temperature, and longer idle time while preserving the curvature of evolution in the solid regime (elastic modulus greater than viscous modulus). Consequently appropriate shifting of evolution of elastic modulus in the solid regime leads to aging time—idle time—salt concentration—Laponite concentration—temperature superposition. The existence of such a superposition suggests the generic nature of microstructure buildup irrespective of mentioned variables in the explored range. The behavior of shift factors needed to obtain the superposition indicate that the energy barrier associated with structural buildup decreases with an increase in idle time and temperature and decreases linearly with an increase in concentration of Laponite and that of salt. The conductivity experiments show that ionic conductivity of the suspension increases with increasing Laponite concentration, salt concentration, temperature, and very importantly the idle time. We also analyze the interparticle interactions using DLVO theory that suggests an increase in idle time, temperature, and salt concentration increases the height of the repulsive energy barrier while it decreases the width of the same when particles approach each other in a parallel fashion. However when particles approach each other in a perpendicular fashion, owing to dissimilar charges on edge and face, the energy barrier for the attractive interaction is expected to decrease with an increase in idle time, temperature, and salt concentration. Analysis of rheological and conductivity experiments suggests a strong influence of attractive interactions on the low energy structures in an aqueous suspension of Laponite.



I. INTRODUCTION

Smectite clay minerals are an important class of colloidal materials with immense academic importance and wide ranging applications.^{1,2} Smectite clays have an oblate shape (layered like) with an aspect ratio in the range 25–1000.¹ Particularly clays embedded in aqueous media are used as rheology modifiers in industries such as petroleum, healthcare, cosmetic, etc.³ Therefore, it is not surprising that rheological and phase behaviors of clays have been very active areas of research over the past several decades.^{1,2,4–17} In the recent literature, a synthetic clay mineral called Laponite has received significant attention due to its rich physical behavior and industrial applications. In addition, an aqueous Laponite suspension shows time dependence evolution of its microstructure and physical properties that is reminiscent of physical aging in molecular, spin, and colloidal glasses.^{18,19} In this work we carry out extensive rheological and conductivity studies on an aqueous suspension of Laponite and analyze various distinct characteristic features of aging observed in this system.

Physical aging is a natural tendency of those materials that, owing to kinetic constraints, have fallen out of thermodynamic equilibrium.²⁰ In a physical aging process, a material explores its phase space and undergoes time dependent evolution in order to progressively attain lower energy microstructures.²¹ There are many soft materials such as concentrated suspensions and

emulsions, cosmetic and pharmaceutical pastes, colloidal gels, clay suspensions, foams, etc. that demonstrate physical aging and have enormous academic and industrial importance.²² Physical aging is, in principle, a reversible phenomenon. The application of a deformation field reverses the effects of aging by rejuvenating the material to higher energy levels.^{23,24} Physical aging is analyzed by monitoring the affected physical properties of the material that show time dependent change. In soft materials, the light scattering techniques are commonly used to probe the structure and evolution of the mobility of the constituents of materials,^{25–30} which also leads to the relaxation time of the same. Bulk rheological techniques are also used to monitor evolution of viscoelastic properties such as elastic and viscous modulus which get strongly affected by physical aging.^{31–33} Recently microrheological techniques have also been used to analyze soft glassy materials.^{34–36} For various soft materials that are thermodynamically out of equilibrium, including aqueous Laponite suspension, ample literature is available that employs scattering as well as rheological techniques to study the aging behavior. However, since the effect of aging in soft glassy materials can be reversed by

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application of deformation field alone, rheological techniques are crucial for studying these phenomena.^{18,31,37–39}

Laponite (hydrous sodium lithium magnesium silicate, $\text{Na}_{+0.7}[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]_{-0.7}$) is a synthetic layered silicate clay mineral available as a white powder. A Laponite particle has a disk like shape with a diameter in the range 25–30 nm with a thickness of 1 nm.⁴⁰ In dry form Laponite particles are present in stacks with sodium ions residing in the interparticle gallery. When dispersed in aqueous medium sodium ions dissociate rendering a permanent negative charge on the faces of Laponite disks. The edge of the Laponite particle, which is composed of hydrous oxides of magnesium and silica, is reported to acquire a positive charge at low pH (below the pH of around 11).⁴¹ Overall Laponite particles share edge-to-face attractive interactions while face-to-face repulsive interactions among each other. Addition of a salt such as NaCl enhances the concentration of cations and anions in the suspension which shield the charges on the particle thereby reducing repulsion among the particles. The addition of Laponite to water, typically beyond 2 wt %, increases its viscosity and elastic modulus by several orders of magnitude over a short duration.³¹ The microstructure of Laponite suspension and its time dependency that is responsible for such enormous increase in viscosity is, however, not completely understood even after more than 15 years of research on this topic.^{42–44} The issue of contention is whether the microstructure of Laponite is an attractive gel (interconnected particles through positive edge–negative face contact)^{16,30,42,45–47} or a repulsive glass (particles in a self-suspended state in a liquid media owing to repulsion among them).^{15,48–50} Some reports claim the existence of both states over a certain concentration regime.⁵¹ Interestingly, several groups have observed Laponite disks to show anisotropic orientation in a suspended state.^{6–9,13} Recently our group reported that anisotropy originates at the air–suspension interface and percolates into the bulk as a function of time.⁵²

The aging behavior of a Laponite suspension can be rheologically monitored by applying a small amplitude oscillatory shear to a shear melted suspension so as to record evolution of elastic (G') and viscous (G'') moduli as a function of time.^{39,44,53,54} However, it has been observed that, unlike many soft materials that show complete reversal of aging when a strong deformation field is applied, the evolution of viscoelastic properties in an aqueous suspension of Laponite is only partly reversible over a time scale of days.^{19,37,39,44} Shahin and Joshi⁴⁴ observed that under large amplitude oscillatory shear (shear melting protocol in an oscillatory mode) an aqueous suspension of Laponite demonstrates a plateau of complex viscosity after a sufficient time of shearing, which has a higher value for samples kept idle over a longer duration since the preparation of the suspension (we represent this time as idle time). In addition, the temporal evolution of G' and G'' after shear melting is stopped shifts to lower times for experiments carried out on higher idle times. It was concluded that the structure formed by Laponite particles in a suspension cannot be completely destroyed by application of shear suggesting irreversibility in aging over a duration of days.^{39,44} This observation suggests that the shear melted sample on a higher idle time is in a more matured (low energy) state. Furthermore, for suspensions having a greater concentration of salt (NaCl) or experiments carried out at a higher temperature, the evolution of G' is also observed to shift to lower times suggesting the rate of formation of the structure to be faster

with an increase in the two mentioned variables.^{31,37,44,55} In this paper we extend this work and analyze the effect of different concentrations of Laponite, different concentrations of salt for each concentration of Laponite, and temperatures on the aging behavior at various idle times by carrying out extensive rheological experiments. We simultaneously perform conductivity studies as a function of the same variables and estimate interparticle interactions using DLVO theory for the Laponite suspension. We believe that both of these studies give complementary information leading to new insights into various features of aging dynamics in this system.

II. MATERIAL AND EXPERIMENTAL PROTOCOL

In this work we have used smectite hectorite clay Laponite RD procured from Southern Clay Products Inc. White powder of Laponite was dried at 120 °C for 4 h before mixing with deionized water having pH 10 and predetermined amount of NaCl. The pH was maintained by addition of NaOH. Mixing was carried out using an ultra turrex drive for a period of 45 min. Subsequent to mixing, suspensions were stored in sealed polypropylene bottles at room temperature. In this work we have used five Laponite concentrations: 2, 2.4, 2.8, 3.2, and 3.5 wt %. For each concentration of Laponite, suspensions were prepared with five concentrations of salt (NaCl) in the range 0.1–7 mM of externally added Na^+ ions (a concentration of 0.1 mM is achieved merely by NaOH used to maintain pH; therefore, this concentration corresponds to a no salt situation). We carried out the rheological, ionic conductivity, and complexometric titration experiments on these 25 samples on various days elapsed since preparation of the suspensions up to 21 days (idle time) at an interval of 3 days (for some samples we also carried out experiments up to 60 days). Complexometric titration⁵⁶ experiments using EDTA were carried out to confirm the stability of these suspensions at regular interval. These experiments did not show the presence of Mg^{2+} ions for any sample over the above-mentioned period, thereby ruling out the possibility of Mg^{2+} leaching from the Laponite particles.^{56,57}

Rheological experiments were performed using a stress controlled rheometer AR 1000 (Couette geometry with a bob diameter of 28 mm and a gap of 1 mm). The procedure employed in the rheological experiments is described in Figure 1. For every experiment, at a

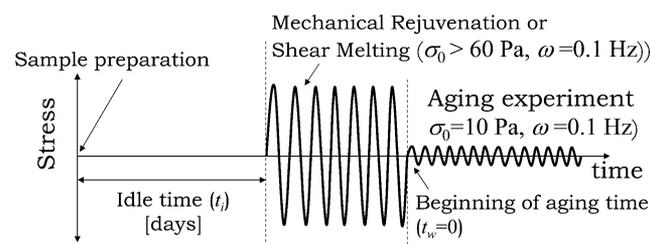


Figure 1. Schematic representing the experimental protocol employed for the rheological experiments.

specific idle time (mentioned in days) a fresh sample was loaded in the Couette geometry using an injection syringe, and proper care was taken to avoid entrapment of air bubbles. After attaining thermal equilibrium the sample was shear melted using an oscillatory stress of 60–80 Pa (varied depending on the concentration of Laponite) and a frequency of 0.1 Hz. The time at which shear melting was stopped marks the beginning of aging time ($t_w = 0$). Subsequent to shear melting, aging experiments were carried out by applying a small amplitude oscillatory shear stress with magnitude 10 Pa at a frequency of 0.1 Hz. An evolution of the viscoelastic properties of a suspension was monitored as a function of aging time (t_w). It should be noted that, owing to a time dependent increase in elastic modulus and viscosity, the rheological linear response regime undergoes continuous broadening as a function of aging time. However estimation of the linear response regime poses some practical difficulties for samples

having a small age. When the time scale associated with the stress sweep experiment is larger than the age of the sample, evolution of viscoelastic properties takes place over the duration of the experiment forbidding the estimation of the linear response regime. At higher ages, the aging experiments were indeed carried out in the linear response regime. Interestingly, irrespective of the age of the sample, the strain response to the stress controlled experiments was always close to harmonic justifying usage of G' and G'' as discussed before in greater detail.^{39,44,58} For all of the above-mentioned concentrations, aging experiments were carried at 10 °C.

We also measured the ionic conductivity (Cyberscan PC 6000) of all of the samples at regular intervals since preparation of suspensions up to 18 days. In order to measure conductivity, suspension samples were shear melted using an injection syringe with a needle having a 0.5 mm diameter and 30 mm length. In this process, the soft solid shear melts and forms a liquid. Our experience suggests that, within experimental uncertainty, the extent of shearing does not show any effect on the conductivity. However, as expected, for a low viscosity sample, the conductivity meter shows a steady state over a shorter duration. For significantly aged samples, measurement of an accurate value of conductivity becomes difficult because of the high viscosity of the suspension. Moreover, under these conditions, measurement of the ionic conductivity as a function of temperatures becomes more difficult owing a faster increase in viscosity of the suspension at high temperatures.

In addition to the experiments at different Laponite and salt concentrations, we also studied the effect of temperature in the range 10–40 °C on the evolution of viscoelastic properties of a 2.8 wt % Laponite suspension with five concentrations (0.1–7 mM) of NaCl. The temperature dependence was studied over idle time duration from 3 days up to 60 days at regular intervals. In all of the rheological experiments a thin layer of low viscosity silicon oil was applied on the free surface to prevent evaporation.

III. RESULTS

We begin by discussing the results of a rheological study. Before starting the aging experiments all of the samples were shear melted until the complex viscosity of the respective suspension attained a steady state plateau. This steady state plateau of complex viscosity demonstrated a higher value for experiments carried out on greater idle times indicating the inability of the strong shear deformation field to destroy the structure formed during aging irrespective of the concentration of Laponite and that of salt. Subsequently, shear melting was stopped and the suspension was allowed to age. It is usually observed that shear melting carried out at different stress levels does not affect the subsequent aging if the applied stress completely rejuvenates the material. Therefore any excessive or otherwise shear melting/history the material is subjected to while loading the sample is erased in the shear melting protocol. Cessation of the shear melting step marks the beginning of aging time ($t_w = 0$). Similar to that observed for the 2.8 wt % concentration system,⁴⁴ evolution of G' typically follows a two-step evolution for other concentrations as well. Usually for experiments carried out on low idle times or with lesser salt concentrations, suspensions are observed to be in a liquid state ($G' < G''$) immediately after the shear melting is stopped. On the other hand, for experiments carried out on higher idle times or with a greater concentration of salt, the suspension directly enters a solid state after the shear melting ($G' > G''$). In the liquid regime, G' shows a stronger enhancement as a function of aging time compared to that of G'' and eventually crosses the same. The point of crossover ($G' = G''$) is represented as a liquid–solid transition in the literature.³² It should be noted that this point of transition does depend on the applied frequency (or a time scale of probe),³⁹ as also observed for glass transition in

molecular glasses.⁵⁹ In the solid state ($G' > G''$), G' increases with a weaker dependence on aging time and G'' decreases after showing a maxima. We also perform aging experiments at different frequencies. Interestingly, G' does not show any dependence on frequency beyond $G' > G''$. However G'' shows a weak decrease with frequency in the solid state.

As mentioned before, evolution of G' and G'' for experiments on Laponite suspension carried out at higher idle times and with greater concentration of salt shift to lower aging times. The representative behavior for a 3.5 wt % suspension is plotted in Figure 2. It can be seen that the curvature of the

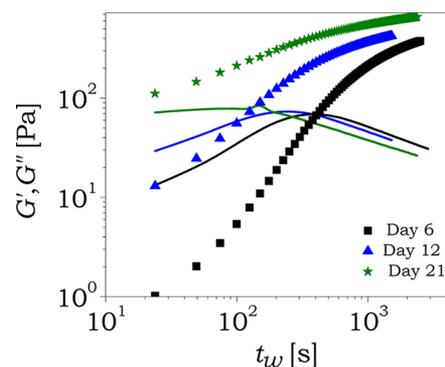


Figure 2. Evolution of storage (symbols) and loss moduli (lines) on different idle times (t_i) for a suspension having 1 mM salt and 3.5 wt % Laponite.

evolution of G' beyond the crossover is self-similar, which leads to an aging time–idle time superposition for various concentrations of salt as shown in Figure 3a. Various superpositions of G' at different concentrations of salt also share self-similar curvature in the solid state ($G' > G''$) and produce aging time–idle time–salt concentration superposition for all of the explored concentrations of Laponite. We report these superpositions in Figure 4a. Similar to the effect of idle time and salt concentration, evolution of the elastic (and viscous) modulus at higher Laponite concentration shifts to lower aging times. In order to get the aging time–idle time–salt concentration superposition at various Laponite concentrations shown in Figure 4a, we have primarily carried out the horizontal shifting of all of the G' evolutions. The vertical shift factor is required for salt concentration dependent shifting, though the value of V_s is observed to be of the order of unity (vertical shift factor V_L shown in Figure 4a is merely used to show the superpositions for various Laponite concentrations clearly). The horizontal shift factors (h_t) associated with idle time shifting (shown in Figure 3b) were observed to increase with the increase in idle time. The salt concentration dependent horizontal shift factors (H_s) plotted as a function of concentration of salt for various concentrations of Laponite are shown in Figure 4b. It can be seen that the shift factors show an exponential dependence on salt concentration represented by $\ln(H_s) \approx C_s$, irrespective of the Laponite concentration in the explored range of 2–3.5 wt %. It should be noted that various shift factors discussed in this work are not independent and separable from others and do depend on values of other variables. For example, in Figure 3a, $h_t = H(C_L, C_s, t_i, T)$, where $C_L = 3.5$ wt % and $T = 10$ °C, and is plotted as a function of C_s and t_i in Figure 3b. Similarly in Figure 3a, $H_s h_t = H(C_L, C_s, t_{iR}, T_R)$, where $t_{iR} = 18$ day and $T_R =$

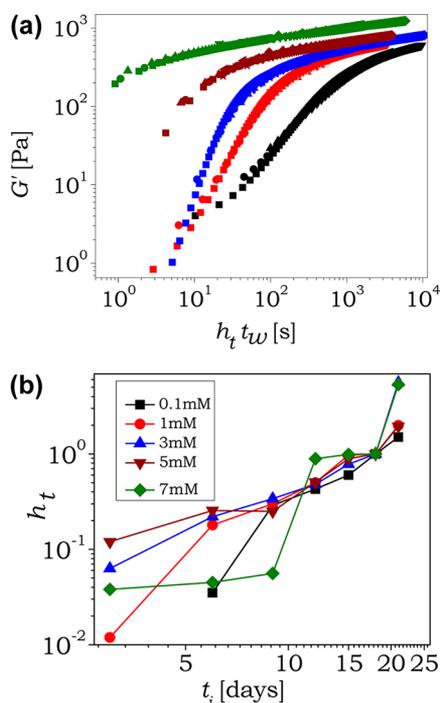


Figure 3. (a) Time–aging time superpositions of the storage modulus for various salt concentrations having 3.5 wt % Laponite. From right to left: 0.1, 1, 3, 5, and 7 mM salt concentrations. Evolutions on various idle times are horizontally shifted on $t_i = 18$ day evolution to obtain superpositions for different salt concentrations. (b) Horizontal shift factor required to obtain the superposition is plotted as a function of idle time (t_i) for storage modulus data shown in Figure 2a.

10°C and is plotted as a function of C_S for different C_L for the specific values of t_{iR} and T_R .

Although the evolution of G' does demonstrate excellent superposition in the solid state (region of weak evolution of G' at higher aging times, $G' > G''$), in the liquid state (region of strong evolution of G' at lower aging times, $G' < G''$) the quality of superposition is poor. The primary reason for this could be the inability of oscillatory flow experiments to access the evolution of viscoelastic behavior in the liquid region.⁶⁰ This point can be understood better by considering the rheological behavior of an aqueous suspension of Laponite to be represented by a single mode Maxwell model (a spring and dashpot in series) with time dependent elasticity and viscosity. For a Maxwell model, $G'' = G'/(\omega\tau)$, where ω is frequency of oscillations and τ is characteristic (or dominating) relaxation time.⁵⁹ The relaxation time, which is very small in the liquid regime increases as a function of time (typically relaxation time shows exponential dependence on aging time in the liquid regime).^{19,53} As a result the point at which the relaxation time becomes of the order of reciprocal of frequency ($\tau \approx 1/\omega$), G' crosses over G'' . Consequently in the liquid regime ($G' < G''$), the relaxation time undergoes a substantial increase over a period of one oscillation ($1/\omega$). Therefore oscillatory flow experiments tend to average the variation in viscoelastic properties over the duration of one cycle and thereby induce error while probing the evolution of G' and G'' . The further the material in the liquid region is from crossover ($G' = G''$), the greater the error is.⁶⁰

Similar to that of G' , the evolution of G'' also shifts to lower aging times for experiments carried out for higher idle times and for higher concentrations of Laponite and salt. However,

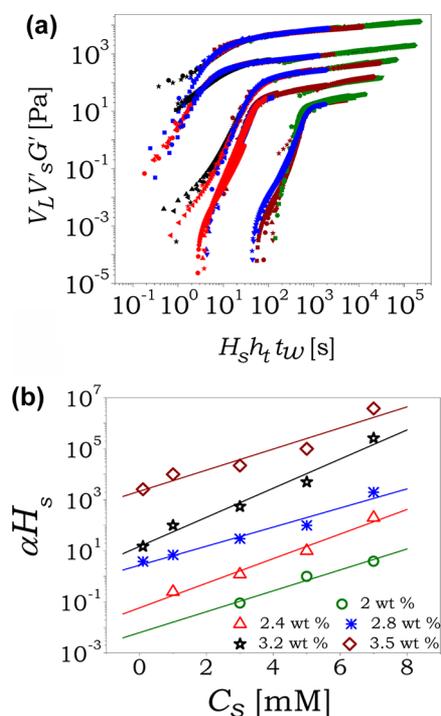


Figure 4. (a) Aging time–idle time–salt concentration superpositions for evolution of G' for various Laponite concentrations. From right to left: 2, 2.4, 2.8, 3.2, and 3.5 wt %. The curves have been shifted vertically with respect to concentration of Laponite for better clarity. (b) Dependence of the horizontal shift factor based on salt concentrations used for obtaining the superposition shown in panel a. Line fitted to the data represents $\ln(H_s) \propto C_s$. The shift factor data has been shifted vertically with $\alpha = 1, 10, 10^2, 5 \times 10^3,$ and 10^5 for 2, 2.4, 2.8, 3.2, and 3.5 wt %, respectively, for better clarity.

G'' shows a very peculiar behavior as a function of concentration of Laponite. In Figure 5 we plot G'' for various

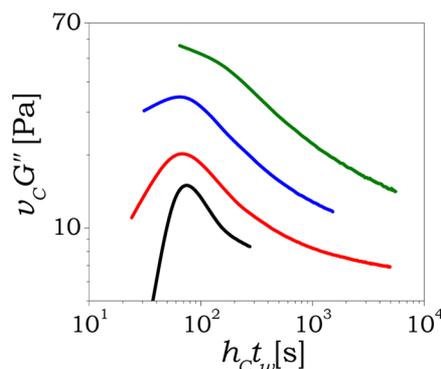


Figure 5. Evolution of the loss modulus for a suspension having 5 mM salt and an idle time of 6 days with varying Laponite concentrations. From top to bottom: $C_L = 3.5, 3.2, 2.8,$ and 2.4 wt %. The respective concentration curves have been shifted in both horizontal and vertical directions to describe the phenomenon more clearly.

concentrations of Laponite having 5 mM salt and an idle time of 6 days. It can be seen that the slope with which G'' decreases on a double logarithmic scale (after the crossover $G' = G''$) becomes weaker with an increase in the concentration of Laponite. Such broadening of the maxima for experiments carried out on greater idle times was reported recently.⁵³ The present observation of broadening with an increase in the

Laponite concentration (over 2.4 to 3.5 wt %) is witnessed irrespective of the concentration of salt present in the suspensions. On the other hand, G'' of 2 wt % suspension shows a different behavior as shown in Figure 6. For this

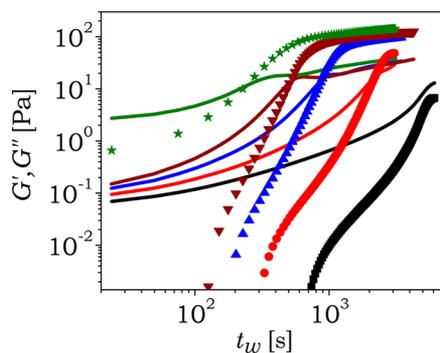


Figure 6. Evolution of G' (filled symbols) and G'' (lines) plotted as a function of aging time on various idle times (t_i) for a suspension having 2 wt % Laponite and 5 mM salt. From right to left: $t_i = 6, 9, 12, 15,$ and 18 days.

concentration evolution of G'' demonstrates either a very weak decrease or a plateau after the crossover. However, unlike a prominent decrease in G'' observed for high concentrations of Laponite, at high aging time, G'' in a 2 wt % suspension can be seen to be increasing with the aging time.

We also study the evolution of the viscoelastic response at different temperatures for a 2.8 wt % suspension with different concentrations of salt over a period up to 60 days after preparation of the same. In Figure 7a,b, we plot the evolution of G' and G'' for a 2.8 wt % Laponite suspension at different idle times and salt concentrations. The plot shown in Figure 7a describes the evolution of G' and G'' for a suspension without any externally added salt (0.1 mM) having an idle time of 18 days. It can be seen that evolution of G' and G'' shifts to lower aging times with increase in temperature. In figure 7b, we plot aging behavior of a 9 days old 2.8 wt % 5 mM suspension. In this case suspension directly enters the glassy state ($G' > G''$) owing to faster aging dynamics in the presence higher amount of externally added salt. In figure 8, we have plotted temperature dependence of 2.8 wt % suspension at 5 salt concentrations for experiments carried out on day 12. On the other hand, in Figure S1 we have plotted evolution of temperature dependence as a function of idle time (day 6 to day 60) for a 2.8 wt % suspension having no salt (0.1 mM). As shown in Figure 6–8, in the solid state, G' follows the same trend of shifting to lower aging times at higher temperatures while preserving the curvature. However, evolution of G'' does not follow the same trend and shows weaker decrease for experiments carried out at higher temperatures. In Figure 9 we plot $-d \ln G'' / d \ln t_w$ for samples having 2.8 wt % Laponite and different concentrations of salt as a function of the reciprocal of temperature, which clearly shows a weaker slope at higher temperatures. In the solid state, self-similar curvatures associated with G' suggest the possibility of superposition upon horizontal shifting. In Figure 7a,b, we represent this superposition by gray symbols. The corresponding shift factors a_T are plotted as a function of the reciprocal of temperature in Figure 7c.

The self-similar curvature of G' in the solid state ($G' > G''$) irrespective of concentration of Laponite shown in Figure 4a and that of as a function of temperature shown in Figure 7 lead

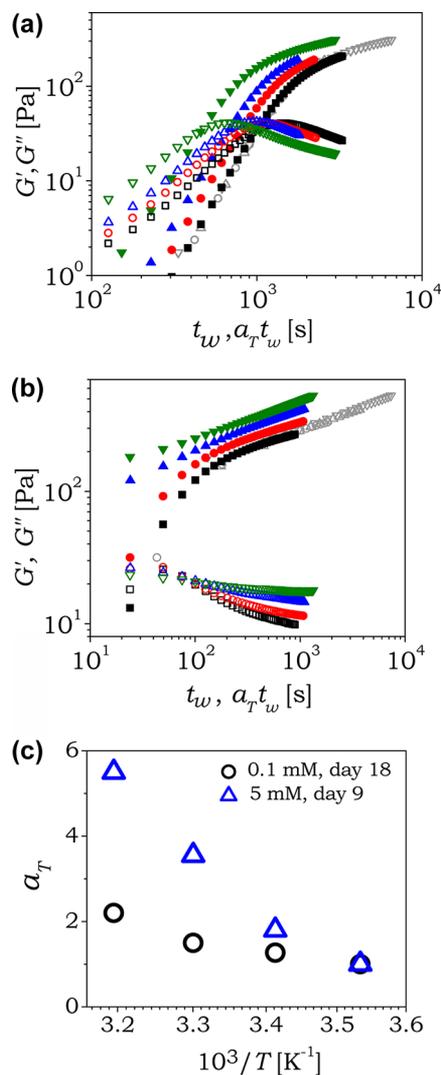


Figure 7. Evolution of G' (filled symbols) and G'' (open symbols) plotted as a function of aging time for different temperatures for (a) no salt system having 2.8 wt % Laponite and an idle time of 18 days. (0.1 mM) and (b) 2.8 wt % Laponite and 5 mM salt and an idle time of 9 days (black, 10 °C; red, 20 °C; blue, 30 °C; and green, 40 °C). The open gray symbols show the aging time–temperature superposition of G' . The corresponding shift factors are plotted with respect to the reciprocal of temperature in panel c.

to an aging time–idle time–salt concentration–Laponite concentration–temperature superposition. This superposition is plotted in Figure 10 which contains 61 evolution curves obtained for different system variables. It should be noted that in order to get the superposition we need only horizontal shifting as a function of idle time, Laponite concentration, and temperature, whereas the vertical as well as horizontal shifting is required for salt concentration variation. In the inset of Figure 10, we plot the horizontal shift factor (H_L) as a function of Laponite concentration. Similar to that observed for salt concentration, the horizontal shift factor associated with Laponite concentration shows an exponential dependence represented by $\ln(H_L) \approx C_L$.

We now discuss the results of the conductivity experiments. As discussed in the Introduction, particles of Laponite in an aqueous media share attractive as well as repulsive interactions among each other. As an apparent quantification of repulsive

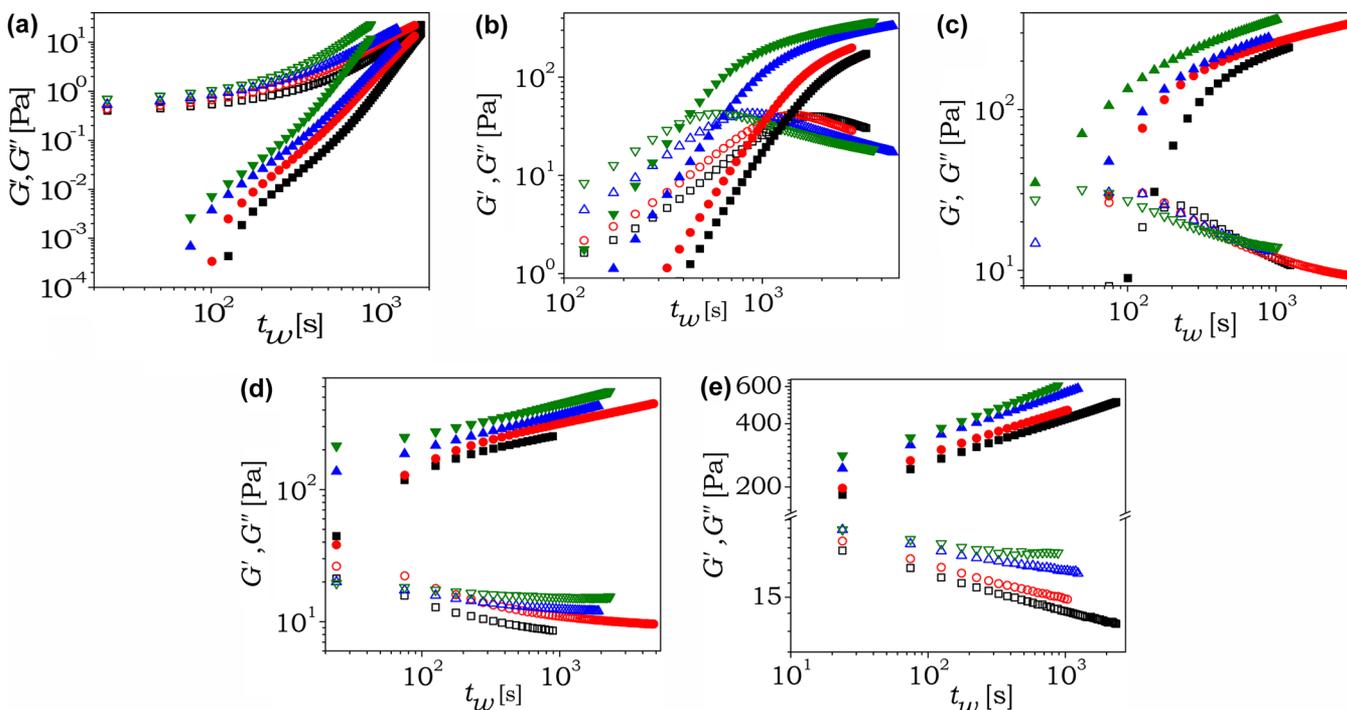


Figure 8. Evolution of storage (closed symbols) and loss (open symbols) moduli at various temperatures for a system having 2.8 wt % Laponite and $t_i = 12$ days. (a) 0.1, (b) 1, (c) 3, (d) 5, and (e) 7 mM salt (black squares, 10 °C; red circles, 20 °C; blue up triangles, 30 °C; and green down triangles, 40 °C).

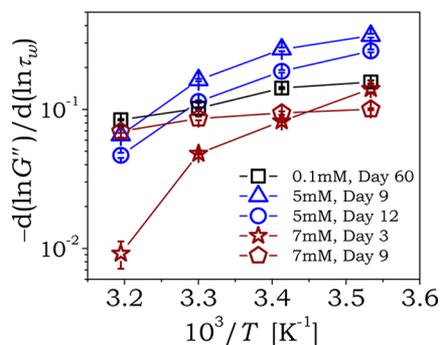


Figure 9. Variation of the slope of the loss modulus with an increase in temperature for various idle times and salt concentrations.

interaction, the electrostatic (Debye) screening length associated with the opposite faces of Laponite and its temporal evolution, if any, may help in understanding the origin of irreversibility in this system. Debye screening length can be obtained with the knowledge of the concentration of cations and anions present in the aqueous media. In order to estimate the same, we measure the conductivity of samples over a span of idle times up to 18 days as a function of concentration of Laponite and that of salt. For some samples we also measure conductivity as a function of temperature. The inset in Figure 11 shows the ionic conductivity of the 3.5 wt % Laponite suspension having various salt concentrations measured at different idle times. As expected, the conductivity of samples having a greater amount of NaCl is higher. In the inset of Figure 12, we plot conductivity as a function of concentration of Laponite having no externally added salt.⁶¹ Conductivity can be seen to be increasing with an increase in Laponite concentration owing to an enhanced counterion concentration. However, very importantly, the conductivity can be seen to be

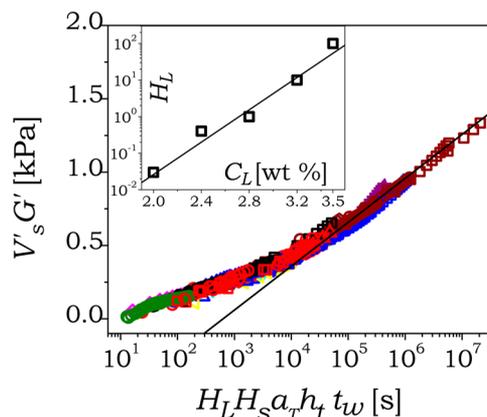


Figure 10. Aging time–idle time–salt concentration–Laponite concentration–temperature superposition for G' . The superposition contains 61 curves obtained at different idle times, Laponite concentrations, salt concentrations, and temperatures. Only the data beyond the crossover of G' over G'' is considered for the superposition. The black line passing through superposition represents $G' \approx \ln(t_w)$. The inset shows the horizontal shift factors H_L used to obtain the superposition as a function of concentration of Laponite. The straight line through the data plotted on semilogarithmic scale demonstrates $\ln(H_L) \approx C_L$.

continuously increasing with idle time over the explored range of 18 days in both of the insets of Figures 11 and 12. Since complexometric titrations have confirmed the absence of Mg^{2+} ions in the suspensions, a continuous increase in ionic conductivity over 18 days may be attributed to slow dissociation of Na^+ counterions from Laponite particles. With knowledge of conductivity, the Debye screening length can be obtained by using the expression⁶²

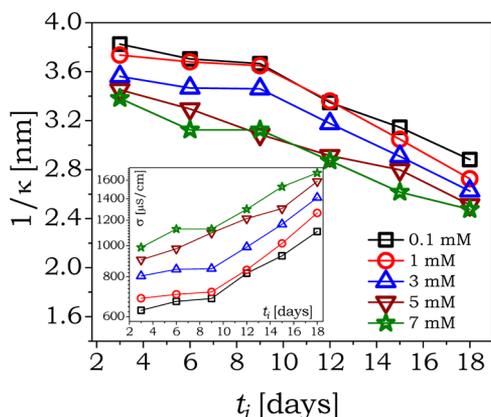


Figure 11. Debye screening length for the 3.5 wt % Laponite suspension having different concentrations of salt as a function of idle time. The inset shows the ionic conductivity for the same.

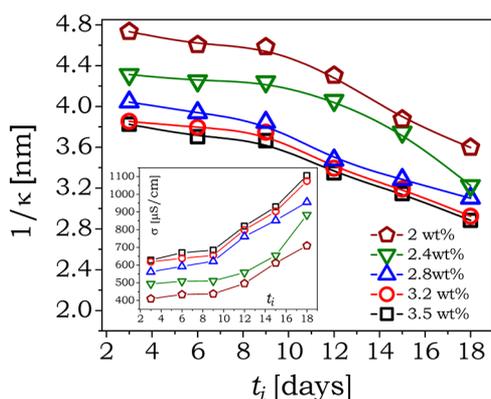


Figure 12. Debye screening length for various Laponite concentrations having no salt as a function of idle time. The inset shows ionic conductivity for the same.

$$\frac{1}{\kappa} = \left(\frac{\epsilon_0 \epsilon_r k_B T}{\sum_i (z_i e)^2 n_i} \right)^{1/2} \quad (1)$$

where ϵ_0 is permittivity of free space, ϵ_r is relative permittivity, k_B is the Boltzmann constant, z_i is the ionic charge number for the i th ion (NaCl is a 1:1 electrolyte), e is the electron charge, and n_i is the total number density of the i th ion. In order to evaluate the denominator, we need to calculate the number density of Cl^- and Na^+ ions. Since Cl^- ions are present in the suspension only through externally added NaCl, its concentration is the same as that of NaCl. On the other hand, the concentration of Na^+ ions can be estimated from the ionic conductivity and is given by $\sigma = e(\mu_{\text{Na}} n_{\text{Na}} + \mu_{\text{Cl}} n_{\text{Cl}})$,⁶³ where mobilities of Na^+ and Cl^- ions are $\mu_{\text{Na}} = 5.19 \times 10^{-8} \text{ m}^2/\text{sV}$ and $\mu_{\text{Cl}} = 7.91 \times 10^{-8} \text{ m}^2/\text{sV}$.⁶⁴

In Figure 11 we plot the Debye screening length estimated for the 3.5 wt % Laponite suspension as a function of salt concentration and idle time, whereas in Figure 12 we plot the same as a function of concentration of Laponite and idle time for a no salt system. It can be seen that the higher the concentration of salt, the lower the Debye screening length associated with a particle. Interestingly changing the concentration of externally added Na^+ ions from 0.1 to 7 mM causes a decrease in Debye screening length of around 10–12% on any studied idle time. Similarly the Debye screening length is observed to decrease with an increase in concentration of

Laponite. Finally and very importantly, the Debye screening length is observed to be decreasing as a function of idle time over the duration of 18 days in all suspension samples due to the continued dissociation of counterions. This proposal of continuous dissociation of counterions from the Laponite particle, in addition to complexometric titration experiments, can also be supported by estimating the maximum possible conductivity achievable for a suspension assuming all of the counterions have been dissociated. Since a single particle of Laponite of 25 nm diameter contains around 1000 unit crystals, the net negative charge on a Laponite particle is around 700 electronic charges.^{3,65} As a result, the maximum possible Na^+ ion concentration of a suspension, in addition to the known amount of NaOH and NaCl added to the same, is 700 ions per particle. In Figure 13a,b, we show that the measured value of

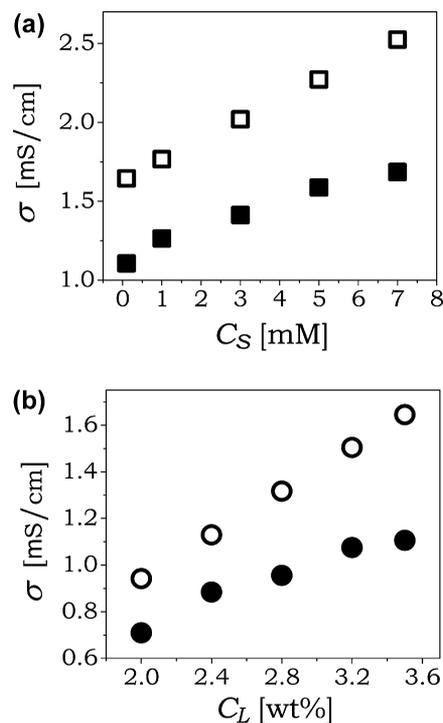


Figure 13. Ionic conductivity plotted as a function of (a) salt concentration for the 3.5 wt % Laponite suspension and (b) the concentration of Laponite for no externally added salt (0.1 mM). Solid symbols represent the measured ionic conductivity at an idle time of $t_i = 18$ days, and open symbols represent the theoretically calculated maximum possible conductivity.

conductivity on day 18 is significantly smaller than the maximum possible conductivity. We also measure the conductivity of a suspension as a function of temperature by equilibrating the same with a temperature bath on a mentioned idle time. Interestingly, as shown in Figure 14, the conductivity can be seen to be increasing as a function of temperature. Consequently the Debye screening length is expected to decrease at a higher temperature.

IV. DISCUSSION

Laponite particles in an aqueous medium share complex interactions among each other due to its anisotropic shape, dissimilar charges on the edge as well as the faces, and screening of these charges due to the presence of ions in the liquid media. These interactions may lead to repulsion between

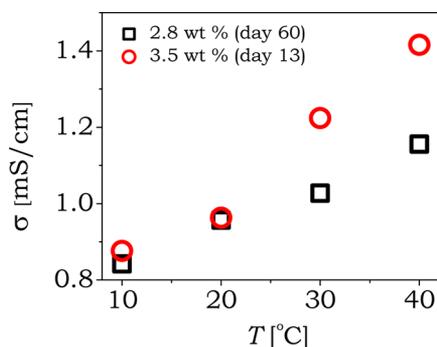


Figure 14. Ionic conductivity of an aqueous suspension of Laponite as a function of temperature for a 3.5 wt % 0.1 mM suspension on day 13 and for a 2.8 wt % 0.1 mM suspension on day 60.

the faces and attraction between the edges and the faces of the particles. In addition, there could be van der Waals attraction among the particles. All these interactions and shape effects are responsible for microstructure of Laponite suspension, which evolves as a function of time causing changes in its viscoelastic character. According to various light scattering and rheological studies, in glassy (nonergodic) state relaxation time of Laponite suspension is known to have a power law dependence on aging time given by $\tau = A\tau_m^{1-\mu}t_w^\mu$ ^{19,27,37,38,53,66} where τ_m represents the microscopic time scale associated structural reorganization (also represented as unit time with which structure builds). The power law dependence of the relaxation time on the aging time is known to be a generic feature of different types of glassy materials.^{20,60,67–69} In Laponite suspension, dynamics of the system can be well represented by considering Laponite particles to be arrested in energy wells, typically represented as cages in the literature.⁶⁶ Under such a situation, mere thermal energy is not sufficient for the particle to escape the cages.^{60,70} However, suspension can experience structural reorganization due to particles undergoing activated barrier hopping or by undergoing motion remaining inside the cage. Both of these events take the suspension to progressively low energy state as a function of time. Assuming that all of the particles occupy the energy wells having same depth E , the relaxation time can be considered to have Arrhenius dependence on E given by $\tau = \tau_m \exp(E/kT)$.⁶⁰ The dependences of relaxation time on E as well as aging time leads to $E = kT \ln A + \mu kT \ln(t_w/\tau_m)$. If b is the characteristic length-scale associated with the suspension, a scaling relation for the elastic modulus of the suspension was recently proposed by Shahin and Joshi⁵³ and is given by

$$G' = \beta E/b^3 = \frac{\beta k_B T}{b^3} \ln A + \mu \frac{\beta k_B T}{b^3} \ln(t_w/\tau_m) \quad (2)$$

where β is a proportionality constant. If we assume that the viscoelastic behavior of a suspension is given by a single mode Maxwell model, the viscous modulus of the same can be written as⁵³

$$\ln G'' = \ln G' - \ln(\omega A \tau_m) - \mu \ln(t_w/\tau_m) \quad (3)$$

Equation 2 suggests that the evolution of G' depends on aging time (t_w) normalized by the microscopic time scale (τ_m). τ_m can be assumed to have Arrhenius dependence given by $\tau_m = \tau_{m,0} \exp(U/k_B T)$, where U is energy barrier related to the microscopic movement within the cage. (It should be noted that E is the depth of the energy well associated with the cage,

and U is the activation barrier associated with the microscopic time scale. In Figure 15 we have represented this scenario using a schematic.)

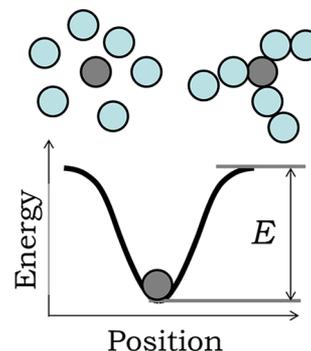


Figure 15. Schematic representing a particle under consideration arrested in a cage-like environment. Irrespective of glass-like or gel-like microstructure, the cage can be represented as an energy well having depth E . The particle undergoes microscopic motion of structural rearrangement within the cage with time scale τ_m such that E goes on increasing as a function of time. τ_m is assumed to have Arrhenius dependence on temperature $\tau_m = \tau_{m,0} \exp(U/k_B T)$, where U is the energy barrier associated with structure formation. Since τ_m sets the time scale of enhancement of energy depth E , it evolves as $E = E(t_w/\tau_m)$.

In the glassy domain, evolution of G' can usually be described by $G' = B + G_0 \ln(t_w/\tau_m)$ as shown by the curvature of the superposition described in Figure 10. Therefore, the power law index μ can be represented by⁵³

$$\mu = b^3 G_0 / (\beta k_B T) \quad (4)$$

where parameter G_0 does not depend on either the concentration of Laponite or the temperature as no vertical shifting is required with respect to both these variables to get the comprehensive superposition of G' as shown in Figure 10. (Vertical shift factor based on Laponite concentration used in Figure 4 is just to show the respective superpositions more clearly. This shift factor has not been used in Figure 10.) Equation 3 qualitatively predicts that, in the glassy regime, G'' decreases with increasing aging time if the third term on the right side dominates the first term. According to this term $[-\mu \ln(t_w/\tau_m)]$, $\ln G''$ is expected to vary as a function of $\ln t_w$ with slope $-\mu$. According to eq 4, μ is proportional to b^3 . If b is considered to be the average interparticle distance given by $b = (\pi R^2 h / \phi_v)^{1/3}$, where ϕ_v is the volume fraction of Laponite in suspension, R is the radius (~ 12 – 15 nm), and h is the thickness (~ 1 nm) of the Laponite particle,^{44,51} we get $\mu \approx G_0 / (\phi_v k_B T)$. This suggests that $\ln G''$ plotted as a function of $\ln t_w$ should decrease more steeply for lower concentrations of Laponite. Interestingly, as shown in Figure 5, we indeed observe that $\ln G''$ decreases more steeply with a decrease in concentration of Laponite. In addition, eqs 3 and 4 also suggest that μ should decrease with an increase in temperature. Remarkably, we also observe this behavior as shown in Figures 7b and 9. For the 2 wt % Laponite suspension, G'' is observed to be increasing as a function of aging time in the glassy domain as shown in Figure 6. Since G' is a continuously increasing function of aging time, increase in $G'' (=G' / (\omega \tau))$ suggests that the increase in τ is weaker than that of G' for the 2 wt % Laponite suspension.

In Figure 10 we observe a comprehensive superposition of elastic modulus irrespective of changes in the studied variables. On the other hand, G'' does not show self-similar evolution as a function of Laponite concentration, temperature, and idle time. However as discussed before, G' can be directly related to the energy well depth E by considering the former to be energy density ($G' = \beta E/b^3$). Self-similarity in G' , therefore, means self-similarity with which system explores low energy states thereby indicating a microstructure buildup of the aqueous suspension of Laponite is generic with respect to change in Laponite concentration, that of salt, aging time, and temperature. The major difference with respect to all of these variables is the time scale of aging (τ_m) related to these variables (the time scale of aging is the same as that associated with structural reorganization). Interestingly eq 2 qualitatively describes the dependence of G' on aging time (t_w) normalized by the time scale of aging (τ_m). The latter is assumed to show Arrhenius dependence [$\tau_m = \tau_{m,0} \exp(U/k_B T)$]. In Figure 10, in order to plot a comprehensive superposition, the aging time is multiplied by horizontal shift factors associated with Laponite concentration (H_L), salt concentration (H_S), idle time (h_t), and temperature (a_T). Since the reference temperature is $T_R = 10^\circ\text{C}$, the reference salt concentration is $C_{SR} = 5\text{ mM}$ and the reference idle time is $t_{IR} = 18\text{ day}$, we can represent the product of shift factors as $H_L H_S h_t a_T = H(C_L, C_{SR}, t_{IR}, T_R)$. Overall, for arbitrary reference points, we can write $\ln(\tau_m) \approx U/kT \approx -\ln[H(C_L, C_S, t, T)]$. In addition, it can be seen from Figure 4b and the inset of Figure 10 that $\ln[H_S] \approx C_S$ and $\ln[H_L] \approx C_L$, respectively. Consequently U decreases linearly with the concentration of Laponite and that of salt respectively in the explored range. Moreover, as shown in Figure 3b, h_t is observed to increase with idle time, suggesting U also decreases with idle time. The effect of temperature is more complicated than the other three variables. Since an increase in temperature increases the conductivity of the suspension as shown in Figure 14, it directly affects the energy barrier so that U decreases with increasing temperature. On the other hand temperature also expedites the dynamics by the thermal activation term in the assumed Arrhenius dependence. Overall, the superposition of the rheological aging data described in Figure 10 clearly shows that the energy barrier associated with structural buildup decreases with idle time and temperature and decreases linearly with an increase in the concentration of Laponite and that of salt.

In addition to the rheological study, the measurement of conductivity and the estimation of Debye screening length gives an independent approach to analyze interactions among Laponite particles as a function of the studied variables. Figures 11, 12, and 14 show an increase in ionic conductivity as a function of the concentrations of Laponite and salt, idle time, and temperature. For these variables, except the salt concentration, enhanced conductivity is due to dissociation of Na^+ ions from the Laponite particles. Greater dissociation of Na^+ ions from the face of the Laponite particle decreases the Debye screening length as shown in Figures 11 and 12. On the other hand, such dissociation makes the face of the Laponite particle more electronegative. Therefore in order to analyze the effect of progressive dissociation of Na^+ ions from the faces on Laponite particles on the energetic interaction (attractive and repulsive) between the same, we solve DLVO theory for the Laponite suspension. According to DLVO theory the free energy per unit area is given by a sum of double layer repulsion

and van der Waals attraction.⁶² The free energy per unit area between two layers of 2:1 clay (planar surfaces) is given by¹

$$W(d) = \left(\frac{64nk_B T}{\kappa} \right) \gamma^2 e^{-2\kappa d} - \frac{A_H}{48\pi} \left(\frac{1}{d^2} + \frac{1}{(d + \Delta)^2} - \frac{1}{(d + \frac{1}{2}\Delta)^2} \right)^2 \quad (5)$$

where n is the number of ions per unit volume, d is half distance between the two plates, A_H is the Hamaker constant ($1.06 \times 10^{-20}\text{ J}$ for Laponite⁷¹), and Δ is the thickness of unit layers between the same plates (6.6 \AA).¹ Furthermore, $\gamma = \tanh(z e \Phi_0 / 4k_B T)$, where z is the valence of ion and Φ_0 is the electric potential on the surface. In eq 5, the first term on the right-hand side represents double layer repulsion and the second term represents van der Waals attraction between the two layers.

In order to compute the free energy using eq 5, we assume complete delamination of all of the Laponite particles. The number of sodium ions dissociated per particle is given by $(n_{\text{Na}} - n_0)/n_p$, where n_0 is the concentration of Na^+ ions due to external sources (externally added NaOH or NaCl) and n_p is number of particles per unit volume. In eq 5 the number of ions per unit volume is therefore related to electric potential on the surface (Φ_0) by $\Phi_0 = e(n - n_0)/(2A_L n_p)$, where A_L is area of one face of the Laponite particle. In Figure 16 we plot the total

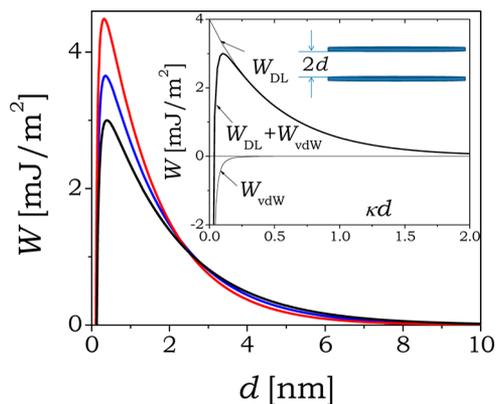


Figure 16. Free energy per unit area between two layers of 2:1 clay (planar surfaces) from DLVO theory plotted as a function of half the distance between the clay layers for the 3.5 wt % Laponite suspension (without any externally added salt) at different idle times. The black line (smallest peak and weakest decay, $\sigma = 628\ \mu\text{S}/\text{cm}$ and $1/\kappa = 3.8\text{ nm}$) represents day 3, the blue line (middle line, $\sigma = 820\ \mu\text{S}/\text{cm}$ and $1/\kappa = 3.3\text{ nm}$) represents day 12, and the red line (highest peak and fastest decay, $\sigma = 1106\ \mu\text{S}/\text{cm}$ and $1/\kappa = 2.9\text{ nm}$) represents day 18. The inset shows the variation of free energy per unit area for the double layer interaction, van der Waals interaction, and their sum as a function of half the distance between the clay layers normalized by the Debye screening length for the 3.5 wt % Laponite suspension (without any externally added salt) on day 3.

free energy per unit area along with the respective contribution from double layer and van der Waals interactions for the 3.5 wt % Laponite suspension without externally added salt for idle times 3, 12, and 18 day. It can be seen that van der Waals attraction is significantly weaker compared to the double layer repulsion except when particles are very close to each other. Interestingly with an increase in idle time, owing to a higher

value of coefficient γ^2 arising from a greater negative surface potential (Φ_0), the height of the repulsive barrier that particles need to cross in order to approach each other in parallel fashion increases. On the other hand, the width of the repulsive barrier becomes narrower as a function of idle time due to stronger exponential decay (e^{-2kd}) caused by a decrease in the Debye screening length $1/\kappa$. We expect a qualitatively similar behavior as shown in Figure 16 when the idle time is replaced by temperature. For the case of externally added salt (C_S), the increase in C_S , for the same extent of dissociation of counterions, will decrease the Debye screening length further without affecting the value of the coefficient γ^2 . However since, $\kappa \approx n^{0.5}$ the coefficient of the double layer repulsion term ($nk_B T/\kappa$) given by eq 5, will still scale as $nk_B T/\kappa \approx n^{0.5}$. This would, therefore, lead to an increase in the height of the repulsive barrier while making its width narrower with an increase in C_S when particles approach each other in a parallel fashion. Therefore the scenario will be qualitatively similar to that described by Figure 16 when the increase in idle time is replaced by an increase in T as well as C_S .

The results of the rheological study suggest a decrease in the energy barrier for structure formation with an increase in idle time, salt concentration, and temperature (time scale associated with increase in G' shifts to lower times with increase in t_i , C_S , and T). Therefore, although the height of the repulsive energy barrier is increasing, the fact that the width of the same is shrinking (reduction in Debye screening length) with an increase in t_i , C_S , and T is intuitively in disagreement with the proposal of low energy structures being repulsion dominated. In order to quantitatively probe effect of repulsive interactions on the low energy structure, we analyze the time scale associated with structure formation at which material undergoes a liquid–solid transition with respect to the Debye screening length. In Figure 18, we plot aging time at which G' crosses over G'' as a function of the normalized Debye screening length (the Debye screening length divided by the average interparticle distance $1/(b\kappa)$) for 1 and 3 mM salt concentration suspensions having different Laponite concentrations (For 2.4, 2.8, 3.2, and 3.5 wt % suspension, value of b is approximately 42, 40, 39, and 37 nm, respectively). We represent this crossover time by t_w^* . As mentioned before, if we assume the material behavior to be represented by a time dependent single mode Maxwell model, the point at which G' crosses over G'' corresponds to $\tau = 1/\omega$. Since, in all of the experiments we have employed fixed $\omega = 0.1$ Hz, t_w^* represents the time at which the dominating relaxation time of the suspension reaches a level of 10 s. It can be seen in Figure 16 that the Debye screening length is around or less than 10% of that of the average interparticle distance. For a given concentration of Laponite and salt, points from right to left suggest an increase in idle time, which causes a decrease in the Debye screening length (or increase in electronegative surface potential) as shown in Figures 11 and 12. Figure 17 shows that t_w^* continuously decreases with a decrease in Debye screening length. Furthermore, for a given concentration of Laponite, an increase in C_S shifts the dependence of t_w^* on $1/(b\kappa)$ to lower values of t_w^* . If low energy structures are repulsive in origin, we would have expected t_w^* to be a decreasing function of $1/(b\kappa)$, contrary to experimental observation. In addition, the overall behavior described in Figure 17 suggests that the concentration of Laponite and that of salt affect the dynamics independently in addition to the Debye screening length. In purely repulsive interactions, we would have expected t_w^* to demonstrate a

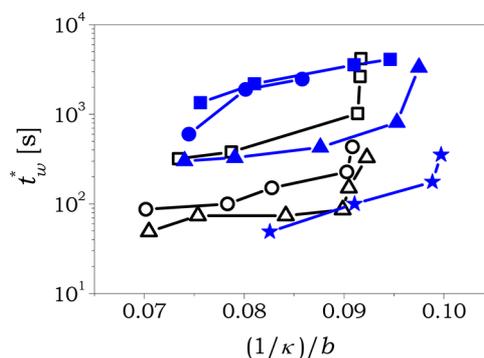


Figure 17. Aging time at cross over (t_w^*) of G' and G'' is plotted against the normalized Debye screening length for various Laponite concentrations [square, 2.4 wt %; circles, 2.8 wt %; triangles, 3.2 wt %; and stars, 3.5 wt %]. Filled blue symbols represent the 1 mM NaCl concentration, and open black symbols represent the 3 mM NaCl concentration.

superposition as a function of $1/(b\kappa)$ irrespective of various system variables.

While undergoing thermal motion, rather than approaching in a parallel fashion, if two Laponite particles approach each other in a perpendicular fashion or from the sides as shown in the schematic in Figure 18, owing to dissimilar charges on the

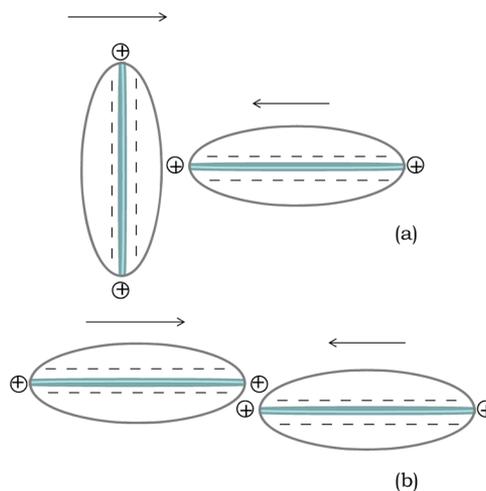


Figure 18. Schematic of a scenario when two Laponite particles, owing to thermal motion, approach each other (a) in a perpendicular fashion and (b) from the sides.

edge and on the face, we intuitively expect the repulsive energy barrier to reduce with an increase in the negative surface potential (Φ_0) and/or a reduction in the Debye screening length. Interestingly, this proposal agrees well with the findings of the rheological study. When particles approach each other in a perpendicular fashion, they form a house of cards structure, whereas when they approach each other from the sides, they form an overlapping coin configuration. Interestingly, a very recent Monte Carlo simulation study inspired by Laponite suspension reports a mixture of both of these configurations.¹⁶ Although simply based on rheological and conductivity results it is difficult to comment on the precise microstructure, various results discussed in this paper make it amply clear that low energy structures associated with an aqueous suspension of Laponite are influenced by attraction among Laponite particles. In the literature it is clearly established that addition of

monovalent salt such as NaCl in aqueous suspension of Laponite increases dominance of attraction.^{42,43,51} In this paper we extend this proposal and state that the increase in Laponite concentration, temperature, and very importantly the time elapsed since preparation of Laponite suspension (idle time) also lead to the microstructures that are influenced by attraction.

In the discussion so far we assumed complete delamination of Laponite particles in a short time followed by a slow but progressive dissociation of counterions. This was considered to be a cause for enhancement in ionic conductivity as a function of time. However, such an increase in conductivity could also be attributed to the slow delamination of Laponite particles (delamination to be a rate determining step), in which the dissociation of counterions can be considered to be faster. In this case the electronegative surface potential (Φ_0) can be assumed to remain constant throughout the process. However, dissociation of counterions would certainly increase n thereby leading to qualitatively the same free energy scenario as shown in Figure 16. The important difference would be the increase in effective particle density as a function of time, which through attractive interactions could lead to enhanced shear modulus.

Shahin and Joshi⁴⁴ had reported the partly irreversible nature of aging in aqueous suspensions of Laponite. We feel that physicochemical effects such as an irreversible increase in the ionic conductivity as a function of idle time, which progressively reduces the width of repulsive barrier (thereby enhancing rate at which attractive interactions may form) among the Laponite particles and an inability of high shear to rejuvenate the evolved microstructure are responsible for irreversible aging in aqueous suspensions of Laponite. Recently Shahin and co-workers observed very strong anisotropic orientation near the air–Laponite suspension interface by observing birefringence when kept in between crossed polarizers.⁵² The anisotropic orientation and its penetration into the bulk were observed to be getting pronounced as a function of concentration of Laponite, concentration of salt, temperature, and idle time. Interestingly, the same variables are responsible for faster aging in this system. We therefore believe that anisotropic orientation near the interface and its penetration in the bulk are related to enhanced conductivity (or reduced Debye screening length or repulsion) in the suspension. In addition, we feel that results discussed in this paper are in agreement with the experiments of Ruzicka and co-workers,⁷² who observed dissolution of a young (around 2–3 days) Laponite suspension having 3 wt % concentration (upon addition of deionized water).⁷³ However, for older samples (~7 day) the suspension did not dissolve but underwent swelling when deionized water was added on top.⁷² They proposed that repulsion is prevalent among the particles in the initial period, whereas attraction develops in the Laponite suspension over long durations. The present study provides a plausible explanation to this observation.

V. CONCLUSION

In this work we carry out an extensive study of the aging behavior of an aqueous suspension of Laponite using rheological and conductivity measurements, as a function of concentration of Laponite (2–3.5 wt %), concentration of salt (NaCl, 0.1–7 mM), and temperature (10–40 °C) at regular intervals up to 60 days after preparation of the suspension (represented as idle time). We observe that rheological experiments carried out on greater idle times do not rejuvenate the suspension to the same initial state upon application of

strong shear suggesting irreversibility in structural build-up. Furthermore, evolution of elastic and viscous moduli (and their crossover), subsequent to shear melting, shift to smaller aging times for experiments carried out on greater idle times, higher concentrations of salt as well as that of Laponite, and temperature. Self-similar evolution of the elastic modulus, which shows monotonic increase with aging time, leads to aging time–idle time–salt concentration–Laponite concentration–temperature superposition in the solid regime. The existence of such a comprehensive superposition suggests the generic nature of the microstructure buildup upon change in the above-mentioned variables over the explored range. On the other hand, in the solid regime a viscous modulus is observed to decrease as a function of aging time with a more pronounced slope for experiments carried out at lower temperatures and on suspensions having a lower concentration of Laponite. Our simple scaling model qualitatively explains this behavior. Variation of shift factors necessary to get the superposition of the elastic modulus suggests that the energy barrier associated with structure formation goes on decreasing with temperature and idle time and particularly decreases linearly with an increase in concentration of Laponite and that of salt. Interestingly, the conductivity experiments carried out on suspensions show a continuous increase in conductivity and therefore a continuous decrease in Debye screening length as a function of idle time. Analysis of interparticle interaction using DLVO theory suggests that when particles approach each other in a parallel fashion, the height of the repulsive energy barrier increases while narrowing its width with increasing idle time, temperature, and salt concentration. However since the edge and face of the Laponite particle have dissimilar charges, attraction between the same is expected to increase when particles approach each other in a perpendicular fashion. Analysis of rheological and conductivity data, therefore, strongly indicates the influence of attractive interactions in forming the low energy structures in an aqueous suspension of Laponite.

■ ASSOCIATED CONTENT

📄 Supporting Information

Additional plots of evolution of elastic and viscous modulus of 2.8 wt % 0.1 mM Laponite suspension as a function of temperature on different idle times. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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