Electronic supplementary information (ESI): Aggregation and stability of anisotropic charged clay colloids in aqueous medium in the presence of salt

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I. ULTRASOUND ATTENUATION SPECTROSCOPY: THEORY AND MEASUREMENTS

Different loss mechanisms such as viscous, thermal, scattering, intrinsic, structural and electrokinetic, result in the attenuation of ultrasound in a colloidal dispersion. The attenuation coefficient α can be written as a sum of the different loss mechanisms, $\alpha = \alpha_v + \alpha_{th} + \alpha_{sc} + \alpha_{int}$, where α_v, α_{th}, α_{sc} and α_{int} are the contributions of the viscous, thermal, scattering and intrinsic loss mechanisms, respectively. Depending on the nature and concentration of the colloidal particles under study, it may be possible to separate the different loss mechanisms in the ultrasound frequency domain. The wavelength of ultrasound in water changes from 1 mm to 15 μm when the ultrasound frequency changes from 1 MHz to 100 MHz. As the wavelength range of ultrasound is much larger than the expected sizes of the particles, scattering loss is negligible. The contributions from structural and electrokinetic losses are typically negligible as the colloids used here are characterized by high particle density contrasts and rigidities. The expression for the complex wave number k of ultrasound propagation [1], derived from the coupled phase model [2, 3] that considers only viscous loss in the long wavelength limit ($ka << 1$), can be written as:

$$\frac{k^2 M^*}{\omega^2 \rho_s} = \frac{1 - \frac{\rho_p}{\rho_s} \sum_{i=1}^{N} \frac{\phi_i}{1 - (9j\rho_m \Omega_i / 4 s_i^2 \rho_p)}}{1 + (\frac{\rho_s}{\rho_p} - 2) \sum_{i=1}^{N} \frac{\phi_i}{1 - (9j\rho_m \Omega_i / 4 s_i^2 \rho_p)}} \tag{S1}$$

where

$$s_i^2 = \frac{a_i^2 \omega \rho_m}{2\eta_m} \tag{S2}$$

$$\rho_s = \rho_p \phi + \rho_m (1 - \phi) \tag{S3}$$

and

$$M^* = \frac{\rho_p \rho_m c_p^2 c_m^2}{\phi \rho_p c_p^2 + (1 - \phi) \rho_m c_m^2} \tag{S4}$$

Here, ω is the angular frequency of the ultrasound waves, M^* is the stress modulus, ρ_p is the density of the particles, ρ_m is the density of the medium, ρ_s is the density of the dispersion, c_m and c_p are the velocities of ultrasound in the liquid and solid media respectively, ϕ_i is the volume fraction of the ith species of the particulate phase, ϕ is the total volume fraction of the particulate phase, a_i is the diameter of a particle of the ith species, η_m is the shear viscosity of the medium and Ω_i is the drag coefficient of a particle of size a_i. The hydrodynamic interactions between the particles is calculated using the Happel cell model [4]. The attenuation coefficient α_v and the sound speed c through the dispersion can then be calculated from the following relations:

$$\alpha_v = -Im(k) \tag{S5}$$

$$c = \frac{\omega}{Re(k)} \tag{S6}$$

In this work, the ultrasound attenuation spectra (attenuation coefficient α_v *vs* frequency ω) and sound speeds in dispersions are measured using a DT-1200 acoustic spectrometer from Dispersion Technology Inc. For each attenuation measurement, the clay dispersion is loaded in a cell containing two identical piezoelectric transducers. The transmitting ultrasound transducer converts input electrical signals into ultrasound tone bursts of different intensities and frequencies. The generated ultrasound pulse propagates through the dispersion and interacts with the colloidal clay particles and water. This interaction decreases the ultrasound intensity, with the predominant loss mechanisms being the viscous loss of the colloids and the intrinsic loss of water. The intensity amplitude of the transmitted ultrasound pulse is received by the detecting transducer and then converted back into an electric pulse for comparison with the initial input pulse. For each frequency, the signal processor receives data for a minimum of 800 pulses to achieve a signal-to-noise ratio of at least 40 dB. The intrinsic loss contribution from water is subtracted from the total intensity loss to estimate the value of α_v. The sound pulses used here are of low power (maximum 10mW) and are not expected to affect the microscopic structures of the dispersion. The sound speed c in the sample is calculated by measuring the time delay between the emitted and received pulses.

An analysis algorithm, developed by the manufacturer and based on the theory described earlier, is used to determine the PSD of clay particles from attenuation spectra [5, 6]. The algorithm assumes a unimodal size distribution and runs a search in the size range from 1 nm to 1 mm for the PSD, using the median and the standard deviation of the particle sizes as the fitting parameters. During the search process, the algorithm calculates the theoretical attenuation values for each PSD using Equations S5 and S6 and fits the experimental attenuation spectrum by minimizing the fitting error. The searching algorithm stops when the fitting error saturates to the lowest value.

II. SUPPLIED VALUES

The following values are used in Eqn. S1 to estimate PSDs.
Density of water at 25°C is $\rho_m = 0.997$ g/cc
Viscosity of water at 25°C is $\eta_m = 0.89$ mPas
Density of Na-Montmorillonite is $\rho_p = 2.6$ g/cc
Sound speed in solid media is c_p= 6000 m/s.

III. ELECTROACOUSTIC MEASUREMENTS

We use a cylindrical electroacoustic probe containing an ultrasound transducer supplied by Dispersion Technology Inc to monitor the stability under gravity of clay dispersions at relatively high particle concentrations. Details of the probe can be found in the literature [7]. An experimental setup using this probe is shown in Fig. S1. In this setup, the front flat surface of the probe is kept in contact with the top surface of the dispersion column. A very thin layer of silicon oil of viscosity 5 cSt is placed between the probe and the dispersion. This keeps the clay particles from sticking to the flat surface of the probe. A low power nondestructive plane ultrasound wave of frequency 3 MHz is launched by the transducer along the height of the dispersion. The ultrasound probe induces small oscillating dipole moments in the EDLs of the clay platelets suspended in the dispersion. The induced dipoles generate electric fields which, in turn, induce a current known as the colloidal vibration current (I_{CVI}) in the receiving transducer circuit of the probe. In a dispersion with added salt, the transducer simultaneously detects an ionic vibration current (I_{IVI}) which arises due to the relative motion between the two ion species of the salt. In this case, the total electroacoustic signal (I_{TVI}) is a vector sum of I_{CVI} and I_{IVI}. The value of I_{TVI} measured in this setup is very sensitive to the distance of the clay particles from the measuring transducer. The settling of the clay particle will therefore lead to a change in the measured values of

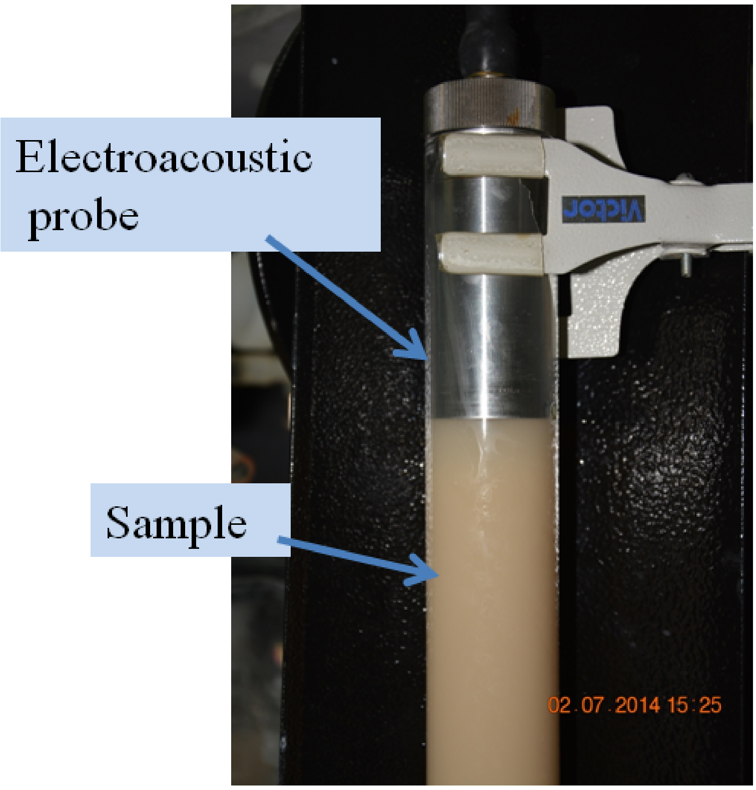

FIG. S1: Experimental setup for monitoring the sedimentation stability of clay dispersions using an electroacoustic probe. The aqueous Na-montmorillonite dispersion is loaded in a cylindrical container with inner diameter of 32.5 mm and a height of 226 mm.

I_{TVI} or I_{CVI}. This feature is exploited here to characterize the gravitational stability of clay gels.

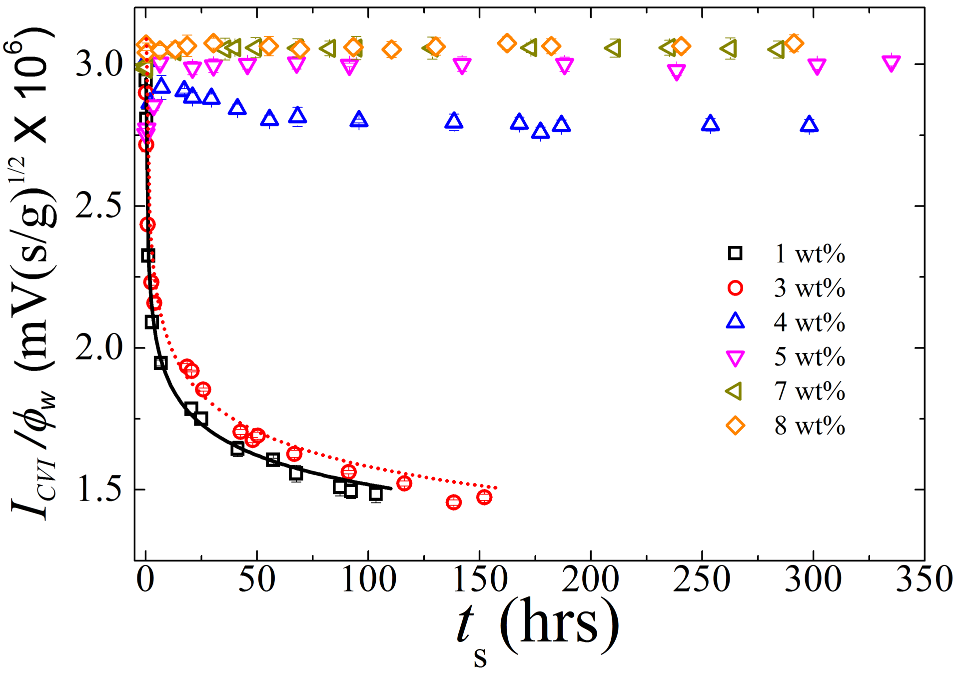

FIG. S2: Evolution of the colloidal vibration current (I_{CVI}) measured in the electroacoustic setup (Fig. S1) versus the age t_s of Na-montmorillonite dispersions with clay concentrations of 1% w/v (□), 3% w/v (○), 4% w/v (△), 5% w/v (▽), 7% w/v (◁) and 8% w/v (◇). For samples with clay concentration below 4% w/v, the clay particles sediment under gravity. This can be seen from the exponentially decreasing I_{CVI} values with increasing t_s. For concentrations above 4% w/v, the clay particles get arrested due to the onset of the glass transition, which renders the particles increasingly stable under gravity. This can be seen from the values of the I_{CVI} which remain almost constant with changing t_s.

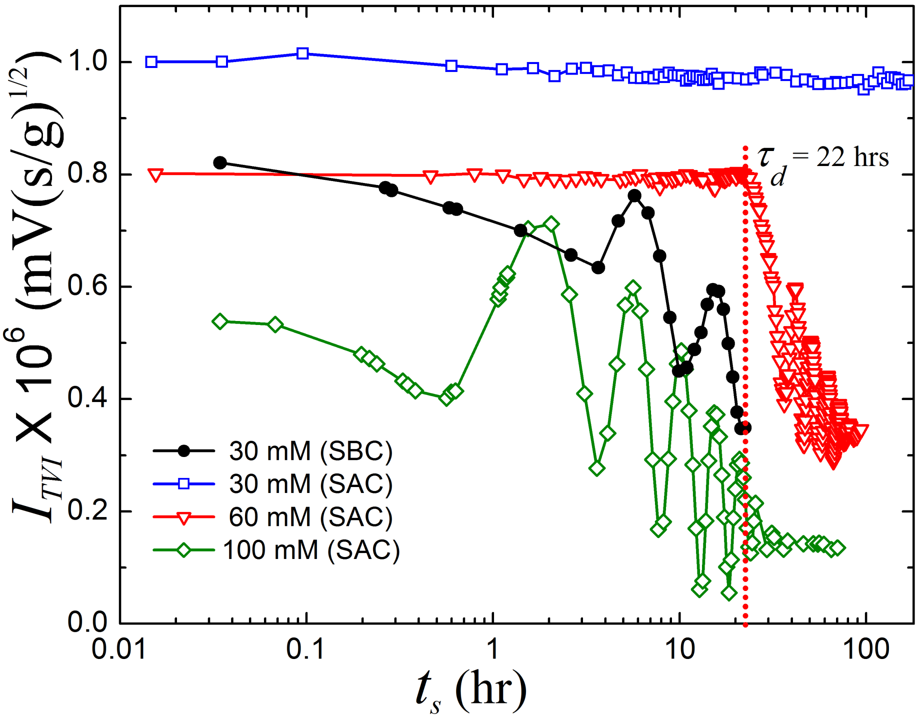

FIG. S3: Evolution of the total vibration current (I_{TVI}) measured in the electroacoustic setup (Fig. S1) with increasing t_s for 3% w/v Na-montmorillonite dispersions with salt concentrations of 30 mM prepared at SBC condition (●) and for 3% w/v Na-montmorillonite dispersions (SAC) with salt concentration of 30 mM (□), 60 mM (▽) and 100 mM (◊). The vertical dotted line shows the position of the delay time $\tau_d = 22$ hrs for the sample with 60 mM salt. The experimental observation presented in this figure is explained in detail in Section A below.

A. Observations in Fig. S3

The stability of clay gels with higher particle concentrations is studied using an electroacoustic method that is suitable for monitoring the small collapse heights in gels of higher clay concentrations. Fig. S3 shows the variation of the total vibration current I_{TVI} measured in the electroacoustic setup (Fig. S1 of ESI) for 3% w/v Na-montmorillonite dispersions with varying C_s prepared in different ionic conditions. It is seen that I_{TVI} for the SAC gel with $C_s = 30$ mM (□ in Fig. S3) remains almost unchanged with t_s. This indicates that the gel is highly stable in the experimental time window. For the SAC gel with $C_s = 60$

mM (▽ in Fig. S3), I_{TVI} remains constant upto a delay time $\tau_d = 22$ hrs. The subsequent decrease in I_{TVI} with increasing t_s is accompanied by oscillations. Such oscillations in I_{TVI} is due to the downward movement of the collapsing gel interface through consecutive half wavelength regions having alternating directions of the ultrasound pressure gradient which is set up by the electroacoustic probe along height h. For an SAC gel with $C_s = 100$ mM (◊ in Fig. S3), oscillations in I_{TVI} start immediately due to the very unstable nature of this gel. In contrast to the 3% w/v Na-montmorillonite SAC gel with $C_s = 30$ mM (□ in Fig. S3), the 3% w/v Na-montmorillonite SBC gel with $C_s = 30$ mM (● in Fig. S3) collapses rapidly after preparation, leading to oscillations in I_{TVI} at very low t_s. Similar stability behaviors of SAC and SBC gels prepared with identical salt concentrations were already observed in Fig. 5 for 0.8% Na-montmorillonite gels in light transmission experiments. Moreover, it can be seen in Fig. S3 and Fig. 8 by comparing data for samples prepared with identical salt concentrations (60 mM) that the 3% Na-montmorillonite SAC gel exhibits better stability ($\tau_d = 20$ hrs, Fig. S3) when compared for the 0.8% Na-montmorillonite SAC gel ($\tau_d = 1.5$ hrs, Fig. 8).

IV. REFERENCES

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