Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Polyphosphates can stabilize but also aggregate colloids

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Sodium Bentonite (SB) tests

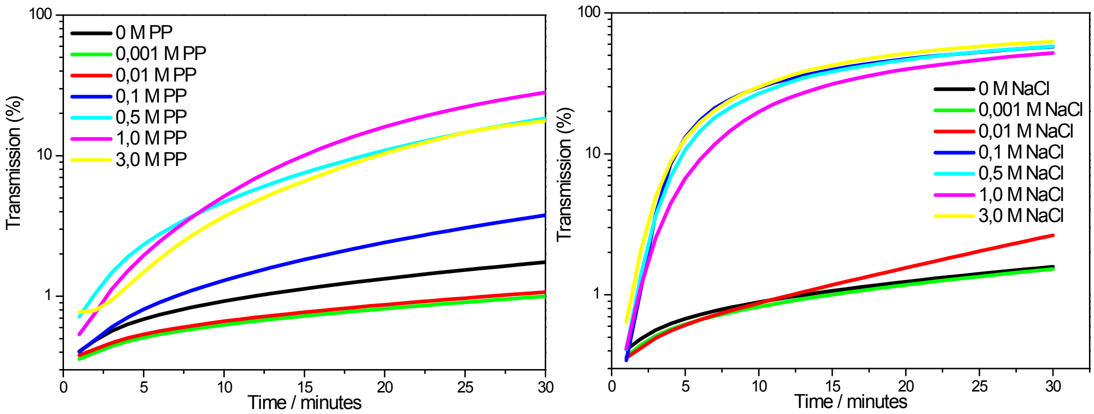

Figure S1 – Sedimentation profile of SB-PPSC dispersions at 1wt% and different molar concentrations of PPSC (left) and NaCl (right), obtained by light transmittance at 1000 nm wavelength.

Sodium bentonite (SB) was purchased from Proquimios-Brazil. The cation exchange capacity was evaluated as the Methylene Blue Index (MBI) = 83 to 89 meq /100 g clay, using the Standard Test Method for Methylene Blue Index of Clay[1].

SB was directly dispersed into water or PPSC solutions at different concentrations of Na^+ cations, according to Figure S1. After 10 min of stirring using a magnetic bar, dispersions were allowed to rest for 24 h. Then, dispersions were again stirred for 5 min, diluted to 0.1wt% of clay in order to avoid interparticle interactions during sedimentation and immediately analysed by light transmittance as a function of time. This was measured using a Shimadzu UV-1800 spectrophotometer at a wavelength of 1000 nm, with the beam positioned just below the dispersion meniscus, passing through the top of the sample (using the minimum volume in the cell in order to determine a transmission signal, resulting in a minimum volume of 2.2 mL in a 1 cm^2 cell) . Sedimentation of particles out of the light beam would lead to an increase of transmission, and particle aggregation would increase the sedimentation rate and hence the rate of increase of the transmission.

SB dispersions were made at 1.0 wt% and 7 different samples with short chain PP (PPSC) were obtained after dilution of PPSC stock solution. Samples were diluted to a clay concentration of 0.1 wt% in order to avoid particle interactions affecting the sedimentation behaviour. As anticipated, for all samples transmission was found to increase with time (Figure S1). The results can be arranged into two groups.

First, the SB without PPSC presents a profile with two main sedimentation rates, a higher initial rate (spanning the first five minutes) and a lower subsequent one, which we interpret to be due to presence of some particle aggregates particles that settle out quickly, followed by the remainder of individual particles. Adding low concentrations of PPSC (up to 0.01 M) results in the well known behaviour of PP molecules, through bonding of PP chains on edges, increasing the net negative charge of particle. That aids in the dispersion of the clay resulting in a reduction in the initial sedimentation rate, as a result of aggregates having been broken up. The late stage (after five minutes) rate of increase of transmission is identical to that in absence of PPSC, which confirms that this reflects the settling of individual particles.

For PPSC concentrations of 0.1 M and above the sedimentation profile changes, increasing the initial sedimentation rate. That can be attributed to an increase in attractive interactions, leading to larger aggregates of SB particles that have a higher sedimentation rate. For comparison, in Fig. S1 (right) a similar set of results is shown obtained using addition of NaCl instead. This shows a marked onset of aggregation at concentrations of 0.1 M and above. Compared to this, the onset of aggregation in the systems with PPSC is less pronounced. PPSC is therefore seen to act as a stabiliser here, and no evidence is found for PPSC acting to enhance sedimentation (compared to NaCl) due to any bridging interactions between clay particles. At high PPSC concentration aggregation still results, due to increase in ionic strength.

Debye length, contour length and arresting

The **Debye screening length** (DL) was calculated for LRD dispersions at 1 wt% and 2 wt%. The systems are counterion-only (no added salt) so calculations are based on the Na^+ ions released by the clay particles. Taking a cationic exchange capacity of 79 mmol / 100 g of LRD[2], this gives 0.008 mol/L of Na^+ for LRD1 dispersion, assuming all the exchangeable cation is Na^+.
For LRD1, the DL was calculated as 4.8 nm, while for LRD2 it was 3.4 nm.

The values follow from the usual expression for Debye length:

$$\kappa^{-1} = \left(\frac{\varepsilon_0 \varepsilon_r kT}{e^2 \sum_i c_i z_i^2} \right)^{1/2}$$

κ^{-1} is the Debye length; ε_0 is the vacuum permittivity; ε_r is the relative permittivity of the solvent; k is the Boltzmann constant; T is the absolute temperature; e is the elementary charge; z is the ion valence and c is the concentration of Na^+.

The contour length of PP chains was calculated multiplying the average distance between charges on chain (2.61 Å) per number of phosphate units per chain:

Polyphosphate	Average phosphate units / chain	Contour length / nm
PPSC	10	2.4 nm
PPLC	100	25.8 nm

Typical length scales (particle distances) calculation

For calculation of the typical distance between two Laponite platelets, we used the following expressions:

Particle volume (for a disc) = $(\pi/4)*(\text{diameter})^2*(\text{height})$
Particle number density = (concentration)/(particle mass)
Typical particle distance = $(\text{particle number density})^{-1/3}$

We used typical values related to Laponite discs: diameter (25 nm); height (1 nm) and Laponite density (2.7 g/cm^3)[2] . For 1 wt% dispersion we calculate volume of the disc ($4.908x10^{-25}$ m^3); particle mass ($1.325x10^{-21}$ kg); particle number density ($7.545x10^{21}$ m^{-3}), leading to a typical particle distance of 51.0 nm. For 2 wt% dispersion, the particle number density was calculated as $1.509x10^{22}$ m^{-3}, giving a typical particle distance of 40.5 nm.

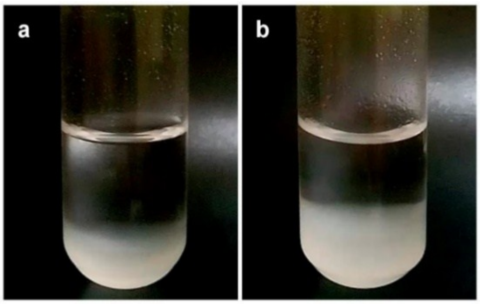

Figure S2 - LRD suspension with sodium chloride ($C_{Na}+ = 10^{-1}$ mol·L^{-1}). (a) C_{LRD} = 1.0%; (b) C_{LRD} = 2.0%.

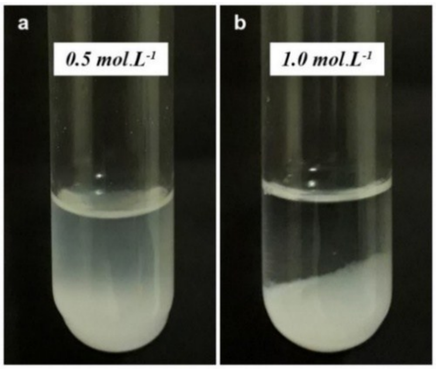

Figure S3 - 36 h after LRD2 addition to (PPSC+H_2O). (a) LRD2-PPSC 0.5 mol·L^{-1}; (b) LRD2-PPSC 1.0 mol·L^{-1}.

Figure S2 illustrates the aggregates that settle down when aggregation is induced by adding NaCl. Similarly, aggregation is obtained when adding PPSC to a sample of 2 wt% Laponite (Figure S3). However noticeably higher concentrations are needed, with a clear supernatant only resulting with 1.0 M PPSC (the concentration refers to the density of phosphate units, not PPSC chains).

1. ASTM C837-09(2019), Standard Test Method for Methylene Blue Index of Clay, ASTM International, West Conshohocken, PA, 2019, www.astm.org

2. M. Pilavtepe, S. M. Recktenwald, R. Schuhmann, K. Emmerich and N. Willenbacher, *J. Rheol. (N. Y. N. Y).*, 2018, **62**, 593–605.