

Manipulating the Large Scale Structure of Plate-like Clay Colloids in Aqueous Suspension

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Abstract

Known for their anisotropy in shape, clay mineral colloids are widely studied due to their formation of liquid crystalline phases and low volume fraction gels. They are used to impart desirable rheological behaviour to cosmetic, agrochemical and pharmaceutical formulations and are often the main constituent of oil-drilling fluids.

The plate-like clay montmorillonite does not form a liquid crystalline phase in aqueous suspension unlike other clay minerals of similar particle shape. A difference in charge distribution within the mineral structure is thought to alter particle interactions bringing about a gel phase. This inhibits entropically driven particle ordering.

We show that the mechanical properties of this system can be dramatically altered by tuning particle surface chemistry. The accompanying structural modification occurs at length scales nearly an order of magnitude greater than the largest particle dimension.

Background

The phase diagram of aqueous platelet suspensions contains a characteristic re-entrant transition from jammed glassy state at low ionic strength to a sol and then a bonded network gel at high ionic strength^{1,2}.

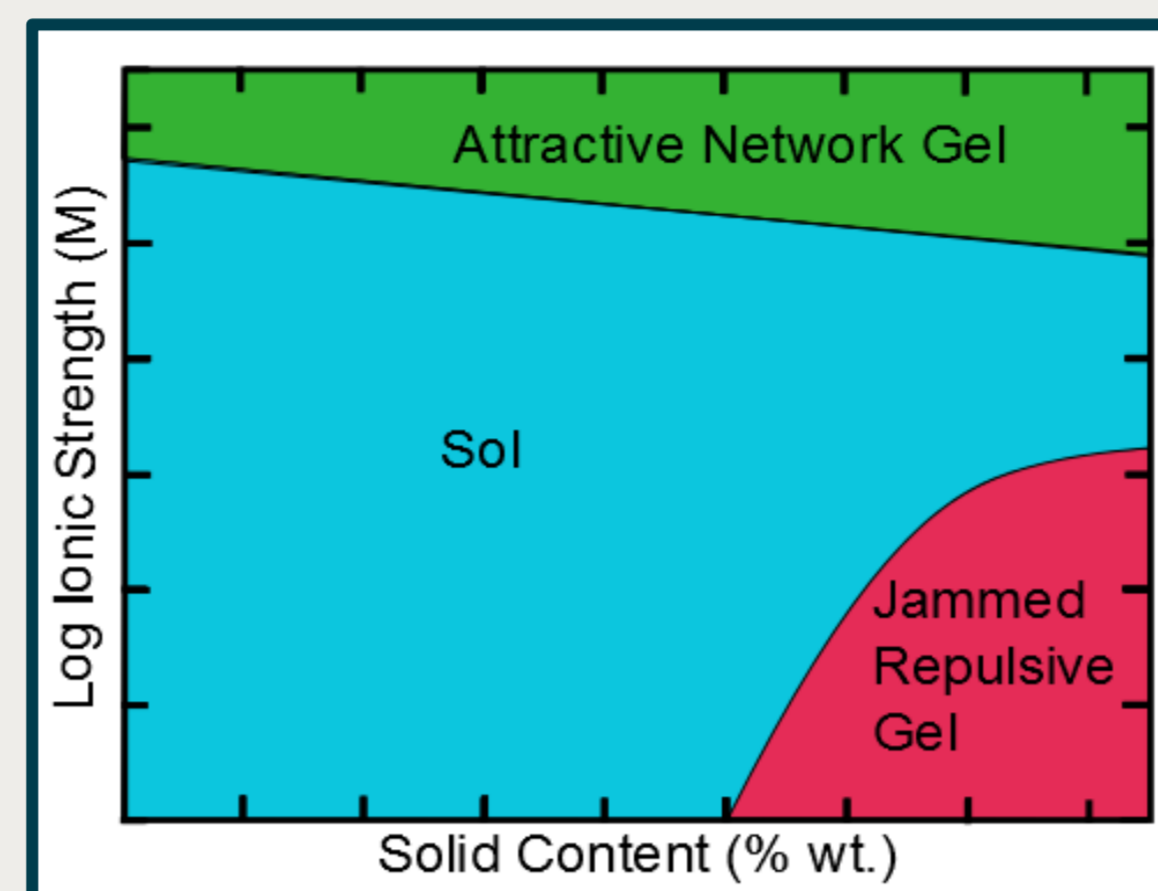


Figure 1: Typical phase diagram for platelet suspensions (redrawn from reference 1)

The adsorption of multivalent anions (such as $P_2O_7^{4-}$) to particle edges has long been used to liquefy clay particle gels³ and it was recently found that adsorbing an amine anchored amphiphilic polymer (Jeffamine M1000) to the particle faces has a similar effect⁴. The full extent of structure and flow control resulting from tuning surface chemistry in this way has not yet been reported.

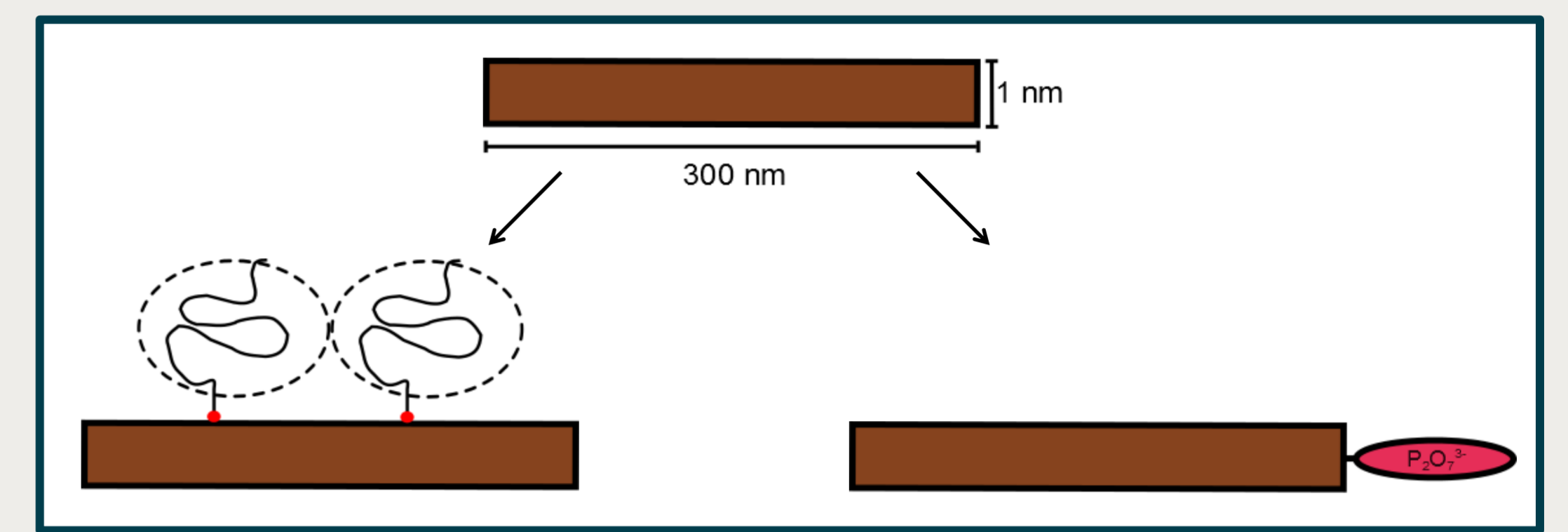


Figure 2: Typical dimensions of a montmorillonite platelet (top), adsorption of M1000 polymer mushrooms (left) and adsorption of $P_2O_7^{4-}$ anion (right)

Scattering Measurements

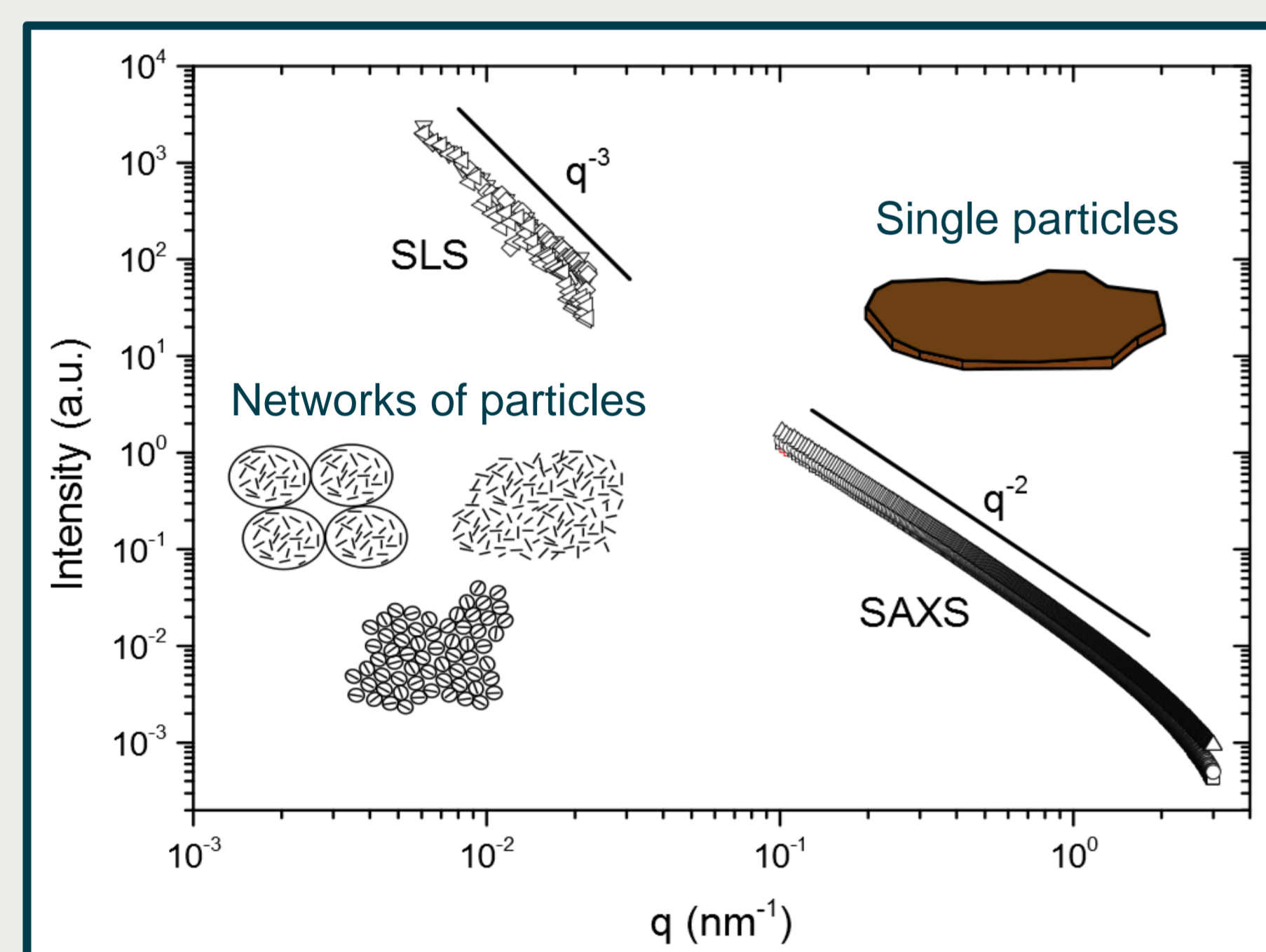


Figure 3: Static light scattering left, small angle X-ray scattering right. Montmorillonite suspensions dispersed in solutions of: 10^{-4} M NaCl (squares), 10^{-4} M NaCl with M1000 polymer (circles) or in 10^{-4} M NaP_2O_7 (triangles)

Small angle X-ray scattering (SAXS) and static light scattering (SLS) of dilute suspensions show that surface chemistry does not change structure on length scales from nanometers to hundreds of nanometers.

Lines represent power laws followed by data. Schematics show structures producing scattering. From left to right: cluster glass, particle glass and network gel all resulting in $\sim q^{-3}$ mass fractal power law and fully exfoliated platelet resulting in q^{-2} power law.

Microscopy

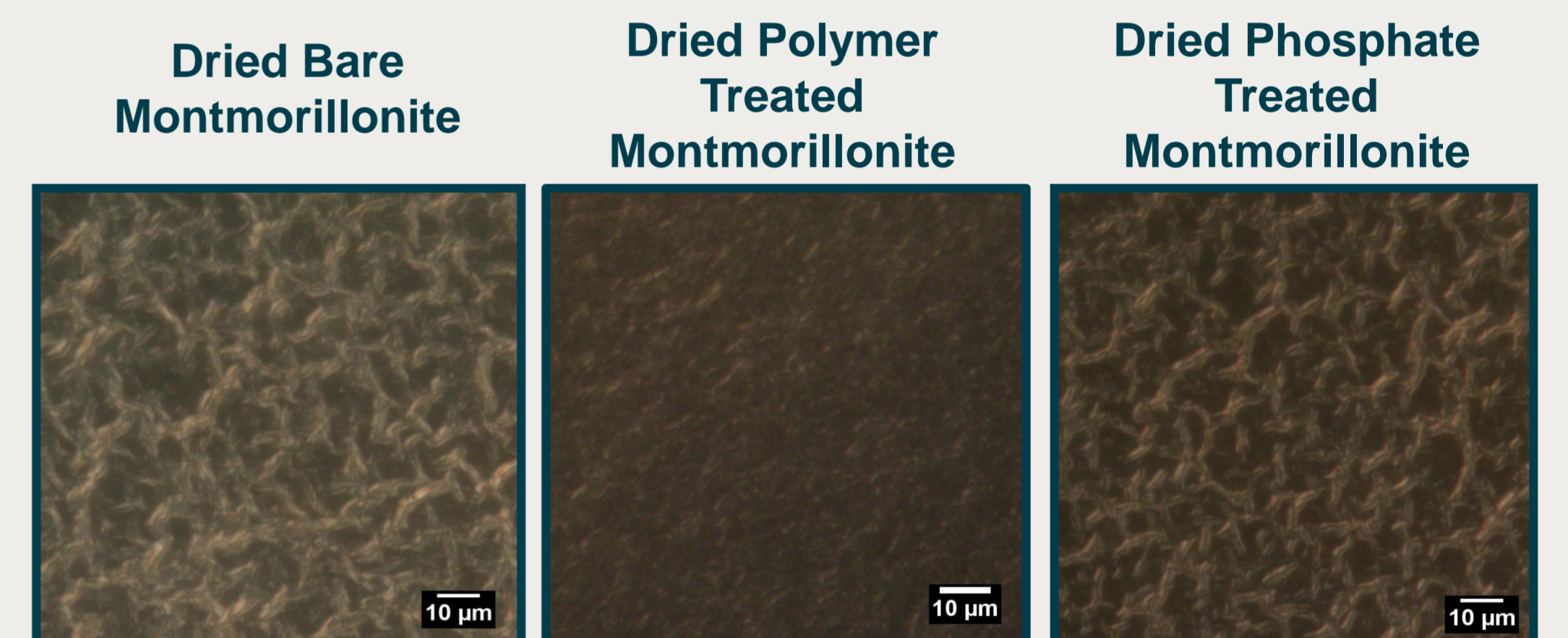


Figure 3: Differential interference contrast micrographs of dilute montmorillonite suspensions at 10^{-3} M ionic strength dried onto glass slides

Large scale ($>1 \mu m$) one dimensional structures have been reported for native montmorillonite suspensions in small angle light scattering and upon dry down under the microscope.

M1000 prevents the formation of the dry structures but $P_2O_7^{4-}$ does not.

Rheological Behaviour

The rheological response to ionic strength around the sol/gel transition line is different for each of the surface treatments.

Pyrophosphate does little to the low ionic strength jammed state but destabilises the high ionic strength gel network and M1000 adsorption disrupts the particle glass yet still forms a bonded particle network.

The surface modification must alter some large structure within the suspensions to bring about this mechanical change.

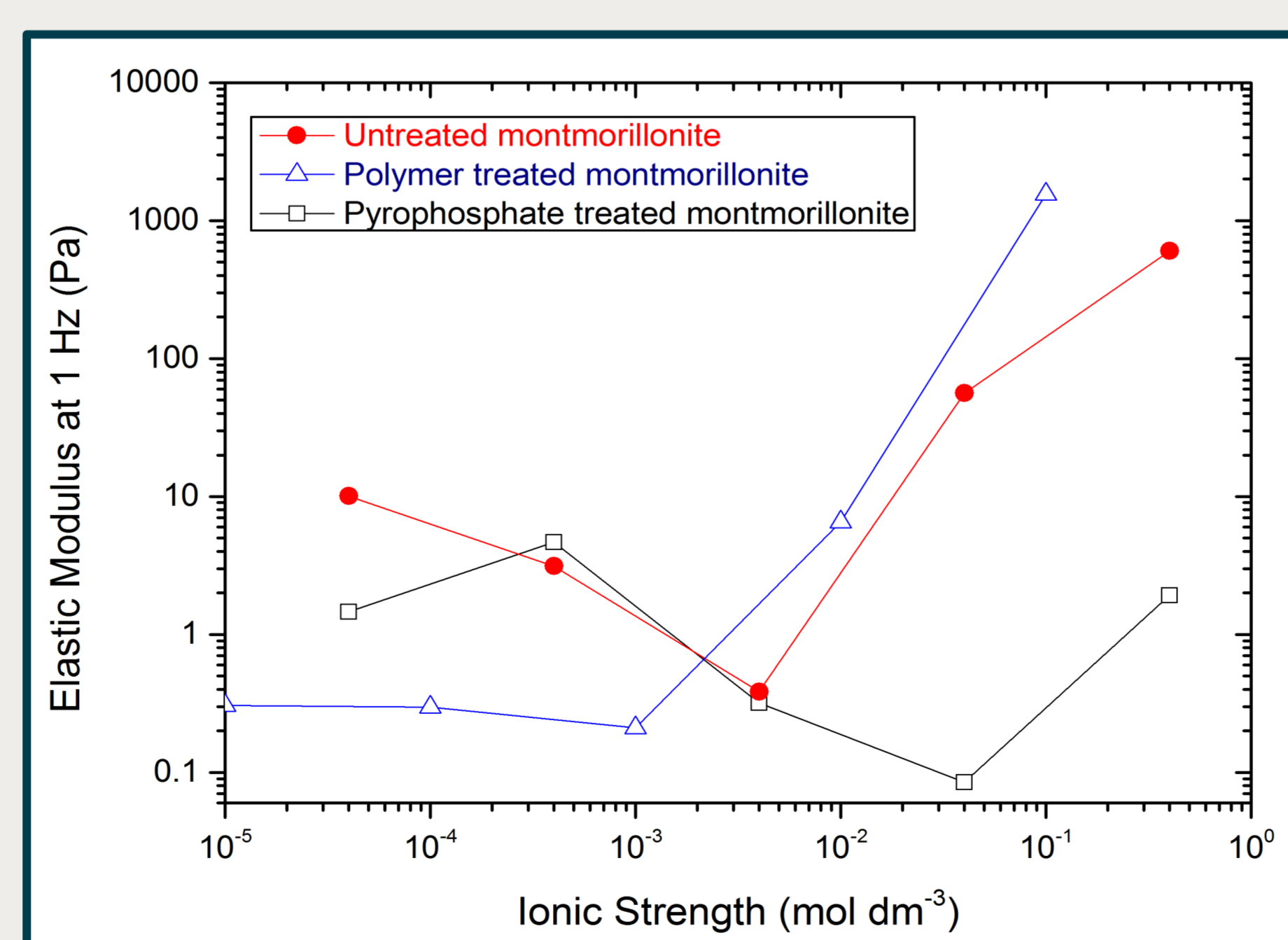


Figure 5: Elastic modulus in linear viscoelastic region at 1 Hz of 3% wt. montmorillonite dispersed in solutions of: NaCl (circles), NaCl with M1000 polymer (triangles) and NaP_2O_7 (squares)

Conclusions and Further Work

- It has been shown that the adsorption of multivalent anions to the edge and amphiphilic polymers to the face of plate-like particles can drastically alter the mechanical response of their aqueous suspensions.
- The response occurs in different regions of the phase diagram for the two species suggesting that steric stabilisation disrupts the jammed state whereas electrostatic stabilisation disrupts the bonded network state.
- Further work will explore more of the rheological phase diagrams of these systems and probe the large scale structure with techniques such as small angle light scattering.

References

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