



Flocculated Laponite–PEG/PEO dispersions with monovalent salt, a SAXS and simulation study

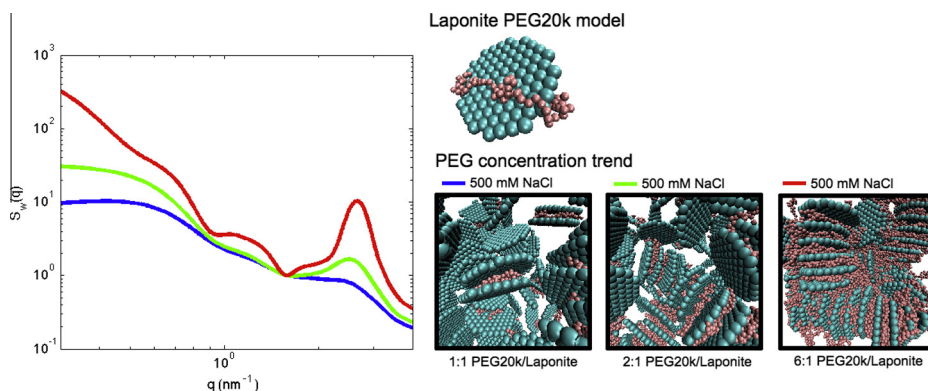


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GRAPHICAL ABSTRACT



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ABSTRACT

It is well-known that clay can form lamellar structures i.e. tactoids, and recently it has been shown that the tactoid formation is dependent on the platelet diameter. To the authors knowledge, no tactoid formation has been observed for montmorillonite platelets with a diameter less than 60 nm. In this study, small angle X-ray scattering in combination with coarse-grained modeling and molecular dynamics simulations have been utilized to study the sediment of Laponite–polyethylene glycol/polyethylene oxide (PEG/PEO) at elevated salt concentrations (150 mM–1 M). Laponite consists of platelets with a diameter of 25 nm and it is known to have a relatively monodisperse size-distribution. At pH 10, the face of the platelets has a strong negative charge, whereas the rim is slightly positive. Here we show that it is possible to induce tactoids for Laponite if two constraints are fulfilled: (1) addition of high amount of salt such as NaCl, and (2) addition of a neutral polymer such as PEG. The role of the salt is to screen the repulsive interactions between the platelets and the role of the polymer is to bridge the platelets together: hence the loss in configurational entropy of the polymer is counteracted by the gain in attractive polymer–platelet interaction. As the concentration of NaCl and/or PEG increases, the Bragg peak becomes sharper, which is an indication of that larger tactoids are formed.

Comparison between Laponite and montmorillonite shows that the interlayer distance between the platelets increases linearly with an increased Debye screening length for both type of clays, whereas the structure peaks of Laponite are broader compared to the montmorillonite. We argue that the main reason to the latter is due to the size of the platelets: (i) smaller platelets are less rotationally restricted

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Total structure factor
Aggregate

and (ii) the effect of positive edge charges is larger when the platelets are smaller, which results in more irregular aggregates. In absence of the polymer, montmorillonite form tactoids above ~ 0.3 M NaCl whereas Laponite does not.

Even though the model used is simple, we find qualitative agreement between experiments and simulations, which verifies that the underlying physics for tactoid formation is captured.

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1. Introduction

Many clay minerals swell in water and yield aqueous dispersions with unusual properties. Swelling 2:1 clays are made of platelets with a thickness of about 1 nm and lateral dimensions varying from 25 nm in synthetic Laponite clays to 1000 nm in natural montmorillonite. Previous experimental studies [1,2] have shown that Laponite exists in dilute suspensions as monodisperse disc-shaped particles. When water is added, the clay platelets become ionized and a rising osmotic pressure in the solution causes the clay to swell [3–5]. Semi-dilute dispersions with volume fractions above 0.5% can behave as gels (they have a yield stress) [5–7]. Upon drying, they form films with excellent barrier properties. These are often used in surface coatings, paper and polymer films, household, and personal care products. Another very interesting area for clay is as storing alternative for the nuclear waste; where the nuclear waste is put into copper containers embedded in bentonite or other source of clay and placed underground [8].

Depending on the size, the platelets can form a lamellar structure making it a seemingly perfect model system for an electrical double layer, where the swelling and stability in saline solution depend strongly on counterion valency and surface charge density [9–11]. The situation is, however, from a structural point slightly less ideal. Clay is normally not a homogeneous lamellar material, it is rather better described as a disordered structure of stacks of platelets, sometimes called tactoids [12–14].

In a tactoid the platelets have agglomerated in a face-to-face conformation with equidistant separation [15]. The tactoid formation of montmorillonite has been studied for several decades [16–19], where Blackmore and Miller [20] were first to introduce the term in clay science. In their study, Ca-montmorillonite was analyzed with X-ray diffraction and a diffraction peak was found at 1.9 nm^{-1} . The diffraction peak gives an estimation of the repeat distance between platelets and the average number of platelets per tactoid. The repeat distance for Na-montmorillonite decreases with increasing NaCl concentration due to the electrostatic screening effect. At high enough NaCl concentration tactoids are formed [21].

Recently, it has been shown that the average diameter of Ca-montmorillonite platelets is related to the average number of platelets per tactoid [22]. By increasing the diameter of the clay platelets, the number of platelets per tactoid increases. To the authors knowledge, it has not been observed that montmorillonite platelets with a diameter less than 60 nm can form tactoids in water with neither NaCl nor CaCl_2 . By generalizing this fact for Laponite, where the diameter is roughly 25 nm (model system for this study), tactoids will not be formed.

Clay/polymer complexes are of considerable importance in the field of colloid science, finding use in a wide range of applications from drilling muds [23,24] to paint. Studies that explore the nature of clay/polymer interactions and how it is affected by the physico-chemical properties of the solution are of fundamental importance since it can affect the bulk properties of the colloidal system such as the stability and the flow. It has been proposed that the polymers are disrupting hydrogen bonding between the water molecules and the silica or alumina functionalities of the clay surface,

and that the glycol molecules competes with water for these sites and also with water hydrating interlayer cations [23].

In the review by Anderson et al. [25] three different mechanisms are discussed for inhibition of clay swelling by addition of polyethylene glycol (PEG): (i) PEG diffuses into and displace water molecules from the interlayer; (ii) enthalpic terms i.e. the energy of the clay-PEG interaction is driving the reaction; or (iii) osmotic dewatering of the clay system. Smalley [26] has suggested a bridging flocculation method; but there has been, and still is, a dispute regarding the main mechanism, as stated by Liu et al. in 2004 [27].

It is well-known that PEG adsorbs onto the Laponite platelets, and at low salt concentration, relatively short PEG inhibits aggregation between the face and edge by steric hindrance [28]. Lal and Auvray [29,30] studied Laponite-PEG composites with Small Angle Neutron Scattering (SANS) using contrast variation techniques. They found that for 2 wt% Laponite with an addition of 1 wt% PEG suspension, the polymers adsorb and saturate the Laponite platelets with a 2–3 nm thick layer. Later, Nelson and Cosgrove [31] used SANS with contrast variation for a range of different molecular weights of PEG and found that the edge adsorption increases slightly with the polymer size whereas the adsorption on the face is more or less constant. By Dynamic Light Scattering studies (DLS) it was shown that the hydrodynamic thickness increases with molecular weight, indicating that the conformation of the adsorbed layer is very compact and it is much smaller than those normally observed for polymer adsorption on flat interfaces [32]. Nuclear Magnetic Resonance (NMR) studies of Na-montmorillonite and PEG have shown that ethylene oxide chains are in closest proximity with the surface [33].

In this article, we present results from our study of sedimented Laponite-PEG composites at pH 10 and at high salt concentrations. A relatively short PEG of molecular weight 20 kDa has been used. The experimental results were obtained by Small Angle X-ray Scattering (SAXS) and complemented by coarse-grained modeling and Molecular Dynamics simulations (MD). At pH 10, Laponite has a strong negative face charge and a weak positive edge charge [34]. Experimentally we show that, despite the small size of the Laponite platelets, it is possible to induce tactoids if two conditions are fulfilled: (1) high ionic strength, and (2) presence of PEG. Hence, it is not enough to only have a high amount of NaCl (as generalized above for montmorillonite) or a high amount of PEG. As the concentration of PEG increases, the number of platelets per tactoid increases and reaches a plateau value. The saturation concentration of PEG is in the same regime as the PEG adsorption isotherm to Laponite found by Mongondry et al. [28].

The experimental findings are compared to MD simulations where the platelets are modeled as negatively charged discs with explicit ions and adsorbing polymers. In the given model, we assume that the effect of the weakly positively charged rim is negligible, therefore only the face charge is taken into consideration. From the simulations, the total structure factor is calculated and compared to the experimental SAXS data. We find the corresponding polymer and salt concentration trends in the simulations as in the experiments. Simulations show that the system can be understood by a competition of electrostatic repulsive forces between the platelets and attractive bridging forces between the platelets

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