

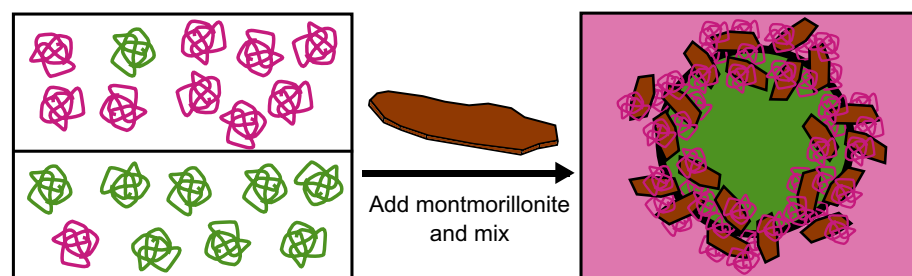
# Stabilisation of water-in-water emulsions by montmorillonite platelets



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## GRAPHICAL ABSTRACT



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## ABSTRACT

The formation of water-in-water emulsions from the aqueous two phase system containing polyethylene oxide and pullulan, stabilised by montmorillonite platelets, was investigated. A novel approach of preparing the emulsions at non-equilibrium polymer concentrations was successfully utilised to control viscosity during mixing and allow the use of low energy emulsification methods. Polyethylene oxide adsorbed to the platelets much more strongly than pullulan favouring the formation of pullulan-in-polyethylene oxide emulsions which remained stable for a period of weeks. Polarising microscopy and small angle light scattering were used to show that droplets were most likely stabilised against coalescence by the adsorption of randomly oriented aggregates of platelets and against creaming by the formation of chains of droplets bridged by the adsorbed aggregates. Montmorillonite platelets were therefore shown to stabilise water-in-water emulsions and their preference for emulsion type was driven by the adsorption of the polymers to the particle surface.

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## 1. Introduction

Traditional emulsions are formed from the dispersion of one fluid into another highly chemically dissimilar one, such as hydrocarbon oils or lipids into water. The emulsion droplets are stabilised by the addition of species that can lower the surface energy such as surfactants, polymers and solid particles. In some

applications, such as in the production of low calorie foods or the encapsulation of sensitive active ingredients, the use of an oil phase is problematic and replacement with another aqueous phase would be more desirable. This can be achieved by using a system of water soluble polymers which separate into two aqueous phases above a certain concentration due to a positive mixing enthalpy and small mixing entropy [1]. These are known as aqueous two phase systems (ATPS) and have traditionally found use in the separation of biomolecules where a target entity with a greater affinity for one of the aqueous phases can be extracted without the use of hydrophobic phases to which it may be sensitive [2].

The majority component in these systems is water and the interfacial tension is typically many times lower than that of an

Abbreviations: ATPS, aqueous two phase system; PEO, polyethylene oxide; Pu, pullulan; SALS, small angle light scattering.

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oil/water interface (of order  $\mu\text{N m}^{-1}$  as opposed to  $\text{mN m}^{-1}$ ) [1]. The total polymer concentration across a water/water interface at equilibrium falls to a minimum in the centre of the interface and the concentration gradient typically extends over a few tens of nanometres [3]. The water-enriched interface is permeable to small solutes (such as ions and surfactants) meaning that to arrest the phase separation of the polymer phases and form an emulsion larger stabilisers, such as colloidal particles, are needed. This approach has been applied successfully and many different types of particle have now been reported to accumulate at the interface between two phase separated aqueous polymer solutions including fats [4], latex particles [5], proteins [6,7], liposomes [8], mineral platelets [9], cellulose nanocrystals [10] and bacteria [11].

One of the first systematic studies into the stabilisation of water-in-water emulsions by solid particles showed that accumulation of particles at the interface does not always result in a stable emulsion [12]. The low adsorption energy means that particles can be thrown off mechanically [12,6,13] and therefore interactions between particles at the interface and the formation of a robust interfacial layer is perhaps more important in the stabilisation of water-in-water emulsions than it is for oil-in-water emulsions [14,5,7].

The increase in number of studies into the stabilisation of water-in-water emulsions by particles has warranted the publication of two recent review papers [15,16] and there are some additional phenomena that are worth noting. The first is the possibility of the polymers comprising the two separated phases adsorbing onto the surface of the stabilising particle and altering its wettability *in situ*. This has been reported to result in an asymmetry in the type of emulsion that is favoured. For example dextran has been shown to adsorb more favourably to cellulose nanorods than polyethylene oxide resulting in particles which only stabilise polyethylene oxide-in-dextran emulsions [10]. Second is that the interaction with either phase can be highly dependent on environmental parameters. Protein stabilised water-in-water emulsions have been shown to be highly pH dependent and only form when the proteins complex with one of the polymers [6,17]. This response to external stimuli has been used to tune the behaviour of the emulsions where a change in pH can trigger destabilisation which may be useful in controlled delivery applications [13].

Non-spherical colloidal particles have the potential to be useful components in these all-aqueous formulations as they are well known to form complex structures in suspension [18] and have already been reported to stabilise water-in-water emulsions [9,10]. Detailed study of their organisation in these polymer-rich systems is therefore warranted as they have the potential to structure the continuous phase of the emulsions whilst also forming a robust stabilising layer at the water/water interface.

Here we take the smectite clay mineral montmorillonite, which can be exfoliated in aqueous suspension to form extremely high aspect ratio ( $\sim 300:1$ ) platelets, and show that it can stabilise pullulan-in-polyethylene oxide emulsions. We use a combination of microscopy, rheology and light scattering to investigate the structures formed by the adsorbing particles and their stabilisation mechanisms. It was found that pullulan-in-polyethylene oxide emulsions were stable for at least 21 days, the adsorption of polyethylene oxide to the surface of the platelets drove an asymmetry in the type of emulsions that could be formed and the platelets were found to adsorb as clay-polymer aggregates.

## 2. Materials and methods

Wyoming montmorillonite (SWy-2) was purchased from the Clay Minerals Society source clays repository at Purdue

University. The composition of SWy-2 is  $(\text{Si}_{7.94}\text{Al}_{0.06})(\text{Al}_{2.88}\text{Fe}_{0.5}\text{Mg}_{0.62})\text{O}_{20}(\text{OH})_4\text{Na}_{0.68}$  [19]. This montmorillonite has a cation exchange capacity of 84 mequiv/100 g [20] and the platelets typically have diameters in the range 200–2000 nm and are 1 nm thick. Polyethylene oxide (PEO,  $M_w = 10^5 \text{ g mol}^{-1}$ ) was purchased from Sigma Aldrich, cosmetic grade pullulan (Pu,  $M_w = 9 \times 10^4 \text{ g mol}^{-1}$ ) was kindly donated by Hayashibara, acridine orange (55% dye content) was purchased from Acros Organics and reagent grade sodium chloride was purchased from Fisher.

Preparation of montmorillonite dispersions was based on a previously described method [21].  $45 \text{ g L}^{-1}$  powdered clay was added to deionised water and stirred for 24 h. The suspension was then dialysed against aqueous NaCl (1 M) for 1 week changing the solution everyday, to remove unwanted ions such as  $\text{Ca}^{2+}$ , and then dialysed against deionised water, changing water every day, until the conductivity of the dialysate was below  $5 \mu\text{S cm}^{-1}$ . The dialysed suspension was then diluted to 1 wt.% and left for 24 h for large impurities such as sand and quartz to settle out. The supernatant was concentrated up by evaporation and used as stock. Our previous work has shown that this results in complete exfoliation of the particles [22].

Polymer solutions were prepared by adding the solid polymer to deionised water and gently rolling at room temperature for a minimum of 12 h. PEO solutions were additionally centrifuged at 20,100g for 60 min in a Labnet Prism C2500 micro-centrifuge to remove silica impurities following a previously reported method [12]. The removed sediment accounted for no more than 2% of the total polymer mass.

Pu/PEO solutions for phase diagram determination were prepared by dissolving Pu into purified PEO solutions at different mass ratios by gentle rolling at room temperature for a minimum of 12 h. Once dissolved the solutions were left to stand in an incubator at  $25 \text{ }^\circ\text{C}$  for 24 h and the presence or absence of a macroscopically visible fluid-fluid interface was noted.

Adsorption of the polymers onto montmorillonite was determined by adding stock montmorillonite suspension to stirring Pu and PEO solutions. The final montmorillonite concentration was 0.2 wt.% and the mass ratio of polymer to clay varied between 1 and 3. The montmorillonite-polymer mixtures were then rolled gently for 24 h and the unadsorbed polymer removed by centrifugation at 20,100g for 30 min in a Labnet Prism C2500 micro-centrifuge. The sedimented particles were then washed with deionised water, air dried and the adsorbed amount calculated by measuring the increase in carbon content using a Euro EA3000 elemental analyser.

Water-in-water emulsions were prepared by combining PEO and Pu solutions (prepared as detailed above) at 27 wt.% and 11 wt.% respectively. The Pu solution was first mixed with stock montmorillonite suspension and NaCl solution (final NaCl concentration in the emulsions was fixed at 0.01 M for all samples tested) by vortex mixing at 3000 rpm for 30 s and then gently rolled at room temperature for 60 min. The solutions were then combined and emulsified by vortex mixing at 3000 rpm for 60 s. The emulsion type was verified as Pu-in-PEO using the drop test where a droplet of emulsion (after being left to equilibrate) was pipetted onto a droplet of either 11 wt.% PEO or 20 wt.% Pu. An example is shown in Fig. 1 where the emulsion can be seen to have mixed with the PEO solution but not the Pu solution showing that the PEO-rich phase is the continuous phase.

The equilibrium Pu-rich phases are much more viscous than the PEO-rich phase making it difficult to shear the droplets sufficiently to achieve break-up using low energy methods such as hand shaking or vortex mixing. To achieve more reproducible results the phases were made at initially non-equilibrium compositions where the Pu-rich phase was less viscous, emulsified and then left to

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