



Pickering emulsions stabilized by amphiphile covered clays

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ABSTRACT

It is shown that all water soluble amphiphilic compounds like surfactants, polymers, block copolymers and proteins bind strongly to clay particles in water. On saturation, the clays bind up to the multifold weight of the additives of their own weight. Prior to saturation some amphiphilic compounds form precipitates with the clays while others do not. The soluble clay–amphiphile complexes do not lower the surface tension of water even though these particles must obviously be hydrophobic. It is concluded from these results that the clays alone are already hydrophobic particles. Solutions or precipitates of these amphiphile covered clay particles are ideal systems for the formation of stable Pickering emulsions. Depending on the used type and amount of amphiphile, the corresponding Pickering emulsions can have either viscous or gel-like properties with large storage moduli. For some combinations both the water and the oil can be removed from the emulsions without collapse of the three dimensional network of the films.

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1. Introduction

Clays are interesting compounds for a wide range of applications [1–3]. The minerals can be exfoliated to single sheets in aqueous solutions. In this state the thin sheets have a thickness of 1 nm. Because of their large surface of about 1000 m²/g, the clay particles can adsorb the manifold weight as their own weight. Clays are therefore used as adsorbers of many waste products like surfactants [4], dyes [5] or heavy metals [6] in the purification process of water. Clays are available either as natural or synthetic products. Natural clays are known under different names like Montmorillonite and Saponite. The diameter of the plate-like clay-particles ranges from 20 nm for synthetic clays to many μm for natural clays. Because of their large anisometry and possible surface modification, clays are often used for various purposes, for example as rheology modifiers [7]. The rheology of industrial formulations can be changed from shear thinning solutions to stiff gels with a few wt% of clays. In recent times clays have been used to strengthen the stiffness of polymers [8] and to improve the impermeability of gases through thin polymer films [9]. In combination with surfactants, clays can be made hydrophobic and these hydrophobic clay-particles can be dispersed in hydrocarbons [10]. In mixture with non-ionic surfactants clays have also been used for the preparation of Pickering emulsions [11]. This application brings up an interesting basic question. The surface of clays is generally considered to be a hydrophilic surface.

Dispersions of clays have the same surface tension as water [12]. It is therefore assumed that clays are not surface active, but this conclusion may not be completely correct. It is known that polymers like polyethylene glycol which are considered to be hydrophilic bind on clays [13,14]. This result makes only sense, if the surface of the clays has somehow hydrophobic features.

Recently it was shown that one to one mixtures of clay–hydrophobin particles stabilize high internal oil in water (o/w) emulsions by synergistic interaction [15]. Only 1 wt% of hydrophobin and clay were needed to prepare homogenous emulsions. However, it was remarkable that both, the clay and hydrophobin protein are negatively charged. Rheological measurements showed that the Pickering emulsion from this combination has a high storage modulus G' (>1000 Pa) and viscosity (1 Pas at $\dot{\gamma} = 100 \text{ s}^{-1}$).

This manuscript focuses on three main aspects. The first part will be about the interaction between amphiphilic compounds and clay. Therefore especially the surface tension behaviour of the amphiphile–clay particles will be discussed in general terms. The second part deals with the question, what kind of one to one mixtures of amphiphile and clay will result in similar emulsions as obtained with the hydrophobin, called H Star Protein B[®] [16]. The influence of the clay coverage with amphiphile on the visual appearance, stability and rheological behaviour to the emulsion is investigated. As a model system we used the cationic surfactant C₁₄-trimethylammoniumbromid (TTMABr) with Laponite XLG as clay compound. Finally, in the third part, we discriminated our emulsion systems from Pickering emulsions prepared with silica particles [17].

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