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SHORT COMMUNICATION

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Aggregation in Pickering emulsions

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Abstract For the first time, the particle distribution and aggregation in Pickering emulsions were made visible by transmission X-ray microscopy. Oil/water emulsions were stabilized by heterocoagulates of a clay mineral and magnesium aluminum hydroxide. Stability is optimum when the particles surround the oil droplets and also assemble to form a network extending through the coherent phase.

Key words Bentonite – Hydrotalcites – Layered double hydroxides – Pickering emulsions – X-ray microscopy

Introduction

Stabilization of emulsions by colloidal solids provides a possibility to reduce the amount of surfactant emulsifier or to avoid surfactant emulsifiers completely. In Pickering emulsions [1, 2] the stabilizing film of emulsifier molecules around the dispersed droplets is replaced by an envelope of solid particles (Fig. 1). This envelope forms a mechanical barrier which impedes the droplets from coalescing with each other. The prerequisite is that the colloidal particles are enriched at the oil/water interface and remain there during collisions of the droplets. The conditions which cause particle agglomeration at the interface were discussed in several papers [3–9].

Weak attraction between the particles should stabilize their enrichment at the interface because the envelope becomes more stable and the risk of movement of the particles into the oil or water phase is reduced. Too strong attractions between the particles may be counterproductive because the envelope contracts, larger aggregates form, and the dense film of particles breaks open.

Recently, very effective stabilization by colloidal particles was observed when smectitic clay minerals (montmorillonites) were compounded with layered double hydroxides (LDHs) [10]. These layered materials have opposite charge distributions: negatively charged layers in montmorillonite with cations as gegen ions [11], positively charged layers in LDHs with anionic gegen ions [12–15].

In recent years aggregation processes in aqueous medium were made visible in situ by X-ray microscopy [16–20]. Because of the shorter wavelength, an X-ray microscope provides better resolution than a light microscope. At an appropriate wavelength (2.34 nm, slightly larger than the K absorption edge of oxygen) the transmission of water is higher than that of other inorganic and organic materials; the phase shift is also smaller. Thus, transmission by X-ray microscope images are created by amplitude and phase contrast mechanisms [21].

Materials and methods

Sodium montmorillonite was prepared from bentonite from Wyoming (Greenbond, sample no. 40A) by the usual procedure [removal of iron oxides by reduction with dithionate in the presence of citrate as an iron

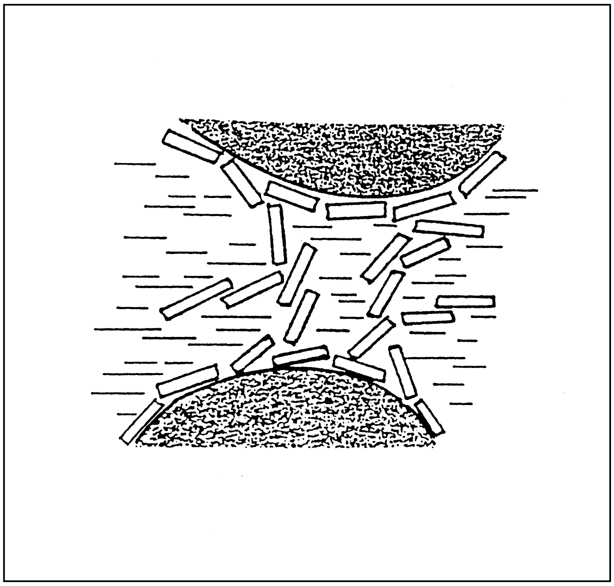


Fig. 1 Stabilization of emulsions by colloidal particles surrounding the droplets and struting them by network formation

chelating agent, oxidation of organic material by hydrogen peroxide, and fractionation ($<2\ \mu$m) by sedimentation] [22].

The layered double hydroxide was a synthetic hydrotalcite-like material with the ideal composition $[Mg_2Al(OH)_6]NO_3 \cdot 2\ H_2O$ [12, 14]. It was prepared by coprecipitation of magnesium and aluminum nitrate in alkaline medium. Colloidal particles were obtained by dispersing the precipitate in water and removing the fine particles by centrifugation [10]. Scanning micrographs showed more or less compact particles of irregular shape, sometimes spherical with diameters above 100 nm. The mean equivalent spherical diameter measured by dynamic light scattering was about 200 nm.

Emulsions were prepared by dispersing the hydroxide in paraffin oil (Merck; density 0.88 g/cm^3, viscosity 150 mPa s) at 80 °C. The oil phase was added in small portions to the dispersion of montmorillonite in water, also maintained at 80 °C. The emulsion was homogenized for 3 min with an Ultra Turrax (24 000 rot/min) [10]. The amounts of colloidal stabilizers were 0.5% magnesium aluminum hydroxide and 0.5% montmorillonite (w/w, related to the total mass, oil + water + solid). The oil volume fraction was 0.38.

For X-ray microscopic examination small amounts of the emulsion were placed in an object chamber which allowed the thickness of the sample to be adjusted. The X-ray images were recorded by a back-thinned, back-illuminated X-ray-sensitive CCD chip. The transmission X-ray microscope of the “Forschungseinrichtung Röntgenphysik” was placed at the electron storage ring BESSY in Berlin [23–25].

▶

Fig. 2a–d Transmission X-ray microscope images of an oil/water emulsion stabilized by 0.5% (w/w) montmorillonite and 0.5% (w/w) magnesium aluminum hydroxide. Paraffin oil volume fraction = 0.38

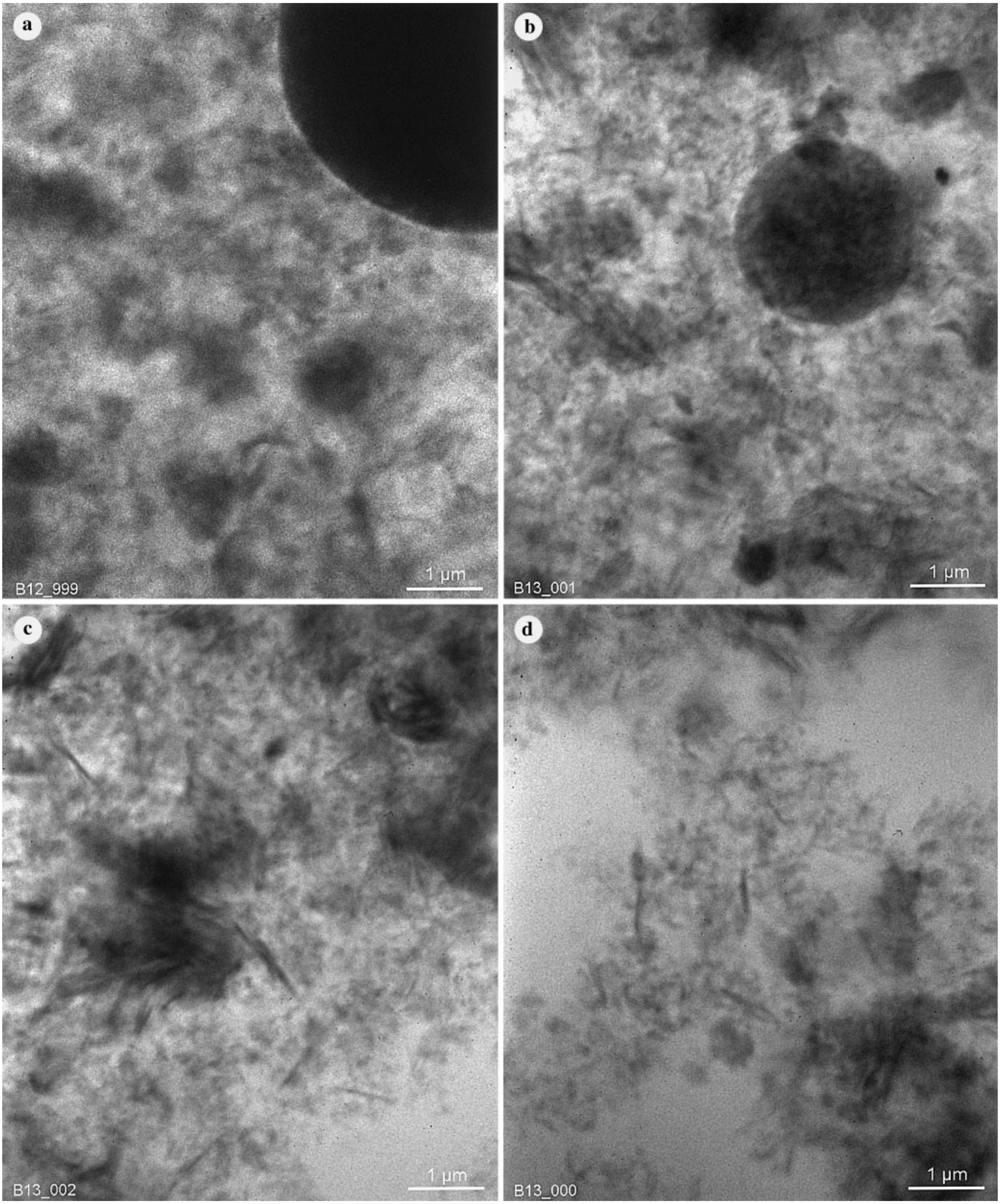
Results and discussion

Figure 2a–d shows, for the first time, in situ aggregation of particles around oil droplets and in the coherent phase of Pickering emulsions. Two types of particles are distinguished: thin, elongated particles, very likely consisting of lamellae of sodium montmorillonite, and more spherical particles of the hydroxide. Larger aggregates of sodium montmorillonite are seen in Fig. 2c. Evidently, hydroxide particles are enriched around the oil droplets but are also distributed between the elongated montmorillonite lamellae. A network of particles is built up in the coherent phase. It consists of a framework of almost equally distributed lamellae, probably montmorillonite, connected by the more spherical particles of the hydroxide.

Network formation of the particles within the coherent phase enhances the emulsion stability because the network struts the oil droplets and protects them from coalescence. The backbone of the network consists of the clay mineral lamellae (Fig. 11a–c in Ref. [10]). The hydroxide particles alone do not build up three-dimensional networks. At the condition for emulsification (low montmorillonite and salt content, pH ≈ 6) the clay mineral particles form weak, fragile frameworks. Addition of the layered double hydroxide strengthens the three-dimensional network. Rheological measurements [10] revealed high elastic contributions during shearing. A graphic model is that the LDH particles act like hinges in the network of the clay mineral particles and give the film a high degree of elasticity.

However, network formation is not a sufficient condition for emulsion stability; the oil droplets must also be encapsulated by the solid particles. The hydroxide improves emulsification because it is more hydrophobic than montmorillonite and is easily dispersed in the oil phase.

Building up a framework of particles increases the viscosity of the coherent phase which also enhances the stability. Experimental observations [26] reveal that this effect is not strong enough to stabilize the emulsion. Rather, optimal stability is attained when the conditions are such that the droplets are surrounded by an envelope of particles and are trapped in a network of additional particles. The X-ray microscopic images provide clear evidence of this model of colloid-laden emulsions.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