Stabilization of emulsions by heterocoagulation of clay minerals and layered double hydroxides

Abstract Paraffin/water emulsions were stabilized by colloidal particles without surface active agents. Mixtures of two types of particles with opposite signs of charge were used: a layered double hydroxide (the hydroxide layers carry positive charges) and the clay mineral montmorillonite (the silicate layers carry negative charges). The emulsions were very stable and did not separate a coherent oil phase. The stability of the emulsion (no oil coalescence after centrifugation) was independent of the mixing ratio of both the compounds when the total solid content was > 0.5%. Solid contents up to 2.0% were optimal. In contrast to stability, flow behavior of the emulsion was dependent on the mass fraction \( \chi \) of the hydroxide. The maxima of viscosity and yield value were observed at \( \chi \approx 0.2–0.3 \); the emulsion showed pronounced antithixotropic behavior. Weak thixotropic properties, smaller viscosities and yield values were observed at \( \chi \leq 0.2 \) and \( \geq 0.5 \). In the absence of the clay mineral, the double hydroxide particles stabilize by forming envelopes around the oil droplets. Addition of bentonites creates a three-dimensional network of particles with high elasticity which impedes coalescence of the oil droplets.

Key words Aluminum magnesium hydroxide – antithixotropy – bentonite – emulsions – montmorillonite – Pickering emulsions – layered double hydroxide – solid stabilized emulsions

Introduction

Stabilization of emulsions by solid materials (Pickering emulsions) [1–6] provides many advantages:

1. The amount of emulsifying agents can be reduced, risky surfactants may be replaced by less hazardous materials, or organic emulsifying agents can even be completely avoided.

2. Many Pickering emulsions are difficult to break by changing the chemical parameters like pH, salt concentration, temperature and composition of the oil phase.

3. By changing the solid content or the type of solid, viscosity and type of flow can be adjusted to required practical applications.

4. In some cases the type of emulsion (O/W or W/O) changes when, at a given composition, a solid stabilizer is added.

Many different solid materials were used as stabilizers: iron oxides, silica, alumina, calcium carbonate, barium sulfate, clay minerals, carbon, polystyrene [3–5, 7, 8], colloidal metals [9] and crystalline organic compounds like glycerol tristearate and stearic acid [6, 8].
Clay minerals should be excellent solid stabilizers because of several favorable properties [10, 11]:

(i) They consist of fine particles ( < 2 μm). If required, fine particle size fractions can be obtained by sedimentation.
(ii) In the presence of sodium ions smectite particles in water delaminate into single silicate layers or thin packets of them.
(iii) At certain conditions the particles or delaminated particles aggregate and form band-type networks or cardhouse structures.
(iv) The clay mineral surface is easily modified by adsorption, ion exchange or grafting.

The clay minerals provide a group of solid materials which are available in large amounts and great diversity. They are easily tailored to stabilizing different emulsion systems. In spite of these aspects only a few papers report the use of clay minerals in emulsions. Recently, emphasis was laid on modifying montmorillonites [12] and kaolinites [13, 14] with asphaltenes because clay minerals play an important role in water-in-crude oil emulsification. Adsorption of asphaltenes and resins from the oil make the clay minerals hydrophobic and changes the wettability of the particles which is crucial in determining the nature and stability of the emulsions. Puskás et al. [15] suggested stabilization of water-in-crude oil emulsions by colloidal hydrocarbons.

Application O/W emulsions in cosmetic and pharmaceutical fields requires non-hazardous surfactants. The use of reduced amounts of surfactants is desirable. Tsugita et al. [16] reported the formulation of O/W emulsions with montmorillonite as the colloidal stabilizer in the presence of glycerol monolaureate, monopalmitate, monostearate and related compounds. In fact, effective emulsifying and stabilizing agents were prepared from sodium montmorillonite combined with glycerol derivatives and other neutral organic compounds (alkyl poly(ethylene oxides), alkyl polyglucoside, lecithine) [11, 17].

A further and final step is the stabilization of oil–water emulsions by clay minerals without surfactants. Stabilization by solid particles depends on their ability to migrate to the interfacial region, to remain there, and to form a film which inhibits coalescence of the droplets. Combination of montmorillonite with a layered double hydroxide (LDH) may fulfill these conditions. LDHs are layered materials with the layers positively charged and separated by anions [18–20]. Because of the opposite sign of the layer charges they interact strongly with the clay mineral. Heterocoagulates between both layer compounds are expected to form a stable, but elastic film around the droplets which should strongly reduce the rate of coalescence.

**Materials**

The clay mineral was a bentonite of Wyoming (sample M40 and M40A). The crude bentonite contained about 80% (sodium, calcium) montmorillonite (molar ratio sodium/calcium about 6.5). This bentonite was used in an air-dried form. The < 2 μm fraction of montmorillonite was prepared from the bentonite by the standard procedure [21, 22].

The cation exchange capacity of the montmorillonite was 1.06 meq/g silicate framework (= 1.03 meq/g sodium montmorillonite, from carbon content of the alkylammonium derivatives [23–25]). The alkylammonium layer charge, $\xi = 0.28$ eq./mol, indicated an interlayer exchange capacity of 0.76 meq/g silicate framework [25]. Crude bentonite had an alkylammonium exchange capacity of 0.82 meq/g and, thus, contained $100 \times 0.82/1.03 = 80\%$ montmorillonite.

The layered double-hydroxide was a magnesium aluminum hydroxide with nitrate as gegenion. The idealized formula is $[\text{Mg}_2\text{Al(OH}_6)]\text{NO}_3\cdot 2\text{H}_2\text{O}$ (the mineral hydrotalcite contains carbonate instead of nitrate). This material easily forms by the coprecipitation of magnesium and aluminium nitrate in an alkaline condition. It crystallizes rapidly and consists of large particles. A sample with colloidal particles was obtained by the following procedure [26]: Amounts of 0.08 mol $\text{Al(NO}_3)_3\cdot 9\text{H}_2\text{O}$ and 0.16 mol $\text{Mg(NO}_3)_2\cdot 6\text{H}_2\text{O}$ were dissolved in 500 ml water. This solution was added dropwise (within 1 h) to a solution of 0.55 mol NaOH and 0.07 mol NaNO$_3$ in 500 ml water. The dispersion was altered 6 days at room temperature under persistent stirring. After this period, the dispersion was centrifuged at 3000 U/min for 30 min (Heraeus Biofuge). The double hydroxide settled completely. The sediment was redispersed in water and centrifuged. Again, the LDH formed a sediment which was redispersed in water. After centrifugation a part of the LDH remained in the colloidal dispersion and made the supernatant turbid. The procedure was repeated several times until a sediment did not form after centrifugation. The turbid supernatents were collected (solid content of about 1%) and spray-dried. As indicated by the broadened reflections of the X-ray powder diffractogram this colloidal material was highly disordered. The molar ratio magnesium/aluminum (= 1.80) was below the theoretical value.

The mean equivalent spherical diameter $d_k$, measured by dynamic light scattering (Zeta Plus, Brookhaven Instr. Corp.), was about 200 nm. Sedimentation experiments (cuvette photocentrifuge Horiba Cappa 500) showed maxima of equivalent Stokes diameters $d_k$ between 150 and 200 nm. The particles were somewhat smaller than the delaminated particles of the sodium montmorillonite.