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ORIGINAL CONTRIBUTION

S. Abend
N. Bonnke
U. Gutschner
G. Lagaly

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

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S. Abend · N. Bonnke · U. Gutschner
Prof. Dr. Dr. h. c. Lagaly (✉)
Christian-Albrechts-Universität
Institut für Anorganische Chemie
D-24098 Kiel
Germany
E-mail: h.mittag@email.uni-kiel.de

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 χ 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 ≥ 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 ($< 2\ \mu$m). 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. (1983) [16] reported the formulation of O/W emulsions with montmorillonite as the colloidal stabilizer in the presence of glycerol monolaurate, 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 $< 2\ \mu$m 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 $[Mg_2Al(OH_6)]\ NO_3 \cdot 2\ H_2O$ (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 $Al(NO_3)_3 \cdot 9H_2O$ and 0.16 mol $Mg(NO_3)_2 \cdot 6H_2O$ 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 supernatent 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_R, 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_S between 150 and 200 nm. The particles were somewhat smaller than the delaminated particles of the sodium montmorillonite

($d_R \approx 500$ nm, d_S: broad distribution between 150 and 500 nm). The different equivalent spherical diameters d_R and d_S indicate that the axial ratio of the hydroxide particles (considered as discs) was ≤ 10 but > 20 for sodium montmorillonite [27].

The theoretical exchange capacity of a LDH of composition $[Mg_2Al(OH)_6]NO_3 \cdot 2H_2O$ is 3.63 meq/g. The analytical composition of the colloidal material indicated an exchange capacity of about 2.9 meq/g [26]. The bentonite had an cation exchange capacity of 0.82 meq/g. A mixture of the hydroxide (anion exchange capacity: 2.9 meq/g) and bentonite with a hydroxide mass fraction $\chi = 0.22$ contained charge equivalent amounts of both solids.

Preparation of emulsions

The bentonite was dispersed in water by intense shaking for 12–16 h. Ultrasound ($\# = 80/160$ W, 40 kHz) was used to disperse the hydroxide in paraffin oil (Merck Comp.; density 0.88 g/cm^3, viscosity 150 mPas). Both dispersions were heated in a water bath to 80 °C. The oil phase, homogenized with an Ultra Turrax (24 000 rot/min), was added in small steps to the aqueous bentonite dispersion. The emulsion was homogenized for 3 min with the Ultra Turrax (24 000 rot/min).

The solid content was varied between 0.02% and 5% (mass fraction, related to the total mass, oil + water + solid). The ratio of hydroxide and bentonite is expressed as a mass fraction of the hydroxide: χ = mass (hydroxide)/mass (hydroxide + bentonite). χ was varied from $\chi = 0$ (bentonite) to $\chi = 1$ (hydroxide).

Emulsion stability

Most emulsions were very stable and did not separate a coherent oil phase even after long periods of sitting (up to two years). To see the influence of the different parameters on emulsion stability, the samples were centrifuged for 30 min at 3000 rot/min (Heraeus, Biofuge). Generally, four phases may be observed after centrifugation (Fig. 1): a sediment of solid particles at the bottom, a layer of water, the creaming layer and the coherent oil phase at the top.

The state of the emulsion is described by (i) the sediment height (volume fraction of sediment, related to the total volume of the system), (ii) the final emulsion volume (volume of the creaming layer to total volume), and (iii) degree of coalescence (volume of coherent oil phase to total volume).

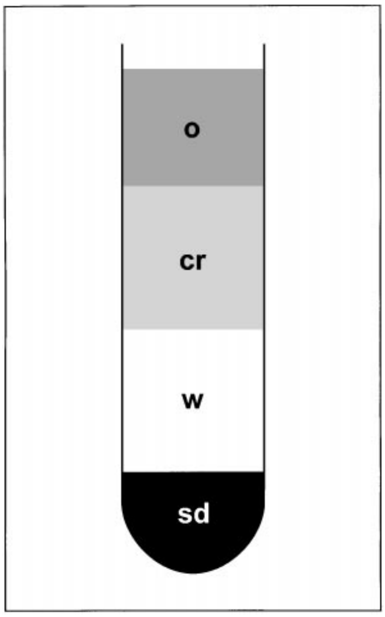

Fig. 1 Solid stabilized emulsions: phase separation after centrifugation (o) coherent oil, (cr) creaming layer, (w) water phase, (sd) sediment of solid particles

Results

Stability

The emulsions were stabilized by very small amounts of hydroxide and bentonite (Fig. 2). Emulsions (oil volume fraction $\Phi = 0.38$) with solid contents between 0.1% and 4% mass fraction did not eliminate a coherent oil phase when the solid was composed of equal amounts of bentonite and layered double hydroxide, $\chi = 0.5$. The ratio χ was not critical to impede oil coalescence (Fig. 3). Oil was only separated at solid contents $\leq 0.5\%$ when the hydroxide mass fraction χ decreased below 0.4. The emulsions were also stabilized by hydroxide alone ($\chi = 1$) when the solid content was above 0.2%.

A sediment was not formed from emulsions with solid contents of 0.5% and hydroxide weight fractions $\chi > 0.4$. At higher solid content not all solid particles were needed for stabilization of the oil droplets and a certain part of both types of particles settled. The sediment height showed a broad maximum at $\chi \approx 0.6$–0.7 (Fig. 4). As the final emulsion volume (s. below) was almost constant for $0.5 < \chi < 0.9$, the maximum of sediment height resulted from distinct sediment structures at these hydroxide/bentonite ratios.

The final emulsion volume (emulsion and creaming layer) after centrifugation occupied 60–70% of the total

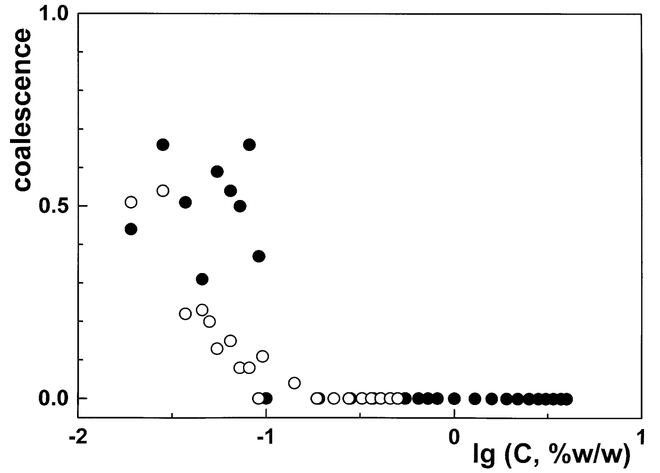

Fig. 2 Coalescence (volume fraction of coherent oil) as a function of solid content. Oil volume fraction $\Phi = 0.38$; (○) magnesium aluminum hydroxide ($\chi = 1$); (●) hydroxide/bentonite (sample M40), $\chi = 0.5$

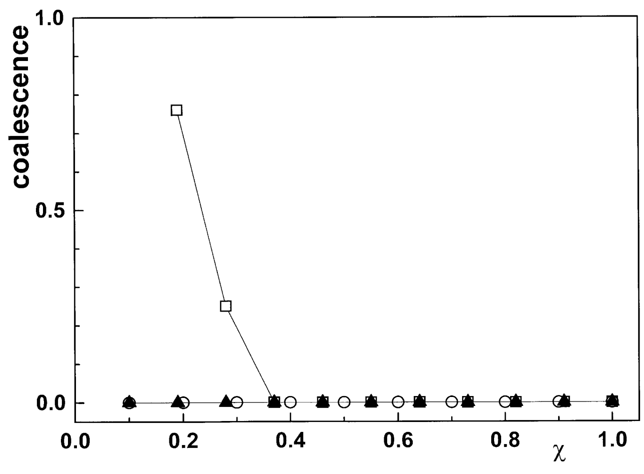

Fig. 3 Coalescence (volume fraction of coherent oil) as a function of the mixing ratio hydroxide/bentonite (M40). χ = mass fraction of the hydroxide; oil volume fraction $\Phi = 0.38$; solid content (mass fraction): (-□-) 0.5%, (-○-) 1%, (-▲-) 1.5%

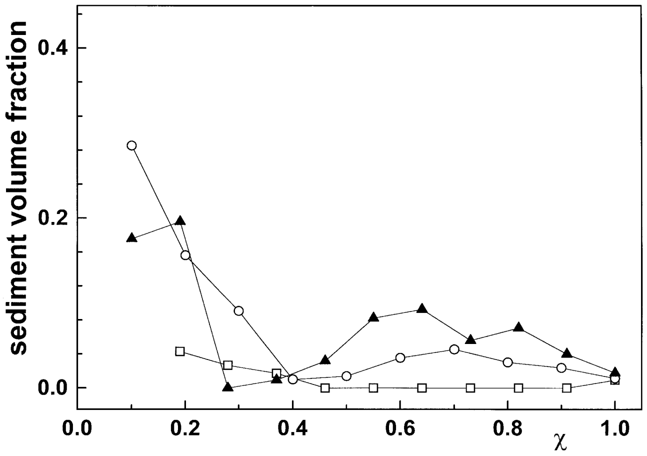

Fig. 4 Height of the sediment (volume fraction) as a function of χ (mass fraction of the hydroxide). Bentonite M40; oil volume fraction $\Phi = 0.38$; solid content (mass fraction): (-□-) 0.5%, (-○-) 1%, (-▲-) 1.5%

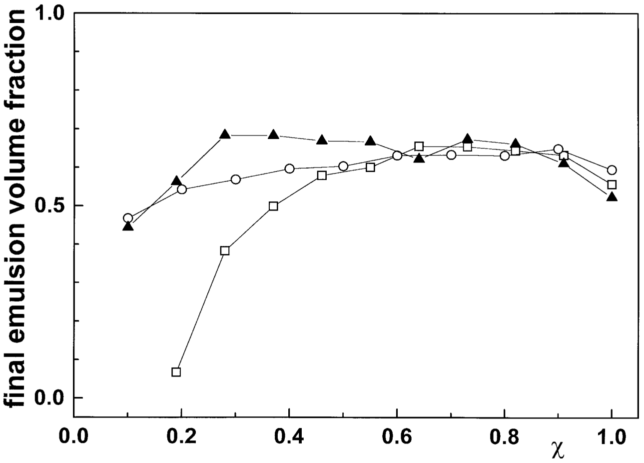

Fig. 5 Final emulsion volume versus χ (mass fraction of the hydroxide). Bentonite M40, oil volume fraction $\Phi = 0.38$; solids content (mass fraction): (-□-) 0.5%, (-○-) 1%, (-▲-) 1.5%

volume (Fig. 5). It was almost independent of the solid content at $\chi > 0.5$ and decreased strongly at $\chi < 0.4$ when the amount of solid was reduced to 0.5%. Pure magnesium aluminum hydroxide ($\chi = 1$) stabilized the O/W emulsions up to oil volume fractions $\Phi = 0.7$, i.e. no coherent oil phase was detected at $\Phi \leq 0.7$. When bentonite was added, the upper limit decreased to $\Phi \leq 0.6$ for $\chi > 0.2$ and 1% solid content (Fig. 6a). The volume fraction of the creaming layer increased with Φ and occupied more than 90% (at $\Phi = 0.74$ and $\chi = 0.5$); coherent oil was discernible for $\Phi \geq 0.66$. With increasing oil volume fraction higher amounts of solids were required to encapsulate the oil droplets so that, at a given solid content, the volume of the sediment (after centrifugation) diminished with increasing Φ. For $\Phi \geq 0.34$ ($\chi = 0.5$) all solid material was enriched in the creaming layer. When the hydroxide content was too low ($\chi = 0.2$, Fig. 6b), the volume fraction of the creaming layer still increased with Φ but oil was eliminated at $\Phi > 0.2$.

The addition of sodium chloride made the emulsions more stable. It increased the final emulsion volume after centrifugation for $\chi < 0.4$ (Fig. 7).

Rheological properties

The hydroxide/bentonite stabilized emulsions exhibited interesting rheological properties. When only magnesium

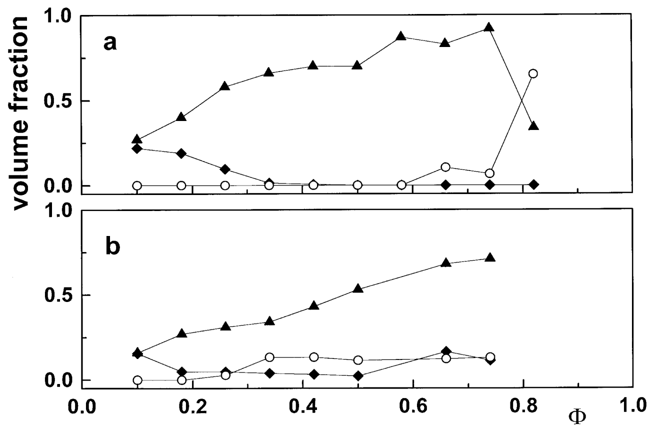

Fig. 6 Volume fraction of the sediment (—◆—), creaming layer (—▲—) and oil (—○—) as a function of oil volume fraction Φ. Bentonite M40; solid content 1% (mass fraction): (a) $\chi = 0.5$; (b) $\chi = 0.22$

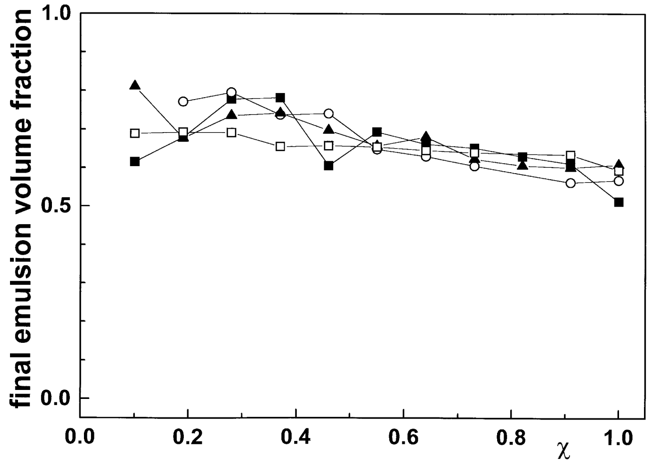

Fig. 7 Final emulsion volume as a function of χ at different NaCl concentrations in the aqueous phase. Bentonite M40; oil volume fraction $\Phi = 0.38$; solid content 1% mass fraction, (—■—) without NaCl, (—○—) 0.006 M NaCl, (—▲—) 0.06 M NaCl, (—□—) 0.6 M NaCl

aluminum hydroxide ($\chi = 1$) was added, the emulsion (1% solid, $\Phi = 0.38$) showed a newtonian flow (Fig. 8, Table 1). Addition of bentonite (χ decreasing from 1 to 0.5) caused the Bingham viscosity to rise slightly and developed yield values of 7–9 Pa. The flow curves formed small hysteresis loops which indicated weak thixotropic behavior. At higher bentonite contents, $\chi < 0.5$, the viscosity and yield value rose to a sharp maximum at $\chi \approx 0.2$ (Table 1). Hysteresis was very pronounced, and the flow behavior changed from thixotropic to antithixotropic. The alternating behavior of thixotropy and antithixotropy is typical of clay minerals [22, 28, 29] and of their mixtures with magnesium aluminum hydroxides [30]. The hysteresis loop contracted strongly at $\chi \leq 0.1$, the yield values were reduced.

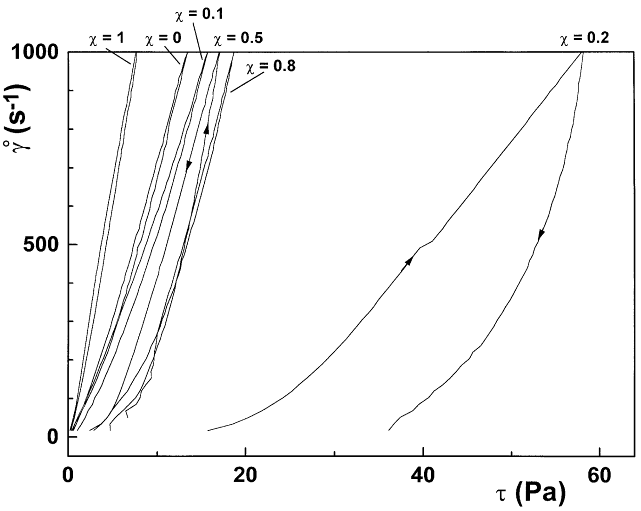

Fig. 8 Flow curves (rate of shear $\dot{\gamma}$ against shear stress τ) of emulsions with different hydroxide/bentonite ratios χ. Bentonite M40A; solid content 1% (mass fraction), oil volume fraction $\Phi = 0.38$

A wide range of linear viscoelastic behavior was observed for $\chi = 0.2$–0.8 (Fig. 9). Elasticity of the system was expressed by high storage moduli at $\chi = 0.2$–0.9 (Fig. 10). The elastic modulus was distinctly smaller for $\chi = 0$ and 0.1 but also for $\chi = 1$, and increased with the frequency of the oscillating measurements. The phase angle became very small for $0.2 \leq \chi < 0.9$ and increased at $\chi \leq 0.2$ and > 0.9, thus revealing the viscous behavior of the emulsions stabilized by almost pure bentonite or hydroxide.

Influence of the clay mineral

The type of bentonite and also the sodium/calcium ratio influenced the stability of the emulsions. Wyoming bentonite and sodium montmorillonite prepared from this parent material were very well suited as colloidal stabilizers. Other bentonites, e.g. a highly charged bentonite from Turkey, produced the required stability only in the presence of an excess of layered double hydroxide ($\chi \geq 0.8$). These effects will be reported in a future paper.

Discussion

Stabilization of emulsions by solid materials requires fine particles which constitute a dense but elastic film around the droplets of the dispersed phase [31–33]. The contact angle θ at the water/oil/solid line is often important [4, 5, 7, 31, 32, 34]. It should not be too far away from 90° [32, 33]. If it is smaller than 90°, O/W emulsions are

Table 1 Rheological properties (yield value τ_0, Bingham yield value τ_B, Bingham viscosity η_B and zero-shear viscosity η_0) of oil/water emulsions stabilized by magnesium aluminium hydroxide and bentonite (M40A); χ = mass fraction hydroxide. Hysteresis expressed by the area of the hysteresis loop

χ	τ_0 [Pa]	τ_B [Pa]	η_0 [mPa s]	η_B [mPa s]	Hysteresis [kPa s^{-1}]
0	0.21	2.67	24	10.7	+0.45
0.1	< 0.1	1.67	21.8	14.1	−0.65
0.2	11.14	23.05	923.0	35.0	−19.08
0.5	8.82	9.12	277.0	8.1	+1.66
0.8	8.82	7.11	131.0	11.6	+0.09
1.0	< 0.1	0	11.1	7.8	−0.37

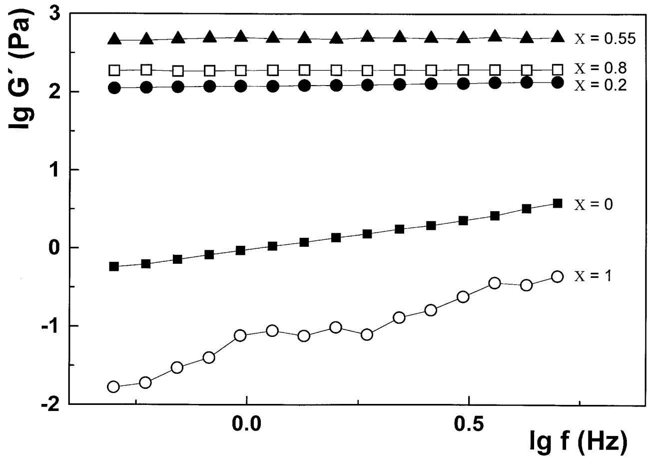

Fig. 9 Elastic modulus G' (frequency sweep, amplitude = 0.5 Pa) of emulsions with different hydroxide/bentonite ratios χ. Bentonite M40A; oil volume fraction $\Phi = 0.38$, solid content 1% (mass fraction)

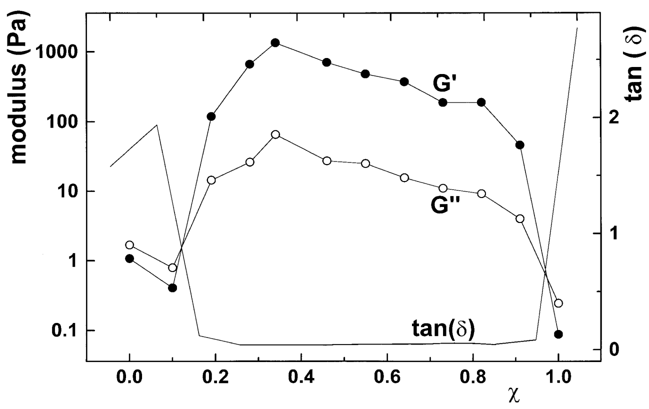

Fig. 10 Elastic modulus G' (—●—), loss modulus G'' (—○—), and phase angle δ (——) at a frequency of 1 Hz as functions of χ. Bentonite M40A; oil volume fraction $\Phi = 0.38$, solid content 1% (mass fraction)

formed. Particles with $\theta > 90°$ stabilize W/O emulsions. The contact angle condition seems to be effective in all cases where the dispersed solid particles themselves do not form a network structure in the coherent phase at the condition of emulsification.

Another mechanism is based on the ability of the solid particles to form a network which encloses the oil droplets: the droplets are captured in the three-dimensional array of particles. In this case particle–particle interaction plays a decisive role. Clay mineral particles with their pronounced ability to aggregate in networks [10, 11] are superior candidates for this mechanism. When the oppositely charged particles of layered double hydroxides are added, the attractive electrostatic forces can increase the stability of the network. Microscopic examination showed the oil droplets being completely immobilized at intermediate χ but moving slightly when χ approached 0.1 or 1.0. In contrast, droplets stabilized by montmorillonite hydrophobized with glycerol monostearate [16, 17] are showed quick movement from one point to the other.

Magnesium aluminum hydroxide particles do not aggregate but form an extended network structure in water and are wetted by paraffin oil. When a hydroxide/oil mixture is dispersed in water with no or low contents of montmorillonite, the hydroxide particles move to the oil/water interface and form a dense film around the oil droplets. The emulsion is predominantly stabilized by these films which impede coalescence when two droplets approach (Fig. 11). With increasing bentonite content (decreasing χ) the hydroxide particles are attracted by the clay mineral particles and, together with them, form a network in the coherent phase (Fig. 11): Stabilization by solid particle envelopes changes into stabilization by a network structure. This is clearly seen by the strong increase of the elastic modulus and the sharply decreasing phase angle at $\chi = 0.9$ (Fig. 10). The high elastic modulus at $\chi < 0.9$ indicates pronounced elasticity of the network because the hydroxide particles link the clay mineral platelets like hinges.

The strong increase of the moduli at $\chi < 0.9$ is not accompanied by a comparable increase of viscosity and yield values which remain nearly constant between $\chi = 0.9$ and 0.5. Viscosity and yield values reach a sharp maximum

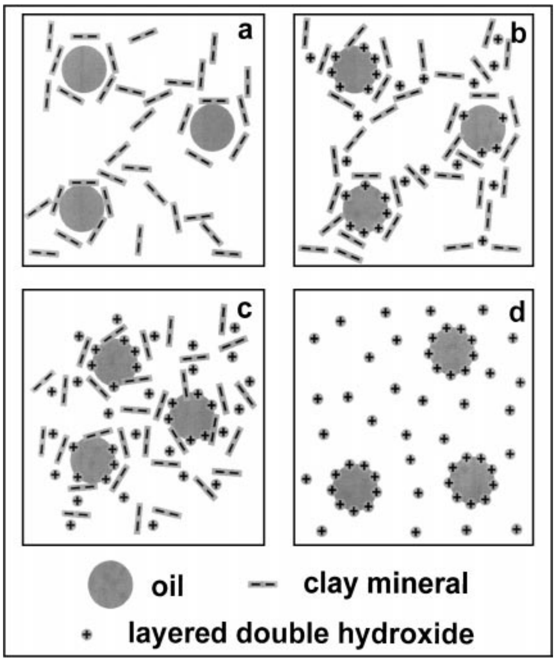

Fig. 11 Schematic representation of stabilization mechanisms at different mass fractions χ of hydroxide (a) $\chi = 0$: the oil droplets are enclosed in the network of montmorillonite particles; (b, c) heterocoagulation of hydroxide and clay mineral particles: formation of three-dimensional networks which impede coalescence of the oil droplets, b → c: increasing content of hydroxide; (d) $\chi \to 1$: the oil droplets are stabilized by envelopes of hydroxide particles

at $\chi = 0.2$–0.3 which indicates the importance of the clay mineral platelets in building up a network of high mechanical stability.

The maxima of viscosity and yield value may correspond to the point of charge equivalency which is placed at $\chi \approx 0.22$ (see above). However, only the charges at the external surfaces are relevant for the particle–particle interactions. As the volume of the hydroxide particles contains a larger part of the charges compared with the delaminated clay mineral, the maxima of viscosity and yield values should be found at χ somewhat above 0.2, which, in fact, is observed.

The high values of the moduli at $0.2 \leq \chi \leq 0.9$ indicate the synergistic effect of the two types of particles. In the absence of hydroxide particles ($\chi = 0$) or at very low contents ($\chi = 0.1$) the clay mineral particles form a weak network. The moduli are higher than in the emulsion containing hydroxide only ($\chi = 1$) because these particles do not build-up a network. The flow behavior of the emulsions with $\chi = 0$ or 0.1 corresponds to the rheological properties of bentonite dispersions. The shear stress of Wyoming bentonite dispersions reaches a minimum at pH = 5–7 [33]. Nevertheless, the aggregation of the clay mineral lamellae is strong enough to impede coalescence of the oil droplets and to make the emulsion stable.

When salt is added, the clay mineral particles coagulate [10, 34]. The aggregation of the particles increases the stability of the emulsion. The effect is most pronounced at high bentonite contents. Salt addition then enhances the final emulsion volume for $\chi < 0.4$ (Fig. 7) and stiffens the creaming layer (after centrifugation).

Conclusion

Heterocoagulation of differently charged particles, layered double hydroxides and clay minerals, provides an excellent way to stabilize oil-in-water emulsions without any surfactant. In case of magnesium aluminum hydroxide and bentonites (or montmorillonites) the stability of the emulsion, at solid contents $\geq 0.5\%$ is almost independent of the mixing ratio of both materials. However, the flow behavior can be adjusted by changing the hydroxide/clay mineral ratio. At low contents of hydroxide ($\chi \approx 0.2$), the emulsion shows high yield values, high viscosity and anti-thixotropic behavior.

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