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Stabilization of emulsions and emulsion films by silica with hexylamine

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The conditions of stabilization of emulsions with silica particles modified by hexylamine and the thickness of free water-in-oil films have been determined.

Emulsions stabilized by solid particles (Pickering emulsions) are well known;[1] solid particles can also stabilize foams.[2,3]

The stability of emulsions is determined[4–8] by (i) the stability of the adsorption layer of an emulsifier on the drop interface and (ii) the stability of the emulsion film (the layer of a continuous phase between the drops).

Previously, it was noted that silica with hexylamine could give extremely stable films.[9] Here, the results of a study of emulsions and free (model) emulsion films stabilized by silica with hexylamine are reported.

The powder of silica (Aerosil A-360) was dispersed in water, and then hexylamine was added. The system was shaken. A 4 M KCl solution was added up to a concentration of 0.1 mol dm^{-3}. Decane was used as the oil phase.

Hexylamine cannot stabilize emulsions and acts as a silica modifier. The silica surface has a negative charge because of the surface dissociation

$$\equiv\text{Si–OH} \rightarrow \equiv\text{Si–O}^- + \text{H}^+.$$

Hexylamine forms positively charged surfactant ions in aqueous solutions:

$$\text{Me(CH}_2)_5\text{NH}_2 + \text{H}_2\text{O} = \text{Me(CH}_2)_5\text{NH}_3^+ + \text{OH}^-.$$

These ions are adsorbed on the silica surface to make it hydrophobic (Figure 1).

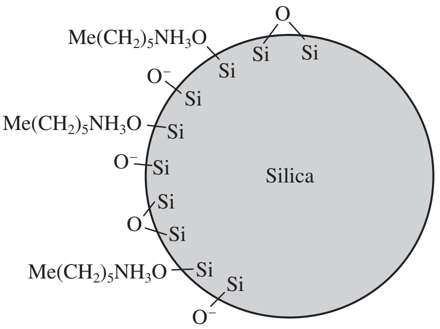

Figure 1 Adsorption of hexylamine on the silica surface.

Table 1 Emulsion stability regions.

C_{SiO_2} (wt%)	n_{Hex}/mol g^{-1}	
	O/W emulsions	W/O emulsions
1	0.002–0.01	0.014–0.021
3	0.0003–0.005	0.007–0.013
5	0.0001–0.003	0.004–0.01
7	0.00004–0.003	0.004–0.007

Usually, the hydrophobicity of a particle is estimated by the contact angle θ.[10,11] Here, the degree of hydrophobicity of SiO$_2$ is estimated by the relative concentration of hexylamine n_{Hex} (mol g^{-1}):

$$n_{Hex} = C_{Hex}/(10\,C_{SiO_2}), \qquad (1)$$

where C_{Hex} is the concentration of hexylamine (mol dm^{-3}) and C_{SiO_2} is the concentration of silica (wt%) in the aqueous phase.

The emulsions were formed by shaking equal volumes of oil and aqueous phases. The type of the emulsion (O/W or W/O) was determined by mixing the emulsion drop and water drop at a glass plate. The stable emulsions of both types were obtained. The emulsion was considered to be stable if it was not destroyed during 24 h (Table 1).

The region of inversion (the transition from O/W to W/O emulsions) was also displaced toward lower concentrations of the solid phase with increasing n_{Hex}.

At a hexylamine concentration corresponding to the beginning of stabilization of W/O emulsions, the appearance of turbidity in the oil was observed at the moment of contact between the aqueous and oil phases (before shaking, when the emulsion was not formed yet). This demonstrated the spontaneous transition of SiO$_2$ particles from the aqueous phase into the oil through the interface. Consequently, the inversion region corresponded to the transition contact angle θ over 90°; therefore, the transition from the water films (in O/W emulsions) to the hydrocarbon films (in W/O emulsions).

In contrast to long-chain ionic surfactants such as cetyltrimethylammonium bromide (CTAB), hexylamine allowed us to reach such a degree of hydrophobicity of SiO$_2$ (n_{Hex} = 0.01–0.02 mol g^{-1}) when the W/O emulsion becomes unstable. Therefore, we can assume that, at this concentration of hexylamine, the angle θ is 150°,[10] while the use of CTAB allows one to achieve the angles θ of no greater than 85–87°.[7,10]

In the region of stable emulsions, appropriate free emulsion films were extremely stable (for 24 h or longer). The water-in-oil films were investigated. The films were formed on a vertical round platinum frame (4.8 mm in diameter) by extension from the aqueous to the oil throw the interface containing the adsorbed solid particles (Figure 2). The adsorption layer of the particles was formed in a chemical glass. Platinum wire (with a thickness of 0.3 mm) penetrated the center of the film, it was the internal

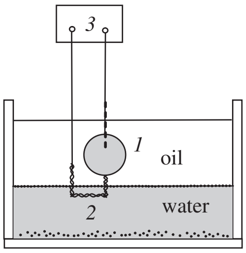

Figure 2 Device for investigating free emulsion films: (*1*) frame with a film; (*2*) bending of wireframe; (*3*) conductometer.

electrode. The frame itself was the external electrode. The electrodes also included liquid menisci. The radii of electrodes were r_1 = 0.28 mm (the internal electrode) and r_2 = 2.25 mm (the external electrode). The internal phase of the film flowed under the influence of gravity, and the film was spontaneously thinning to the thickness *h*:[7,9]

$$h = \text{æ}_\text{f}\ln(r_2/r_1)\,nB/(2\pi\text{æ}_\text{sp}), \qquad (2)$$

where æ_f is electroconductivity of the film; æ_sp is specific electroconductivity of the aqueous phase; *n* is the expansion ratio in the solid-stabilized film; and *B* is an empirically determined coefficient. Here, $nB = 3$.

A noticeable thinning of the films was observed within 5–15 min, and then their thickness varied very slowly. Table 2 shows average thicknesses measured after 15 min. Aerosil [A (%)] and hexylamine (Hex/mol dm^{-3}) concentrations are given.

Thus, sufficiently thick films were formed (for comparison, from 0.5–3% suspensions of silica modified by CTAB films thicknesses of 0.5–22 μm were obtained[7]). At high concentrations of SiO_2 (5–7%), the film thickness increased with the degree of hydrophobicity of particles: in the order (7% A + 0.05 Hex) → → (7% A + 0.07 Hex) → (5% A + 0.07 Hex) → (7% A + 0.1 Hex) hydrophobicity increased and the film thickness increased by a factor of 2.5. At low concentrations of SiO_2 (1%), all films had the same thickness of 27–37 μm irrespective of the hydrophobicity of particles.

Table 2 Free emulsion film thickness *h*.

Stabilizer combination $C_{SiO_2} + C_{Hex}$	h/μm	Stabilizer combination $C_{SiO_2} + C_{Hex}$	h/μm
1% A + 0.05 M Hex	36	5% A + 0.07 M Hex	95
1% A + 0.07 M Hex	27	7% A + 0.05 M Hex	67
1% A + 0.1 M Hex	37	7% A + 0.07 M Hex	134
3% A + 0.05 M Hex	37	7% A + 0.1 M Hex	170

In conclusion, highly stable emulsions and films were prepared from silica with hexylamine, due to structuring of the particles. A large concentration and a considerable degree of hydrophobization of the particles determined the conditions of gelation in the continuous phase including the adsorption layers.

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