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Influence of hydrophobized solid particles on the reduction of interfacial tension

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The adsorption of solid particles causes a significant reduction in the interfacial tension of an oil/water interface, as compared with that of a water/gas interface.

In terms of thermodynamics, the excess free energy at an interface is the reason for the instability of disperse systems (foams and emulsions). In general, the excess free energy for a unit interface area (liquid/gas or liquid/liquid) is called interfacial tension. The interfacial tension of the liquid/gas interface is called surface tension.

The presence of solid particles at the interface leads to the reduction of the interfacial tension of liquid/liquid[1,2] and the liquid/gas[3,4] boundaries.

If monodisperse spherical particles form a dense monolayer at the interface, the interfacial tension decreases with a change in the contact angle θ from 0° to 90° (and from 180° to 90°):[5]

$$\sigma_\mathrm{p}/\sigma = 1 - \pi(1 - \cos\theta)^2/(4\sqrt{3}), \tag{1}$$

where σ_p is the effective interfacial tension in the presence of the solid particles, and σ is the interfacial tension in the absence of the particles.

The aim of this work was to analyze the effect of solid particles on the interfacial tension of water/gas and oil/water interfaces and changes in the properties of the dispersed systems (foams and emulsions) with the interfacial energy.

The silica particles hydrophobized by adding hexylamine or cetyltrimethylammonium bromide (CTAB) were used as solid stabilizers. These surfactants contribute to the hydrophobicity of the particles n_g (mmol g^{-1}), which was calculated by the formula

$$n_\mathrm{g} = C_\mathrm{S}/C_{\mathrm{SiO}_2}, \tag{2}$$

were C_S is the surfactant concentration (mmol dm^{-3}), and C_{SiO_2} is the silica content of the aqueous phase (g dm^{-3}).

Aerosil-380, Aerosil-200, Ludox-HS-40, Ludox-HS-30 and S-3 (with a particle radius of 270 nm; synthesized according to a published procedure[6]) silicas were used.

The contact angle θ was determined by the method of a glass sphere hydrophobized together with silica. The interfacial tension was determined at 25 °C by a maximum bubble pressure, drop volume or platinum frame weighing method.

Table 1 presents the values of σ_p and σ for the water/gas and oil/water interfaces.[2,4]

The particles with low hydrophobicity (n_g = 0.5 mmol g^{-1} for hexylamine) did almost not reduce the water/gas interfacial tension. Increasing the hydrophobicity contributes the reduction of the interfacial tension due to the adsorption of particles. For example, for a 2% suspension of Aerosil, the maximum reduction of the water/gas interfacial tension was 5.36 mN m^{-1}, which corresponds to a hexylamine concentration of 48 mmol dm^{-3}.

Table 1 Interfacial tension of water/gas (1–3) and oil/water (4) in the presence of the solid particles (σ_p) and without the particles (σ).

Entry no.	Aqueous phase	n_g/ mmol g^{-1}	θ_W/ deg	σ_p/ mN m^{-1}	σ/ mN m^{-1}
1	0.6% Aerosil-380 + hexylamine	4.12	52	49.53	55.55
2	2% Aerosil-380 + hexylamine	0.50	20	70.80	70.94
		1.39	34	61.30	64.40
		2.40	50	41.49	46.85
		3.69	—	40.85	42.43
3	2% LudoxHS-40 + hexylamine	0.65	26	56.75	58.21
		1.80	38	40.75	45.11
		2.29	46	34.92	40.75
4	0.5% Aerosil-200 + CTAB (the oil is octane)	0.0001	10	21.30	42.50
		0.001	35	18.90	42.70
		0.02	40	20.90	41.60
		0.1	55	21.20	40.10

The reduction of the interfacial tension is

$$\Delta\sigma = \sigma - \sigma_\mathrm{p}. \tag{3}$$

The relative reduction of the interfacial tension $\Delta\sigma/\sigma$ is shown in Figure 1. For the oil/water boundary, the relative reduction of the interfacial tension is more significant than that for the water/gas boundary. Furthermore, the curves of $\Delta\sigma/\sigma(\theta_\mathrm{W})$ have maximums corresponding to the angles $\theta_\mathrm{W} \approx$ 45° and 30–40° for the water/gas and oil/water interfaces, respectively.

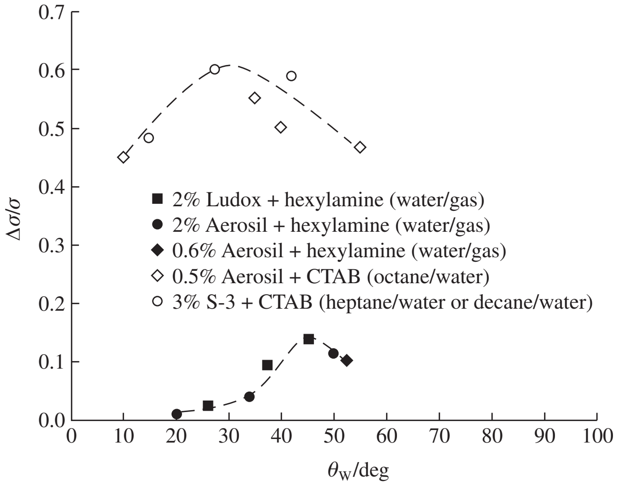

Figure 1 Dependence of the relative reduction of the interfacial tension $\Delta\sigma/\sigma$ on the contact angle θ_W.

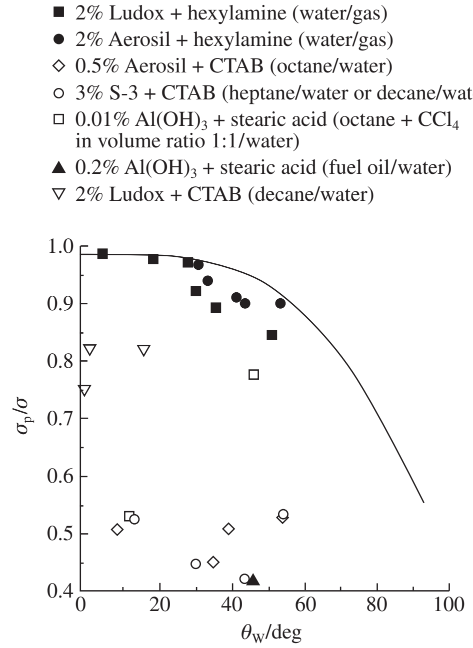

Figure 2 Dependence of σ_p/σ on the contact angle θ_W. The curve was calculated by equation (1), and the points refer to experimental values.

Figure 2 compares the experimental and theoretical data in terms of the σ_p/σ ratio, which also characterizes the degree of the interfacial tension reduction. According to equation (1), the maximum reduction degree corresponds to $\sigma_p/\sigma = 0.55$ at the angle $\theta_W = 90°$. In our experiments, the values of σ_p/σ were 0.41–0.83 and 0.85–1 for the water/oil and water/gas interfaces, respectively.

The values of σ_p/σ most similar to that calculated by equation (1) were obtained for the water/gas boundary (filled symbols in Figure 1). For the oil/water interface, the experimental values (open symbols in Figure 1) were much smaller.

As for the water/gas interface definite dependence of σ_p/σ on the contact angle, for the water/oil interface the ratio σ_p/σ changed little with increasing the hydrophobicity of the particles: for the angle θ_W from 10° up to 55° the ratio σ_p/σ was in the range of 0.41–0.53. Furthermore, in this range of θ_W the thickness of the free emulsion aqueous films also changed little.[2]

Several points for oil/water in Figure 2 differ from the rest of the abnormally high σ_p/σ ratio. These data were obtained for 2% Ludox with low hydrophobicity and for 0.01% $Al(OH)_3$ with a low concentration of solid particles (stearic acid was a hydrophobizing agent). Probably, this fact is explained by the small sizes of the solid particles. The particle radius of Ludox was 30 nm (not aggregated particles with θ_W = 1–2°) or 70 nm (loosely aggregated particles with $\theta_W = 17°$). However, the radius of particles whose adsorption greatly reduced the interfacial tension was 270 nm (not aggregated S-3 with at $\theta_W = 15°$) or 3–6 μm (for everyone else θ_W for S-3 and Aerosil).

At the values of $\sigma_p/\sigma \approx 1$, $\theta_W \leqslant 30°$ (for the water/gas interface) the sols of 2 and 20% Ludox HS-40 (with hexylamine) formed bilayer free foam films with a height of 8–10 μm.[7,8] In this case, the bulk foams (height of 1–2 cm) became unstable under the action of the applied pressure drop[9] ΔP = 5 kPa and destroyed in layers without the gelling of a continuous phase. These foams were characterized by the liquid volume fraction in the range of 0.01 to 0.005. Although a further increase in the contact angle from 30° up to 46° led to a slight decrease in the interfacial tension and the σ_p/σ ratio (from 0.92 to 0.85, Figure 2), the properties of the foam films and foams varied significantly. At the angle $\theta_W = 46°$, the thicknesses of the free foam films formed from the sols of 2% and 20% Ludox HS-40 with hexylamine were 25–100 μm. Foams obtained from these sols were characterized by an increase in the volume fraction of liquid to 0.05–0.016, gel formation in the dispersion medium, and greater stability. The same pattern was observed for Aerosil-380. The maximum reduction in the water/gas interfacial tension ($\Delta\sigma$ = = 5.36–6.02 and $\sigma_p/\sigma = 0.85$) was consistent with the formation of stable foam films and foams.[4,7,8]

Thus, we found that the adsorption of solid particles leads to a significant reduction in the interfacial tension of oil/water and a relatively small reduction in the surface tension of a water/gas interface. Micrometer-sized particles cause a greater reduction in the interfacial tension than the particles of nanometer sizes.

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