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Capillary pressure in a thinning emulsion film stabilised by spherical solid particles

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The capillary pressure isotherms in an emulsion film stabilised by solid spherical particles were obtained, and a threshold pressure required for the rupture of the film was calculated.

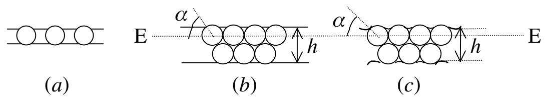
The investigations of emulsions stabilised by solid particles revealed the main factors responsible for the type and stability of emulsions.[1–6] It was found that if the wetting angle θ measured in a polar phase is less than 90°, oil-in-water (O/W) emulsions are formed, and at $\theta > 90°$, the water-in-oil (W/O) emulsions are formed. The most stable O/W emulsions are formed in the angle range 60–85° and the most stable W/O emulsions, at the angles of 95–120°.[1–6] The particles of a solid emulsifier have to be finely divided. The ratio of a particle radius to a liquid drop radius is determined by the equilibrium wetting angle.[6] The receding and advancing angles of water (or oil) define the hysteresis (which is determined by the direction of three-phase contact line's moving), and the difference between these angles can be as high as 50–150°.[2,6]

When the flowing out of a continuous phase is caused by a gravity force or an applied external reduced pressure, the drops are deformed and the films appear between them. The films control the equilibrium state and the stability of the emulsions. The existence of these films in an emulsion with a high expansion ratio was demonstrated.[7] The film stability depends on the particles attaching energy.[4–6]

Denkov *et al.*[9] considered a model film stabilised by one layer of spherical particles, which bridge this film [Figure 1(*a*)]. This type of films can be formed between drops at a low concentration of a solid phase or under specific conditions of model film formation.[8]

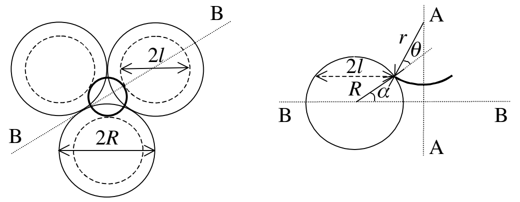
At a high concentration of solid particles when highly stable emulsions are formed, the surface of each droplet is coated with a close-packed well-ordered monolayer of the particles. Such droplets can be seen in the micrographs of individual oil (in water) and water (in oil) droplets stabilised by silica spheres[4] (the particle concentration was 0.005–0.025 g cm^{-3}). If the concentration of a solid phase is so high that drops are completely covered by a layer of particles and if the particles attaching energy is high, a more realistic model is a film that consists of two layers of 'adsorbed' particles with a liquid interlayer between them [Figure 1(*b*)]. Such model films were obtained in our experiments. Further thinning of the film creates a capillary pressure P_c (an analogue of disjoining pressure[9]) in the porous space between the particles. The capillary pressure (stimulated by the film thinning) depends on the size and shape of particles, the contact angle and the film thickness.[6] This P_c must be overcome to rupture the film.

These two mechanisms of rupture of the emulsion film regulate the region of stable emulsions: (1) at small θ (for O/W) and very large θ (for W/O) the film becomes unstable because of a small energy of particles attaching; (2) at θ close to 90° the film becomes unstable because the capillary pressure is equal to zero (as shown below).



(*a*) (*b*) (*c*)

Figure 1 Emulsion film models: (*a*) containing one layer of solid particles, (*b*) stabilised by two layers of solid particles at the instant when the 'adsorbed' layers are in contact and (*c*) when the capillary pressure arises [*h* is the film thickness, α is the slope angle of the particle's radius that drown to the three-phase contact line (at $\alpha = 90° - \theta$, at the moment when 'adsorbed' layers are in contact), EE is the equatorial plane of particles].



(*a*) (*b*)

Figure 2 Spherical meniscus, (r is the radius of the interface curvature, R is the radius of particles, l is the radius of the three-phase contact line, θ is the contact angle of the continuous phase receding and AA is the central axis of porous space between the particles).

The threshold capillary pressure ($P_{c,\,max}$) in a film for spherical monodisperse particles with close packing on the liquid–liquid interface was calculated, and the quantitative dependence of P_c on the film thickness (h) for particles having various contact angles was established.

The coefficient of proportionality between P_c and interfacial tension σ is the curvature of a meniscus interface ($C = 1/r_1 + 1/r_2$):

$$P_c = C\sigma = C_{norm}\sigma/R \tag{1}$$

where R is the particle radius; r_1 and r_2 are the surface curvature radii; $C_{norm} = CR$ in the normalised curvature.

On the assumption that the meniscus is a part of a sphere (Figure 2), *i.e.*, two radii of curvature are equal and the liquid–liquid interface between three particles forms the contact angle θ with the solid particle of radius R, we have:

$$C = 2/r = 2\cos(\theta + \alpha)/\{R[1/\sin(\pi/3) - \cos\alpha]\} \tag{2}$$

where r is the radius of surface curvature, α is the slope angle of the particle radius that is drawn to the three-contact line [as shown in Figures 1(*b*) and (*c*)].

Equation (2) allows the calculation of P_c as a function of the angles α ranged from 0° to (90° – θ).

The dependence of the film thickness on angle α (Figure 3) is given by the equation

$$h = \mathrm{tg}(\pi/3)R + 2\{R\sin\alpha - r[1 - \sin(\theta + \alpha)]\} \tag{3}$$

Here, the film thickness is the lowest distance between menisci taking place on the film opposite sides (Figures 1 and 3).

To take into account the deviation from a spherical meniscus shape, the Mayer–Stowe–Princen (MPS) method[10,11] can be used. In this case, the interface in a space between three spheres consists of three 'wedge menisci' and one 'terminal meniscus'.[10,12] Using the MSP method, we calculated the function $P_c(\theta, \alpha, R)$ for a close hexagonal packing of spherical particles.

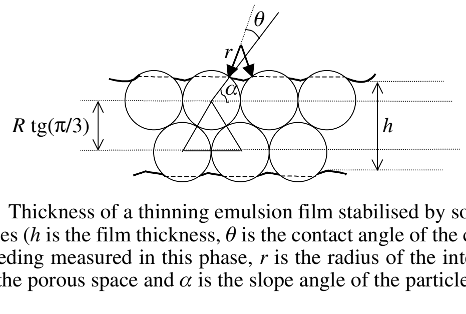


Figure 3 Thickness of a thinning emulsion film stabilised by solid spherical particles (h is the film thickness, θ is the contact angle of the continuous phase receding measured in this phase, r is the radius of the interface curvature in the porous space and α is the slope angle of the particle's radius).

Table 1 The dependence of $CR(\alpha)$ for some θ in the porous space of a hexagonal packing of solid spherical particles.

	α	0°	10°	20°	30°	40°
CR	$\theta = 50°$ (and 130°)	8.31	5.89	3.18	1.20	0
	$\theta = 60°$ (and 120°)	6.46	4.03	1.61	0	–
	$\theta = 70°$ (and 110°)	4.42	2.04	0	–	–
	$\theta = 80°$ (and 100°)	2.24	0	–	–	–

The MSP theory assumes that the meniscus should have a shape that agrees with the lowest curvature and hence a minimum of the surface square relative to all possible shapes.[10]

The calculated values of normalised curvature in pores between spheres with a hexagonal packing suggest that the deviation from a spherical meniscus shape appears at the angles $\theta < 50°$ and $\theta > 130°$. For these angels θ, the meniscus curvature and the capillary pressure should be calculated by the MSP method. At θ of 50°–90° and 90°–130°, *i.e.*, in the region of the most stable emulsions, the minimal curvature values are given by equation (2). Table 1 shows the calculated values of normalised curvature in pores between spheres with a close packing depending on the angles α and θ.

For example, for a close hexagonal packing of particles, when $R = 1$ µm, $\sigma = 10$ mN m^{-1} and $\theta = 60°$, the maximum capillary pressure is equal to $P_{\mathrm{c,\,max}} = 64.7\times10^3$ Pa.

The combined solution of equations (3) and (2) gives the capillary pressure isotherm $P_{\mathrm{c}}(h)$.

To verify the above equations, we performed experiments to determine the maximum capillary pressure as a function of the contact angle in porous space between three glass cylinders and between three glass spheres at $\alpha = 0°$. The maximum meniscus curvature between the spheres (at $\alpha = 0°$) of a definite diameter is equal to that between cylinders of the same diameter. The radius of spheres was 3.15±0.1 mm. The radius of cylinders varied from 1.15±0.03 to 3.35±0.05 mm.

The measurements were carried out at water–air and water–oil interfaces for receding and advancing wetting angles.

A 0.5% solution of a commercial non-ionic surfactant oxyethylated octylphenol (OP-10) was used as a perfectly wetting liquid.

Various contact angles were made by modifying glass spheres and cylinders in the solutions of cationic surfactants in distilled water with various concentrations. The cationic surfactants were dodecylamine hydrochloride (DAHC, pure) and *N*-cetyl-*N*,*N*,*N*-trimethylammonium bromide (CTAB, analytical grade).

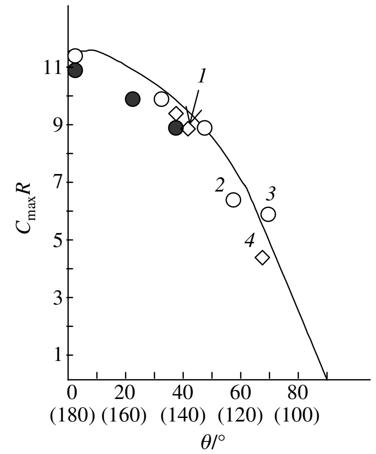


Figure 4 Maximum normalised curvature as a function of the contact angle in a porous space between three spheres $C_{\max}R(\theta)$ [○ (oil phase is DF), ◇ (octane) are the values of the interface curvature in pores formed by cylinders, (*1*)–(*4*) – the receding of the oil phase (θ_{recede} of oil or $\theta_{\mathrm{advance}}$ of water); ● are the values of the curvature in pores formed by spheres].

The advancing and receding angles were determined from depth (H) of immersion in water of a single glass sphere with radius $R = 4.9\pm0.1$ mm on the free oil–water or air–water interface, when the interface near the sphere became flat.[13] The angle θ was calculated using the equation:

$$\cos\theta = (H - R)/R \qquad (4)$$

Capillary pressure was determined by the method of capillary rise of a solution in the porous space between cylinders (spheres) relative to the solution level in an external reservoir. The refraction by the glass sphere was taken into account using a calibration curve, which was based on measurements of glass plate height directly and through the sphere. The influence of gravity was taken into account using the Rayleigh correction.[10,13]

The immersion depth H and the capillary rise were measured by an KM-6 cathetometer to within 0.01 mm.

The interfacial tension was determined by the method of weighing a platinum frame with the emulsion film and without it.[6]

Octane (pure) and diesel fuel (DF, summer) were used as an organic phase.

Figure 4 shows the theoretical dependence of the maximum of normalised curvature on the contact angle $C_{\max}R(\theta)$ and experimental values of $(P_{\mathrm{c,\,max}}R/\sigma)$. The theoretical values of $C_{\max}R$ for θ of 0–50° were found by the MSP method. The open circles and rhombs indicate the values of curvature in pores formed by cylinders; dark circles show the values in pores made by spheres. The contact angles from 0° to 50° were at the receding of water. The angles of 50–70° (DF) and 140° (octane) were at advancing water.

Thus, the experimental values are consistent with theoretically predicted data.

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