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DRAINAGE OF CTAB FILMS CONTAINING SOLID PARTICLES

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ABSTRACT

In this paper, marginal regeneration in films drawn from CTAB (=cetyltrimethylammoniumbromide) solutions in a frame will be discussed. The film thickness was measured as a function of time and height, using interference colours which were evaluated by a computer program, and a film thinning relation was derived for this type of films. The program used for calculating film thicknesses is briefly discussed.

Film thickness measurements were performed on polystyrene (PS) dispersions in CTAB solutions up to 25 vol% PS. The thinning velocity of the film was related to the viscosity of the dispersion.

PS particles in the film could be observed through their light scattering. The particles were present in a film from the bottom up to a height where the film had a certain thickness. This thickness could be correlated with the particle diameter and the contact angle of the PS particles with the CTAB film.

KEYWORDS

Free liquid films, measurements of film thickness, polystyrene latex, marginal regeneration, contact angle, foam film stability, viscosity.

INTRODUCTION

Three phase systems are often used in industrial processes. In the flotation process for example, particles are separated from the liquid by creating foam in which the particles disperse preferably. The present investigation deals with the influence of solid particles on foam.

Some particles lower the surfactant concentration and therefore act as a destabilizer (Kruglyakov, 1972). Most investigations showed that hydrophobic particles have a destabilizing effect on foam (Garret, 1979), whereas hydrophilic

particles in general have a stabilizing effect (Hudales and Stein, 1990b). Fang-Qiong Tang *et al.*, (1989) however found that small hydrophobic particles could also have a stabilizing effect which was ascribed to the reduction of Ostwald ripening in foam.

The destabilizing effect of hydrophobic particles has been theoretically discussed (Frye and Berg, 1989) and was found to be due to promotion of film rupture. Aronson, (1986) showed that hydrophobic (solid) particles stimulate rupture more strongly than hydrophobic droplets because of higher surface roughness. Aronson also found that particles can be swept out of a microscopic foam film into thicker regions of the film. Dippenaar, (1982) used high-speed cinematography to study the behavior of large glass and silica particles ($>160\text{ }\mu\text{m}$) in small films. These measurements showed that particles moved in thin films in order to have the right contact angle with the liquid.

The drainage of the type of films studied, is determined by marginal regeneration (Mysels, 1959), (Hudales and Stein, 1990a).

In this work we used monodisperse PS particles (1900 nm, 1070 nm and 300 nm) in 20mm $\times$ 15mm films drawn from CTAB (=cetyltrimethylammoniumbromide) solutions. The maximum height that the particles reach in the film is correlated with the film thickness measured with a Fizeau interferometer. The influence of higher volume fractions of PS on the drainage rate is studied.

THEORY

A film of thickness d reflects in normal direction an amount of light I :

$$I = I_0 \sin^2(2\pi nd/\lambda) \quad (1)$$

In this equation n is the refractive index of the liquid film (1.33), and λ is the wavelength of the light (546 nm). The absolute value of the film thickness can be calculated at the top of the film as soon as a black film becomes visible. Equation (1) can be used for a film region with no or only minor quantities of solid particles, because in films containing solid particles the scattering of light makes observation of interference fringes difficult, so that equation (1) cannot be used for evaluating their thickness.

We observed a particle borderline (above which there are no particles in the film) as the films were draining. We will first show that this effect is not directly caused by diffusion or by gravity (the particles did not fall down), but indirectly.

Diffusion cannot cause the downward motion of the particles, because this is in one direction only. Diffusion might counteract this downward motion. However no distinct blurring of the transition (particle containing film)/(particle free film) was observed. Diffusion translates particles over a distance S :

$$S = \sqrt{2kT/(6\pi\eta d)} * t \quad (2)$$

The particles used can be displaced by diffusion in the drainage time applied, in the experiments reported here over distances of the order of:

$d=2 \mu\text{m}; t=20 \text{ s}; S=2 \mu\text{m}$

$d=0.3 \mu\text{m}; t=250 \text{ s}; S=20 \mu\text{m}$

The observed displacement of the particle borderline was about 13 mm.

It is seen that diffusion can be neglected.

The effect of gravity on the particle velocity in an infinite amount of liquid or gas can be calculated with equation (3) (a balance between gravity and viscous forces on a single particle):

$$v = \frac{\Delta \rho g}{18\eta} * d^2 \quad (3)$$

The velocity in water and air according to this equation:

Air: $\eta=1.8 \times 10^{-5} \text{ Pas}$, $\Delta \rho=1000 \text{ kg/m}^3$, $g=9.81 \text{ m/s}^2$, $d=2 \times 10^{-6} \text{ m}$

Water: $\eta=1.0 \times 10^{-3} \text{ Pas}$, $\Delta \rho=70 \text{ kg/m}^3$, $g=9.81 \text{ m/s}^2$, $d=2 \times 10^{-6} \text{ m}$

The Reynolds number (Air): $\rho v d / \eta = 1.2 (\text{kg/m}^3) \times 1.3 \text{e-}5 = 1.6 \text{e-}5$

Calculated velocities: $V_{\text{air}}=0.12 \text{ mm/s}$; $V_{\text{water}}=0.00015 \text{ mm/s}$

The Reynolds number is small enough for neglecting turbulence (Clift *et al.*, 1978), equation 3 can be applied.

We can conclude from the fact that the particles would fall slower in air than they do in the foam film (measurements: 0.56 mm/s), that gravity does not play a significant role, and that there must be another reason for the separation of the particles from the liquid. This will be shown to be the contact angle phenomenon.

EXPERIMENTAL METHODS

The Apparatus

A film was drawn in a vertical brass frame (see fig.1), which was held at a fixed position. The four legs of the frame formed four identical films. A fifth film in the middle of the former four mentioned, was a film with completely free Plateau-zones. The frame was positioned in a thermostatted tank in order to avoid evaporation of the liquid. The film could be observed from both the front as well as the back through two windows in the tank. From the front the film was illuminated by a 50 W super pressure mercury lamp (Osram HBO 50 W) (see fig.2). Through the front window, the interference pattern between light reflected from the front and rear surfaces of the film was observed; through the rear window, light scattering information was obtained.

Fig.1. The brass frame in which the films were drawn

Fig.2. The Fizeau interferometer

We placed a light filter (SFK21 Schott, 546 nm) in the beam in order to separate the (green) light from the other wavelengths.

Film thickness measurements

The film was observed with a Panasonic CCTV camera through the semi-reflecting mirror (fig.2), and the pictures were analyzed on-line with a computer. The program which calculated the film thickness from the interference pattern was as follows. First we determined the exact position of a film in the picture and the magnification (mm/byte). After forming a new film in the frame, pictures (384*288 byte, 256 grey levels) were taken with a variable interval (0.5 s to 10 s). We masked every picture so that only film information was visible. We added all bytes in horizontal direction and put the result in a word (16 bit information). It appeared that the value (so calculated) never exceeded the maximum value of a word. This array of words was stored in a file and processed afterwards. The film thickness was determined by using equation (1). All films were measured until the black or silver-black film was visible.

Light-scattering measurements

The presence of the PS particles could be easily detected by their light scattering causing a hazy aspect of the film (see fig.3).

Fig.3. The particle borderline and marginal regeneration
a 10 vol% dispersion of PS (sample 1, 1900 nm)

Therefore we measured the decrease of the height with time. For these measurements we again crunched the pictures into an array of words. This array was processed afterwards in order to calculate the height of the particle borderline.

The preparation of the PS particles

We used for our experiments three PS samples. The preparation of the first sample is described below. The second and the third samples were kindly donated by H. Leendertse, and B. Krutzer respectively. The second and third samples were prepared surfactant-free.

We used a recipe similar to the one described by Almog *et al.*, (1986). We used PVP, ACPA and CTAB >99% (the recipe gives also good mono-disperse particles if SDS is used instead of CTAB). The PVP (polyvinylpyrrolidone, average MW 40000) was used for steric stabilization, and the ACPA (4,4'-Azo-bis(4-cyanopentanoic acid), >98%) is the initiator for the emulsion polymerization. The styrene (99%) was stabilized with 10-15 ppm p-tert-butyl-cathochol.

We prepared the particles in a batch reaction at 70°C in 1000 ml. ethanol. The PVP (40 gram in 150 ml ethanol) was added with the CTAB (12 gram in 50 ml ethanol). We mixed 2.8 gram of ACPA in 100 ml. ethanol and after stirring (the ACPA did not dissolve completely), 300 ml of styrene was added to the ACPA. This was stirred for 5 seconds and added to the reactor. The emulsion was slightly turbid after 10 minutes. The reaction stopped after 24 hours. The PS was centrifuged 4 times with water.

The characterization of the PS particles

The particle diameter was determined both with the Coulter counter ZM and with the Coulter LS 130 (see table 1). The ζ -potential of the particles was determined with the Malvern ζ -sizer 3 (see table 1) in a 0.002 M CTAB solution.

Table 1. The particle size and ζ -potential of the particles

Sample 1	diameter (μm)	stand.dev (μm)	ζ -pot. (mV)
Coulter LS130	1.895	0.281	+15
Coulter Counter ZM	2.032	0.187	
Sample 2			ζ -pot. (mV)
Coulter LS130	0.270		+64
Electron microscopy	0.300		
Sample 3			ζ -pot. (mV)
Coulter LS130	0.980	0.050	+72
Coulter Counter ZM	1.034	0.125	

RESULTS

The film is essentially free from particles above a certain height. This will be indicated as "particle borderline". This is what we can see in fig.3, a picture taken through the rear window. We can also see that marginal regeneration causes thin film elements, near the Plateau-border, which rise in the film.

We will first compare the height at which the particle borderline is visible to the height at which the film has the thickness of the particles for all the PS samples (see fig.4,5). The volume fraction of PS in the bulk was lower than 0.5%.

Both the 300 nm and the 1070 nm particles have almost the same diameter as the thickness of the film at the height of the particle borderline, therefore their contact angle with the film is $\arccos(1)=0$ degrees. The 1900 nm particles can be incorporated into a significantly thinner film. This indicates that the hairy stabilizer present at the 1900 nm particles, decreases the amount of CTAB at the surface. This is supported by the fact that sample 1 has surfaces which are only partially covered by CTAB (as shown by the ζ -potential) whereas samples 2 and 3 have surfaces which are covered by a micellar layer of CTAB. Our results suggest that the smaller amount of CTAB adsorbed at the PS surfaces in the presence of polyvinylpyrrolidone (sample 1) result in a hydrophobicity, and that this sample has a finite contact angle. From table 2 we calculate this angle to be $\arccos(1310/1900)=46$ degrees.

Fig.4. Drainage of hydrophobic polystyrene (sample 1)

Fig.5. Drainage of hydrophilic polystyrene (samples 2 and 3)

We checked the existence of the particle borderline for glass particles $1.61 \mu\text{m}$, $\text{s.d.}=0.44 \mu\text{m}$. The film was after a while free of particles as far as detection by light scattering is concerned. The glass particles were not as monodisperse as the PS particles, therefore a sharp particle borderline was not observed. This is to be distinguished from the microscopic measurements (Hudales and Stein, 1990b), in which they observed glass particles which became visible after a while, when the film was much thinner already. The explanation for this might be that they looked at reflected light, while our measurements are based on transmitted scattered light.

If the logarithm of the film thickness is plotted against the logarithm of time at a fixed height, then a straight line results in agreement with measurements by Hudales and Stein, (1990a) (see fig.6). Equation (1) in their paper $Q=kd^n$, where Q is the volume flow out of or into the film per unit length (in height) can be rewritten to :

$$d=A \times t^b \quad (4)$$

Here d represents the film thickness, t time, and A and b are constants (see appendix A).

We made double logarithmic plots for the glass dispersion (glasscontent $<0.5\%$ v:v), and for a 0.002 M CTAB film at two temperatures. At this glasscontent, the presence of glass particles did not have any effect on the film drainage, and a temperature increment of 6.5°C increased the thinning velocity slightly.

Secondly we investigated whether the particle concentration has any effect on the film thickness at the particle borderline. Therefore we calculated for all films (volume fractions <0.5%, 11.1%, 17.4% and 25.0%) the film thickness at the particle borderline for all pictures. The average value and standard deviation is given in table 2. From this we can see that the particles can be incorporated into the film at a rather well defined thickness (1310 nm).

Fig.6. The influence of temperature and glass particles

Table 2. The Film thickness at the particle borderline

Vol % PS	Thickness average [nm]	Thickness σ [nm]	Number of points
<0.5	1371	79	37
11.1	1500	156	17
17.4	1384	127	32
25.0	1109	75	49
25.0	1201	210	46

The influence of the particles on film thinning can be seen in fig.7, if the amount of PS (sample 1, 1900 nm) increases, the film thinning process becomes slower.

There may be a difference between the height down to which the film thickness can be measured by interference, and the height of the highest particles, because near the particle the film may not be exactly plane parallel. However in films containing small amounts of particles, interference fringes could be observed both in the film region containing particles as well as in film regions free of particles. In these cases no discontinuity at this transition was observed. These facts give us confidence that there is no substantial difference between the film thickness measured by interference just above the highest particles, and the film thickness at the height of the highest particles.

Fig.7. The drainage of the particle borderline as a function of vol% PS (sample 1, 1900 nm)

The lines in the figure can be extrapolated to zero-height, and the corresponding time can be used as a measure for the film thinning velocity. In order to check the influence of flow by the particles on the flows in the film, we measured the bulk viscosity of suspensions of latex particles. Although in principle there may be a difference between the viscosity of a 3-dimensional bulk suspension and the suspension in the film containing a 2-dimensional array of particles, this difference is neglected here as a first order approximation (no data on the viscosity of two-dimensional thin arrays being available). We measured the viscosity of the dispersions with an Ostwald viscosimeter. The data fitted reasonably well with the Mooney equation, with $\phi_{\max}=70.0$ vol%. Although this is not a realistic value for the constant $\phi_{\max}$, we will use it for interpolation since it fits the measurements satisfactorily. Table 3 gives the film thinning velocity in relation with the viscosity of the dispersion.

Table 3. Film thinning velocity as a function of the bulk viscosity

Vol % PS	Total film	Extrapolated	Velocity $V \times \eta / \eta_0$		CTAB
	Height [mm]	Time [s]	V[mm/s]	[mm/s]	[mol/l]
<0.5	13.4	24	0.56	0.56	2.0e-3
11.1	13.5	30	0.45	0.63	5.1e-3
17.4	13.0	42	0.31	0.55	5.1e-3
25.0	12.5	65	0.19	0.50	6.7e-3

DISCUSSION

In fig.3 we can see an interesting phenomenon. The process of marginal regeneration has been made visible by means of the PS particles. Marginal regeneration creates thin film parts which rise (rapidly) in the film. These parts again are essentially free of PS particles. This indicates that neither gravity nor diffusion is the reason for the fact that the particles used can not be present in a film which is much thinner than the particle diameter itself.

The place of the particle borderline (above which there are no particles in the film), can be explained in agreement with Dippenaar (1982) by the contact angle between glass particles in a film.

The film is expected to thin until it has reached a slightly smaller thickness than the particle diameter (see fig.8). The particles will create a contact angle and fall dry for a part. The film continues thinning until it has no radius of curvature near the particle. The particle will be pushed downward into a thicker region. In our case it is not clear whether the last drawing of fig.8 will be reached in the thinning process, since the film dimensions in directions parallel to the film surface are very large compared to the particle diameter. The film therefore has no significant radius of curvature.

Fig.8. A particle in a film, the drainage process of the particle in the film.

The hydrophilic particles (both 300 nm and 1070 nm) were pushed out of the film when the film reached their own thickness. Hydrophobic particles could be present in a film which is thinner than the particle diameter. This can be explained by the larger contact angle of the hydrophobic particles. From geometrical considerations, assuming flat film surfaces up to the contact line on a particle, we calculated this angle to be 46 degrees. The small particles act in the same way as large particles ($>160\text{ }\mu\text{m}$) with which Dippenaar (1982) performed experiments. The contact angle causes drainage of the particles which follow the drainage of the film completely. If the particles stick to the surface, their Brownian motion will be suppressed by the Marangoni effect and by contact angle hysteresis. They will thus tend to follow the motion of the film. This phenomenon appears to be strong enough to suppress even the Brownian motion of the 300 nm spheres. We found a similar behaviour for glass particles ($1\text{--}2\text{ }\mu\text{m}$) which did not have a distinct effect on the film thinning process of films from CTAB solutions unless they lower the CTAB concentration by adsorption. This however could not happen at the volume fractions used ($<0.5\%$). The hydrophilic glass particles were not monodisperse, and the particle borderline therefore was not very sharp.

In table 3 we find within experimental accuracy a linear

correlation between the thinning velocity (V) and the viscosity of the liquid:

$$V = 0.56 \times \eta_0 / \eta \quad (5)$$

The result of the present investigation indicates that marginal regeneration is inversely proportional to the viscosity of the solution, since marginal regeneration is the major mechanism of film drainage.

CONCLUSIONS

The actual thickness of the film at the particle borderline is determined by the hydrophobicity of the particles. This is in agreement with other investigations (Dippenaar, 1982). The particles do not flow downwards because of direct effects of gravity. Diffusion can be neglected.

The thinning rate of foam films of PS dispersions in CTAB (up to 25 vol% PS) is linearly correlated with the reciprocal value of the viscosity. This suggests that marginal regeneration is also linearly correlated with the viscosity, because marginal regeneration is the major mechanism of film thinning in this type of films.

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APPENDIX A

We consider a film element with height Δh , width b and thickness d . The volume V will therefore be $V=b*d*\Delta h$. The flow per unit of height out of such a element will be :

$$Q = \frac{1}{\Delta h} * V' = b*d'$$

Hudales found Q to be equal to $Q=k*d^n$ were k and n are arbitrary constants. Separating thickness d from time t , and integration in time leads to:

$$(1-n)kt/b = d^{1-n}$$

Here we assumed the film to be infinite thick at $t=0$, and $n>1$. A double logarithmic plot gives information about k/b and n :

$$\ln(d)=1/(1-n) * \ln(t) + 1/(1-n) * \ln(k(1-n)/b)$$