

Comments

Effects of Electrolytes on Bubble Coalescence

The observation that a wide range of solutes in aqueous solution stabilize foaming has been applied in areas as diverse as the food industry, the separation of minerals by froth flotation, cleaning processes, and detergency. Foams are stabilized by surface active solutes or colloids and have a wide range of stability times. Although never thermodynamically stable, they can exist under suitable conditions for long periods of time (i.e. months). Many everyday and industrial uses, however, require only short time stability of the order of minutes.

The first stage in foam formation involves the approach of two gas bubbles in solution. The bubbles deform because of the hydrodynamic force acting to oppose film drainage, and it is this resistance to thinning which gives foam stability at the early stage of foam formation. For surface active solutes, such as ionic surfactants, there is an additional resistance to thinning for films approaching thicknesses typical of electrical double-layer interactions (i.e. 10–100 nm). For nonionic surfactants a very short-range repulsion is apparently generated by the solvation water surrounding the polar surfactant head-group.¹ This repulsion stabilizes very thin Newton or common 'black' films. Spots of thin black films have been observed in regions of thick soap films formed from nonionic surfactants.²

For the stability of foams, it is also important to create a reasonable degree of mechanical stability, so that the foam can withstand perturbations without breaking. This stability can be enhanced both by increasing the viscosity in the film or plateau borders and by creating a significant surface elasticity at the two facing interfaces. The former has the effect of preventing rapid drainage in response to external forces, whereas the second forms a restoring force which opposes any stretching of the interfaces. Surface elasticity can be generated in response to stretching of the film, when the surface diffusion time is slow relative to the perturbation time. Stretching of the surface immediately generates a region depleted in surfactant and of high surface tension, and hence a restoring force acts to minimize film thinning.

The degree of foam stability created by nonionic surfactants appears to be based on this surface elasticity, but there also may be a contribution from rapid surface surfactant transport to the stretched and depleted section of the film. This transport of surfactant molecules driven by a high local surface energy will also carry associated solvation water to the thinning region of the film. This effect will also act to prevent thinning and hence stabilize the film.

Water-soluble short-chain alcohols can also stabilize foam by this mechanism, but at high concentrations they are equally effective at destroying foams produced by even ionic surfactants. The latter effect is due to the fact that at high concentrations the bulk to surface diffusion rate is rapid and the stretched surface rapidly adsorbs the alcohol, reducing the local surface tension and removing the surface elasticity.

In a typical foam the forces initially acting to drain the film are relatively weak and are caused by the hydrostatic suction pressure. For example, a foam of height 1 cm has a suction pressure of about 100 Pa. Foam lifetime has been closely correlated with foam height.² As the film drains, an opposing hydrodynamic force is produced, which increases rapidly as the thickness is reduced and the area of the film increases. One of the oldest and simplest theories of the effect of this opposing force on the film drainage rate is that of Reynolds.^{3,4}

The film thickness (h) with drainage time ($t - t_0$) for parallel disks of radius r , with the zero slip condition at the liquid-wall interfaces, is given by the simple relationship

$$h = \left[\{4P(t - t_0)/(3\eta r^2)\} + 1/h_0^2 \right]^{-1/2}$$

where h_0 is the initial film thickness at time t_0 , P is the drainage pressure, and η is the viscosity of the fluid. This relationship predicts film drainage for pure water reasonably well,⁴ and a typical drainage curve calculated using this model is shown in Figure 1. This hydrodynamic repulsion creates dynamic, short-lived foam stability, even in systems where there is no long-range repulsion acting between the facing surfaces.

As two bubbles collide, the flattened region between two contacting bubbles arises as a consequence of the forces acting to pull or push them together. Several theories on the coalescence of bubbles incorrectly assign the Laplace pressure across the curved bubble interface as the suction pressure draining the film formed between bubbles.^{5,6} For example, imagine two pairs of bubbles of different size colliding in water. It would be incorrect to say that the collision between the smaller bubbles will be more successful via rapid film drainage because of their larger Laplace pressure. During transient collisions bubbles flatten in response to the drainage force which acts to prevent coalescence. A related situation occurs for bubble persistence at the water surface, where bubbles of different radii have different persistence times based on drainage rate not Laplace pressure, since bubbles trapped at the water surface generally deform the surface to follow the curvature of the bubble during film drainage. Studies on oil droplets in water clearly demonstrate the dependence on film drainage rather than the Laplace pressure.⁷

In pure water, surface elasticity is zero and the approaching bubbles drain to form films which are unstable and rupture at film thicknesses of about 110 nm.⁸ The rupture mechanism is still not clear because of the limited range of van der Waals forces in this system, which are very weak even at 50 nm separation. Rupture most likely occurs due to the contact of the peaks of capillary waves formed at each of the two facing surfaces. We have pointed out in earlier work that the hydrophobic attraction should operate between two bubbles in aqueous solution to pull the interfaces together.^{9,10} This force is

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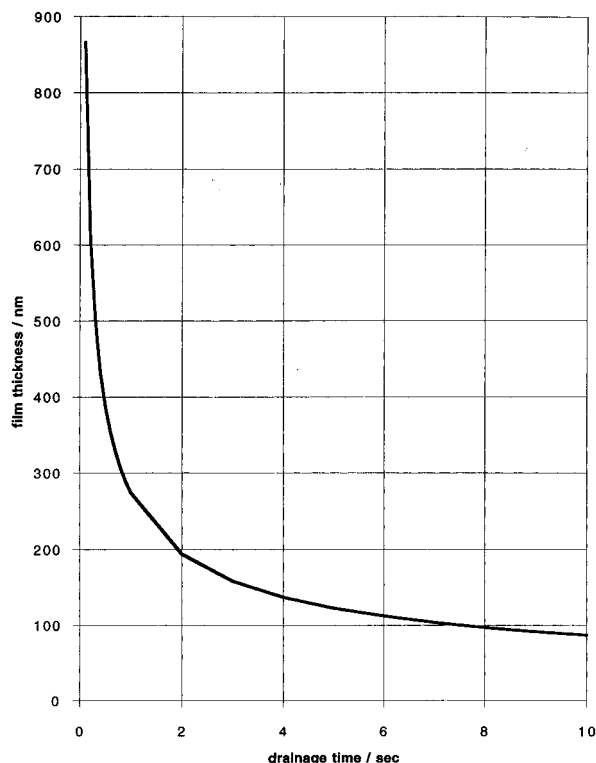


Figure 1. Drainage time calculated using the Reynolds equation for a parallel water film of radius 0.1 mm with a drainage pressure of 100 Pa. The film was assumed to be infinitely thick at the initial drainage time (t_0).

Table 1. Comparison of van der Waals Forces in a Water Film and Those Experimentally Observed between Strongly Hydrophobic Solid Surfaces in Water

film thickness/nm	5	10	50	100
F/R (vdw) ¹¹ (mN m ⁻¹)	-0.29	-0.057	-9.3×10^{-4}	-1.5×10^{-4}
F/R (obs) ¹² (mN m ⁻¹)		<-10	-3.5	-1.0

much stronger than the van der Waals force and should act to increase the amplitude of opposing surface perturbations, which may become strongly correlated even for relatively thick water films of 100–200 nm. A comparison of the van der Waals interaction (with retardation) expected for a water film¹¹ and the interaction recently measured between strongly hydrophobic solid surfaces in water¹² is given in Table 1. At all film thicknesses the hydrophobic interaction is several orders of magnitude stronger than van der Waals forces. In addition, the hydrophobic attraction is significant even at 100 nm, where water films are observed to rupture. At these distances van der Waals forces are negligible.

The persistence of air bubbles in water has been suggested as a sensitive test for surface active contamination.¹³ However, it has been known for many years that addition of electrolytes to water above a critical concentration produces a substantial increase in foam stability.^{5,14,15} This effect extends the lifetime of bubbles from less than 1 s in clean water to 5–10 s for some salts. This situation is more difficult to understand and has recently been made more curious by the discovery of anion–cation

combining rules,^{9,16} which can be used to predict which salts will give this effect and which will not.

Electrolytes do have a weak effect on surface tension, which in the majority of cases is to slightly increase it, due to their desorption from the low-dielectric-constant air phase. That some electrolytes exhibit completely different foaming behavior from that of others ought to lead us to some explanation for this phenomenon. Recently, Christenson and Yaminsky,¹⁷ utilizing newly available data, have been able to correlate the effects of electrolytes on bubble coalescence with the parameter $(d\gamma/dc)^2$, where $d\gamma$ is the change in surface tension and dc is the change in bulk concentration of the electrolyte. This correlation was originally demonstrated, with limited data, by Marrucci and Nicodemo.¹⁸ If the parameter $(d\gamma/dc)^2$ is large, then the electrolyte will inhibit bubble coalescence, and if it is small, bubble coalescence remains unaffected. Generally the transition from one type of electrolyte to the other occurs when the value of $(d\gamma/dc)^2$ drops below ~ 1 (mN m⁻¹ M⁻¹).² The importance of this parameter in bubble coalescence has been related to the elasticity of the interface¹⁷ through the Marrucci model of electrolyte film drainage. Unfortunately, however, this model involves the basic assumption that the interlayer water must thin as a parallel film down to a thickness of a few nanometers, which is not observed experimentally. Several studies have demonstrated that films formed from water and electrolyte solutions rupture suddenly at thicknesses in the range 50–110 nm, probably due to the bridging of surface waves across the film.^{4,8}

The Marrucci model requires the assumption of rapid, parallel film drainage to a thickness of several nanometers. It is proposed that this rapid drainage results in a significant increase in the film electrolyte concentration, via the exclusion of electrolyte from the now increased surface area. Assuming that the electrolyte cannot diffuse away during rapid drainage, this will raise the surface tension of the film and, in a similar manner to that for the surfactant case, this increase in surface tension would then act to oppose film drainage in electrolyte solutions. At the high concentrations of electrolyte required to prevent bubble coalescence, diffusion will be rapid. This rapid diffusion will quickly negate any surface tension gradients produced in response to a change in interfacial area, as equilibrium conditions are rapidly restored.

The very rapid thinning to small separations, upon which the Marrucci model depends, has also been shown to be incorrect by direct experiments. Cain and Lee⁴ have demonstrated that films between a bubble and a hydrophobic flat thinned quickly before rupture at separations of 95–55 nm in KCl solutions. Also, rapidly thinning films form dimple-shaped films¹⁹ not flat films, as assumed in the Marrucci theory.

Further problems arise because the Marrucci model uses the van der Waals force as the attractive component, but this will actually be negligible at the film thicknesses relevant to film rupture, as pointed out by Doublet.²⁰ It now seems clear that the hydrophobic interaction offers a more likely mechanism. In a recent study, it has also been demonstrated that the correlation obtained by application of the Marrucci model to bubble coalescence studies is weak, and a much better correlation can be

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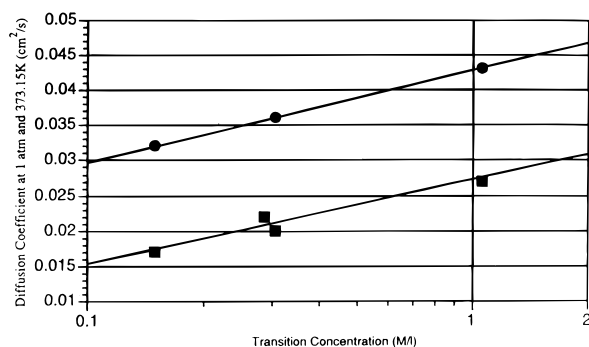


Figure 2. The transition concentrations of MgSO_4 (squares) and CaCl_2 (circles) versus the diffusion coefficient of the sparging gas. The gases used from left to right were SF_6 , Ar, N_2 , and He. The diffusion coefficients (see CRC Handbook) used were measured in air at atmospheric pressure, except the diffusion coefficient for nitrogen (0.307), which was measured in O_2 as the data in air were not available. The error associated with this value is expected to be less than 1%.

obtained on the basis of electrolyte effects on dissolved gas solubility.^{21,22} These observations bring us back full circle to the original suggestion that dissolved gases play a role in the hydrophobic interaction,⁹ for which there is now some evidence.^{23,24}

However, experiments using sparging gases with solubilities varying from 1.0 to 34 mL L^{-1} have shown that the variation in transition concentration is not in direct relation to the gas solubility.⁹ Rather we have found that a good correlation is revealed between the diffusion coefficient of the sparging gas and the transition concentration (see Figure 2), but the effect of electrolytes on the diffusion of gas shows no correlation with bubble coalescence behavior. This somewhat confusing and apparently contradictory situation is summarized in the points listed below.

(i) The effect of an electrolyte on dissolved gas solubility correlates with its effect on bubble coalescence.

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(ii) The diffusivity of the sparging gas correlates with the transition concentration for a given salt.

(iii) The parameter $(d\gamma/dc)^2$ gives a reasonable correlation with bubble coalescence behavior and with dissolved gas solubility for a wide variety of electrolytes.

Whereas:

(iv) The solubility of the sparging gas does not correlate with the transition concentration for a given salt.

(v) The effect of an electrolyte on diffusivity does not correspond with its effect on bubble coalescence.

If bubble coalescence proceeds via bridging of surface capillary waves, it is not completely surprising that reducing the level of dissolved gas in solution and reducing the diffusivity of the gas in the bubble favors prevention of coalescence. High gas diffusivities may favor rapid growth of surface waves, and high gas levels in solution may favor their fusion across a thin liquid layer.

Although the current explanation for film rupture and bubble coalescence in water and electrolyte solutions is rather unsatisfactory, there are some clear paths forward. A proper model must be based on the growth of surface waves and their subsequent fusion. The hydrodynamic flow within the water film must be correlated with the long range hydrophobic attraction operating between the fluctuating water surfaces. An initial attempt in this direction has already been made,²⁵ and much further work is required. The effect of electrolytes on bubble coalescence is clearly even more complicated and stretches our rather limited understanding of the effects of electrolytes on both the hydrophobic interaction and the behavior of surface waves. There is much to be done in this area to establish a complete description of this quite fundamental process.

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