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On the role of surfactants in emulsions and foams

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This perspective article is centered around my work related to surfactant science. The field is multidisciplinary, linked to physics, chemistry and biology. It is part of the field of soft matter and is well connected to industrial applications. My particular expertise deals with liquid surfaces, an area that expanded considerably with the advent of miniaturization, *i.e.*, when surfaces begin to matter. I started my research with surface light scattering and surface rheology investigations. The light scattering technique allows measurements of low interfacial tension systems, and led me to investigate microemulsions. After this work, I used my knowledge in surface rheology to investigate emulsions and foams, which are not thermodynamically stable, in contrast with microemulsions. The work is still ongoing, in particular to reach a better understanding of coalescence of bubbles and drops. I will show how interesting it is to use knowledge on surface layers at macroscopic interfaces to better understand microemulsions, emulsions and foams. I conclude with considerations on the perspectives of the research field.

1. Introduction

Surfactants are molecules made of two parts: a hydrophilic group soluble in water and a hydrophobic group, soluble in oils. As a result, these molecules adsorb at a variety of interfaces, solids or liquids, and are widely used in applications as detergents, emulsifiers and foaming, dispersing and wetting agents.[1]

The hydrophobic groups are generally alkyl chains, for instance in soaps, which are fatty acid salts and are the most commonly used surfactants. The hydrophilic groups are either anionic (negatively charged), as in soaps, cationic (positively charged) or nonionic. While soaps have been used for millennia, other surfactant types are now widely used, such as alkylbenzene sulfonates, products derived from petroleum. With the biodegradability of synthetic surfactants being limited, new surfactants produced from biomass are being investigated. In this article, I will focus on the research performed with common synthetic surfactants, having single alkyl chains and small polar groups, such as sulfates or sulfonates (anionic), quaternary ammonium (cationic) and ethylene oxide groups (nonionic). I will also focus on liquid interfaces, either air–water or oil–water, and discuss the relationship between interfacial properties and the behavior of emulsions and foams.

Surfactants are associated with polymers, proteins and/or particles in many practical systems. I will not discuss the mixed systems in this article, information and references can be found in a book that I published recently.[2]

2. Surfactant layers at macroscopic interfaces

It was recognized early that surfactants decrease the interfacial tension between fluids. It is still sometimes believed that the tension change is sufficient to explain the surfactant behavior. This is clearly wrong: for instance, the surface tension of surfactant solutions is usually similar, around 40 mN m^{-1}, but the stability of the foams made with these solutions can differ largely. Another example is the behavior of surface deformations when surfactants or oils are spread onto water: because surface tension is lowered, surface deformations should be larger (the surface energy being decreased), whereas the opposite is observed, the deformations are damped. This phenomenon was used by Benjamin Franklin in the 18th century to show that matter is discontinuous (Fig. 1).[3]

In his well-known experiment, Franklin spread a teaspoon of oil on the surface of a pond and observed that only a fraction of the lake surface became still, suggesting that the oil could not fractionate indefinitely (otherwise the whole lake would have become still). Interestingly, the estimated thickness of the oil layer was about 1 nm, *i.e.* close to the size of an oil molecule. The notion of molecules was controversial at that time but was confirmed later on. Franklin was also puzzled by the fact that such a thin layer could dampen surface waves. Clearly, something other than surface tension was at play. At the beginning

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Fig. 1 Left: Benjamin Franklin (1706–1790). Right: Clapham pond after the addition of oil to repeat Franklin's experiment.

of the 20th century, Boussinesq introduced the notion of surface viscosity[4] to explain another peculiar feature: bubbles in water move upward with the velocity of a solid particle with the same radius, whereas air recirculation in the bubble should increase the velocity by 50%. Boussinesq proposed that surface-active contaminants could induce viscous damping and suppress air recirculation. However, the correct explanation was provided by Benjamin Levich, who attributed the phenomenon to surface elasticity:[5] when bubbles move upward, the adsorbed surface-active substances are entrained downward, surface tension gradients arise and oppose the surfactant motion, internal air circulation is stopped, and the bubbles behave like solid particles. Levich also showed that surface tension gradients are responsible for the damping of surface deformations by monolayers of oily substances. He introduced the compression modulus.

$$E = -A\frac{\mathrm{d}\Pi}{\mathrm{d}A} \tag{1}$$

where A is the area, and Π is the surface pressure in the layer, which can be calculated using the following equation:

$$\Pi = \gamma_0 - \gamma \tag{2}$$

where γ is the surface tension, and γ_0 is the surface tension of the bare surface. Eqn (1) shows that E is the two-dimensional analog of the compression modulus of a bulk fluid: $-V\,\mathrm{d}P/\mathrm{d}V$, where V is the volume, and P is the pressure.

When the molecules in the surface layer are insoluble in the bulk fluids, their surface concentration Γ is inversely proportional to surface area A. Eqn (1) can be rewritten as

$$E = -\Gamma\frac{\mathrm{d}\gamma}{\mathrm{d}\Gamma} \tag{3}$$

The modulus is smaller for soluble molecules because when compressed, they can dissolve in the bulk fluids, lowering the resistance to compression. Levich proposed expressions for the effective modulus in the case of air–water interfaces. He showed that the decrease in the modulus was accompanied by the appearance of an effective viscosity. Expressions for the case of oil–water interfaces were proposed recently by Kovalchuk *et al.*[6]

With the thickness of the surface layers being much smaller than the characteristic lengths involved in surface motion, surface elasticity and viscosity are usually handled as excess quantities, as proposed by Gibbs.[7] It should be pointed out that most surfactant layers are compressible, in contrast to bulk fluids (except at high frequencies). Surfactant layers are also fluid-like and have only a viscous resistance to shear (as bulk fluids). Note that the layers of some bio-surfactants, such as saponins, have a finite surface shear modulus and a more complex viscoelastic behavior.[8,9]

The notion of surface viscoelasticity took some time to be accepted, especially because the corresponding parameters are difficult to measure. The first compression experiments were made with Langmuir troughs and limited to very low frequencies. Oscillating bubble/drop devices have been commercially available since the 90s and are widely used nowadays. Shear viscosity measurements were not precise enough to detect the viscosity of surfactant layers until very recently, and high-sensitivity oscillating ring devices are also now commercially available.[10]

When I started my research work in the late 60's, surface viscoelasticity, also called surface rheology, was still little explored. Lasers were discovered in 1965, and it was soon realized that, because of their remarkable frequency definition, they could be used to detect small frequency shifts. This was particularly interesting for light-scattering experiments, formerly limited to Raman and Brillouin scattering. Light-scattering studies of Brownian motion of colloidal particles became possible, and commercial instruments were soon available for these types of experiments. In the late 60's, Jean Brossel was the head of my laboratory. He discovered, together with Alfred Kastler (Nobel Prize 1967), the method of optical pumping, used afterwards in lasers. The laboratory (part of the Physics Laboratory of the Ecole Normale Supérieure, Paris) specialized in spectroscopy and detection of weak optical signals. Seeing the potential interest of the new light scattering techniques, and knowing that his laboratory had the necessary expertise, Brossel decided to introduce light scattering studies, both in bulk and at surfaces. My colleague Jacques Meunier built a surface light scattering set-up using light beating spectroscopy. Together with Jean Brossel and my thesis adviser, Marie-Anne Bouchiat, he published the first experiments of this type in 1968, the same month as Katyl and Ingard in the USA. In this method, one detects the thermally excited surface waves, which wavelength is related to the scattering angle, as for other types of fluctuations in bulk light scattering. With the new set-up, I undertook first the study of surfaces of simple liquids and of liquid crystals (see ref. 11 for details). I began surfactant studies with monolayers of insoluble fatty substances at the surface of water.

2.1. Insoluble monolayers at the surface of water

As with the large amplitude deformations observed by Franklin, the monolayers dampen the surface waves observable in light-scattering experiments, and the spectrum of the scattered light is broadened (Fig. 2). Note that these waves are capillary waves (wavelength smaller than the capillary length, about 2 mm for water), whereas the waves observed by Franklin were gravity waves, but both are affected by surface layers. Capillary waves also shift the laser frequency (by the Doppler effect) because they propagate on water.

With this technique, I studied various types of monolayers, fatty substances and polymers.[12] Various differences were observed depending on monolayer type, expanded (liquid-like) or condensed (solid-like). The spectra were analyzed using the dispersion equation of the capillary waves, including three parameters: surface tension, surface compression modulus and viscosity. When the monolayers are very dense, variations in the compression parameters no longer affect wave propagation, and the layer behaves like a thin solid plate.[5] However, the data interpretation for condensed monolayers required the introduction of a transversal viscosity, which should be zero in the linear viscoelastic regime. Many studies were performed to elucidate this question, but to date a clear picture is still missing.

Fig. 2 represents an example of the largest changes produced by monolayers, evidencing that these changes are quite small. This is because capillary waves are weakly coupled to compression (longitudinal) waves and produce only a small compression of monolayers at air–water interfaces. The coupling almost vanishes at oil–water interfaces,[5] and the scattering technique cannot be used for the determination of the compression parameters at these interfaces. There is also a significant spectral broadening due to the finite size of the laser beam at the small scattering angles that are used: unlike bulk light scattering, the scattered intensity decreases rapidly with increasing scattering angles and cannot be performed at angles larger than a few degrees. The accuracy of the surface light-scattering experiments is thus limited, even at air–water interfaces. Another difficulty is the necessity to avoid the contamination of the sample by surface-active impurities, which significantly affect the surface compression modulus, much more than the surface tension. All this explains why the technique has been little used to date and why instruments are not commercially available, in contrast to bulk light scattering.[13]

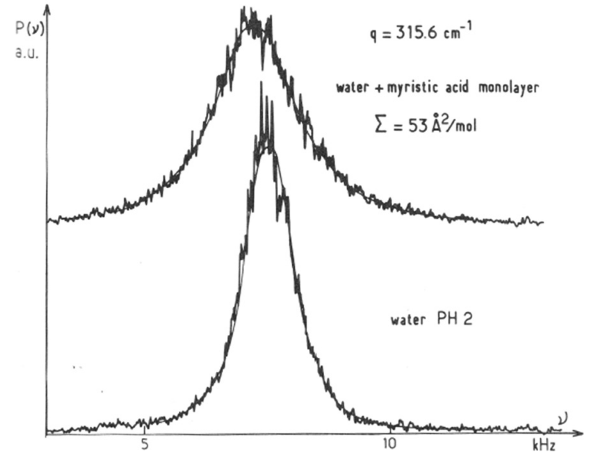

Fig. 2 Spectra of the light scattered at the surface of water (bottom) and water covered by a myristic acid monolayer (top). The wavelength is $2\pi/q \sim 200$ μm. Reproduced from ref. 12 with permission from Elsevier, copyright 1981.

2.2. Low interfacial tension in microemulsion systems

Microemulsions, as emulsions, are dispersions of oil and water. They can be made of oil drops dispersed in water (O/W) or water drops dispersed in oil (W/O), and unlike emulsions, they are thermodynamically stable. This is because, despite the drop size being much smaller (tens of nanometers instead of microns), the interfacial tension between oil and water is small (typically 0.01 mN m^{-1} instead of a few mN m^{-1} for emulsions), and the surface energy can be balanced by dispersion entropy.[14] Because of these low tensions, microemulsions can remove oil from porous rocks, and they began to be extensively investigated in relation to enhanced oil recovery in the 70's. At that time, there were no commercial instruments that were able to measure very low tensions: spinning drop instruments were being developed in the laboratory of the University of Texas and were only commercialized later. We then started a collaboration with the Institut Français du Pétrole, in order to measure the tensions with the light scattering technique. Microemulsion systems were, in fact, ideal for the technique because interfacial roughness is large when the tension is small, and the scattered intensity is large, making the experiments easier. Because, as mentioned earlier, capillary waves at oil–water interfaces do not induce significant compression in the layers, the technique is only sensitive to surface tension. We began with a model system containing water, salt (NaCl), toluene, sodium dodecyl sulfate (SDS) and a cosurfactant, butanol. The appearance of the samples is shown in Fig. 3. These systems are currently called *Winsor systems* (see ref. 2 for a review).

At low salinity, an O/W microemulsion coexists with excess oil (Winsor I equilibrium). This is because the drops' curvature cannot be less than their optimal curvature (close to their spontaneous curvature $\mathcal{C}_0$): when there is not enough surfactant to cover the whole air–water interface, the excess oil is rejected to an upper phase. The same occurs at high salinity; when the water drops reach their optimal curvature, the excess water is rejected to a lower phase (Winsor II equilibrium). By convention, $\mathcal{C}_0$ is positive in the first case and negative in the second.

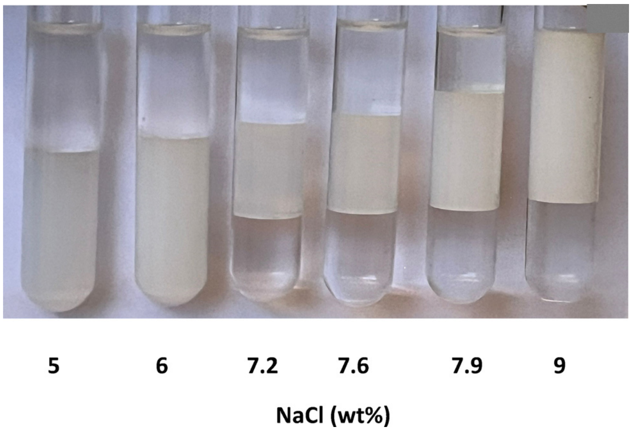

Fig. 3 Appearance of water–NaCl–toluene–SDS–butanol mixtures of increasing water salinity. At low salinity, an O/W microemulsion coexists with excess oil (Winsor I); at high salinity, a W/O microemulsion coexists with excess water (Winsor II); and at intermediate salinity, a microemulsion coexists with both excess oil and water (Winsor III).

The microemulsion coexisting with both excess oil and water does not contain drops (Winsor III equilibrium). It is made of strongly fluctuating surfactant layers at the interface between oil and water domains; the microemulsion is bicontinuous and also called sponge phase. In the salinity range of the three-phase equilibria, the spontaneous curvature is close to zero, meaning that a lamellar structure could have been expected. The structure is not lamellar because the curvature energy is small and of the order of the thermal energy k_BT (k_B = Boltzmann constant, T = absolute temperature). The form of the curvature energy was proposed by Helfrich:[15]

$$E_c = \int_A \mathrm{d}A\left[\frac{1}{2}K(\mathcal{C}_1+\mathcal{C}_2-2\mathcal{C}_0)^2+\bar{K}\mathcal{C}_1\mathcal{C}_2\right], \qquad (4)$$

where $\mathcal{C}_1$ and $\mathcal{C}_2$ are the two local principal curvatures of the surfactant layer, K is its bending modulus and $\bar{K}$ is its Gaussian modulus.

Fig. 4 shows a plot of interfacial tensions measured in this system *versus* salinity. The largest tensions in the three-phase region are minimum at a salinity S^* called optimal salinity.

It was argued in the 70's that the tensions were low because of the vicinity of critical points that are numerous in multicomponent systems (hypersurfaces in the phase diagrams).[17] In the two-phase region, the tensions between the excess phase and the microemulsion or of its continuous phase (in which the drops have been removed) are the same. This means that the low tensions are not due to the vicinity of a critical point (that could not be close, the continuous phase of the microemulsions being almost pure oil and water). This proved that the low tensions are due to the high surface pressure of the surfactant monolayers.[18] In the three-phase region, critical points should also be far in the systems without the middle phase. It was argued that a thin layer of microemulsion could still be present between oil and water. However, in this case, the tension γ_{ow} between oil and water should be the sum of the tensions between the microemulsion and water γ_{mw} and microemulsion and oil γ_{om}. This is not the case, for instance, at the optimal salinity, $\gamma_{mw} = \gamma_{om}$ and γ_{ow} should be twice γ_{mw} (or γ_{om}), whereas $\gamma_{mw} = \gamma_{om} = \gamma_{ow}$ (see Fig. 4). This result was puzzling, because close to a critical point $\gamma_{ow} = \gamma_{mw} + \gamma_{om}$ and middle

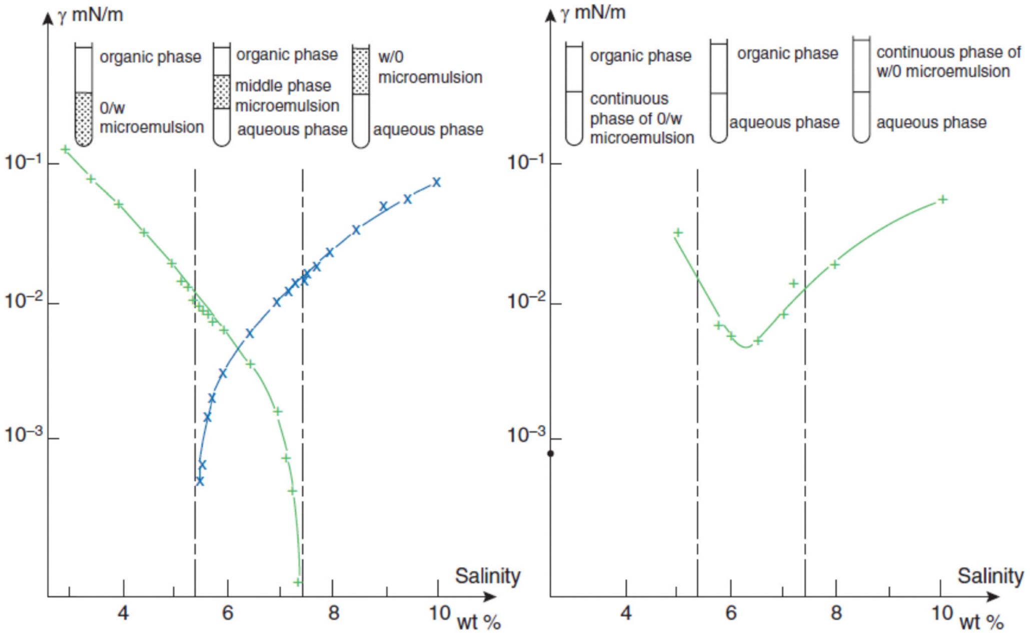

Fig. 4 Left: Interfacial tensions between microemulsions and excess oil and/or water *versus* salinity. Right: Interfacial tensions between the microemulsion's continuous phase and excess oil or water in the two-phase regions and between oil and water in the three-phase region *versus* salinity. The water–NaCl–toluene–SDS–butanol mixture system shown in Fig. 3 is used here. Adapted from ref. 16 with permission from Elsevier, copyright 1982.

phases wet the interface between upper and lower phases.[19] At that time, microemulsion models began to be established. Pierre Gilles de Gennes and Christiane Taupin proposed a space-filling model dividing all space into consecutive cubes, each cube being filled either with oil or with water.[14] This work stimulated the development of Ising microemulsion models. Benjamin Widom elaborated on one of them and predicted that the middle phase should not wet the oil–water interface.[20] He suggested to us to check if this was the case in our three-phase samples. As expected, we observed that small quantities of the middle phase indeed collect in the corner of the liquid cell, without covering the oil–water interface.[21] These measurements definitely proved that the low tensions were due to high-surface-pressure monolayers sitting at the oil–water interface. Only the lowest branches of Fig. 4a in the three-phase region are due to the vicinity of critical points.[16] Ising models also predicted an evolution from non-wetting to wetting behavior of the middle phase when the surfactant molecules become less surface-active, and our later experiments confirmed the existence of this transition.[22]

De Gennes and Taupin proposed that there should be a characteristic size in the bicontinuous microemulsions of the order of the persistence length of the surface layer:

$$l_{\mathrm{p}} = a\exp\left(\frac{2\pi K}{k_{\mathrm{B}}T}\right) \tag{5}$$

where a is a molecular length. We determined K using ellipsometry, which allows measurement of the amplitude of surface thermal fluctuations.[23] We showed that the characteristic size varies exponentially with K, as predicted by eqn (5).[24] Because the interfacial tension depends on a combination of K and $\bar{K}$, it can be used to determine the values of $\bar{K}$.[25] These values were in agreement with our later neutron spin echo measurements, performed after I moved to the Centre de Recherche Paul Pascal in Bordeaux in 1994.[26,27]

Funding for microemulsion research substantially decreased after the 80's due to the decrease in oil price, making the use of microemulsions in oil recovery too expensive. I could, however, secure funding for other topics, antifoams and emulsion stability. This led me to study in parallel the behavior of monolayers of soluble surfactants, work which is described in the next section.

2.3. Soluble layers

Because of the limited accuracy of the surface light-scattering technique, I decided to develop excited wave techniques, where not only the amplitude of the waves is larger but the frequency is fixed by the instruments and there is no instrumental broadening affecting the wave damping. We built devices for the study of both capillary and compression waves. The second device was intended to determine the compression properties of layers at oil–water interfaces where the coupling with capillary waves almost vanishes. An example of the measurements with aqueous solutions of a nonionic surfactant decyl pentaethylene glycol ether ($C_{10}E_5$) is shown in Fig. 5. The measured compression modulus differs from the intrinsic modulus E defined by eqn (3) and is an effective modulus denoted by E_{eff}.

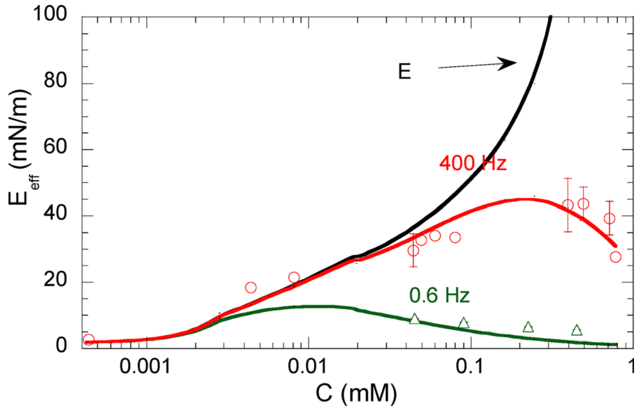

Fig. 5 Effective surface elastic compression modulus E_{eff} *versus* surfactant bulk concentration C in $C_{10}E_5$ aqueous solutions. Circles: measurements using excited capillary waves; triangles: measurements using excited compression waves; black line: calculated intrinsic modulus E; red and green lines: calculated E_{eff} using the bulk surfactant diffusion coefficient: 4×10^{-6} cm^2 s^{-1}. Adapted from ref. 28 with permission from Elsevier, copyright 1995.

The intrinsic modulus E has been calculated using eqn (3). In order to determine the surface concentration Γ, many authors use an equation of state relating surface and bulk concentration. The simplest one is the Langmuir equation of state, which assumes that there are no interactions between surfactants in the monolayers. In Frumkin's equation, binary interactions are included, and this equation usually allows for obtaining good fits of the surface tension variation with bulk concentration C. However, the calculations of the modulus E at concentrations at which the monolayer becomes compact lead to unrealistically large values.[28] Higher-order terms are sometimes included, but the necessity of determining additional parameters limits the accuracy of the calculations. In addition, these equations of state lack thermodynamic bases.[29] In order to avoid errors, it is safer to use the Gibbs adsorption equation, which is written for a nonionic surfactant as:

$$\Gamma = -\frac{1}{k_{\mathrm{B}}T}\frac{\partial\gamma}{\partial\ln C} \tag{6}$$

This method requires accurate measurements of $\gamma(C)$ because E is a second derivative of this function. The black line in Fig. 6 was calculated in this way.

One sees in Fig. 5 that, the smaller the frequency, the smaller the effective modulus. This is because upon monolayer compression, the surfactant is expelled in the bulk and comes back during the following expansion (the waves alternatively decrease and increase the surface area). Assuming that the surfactant motion in the bulk involves diffusion only and that there are no adsorption/desorption barriers, Levich calculated the effective compression modulus E_{eff} describing the response to a sinusoidal compression of the surface with a frequency ω[5]:

$$E_{\mathrm{eff}} = E\frac{1+\Omega}{1+2\Omega+2\Omega^2} \quad \text{with} \quad \Omega = \sqrt{\frac{D}{2\omega}}\frac{\partial C}{\partial\Gamma} \tag{7}$$

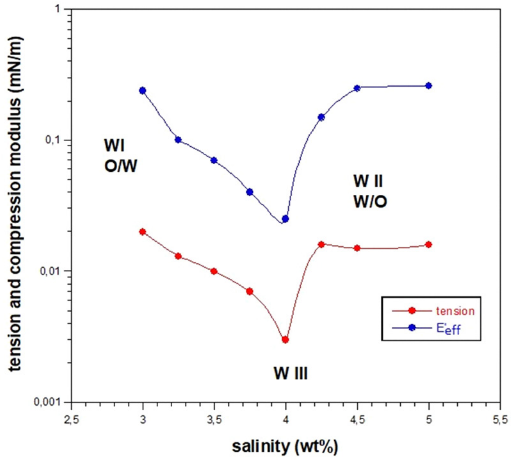

Fig. 6 Interfacial tension and effective compression modulus at 0.1 Hz *versus* salt concentration in a water–NaCl–cyclohexane–sodium dodecyl benzene sulfonate–*sec*–butanol system. Adapted from ref. 32 with permission from ACS, copyright 2018.

where D is the surfactant diffusion coefficient in bulk, and Ω is a reduced frequency. The effective modulus E_{eff} is close to E at high frequencies and close to zero at low frequencies. The red and green lines in Fig. 5 are calculated using eqn (3), (6) and (7). The agreement with the experiments is quite good. When the surfactant is ionic, eqn (7) is no longer applicable because of the electrostatic adsorption barriers, and E_{eff} is closer to E. More complex calculations are then needed to evaluate E_{eff}.[30]

Oil–water interfaces can have interfacial tensions lower than a few mN m^{-1}, for instance in the Winsor systems such as those of Fig. 4. In this case, the compression modulus cannot be measured either using capillary wave techniques or oscillating pendant techniques. An oscillating spinning drop device was developed recently by the group of Jean-Louis Salager.[31] Thanks to an exchange program between France and Venezuela, I could spend time in Salager's lab and perform experiments with Ronald Marquez, who was completing his PhD thesis. Fig. 6 shows an example of the results obtained with Winsor systems similar to those shown in Fig. 3 but containing less surfactant to avoid rapid dissolution upon compression.

As in other Winsor systems, the tension is minimum at an optimal salinity S^*. Surprisingly, E_{eff} is also minimum at S^*, whereas the surface pressure is maximum. This is the consequence of the exchanges: at S^*, the partition coefficient of the surfactant between oil and water is equal to one, so the role of the exchanges is quite significant.[32]

3. Aqueous foams

Aqueous foams are dispersions of bubbles in water. They can be stabilized by surfactants that cover bubble surfaces. There are three main foam destabilization processes:

- Gravity drainage
- Disproportionation: gas diffusional exchange between small bubbles in which the capillary pressure is high and larger bubbles in which the pressure is lower. The exchanges lead to the disappearance of small bubbles and to the growth of large bubbles as time elapses. This process is similar to Ostwald ripening, but the growth laws are different, so it is sometimes called coarsening.
- Coalescence: fusion of bubbles, caused by the rupture of films between them.

The three processes occur simultaneously, and it is quite difficult to distinguish between disproportionation and coalescence as both lead to bubble growth.

3.1. Antifoams

I began foam studies in the late 80's investigating the mechanisms of action of the antifoams commercialized by Rhone Poulenc. These antifoams are silica particles agglomerated in silicon oils and emulsified in water. They are very efficient and destroy foams in seconds, during which foam drainage and disproportionation have no time to take place. They therefore act by breaking the films between bubbles. My view was that film rupture is thermally activated and originates from surface concentration fluctuations in the films with an activation energy on the order of EA_{hole}, where A_{hole} is the area of the hole nucleated in the film (Fig. 7).

We then started surface rheology studies with surfactants and silicon oils. The stochastic rupture mechanism was later found to be relevant to more stable foams (or emulsions) (see the discussion in Section 3.4). Film rupture by antifoam particles is rather deterministic and occurs during film thinning, once the film thickness is comparable to the particle size; the particle bridges the two film surfaces, and film rupture follows due to particle dewetting. We could, however, propose an interpretation for the loss of efficiency of the antifoams with time,[33] which we validated later with experiments in microgravity, performed after I joined the Laboratoire de Physique des Solides in Orsay.[34]

Antifoaming action can also be observed with surfactant solutions during a phase separation, such as that occurring in nonionic surfactant solutions above the cloud point: the solution phase separates into surfactant-poor and surfactant-rich phases. The surfactant-rich phase nucleates in the form of drops that behave like antifoam particles, bridging film surfaces and breaking them by dewetting. We explained in this way why the foams made with nonionic surfactant solutions are unstable above the cloud point.[35] Interestingly, the same phenomenon was observed in emulsions.[36]

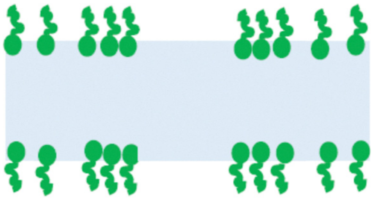

Fig. 7 Sketch of the concentration fluctuation at the surfaces of a soap film leading to the formation of a hole in the film.

3.2. Foam drainage

After the antifoam work, I decided to investigate foam stability, work that took me much longer and is still ongoing. At that time, Denis Weaire introduced the concept of forced drainage, where a surfactant solution is added on top of a foam column. Forced drainage experiments proved to be less difficult to interpret than free drainage experiments. A flat frontier forms between the added liquid and the foam, with the frontier travelling downwards at a constant velocity V. The experiment is similar to imbibition of porous solids, except that in porous solids, the frontier broadens. The liquid channels in the foams are the film borders, called Plateau borders, the films being much too thin to transport a significant fraction of liquid. Plateau borders are interconnected and can expand during the passage of the liquid, in contrast to solid pores. Weaire and his coworkers showed that surface tension opposes border expansion and that the different forces at play lead to the propagation of a soliton, as observed.[37] They showed that the soliton velocity V is related to the flow rate Q by a power law: $V \sim Q^{\alpha}$, where $\alpha = 1/2$, in agreement with their experiments. Howard Stone and his coworkers performed similar forced drainage experiments with a different surfactant solution; they also found a soliton propagation but with a different exponent $\alpha = 1/3$. In order to explain this result, they modified the theory assuming that the velocity at the Plateau border surface is not zero, as in the model by Weaire *et al.* (Poiseuille flow in the Plateau borders), and that the flow in the Plateau borders is plug-like.[38] Suspecting that the difference was due to a different resistance of the surfactant monolayers to the flow, we investigated foams made with SDS solutions with and without a cosurfactant, dodecanol. In microemulsions, a small cosurfactant is frequently needed to fluidify the surface layers; however, here we wanted to increase its rigidity, and we used dodecanol, a cosurfactant of the same chain length as the surfactant. As expected, we found that the exponent α increased when dodecanol was added.[39] The different behavior of the surface layers is not due here to the compression modulus as in foam films such as those studied by Mysels *et al.*:[40] the Plateau borders are thick (fraction of mm) and the surfactant concentration high, so E_{eff} is close to zero. The difference rather comes from the surface shear viscosity η_S, which is much larger when dodecanol is present. Our result showed that the theories of the Weaire and Stone groups apply to different extreme cases in which the surfactant monolayer is either fully rigid or fully mobile.

3.3. Foam coarsening (disproportionation)

The study of foam coarsening in draining foams is difficult because the liquid fraction ϕ changes with time, until ϕ reaches values of a few percent, depending on the bubble size and foam height.[41] These foams are called dry foams. In order to study coarsening of foams containing larger amounts of liquid, called wet foams, we submitted a project to the European Space Agency for the study of foams in the International Space Station (ISS). The plan was to study a large range of liquid fractions up to the jamming transition (at which bubbles unjam) and beyond, in bubbly liquids (Fig. 8). The project was selected in 1999, and the experiments started in 2020.

A theoretical description of the process only exists in the limits of small and high liquid fraction ϕ: the average bubble size is predicted to increase with time t as t^{β} with respectively $\beta = 1/2$ for dry foams and $\beta = 1/3$ for bubbly liquids in which the process is similar to Ostwald ripening. The intermediate growth regime remained mostly unexplored, both experimentally and theoretically. The transition between the two growth regimes was expected to occur at the jamming point, where ϕ is equal to the random close packing volume fraction ϕ_{rcp}, beyond which the bubbles become spherical ($\phi_{\text{rcp}} = 0.36$ for monodisperse bubbles) (Fig. 8). Similar jamming transitions are encountered in other assemblies of randomly packed objects (sand, clay, emulsions; pedestrian and car traffic) and currently attract much interest.

We observed that bubble size distributions evolve towards a hierarchical stationary regime in which small bubbles are over-represented compared to observations on Earth[42] (see Fig. 9). This was completely unexpected as numerical simulations predicted monomodal distributions. We explained the origin of the peculiar size distribution by arguing that the Plateau borders are larger in wet foams and can accommodate small bubbles, disconnected from the foam network (called roaming bubbles), which coarsens much more slowly.

The change in exponent β was found to be more rapid than expected and to occur at a liquid fraction ϕ (~39%) larger than ϕ_{rcp} (31%, estimated taking into account bubble polydispersity). This other unexpected phenomenon was related to adhesion

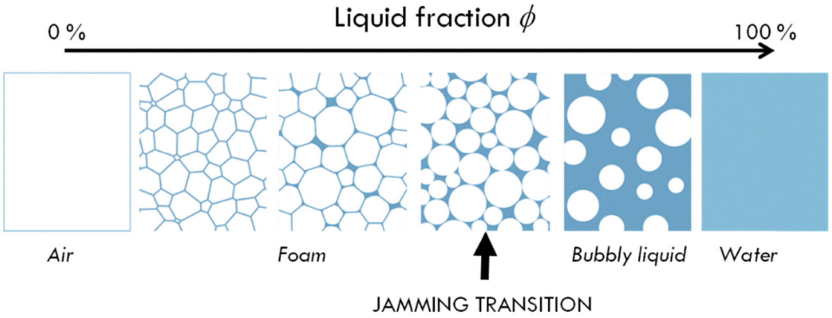

Fig. 8 Sketch of the evolution of the foam structure with increasing liquid fraction (jamming occurring at the random close packing volume fraction ϕ_{rcp}).

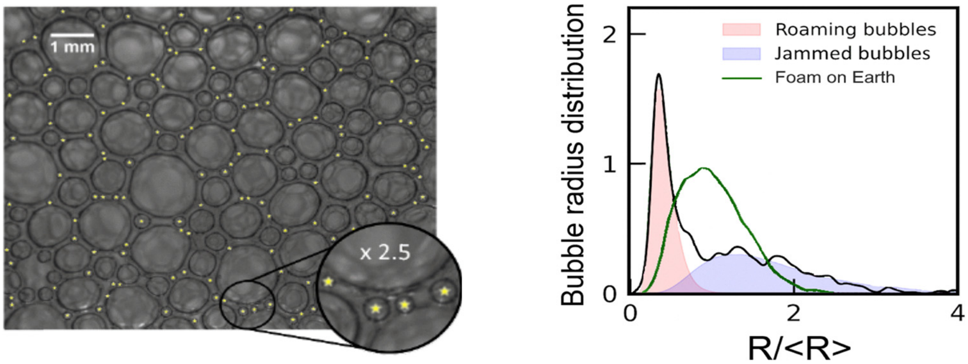

Fig. 9 Left: Wet foam image, obtained under microgravity conditions, revealing the presence of small bubbles disconnected from the bubble network. ϕ = 15%. Right: Bubble radius distributions. Reprinted from ref. 42.

between bubbles.[43] The coarsening rate was found to be proportional to the fraction of bubble surface covered by flat films but only up to ϕ_{rcp}.

Measurements of the coarsening rate performed with different foaming solutions were found to be in very good agreement with the theoretical predictions up to $\phi = \phi_{\text{rcp}}$.[44] This agreement was questioned before, on the basis of measurements made on Earth. However, the discrepancies likely arise from contributions of drainage and coalescence, which introduce errors.[45] Above the ϕ_{rcp}, an appreciable quantity of gas begins to diffuse across film borders, introducing unexpected differences depending on the surfactant.

Multiple light-scattering experiments were also performed and are being analyzed. The modeling of wet foams needs to be improved to achieve a full understanding of the ISS experiments.

3.4. Coalescence

In this section, I will address the topic of coalescence at rest and in the absence of antifoam agents. There are numerous papers in the literature on the topic of coalescence that relate the probability of film rupture to various parameters, liquid fraction ϕ, capillary pressure P_{cap}, and bubble radius R. These parameters are in fact linked; for a small ϕ, for instance:

$$P_{\text{cap}} = \frac{\gamma}{R\sqrt{\phi}} \tag{8}$$

In order to identify the critical parameter, we performed experiments with 2D foams in which the capillary pressure can be varied in a controlled way. We found that film rupture is stochastic and that the control parameter is the contact area between bubbles (film area, see Fig. 10).[46]

Note that this hypothesis was put forward by de Gennes in the 90's[47] and used by Jérome Bibette and his coworkers in order to interpret emulsion experiments.[48] As mentioned earlier, one possible coalescence mechanism involves holes opening in the films during surface concentration fluctuations (Fig. 7).

De Gennes proposed a complete model for emulsion film rupture, which was unfortunately unpublished.[47] He wrote the frequency of coalescence per unit area as

$$\omega = \omega_0 \exp\left(-\frac{U*}{k_{\text{B}}T}\right) \text{ with } \frac{U*}{k_{\text{B}}T} = \frac{(\Delta\Gamma)^2}{\delta\Gamma^2} = \frac{(\Delta\Gamma)^2 E A_{\text{hole}}}{\Gamma^2 k_{\text{B}} T} \tag{9}$$

where $U*$ is the activation energy, ω_0 is a molecular frequency ($1/\omega_0$ being on the order of the hole dimension, times the velocity of compression waves), $\delta\Gamma^2$ is the mean square value of the fluctuations of the surface concentration Γ and $\Delta\Gamma$ is the variation in Γ necessary to suppress the repulsion forces between film surfaces that forbid coalescence.[47] The coalescence process is similar in foams; thus, the model applies to both types of dispersions.

The activation energy in eqn (9) is proportional to the intrinsic modulus E because the nucleation of holes is extremely rapid (~1 ns) and the surfactant has no time to dissolve in the bulk. This was confirmed with experiments on soap films by Karol Mysels and coworkers,[49,50] who showed that the

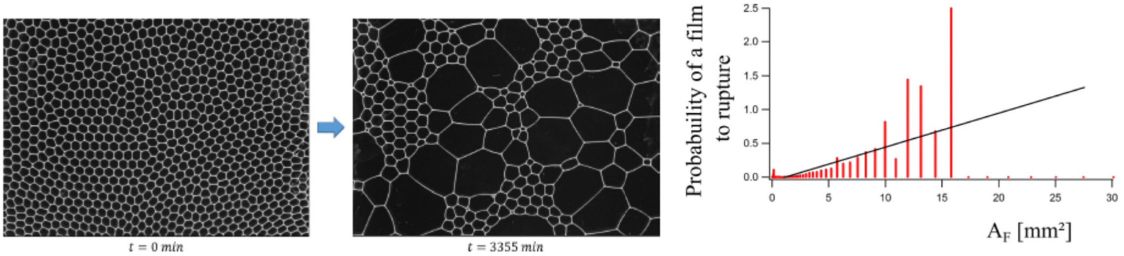

Fig. 10 Left: 2D foam images at different times. Right: Probability of film rupture *versus* film area. Reprinted from ref. 46 with permission from APS, copyright 2019.

surfactant layer was indeed compressed at the film surfaces during hole expansion.

Foam stability experiments confirmed that the higher the E, the more stable the foams are, as predicted by eqn (9).[51] However, there are some exceptions; foams made with solutions of nonionic surfactants ($C_{12}E_6$) are much less stable than those made with dodecyl maltoside ($C_{12}G_2$), despite the modulus E being about the same. The difference between the two surfactants possibly arises from differences in the surface shear viscosity η_S that may affect ω_0, with the η_S being larger for $C_{12}G_2$.[52] This viscosity difference could arise from hydrogen bonding, shown to affect foam stability by Cosima Stubenrauch and coworkers.[53]

Note that the energy of activation is proportional to the A_{hole} that is unknown. $A_{\text{hole}} = \pi a^{\star 2}$, where $a^\star$ is the critical hole radius below which holes close up and above which they open. It is generally assumed that $a^\star$ is comparable to the film thickness, but proofs are missing.

4. Emulsions

Emulsions, as foams, are dispersions stabilized by surface layers. The main difference lies in the sizes, as drops are generally smaller than bubbles.[2] As in foams, gravity promotes the separation of the continuous phase: drop sedimentation or creaming leads to the formation of concentrated emulsions in which drops are jammed. Larger drop concentrations can be reached by centrifugation or osmotic compression. These emulsions are called high internal phase emulsions (HIPE) and have a structure similar to that of foams; they were called biliquid foams by Cabane and coworkers.[54] In turn, dilute emulsions are similar to bubbly liquids.

As foams, emulsions destabilize with time due to several processes: gravity-induced creaming or sedimentation, possibly accelerated by the formation of drop clusters (flocculation), Ostwald ripening and drop coalescence. Although creaming and sedimentation are qualitatively understood, the classical Ostwald ripening model fails.[55,56] My work was devoted to the coalescence process, which is also still poorly understood. Because of the numerous open problems, I will first describe the present state of the art.

4.1. O/W or W/O structure

As microemulsions, emulsions can have O/W or W/O structures. How these structures are obtained depends on the emulsification process, on the O/W ratio and mainly on the type of surfactant used. Bancroft proposed in 1913 that emulsions that form are those for which the surfactant is soluble in the continuous phase.[57] The origin of this rule is still under discussion. It was postulated early that there is a correlation between the monolayer spontaneous curvature $\mathcal{C}_0$ and emulsion type, as in the case of microemulsions. In their oriented wedge theory of 1917, Harkins *et al.* and Langmuir proposed that the surface tension of drops is smaller if the surfactant layers have a suitable curvature[58,59] (see Fig. 11a). Hildebrand criticized this viewpoint in 1941, saying that the surfactant layer curvature cannot significantly affect the surface tension of large emulsion drops and that a thermodynamic explanation would fail anyway because emulsions are only kinetically stable.[60] Another explanation was put forward by Kabalnov and Wennerstrom, who revisited the oriented wedge theory of Harkins and Langmuir.[61] They proposed that the film rupture is thermally activated through the nucleation of holes and that the activation energy is related to the curvature energy of the surfactant layer covering hole edges (Fig. 11b): the edge curvature for the hole with the smallest activation energy is of the same sign as the spontaneous curvature $\mathcal{C}_0$. Note that, as stated by the authors in the introduction of their paper, the model is limited to the case of "stable" emulsions formed with an excess of surfactant above the Cmc, whose lifetimes are on the order of hours or more. The short-term rupture (occurring at low surfactant concentrations) depends on film thinning hydrodynamics and hydrodynamic stability, while the long-term stability is controlled predominantly by hole nucleation in emulsion films.

In order to explain the Bancroft rule, Hildebrand proposed a different argument in 1941, which is kinetic in nature and applicable to both stable and unstable emulsions: when oil and water are shaken, both oil and water drops are produced;

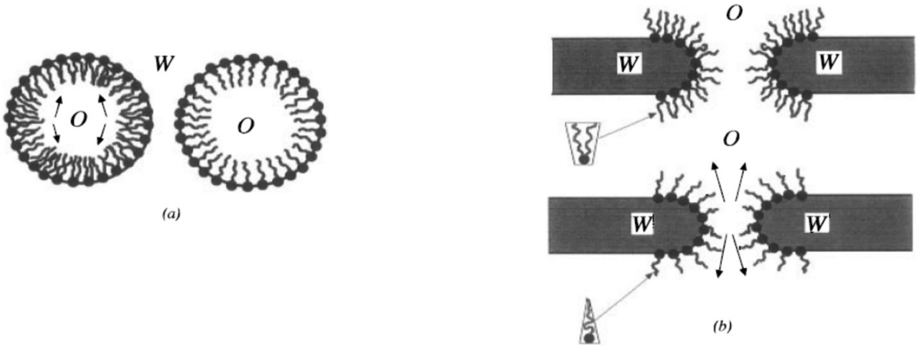

Fig. 11 (a) sketch showing that two-chain surfactants have difficulties forming oil drops in water; (b, top) monolayer spontaneous curvature fits that of the hole edge and the rupture occurs without a barrier. (b, bottom) monolayer at the edge of the hole nucleus is frustrated and a barrier for hole nucleation is present. Reprinted from ref. 61 with permission from ACS, copyright 1996.

during drop encounters, films are formed and resist thinning due to the surface tension gradients generated.[60] Citing Hildebrand: ''the resistance to sudden rupture is much stronger if the emulsifying agent is present in the film liquid, which is the external phase, than if it is in the larger mass of emulsified drop, the internal phase. The reason for this is that there is very little soap available in a thin film to migrate to the new surface and weaken it, while there is an ample supply if it is soluble in the liquid outside of the film'' While both oil and water drops are produced, only those with the lowest coalescence rate survive, in agreement with the Bancroft rule. A cartoon illustrating these ideas is shown in Fig. 12.

During thinning of films between approaching emulsion drops, the surfactant is entrained toward film borders. Because the surface tension is smaller when the surface concentration Γ is larger, tension gradients appear, giving rise to forces opposing film thinning, called Marangoni forces. As Hildebrand proposed, surface tension gradients persist longer when the surfactant is solubilized in the continuous phase because when the films are very thin, they do not contain enough surfactant to replenish film surfaces. In turn, when the surfactant is in the drops, surface replenishment is rapid, Marangoni forces are suppressed and film thinning is very rapid; instabilities may then lead to film rupture, even before an equilibrium thickness is reached. Fig. 12 represents two drops separated by a film of uniform thickness. Films between approaching drops are frequently deformed and might not even form at all if the drops are small and the velocity of approach is small.[62] But if the local distance between film surfaces is small enough, Hildebrand's argument remains valid.

Various experiments confirmed this picture: films in Sheludko cells,[63] films between drops and macroscopic oil–water interfaces[64] and antibubbles (air films immersed in a surfactant solution).[65]

In summary, there are two main types of coalescence processes in emulsions (and foams):

- Rapid coalescence (a few minutes or so): when drops approach rapidly and no equilibrium film is formed before they coalesce; this is either because there are no repulsive forces between drops, or because these forces, as well as the Marangoni forces and the surface viscosities, are small, and hydrodynamic instabilities develop.[66,67] The films rupture generally at a critical thickness h_c on the order of $(A_H R/\gamma)^{1/3}$, where A_H is the Hamaker constant, and R is the drop radius; typically, h_c is a few tens of nanometers.[68] This type of coalescence is generally deterministic and occurs, for instance, when the surfactant concentration is well below the critical micellar concentration (*C*mc).
- Slow coalescence (hours and more): occurring well after equilibrium films between drops are formed. The film rupture is stochastic and is expected to occur through thermally activated nucleation of holes in the films.

4.2. Coalescence in unstable emulsions

Unstable emulsions generally contain small surfactant quantities. Exceptions are emulsions made with Winsor systems close to the interfacial tension minimum: despite containing large quantities of surfactant, these emulsions are very unstable. This feature was well known for 50 years[69] but remained unexplained until measurements of the surface compression modulus in low interfacial tension systems became possible (Section 2.2). Fig. 13 shows the time required for the separation of water and oil in a cyclohexane–water–SDBS–*sec*–butanol–NaCl system.[32] Water separation is due to creaming in O/W emulsions and coalescence in W/O emulsions. Oil separation is, in turn, due to coalescence in O/W emulsions and to sedimentation in W/O emulsions.

It can be seen in Fig. 13 that the separation times are fractions of minutes close to the optimal salinity, similar to

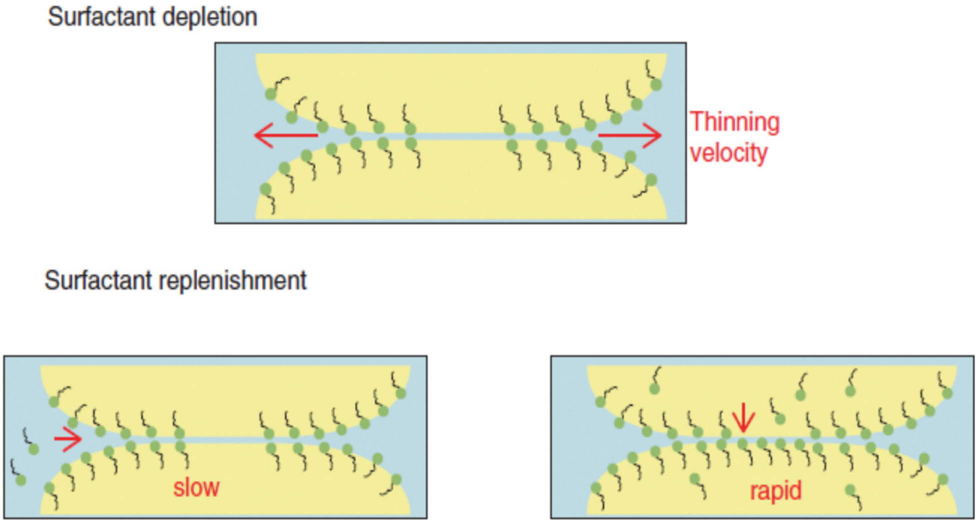

Fig. 12 Schematic representation of the thinning of films between approaching emulsion drops; top: surfactant is entrained during thinning towards the film borders, resulting in surface tension gradients; hence, Marangoni forces oppose film thinning; bottom: the tension gradients heal more rapidly when the surfactant is present in the drops.

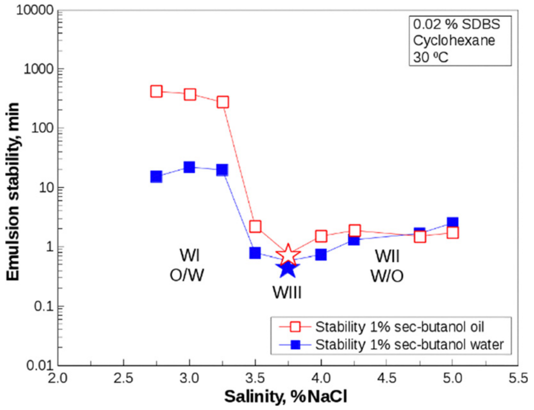

Fig. 13 Plot of time to resolve 60% of oil (red points) or water (blue points) *versus* salinity in a cyclohexane–water–SDBS–*sec*–butanol–NaCl system. Reprinted from ref. 32 with permission from ACS, copyright 2018.

those of surfactant-free emulsions. In this case, equilibrium films likely do not have time to form, and film rupture is related to hydrodynamics. Note that Ostwald ripening is much slower than the rapid coalescence observed in these systems and cannot influence the separation times. The partition coefficient of the surfactant between oil and water was measured in the system shown in Fig. 13 and found to be equal to 1 at the optimal salinity. The drop approach is very rapid because when the surfactant is equally soluble in oil and water; whatever the type of emulsion film, surface tension gradients heal rapidly. The Marangoni forces are related to the modulus $E_{\text{eff}}\,(\omega)$, where $1/\omega$ is of the order of the time of approach of drops (see Fig. 6). In view of the lifetimes shown in Fig. 13, this time is on the order of seconds, hence close to the frequency at which E_{eff} has been measured and found to be very small (Fig. 13). The drop approach is rapid but not rapid enough to prevent surfactant dissolution in the bulk, explaining why the Marangoni forces are much smaller than those expected from the intrinsic modulus E. As the drop approach is rapid, hydrodynamic instabilities may then develop and coalescence may occur before equilibrium films can form.[32] Similar results were obtained for all the other systems investigated.[70]

4.3. Demulsifiers

Demulsifiers are molecules used to accelerate emulsion separation when one of the phases needs to be recovered. They are usually small molecules, unlike antifoam agents, which are not efficient with emulsions. Salager and coworkers have shown that efficient demulsifiers should be surface-active and added at a concentration $C_D{}^*$ in order to reach the so-called optimum formulation.[71] The fact that the demulsifier should partition equally between oil and water was also demonstrated in later studies of Darsh Wasan and his coworkers.[72] It was tempting to investigate if the compression modulus was also minimum for a demulsifier concentration $C_D{}^*$. Our measurements with a variety of systems confirm this fact and support the interpretation discussed earlier, namely that Marangoni forces are almost suppressed during the approach of drops and that these drops can coalesce rapidly when in close contact without forming equilibrium films.[73,74]

4.4. Coalescence in stable emulsions

When equilibrium films have time to form, the rupture process is different, thermally activated and stochastic, instead of being ruled by the hydrodynamics of film thinning. Two models for film rupture were proposed, one related to monolayer compression described in Section 3.4 and one related to monolayer curvature described in Section 4.1. In the second model, Kabalnov and Wennerstrom proposed that the curvature of the edge of the hole of which the activation energy is the smallest is of the same sign as the spontaneous curvature. This model explains the Bancroft rule as well as its exceptions.[75] It also explains why the emulsions obtained with Winsor I and Winsor II systems have a stability that decreases with decreasing surface tension, whereas the opposite is expected from the model involving monolayer compression.

Bibette and coworkers performed experiments with monodisperse emulsions made with SDS and silicon oil (to avoid Ostwald ripening). The emulsions were concentrated using osmotic compression. They found that the lifetime of the emulsion decreases when the drop fraction ϕ_d increases.[76] Assuming that this variation is due to that of the fraction of drop surface covered by films $f(\phi_d)$, I plotted in Fig. 14 the results together with a calculation of $f(\phi_d)$ made using the recent model by Reinhard Höhler and coworkers.[77]

This confirms that the frequency of coalescence is proportional to the area of contact between drops, as discussed in Section 3.4. Bibette and coworkers later elaborated a model for the frequency of coalescence from experiments with concentrated emulsions.[79] They performed experiments with silicon oil-in-water emulsions stabilized by nonionic surfactants and varied the temperature to determine the activation energy U^*, which was found to be on the order of 50 k_BT. De Gennes

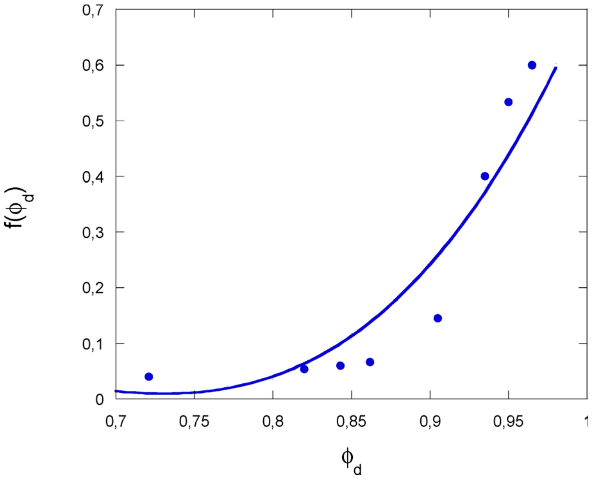

Fig. 14 Fraction of drop surface covered by films deduced from measurements of coalescence frequency in silicon oil-in-water emulsions plotted as a function of the drop volume fraction. Reprinted from ref. 78 with permission from Elsevier, copyright 2025.

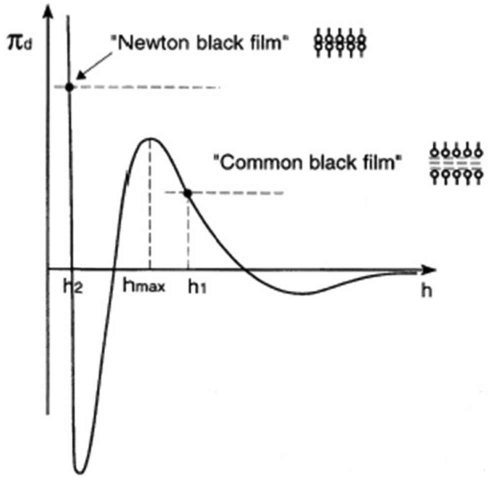

Fig. 15 Schematic of variation in force per unit area (disjoining pressure π_d) between water film surfaces with film thickness h for water films and ionic surfactants.

estimations of U^* were larger, which led him to unrealistically large emulsion lifetimes and to propose that coalescence cannot be thermally activated and occurs due to the presence of contaminants acting as antifoams.[80] However, his estimations were too large because he used the value of film thickness for ionic surfactants, whereas films of nonionic surfactants are much thinner (see Fig. 15).

Fig. 15 shows the force per unit area between water film surfaces (disjoining pressure π_d) covered by monolayers of ionic surfactants, including van der Waals attractive forces and electrostatic and short-range repulsive forces, *versus* film thickness h. The short-range force is attributed to hydration and hydration forces.[81] Under moderate applied pressures, the equilibrium thickness h_1 is large, a few tens of nanometers, and the film contains a significant amount of water and is called a common black film. When the applied pressure is larger than the maximum in π_d, the film is a much thinner surfactant bilayer and is called a Newton black film. When the surfactant is nonionic, the electrostatic repulsion is generally absent, and the films are Newton black films ($h_2 \sim 5$ nm).

In order to investigate the possible role of the modulus E, we planned experiments with O/W emulsions made with two alkanes, decane and tetradecane, and the surfactant diethylhexyl sulfosuccinate (AOT)[82] during the PhD thesis of Annie Colin. The emulsions were concentrated using osmotic pressure in order to decrease their lifetimes. We first found that decane emulsions are much less stable than tetradecane emulsions, although E is smaller at tetradecane–water interfaces. The stability difference is, in fact, due to Ostwald ripening because decane is more soluble in water than tetradecane. Traces of tetradecane were added to decane to halt ripening, and the decane emulsions became then the most stable, as expected.

We later performed experiments in collaboration with Véronique Schmitt. We used other concentrated emulsions (ϕ_d = 78%) made with octane and different surfactants, ionic (alkyl trimethyl ammonium bromides C_nTAB) and nonionic ($C_{12}E_6$ and $C_{12}G_2$).[83] The emulsions made with DTAB were found to be less stable than those made with TTAB and CTAB emulsions, that evolve very similarly, and still more stable emulsions were obtained with $C_{12}G_2$. This is in qualitative agreement with the measurements of the compression modulus: $E(C_{12}TAB) < E(C_{14}TAB) \sim E(C_{16}TAB) < E(C_{12}G_2)$. The frequency ω could not be determined accurately because these emulsions have very long lifetimes. The same unexplained difference as for foams was found between $C_{12}E_6$ and $C_{12}G_2$. The emulsions made with $C_{12}E_6$ were so unstable that they could not be concentrated up to ϕ_d = 78%, whereas the E values for the two surfactants were similar.

More recently, we undertook experiments with the same surfactants, in which we allowed the emulsions to concentrate upon creaming. These experiments are similar to those of François Lequeux and coworkers who showed that they allow determination of the frequency of coalescence.[84] The aim was to relate more quantitively the experiments with the compression modulus. Unfortunately, the emulsions were still more stable than in the previous experiments, because ϕ_d was smaller (close to the jamming value). The accuracy of the measurements was still insufficient to make a precise comparison with models, with the exception of C_{10}TAB, for which U^* was found to be proportional to E. The same unexpected differences were found between $C_{12}E_6$ and $C_{12}G_2$. The concentrations used for C_{12}TAB, C_{14}TAB and C_{16}TAB were smaller than for C_{10}TAB (the Cmcs are smaller), and the electrostatic interactions are larger. The results obtained with the long-chain TABs suggested that coalescence might proceed in two steps, first a transition between CBF and NBF, and then NBF rupture.

The curvature model by Kabalnov and Wennerstrom accounts for the fact that emulsion stability decreases with interfacial tension in Winsor systems, whereas the compression model predicts the opposite. However, the curvature model implies that the surface concentration is constant: the surfactant should therefore desorb during hole opening, although the opening time is expected to be much shorter than the time of surfactant exchange between film surfaces and bulk. It is possible that when the interfacial tension is low and the interfacial roughness is large, the surfactant expelled from the hole remains in the film, resulting in a transient increase in the roughness, as during the opening of holes in vesicles.[85]

In their experiments, Lequeux and coworkers used W/O emulsions stabilized with a nonionic surfactant (Span 80).[84] Afterwards, they performed experiments with mixtures of Span 80 and Tween 20 to vary the spontaneous curvature of the surfactant layer. Their results are consistent with the model by Kabalnov and Wennerström.[86] More work is clearly needed to identify the origin of the activation barrier (compression or curvature energy) and the possible role of surface thermal roughness, and to elucidate how thick common black films rupture.

5. Conclusions

Surfactants allow one to obtain extremely varied model systems, with very rich behavior, and are connected to many fundamental problems in the field of soft matter. Foam films, for instance, allow us to explore the new world of nanofluidics. It is a domain where physics and chemistry are strongly interrelated: an understanding of the problems requires knowledge of the chemical composition of the systems. The domain is connected to many practical problems of our everyday life: food, cosmetics, detergents, *etc.*, hence the interest from many industrial companies in this field of academic research.

In this review, I showed how useful it is to relate the properties of surfactant monolayers to the behavior of microemulsions, emulsions and foams. Although the equilibrium properties of surfactant layers are reasonably well understood, their dynamic properties are not. There are still many open issues, even with classic synthetic surfactants, for instance, in the long-standing coalescence problem. Knowledge of surface rheology is still insufficient, and the frequency dependence and the non-linearities of the different moduli should be investigated in more detail. New biodegradable surfactants are beginning to be investigated: they frequently form solid-like layers, the rheological behavior of which is more complex and is being investigated. Stimuli-responsive surfactants also have an interesting future, as well as surfactants for ionic liquids. Not mentioned in this review are the mixed systems between surfactants, polymers, proteins and/or particles, which are frequently found in applications and the behavior of which is still more complex. Better knowledge of surface rheology will help to achieve, among other purposes, a better control of emulsion and foam properties. Because microemulsions are thermodynamically stable, a good understanding of what controls their properties has been available since the 80's. However, the main control parameters are the curvature moduli, which are difficult to measure. Numerical simulations of surfactants are becoming more accurate and will certainly help progress in the future.

Conflicts of interest

There are no conflicts to declare.

Data availability

There are no data from new experiments in the paper.

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