

HOW SURFACTANTS STABILIZE EMULSIONS

Copolymer surfactants start on page 10

I. Stabilization of a concentrated emulsion with a very viscous dispersed phase

Daniel D. Joseph, Oct. 6, 1996

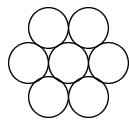
- These are tentative thoughts about how surfactants might suppress coalescence in the case of orimulsions.

I think that the fact that the dispersed phase is very concentrated and very viscous alters the mechanisms which have been proposed for stabilization and they appear not to have been discussed in the literature I read:

- [1] D.A. Edwards, H. Brenner, Darsh T. Wasan, Interfacial transport processes and rheology. Butterworth – Heinemann Boston, 1991.
- [2] Ivan Ivanov, Interfaces, foams and emulsions, Course notes, 1994 (unpublished).
- [3] A.K. Malhatori and D.T. Wasan, Effect of surfactant adsorption – desorption kinetics and interfacial rheological properties on the rate of drainage of foam and emulsion films. *Chem. Eng. Comm.*, **55**, 95–128 (1987).

I read many other works, which will be cited as needed, but the ones listed above form the basis for the discussion below.

- COALESCENCE. For two or more drops



to coalesce, 1.) The water between the drops must be squeezed out. In the literature this is considered under *drainage* (into Plateau borders). I prefer to think of ringing out the water in wet clothes before drying them rather than “collisions” which is a concept from the kinetic theory of gases which I think inappropriate for orimulsions. 2.) The drained film must *rupture*; as long as there is a film between, the drops won’t coalesce.

So we have to deal with

1. DRAINAGE
2. RUPTURE

- DRAINAGE: It is generally thought that Maragnoni effects oppose film drainage. I am going to present arguments which say that Maragnoni effects are not important in the stabilization and further, the surpassingly high viscosity of the dispersed phase already leads to maximum inhibition of drainage, according to Reynolds theory.

The squeezing is the driving motion producing drainage. The velocity and shear tractions are continuous across the oil/water interface when there is no interfacial dynamics due to surfactant. The circulation in the drop drives a tangential motion in the film which is regarded as a basis for the drainage problem [2]:

“5. THINNING AND RUPTURE OF EMULSION FILMS (Ivanov [2])

5.1 THINNING AND EMULSION OF FILMS IN THE ABSENCE OF SURFACTANTS

The theory of emulsions is considerably more difficult than that of foams due to the need to account for the circulation of the fluid *inside* the droplets and its coupling with the fluid motion in the continuous phase.”

All the other authors cited here base their thinking about Maragnoni effects on secondary motion in drops. A cartoon of this from [2] is shown below:

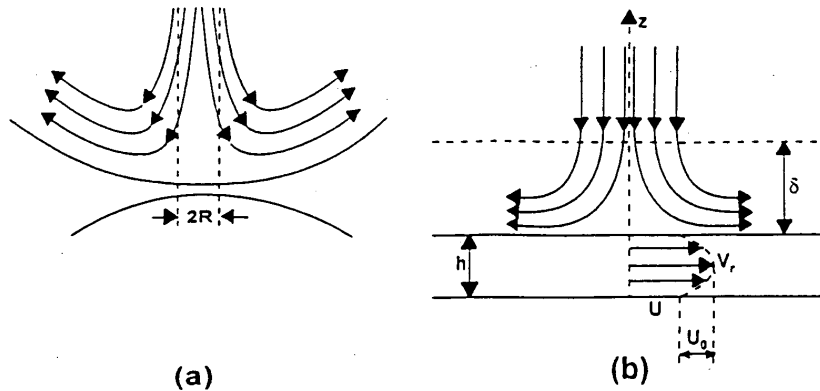


Figure 5.1

Another cartoon from [1] shows how the surfactant works to restore a no-slip condition at the oil-water surface. Figure 5.1(a) shows how the squeezing motion creates a tangential motion of the fluid in the drop which produces a tangential motion of the interface shown in figure 5.1(b) and in figure 11.3-3([1], pg 296)

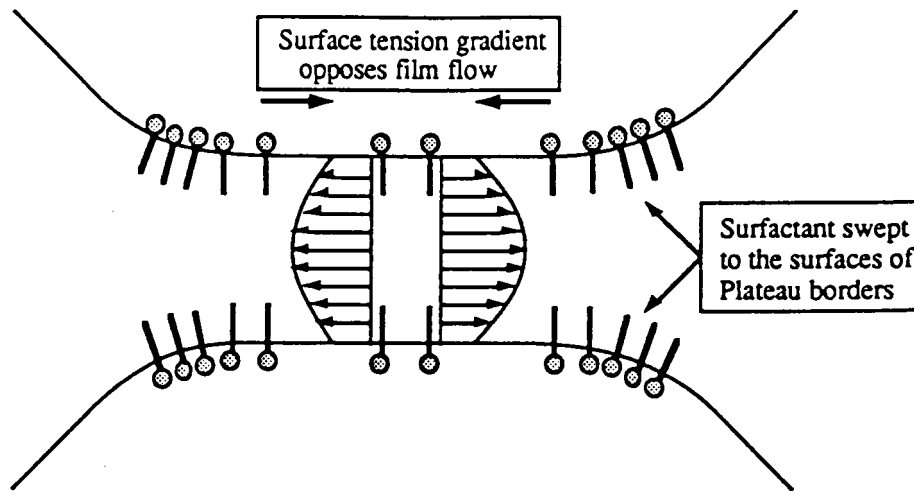


Figure 11.3-3 Marangoni effect in the thin film drainage process. Surfactant is swept to the Plateau borders by flow in the film and droplet phases, thereby creating surface concentration gradients which engender surface tension gradients.

It is this tangential motion which is inhibited by surfactants absorbed on the interface. The tangential motion generated by squeezing sweeps surfactant out of the gap. This depleted region gives rise to an increased surface tension locally because surfactant lowers tension. The increased surface tension gives rise to a shear stress which opposes the sweep-out motion due to squeezing. The most extreme form of opposition would completely immobilize the interface.

- A SPHERICAL DROP OF A DIFFERENT FLUID

V.G. Levich, *Physico-chemical Hydrodynamics*, Prentice-Hall 1962, was the one who popularized the notion that a fluid-fluid interface could be rendered immobile by Marangoni effects. Batchelor, *An Introduction to Fluid Dynamics*, Cambridge University Press, 1967, p. 237:

The speed of a spherical gas bubble rising steadily under gravity is thus given as $\frac{1}{3}a^2g/\nu$. However, observation of the terminal speed V of very small gas bubbles suggests that the drag is often closer to the value $6\pi a\mu V$ than to the expected value $4\pi a\mu V$; this is believed to be because any surface-active impurities present in the liquid are likely to form a mesh of large molecules at the bubble surface and to cause the interface to act partially like a rigid surface.

Batchelor's explanation of how the surfactant immobilizes the surface is, of course, way over-simplified. The way which surfactants work, which we discussed above, is exhibited for the moving drop in the cartoon shown in figure 5.6-1 from Edwards et al [1] which is shown below and on the cover of their book:

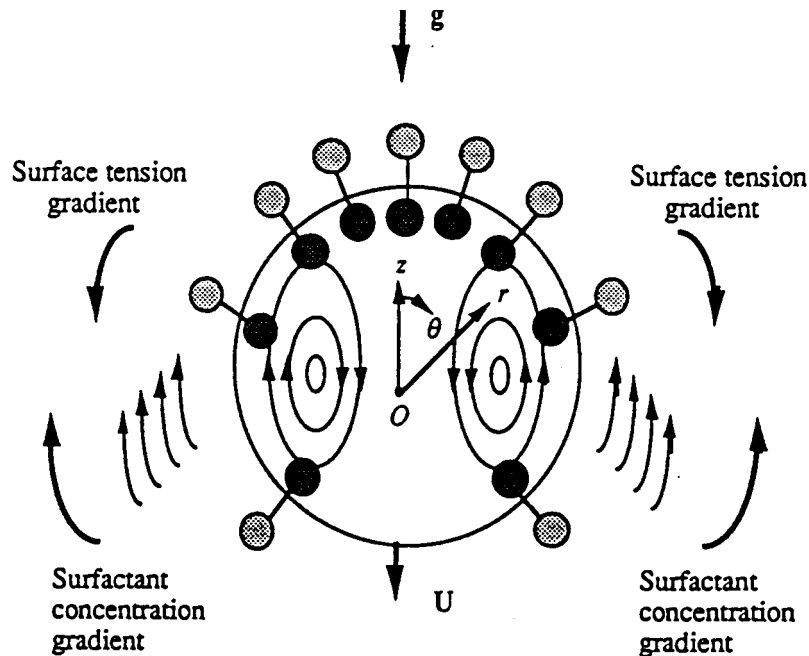


Figure 5.6-1 Surface tension gradients are created by the convective sweeping of absorbed surfactant to the rear of the settling droplet. This phenomenon acts to diminish the sedimentation velocity of the droplet as a whole. (Surfactant molecules are disproportionately idealized in the figure.)

- MARAGNONI EFFECTS ARE TOTALLY SUPPRESSED WHEN THE VISCOSITY RATIO IS LARGE

A cartoon of the spherical drop moving in a different fluid is shown here (from J. Happel and H. Brenner, Low Reynolds Number Hydrodynamics, Prentice-Hall, Inc., 1965, pg 129).

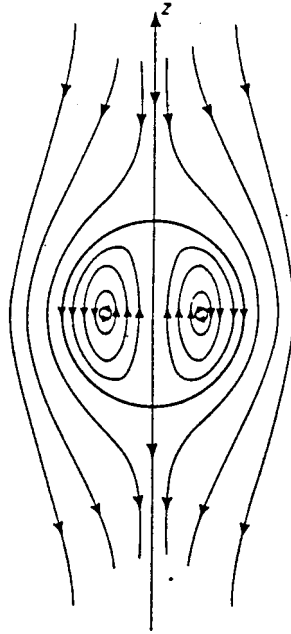


Figure 4-21.1. Streamlines for liquid droplet showing internal circulation.

The drag on the drop is given by

$$\frac{3}{2} \left(\frac{\mu + \bar{\mu}}{\mu + \frac{3}{2}\bar{\mu}} \right) \text{ times } \left(\begin{array}{l} \text{drag on a} \\ \text{solid sphere} \end{array} \right)$$

where $\bar{\mu}$ is the viscosity of the drop and μ is the viscosity of the other fluid. When $\frac{\bar{\mu}}{\mu} \rightarrow \infty$ (solid drop and orimulsion $\mu = \frac{1}{100}, \bar{\mu} = 1000, \frac{\bar{\mu}}{\mu} = 100,000$). when $\frac{\bar{\mu}}{\mu} \rightarrow 0$ the rise velocity is $\frac{3}{2}$ times the gas bubble.

The velocity on the sphere is continuous but this continuous velocity can be zero in a frame in which the sphere is at rest as it is in the case of a solid sphere. The force that drives the secondary motion in the drop is the shear rate at the

boundary of the drop, just inside. If $\overset{\circ}{\gamma}_o$ is shear rate in the oil and $\overset{\circ}{\gamma}_w$ is the shear rate in the water. The continuity of the shear stress is given

$$\mu \overset{\circ}{\gamma}_w = \bar{\mu} \overset{\circ}{\gamma}_o,$$

hence

$$\overset{\circ}{\gamma}_o = \frac{\mu}{\bar{\mu}} \overset{\circ}{\gamma}_w$$

Since $\frac{\mu}{\bar{\mu}} \rightarrow 0$, $\overset{\circ}{\gamma}_o \rightarrow 0$ and there is nothing to drive the secondary motion in the drop.

You should not be fooled by the streamlines shown in the cartoon; they are always there in Stokes flow, just as shown. The question to ask is how fast is the flow following the streamlines. In the case of the bitumen drops it could take a lifetime for a fluid particle to circulate just once.

- CONCLUSION: The fact that the viscosity of a bitumen drop (10^3 p) is so much larger than water (10^{-2} p) means that the surface of the bitumen drop is immobile. Surfactant action at an interface restricts the mobility of the surface but in the case under consideration the surface is already maximally immobile.

It follows from the arguments just given that Maragnoni inhibition of drainage is not a factor for orimulsions. Drainage is already maximally inhibited by the high viscosity of the drop.

In a subsequent section I will look at the question of surfactant mobility. Formerly, I thought that if the surfactant was not miscible in the oil it could move under Maragnoni forces, but now I think even if the surfactant was not firmly attached it would not move.

- PRACTICAL TEST. We need a test to see if the drop surface is immobile. If the surface is immobile we can predict the drainage rate from the Reynolds lubrication theory.

Malhorta and Wasan [3] describe many drainage tests which might be used by us. They were looking to confirm their theory which does not consider the effects associated with the big difference in viscosity which immobilizes the interface.

Here are some of the results they cite:

DRAINAGE OF FOAM AND EMULSION FILMS

Several investigators (MacKay and Mason, 1963; Sheludko, 1967; Sonntag and Strenge, 1972) have employed the Reynolds equation to describe the film drainage rate. According to Reynolds (1886) model the film thinning velocity, V_{Re} is given by

$$V_{Re} = -\frac{dh}{dt} = \frac{8h^3}{3\mu R^2} \Delta P \quad (1)$$

where

h is half film thickness,

t is time,

μ is viscosity of the film liquid,

R is the film radius,

Δp is the pressure causing drainage.

Equation (1) is similar to the expression obtained by Reynolds to describe the axi-symmetric drainage of a liquid film between two rigid parallel discs. This restricts the applicability of the Reynolds equation to liquid flow between plane-parallel and tangentially immobile film surfaces. Hartland (1967) has shown that due to the mobility of the film surfaces, the rate of film drainage can be several times greater than predicted by the Reynolds model. Several other investigators (Levich, 1962; Jeffreys and Hawksley, 1965; Lucassen *et al.*, 1970; Berg, 1972; Woods and Burrill, 1972; Liem and Woods, 1976) have shown that the hydrodynamic behavior of systems with liquid-liquid interfaces is dependent on the flow in both phases as well as surfactant congregation at the interface.

Johannes and Whitaker (1965) analysed the gravitational thinning of a soap film stabilized by surface active agents. They compared the experimental results with the predictions of the theory and concluded

that either the dilational surface viscosity is several orders of magnitude higher than the shear viscosity or the variation in surface tension gradient is an important stabilization mechanism.

Lee and Hodgson (1968) have examined the influence of interfacial tension gradient on the tangential movement of the interfaces and have discussed its effect on drop coalescence times in dispersions. Ivanov and Dimitrov (1974) included the influence of surface viscosity on the rate of drainage of surfactant stabilized foam films. Their analysis shows that the effect of surface viscosity can be neglected on the rate of film thinning.

Rodoev *et al.* (1974) developed a theory for the drainage of foam films which accounts for the effect of bulk and interfacial diffusion in promoting interfacial mobility. However, their model does not take into consideration the effect of interfacial shear and dilational viscosities on the drainage velocity. The results of their analysis demonstrate that actual velocity of thinning is several times larger than predicted by the Reynolds model and the effect of surface diffusion on drainage velocity increases with decrease in film thickness.

Traykov and Ivanov (1977) have analyzed the effect of surfactants on the rate of drainage of plane-parallel emulsion films. However, they too neglected the effect of interfacial shear and dilational viscosities. They examined the limiting cases, in which the surfactant is soluble only in the continuous phase or the dispersed phase. Their analysis shows that the velocity of thinning is essentially dependent on the bulk viscosity of the film phase liquid. In the presence of a surfactant soluble in the continuous phase, the velocity of thinning is slightly different from that of a foam film, whereas when the surfactant is soluble only in the dispersed phase, the velocity of thinning is much higher and is the same as in a system with no surfactant.

On pages 122 and 123 you can find the following conclusions, which are correct, but show that they have not considered the effects of a surpassingly viscous dispersed phase.

Furthermore, the predictions of the Reynolds model agree with the experimental data only for systems containing high surfactant concentration in the film. This is not surprising in view of the fact that the Reynolds model ignores the impact of interfacial mobility on film thinning by assuming the film surfaces to be tangentially immobile, an assumption justified only at high surfactant concentration. The present

model predicts results which are in fair agreement with the experimental data for all the systems. As remarked by Zapryanov *et al.* (1983), comparison using the model of Traykov and Ivanov (1977) and Good (1974) resulted in poor comparison for systems with low surfactant concentrations in the film phase (system 1 & 3) and at higher surfactant concentrations (systems 2 & 4) the drainage times were identical to those predicted by the Reynolds model.

- SURFACTANT MOBILITY

When you were here last, I was interested in how a surfactant molecule attached to the bitumen. The hydrophobic part of the molecule need not be miscible in the oil and it could attach to the bitumen weakly, not so much because it loves bitumen but because it hates. After thinking about this I concluded that even if the molecule could slide against friction on the bitumen surface it still would not effect drainage. The only way drainage could be altered by surfactant is if it introduced a lubrication layer, a layer of sensible thickness with a greatly reduced viscosity. I can't see this as a possibility so I am led to the conclusion that surfactants don't effect the drainage in the case of orimulsions.

- CLARA'S EXPERIMENT.

Triton 100 (non-ionic) protects bitumen from sticking to itself and from sticking to glass (very astonishing wall treatment). I am asking Clara to write about it in her own words:

An inspiring idea came to us, when setting up an experiment in which two different fluids, water (1cS) and a 400 cS silicon oil, had to be poured within the gap of two concentric cylinders in a vertical position. Then the cylinders had to be sealed and turned to a horizontal position. Finally, we had to wait until the water settled down, due to its higher density, so a perfect horizontal interface appeared. We accidentally noticed that when a non ionic surfactant (Triton-100) was added to the water, the settling period was considerably shorter than with water alone. We decided to test what would happen if instead of silicon oil, we used Zuata.

Due to the high viscosity of this bitumen, we did a different experiment. We prepared a 0.75% surfactant solution, using Triton-100 and distilled water. Then we set up two glass tubes, in a vertical position. We poured distilled water into one of them and the surfactant solution into the other; only half way so we could fill the other half with Zuata. We warmed it up so we could pour it more easily.

We found that when pouring the bitumen into the tube with distilled water alone, a long finger of bitumen entered the water and rapidly went up again, as it was less dense than water. Then, as more bitumen was poured, it just accumulated and stuck on the glass and on itself.

A totally different scenario appeared when pouring the bitumen into the second tube. The same finger entered the surfactant solution and, as soon as it reached the bottom it just made its way up and down several times, before it started to accumulate mainly on top of the solution. However, the early fingers never stuck to themselves or the tube and there was always a small amount of solution rising

along the glass, protecting the bitumen not only from sticking to the glass (very astonishing wall treatment), but from sticking to itself.

After minutes, the bitumen settled down to the bottom of the tube with the surfactant solution; however, even after days, the bitumen has not moved at all in the other tube. In order to clarify if this was a matter of densities, another test was carried out. Bitumen was poured into wide jars with distilled water and the same surfactant solution. In both cases the bitumen settled down.

II. Surfactant Effects of Copolymers

Daniel D. Joseph, Oct. 8, 1996

Block copolymers, because of their amphiphilic character and resulting affinity of homopolymer interfaces, have the potential to reduce the interfacial tension between the immiscible homopolymers.

Edwards, Brenner and Wasan [1] say that:

Synthetic and natural polymers often exhibit a significant surfactant tendency, particularly when the hydrophobic and hydrophilic parts of the molecule are sufficiently separated, as with block and graft copolymers. Carboxylic polymers, sulfonated polymers, phenolic polymers and polyvinyl polymers constitute further examples of polymeric surfactant molecules.

- STABILIZATION OF POLYMER BLENDS

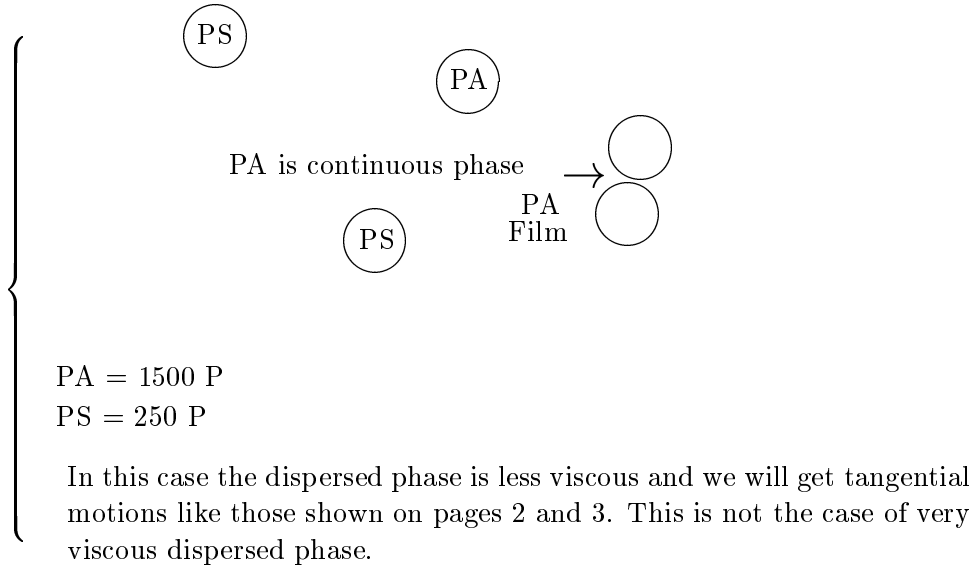
The stabilization is done with copolymers. It appears *not to be known* whether or not the copolymers follow exactly the mechanisms which are known to work for other surfactants. These mechanisms are described in Joseph's Oct. 6 memo and in the references there. The mechanisms for stabilization are

1. MARAGNONI SUPPRESSION OF DRAINAGE
2. FILM RUPTURE

Film rupture is controlled by Van der Waals forces and electric double layers and is described by DLOV theory. There is nothing known about this for polymeric solutions and the effects of copolymer surfactants is also not understood.

YOU CAN'T COALESCE WITHOUT FILM RUPTURE.

Figure 1



SURFACE TENSION IS NOT SO IMPORTANT

(but you must get a decrease when you add the copolymers)

SURFACE TENSION GRADIENTS ARE VERY IMPORTANT

Actually the important quantity is the Gibbs elasticity which is a measure of how fast the surface tension changes when you change the bulk concentration. The surfactant (copolymer) gets absorbed on the interface $\frac{\phi_{PA}}{\phi_{PS}}$. The copolymer is soluble in one or both phases. The solubility appears not to be known. Both cases, (1) the surfactant is soluble in the continuous phase and (2) the surfactant is soluble in the dispersed have been discussed in the literature, (Ivanov [2]) has a nice discussion. The excess of surfactant is called Γ , and the concentration of surfactant (copolymer) in the bulk is ϕ . A Gibbs isotherm relates Γ to ϕ

$$\Gamma = \Gamma_{\infty} \frac{\phi}{\phi + a}$$

where $\Gamma = \Gamma_{\infty}$ when $\phi = \infty$. (We have to watch units, I am being careless). You get the parameters Γ_{∞}, a for this from surface tension versus ϕ measurements (see

Guitian-Joseph on the Shaker bottle, and standard literature). The ideal surface tension curve is of the form:

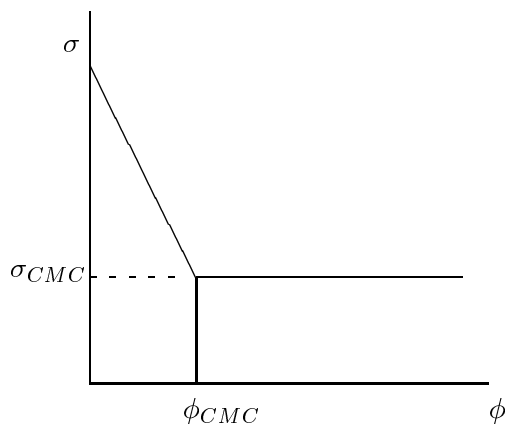


Figure 2. Surface tension σ versus bulk concentration ϕ . ϕ_{CMC} is the critical micelle concentration, σ_{CMC} is the maximally reduced surface tension. The bulk concentration is related to the surface excess by the Gibb's isotherm. We need this kind of graph for block copolymers. I don't think there are any in the literature. The important quantity is the slope $d\sigma/d\phi$; we can get any slope even when the reduction of tension is not so great.

- EVALUATION of the paper

S.T. MILNER & H. XI, How copolymers promote mixing of immiscible homopolymers, *J. Rheol.*, **40**(4), 663–687 (1996)

They are correct to say that the reduction in surface tension is not the main issue. They are looking for the Maragnoni effects of the kind discussed in this memo, but they are very confused. They seem not to have any idea that film rupture is required for coalescence. The surface pressure they talk about is a mystery to me. Their kinetic theory approximations are *totally inappropriate* to a system in which the continuous phase viscosity is 1500P. The use of the ballistic formula (6) here is *ridiculous*. There is no reason for us to consider their confused understanding of Maragnoni suppression of drainage (without rupture; ugh).

- ACTION ITEMS

1. Identify immiscible homopolymers for which we can measure the tension.
2. Identify a copolymer surfactant which is soluble in one phase mainly. This is the phase in which micelles should form after the CMC.
3. Measure σ as a function of ϕ to get a figure like 2.
4. Do this also with melted polymers.