MEMORANDUM

In this document we present some general ideas regarding emulsion stability which we would like to discuss with the group.

COALESCENCE REQUIRES THAT DROPS "TOUCH"

I. Conceptual organization of the idea of touching drops for Orimulsion

How should touching be defined? Is there a minimum distance (say 1000 Aº) behind it? Do we want touching drops to be deformed?

What are "colliding" drops? Should we think of "colliding" as impact, like billiard balls?

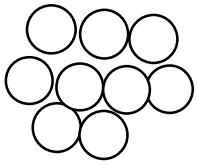
To make "colliding" drops coalesce, we have to have driving mechanisms strong enough and long enough to rupture the film. We should understand the nature of this driving mechanism.

One drop may collide with and then stick to an aggregate.

Squeezing together of many (an array) vs the collision of two drops.

Squeezing requires that you push the water from between the drops of the orimulsion dispersion. The water will move through the bitumen, probably seeking percolated paths which will drain film water from tributaries. It is like ringing water from wet clothes. Squeezing, rather than collisions, is the way we get bitumen drops to coalesce between eccentric rotating cylinders (coalescence meter).

II. MANY AGGREGATED PARTICLES



The words

aggregation, coagulation, flocculation appear to be used as synonyms

Hunter [1993] pg. 47 says that "a systems is said to be colloidally unstable if collisions lead to the formation of aggregates; such a process is called coagulation or flocculation".

We've learned that Orimulsion flocculates. There is evidence of increased viscosity of static emulsions. This flocculation can be remedied by adding electrolyte. All of these is known already, but we can continue to pose questions.

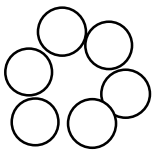
Flocs can be broken by flow.

Does flocculation have any influence on coalescence?

Does preventing flocculation help to prevent coalescence?

III. CONCENTRATION OF DROPS BY FLOW

We discussed local inversion in regions where the emulsions are concentrated by flow; this is different than flocs. We imagined that many drops coalesced at (or near) the same time. This leads to trapping of water in plateau borders. Water was found in coalesced drops.



Do you think many drops can coalesce at or at nearly the same time?

"Nearly" the same could be a rather long time since the coalescence could take a rather long time, even after rupture, because the drop is so viscous. So its shape many not change much for a time.

IV. SHAPE OF ORIMULSION DROPS IN EXTRAORDINARILY CONCENTRATED EMULSIONS

Let us say we have 90% bitumen dispersed into water and the emulsion is in a container open at the top.

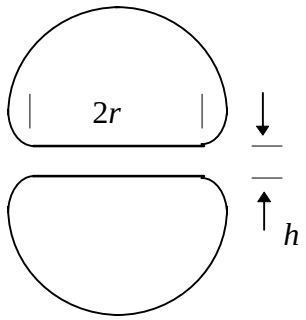
Are the drops spheres or are they distorted?

Obviously you can obtain greater and greater disperse phase fractions by squeezing the drops together. But capillary forces want them to be spheres. If there are no forces to keep the drops deformed, they will become spheres. The height of this dispersed phase oil will rise; more water will be needed to fill the interstices.

Drops of concentrated emulsions will distort in flow. The more concentrated, the greater is the risk of coalescence.

V. SHAPE OF COALESCING DROPS

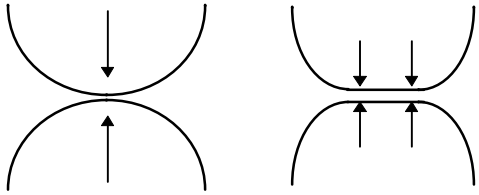
You see cartoons like this (e.g. Ivanov)



Does this picture require an external force to push the spheres together and flatten them?

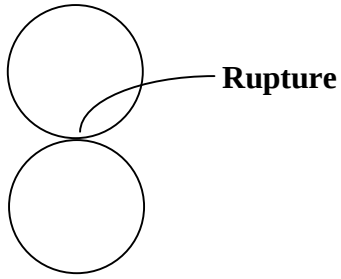
If the answer to the previous question is yes, then h and r could depend on forces arising at remote boundaries.

Another way to ask the previous question is: two-spheres are being pulled together by VW forces, but the film in between does not allow them to coalesce; so the pulling action spreads along a flat film. The film resistance of a draining film first balances the VW forces

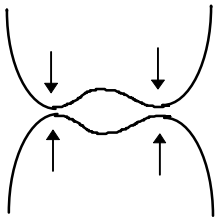


VI. FILM RUPTURES

Can you get rupture at the touching point of good spheres?



Sometimes there is a dimple.



Then rupture could occur at the distinguished points.

Does the rupture always occur at a weak point; then propagates or spreads?

I didn't read anything about this but it seems to me that it is the only possibility. Of course, rupture sites could occur at many points, nearly simultaneously, in a crowded dispersion.

If the rupture occur at weak points, you really need a good covering of surfactant which will protect even the weak points.

VII. VAN DER WAALS FORCES

Usually people use Hamaker's theory in which the van der Waals force is always attractive. Israelachivili data shows a big 3-4 fold difference between

Hamaker's constant computed by Hamaker and Lifshitz theory for H_20-vaccuum-H_20 layers. The Lifshitz theory agrees will experiments and there is no check of Hamaker's theory with experiments (see Table 3.1 of Ivanov notes).

For us, it is important to note that the van der Waals forces fail for water between hydrophobized surfaces because bitumen drops are hydrophobic. In a letter by Ruckenstein and Churaev to J. Colloid Int. Sci. titled "A possible hydrodynamic origin of the force of hydrophobic attraction" one reads:

"Recent experiments (1-10) have revealed strong long-range attractive forces between hydrophobized surfaces immersed in water. These can be greater by orders of magnitude than those predicted on the basis of van der Waals interactions. These attractive forces obey an equation of the same form as the hydration repulsive forces

$$F = K e^{-h/l}$$

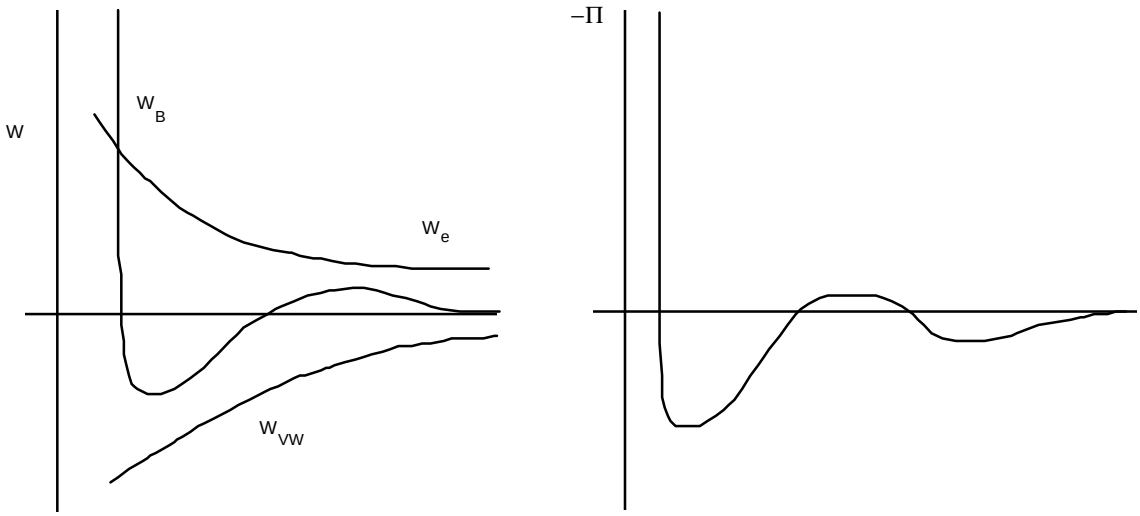
but with K < u and much larger decay length λ. The value of the decay length λ depends markedly on the hydrophobicity of the surface...."

We will raise the idea that the covering of the bitumen drop with surfactant changes the surface of the drop from hydrophobic to hydrophilic. Then the extra strong attractive force would be reduced to something more usual.

As an aside, I would like note that expressions for the van der Waals forces which collapse tiny air bubbles, leading to dissolving of air in water, and expressions for the molecular force which lead to the final breaking of a capillary jet seem not to have been given.

VIII. DISJOINING PRESSURES, DLVO THEORY

The usual picture is:



$$\Pi = \Pi_{VW} - \Pi_e - \Pi_B$$

Π_B is the steric part which depends on surface covering (It's called a Born Layer)

Π_{VW} is the van der Waals attractive force

Π_e is from electric double layer

The DLVO theory is the one you get when the steric part is neglected; it can't be good when steric effects are important. According to Ivanov and others it's not a good quantitative approach even when steric effects are negligible.

IX. STERIC EFFECTS

These appear to be associated with surface covering in which the covering protect the drops from coalescing. Good [1974] says that the Born repulsion pressure is due to steric hindrance between surfactant molecules on opposing interfaces and represent the barrier to further thinning, setting an absolute

minimum on equilibrium film thickness. He says that E.M. Duyvis "The equilibrium thicknesses of free liquid films" PhD thesis, Delft (1962), suggests that the simplest form for Π_B would be to have a zero Born pressure for film thicknesses greater than some minimum value, and an infinite pressure for film thicknesses less than this minimum. Ivanov described the steric effect of nonionic surfactant molecules anchored on the liquid interface.

Can you get a rupture of protected surfaces where the repulsive forces are infinite?

Probably not, unless you break the protection which could be a good idea for Orimulsion.

What is the mechanism by which steric forces create a repulsion?

I think that water is the real protection and that lubrication forces in the water produce the protection. The covering holds water perhaps like a paint brush, which will remain wet for a large time even though the water is not chemically bound.

An analogous kind of protection is powdering the dough with flour. The non powdered dough is sticky, but if the dough is well covered with flour it won't stick.

You can cover bitumen with clay particles suspended as a colloid in water. If there is enough clay in the water, it will protect the bitumen from sticking to itself. This may be because the clay holds the water.

Is it possible to get a scanning electron microscope photograph of bitumen covered and not covered by Intan 100?

X. THE MAIN STABILIZING EFFECTS OF ADDING INTAN 100 TO ORIMULSION.

The main effect is to change the hydrophobic surface to a hydrophyllic surface by covering it with surfactant with hydrpohillic heads. If other hydrophillic moeties are on the bitumen drop, so much the better. Here are some properties to consider.

The covered surface gets a strongly steric barrier, stronger when the bitumen is well covered. The degree of covering is an important quantity given as a % of surface covered.

The strong exponential long range forces known to exist between hydrophobic surfaces are reduced to the usual power law Hamaker values by changing the surfaces to hydrophilic. Attractive forces leading to coalescence are reduced by orders of magnitude.

Since Intan is non-ionic, electrical double layers should be less important. The addition of Mg reduces the charge density even further. Cardenas, Rossi and Rivas have shown that the negative charge density on Orimulsion is reduced to nearly zero by adding salts.

These three effects imply that van der Waals forces fight steric forces.

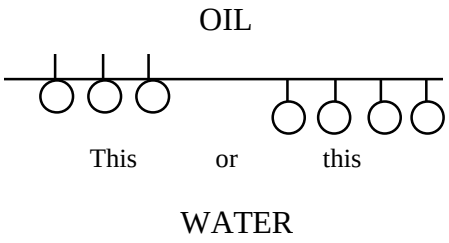
If these ideas are correct DLVO would be a useless theory for the stability of Orimulsion.

XI. HOW IS INTAN 100 ABSORBED ONTO BITUMEN

The issue here is tied to whether or not the surfactant is miscible in bitumen, according to Raad, Intan 100 is immiscible in bitumen, but there is some miscibility when some small amount of toluene is mixed in the bitumen.

The hydrophobic tail need not be miscible in the oil. Obviously, the hydrophobic part is not miscible in air at an air water interface. Different oils can be immiscibile. The difference here is probably in the nature of the absorption with miscible surfactants firmly anchored in the oil bulk while the

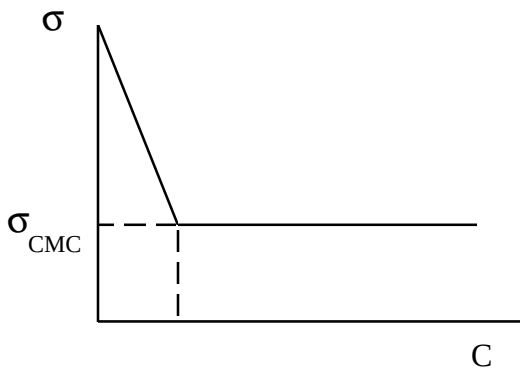
non-miscible are attached like a magnet to the surface. Surfactants absorbed on a solid surface are attached like a magnet but there are different degrees of attachment.



Is the nature of attachments of Intan 100 to bitumen an issue worthy of study?

XII. SURFACE COVERING, MULTIPLE LAYERS

The typical idealized interfacial tension versus bulk concentration is as follows.



Two parts of this curve are

1. The CMC and σ_{CMC}

2. The slope $d\sigma/dc$

Which of these two is most important?

We need $d\sigma/dc$ to calculate the Gibbs elasticity

$$Eg = A \frac{ds}{dA}$$

where dA/A is a strain based on the change of the area of the surface. Actually σ cannot depend on A since A is neither a thermodynamic nor a material variable. Eg is defined strangely and needs interpretation. We may write:

$$\frac{d\sigma}{dA} = \frac{d\sigma(c)}{dc}\frac{dc}{dA}$$

Obviously $d\sigma/dc$ is a well defined concept and we can think that the bulk concentration c evaluated on the surface is changed when you change the area of the surface. Evidently we can express A in terms of the surface molar concentration. For a fixed number of moles

$$\frac{dA}{A} = \frac{d\Gamma}{\Gamma}$$

(I remember this, but I would like to understand this better). Then

$$Eg = \Gamma \frac{d\sigma}{dc}\frac{dc}{d\Gamma}$$

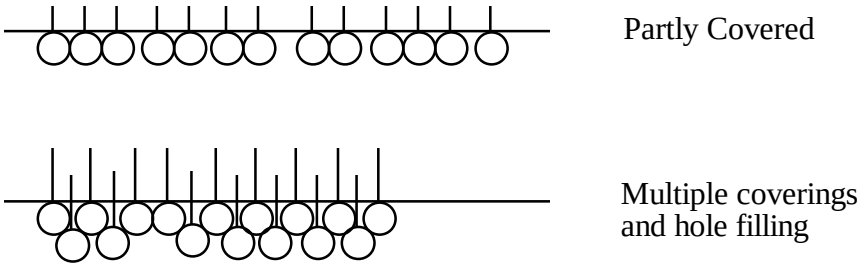
$d\Gamma/dc$ is a derivative which expresses how fast the surface excess concentration changes when you change the bulk concentration evaluated at the interface.

I think that $d\sigma/dc$ is related to the area/molecule. From the area/molecule we can calculate the percent of the surface covered by surfactant. Raad calculates this in a typical case to be 34%.

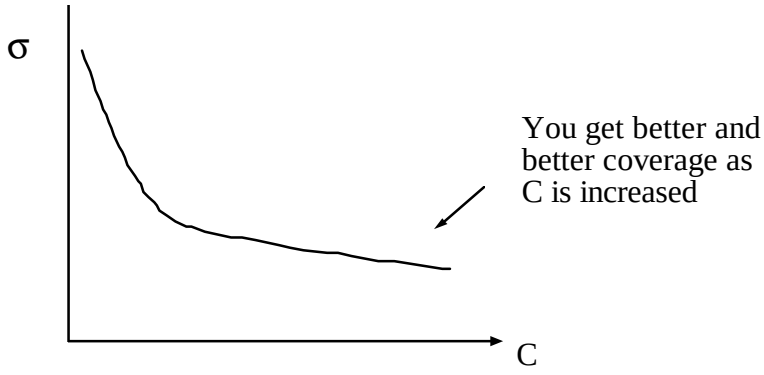
Customers and managers will understand the % of surface covered by surfactant much better than the area/molecule. Probably data should be given this way.

34% may seem like a small covering but Raad says that there are natural hydrophobic moities already on the drop before surfactant is applied; this would impede covering the drop with a higher percentage of surfactant.

Multiple covering of drops could be considered as is suggested by the following cartoon.



It could be augued that nonideal isotherms can be explained by hole filling and multiple layers.



Is There a relation between the CMC and the % covered?

XIII. CASES IN WHICH CMC DOES NOT SEEM RELEVANT

People have noted that they get smaller and smaller bitumen drops at constant energy of mixing when they increase the concentration of surfactant. They also note that the CMC seems irrelevant. Raad says that there is a limiting value for reduction of the drop size which is reached when the concentration of surfactant is maybe 20 times the CMC.
Another case where the CMC is apparently irrelevant is for the creation of stable foams in Jose's slit reactor.

These two cases have something in common. They both have rapid deformations which stretch surfaces. We could say that fresh surfaces are being created by stretching. This fresh surface is not covered by surfactant even when the amount of surfactant in the water is well beyond the CMC. However, the diffusion of surfactant to freshly exposed surfaces would be promoted by having more surfactant in the water. This doesn't explain why smaller drops form. It may be important to have a steep $d\sigma/dc$; or better yet a large Gibbs elasticity. Then the <u>changes</u> of interfacial tension induced by expanding surface would be great, more or less independent of the values of the CMC and σ_{CMC}.

It is certainly relevant to note that any deformation of a spherical drop will increase the surface area.

It would be interesting to carry out experiments, maybe mixing experiments like Gustavo's with surfactants with very different values of Gibbs elasticity. It would be nice to study systems with different Gibbs elasticities but nearly the same σ_{CMC}

How to determine the % coverage of surfactant?

1. Measure the tension σ as a function of concentration of surfactant c.
2. Calculate the surface excess Γ from the slope of the plot σ vs ln c.
3. Calculate Γ from the equation

$$slope = \frac{-\Gamma}{RT}$$

In order to calculate the % coverage of the total area of a drop of radius r, assume an area per molecule of I-100 A_i, a typical value of surface excess at bitumen/water interface Γ_b at 30ºC is 9,3 x 10-11 moles/cm^2 therefore,

Nº of molecules of I-100 covering a drop of bitumen

$$N = \Gamma_b A_d N_a$$

where A_d is the area of a typical drop approximately 20μm, and N_a is avogadro's no.

Assuming full coverage by the surfactant, the total area that the surfactant would occupy is given by

$$A_t = A_i N$$

The % coverage is calculated from

$$\% \text{ coverage} = \frac{A_t}{A_d} \times 100$$

The % coverage for the surfactant I-100 at 30ºC is then calculated to be 48% of the total area of a 20 μm.

Γ mol/cm^2
RT erg/mol
A_t, A_i, A_d cm^2
r cm

- What is the nature of fluid dynamics in mixer like Gustavo's that lead to emulsification?

- What are the fluid dynamic mechanisms that lead to spontaneous emulsification in surfactant solutions?

I could not find any analysis of these fundamental problems anywhere. I think that the major mechanism is associated with the normal stress balance at the interface. The first order effects are associated with the balance of shear stress in which the difference of the shear stress on either side of the interface is equal to the surface gradient of the surface tension. This gives rise maragnoni effects. The other balance says that the difference in the normal stress Tnn is balanced by surface tension times the mean curvature.

$T_{nn}(1)$ $\qquad$ $[T_{nn}] \equiv T_{nn}^{(1)} - T_{nn}^{(2)}$

$T_{nn}(2)$ $\qquad$ $[T_{nn}] = s\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$

Let α be some parameter like C on which σ depends

$$\frac{\partial}{\partial a} = [T_{nn}] \frac{1}{R_1 + R_2} \frac{\partial s}{\partial a} - s\left(\frac{1}{R_1^2} \frac{\partial R_1}{\partial a} + \frac{1}{R_2^2} \frac{\partial R_2}{\partial a}\right)$$

For Newtonian fluids $T_{nn} = p + \mu \frac{\partial u_n}{\partial n}$

XIV. NATURAL SURFACTANTS

Natural surfactants are not transported to the surface by diffusion. Since the inactive surfactants are on the drop surface only, Gibbs isotherms are not literally possible. However, after a discussion with Hercilio we came to consider the possibility that quantity equivalent to Gibbs isotherm could possibly be defined in terms of OH^- ions which are present in the water and diffuse to the surface where they activate the surfactant. Hercilio says that the surface tension goes down very rapidly with OH^- but the drops are larger when there are only very small amounts of OH^- in the water. Perhaps we can measure a "Gibbs isotherm" in term of OH^-.

For purposes of discussion only, put $\frac{\P[T_{nn}]}{\P a} = 0$; then

$$\frac{\P(R_1 + R_2)}{\P a} = \frac{(R_1 + R_2)}{s}\frac{\P s}{\P a}$$

If we think that α = C and

Look at this; the radius of the tip decreases and it decreases more strongly when σ is small and $d\sigma/dc$ is large.

Antonio says that the activated surfactant is strongly charged and can be considered as anionic, that steric effects are not important and the DLVO theory appears to apply.

The double layer repulsive force may hold drops further apart than the steric repulsion, so that the emulsion is very well protected.

We should run emulsions stabilized by natural surfactant through the coalescence meter.

Try to measure s vs OH^-, for a fixed chemistry, on a spinning drop tensiometer.