ANNUAL TRANSACTIONS OF THE NORDIC RHEOLOGY SOCIETY, VOL. 23, 2015

Characterization of microscopic drainage and breaking mechanisms in non-Newtonian water-oil emulsions

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ABSTRACT

Emulsions of oil and water are one of the most common types of naturally occurring fluid systems, from living organisms to complex industrial fluids. In chemical industry, cosmetics and for food the stability and behaviour of such is of high importance for quality. In oil production from petroleum reservoirs emulsion are often problematic both in pipeline transport and in separators. So called "rag layers" in separators are oil-in-water and ater-in-oil emulsions with long decay times. This project has studied self-organized processes that de-stabilize emulsion leading to gradual separation. Such rag layer emulsions consist of very small and finely dispersed elastic droplets that rarely coalesce as long as the droplet concentration is low. When the particle fraction becomes higher it might reach a critical concentration where coalescence takes over, so that even massive burst-percolation flows start.

INTRODUCTION

In this project "rag layer" micro-emulsions where created artificially by using small amounts of non-ionic surfactants ("Span 80" and "Tween 80"). Mixing was then applied in various ways, both with «ordinary» process mixing, but also with the use of a so-called "acoustic horn". This device induced very strong ultrasonic waves in the liquid, which causes cavitation, strong mixing and intense droplet fragmentation. Ordinary mixers produce droplets from 100 micron to several millimetres. Cavitation on the other hand, readily generates droplets 10 micron and less, thus forming micro-emulsions. The micro-emulsions were studied microscopically by also adding colour dye the water (Lissamine red) or to the oil phase (Sudan blue).

Using microscope and camera it was possible to observe reordering transitions of the oil and water as the emulsion gradually broke down, or dehydrated in cases of water dry-out. It is often assumed that dehydration is a diffusion dominated process. This work shows however that the dehydration and separation process is taking place via several heterogeneous transport mechanisms including breaking of larger lamellae and also massive channelling. The microscope imaging showed several types of such breaking processes. Chemical effects of surfactants and colour dyes, and their impact on surface tension are discussed. Also the impact of non-Newtonian emulsion with water soluble polymer (PolyAnionic Cellulose – PAC) was studied.

Background

Dispersions, suspensions and emulsions play an important role in nature as well as in industrial processes, both as a "helping agent" - or in other contexts, as a problem.

This project was initiated to study so-called "rag layers" in oil production. Natural ground water from reservoirs flows together with the oil often as dispersed droplets, sometimes as emulsions, and may take very long times to separate out. In such flows there are often other components like asphaltene aggregates (Kelesoglu et al[11]), sand particles and wax crystals which contributes as natural stabilizers. Good decriptions of the problem of emulsions in oil production are given by Sjøblom et al[1], Azuraien et al[2], MadjlessiKupai[3], Manar El-Sayed[4]. To enhance the emulsion breakdown various techniques are used, amongst the most frequently used are electrostatic separators, Amarzguloui[5]. In this paper we present results from the study of the stability of artificially made emulsions using a synthetic mineral oil (silicon oil - EDC 95/11) together with de-ionised water in combinations with polymer, PAC, and surfactants. The range of tests carried out is however too comprehensive to be presented in detail in this short paper, and will be published more consistently in a larger paper.

Theory

Good descriptions of the theory of emulsion can be found in Davies[6], Nagarjan[7], and the IUPAC Goldbook[8]. Dispersions are created naturally in strong turbulent oil-water flows in pipelines, or by strong mixing as in choke valves. Sufficiently energetic, the mixing produces small droplets, but rarely smaller than 10 microns. Emulsions on the other hand are more or less spontaneous processes where, in principle, immiscible liquids like oil and water by the action of surface active agents (hydrophilic / lipophilic "emulsifiers") go into very small droplets. The size is determined thermodynamically by minimum Gibbs free energy. A special case of emulsions are micellar emulsions which are thermodynamically stable in the finely mixed stated due to presence of amphiphilic chemicals.

The breakdown of emulsions (and foams) is closely linked to the dynamics of the separating film between droplets or bubbles. In flowing systems there is a "population dynamics" involving a continuous competition between collision-coalescence processes and breakup. In this work the focus is on stagnant non-flowing fine dispersions and emulsions, with influence of large scale convection and turbulence. The stability of the "film" which separates the droplets is linked to the electrochemical hydrophobe – hydrophile balance ("HLB"). The HLB influences the surface tension and viscosity of the film. These parameters also depend on temperature, water salinity and pH. The temperature is important also via collision impacts of Brownian motion of very small droplets. In water this essentially means smaller than a few micron at room temperature.

The HLB system

The HLB system was introduced (ICI[12a], and Griffin[12b]) in the late 1940's, somewhat analogous to the octane number for car fuels. The system was meant as a tool for designing stable emulsions. When needed, e.g. in food and medical industry, one should select emulsifiers with similar number to the oil or fat which is used. HLB numbers 0-10 are lipophilic, while 1-20 are hydrophilic.

In this work the interest is on the contrary focused on unstable emulsions. (see e.g http://petrowiki.org/Oil_demulsification)

In order to enhance the emulsification, low doses of Span80 and Tween80 were used as a surfactant/co-surfactant system in concentration 0.01% wt. Span and Tween are brand names by Croda International PLC. The molecular structures of both are shown in Fig.1

Span[13] (sorbitol monooleate) is a sorbitan ester, belonging to a class of food additives known as Polysorbates. It is widely used in food products and oral pharmaceuticals. It is oil soluble with specific gravity 0.99 and HLB number 4.3

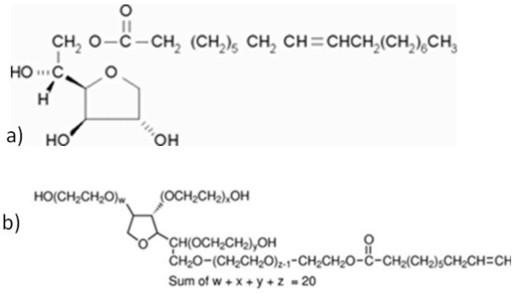


Figure1 a) Span 80 b) Tween 80

Tween[14] is a hydrophilic polyethylene sorbitol ester, an ethoxylated Span, with specific gravity 1.07 and HLB of 15.

EXPERIMENTS AND SETUP

A range of different dispersions and emulsions were prepared and investigated. Oil and water systems were prepared with small doses of surfactants and dye colours for phase identification. They were then mixed either with impeller mixers Silverson L2R and L4RT-A at 400 rpm. For strong mixing an “acoustic horn” Hielscher UP400S was used as in Time et al [25]. It has 400W as maximum power. See Fig. 2. The horn was operated at 40% of maximum amplitude, and a repeated duty of cycle 0.5s for five minutes.

For phase identification in pictures and videos colour dyes “Lissamine red” was added to the water, while “Sudan blue” (both from Merck) was added to the oil.

Macro-emulsions (dispersions) which separate easily were made straightforward by mixing of oil and water with the Silverson L4RT-A mixer.

a) Acoustic horn b) Shear mixer

Figure 2: Mixers a) Acoustic horn - Hielscher UP400S b) Silverson L4RT-A

The emulsions were then set to separate, and photographed at given intervals during 72 hours. Initially the frame rate was one picture minute, but as the emulsion separation speed decreased only one picture was taken.

“Stubborn emulsions” on the other hand were made either by use surfactants in combination with either simple mixing or with use of the acoustic horn. Somewhat similar effects were obtained by adding PAC (PolyAnionic Cellulose) to the water (concentration 4g/Liter).

Altogether 11 different “Newtonian” oil-water mixtures and 4 oil polymer (PAC) were tested as shown in Table 1.

- Newtonian: Oil - water (deionized) system
- Non-Newtonian: Oil – polymer (deionized water + PAC solution)

In addition some microscopy reference analyses were done on milk (“*emulsion*” - from latin “*made as milk*”), fat milk, sour milk - and also hand soap emulsion.

Sample	O:W proportion	Emulsifier weight proportion	HLB	Emulsifier premixed with	Mixer
S1	20:80	-	-	-	Silverso L4RT-
S2	20:80	-	-	-	Ultrason
S3	80:20	-	-	-	Silverso L4RT-
S4	80:20	-	-	-	Ultrason
S5	80:20	0.01wt% surfactant	7.8	Water	Silverso L4RT-
S6	80:20	0.01 wt% surfactant	7.8	Water	Ultrason
S7	80:20	0.1 wt% surfactant	7.8	Water	Ultrason
S8	80:20	0.01 wt% surfactant	7.8	Span in oil, Tween in water	Ultrason
S9	80:20	0.01 wt% surfactant	7.8	Span in oil, Tween in water	Ultrason
S10	20:80	0.01 wt% surfactant	7.8	Span in oil, Tween in water	Silverso L4RT-
S11	20:80	0.01 wt% surfactant	7.8	Span in oil, Tween in water	Ultrason
S12	80:20	PAC 2g/l	-	Water	Silverso L4RT-
S13	80:20	PAC 2g/l	-	Water	Ultrason
S14	80:20	PAC 4g/l	-	Water	Silverso L4RT-
S15	80:20	PAC 4g/l	-	Water	Ultrason

Table 1: List of emulsion samples prepared (from Pedersen[27]).

A number of different emulsion system were analysed in microscope (brand “Swift”), at magnifications up to 1000X. A digital camera (14 Megapixel, “Toupcam U3CMOS” 14000KPA) as in Fig. 3 was used to acquire and store images to PC at given intervals.

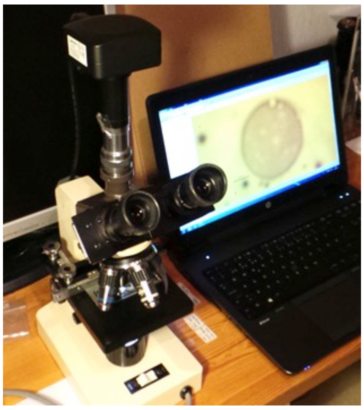


Figure 3. Microscope with camera and laptop.

The prepared emulsions were left to settle in a temperature stabilised room for a couple of days in order to separate out the large oil and water droplets. Then samples were extracted from the mid-layer and analysed in the microscope. Microscope slide glasses as in Fig.14 with a concave centre region (15 mm diameter, 0.8 mm deep) were used to prepare sections of emulsions thick enough to be considered 3D.

Fluid properties

Solutions of PAC were used for standard non-Newtonian analysis. The rheological properties were measured with an Anton Paar MCR 302 rheometer as shown in Fig.4.

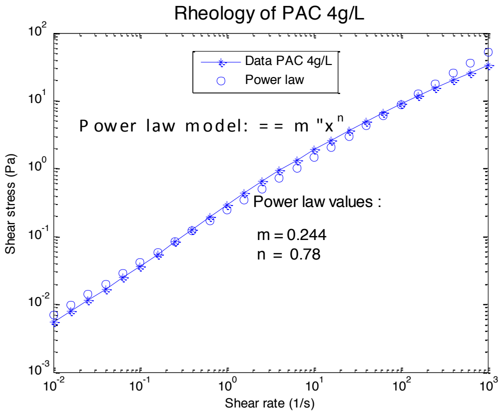


Figure 4: Rheology of PAC (4g/L)

The interfacial tension between oil and water-polymer solutions was measured with a Du Noüy Ring Tensiometer. For oil and water without surfactants but with color dyes it was measured to 33.7 mN/m. For the oil and PAC water solution (4g/L) the value was 40.2. For oil and water with surfactants the value was too low to be measured accurately.

ANALYSIS AND DISCUSSION

Most of the tests involved oil with small amounts of surfactants in water. The aim was to provoke emulsification as observed during petroleum production from oil reservoirs without creating full emulsions.

A low dose of both Span and Tween 0.01% (weight, “wt”) was used. Only in one single feasibility test 0.35 % (wt) was used. This test as expected showed much stronger emulsification. In addition some “side-track” tests were carried out to study microscopically the breakdown of known emulsions as milk and hand soap with the aim to see what can be gained from long time microscopy recordings. Some of these will be shown in the presentation.

The following Fig. 5 shows the typical appearance of small “mushrooms” growing up from the top of the mid-layer emulsion.

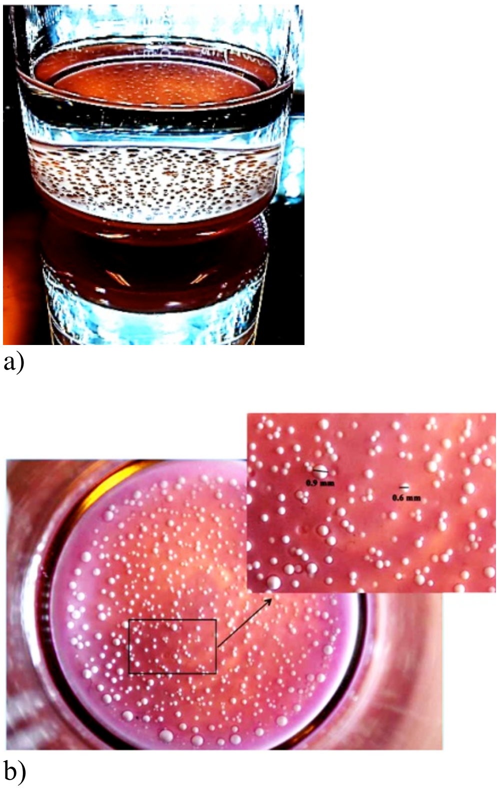


Figure 5: Aggregates of oil droplets in the mid-phase are prevented from draining up into the oil phase due to surrounding water film a) side view of beaker glass standing on a mirror b) top view

These are oil-in-water structures with small amounts of oil droplets that are prevented from draining into the oil above.

Similar patterns were observed at the underside of the mid-layer. These hanging aggregates consist of microscopic water droplets encapsulated in water film. Drainage patterns of oil and PAC emulsion like these were also seen in the microscope as shown in the Fig.6.

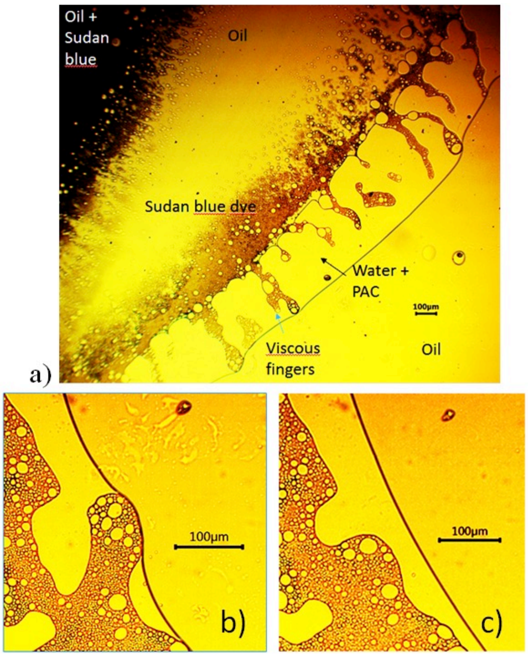


Figure 6: Oil and PAC (4g/L) water solution draining from the central reservoir of the microscope slide out to the edges of the cover glass observed during a week.
a) Overall picture b) detail of the process where oil fingers (darker, in the middle) containing water are separated from the continuous oil zone to the right by a thin water film. The fingers drain water droplets into the separating water film (light) but remain separated from the oil zone due to the water film.
c) The finger has drained out water and retracted

Effect of mixing and additives

Four samples shown in Fig.7 were selected for thorough microscopic analysis. The numbers on the bottles are linked to the to the sample numbers in Table 1 (in parenthesis) and oil-water ratios (O:W) as follows:

- Nr 1(S11): **O20:W80**, with both Span and Tween, mixed with ultrasonic (US).
- Nr 2 (S10) - sample S10: **O20:W80** with both Span and Tween, mixed “ordinary” (Silverson mixer).
- Nr 3 (S9): **O80:20W**, both Span and Tween, HLB = 7.8 – US mix. These first three all contained 0.01% (wt) surfactants, with HLB = 7.8.
- Nr 4 (S15) **O80:W20**. No surfactant, only PAC (4g/L) and “US” mixed US.

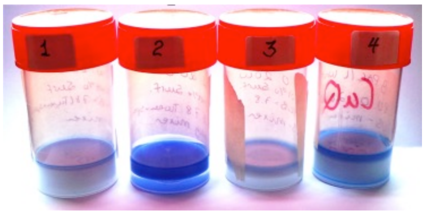
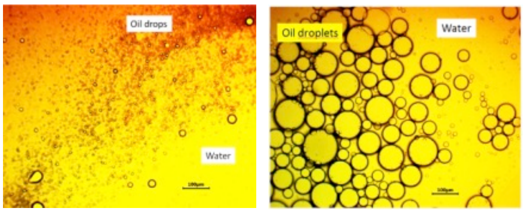


Figure 7: Bottles of samples for microscopy tests.

Fig. 8 shows microscope images from samples 1 and 2. The ultrasonic mixing used in a) gives much smaller droplets that with ordinary mixing as in b).



a) b)

Figure 8: a) Bottle nr 1 20:80 O/W – ultrasonic mixing b) Bottle nr 2, as a) but with ordinary mixer

In Fig. 9 and 10 from sample 3 is shown a detail which seem to indicate visco-elastic behaviour, perhaps due to intense ultrasonic treatment of the oil. A thin filament develops as the oil droplet stretches. Koplik[22] has simulated similar structures using molecular dynamics.

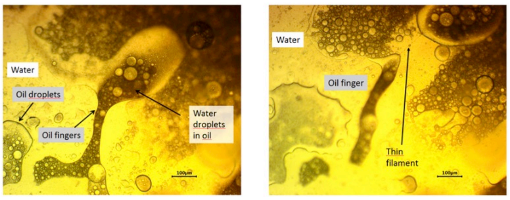


Figure 9: a) Bottle nr 3 – showing an oil finger developing and moving up to the right b) Same as in a) but now with a very thin wire is stretching from the droplet moving up-right.

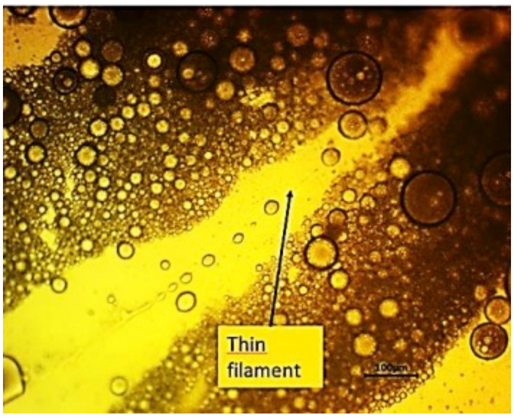


Figure 10: Same as previous, but ten minutes later, and with higher magnification. Droplets now have organized as a pearl necklace along the thin filament which is still visible.

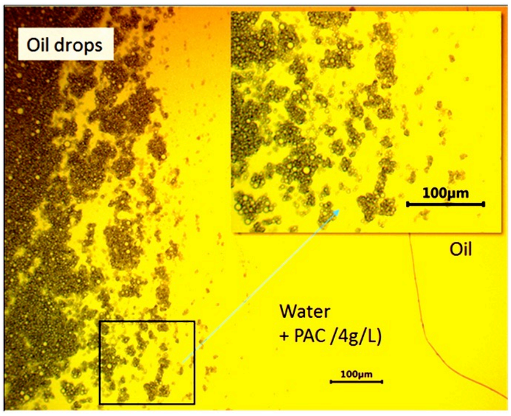


Figure 11: Bottle nr 4. Oil and PAC solution. Water is draining (upwards in the picture) in a slow dry-out process and start to organize as long chains

The emulsion of oil and water with PAC polymer is shown in figure 11. Alignment of droplets is seen. It is organized in parallel with the direction of flow which is typical for shear thinning liquids. Similar patterns were reported by D'Avino[19], Feng[20] and Mirsepassi[21] for viscoelastic liquids.

Microscopic PIV

A small feasibility study was done for calculation of the flow profile in emulsions. Sequences of microscope images from the mixture S5 were used. The images in these cases were recorded with 30 seconds interval. One image was recorded with reference length scale included as shown in Fig. 12. From this the pixel to real world coordinates was calculated (4318750 px/m).

MatPIV by Sveen[27] was used for the analysis. The figures below show a typical outcome from the analysis. The authors have earlier used this method in several papers, e.g. Time[25] and Rabenjafimantsoa[26].

The PIV analysis as shown in Fig. 13 indicates that the larger particles move differently from the smaller particles. The drain-out process causes a flow which drags the large particles. The display frame rate of the camera was 50Hz and clearly revealed that the smallest particles display a much more irregular Brownian. Images were stored with 30 seconds interval which is too slow to track the Brownian motion. The large particles on the other hand are very little influenced by the irregular Brownian over such time scales. Being able to capture the Brownian motion would be interesting since it could potentially be used for measurement of viscosity, even in very small samples and very low shear rates. This has been discussed in Greczyło[16] and Qian[17] with a useful microscopy recipe in[18]. This will be followed up in a new project.

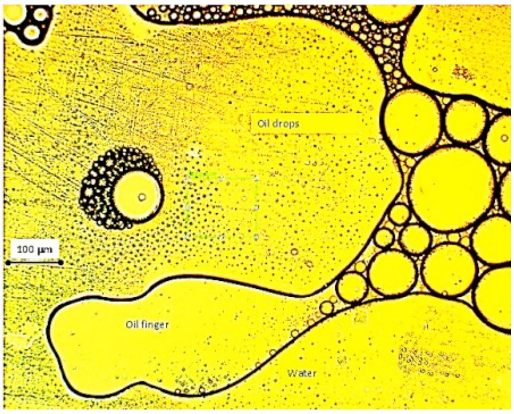
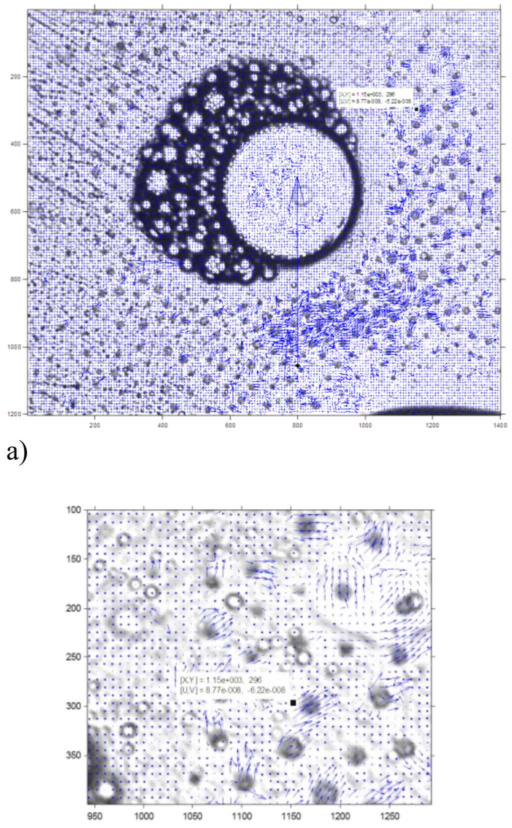


Figure 12: Images used for micro-PIV of emulsions. Length scale 100 µm shown to the left.



a)

b)

Figure 13: PIV analysis around a selected part of the image. a) Velocity vector are blue. Some velocity vectors are clearly erratic. b) Showing an enlarged section of a) at the upper right if the large bubble

Flow regimes in emulsion breakdown

The microscopic slides were prepared as shown in Fig. 14. The microscopic analysis revealed several regimes of emulsion breakdown, depending on whether the process was

- sealed at the glass edge, with no loss of water
- a dry-out process where water evaporates at the glass edge
- if chemical degradation and thermal effects were present

In the case of sealed (no leakage) processes it was found that breakdown was connected to breaking of the separating film between droplets as expected. On longer time scales the films became longer and thin and still quite resistant to breakdown. Whether this stabilisation was caused by tiny particles ("Pickering stabilisation") or by increase in film viscosity was not revealed. The Pickering effect has been found both to stabilize (Li et al[10], Keleşoğlu[11]) and destabilize (Juarez and Whitby[9]) emulsions. The interpretation of the microscopic fingering separation is challenging, amongst others because of some ambiguity in phase identification.

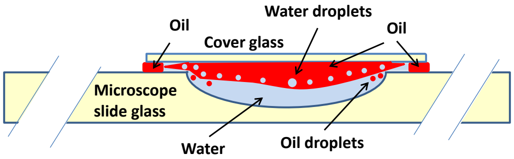


Figure 14: Cross section of oil and water distribution in the microscope slide glass concavity. In this case the emulsion is sealed by an outer non-evaporating oil barrier.

Dry-out processes involving water dissipation were much more dynamic. In these cases the mass transport to the edge of microscope cover glass over the samples caused internal shear. Very complex transport mechanisms were found with collective effects over "long distances" (millimetres). These could be termed "landslides" or "dambreaks", in analogy to geological surface processes. Due to the limited view field of the microscope it was difficult to determine typical correlation lengths of these phenomena. In many cases of far developed separation however it was easily observed how a film breakage at some point caused pressure-stress-mass transport that initiated deformation or breakage at locations nearby. Several more examples of this will be shown in the conference presentation.

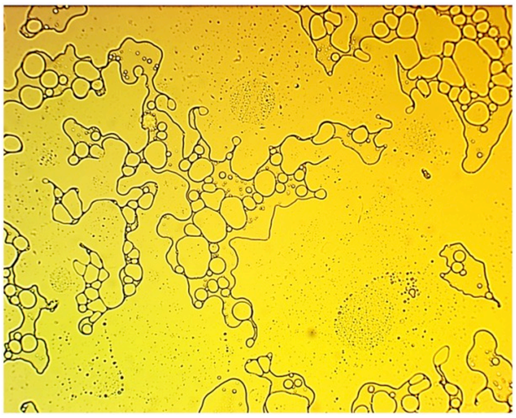


Figure 15: A late stage of oil water emulsion separation. The ("island") regions are oil surrounded by water. Long thin filaments remained for many days.

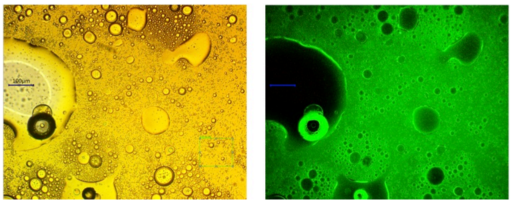
Dimension of emulsions

In several of the mixtures the water obviously contained dissolved air (nitrogen and oxygen) which over time separated out and at least locally caused three phase foam like emulsions in which the gas bubbles surfaces influenced the liquid films and in the "2D confined" microscope samples captured and immobilised liquid droplets as well. In particular when using ultrasonic mixing, sub-micron bubbles are created by cavitation and may gradually coalesce into larger bubbles.

These observations also point out a question whether the dimensionality of the emulsions is an important parameter. Will breakdown of "3D emulsions" (e.g. in the microscope slide cavity in Fig. 14) be different from an emulsion squeezed directly between the glass plates? Questions arise as to whether the glass plate walls also cause additional (e.g. surface electric) phenomena.

Phase identification with fluorescence

Based on the challenges with phased identification, at the end of the project it was attempted to use fluorescence for phase identification. Water with Uranine (Na-fluorescein, 1.5 g/L) was mixed with oil with impeller mixer. Uranine is not soluble in oil. The two images in Fig. 16 show the difference between normal lamp light and UV light. The light areas in b) are water, while the dark areas are oil. In colour microscopy photo the fluorescence appears green, due to the low light level with the UV lamp. Combined with normal lamp light the fluorescence is yellow.



a) Normal light *b) Fluorescence UV–light*

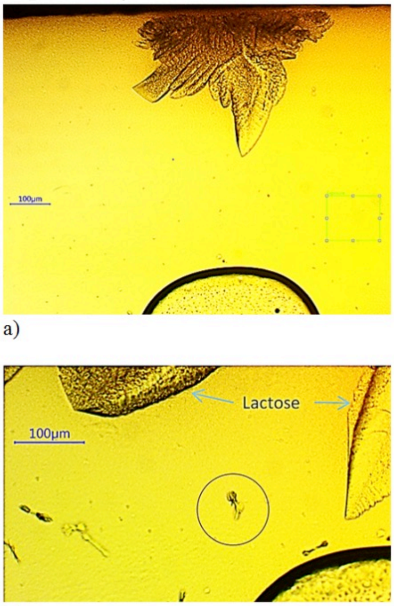
Figure 16: Comparison of pictures in normal light and with Uranine added

Other emulsions

Breakdown of milk via dehydration was studied for reference, since milk is so finely dispersed that it is stable over long time. However milk in addition to water and fat droplets ("oil") contain lactose and casein proteins. Thus chemical effects arise during the dry-out process. Some very interesting transport modes were found in addition to crystallization of lactose close to the glass edge, see Fig.17. Possibly this is a combination with polymerization of casein.

SUMMARY AND CONCLUSIONS

The main objective of this work was to reconstruct "flow regimes" in microscopic break-up of long-lived emulsions.



a)

b)

Figure 17: a) Lactose crystallizes as water evaporates at the edge of the cover glass (top of picture). A gas bubble is at the bottom right b) An hour later than picture a) the lactose crystals have grown, and at the same time small "tree-like" structures grow from the bottom slide glass as shown in the ring near the centre of the image. The chemical composition of these structures was not determined.

Inspired by difficult "rag-layers" in petroleum oil-water separation the idea was to make such emulsions using a simple well known oil plus water without the chemicals and particles which naturally follow the petroleum stream from the reservoirs.

By use of small amounts of surfactants the interfacial tension in the oil-water system could be reduced without making spontaneous emulsions, still making it harder to break. The two mixing methods – mechanical and ultrasonic are very different in terms of energy deposition and spatial focus. The ultrasonic due to cavitation causes pressure and temperature variations (< 1000 Kelvin) over short intervals so that chemical reactions can be induced. This is discussed in Margulis[23], Mohod[24] and Time[25]

Microscopy and emulsion dimensionality

The emulsion decay was studied first macroscopically in beaker glasses for several days. Then small samples of the mid-phase were extracted by pipette and picture recorded over many days in microscope. The microscope slide glasses had a concave cavity (Fig.14) so that both "3D" and "2D" effects could be studied. The breakdown regimes were different for samples enclosed by an outer oil barrier, compared to if the emulsion water could escape at the glass edge and evaporate in a dry-out process.

Dry-out processes

Dry-out processes involve transport of water and introduce small shear (creep) flow. For dry-out processes, in regions with high droplet density, quite complicated collective phenomena showed up - as "landslides" and "dam breaks" with sudden flows of larger domains of the emulsions.

For dry-out processes involving milk a lot of effects showed up. Crystallization of lactose was fast. Possibly this was in combination with polymerization of casein although normally pH or enzymes are needed for this.

Enclosed processes

For "enclosed" oil-water emulsions as in Fig. 6 "fingering separation" was found – as in macroscopic open 3D systems (Fig.5). In late stages of 2D emulsion as in Fig. 15 the remaining films stay as filaments. In presence of glass walls these seemingly had life-times over many days.

Non-Newtonian behaviour

For emulsions of pure Newtonian liquids this would presumably be a uniform flow. However the emulsions become non-Newtonian for several reasons: 1) droplet-film systems are controlled more by surface tension at least as much as viscosity, 2) the small amounts of Span and Tween may cause the oil and water to become non-Newtonian, 2) PAC is intended for shear thinning of water, and 3) ultrasonic mixing may induce reactions in the oil which may modify the rheology.

Non-Newtonian liquid behaviour was seen in Fig. 9 and 10 with spontaneous long thin filaments as if very long polymers were present. This system of oil and water had been mixed with the ultrasonic horn. In PAC treated emulsions as with hand soap fluids the microscope images Fig. 11 showed clear orientation of droplets as chains in the flow direction (these were prepared as "dry-out processes").

Challenges and spin-off

Some challenges turned out from the microscope analysis. One quite obvious was phase identification of oil-and water. Even if coloured and well discriminated in the beaker glass, it was very difficult to see the colours in thin layers in the microscope. Fluorescence seems to be a useful method.

Additional spin-off of this analysis was the possibility of using (micro-) PIV, as in figure for measurement of transport rates in emulsions. Also the observations of clear differences in Brownian motion in oil, water and polymer liquid parts of the emulsions initiates new studies, with the aim to be used for micro-rheology.

ACKNOWLEDGEMENT

We greatly acknowledge the work and input from our bachelor student Marianne Pedersen in to this work. Also we appreciate valuable input from Dr. Azuraien Bt at Petronas University in Malaysia about realistic process conditions and published findings.

REFERENCES

1. Sjöblom, J., et al. (2003): "Our current understanding of water-in-crude oil emulsions.: Recent characterization

techniques and high pressure performance", *Adv. Colloid and Interface Science*, Vol. 100 –102, pp. 399–473

2. Azuraien, J-J. et al (2014): "Investigation on demulsification performance of combined demulsification method and rag layer characterization", *SPE conference, Flow Assurance–Further, Deeper and towards excellence*, Bali, Indonesia.

3. MadjlessiKupai, M. (2012):" Study of the Rag Layer: Characterization of Solids", *MSc thesis*, University of Alberta

4. Manar El-Sayed (2012):" Factors Affecting the Stability of Crude Oil Emulsions", Chapter 10 in book "*Crude Oil Emulsions - Composition Stability and Characterization*", ISBN: 978-953-51-0220-5

5. Amarzguloui, M., and Jacobsen, P. (2014): "Overcoming Separation Challenges by Use of Electrocoalescence Technology", *SPE-171483-MS.*

6. Davies, J.T. (1957), "A quantitative kinetic theory of emulsion type, I. Physical chemistry of the emulsifying agent", *Gas/Liquid and Liquid/Liquid Interface, Proceedings of the 2nd International Congress of Surface Activity*, pp. 426–438

7. Nagarjan, R. (1980): "Thermodynamics of Surfactant-Polymer Interactions in Dilute Aqueous Solutions", *Chemical Physics letter*, Vol. 76 No. 21

8. IUIPAC Goldbook; http://goldbook.iupac.org/E02065.html

9. Juárez, J. A. and Whitby, C. P. (2012): "Oil-in-water Pickering emulsion destabilisation at low particle concentrations", *J. Colloid and Interface Science*, Vol. 368(1), pp. 319-325.

10. Li, C., et al (2009): "Pickering emulsions stabilized by paraffin wax and Laponite clay particles", *J. Colloid and Interface Science*, Vol. 336, pp. 314–3214.

11. Keleşoğlu, S., et al (2015): "Rheological properties of highly concentrated dense packed layer emulsions (w/o) stabilized by asphaltene", *J. Petr. Sci. and Eng.*, 126(0), pp. 1-10.

12a. ICI Americas Inc.: "The HLB system – a time saving guide to emulsifier selection", http://www.firp.ula.ve/archivos/historicos/76_Book_HLB_ICI.pdf

12.b Griffin, W. C. (1949), "Classification of Surface-Active Agents by 'HLB'" (PDF), *Journal of the Society of Cosmetic Chemists,* Vol. 1 (5), pp. 311-26

13. Sigma-Aldrich (2015): Span 80, from http://www.sigmaaldrich.com/catalog/product/sigma/s6760?lang=en&region=NO

14. Sigma-Aldrich (2015): Tween80, from http://www.sigmaaldrich.com/catalog/product/sigma/p4780?lang=en&region=NO

15. Capdevila, M., et al. (2010): "Preparation of Span 80/oil/water highly concentrated emulsions: Influence of composition and formation variables and scale-up*", J. Colloid and Interface Science*, Vol. 345, pp. 27–33

16. Greczyło, T. and Dębowska, E. (2005): "Finding viscosity of liquids from Brownian motion at students' laboratory", *Eur. J. Phys.*, Vol. 26, pp. 827–833

17. Qian, H. (2000): "Single-Particle Tracking: Brownian Dynamics of Viscoelastic Materials", *Biophysical Journal*, Vol. 79, July, pp. 137–143

18. Brownian motion in milk: http://www.microscopy -uk.org.uk/mag/imgjun09/Brownian-motion-in-milk.pdf

19. D'Avino, G. and Maffetone, P.L. (2015): "Particle dynamics in viscoelastic

liquids", *J. Non-Newtonian Fluid Mech*, Vol. 215, pp. 80–104

20. Feng, J. and Joseph, D.D (1996):" The motion of solid particles suspended in visco-elastic liquids under torsional shear", J. Fluid Mech. (1996), vol. 324, pp. 199-222

21. Mirsepassi, A., et al (2012): "Particle chaining and chain dynamics in viscoelastic liquids", *J. Non-Newtonian Fluid Mech*. Vol. 179–180, pp. 1–8

22. Koplik, J. and Banavar, J.R. (2003); "Extensional rupture of model non-Newtonian fluid filaments, Phys. Rev. E, Vol. 67 , 1- 011502

23. Margulis, M.A. (1995): "Sonochemistry and Cavitation", Book, Gordon and Breach Publ.

24. Mohod, A.V and Gogate, P.R.: "Ultrasonic degradation of polymers: Effect of operating parameters and intensification using additives for carboxymethyl cellulose (CMC) and polyvinyl alcohol (PVA)", *Ultrason. Sonochem.*, Vol. 18 (2011), pp. 727–734

25. Time, R.W. and Rabenjafimanantsoa, H.A (2011): "Bubble Dynamics and Cavitation in Non-Newtonian Fluids Exposed to Strong Acoustic Fields", *Annual Transactions of The Nordic Rheology Society*, Vol. 19, 2011

26. Rabenjafimanantsoa, H. A, Wrobel, B. M. and Time, R. W.: "PIV Visualization of Acoustic Streaming in Non-Newtonian Fluid", *Ann. Trans. of the Nordic Rheological Society*, Vol. 17, 2009.

27. Sveen, J.K.: "MatPIV", Department of Mathematics, University of Oslo, (2004).

28. Pedersen, M. (2015): "Separation properties of synthetic oil-water and oil-polymer rag layer emulsions with small additions of surfactants", *BSc thesis*, University of Stavanger