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Effect of small amounts of surfactant on oil-water dispersion

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University of Stavanger, 2014

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ABSTRACT

The present work reports the study of oil-water dispersions in static conditions. All experiments were carried out with a mineral oil and tap water in glass beakers with mixing of the phases. Small amounts of non-ionic surfactants were used to stabilize the emulsion systems. This simple system gives a good formation of oil-water emulsions.

The objective of the present work is better understanding of emulsion behavior. The study was conducted with increasing agitation speed of impeller and different proportion of Span 80 and Tween 80. The understanding of emulsion changes with increase HLB value from 4.3 to 15 was studied on both O/W and W/O emulsion types. The emulsions, which did not show immediate separation trends, were analyzed for 72 hours with pH meter, a microscope. The unstable emulsions separated due to creaming and coalescence processes. Droplets of the short-stable emulsion were growing in size along time, what signals about coalescence.

During guest's presentation out of Mettler Toledo Company it was a great luck to use FBRM and PVM probes to confirm states made with simple measurement tools and compare the results. The results achieved with FBRM and PVM tools, also prove that the droplets sizes decrease with addition of a very small amount of surfactants and/or increase of stirring speed of an impeller.

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ABBREVATION

AV	Apparent Viscosity
BHP	Bottom Hole Pressure
DSD	Droplet Size Distribution
ECD	Equivalent Circulation Density
FBRM	Focused Beam Reflectance Measurement
HLB	Hydrophilic-lipophilic Balance
MPD	Managed Pressure Drilling
PV	Plastic Viscosity
PVM	Particle Video Microscope
SARA	Saturate, Aromatic, Resin and Asphaltene

1 INTRODUCTION

Permanent emulsion is important for many industries like food, cosmetics, pharmaceuticals and many others. Petroleum emulsion have frequent, important and widespread occurrence in the industry. Many emulsions encountered in the petroleum industry are undesirable and may be an effect of high costs in drilling, refinery and transportation processes. Any of these dispersions might be stabilized to assist one stage of oil recovery, but another emulsions may be undesirable. For example, emulsion drilling fluids are desirable, but emulsions during oil production are undesirable, see table 1 (L. Schramm, 2005).

Undesirable	
Producing emulsions	W/O
Fuel-oil emulsions	W/O
Oil-flotation process froth emulsions	W/O, O/W
Oil-flotation process diluted froth emulsions	O/W/O
Oil-spill mousse emulsions	W/O
Tanker bilge emulsions	O/W
Desirable	
Heavy-oil pipeline emulsions	O/W
Well-stimulation emulsions	O/W, W/O
Oil and oil-sand flotation-process emulsions	O/W
Emulsion drilling mud	O/W, W/O
Asphalt emulsion	O/W
Enhanced oil recovery in-situ emulsions	O/W
Transportation fuel emulsion	O/W, W/O

Table 1: Some emulsions in the petroleum industry (L. Schramm, 2005)

1.1 Project work

The objective of this work is to study the emulsion behavior (stability, viscosity, DSD, separation efficiency) created with small amount of additives and without applying of much energy of agitation. The work was conducted with a purpose of establishing of long–term stable dispersions with big droplets; meanwhile those droplets could enable to separate the dispersion into two initial phases by the gravitational force. The experiments were conducted in glass beakers with oil-water system emulsified by using of different proportion of Span 80 and Tween 80 in amount equal to 0,01% of total volume of the system. Droplets were generated with a mixer until homogeneous conditions. In contexts of the work, maximum droplet sizes were suggested to determinate with using of a light microscope.

1.2 Motivation for drilling

Recent tendencies show that drilling and production become more and more difficult. The time of easy extracting oil is over. Nowadays, drilling takes challenges in harsh environment, complex geological structures, heavy oil deposits and increase of extraction coefficient. The last point is directly associated with drilling through reservoir section and contamination around the wellbore. Direct and invert emulsion were invented to solve that problem. Invert emulsions posses lubricating features what enables to drill highly deviated and horizontal wells. Otherwise, stable invert emulsions have a high percentage of surfactants in its composition what could lead to wellbore damage. Another problem is low electrical permeability of invert emulsion drilling fluid system. It is a cause of unsuccessful well logging. Use of direct emulsions solves that problem, but it makes difficult to drill long-distance horizontal section and control shale stabilization.

Ideally, drilling fluid system possessing properties of both systems could solve all these problems. One of such solutions could be reversible oil/water dispersion. Such system could be changed from oil-in-water dispersion to water-in-oil dispersion in dependence on technological requirements. The drilling fluid system might provide drilling and shale control of an oil-base mud with the mud cake removal efficiency and non-damaging characteristics of a water-base fluid.

With increasing of Managed Pressure Drilling (MPD) technology utilizing, the question about reservoir fluid influx handling is one of most discussed. During drilling operations utilizing MPD equipment, the main focus for drilling is to keep Bottom Hole Pressure (BHP) in the well slightly higher pore pressure. However, due to uncertainties in pore pressure during drilling, pore pressure might be higher BHP. This can lead to influx of reservoir fluid and kick situation occurring. According to traditional procedures for kick circulations out, the mud pumps should be switched off and the well shut-in. These procedures lead to reducing of the BHP, with following circulation of influx and increasing of mud weight.

In case of reservoir fluid influx for the MPD drilling “dynamic” shut-in procedure exists. The main idea of the procedure is to avoid reducing of the equivalent circulation density (ECD) by no stopping mud pumps, but instead to increase the BHP by increasing of backpressure in the annulus with adjusting of drilling fluid mixture and choke valve opening, whilst controlling the bottom hole pressure above the pore pressure. While control of choke valve opening became automatically adjusted, the adjusting of drilling fluid mixture for well kill procedure still requires more studies and new solutions. One of the solutions might become emulsion system, which can be achieved by mixing of oil and water with small amount of emulsifiers (Liv A. Carlsen, 2008).

Potentially, using of the system might give an increase in drilling and completion efficiency as a result it might reduce well cost.

1.3 Motivation for production and transportation of oil

Actual problem in oil field development is remoteness from refineries and consumers. Therefore, oil must be transported in pipelines. There is a great challenge for flow assurance of multiphase flow due to changes in properties of oil during transportation.

A reservoir fluid is rarely pure crude oil; usually it is polluted with water, gas and different particles. Before being transported oil needs to be treated near the reservoir. For this purpose collected crude oil goes through separation and cleaning processes. The biggest issue for transportation is water; excessive volume of water has to be removed before oil can be carried.

Produced oil usually contains emulsified water; water cut may reach up to 90%. In fact, water content 0.5%-2% has been specified as the tolerable amount in a crude oil for transportation by pipelines. In such highly water produced amounts dispersed flow is dominated and phase inversion process takes place. The volume phase fraction at which this phenomenon takes place depends on several factors. The water and oil properties such as density, interfacial tension and viscosity appear to be most crucial. The presence of surfactants, which accumulate at the phase interface, lead to reduction of interfacial tension promoting a stable dispersion.

There is a main problem for transportation: control of phase inversion by additional of small amount of surfactants. Due to this problem, accurate prediction and control of inversion point is vital for an appropriate design and operation of the production system.

2 THEORY OF EMULSION

There are several theories of emulsion formation, but the most common used that emulsion is the colloidal system in which small drops of a liquid phase are dispersed in another phase where both liquids are immiscible. Oil and water form an emulsion by shear motion, but pure emulsion is rarely stable and starts to separate immediately after motion has been stopped.

There are two general types of emulsion depended on nature of the dispersed phase. The type of emulsion in which oil droplets are dispersed in water phase (continuous phase) is called an oil-in-water emulsion (O/W). A water-in-oil emulsion (W/O) is the type of emulsion in which water drops are dispersed in oil medium (continuous phase) (Bin Hu et al., 2006). It is also possible to create emulsion more complex structures like W/O/W and O/W/O where water dispersed within oil droplets of O/W type emulsion or vice verse, see Fig.1 (Abdel-Raouf, 2012). In water-in-oil in water dispersion: water-in-oil mixture remains stable and might be dispersed as droplets (partly or fully) in the water continuous phase. Such emulsion is unstable, what means water can easily segregate under quiescent conditions while fraction of water dispersed in oil may remain stable (J. Cabanillas, 2013)

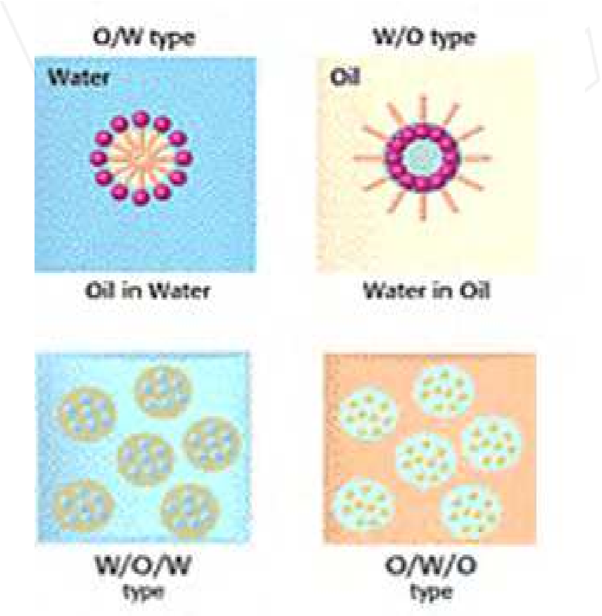


Fig.1: Types of emulsion (Manar El-Sayed Abdel-Raouf, 2012)

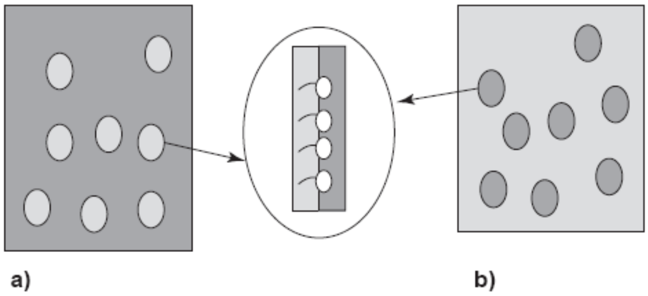


Fig. 2: Schematic representation of emulsion structures a) O/W emulsion b) W/O emulsion. Encircled: enlarged view of a surfactant monolayer sitting at the oil-water interface (Abdel-Raouf, 2012)

There are three main criteria needed for creature of oil emulsion (H. Schubert, 2005):

1. Two immiscible liquids must be brought in contact.
2. Surface active component must present as the emulsifying agent.
3. Sufficient mixing or agitating effect must be provided in order to disperse one liquid into another as droplets.

During emulsion production, the deformation of drop is opposed by the pressure gradient between the external (convex) and the internal (concave) side of an interface. Agitation provides the pressure gradient and velocity gradient essential for emulsion formation. Very high shear velocity enables to produce emulsion of small droplets, what requires much energy.

This problem can be solved by addition of certain surfactant to the system that reduces the agitation energy required to produce small droplets. In practice the same effect can be achieved with phase inversion what requires much less energy. For example, if a water-in-oil emulsion is desired, then an oil-in-water emulsion is first prepared by the addition of mechanical energy, and the oil content is gradually increased. At some volume fraction above 60-70%, the emulsion will suddenly invert and produce a W/O emulsion of much smaller water droplet sizes than were the oil droplets in the original O/W emulsions (L. Schramm, 2005).

2.1 Characterization of Emulsions

Appearance and Emulsion type

Emulsions are presented in a vast range of appearance, depending on the droplet sizes and the difference in refractive indices between phases (L. Schramm, 2005). Emulsion can be transparent if the phases indices are the same or the droplets of the dispersed phases are sufficiently small compared with the wavelength of the light. For instance, an O/W micro-emulsion of crude oil and water may be transparent.

Texture

O/W emulsions feel like “watery or creamy” otherwise W/O emulsions feel “oily or greasy”. These feelings tell about the texture of an emulsion reflects that of external phase. However, with increase in emulsion viscosity it becomes hardly to distinguish the emulsion types.

Mixing

An emulsion easily mixes with a liquid phase that is miscible with the continuous phase. It means that O/W emulsions can be diluted with water while W/O emulsions can be diluted with oil.

Dyeing

Any dyes, which added into an emulsion, color the continuous phase in which they are soluble.

Inversion

Once a very concentrated emulsion is diluted with additional internal phase, it will probably invert.

2.1.1 Oil composition

A good understanding of emulsion behavior is necessary within all stages of petroleum activities in the field, hydrocarbon transportation and refinery. Many studies have been done over the last years but many questions still have to be solved in emulsion behavior.

Oil composition plays a major role in the emulsion behavior, especially the surface-active molecules contained in the oil. These molecules cover a spread range of chemical structures, molecular weight and HLB (Hydrophilic-lipophilic-balance) values; they can interact between each other and/or reorganize at the water/oil interface (G. Nunez, 1996) (D. Fruman, 1983). The scheme of dividing of oil into four groups is illustrated in Fig.3.

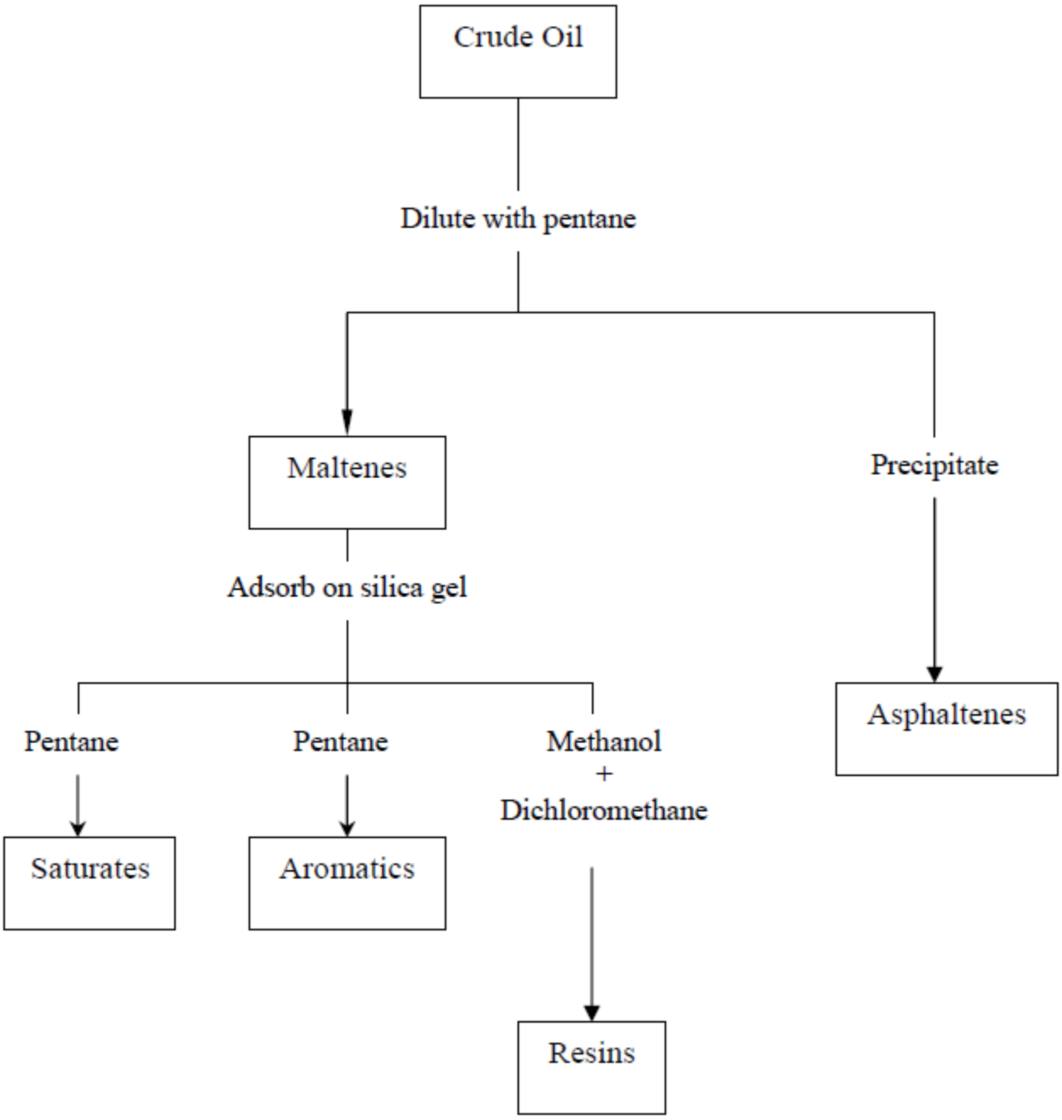


Fig.3: Schematic of SARA fractionation of oil

Oil composition usually classified as saturates, aromatics, resins and asphaltenes. This composition analysis is known as SARA analysis and it helps on the prediction of crude oil behavior in oil-water mixtures.

The formation of water-in-oil stable dispersions and water-in-oil in water unstable multiple dispersions occur due to the chemical composition of oil. Oil composition facilitates the formation of water-in-oil emulsion when none of surfactants are in the mixture. The complex crude oil chemical composition and the presence of solid particles will affect the interfacial tension between both phases as well as the stability. The crude oil composition obtained from the SARA analysis is used as a tool to predict the stability of these water-oil emulsions. The SARA analysis test may provide information about the degree of stability of crude oil-water emulsion. The degree of stability is important because it affects the inversion point and effective mixture viscosity (J.L. Cabanillas, 2013)

Asphaltenes are high molecular weight polar components of oil, many studies recognized asphaltenes as a main natural stabilizer of water-in-oil emulsion (M.F. Ali, 2000). Asphaltenes stabilize water-in-oil dispersion by various mechanisms of action. Once asphaltenes disperse at the water/oil interface, the layer adsorbed onto the interface behaves as a barrier that prevents the droplets to coalescence and phase separation into oil and water. J. Sjoblom, 2001 suggests that asphaltenes forms hydrogen bonding between water molecules and asphaltenes, what stabilizes the emulsion. Other crude oil components, such as resins, fatty acids (wax crystals, porphyrins, naphthentic acids, etc.) also affect to emulsion stabilization. However, there are still controversies about their positive or negative impact on stabilization process. The well-known fact that they are not able to form stabile emulsions alone but they can to associate to asphaltenes. Resins make asphaltenes soluble in oil and remove them from interface what lowers emulsion stability. Naphthenic and other fatty acids are not able to stabilize emulsion alone, however they create desirable conditions for the emulsion stability upon water pH (J. Sjoblom, 2003).

In addition to the indigenous components, particles such as silica, clay, iron oxides, etc. are defined as emulsifier agents. These particles are naturally hydrophilic, but can turn into lipophilic because of long time exposure to the oil in the non-water environment. Wax in crude oil also adsorbs on the interface and contribute to the stability. To know the temperature at which waxes form crystals is vitality. Below that temperature wax crystals precipitate and interact the oil-water interface increasing the stability. Otherwise, once temperature grows up the wax crystals melt and the emulsion stability decreases tremendously.

2.1.2 Phase inversion

Phase inversion phenomena take place at phase inversion point. It refers to the state of dispersed flow when the continuous and dispersed phases spontaneously invert. For example, in water-oil system systems a dispersed of water droplets in oil become a dispersion of oil drops in water, or vice versa. An abrupt change in rates of momentum, mass and heat transfer between the continuous and dispersed phases and between the dispersion and boundaries of the system are associated with phase inversion. Also, the droplets size distribution depends on the type of dispersion.

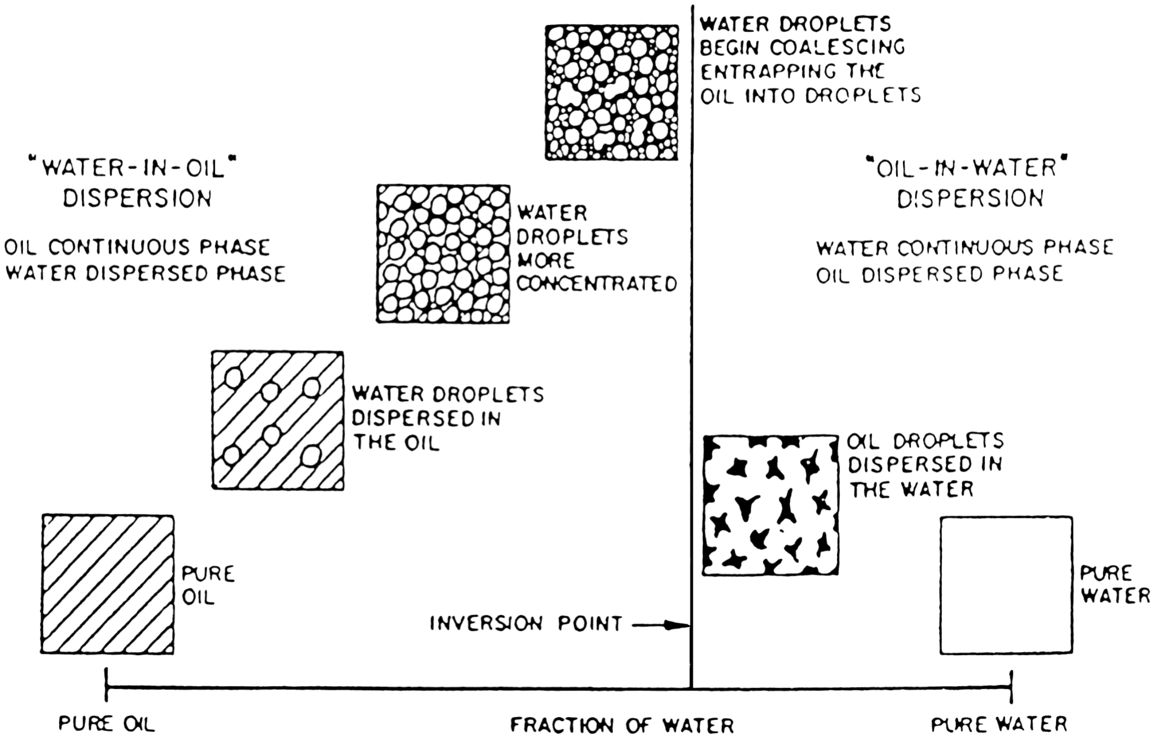


Fig.4: Phase Inversion Process for an Oil-Water Dispersion System (Arirachakaran et al. 1989)

As it is shown in Fig.4, when volume of the dispersed phase increases, the dispersed droplets become more concentrated and begin coalescing entrapping the initial continuous phase into droplets. As a result, phase inversion process occurs.

The phase inversion point is defined as the critical volume fraction of the dispersed phase over which this phase becomes the continuous phase after small changes have been made to the physical properties of system (density, viscosity, chemical composition, interfacial tension), the geometry factors of a vessel (agitation speed, material type, wettability effect), phase ratio, energy changes (temperature), the presence of surfactants (decrease interfacial tension) (J.L. Cabanillas, 2013). All those parameters are regarded as influence factors on phase inversion and ambivalence range.

Ambivalence range is defined as a range of volume fraction a phase above which that phase is always continuous and below which it is dispersed. In the ambivalent range, either one of the two phases can be the dispersed phase. It has been marked that the percentage maximal dispersed phase fraction can be higher 74% and even reach 90% (R. Pal, 1986) (N. Brauner, 2000).

Phase inversion process has been studied for the last 30-40 years but there is still little knowledge about the mechanism of phase inversion process. Nevertheless, many researches are still required in order to understand the phase inversion process and the mechanisms behind it.

A proportion between water volume fraction and oil viscosity was established: the amount of water decreases with increasing of oil viscosity. The frictional pressure drop was also found to increase when the mixture reaches the inversion point. Due to the significant pressure drop and increasing of the effective viscosity of the mixture accompanied phase inversion, more detail studying of phase inversion process and point is essential (Arirachakaran et al. 1989) (see Fig.5).

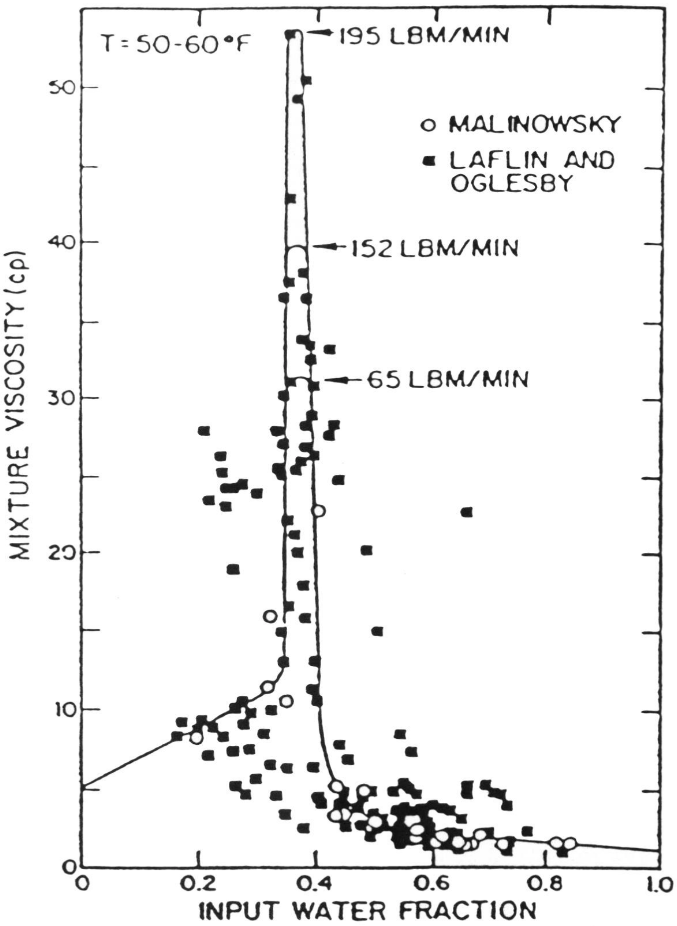


Fig.5: Mixture viscosity as a function of input water volume fraction for low viscosity oils (Arirachakaran, 1989)

It can be seen that the effective viscosity of the mixture reaches a peek at the point of phase inversion simultaneously with increasing of the volume fraction of the dispersed phase. S.L. Kokal (2005) stated that the droplet sizes of the dispersed phase, temperature, the viscosity of oil and water, the amount of solids and shear rates could affect on the effective viscosity of dispersion. This effect increases with increase of concentration of dispersions with significant interactions between droplets. R. Pal (1996) defined that decreasing of droplet sizes could increase the effective viscosity of the mixture in stable dispersions. The effect is highly dependent on dispersed phase volume fraction. R. Pal demonstrated the dependence of the effective viscosity on droplet size distribution (Fig.6). The figure exhibits that higher differences exist for low shear stress. At low shear stresses (about 0.1-10 Pa) a shear thinning behavior of the dispersion is observed to be stronger in the fine dispersion. The volume fraction of the dispersed phase also plays an important role where higher dispersed phase concentrations result in significantly higher effective viscosities.

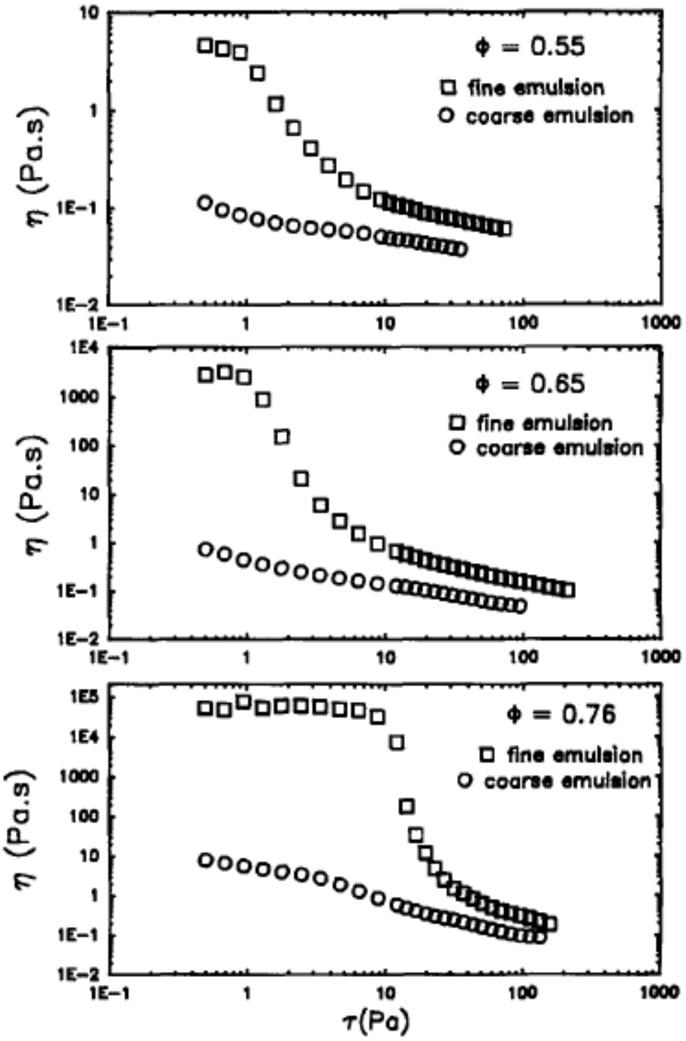


Fig.6: Influence of droplet sizes on effective viscosity in water-in-oil stable dispersions (R. Pal, 1996)

The shear rate becomes a very important parameter of droplet formation and size distribution. It is observed that an increase of shear rate has reduction effect on droplet sizes. Summer et al. (1992) stated that the droplet sizes increase simultaneously with an increase of the dispersed volume fraction in the water-in-oil system, see Fig.7.

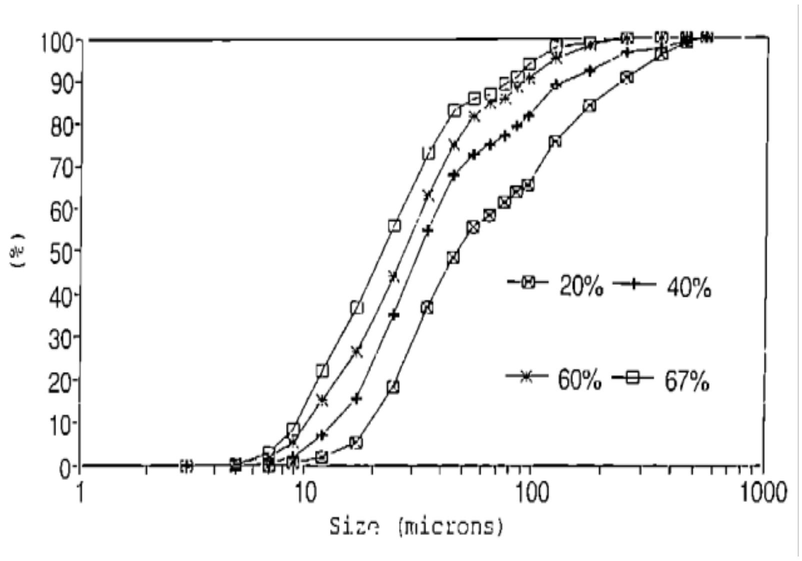


Fig.7: Droplet size distributions at different volume fractions of the dispersed phase (Summer et al., 1992)

2.2 Stabilization of the emulsion

There exist several factors that contribute to formation of stable emulsion such as low interfacial tension, small sizes of droplets of the dispersed phase, small volume of the dispersed phase, small density differences between the phases, steric repulsions and high viscosity of the continuous phase. The best result of stabilization is achieved by stabilization of the phase boundary. There are the factors favoring emulsion stability (L. Schramm, 2005):

1) Low interfacial tension- low interfacial free energy makes it easier to maintain large interfacial area.
2) Strong interfacial film acting as a barrier - it makes hard droplets to coalescence
3) Steric repulsions- these repulsions act to prevent collisions and aggregations and then coalescence.
4) Small dispersion force attraction- this decrease the rate of aggregation and coalescence.
5) Small droplets size, if the droplets are electrostatically or esoterically interacting
6) Small volume of dispersed phase- this reduces the frequency of collisions and aggregations.
7) Small density difference between the phases- this reduces the rate of creaming and aggregation.
8) High bulk viscosity- this reduces the rates of creaming and coalescence.

2.2.1 Steric stabilization of the interface

Solids at interfaces might give a rise of repulsive surface forces that thermodynamically stabilize the emulsion. For particles possessing intermediate wettability (partially wetted by both oil and water phases) solid's properties contribute large amount of free energy of absorption at stabilizing emulsion interface (P.M. Spiecker, 2003). On the one hand, certain emulsion are stabilized superbly by the irreversible adsorption. Otherwise, such behavior is cardinally different to the behavior of surfactants, which leads to the thermo-dynamical equilibrium between continuous phase and the phase interface. If we look at stabilization mechanism of asphaltene, it is observed that coalescence needs free-particles zone at the droplets contact region. Many researches suggest that lateral displacement is most likely, because of a huge amount of energy required for droplets movement into either phase out of the interface (S. Acevedo, 1993) (R.F. Lee, 1999). The steric stabilization effect for water drops is demonstrated in Fig.8, where a physical barrier around the particles prevents droplet contact. The rheological properties of water-asphalted oil interface dependent on the nature of solvent used for dilution, the oil concentration, the asphaltenes and resin concentrations, the resin to asphaltenes ratio, etc. (J.D. Mclean and P.K. Kilpatrick, 1997) (E. Strassner, 1968).

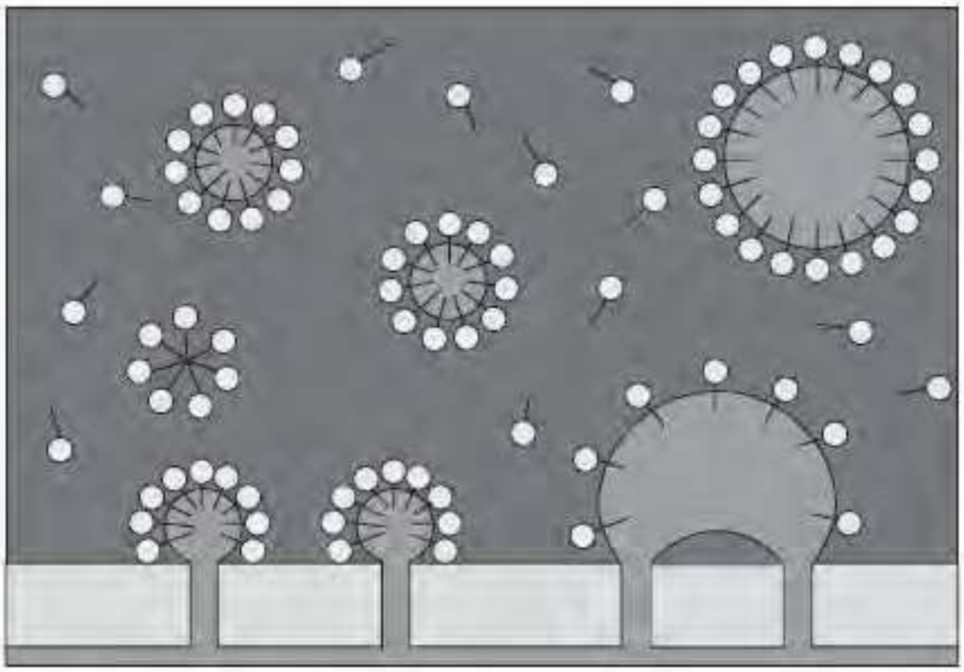


Fig. 8: Steric stabilization of the interfaces (J.D. Mclean, 1997)

2.2.2 Electric stabilization of the interface

Surfactants and polymers with protruding molecular chains use electrical double layer repulsion or charge stabilization to prevent the droplets from interaction between each other (T.H. Plegue, 1986) (P.R. Garrett, 1983). Another mechanism of surfactants that helps to prevent coalescence is creation of a mechanically strong and elastic interfacial film. In order to stabilize the emulsions the particles should be least one order of magnitude smaller in size than the emulsion droplets and in sufficiently high concentration. Stable water-in-oil emulsions demonstrate high interfacial viscosity and/or elasticity modulus.

2.2.3 Stable versus unstable oil-water dispersions

Dispersed flow with crude oil and water mixtures is very unstable and normally segregate under quiescent conditions. Otherwise, the complex oil composition including natural surface-active components and particles reduce the interfacial tension between the phases and tend to stabilize dispersions. By adding of lipophilic surfactants stable dispersion can be achieved.
The type of surfactant and the amount are adjusted in order to get the desired stability. In general emulsifiers reduce the interfacial tension between the two phases forming a barrier at the interface. That leads to stabilization of dispersion as a result smaller droplet sizes are achieved and enhanced stability of the dispersion. Oil-in-water or water-in-oil dispersions may be formed depending on the type of emulsifier used. The hydrophilic-lipophilic balance (HLB) of the surfactant plays the major role in determination of the type of stable emulsions, Bancroft´s rule states that the liquid in which the stabilizer has a higher solubility will form the continuous phase (Bancroft, 1912).

2.3 Emulsion destabilization

The process by which the emulsions completely break is named coalescence. The system separates into two initial immiscible oil and water phases. The process is governed by emulsion destabilization mechanisms: creaming (sedimentation) and aggregation (flocculation), see fig.9.

Creaming, or sedimentation is a result from the density difference between the dispersed and continuous phases (L. Schramm, 2005). Creaming is not actually breaking, but produces two separate layers of emulsions. One of which (the cream) is raised upper over the other and contain an enhanced concentration of dispersed phase, which may produce aggregation.

Flocculation is aggregation of droplets, when two or more droplets clump together without coalescence occurring. Important point of flocculation is that all droplets save their own integrity with no change in the total surface area.

Coalescence is when two or more droplets fuse together to foam a singe larger droplet, reducing the total surface area. In contrast to aggregation, in coalescence process droplets lose their integrity and become a part of a new unit.

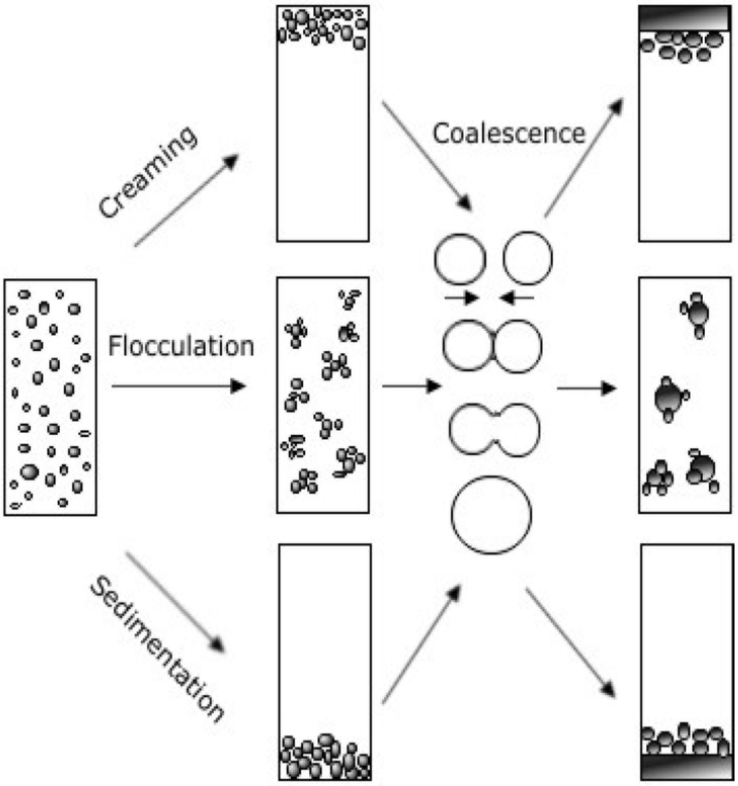


Fig. 9: Destabilization mechanisms of emulsions

2.4 Parameters influencing DSD

It is well known that properties of a system and parameters of processes have influence on DSD. Some of these parameters are described in the following.

2.4.1 pH-value

The coalescence mechanism is particularly affected by pH. Different methods for changing coalescence behavior are known in literature, one of the most used is adding of surfactants to immobilize the droplet surface and cause the change in interfacial tension and deform droplets.

Gäbler et al. (2006) focused on changing the coalescence behavior with increasing the pH-value and thereby the droplet charge.

They conducted their tests in a baffled-glass vessel with toluene as dispersed phase (φ =5-50%), and stirrer speed between 400 and 700 rpm. From the received results, pH has got a great influence on the steady-state distribution of the droplets. In fact with higher pH, coalescence is hindered considerably.

2.4.2 Viscosity

Calabrese et al defined that droplets are stabilized in agitated two liquids systems by surface and dispersed-phase viscous forces and are broken by forces associated with the continuous-phase turbulence (R.V. Calabrese, 1986).

The dispersed-phase viscosity has influence on the DSD and the mean drop size. Calabrese et al conducted their test with dispersed oil in water and analyzed the influence of dispersed-phase viscosity on the DSD at constant interfacial tension. It was noticed that at constant mixing conditions, the steady-state DSD increase significantly as dispersed-phase viscosity increases.

The size of the smallest droplets decrease while their number increases; the size of the largest droplets increase while their number decreases and the drop size distribution gets wider.

2.4.3 Dispersed phase fraction

Dispersed-phase concentration has profound effect on coalescence, dispersion process. For instance: coalescence rates increase with increasing of dispersed phase volume fraction. With increase of concentration, collision frequencies also increase and rheological properties get changed that enables to get longer contact intervals.

El-Hamouz et al. (2009) derived that there is a weak dependence of the equilibrium the mean droplet size on dispersed-phase concentration but a high concentration of dispersed phase affect small scale turbulent eddies, reducing their intensity and making them less able to disperse droplets. As a consequence of it the breakage decrease and the mean size diameter increase, the dependence demonstrated in Fig.10.

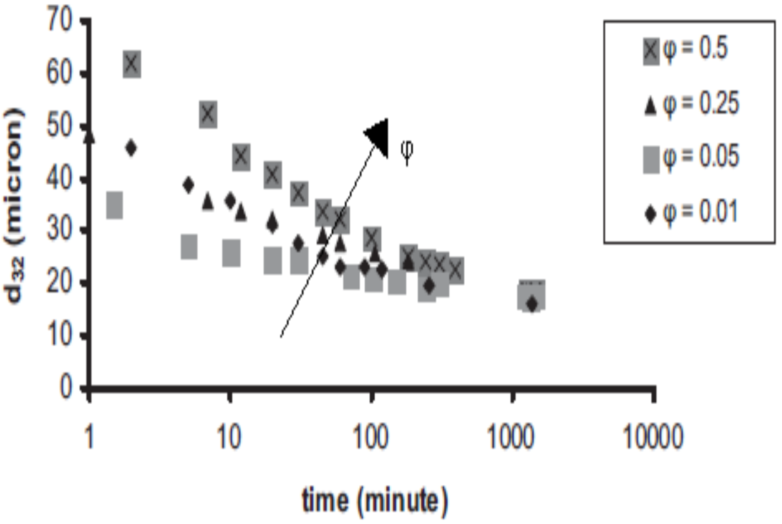


Fig.10: Mean size diameter for different phase fractions, with high viscosity silicone oil (El-Hamouz et al, 2009)

3 MATERIALS AND EXPERIMENTAL SETUP

3.1 Material description

The following surface-active components were used to stabilize dispersions:

The lipophilic surfactant was Span 80 from Croda GmbH (Germany). Span 80 is soluble in oil and partly soluble in water.

The hydrophilic surfactant was Tween 80 from Croda (Germany). Tween 80 is insoluble in oil and soluble in water.

Span 80 based on unsaturated or branched chain fatty acids acts as effective water in oil emulsifiers. Span 80 is efficient co-emulsifier for oil in water systems when it combined with the corresponding Tween 80. Table 3 details the approximate HLB (hydrophilic-lipophilic balance) values of each surfactant. By adjusting the Span to Tween ratio, various HLB values can be achieved allowing the emulsification of many industrial raw materials (Span and Tween).

Product name	HLB	Product name	HLB
Span 80	4.3	Tween 80	15.0

Table 2: HLB values of Span and Tween

A combination of a high and low HLB emulsifiers is often more effective compare to the use of a single emulsifier. Combinations of Span and Tween products can therefore be used to develop stable oil-in-water emulsions of various materials. In this case of study, a blend of Span 80 and Tween 80 would be recommended to emulsify oil and water dispersion.

The mineral oil EDC 95/11 was chosen as oil phase with the following properties: density- 815 kg/m^3, viscosity- 3,4 mm^2/s.

Tap water was used. Due to transparence of both of phases, Lisamine red was premixed with water to dye the water and therefore to distinguish phases.

3.2 Preparation of Emulsions

As said earlier, for experiments Span 80 and Tween 80 were chosen as two of the most used non-ionic emulsifiers for preparation of W/O and O/W emulsions. Moreover, various emulsifiers were prepared using in various weight proportions of Span 80 and Tween 80 by mixing them. In order to calculate average HLB number the provided equitation 1 was used (A. Shrestha, 2011).

$$HLB_R = x_1 HLB_1 + x_2 HLB_2 \qquad (1),$$

Where:

HLB_R- compound HLB value

x_1, x_2- weight fractions of the surfactants

HLB_1, HLB_2 - HLB value of the surfactants

Obtained HLB numbers are demonstrated in the following table 6:

Number	Span 80: Tween 80	HLB
1	1:0	4,3
2	4:1	6,4
3	2:1	7,8
4	4:3	8,9
5	2:3	10,7
6	1:4	12,9
7	0:1	15,0

Table 3: Obtained HLB number

The emulsions were prepared by mixing of 0,01% of emulsifier with either weight proportion: 1) 20% of oil/ 80% of water or 2) 20% of water/ 80% of oil. To get the full picture of emulsion behavior surfactants were premixed with one of phase and the other phase was added after. All phases together were homogenized continuously for 5 min at 400 rpm using Silverson L4RT-A mixer, see Fig.11.

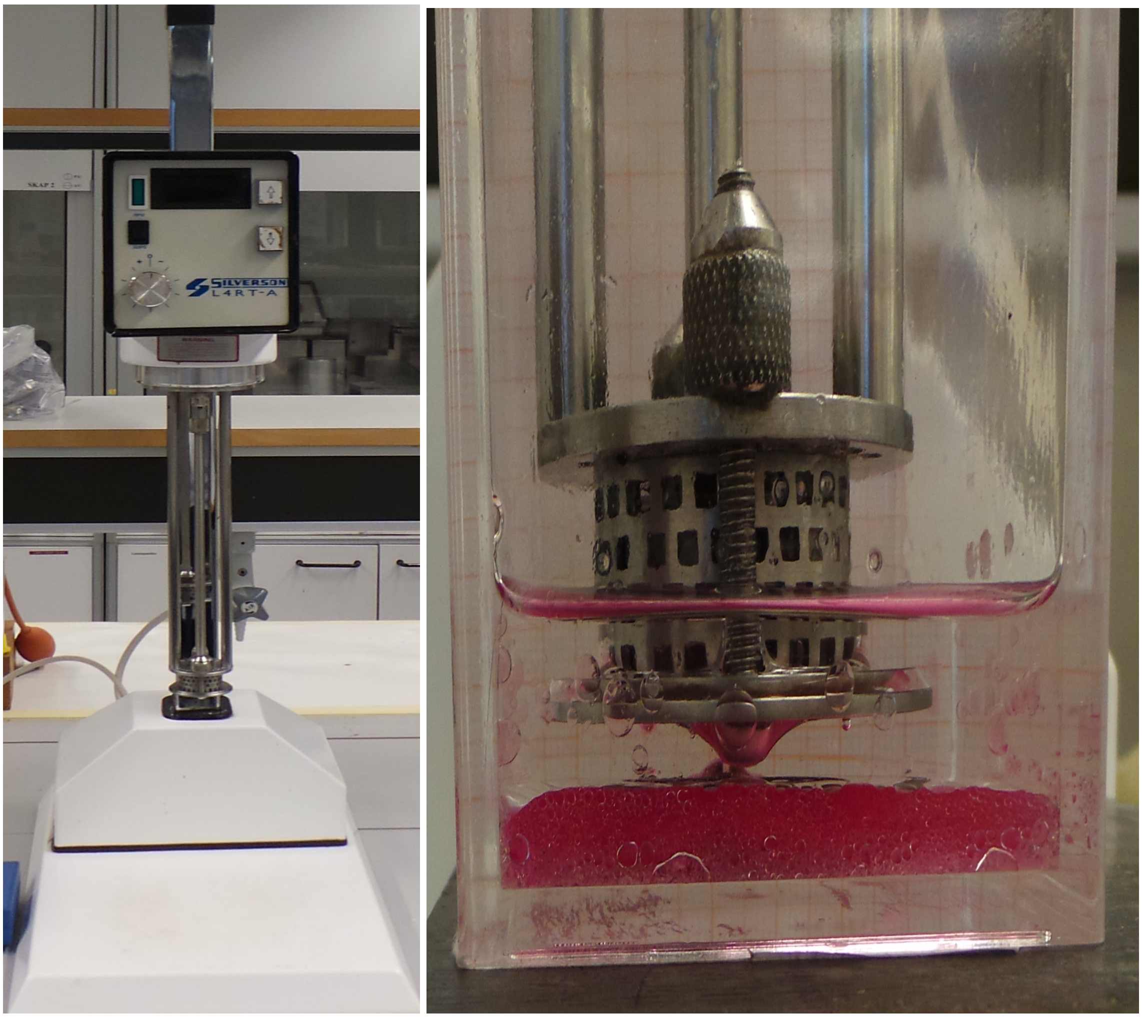


Fig.11: Experimental setup

The resulting compositions of the emulsions are tabulated in table 7. The emulsions were observed over 2 hours at room temperature. If any of prepared emulsions did not show signs of destabilization, the emulsions were considered as stable. The emulsions were continuously observed for next 72 hours to notify destabilization processes. Emulsions that demonstrated a strong tendency to full separation in first 2 hours were regarded as short-term stable.

Sample code	Water % /Oil % weight proportion	HLB	Surfactant weight proportion %	Surfactant premixed with	Phase added
S1	20:80	4,3	0,01	Water	Oil
S2	20:80	4,3	0,01	Oil	Water
S3	80:20	4,3	0,01	Water	Oil
S4	80:20	4,3	0,01	Oil	Water
S5	20:80	6,4	0,01	Water	Oil
S6	20:80	6,4	0,01	Oil	Water
S7	80:20	6,4	0,01	Water	Oil
S8	80:20	6,4	0,01	Oil	Water
S9	20:80	7,8	0,01	Water	Oil
S10	20:80	7,8	0,01	Oil	Water
S11	80:20	7,8	0,01	Water	Oil
S12	80:20	7,8	0,01	Oil	Water
S13	20:80	8,9	0,01	Water	Oil
S14	20:80	8,9	0,01	Oil	Water
S15	80:20	8,9	0,01	Water	Oil
S16	80:20	8,9	0,01	Oil	Water
S17	20:80	10,7	0,01	Water	Oil
S18	20:80	10,7	0,01	Oil	Water
S19	80:20	10,7	0,01	Water	Oil
S20	80:20	10,7	0,01	Oil	Water
S21	20:80	12,9	0,01	Water	Oil
S22	20:80	12,9	0,01	Oil	Water
S23	80:20	12,9	0,01	Water	Oil
S24	80:20	12,9	0,01	Oil	Water
S25	20:80	15,0	0,01	Water	Oil
S26	20:80	15,0	0,01	Oil	Water
S27	80:20	15,0	0,01	Water	Oil
S28	80:20	15,0	0,01	Oil	Water

Table 4: Emulsion composition

3.3 Microscopy studies of emulsion

The microstructures of the emulsions were studied with a light microscope Ziess Stemi DV4. All samples of emulsions were studied at time intervals: 30 min, 2 hours, 24 hours and 72 hours. AxioVision enabled to measure the size of droplets.

Fig.12: Light microscope Ziess Stemi DV4

3.4 Determination of emulsion type

Dye solubility test was conducted on the long-term stable emulsions to determinate an emulsion type. The dye solubility tests were performed with Lisamine red as a dye indicator. If the type of the emulsion is water-in-oil either Lisamine red will float on the surface of the emulsion or else the dye will dissolve and cause a change in the color of the emulsion from white to purple.

3.5 pH measurements

The changes in the pH of the stable emulsion were measured with a digital pH meter Orion Research model 201. pH values were taken every 12 hours during 72 hours.

Fig.13: pH meter Orion Research

3.6 Viscosity measurements

Rotational technique tests were conducted on the emulsions to determinate rheological characteristics of the emulsions. All samples were tested under shear rate from 400 to 1400 RPM with an increasing step 200 RPM. There are some rheological measurement problems due to phase separation that may occur during conduction of measurements, what makes the measurements non-reproductive. Careful observations may be needed to identify these problems.

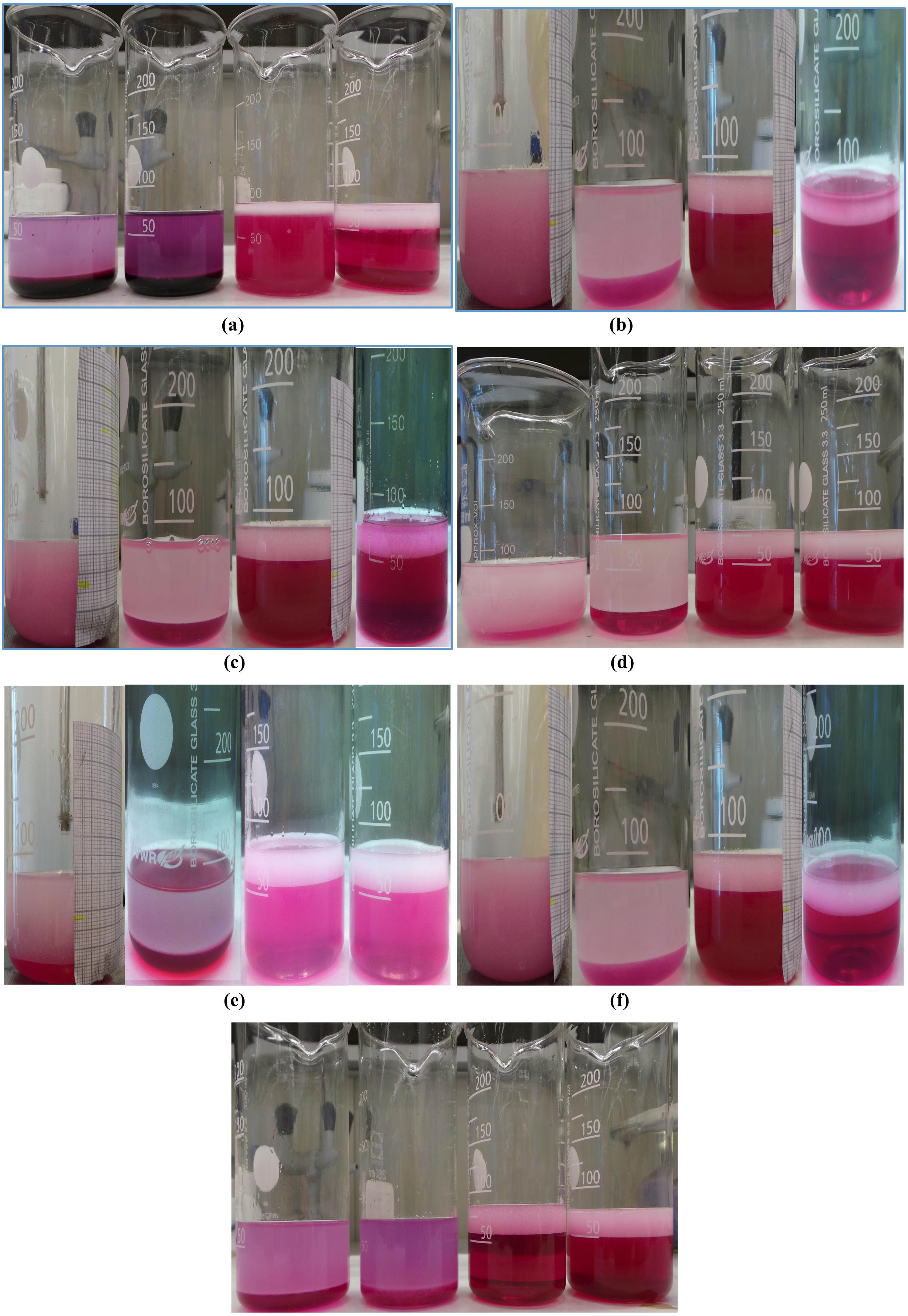
3.7 FBRM and PVM measurement techniques

FBRM and PVM measurement probes are ones of the most recent equipment that allows measuring real time droplet distribution and microstructure of emulsions. Due to a very short availability of these units it was not possible to conduct all experiments but the major states of emulsion behavior were also proved and used as the reference states for the work.

4 RESULTS AND DISCUSSION

4.1 Emulsion preparation

The emulsions were prepared in glass beaker with liquid volumes: 65 ml (80%) and 17 ml (20%) (fig.14). The prepared emulsions were put aside without disturbing for 2 hours. The emulsions (S1, S5, S10, S14, S18, S22, S25) with weight fraction of the mineral oil:water equal to 80%:20% destabilized immediately after mixing. All emulsions with weight proportion of mineral oil:water was 20%:80% (S3, S4, S7, S8, S11, S12, S13, S15, S16, S20, S23, S24) demonstrated disability to produce long-term stable emulsions and separated immediately after stirring. For those emulsions with all HLB number it shows that surfactants did not produced O/W emulsion. The destabilization of the emulsions may be attributed to the separation of the emulsions. This may be because small droplets merge and procreate larger species, what leads to the separation of the continuous phase from the emulsion and breaking of the surfactant barrier with continuous coalescence of the smaller droplets. This kind of destabilization has been regarded as the inability of such small amount of surfactant to create a fairly enough strong physical barrier around the droplets what prevents the droplets from contact and merge. This destabilization is an obvious signal of short-stable emulsions. Four emulsions were found to be stable for 2 h. They were subsequently kept undisturbed at room temperature up to 72 h.



(a) (b)

(c) (d)

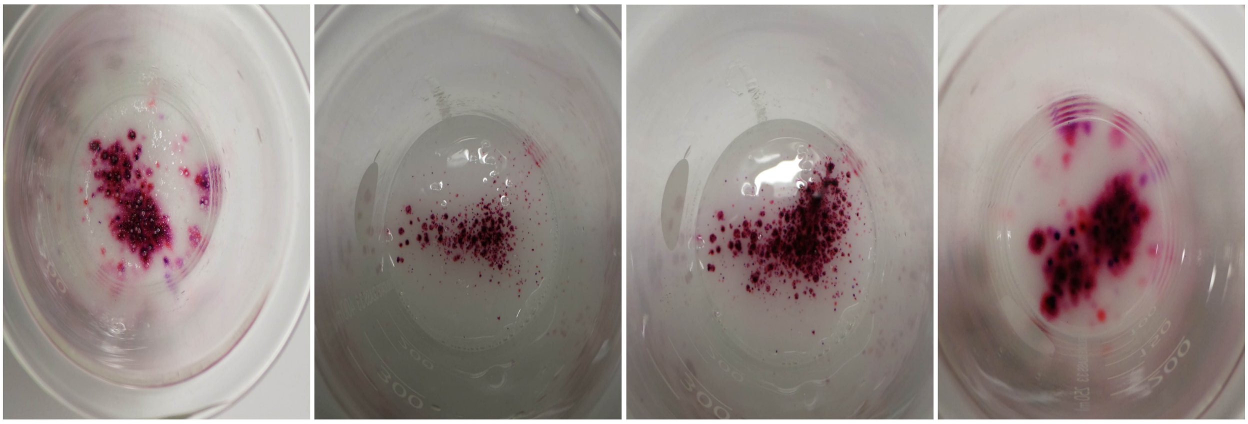
(e) (f)

(g)

Fig.14: ECD 95/11 mineral oil and water-based emulsions. (a) S1-S4 (HLB 4.3); (b) S5-S8 (HLB 6.4); (c) S9-S12 (HLB 7.8); (d) S13-S16 (HLB 8.9); (e) S17-S20 (HLB 10.7); (f) S21-S24 (HLB 12.9); (g) S25-S28 (HLB 15)

4.2 Determination of emulsion type

To determinate the emulsion type, dye solubility tests were performed on the long-term stable emulsions (S9, S13, S17, S21). The results of the tests indicate that the long-term stable emulsions were water-in-oil type emulsions, which showed that Lisamine red did not dye a continuous phase and remained onto the surface in the emulsion as powder substance, see Fig.15.



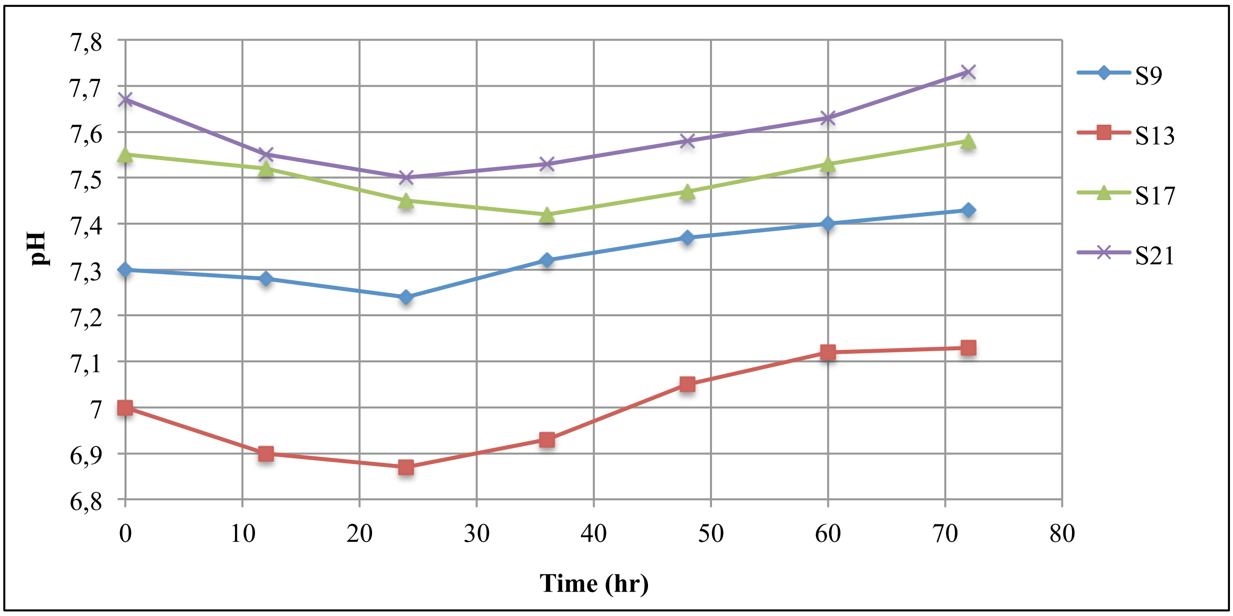
(a) (b) (c) (d)

Fig. 15: Dye solubility test for long-term stable emulsion. (a) S9; (b) S13; (c) S17; (d) S21

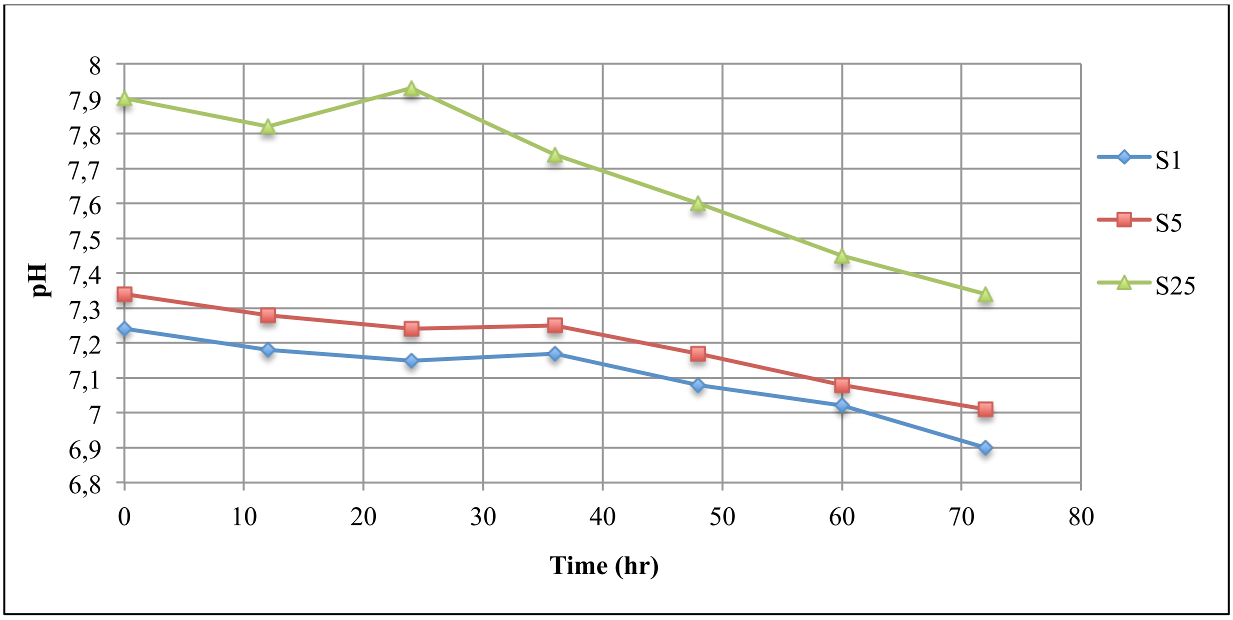
According to the HLB scale classification and definition, surfactants with HLB values in the range 3-8 promote water-in-oil emulsion while oil-in-water emulsions are created with emulsifiers having HLB values in the range 8-18 (L. Schramm, 2005). The dye tests gave an interesting result. Samples S17 and S21 were water-in-oil emulsions despite they were prepared with emulsifiers having HLB values: 10,7 and 12,9 accordingly.

4.3 pH measurement

The pH values of emulsions were taken for 72 hours with interval of each measurement in 8 hours (Fig.16). It was found that pH values for long-term stable emulsion (S9, S13, S17, S21) were slightly fluctuating around the initial point of pH value with a small increase in the pH value after 36 hours. Otherwise, the short-stable emulsions (S1, S5, S25) demonstrated a continuous decrease in pH values. The results of long-stable emulsions proves that with an increase in pH values coalescence increase, what can be seen that in 36 hours pH values started slightly increasing, what gives an increase in coalescence and further separation.



(a)

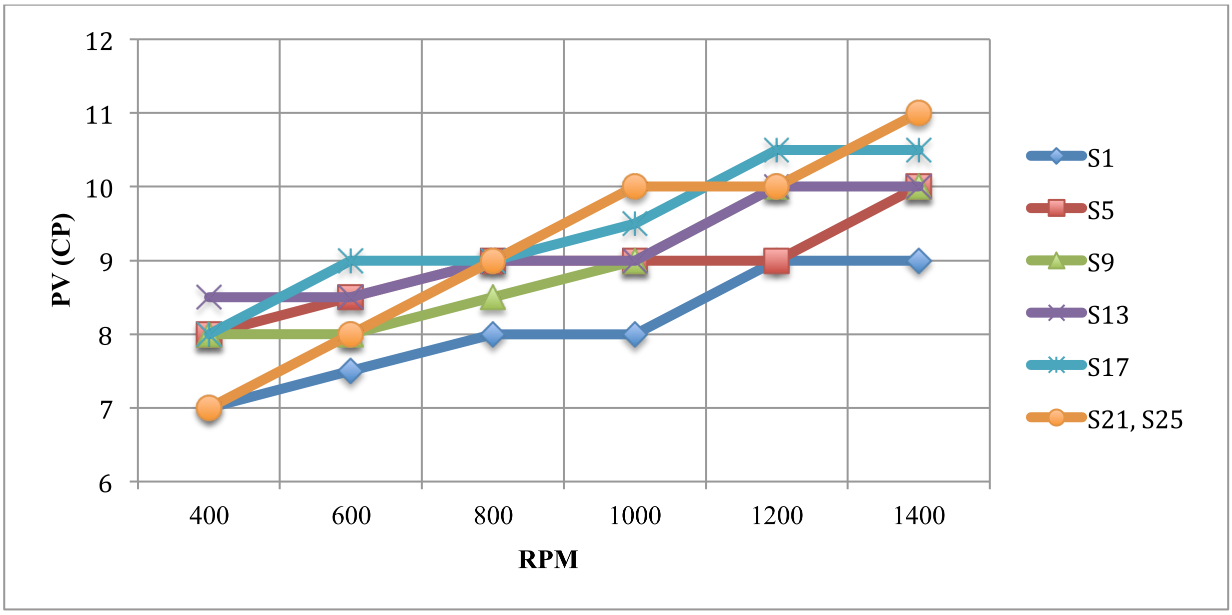


(b)

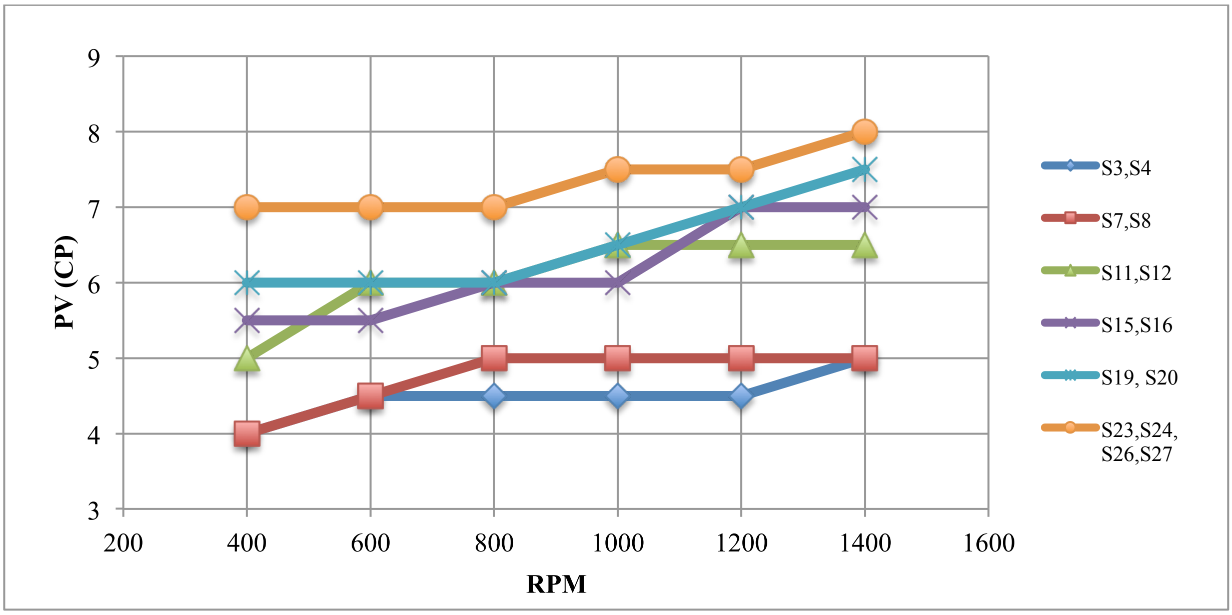
Fig. 16: pH values of emulsions (a) Long-term stable emulsions (b) short-term stable emulsion.

4.4 Viscosity

In order to determinate the dependency of mixture viscosity and shear rate, all emulsions were subjected to rotational tests of viscosity measurements. All samples were tested under shear rate from 400 to 1400 RPM with an increasing step 200 RPM. The diagrams demonstrate that as shear rate increases therefore mixture viscosity increases. Conclusion from such behavior is that the emulsion systems are dilatants (shear-thickening). The emulsions with water content 80% had lower viscosity values than the emulsions with 20% of water content, what could be considered as an indication of phase inversion occurrence in the water fraction between 20% and 80%. Dilatancy can be due to dense packing in very concentrated emulsions for which at low shear rate, the droplets can move past each other but at high shear rate they get wedged together such that can not easily move and the viscosity increase (L. Schramm, 2005). The conducted studies showed another dependency that with an increase of the HLB values, the viscosity of the emulsions also increases. What gives an enough strong barrier to coalescence and enhance the emulsion stability.

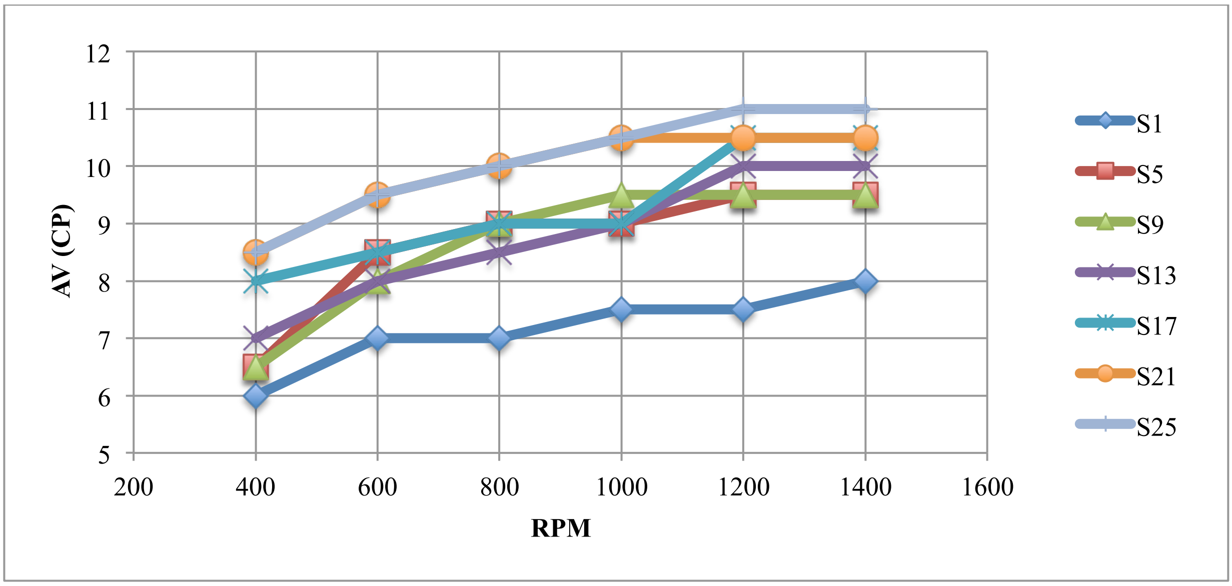


(a)

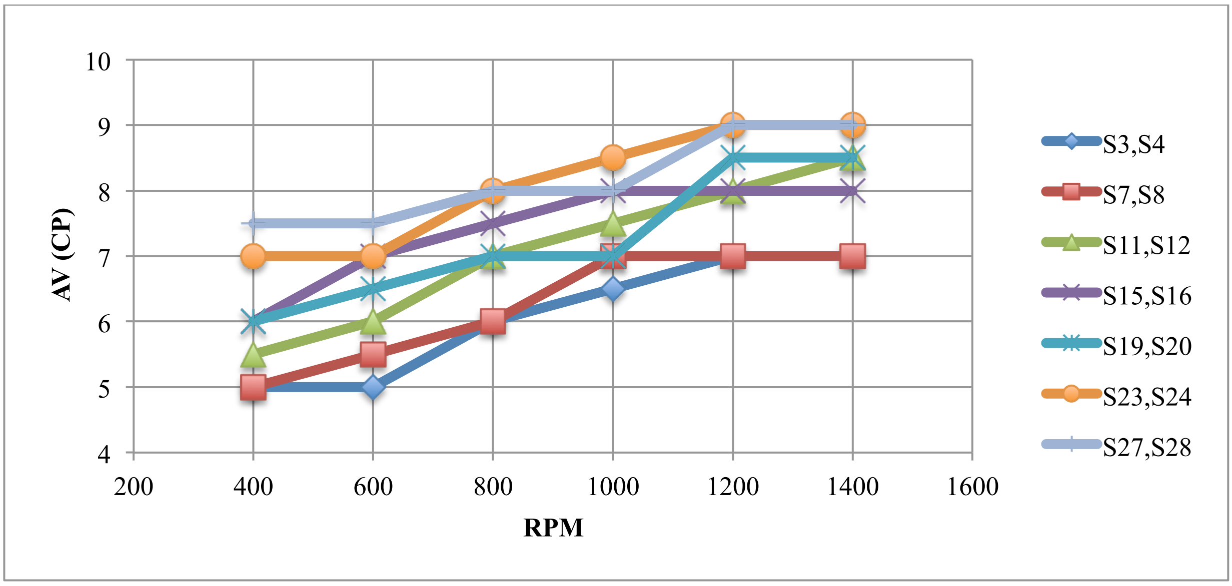


(b)

Fig.17: Plastic mixture viscosity versus shear rate: (a) emulsions with water fraction 20% (b) emulsions with water fraction 80%



(a)



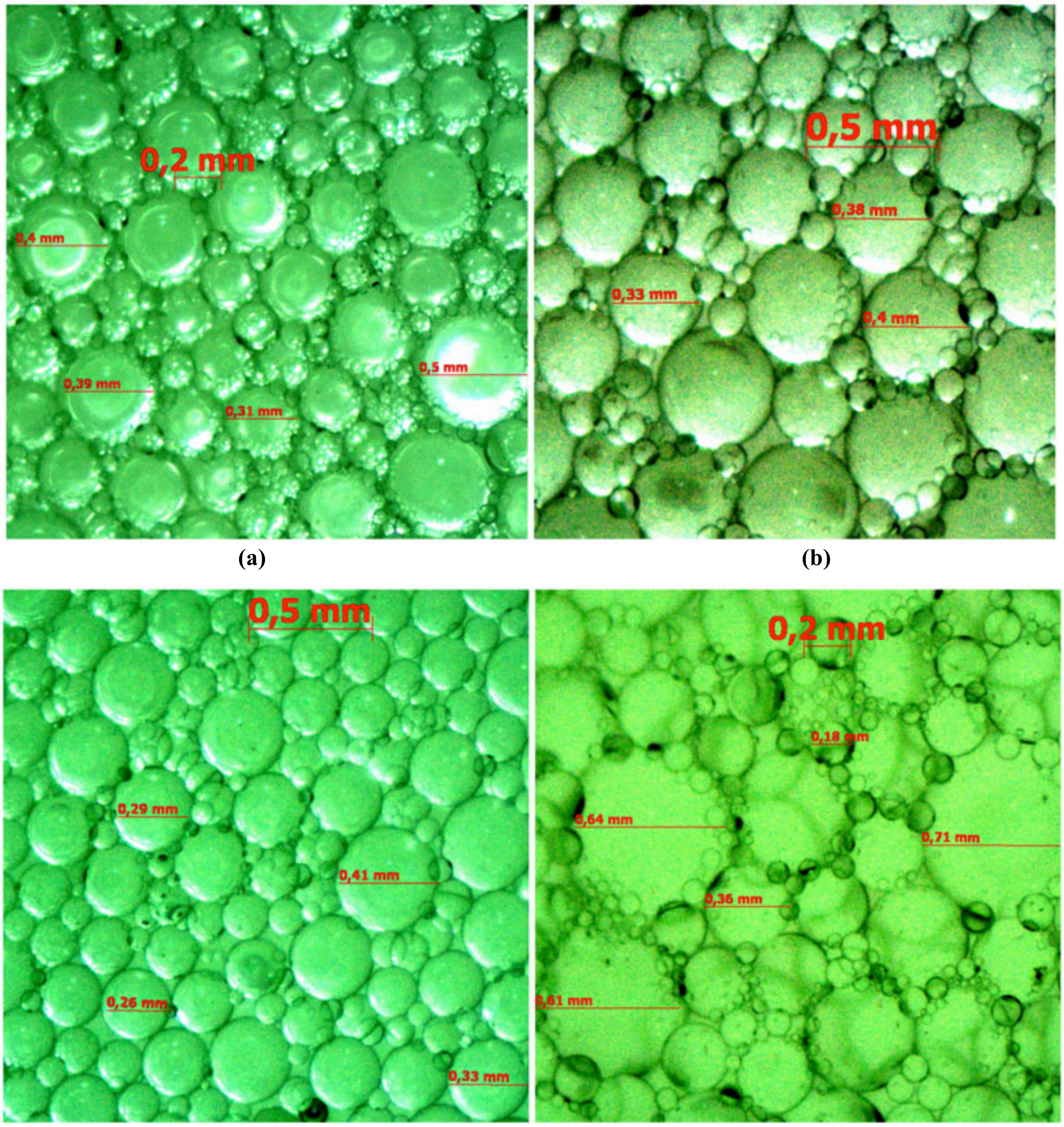
(b)

Fig.18: Apparent mixture viscosity versus shear rate: (a) emulsions with water fraction 20% (b) emulsions with water fraction 80%

4.5 Microscopic studies

Microscopic studies were conducted on all emulsion with an optical microscope Zeiss Stemi DV4. According to general description of emulsion preparation by mechanical mixers dispersed phase present as circular droplets. The micrographs of long-term stable emulsions proved that state. The dispersed water phase was present as droplets with a range of droplet sizes rather than droplets of a certain size.

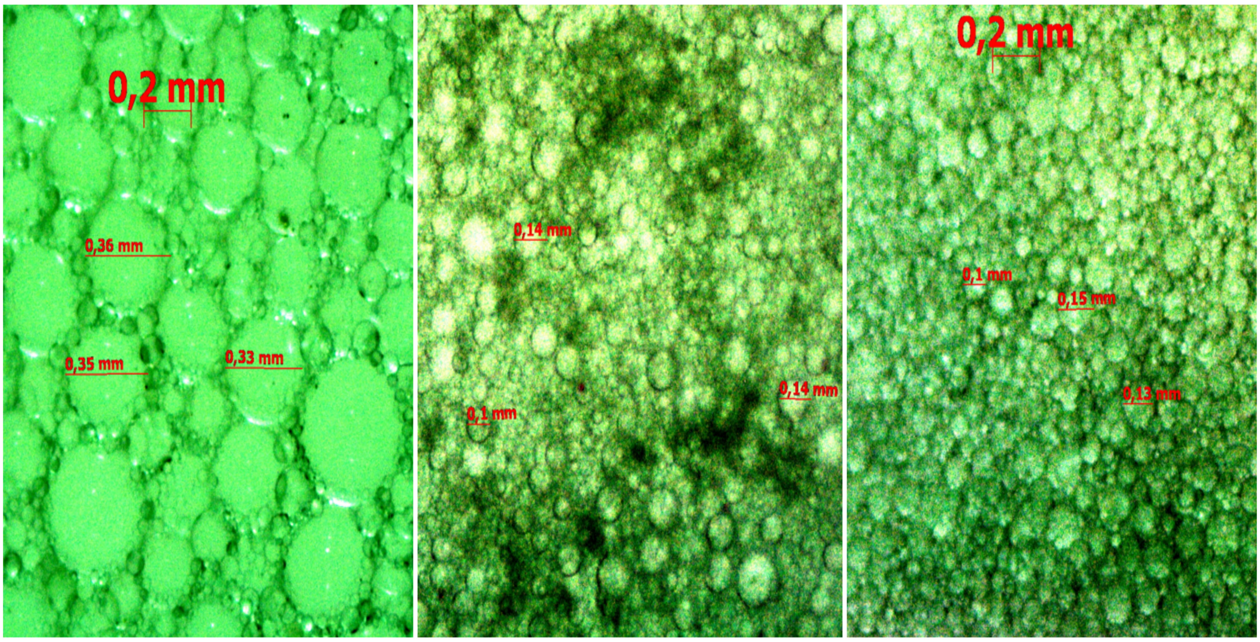
The sizes of droplets were measured using AxioVision software from the microstructures. The results indicate the broad range of droplet size distribution rather than a particular size of droplets.



(a) **(b)**

(c) **(d)**

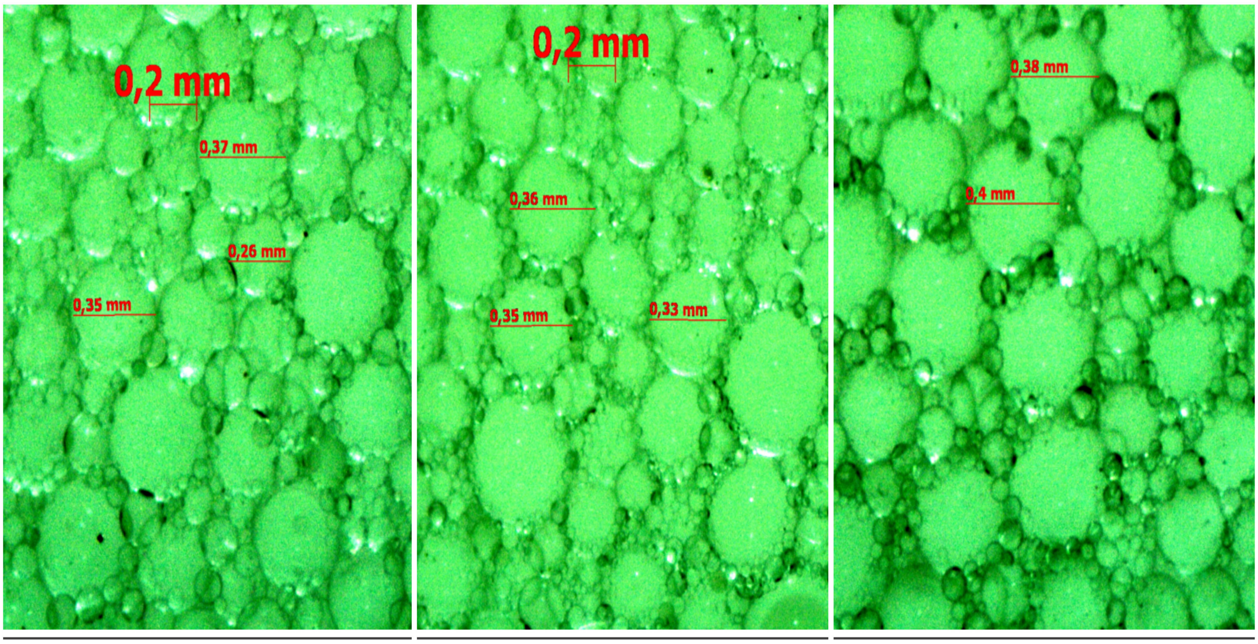
Fig.19: Micrographs of long-term stable emulsions. (a) S9 (b) S13 (c) S17 (d) S21



(a) (b) (c)

Fig.20: Structure of short-stable emulsions. (a) S5 (b) S1 (c) S25

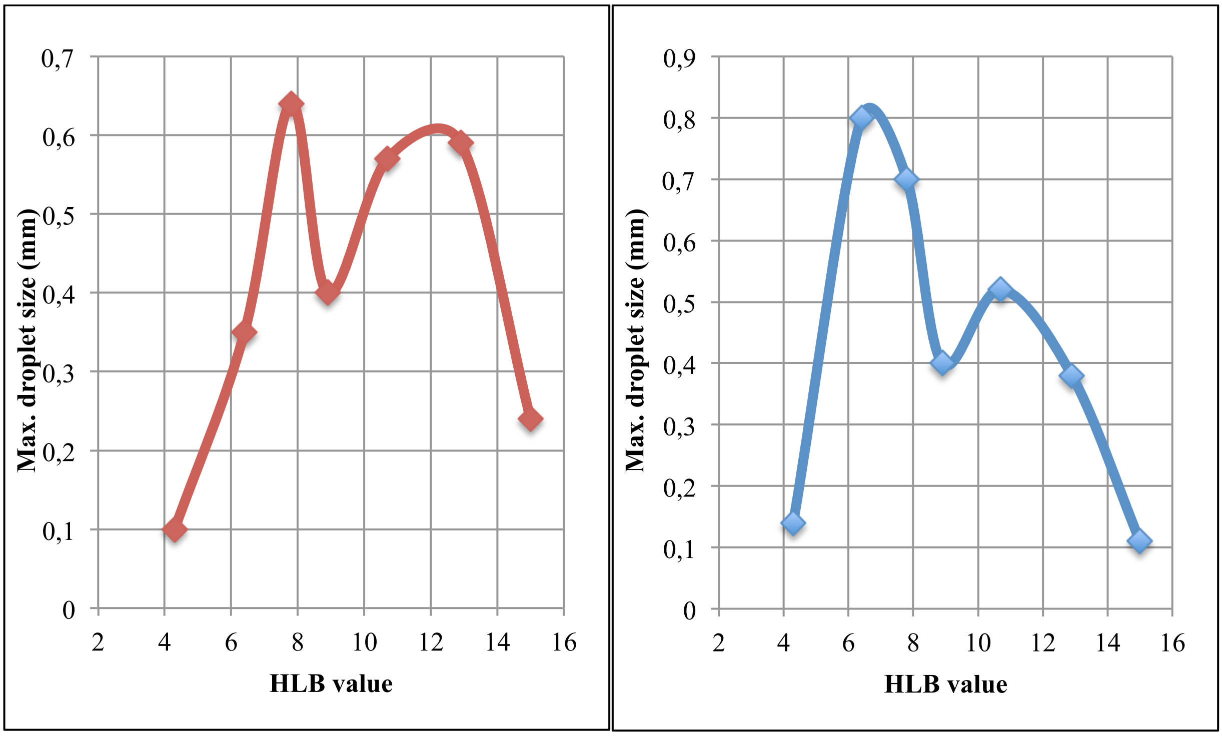
In spite of emulsions S1 and S25 had the smallest droplets in its microstructure, the emulsions did not stabilized for a long time. The emulsions with water fraction equal to 80% required longer time than 5 min to form homogeneous emulsions, which occupied the full volume of beakers. However, an increase of agitation time did enhance stability of the emulsions, which separated out almost completely after stop of agitation.



(a) (b) (c)

Fig.21: Example of micrographs of S5 taken in time. (a) 2 hr (b) 24 hr (c) 72 hr

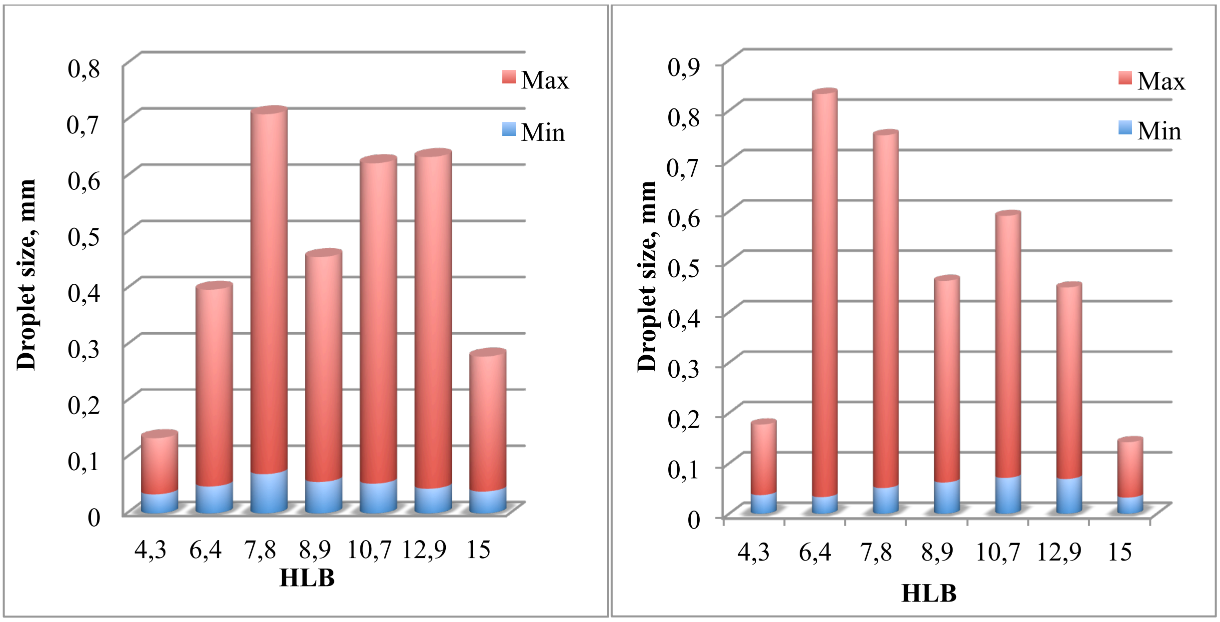
Fig.21 shows the microstructure of the short-term stable emulsions after 72 hours. It reveals that the possible cause of emulsion destabilization is aggregation. The microstructures demonstrate that the short-term stable emulsions were forming aggregates, with following coalescence. As these large species are formed, they were affected by the gravitational force and follows Stoke's law of sedimentation.



(a) **(b)**

Fig.22: Proportion of maximum droplet size and HLB value. (a) emulsions with water fraction 20% (b) emulsions with water fraction 80%

Fig.22 shows the distribution of maximum of droplet size as a function of the HLB value of the surfactants. The graphs indicate a bimodal distribution. The tendency of an increase of the droplet size is clearly seen with an increase of the HLB value from 4.3 to 7.8 with the maximum droplet sizes between 0.64 mm for 20% of water and 0.81 mm for 80% of water in the system. The following increase in HLB value up to 8.9 characterizes with a drop in the droplet size of emulsions to 0.4 mm. There is an increase in the droplet size up to 0.5 mm for both emulsion systems accompanied with an increase in the HLB value to 12. Thereafter, onwards increased HLB value to 15 demonstrated tremendous decrease in the droplet size to an initial droplet sizes.



a) **b)**

Fig.23: Range of droplet sizes versus HLB value.
(a) emulsions with water fraction 20% (b) emulsions with water fraction 80%

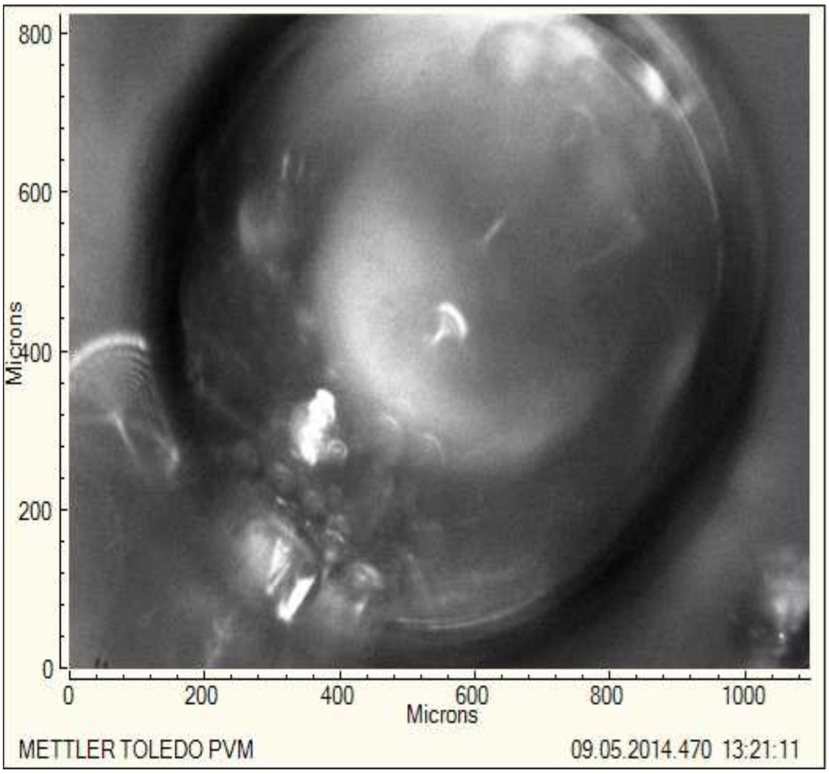
The range of droplet size is vast; it varies from 0,03mm to 0,8mm. The minimum size of droplets grows up along increase of HLB value, otherwise pure Span 80 and Tween 80 form almost equal minimum size droplets, which did not stabilize emulsions. With increase of water volume fraction minimum droplet size increase with increase of HLB value. The widest range of droplets size for both water volume fractions is achieved at point HLB value equal to 8, when emulsifiers convert from water-in-oil emulsion producers to oil-in-water emulsion producers.

All measures of droplet size are based on taken picture of emulsion structure with dimensions 2500*2000 pixels. The initial pictures were divided into squares with sides 500 pixels. The minimum and maximum sizes were observed in each square with approximation in droplet size ±0,02. The mean droplet sizes were calculated with that approximation.

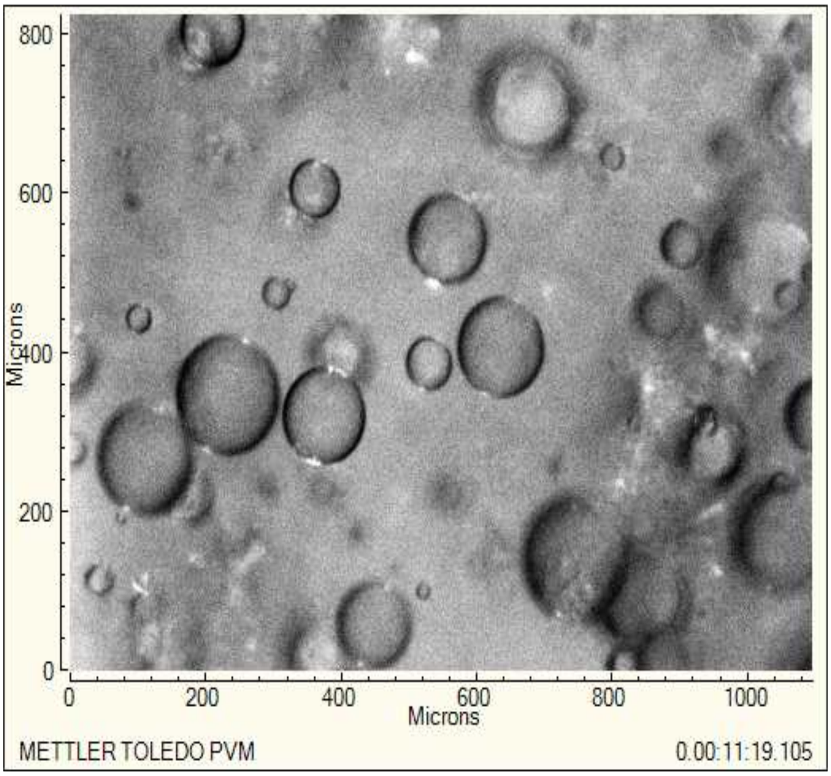
4.6 FBRM and PVM measurement techniques

FBRM and PVM studies were conducted on an oil-water emulsion with addition of Span80. The short-time studies allowed better understanding of emulsion behavioral changes under different conditional changes, like: increase of stirring speed, continuous adding of the emulsifier.

Fig. 24: FBRM and PVM experimental setup


800
600
400
200
0
Microns
0
200
400
600
800
1000
Microns
METTLER TOLEDO PVM
09.05.2014.470 13:21:11

a)


800
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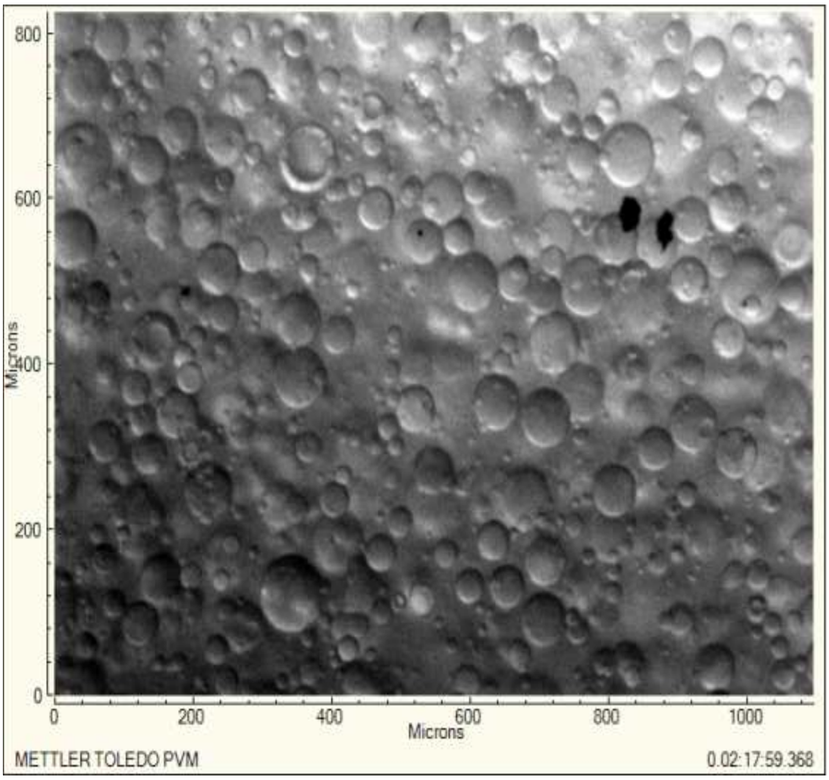
0.00:11:19.105

b)



c)

Fig. 25: Example of emulsion microstructure taken by PVM.
a) at 400 rpm b) at 1200 rpm c) at 1200 rpm+ 0,001% Span80

The pictures above taken by PVM demonstrate the difference in shapes and sizes of oil droplets with increase of stirring speed and addition of Span 80. It is well seen that the increase in agitation speed leads to decrease in droplet sizes, as well as addition of the surfactant. The fall in sizes of droplets from 800 µm to droplet size smaller than 100 µm is observed.

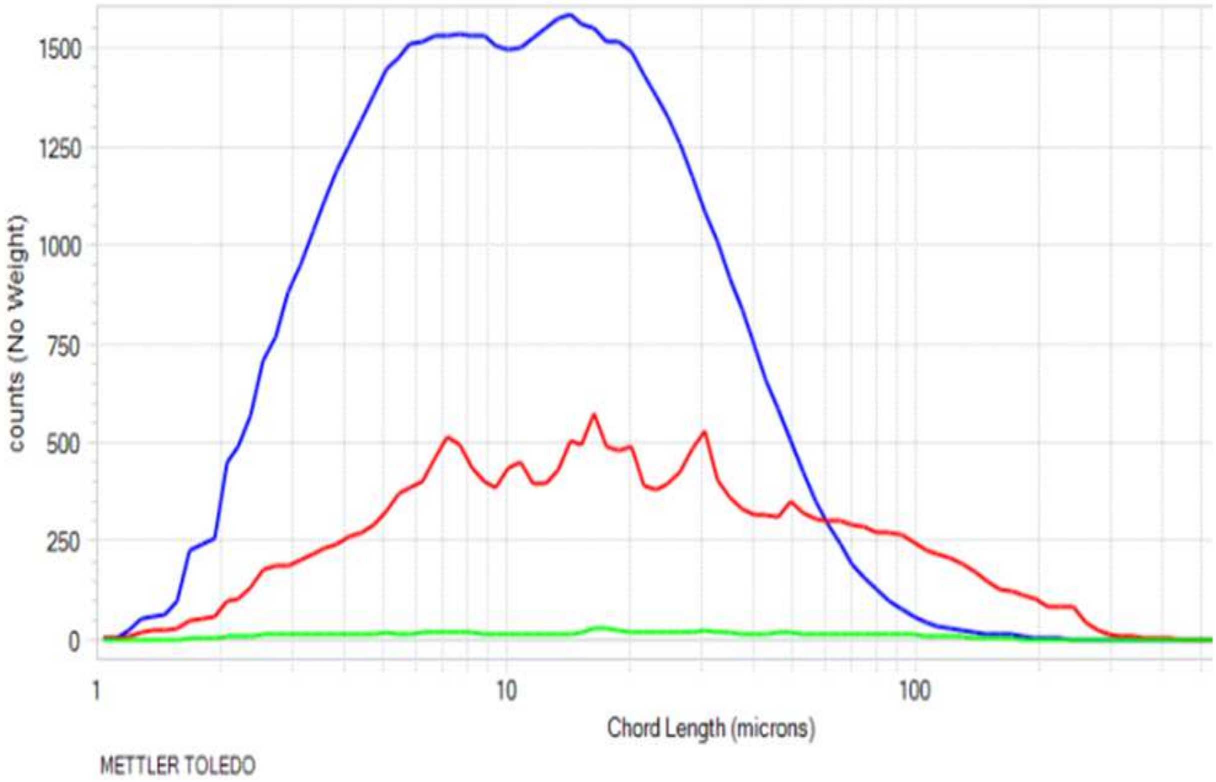


Fig.26: Example of FBRM distribution measurement

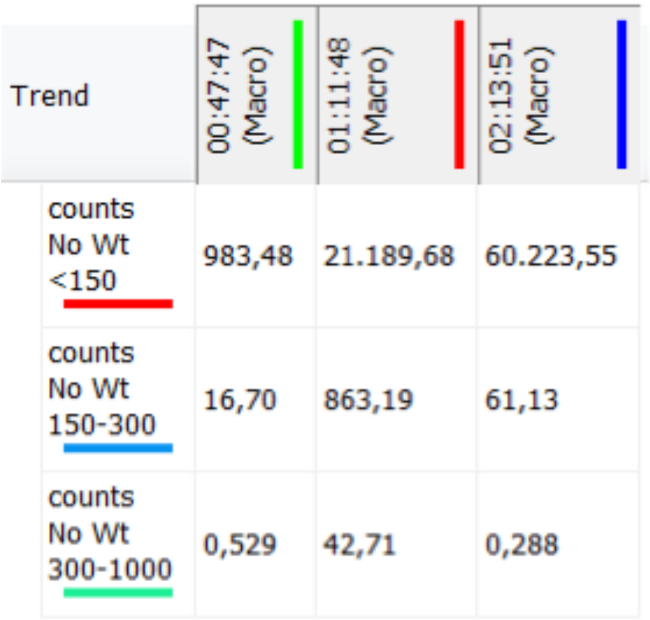
Where:

🟩 at 400rpm

🟥 at 1200rpm

🟦 at 1200rpm+Span 80

The Fig.26 proves that with an increase of agitation speed and addition of surfactants the droplets sizes become smaller. As it can be seen a small amount of Span 80 decreased the droplet size, chord length indicates it, and the number of smaller droplets tripled.



Trend	00:47:47 (Macro) 🟩	01:11:48 (Macro) 🟥	02:13:51 (Macro) 🟦
counts No Wt <150 🟥	983,48	21.189,68	60.223,55
counts No Wt 150-300 🟦	16,70	863,19	61,13
counts No Wt 300-1000 🟩	0,529	42,71	0,288

Fig. 27: Counted numbers of droplets

An accurate numbers of droplets are present in Fig.27. From the picture above, the numbers of droplets with chord length range smaller 150 μm is clear seen that increased after addition of Span 80. Meanwhile, the numbers of droplets with chord length range 150-300 μm decreased significantly, what says about overall droplet size decrease.

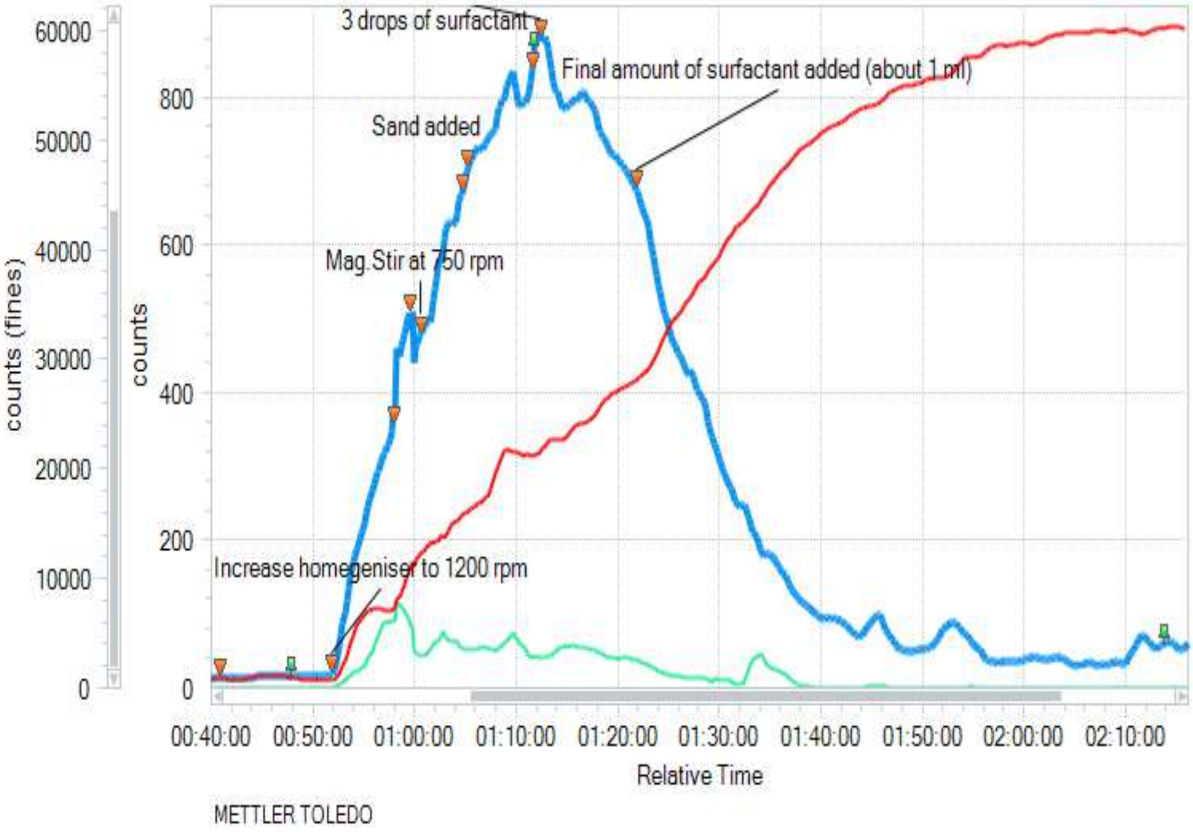


Fig. 28: Example of FBRM trends measurement

Where,

🟥 < 150 μm
🟦 150-300 μm
🟩 300-1000 μm

At point of time from 40 min to 50 min stirring speed was 400 rpm PVM captured big sized droplets around 1000 μm. After increase of impeller rotation speed up to 1200 rpm at 50 min we observed the number of droplet in chord length range 150 μm and 1000 μm increased, in Fig.28 it demonstrated with the blue and green lines. At the pick when the small amount of surfactant was added the FBRM counted a decline in amount of droplets with chord length 300-1000 μm and an increase of amount of droplets with chord length 150-300 μm. All this proves that an increase of agitation speed and addition of surfactants leads to decreasing of droplet sizes.

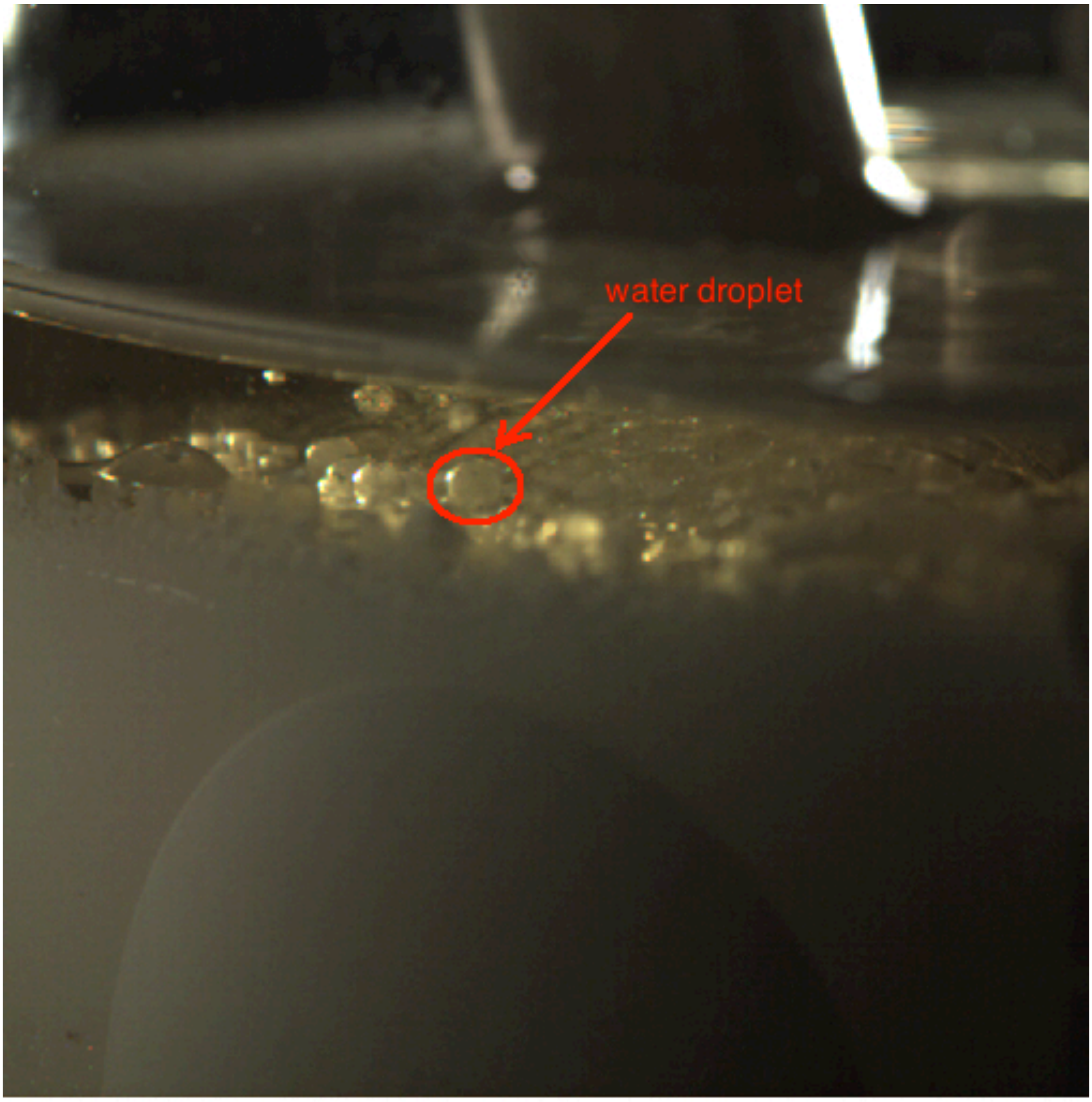


Fig. 29: Water droplets in oil

A close-up picture of water droplets in oil demonstrated in Fig.29. Span 80 have HLB value 4.3, the emulsifier produces water-in-oil emulsions. A good example of water droplets can be seen in the oil layer.

In combine with PVM results FBRM probe provides a good picture of droplet size distribution and changes occurring in emulsion in real time. These techniques could be used in studies of emulsion stability with desired droplet size distribution.

5 Conclusion

The study reports the successful implementation of very small amount of surface active agents of various HLB numbers for development of stable mineral oil-water emulsions without applying of much energy. The study indicated that once the HLB value had been changed the properties of emulsions changed, as well. The maximum droplet sizes of the emulsions varied from 0,1 mm to 0,8 mm. The results demonstrated that the main reason of emulsion destabilization of unstable and short-term stable emulsions was creaming leading to emulsion separation.

The case study proved facts about the emulsions with two different techniques. Stabilization of emulsion can be achieved by increasing of amount of emulsifiers and/or increasing of agitation energy, what leads to decrease of the droplet sizes and enhance emulsion stabilization.

6 FURTHER WORK

- In this project, only static conditions tests were conducted. It would be interesting to run experiments with the emulsions in pipeline flow loop.
- In the experiments only non-ionic surfactants were used. In the future works cationic surfactants might be used because of their promising separation abilities. Moreover, different separation techniques could be used.
- Phase inversion process requires investigation. Investigation of how small amount of surfactant will increase water volume fraction needed that phase inversion could occur.
- Accurate droplet size distribution analysis is required to study the effect of surfactants on the emulsion. With this purpose FBRM and PVM measurement techniques might be used.

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APPENDIX

Time, hours	Sample code and pH values			
	S9	S13	S17	S21
0	7,3	7	7,55	7,67
12	7,28	6,9	7,52	7,55
24	7,24	6,87	7,45	7,5
36	7,32	6,93	7,42	7,53
48	7,37	7,05	7,47	7,58
60	7,4	7,12	7,53	7,63
72	7,43	7,13	7,58	7,73

Table 5: pH values of long-term stable emulsions

Time, hours	Sample code and pH values		
	S1	S5	S25
0	7,24	7,34	7,9
12	7,18	7,28	7,82
24	7,15	7,24	7,93
36	7,17	7,25	7,74
48	7,08	7,17	7,6
60	7,02	7,08	7,45
72	6,9	7,01	7,34

Table 6: pH values of short-term stable emulsions

RPM	**Sample code and PV values (CP)**					
	S1	**S5**	**S9**	**S13**	**S17**	**S21, S25**
400	7	8	8	8,5	8	7
600	7,5	8,5	8	8,5	9	8
800	8	9	8,5	9	9	9
1000	8	9	9	9	9,5	10
1200	9	9	10	10	10,5	10
1400	9	10	10	10	10,5	11

Table 7: Plastic mixture viscosity values (CP) of emulsions with water fraction 20%

RPM	**Sample code and PV values (CP)**					
	S3, S4	**S7, S8**	**S11, S12**	**S15, S16**	**S19, S20**	**S23, S24, S26, S27**
400	4	4	5	5,5	6	7
600	4,5	4,5	6	5,5	6	7
800	4,5	5	6	6	6	7
1000	4,5	5	6,5	6	6,5	7,5
1200	4,5	5	6,5	7	7	7,5
1400	5	5	6,5	7	7,5	8

Table 8: Plastic mixture viscosity values (CP) of emulsions with water fraction 80%

RPM	Sample code and AV values (CP)						
	S1	S5	S9	S13	S17	S21	S25
400	6	6,5	6,5	7	8	8,5	8,5
600	7	8,5	8	8	8,5	9,5	9,5
800	7	9	9	8,5	9	10	10
1000	7,5	9	9,5	9	9	10,5	10,5
1200	7,5	9,5	9,5	10	10,5	10,5	11
1400	8	9,5	9,5	10	10,5	10,5	11

Table 9: Apparent mixture viscosity values (CP) of emulsions with water fraction 20%

RPM	Sample code and AV values (CP)						
	S3, S4	S7, S8	S11, S12	S15, S16	S19, S20	S23, S24	S26, S27
400	5	5	5,5	6	6	7	7,5
600	5	5,5	6	7	6,5	7	7,5
800	6	6	7	7,5	7	8	8
1000	6,5	7	7,5	8	7	8,5	8
1200	7	7	8	8	8,5	9	9
1400	7	7	8,5	8	8,5	9	9

Table 10: Apparent mixture viscosity values (CP) of emulsions with water fraction 80%

Min droplet size, mm	Max droplet size, mm	HLB value
0,034	0,1	4,3
0,048	0,35	6,4
0,07	0,64	7,8
0,056	0,4	8,9
0,053	0,57	10,7
0,044	0,59	12,9
0,039	0,24	15

a)

Min droplet size, mm	Max droplet size, mm	HLB value
0,037	0,14	4,3
0,033	0,8	6,4
0,051	0,7	7,8
0,062	0,4	8,9
0,071	0,45	10,7
0,069	0,38	12,9
0,032	0,11	15

b)

Table 11: Range of droplet sizes versus HLB value
a) 20% water volume fraction b) 80% water volume fraction