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Theoretical Survey and Experimental Assessment on the Comercial Surfactants to Produce Stable Water-in-Petroleum of Miri Light and Kuwait Heavy Crude Oil Emulsions

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Abstract

In this research the formulation of the experimental w/o emulsions was investigated based on two diferent crude oils, the crude oils used in this study were Miri light oil from malaysia and Kuwait heavy oil from middle east, the study was conducted with particular emphasis on the qualiy as well as quntity of the emulsifying agents,on purpose of selecting a suitable emulsifying agent to produce stable water-in-oil emulsions of the aforementioned oils, three types of emulsifying agents were tested namely Triton x-100, SDDS and SPAN 80, at various concentrations of 1, 3 and 5%, the water to oil ratios in the emulsion samples were 50-50% and 20-80%, from the results of this study SPAN 80 had produced very stable emulsions which showed no water separation within the observation period of one week for 50-50 as well as 20-80% w/o emulsions, while the other emulsifiers (Triton x-100 and SDDS) were found to be not effective, thus for emulsions with respect to the minimum emulsifiers' concentration of 1% and 50-50%, water to oil ratios, the separation rate of the Triton x-100 stabilised emulsions withinthe first 24 hours was, 70% for Miri oil emulsion and 50% for Kuwait oil emulsions, while the separation rate for SDDS stabilised with the same formulation was 60% for Miri emulsion and 55% fror Kuwait emulsions, but no water separation was observed with the SPAN 80 stabilised emulsions of the same compositions.When the water content was decreased to 20%, there was some increase in the stability, hence again with the minimum emulsifiers' concentration of 1%, and 20-80% water-in-oil emulsions, the amount of water separated from the Triton x-100 stabilised emulsions were 38 % for Miri emulsions, 0.4% for Kuwait emulsions, while the percent amount of water separated from SDDS stblised emulsions were, 38% for Miri emulsion and 1% for Kuwait emulsion, but again there was no water separation for SPAN 80 stabilised emulsions of same formulation. Based on theses observations SPAN 80 was found to be the most effective emulsifiers to produce experimental emulsions from Miri light and Kuwait heavy crude oils.

Keywords: emulsion, comercial emulsifiers, petroleum emulsion, stability investigation

Introduction

Emulsion refers to a mixture of two immiscible liquids that are mixed in the presence of an emulsifying agent, one of the phaces should be dispersed in the forms of small droplets into the other and perhaps vigorous mixing, in order for the emulsion to ocur, moreover, one of the phases should be polar and the other is nonpolar so that the emulsifying agent which is normally amphiphilic can position itself well at the interface and eventually promoting a stable homogeneous mixture (Emulsion) (Alejandro A. Pena 2003), (J. Fukushima, et al., 2008).

In some cases some oil phases pocess both non-polar (Hydrocarbone chain, Naphtenic or aromatic ring) and polar groups (structure with heteroatoms O, N, S), for exemple long chain alcohols, flourinated amines and ethers can represent the oil phase in what so called flourocarbon emulsions(Alejandro A. Pena 2003) .

Emulsions are encountered in various areas such as Food, pharmaceutical, cosmetics, agricultural, consumer products as wellas ptrochemicals, however the current research is concerned with the petrochemical based emulsions (D. Clausse et al., 2005), (Youngsum Kong et al., 2010).

Basically peroleum emulsions occur in various locations starting from reservoirs to refineries, thus in the reservoirs water and oil can mix naturally or as aresults of enhanced oil recovery process. In refineries emulsions occur either during the washing process whereby fresh water is added as solvents to extract the unwated water solubles salts or while injecting steam to enhance fractionations (Olga Victorovna Gafonova 2000), (Delphine Daniel-Daved et al.,2005), (A. M. Al-Ghamdi, 2007).

Types of emulsions

There are numerous types of emulsions occuring in the petroleum industries that are classified according to which of the two phases is host (continuous) and which is dispersed (droplets).

The two major types of crude peroleum emulsions are either Water-in-oil (w/o) when water exist as dispersed droplets in oil continuous phase (Host), and/or Oil-in-water (o/w) in the opposite case (Olga Victorovna Gafonova 2000). Some morphological structures of the types of emulsions are shown in figure1.

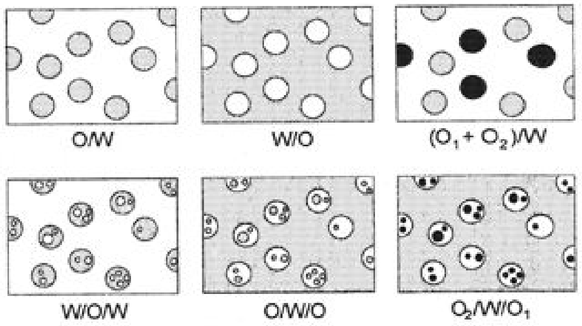

Figure 1: Morphology of some emulsion types(Modified from Alejandro A. Pena 2003)

Some typical exemples of oilfield emulsions and their place of occurence are given in table1

Table 1: Typical exemples of oilfield emulsions and locations of occuring (Modified from Alejandro A. Pena 2003)

No.	Location of occurence of the emulsions	Types
1	Well-head emulsions	w/o
2	Oil sand flotation process	w/o or o/w
3	Oil spill mousse emulsions	w/o
4	Heavy pilpline emulsions	o/w
5	Oil sand floatation process slurry	o/w
6	Emulsion drilllimg fluid, oil emulsion mud	o/w
7	Emulsion drilling fluid oil-base mud	w/o
8	Asphalt emulsions	o/w
9	Enhanced oil recovery in situ emulsions	o/w

Petroleum emulsion and stability

Petroleum emulsion is said to be stable when the quantity of the amphiphilic particles and surfactants found naturally in the crude oil , namely Asphaltene, Resins, Naphthenic acids clays, heavy metals and the like is large enough to surround and encapsulate each and every individual water drops in the mixture.

Figure 2 shows how the individual molecules align themselves between the two phase, once an emulsifying agent of surfactant (Surface active agent), is placed in the mixture, immidiately it will reorient itself at the interface, the polar head group will be attashed to the aqeous phase and the hydrophobic tail group will pretruded into the oil phase and this orientation will lead to the formation of mechanical barrier that serve as atrap to separate the droplets from each other (Clausse et al., 2005).

Technicaly speaking, food, cosmotic, pharmaceutical and personal care emulsions are made to keep their stable structure for lon time (shelf life), while petroleum emulsions are made to break and separate into two phases to recover the pure oil and discard the aqueous phase (D. Clausse et al., 2005).

Stability is defined as the strength with which this interfacial film hold the droplets in a an stagnent state, and prevent against the natural attractive foces such as vander waals, hydrodynamic and gravitational forces that tend to attract the droplets and let them merge together (coalescence) and form a separate phase that is what so called destabilization or demulsification.

Generally emulsions are thermodynamically unstable, that mean the coolective of droplets keep their natural tendency to attract to each other, hence in any stables emulsion there are several mechanis that hapen simultaneously in microscopic level,As such Steric stabilisation because of the adsorbed surfactant layer at the interface, Deplation destabilization because of the depleted volume of the surfactants from the interfsce, this is attractive, and structural destabilization due to the long chain colloidal structure (K. Kumar et al., 2001), (Snull 2005).

Therefore stability is all about creating a strong interfacial filmthat can resists the interparticle attraction forces (Christophe Diecharry et al., 2006), (K. Moran et al., 2006).

The interparticle interaction forces exists permenatly in every stable colloidal system, and that is the reason why the colloidal systemsare thermodynamically unstable, that means if the repulsive form dominates, the system is considered stable, And the reverse is true when the attractive forces dominate (Dou Dan and Gong Jing, 2006).

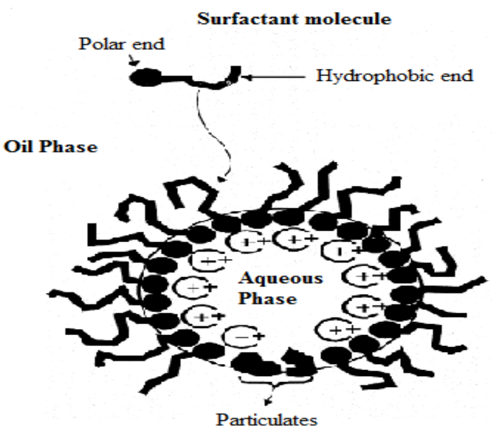

Figure 2: Alignment of surfactants around aqueous droplets, (Modified from D. Clausse et al., 2005)

Creating or making a stable emulsion with rigid and strong interfacial film, depends on various factors some of which are type of surfactants, amount of surfactants, mechanical mixing and temperature.

Surfactants(types as well as concentration) play very significant role in emulsion type as well as stability, furthermore, the hydrophilic lipophilic balance (HLB) of the surfactants also play a significant role on types of emulsions, thus High HLB will favor the formation of aqueous micelles promoting o/w type emulsion and are designated as weisor I systems, while low HLB will faver the opposite and are designated as weisor II systems (B. P. Binks et al., 2000), (Ahmed M. Al-sabagh, et al., 2002).

Although the solid dispersion bahavioursand stability were throughly delinated by the well stabilished DLVO theory, yet emulsions are complex because droplets can deform at any time, since they are considered thermodynamicaly unstable and the surfaces are fluid. These two factors affect greatly the interdroplets and hydrodynamic interaction forces between the fluid particles, further more; the complesxity increses with increasing the droplet phase volume fraction, DLVO forces are normally observed within the charged interface with low concentration of charges, while non DLVO forces such as steric and surface forces are observed at high electrolyte concentration. (Johan Sjoblom et al., 2003), (Dou Dan and Gong Jing, 2006), (Stoyan I. Karakashov et al., 2008), (Dotchi Exerowa, et al., 2009).

It was proved that when two large drops (few millimeter sized) approaches one another, their spherical shape will deform and a planer film barrier forms betweem them. The rate of drainage and thining of this film and resistance to rupture will define the credibility of the stability (B. P. Binks et al., 2000), (Dotchi Exerowa, et al., 2009).

The process ofdestabilization or demulsification occurs when the attraction forces between the droplets exceeds the repulsion forces,and governed by several steps that occurs concurrently named sedimentation/creaming, flocculation and coalescence as depicted in figure 3, creaming and sedimentation depends on which of the two phaces have higher density to sediment down and the other way around.

Coalescence hapens in two steps that are film drainage and film rapture. Electrical double layer repulsion or steric stabilization by polymer and surfactants may prevent the droplets to come into direct contact with one another via constracting rigid barrier against aggregation. However; the efficiency of this barrier depends on some intrinsic parameters as such the size of the surfactats molecules, and the interdroplet contact angles,the surfactants msut be smaller in size than the droplets, and the contact angle had better to be preferentially around 90°, other extrinsic parameters are low temperature, low viscosity, low interfacial force, small amount of dispersed phase, and short droplets diameters (Ing Harald Auflem 2002).

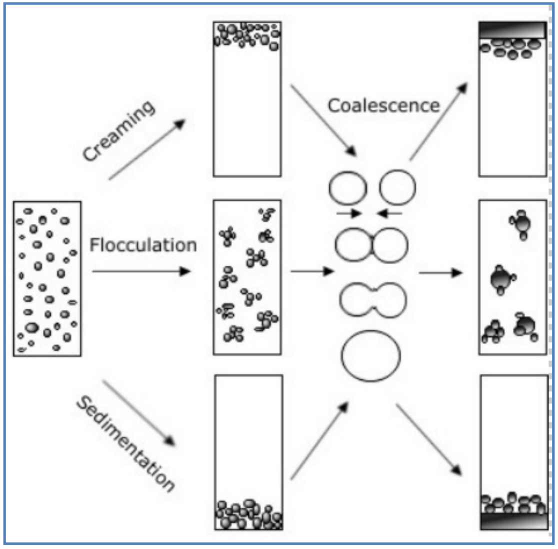

Figure3: Mechanism of destabilization (from Ing Harald Auflem 2002)

Monitoring emulsion stability means to control the life of the interfacial film, because once the interfacial film colaps; the droplets will gradually aggregatetoward each other, then come to contact (two or more drops at a time) and merge together forming a biger drops that in turn merge with another and eventually leading to the separation of the phases, hence one way to study the stability is to measure the droplet sizes as function of time, but this is only applicable for dilute emulsion (K. Moran et al., 2007) .

Another more effective technique to study the stability is bottle test, whereby emulsion is placed in a graduated measuring cylinder and the amount of water separation is measured with time (D. Clausse et al., 2005).

Comercial stabilizers and water/oil interface activity

The purpose of using surfactants is to lower the interfacial repulsive free energy that arises when the surfaces of two incompatible materials come together, thus reducing the strength of the free energy between surfaces or interfaces (Surface or Interfacial tensions). Commonely, every emulsifier molecule pocess one hydrophilic polar head group, and one or two lipiphilic chain tail of hydrocarbone or florocarbone, the hydrocarbone chain is insoluble in water therefore it would be attashed to the oil phase while the hydrophilic ionizable head group will be attashed to water phase, this particular character render the surfactants to accumulate along the interface reducing both surface and interfacial tension, when the concentration of surfactants reach centain threshold known as Critical Micelle Concentration (CMC), the surfactants will aggregate and form micelles of their own (J-L. Li et al., 2002).

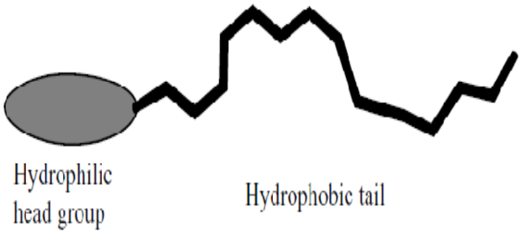

Figure 4: Sheamatic diagram of surfants molecules (from Krister Holmberg et al., 2002)

Thogh comercial surfactants are used in almost everywhere in human daily live consumptions, however their selective applications rely heavily on their HLB, and their charges.

HLB of surfactants are ranged from Zero oil soluble to more than 10 water soluble, in another words low HLB below 10 normally favor the formation water-in-oil emulsions, while high HLB more than 10 normally favour the formation of oil-in-water emulsions.

According to electrical charges og their polar head groups, surfactants are divided into ionic and nonionic, based on the charges on their head groups, thus the heat groups of the ionic surfactants are either carboxilates, sulfates and sulfonates which confer them negative charges and the surfactants under this category are disgnated as anionic surfactants, the most impotant and widely used of which is Sodium Dodecyl Sulfate (SDS), or amine and quaternary amonium that confer them positive charge, and the surfactants under this category are termed as Cationic srfactants (Krister Holmberg et al., 2002).

Ninionic surfactants normally pocess polyether or poly hydroxyl unit as a polar hydrophilic head groups. Indeed there are also the zwitterionic surfactants that pocess both charges simultaneously.

Previous studies on surfactants

Almost all types of industrial emulsions and to some extent the petroleum emulsions are produced with the help of surfactants, and that is because the droplets or particles in the continuous medium aggregate easily and separate if surfactants were not added, hence the addition of surfactants would induce the formation of repulsive barrier around each droplets and that will retard the aggragation rate and consolidate the emulsion stability (Yoichikanda, et al., 2004), (J. Perkowski, et al., 1995). When a surfactant molecules solibilise in a single phase they tend to self associate forming micelles, but when they disolve in two phases mixture, they tend to migrate and accumulate at the interfaces forming manomeric layer(J. Perkowski, et al., 1995).

Although numerous research have been conducted on vast latitude thus far to study the attitude of surfactants, yet only the water-in-oil, and prefrential petroleume related studies are considered in this paper. Generally petroleum emulsion occurs either inside the reservoir when oil and water come into contact or as aresults of delibrate treatments such as enhanced oil recover (EOR),washing and stean injection in refineries to improve fractionation(Olga Victorovna Gafonova 2000).

However, emulsions are mostly undesired in petroleum industry, and have to be breaked (Demulsified) to remove the water, while personal care, household and baverage emulsions are meant to retain their stable structure for as long as possible (shelf life) (D. Clausse et al., 2005).

Youngsum and coworkers have studied the effect of nonionic surfactants based on the aggregation pathern (Miceller formation) at the oil water interfaces from microscroscopic point of view whereby emulsion stability is defined by speed with which the individualy dispersed emulsion drops will agregate or flocculate to eventually coalesce (separate from the host phase) (D. Clausse et al., 2005).

Other researcher have used the anionic sodium Bis(2-ethylhexylsulfosuccenate) emulsifiers to stabilise an heptane-in-water mixture(model emulsion) and reported that the creaming rate of the saied emulsion decreased with increasing the emulsifiers' concentration (B. P. Binks et al., 2000).

In another article the ability of montmorillonite clays and calcium chloride as emulsifiers to produce o/w emulsion was reported(K. Moran et al., 2007). Beside that the complexity of the emulsion was also reported to increase with increasing the dispersed phase volume frction and perhaps mixing (Dou Dan and Gong Jing, 2006). Similarly others have investigated the effect of certain nonionic surfactants namely Tritonx-100, Tween 20 and Tween 80 on model emulsion that is consisted of water and poly cyclic aromatic hydrocarbone (PCAHs), how ever they found that the droplets aggregation was increased with increasing temperature (J-L. Li et al., 2002).

Other group have studied the effect of surfactant made by the incorporation of mineral salts namely, sodium naphthenate, ferro oxide, and calcium hydroxide with naturally occuring species, indeed combination of polybutadiene with asphalte and devulcanized rabber was found to induce steric stabilizaton (Andrew P. Sullivan et al., 2002), (K. Moran et al., 2007).

Elsewhere, the dropet coalecesnce rate of liquid parafine emulsions made out of 3% noninic surfactants named Polyoxyethylene dodecylether was investigated, also the efect of the concentration of the nonionic surfactants on the steric stabilisation was reported in similar work, however, the concentration was varied in the range between 0.06 to 2% (Stoyan I. Karakashov et al., 2008), (N. Lazaridis et al., 1999). In another report the nonioni surfactants prcisely sorbitan monooelate (Span 80) are used to to prepare water-in-oil emulsions of soy bean as well as canola oil (Fukushima et al., 2008).

Another work by Nael N. Zaki and colleagues have related the stability ofcertain nonionic surfactants stabilised petroleum emulsion to several parameters based on their observation, they observed that emulsion stability and viscosityincreses with increasing the concentration of emulsifiers, volueme fraction of the external phase, and mixing speed, they also observed that the the values of the pour point for emulsions were always greater than that of starting pure oil (Nael N. Zaki 1999).The effects of PH and counterions in the stability of the that nonionic surfactants stabilised emulsion also reported elsewere (Muhannad Jumaa, et al, 1998).

Another group of researchers have investigated the effect of asphaltene and oil field native solids on the stabilty of petroleum emulsions, however, their system was a simulated emulsion of water and hydrocarbone mixture of toluene plus heptan (simulated oil phase) (Danuta M. Sztukowski, et al., 2005).

Elsewhere, the effects of zwittrionic surfactants on the emulsion stability also was investigated based on their ability to stabilise solid prticles in liquids (Dispersion) (Kenichi saki et al, 2007).

Other comperhensive investigation on nonionic surfactants stabilised asphalte emulsion revealed that for 30% internal phase volume fraction emulsion, low HLB surfactants (HLB 4-6) would produces water-in-oil emulsion, while high HLB (HLB 10-13) will produce o/w emulsion, they also proved that the length of the hydrocarbone chanin of the surfactants molecules would tremendously affect the emulsion stability, and that is because it will controbutes on increasing emulsion viscosity (Ahmed M. Al-sabagh 2002).

Materials and Method

Materials: two types of crude oils were used, their physical characteristics were measured in laboratories and reported as follows, one is malaysian miri light crude oil having API gravity of 35 and dynamic viscosity of 23.7 cp, the other is Kuwait heavy oil having API gravity of 24.5 and dynamic viscosity of 161.8 cp.

Three types of comercial emulsifiers were used, namely SDDS (anionic), Tritonx-100 (nonionic), and Span80 (nonionic), at different concentrations (1, 3%) for Span 80 and (1, 3, 5%) for the others.

Water-in-crude oil emulsions were prepared using the agent in oil method, emulsifiers were first disolved in the oil phase with gentle mixing for two minutes then water was added gradually while mixing went on for a total emulsification time of seven minutes, three blade mixture was used at speed of 1000 rpm.

After preparation emulsion types were assessed using filter paper test as well as bottle test, all emulsions were found to be water-in-oil emulsions. Then the stable emulsions were put in a graduated cylinders and left to settle for stability test for total period of one week, the amount of water separation from the emulsions were recorded everyday.

Results and Discussions

Stability assessment is probably the first and most important step in producing experimental emulsions for industrial as well as real life applications, as such crude oil spillage, pipeline transportation, oil production from reservoir, enhanced oil recovery, in addition to the wide spread food, cleaning, personal cares, and pharmaceutical applications (Gannam., 2005). Stability study is normally conducted to find out the optimal formulation for desired products, either to observe shelf long life as in beverage and other industrial applications excluding crude oil, or for transportation, recovery, combustion in petroleum industries and refineries, emulsions are sometime prepared in laboratory purposely for testing new demulsifiers or new demulsification techniques as in the current research.

Three types of emulsifiers have been chosen based on previous studies they are commercially named Triton-x100, SDDS and Span 80 applied in two different crude oils one was heavy type oil from Kuwait and the second was light type oil from Malaysia. SDDS is an anionic surfactant while the others are nonionic surfactants, the HLB of the surfactants are, SDDS (HLB 40) , Tritonx-100 (13), and Span80 (HLB 4), The main purpose of this screening process was to find the best formulation in terms of emulsifiers' type as well as concentration, since concentration is very significant from economic point of view. Thus in every experimental emulsification studies, stability test is required to find out the best and reliable emulsion at lower cost, hence the effectiveness of the emulsifiers was accessed by measuring the rate of water separation from emulsions (Zaki et al., 1996).

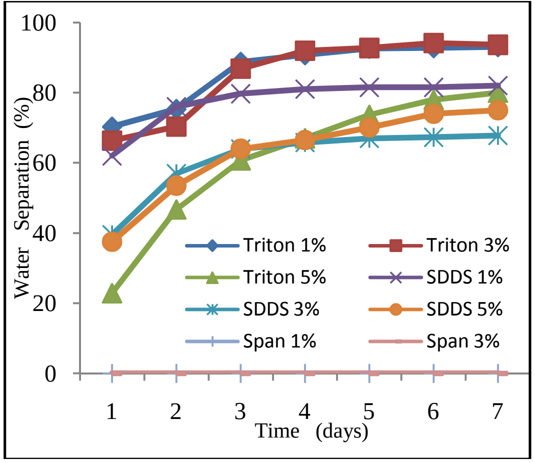

Figure5: Effects of types of emulsifiers and their concentrstions on the stability of 50-50% (w/o) emulsions from Miri light crude oil

The effect of three different emulsifiers on the stability of Malaysian light crude oil (miri) was depicted in figure 5.The dosages of the emulsifiers were varied as 1, 3 and 5% For Triton-x100, SDDS, while for Span-80 only two concentrations of 1, 3% were used besed preliminary tests.

Firstly considering the Triton x-100 stabilized emulsions the percentage of water separated in the first day was around 70%, 68% and 20% for 1%, 3% and 5% concentration respectively and from this observation, 5% result was truly in accordance with what was expected, since triton x-100 is nonionic surfactant same as Span80; so the types of interfacial barrier they make is called steric barrier as mentioned earlier and their stability is termed steric stabilization.

This current experimental result showed that emulsion stability (less water resolution) increases with increasing the emulsifiers' concentration, therefore concentration was found to be the most particularly effective parameter for Triton x-100 emulsifier, yet it is not the suitable choice since it lost around 20% of its water within the first day, and as time goes on; separation rate was increased until it reached 72% for the 5% concentration and 90% for each of the rest two concentrations during the total observation period of one week.

This instability might be due to low viscosity of the continuous phase together with HLB and solubility of the emulsifiers will ease the agglomeration and offer paths to the agglomerated drops and flocks to settle and sediment in accordance with stokes' law of settling velocity which says the settling velocity and separation rate of the emulsion droplets will increase with reducing continuous phase viscosity. Since Triton x-100 is nonionic surfactant but it is reported to favor partitioning in aqueous phases more than the oil phases, this may also contribute massively in lowering the stability since the surfactant are most likely assumed to be intended to produce water-in-oil types emulsion with regard to their solubility behavior, and that is by being more soluble in the aqueous droplets instead of protruding their long chain polymer part in the bulk continuous oil phase and just surround the drops to produce water-in-oil emulsion as expected,

Ghannam reported the significance of 1% tritonx-100 addition in water-in-crude oil emulsion, of low water contents of 20% and found to increase emulsions stability over the emulsifiers' free emulsion, then stability decreased with increasing water contents hence the most unstable emulsion was found at 50% water concentration that is in accordance to the current study (Ghannam et al., 2005).

With regard to SDDS stabilized emulsions; the general trend for 1, 3 and 5%, stabilized emulsions were 60%, 40% and 35%, it is generally similar to it previously discussed tritonx-100 counterpart although the numerical values are a bit different. SDDS is anionic surfactant and the mechanism with which anionic surfactants behave at the interface is as reported in the literature is basically through the formation of well known electric double layer which is normally formed by the positioning of the surfactants molecules at the interface. Normally the polar head groups are attached to the water phase and the non-polar tail to the oil phase. The charges of the head groups will surround the droplets while the counter ions would be dispersed randomly in the vicinity of charged interface and altogether will form what is known as the electric double layer which acts as an electrical barrier prevents the neighboring droplets from merging or coalescing. Indeed the coalescence of the droplets is proportional to the strength or potential of this interfacial layer, although the stability of the layer is affected by many parameters such as surfactant concentration, pH, salinity and temperature, fundamentally there are two mechanisms affecting the strength of the double layer these are; the random molecular motion which tends to fix a uniform concentration in the vicinity of diffuse layer.

secondly the columbic attraction force between the adsorbed charges and the free moving charge which tends to keep the cations in close proximity to the interface, and induces repulsion when the approaching surfaces of the neighboring droplets overlap, this double layer extends over certain effective distance around $500A^0$ (Angstrom) from the interface known as the Debye length which increase with increasing surfactant or electrolyte concentration.

Hence from this fact, at low concentration of 1% and 3% ; the strength of the charged interfacial layer might be less effective in holding the counter ions in equilibrium at close proximity and that will lead to the reduction of Debye length and faster flocculation and coalescence of the droplets, and this will eventually leads to unstable emulsions, another explanation is that the anionic surfactants SDDS in this case are water soluble and hence will tend to dissolve in the water phase rather than oil phase and this lead them to form stables bubbles of water, SDDS gave better result than Triton x-100. This was expected to occur since SDDS is anionic surfactant which is water soluble, add to that its detergent like character will lead to the formation of foam or bubles at higher water content, this is most probably what happened in this situation of high water content (around 50%). Thus the stable bubbles making the foam are expected to be surrounded by surfactant layer. Hence this mixture of bubble plus droplets plus bulk oil will make the emulsion even more stable, however this situation was changed when the concentration was increased to 5% where triton x-100 stabilized emulsion was more stable, this may be due to the surfactant adsorption at the interface since the interface only can accommodate certain amount of surfactant concentration beyond which they either consolidate the existing monolayer and form what is known as cylindrical layer which in turns transform with increasing concentration to lamella liquid crystal or they are no longer effective in stabilizing the emulsion. Weixing and coworkers have examined the solubility behavior of some anionic surfactant and confirmed the increase of solubility with solid concentration (weixing et al., 2004).

Indeed with regard to Span80 stabilized emulsions, there was no water separation observed in all dosages tested (1%, 3% and 5%), which mean Span 80 prepared emulsions were very stable.

With regard to the types of emulsifiers used in this research, emulsions composed of 1% concentration of the three aforementioned emulsifiers (Triton-x100, SDDS, and Span-80), as shown in figure5. During the fist 24hours 1% triton stabilized emulsion had lost around 70% of its water content that means it was not stable at all so 1% triton-x100 was not sufficient in stabilizing 50-50% w/o emulsion of miri (A) crude oil, similarly SDDS stabilized emulsion had lost around 60% of its water thus 1%SDDS was not sufficient in stabilizing 50-50% emulsion of miri (A) crude oil, while that was not the case in 1%Span-80 stabilized emulsion since the curve showed there was no water separation for the whole week, but it was observed that there was some oil was floating over the emulsion layer but no water separation at all.

Indeed in the subsequent day, the separation rate of 1%SDDS stabilized emulsion was around 72% and there was very minor increase in the in the days after until the day 7. For 1%triton-x100 stabilized emulsion, the rate had augmented to around 82% by the third day after that no much increase until the day 7, in contrast to the previous two cases, the 1%span-80 stabilized emulsion was stable for the whole week with regard to water separation despite some oil had separated from the emulsion, and that may be due to the light nature of miri crude oil (low viscosity).

Secondly; the effect of concentrations on the emulsions stabilized solely by SDDS was investigated and it was found that the resolved water was ranged again as 60%, 40% and 39% for 1%, 3% and 5% respectively in day one of the test, a result which is more or less in accordance with its previous counterpart (triton X-100), and indeed; the overall comment is simply that 1% concentration was not enough to stabilize 50-50% water-in-crude oil emulsions of miri light crude in both aforementioned emulsifiers (SDDS and Triton X-100).

3% and 5% SDDS stabilized emulsions had given almost identical results, unlike in the case of Triton X-100. In the case of SDDS the stability mechanism as described in literature is an electrostatic mechanism where by several attraction and repulsion forces will interact to promote stability when repulsive forces are dominant, and instability when the attractive forces are dominants, the repulsive forces for ionic surfactants (SDDS) are normally created when two charged interface approaches each other and their electric double layers overlap and its named columbic repulsion force whose function is to oppose any minimization to the separating distance between the two dropltes, and its sometimes expressed as the potential energy of repulsion. There are other repulsive forces that can rises referred to as born repulsion, in the stable conditions these forces are normally balanced by what so called attractive forces created form the orientation of the dipoles which in turn categorized to either; Dipole-Dipole attraction force (Keesom dispersion forces), Dipole induced-dipole attraction (Debye dispersion forces), or induced dipole-induced dipole (London dispersion forces) (Laurier L. Schramm., 2006), however these electrostatic affect was not measured in this study since the aim was to produce water-in-oil emulsion which known to show very poor electrostatic properties, and that may be one reason why the SDDS stabilized emulsions were unstable losing most of their water contents during the first day of preparation because it hase poor solubility in the oil phase and that may lead then to form oil trapping surfactant micelles when they first added in the continuous phase and agitated before the addition of the water droplets, remember that in the current method used to produce the actual emulsion; the mixture of oil and surfactants was agitated vigorously for 2 minutes before adding the water as drops.

During the mixing the polar heads of the anionic water soluble SDDS surfactant are assumed to be oriented in a circle shaped micelles as they are trying to group themselves faraway from the nonpolar oil phase and some may also dive freely in the oil phase, indeed the circulated micelles my entrap some oil within the micelle forming miceller solution and that may be the reason why an unstable foam was observed to form when water was added instead of emulsion, then within a few minutes from preparation the foam would vanish and three layer would form, the upper most is either oil or oil rich emulsion, the down most is either water or water rich emulsion and middle layer is particularly assumed to be the surfactant or micelles rich very stable emulsion which appeared to be reddish in color and also was observed to increase with increasing surfactants concentration, this situation considered to support the idea of micelles orientation.

The increases in the amount of the surfactants will leads to more micelles and probably micelles swollen micro sized oil droplets and more freely diving surfactant which can be oriented at the interface according to their nature; and that will eventually increase the middle emulsion layer when the emulsion is put in measuring cylinder for observation.In terms of quantitative observation; the addition of surfactants beyond this optimal concentration (say from 3% optimal to 5%) in this case; shall not much disperse solely but rather accumulate to the already dispersed ones (optimal condition) and consolidate the stability by forming what so called the lamella liquid crystals this claim is proved by observing the rate of stability in the following days as seen in figure 5.1, the two results were converged in the third day and remained equal until the forth day, after which the 3% had reached a plateau and the other 5% continued to separate until it reached to 70% by day 7. anyhow the results were contradictory to each other and observation marked for 50-50% miri light crude oil emulsion stabilized by SDDS in the previous four days; 5% concentration had given more stable emulsion with less water separation then from day four until day 7 the 3% stabilized emulsion had given a better results and reached a plateau at 60% water resolution, every emulsion produced from SDDS surfactant was not stable enough to be considered but as it is well known that every surfactant molecule can migrate to interface and reside there with certain arrangement when its placed in mixture of two immiscible liquids, normally the polar head groups are oriented toward the aqueous polar phase, and the hydrophobic non polar tails are protruded into the hydrocarbon or oil phase, and that arrangement will lead them to construct a mechanical or potential barrier that hinder the neighboring drops from coalescence, thus in the case of SDDS the more surfactant are put; the thicker and stronger the film will be and that would lead the high stability.

Thirdly the case of span80 was totally unique and different than the other two cases hence for all observation there was no any water resolution reader may need to refer to figure 5.2. According to the theory, Span 80 and triton X-100 of same category of nonionic surfactant with triton X-100 is considered as more water soluble (HLB>10) and span 80 is more oil soluble (HLB<10), indeed the mechanism of nonionic surfactants' stabilization is based on what so called steric stabilization; a mechanical film formed at the interface in the nonionic or polymer stabilized emulsion, hence when the two interface come to proximity in another word; when the two neighboring drops are close enough then the steric film is formed as a result of either head groups overlap and fluctuation in interface, this type of steric stabilization is normally stabilize or help to increase the stability of the emulsion, other type is called bridging flocculation wherein some materials are adsorbed on the particle surfaces and it normally tends to decrease the stability(Laurier L. schramm., 2006).

Finally this paragraph would be concluded by a summary of all the observations discussed. Generally at low concentration of 1% in all cases excluding Span80,the stability was very poor for miri crude oil, then when the emulsifiers increased further to 3%, the Span-80 stabilized emulsion has not shown any effect and remained stable with zero water separation, indeed the 3% tritonx-100 stabilized emulsion had almost the same pattern as in 1% stabilized emulsion, while the 3% SDDS stabilized emulsion was observed to be slightly stable than at 1%, hence the separation rate was 40% during the first day and increased further to 55% in the second day then to around 60% in the following days.At 3% emulsifiers concentration, the separation rate of the tritonx-100 stabilized emulsions had reduced to 20% in the first day but it had doubled in the second day to 40% then to around 55% by the third day and continued to around 70% on day 7.

Similar trend had observed with 3% SDDS stabilized emulsion which had lost around 35% of its water content in the first day, 50% in the second day, 60

% by the third day and to around 70% by the day 7, and again there was no water separated from 3% span-80 stabilized emulsion but there were some abnormalities such forming two layered emulsion; a situation in that appeared in span80 stabilized emulsion that is contradicted the usual stability pattern of only water separating out of the stable emulsion by seeing three or two layers the top-most layer consist of either pure oil or oil rich mixture, the lowermost layer consists of either cloudy water or water rich mixture which might be referred to as micro-emulsion surfactant micelles swallowed oil droplets in the excess water phase.

Concerning the middles layer which appeared brownish in color is assumed to the most stable formulation within the individual emulsion samples, the point is that in span 80 stabilized emulsions; the intermediate layer was found to be either absent (uniform emulsion) or the dominant layer compared to the other tow types stabilized emulsions. From this observation there was a clear view and there was no minor doubt to choose the Span 80 as the best emulsifiers to be selected to produce high water contained miri light crude oil emulsion (50-50% w/o emulsions).

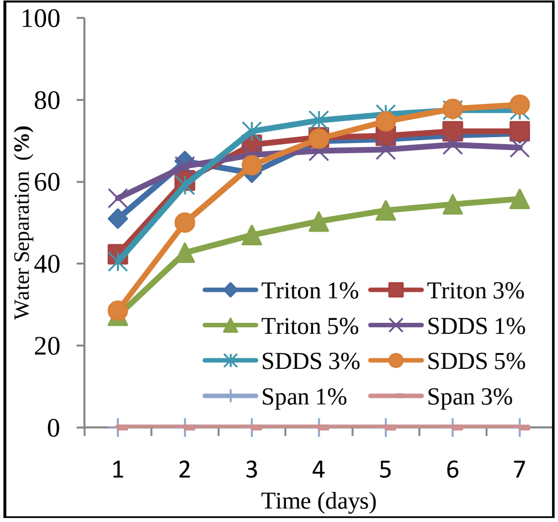

Figure 6: Effects of types of emulsifiers and their dosage on 50-50% (w/o) of Kuwait oil (B) emulsions

Curves in figure 6 are plotted from the experimental data obtained from the same three emulsifiers and their dosage as stated earlier in figure 5, but this time in different crude oil that is apparently more viscous than the Miri (A) and it is originally from Kuwait and named as (B) in this part of the study,emulsifiers were shown to be more efficient in promoting and stabilizing the emulsion in oil (B) compared to (A), thus in 50-50% water-in-oil emulsions, the effect of the different concentration of three emulsifiers had plotted in Figure6, again in here the span 80 was found to promote a very stable emulsion at all concentration hence there was no water or oil separation was observed within the whole one week observation time.

The experimental results also proved that different crude oils have different stability pattern even with the same emulsifiers, this can be seen by comparing the experimental results obtained from 50-50% emulsions prepared by Triton X-100 for two different crude oils (A and B), for oil B the stability result was 50%, 40% and 26% for 1%, 3% and 5% triton x-100 respectively but thy were 70%,68% and 20% for oil (A) with the same formulation, this means Triton x-100 was more effective in oil B than oil A, a situation which could be attributed to the physical and chemical composition of the crude oils since Kuwait crude oil is heavier, denser and more viscous than miri light crude oil, and thus it is assumed to content more of incompatible materials such as asphaltene, solid particles and clays which play a very important role in promoting crude oil emulsion. Previously similar results were reported by Mervin and coworkers in different crude oil emulsions having similar formulation to the current systems, and concluded that stability is more or less a strong function of viscosity of the continuous phase (crude oils) in addition to the surfactants and agitation, and they also evidenced experimentally that heavy crude oils contains more asphaltene than the light ones.

Asphaltenes would either catalyze the mechanism of surfactant adsorption at the interface or would be located at the interface and consolidate the strength of the film formed by the surfactants molecules that acts as a mechanical barrier hindering the droplets from flocculation and coalescence and eventually promoting a stable water-in-crude oil emulsion (Fingas and Ben., 1996).

Similar observations were found with SDDS stabilized crude oil B emulsions which gave 55%, 40% and 27% just similar to the triton X-100 but in comparison with the same formulation of SDDS from the previously discussed with crude oil (A), the amount of water resolution was 60%, 40% and 39% reader may need to refer to Figure5, If the effects of tritonx-100 and SDDS were compared for oil B alone; it is clear that the effect is almost similar in contrast to the effects on oil (A), which was obviously fluctuating and alternating with concentrations for example at low concentration of 1%; the amount of water separated from miri light crude oil (A) emulsion were 70% and 60% for triton and SDDS respectively that means at low concentration SDDS gave better result over triton X-100, As the concentration increased further to 3%, the water separation was 68% and 40% for triton and SDDS respectively here, still SDDS gave better result, at 5% concentration; the water separations were 20% and 39% for triton X-100 and

SDDS respectively Triton gave better result, this contradict the previous result, in another word; at 1% emulsifiers' concentration of triton x-100 and SDDS the percentage of water lost was around 50 and 55% respectively, this case was slightly stable compared to same composition in oil (A), in which the separation rate was 70 and 60% for triton and SDDS respectively, further more as the concentration had increased to 3%; both triton and SDDS emulsions had lost around 40% of their water content in the first day then they all reached plateau by the third day at separation range between (60-74%). Indeed when the concentration had increased further to 5%; the stability of both tritonx-100 and SDDS had enhanced, and the percentage of water separation had reduced to 28% in the first day, but immediately increased the next day hence triton satbilised emulsion had reached a plateau at 40% separation by the second day, while the SDDS stabilized emulsion continuously separating and reached around 80% within one week figure 6.

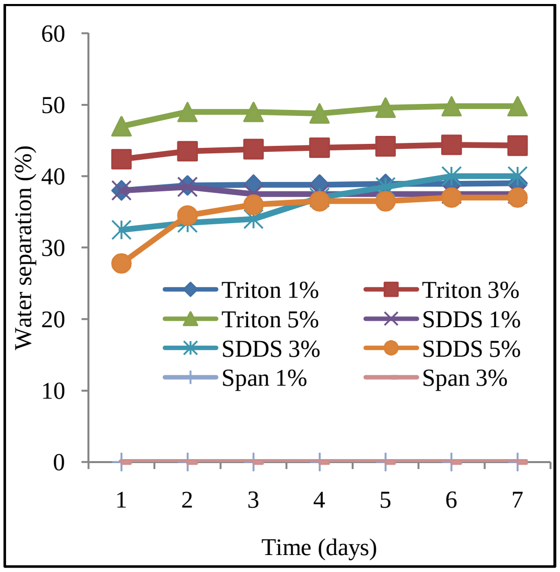

Figure 7: Effects of types of emulsifiers and their dosage on stabilizing 20-80% (w/o) emulsions from Miri oil (A) crude oil.

With respect to water content of emulsions and its effect on emulsifiers' action; data on Figure 7 were obtained from 20-80% water to oil ratio emulsions prepared from crude oil (A), however, results in here were some how different from the 50-50% emulsion, thus for 3 and 5% Triton-x100 stabilized 20-80% w/o emulsions, it was observed that they were not stable and separated immediately to two distinct layers, more importantly the water layer was not pure water it was rather a mixture that content some oil droplets in it, beside that water rich bottom layer there was also a thin emulsion layer in the middle, and finally a black oil layer on top of measuring cylinder, so altogether there were three layers, the top layer is the oil-rich layer and the middle layer might be an emulsifiers rich layer that had formed from the excess emulsifiers that may have formed some micelles at the interface between the two phase and trapped some water droplets and promoted a stable emulsion layer.

Beside that the down bottom layer that is rich in water also definatly consists of three components with water being the most prominent element that is why it appeared as turbid water which consists of small oil droplets trapped in water and surrounded by the dissolved surfactant molecules, as the surfactant concentration was reduced further to 1% Triton x-100; the turbid water layer has reduced to 38%, which means this concentration of triton is not enough to keep the oil drops trapped within the turbid layer so they have escaped and transferred either to the surfactant rich emulsions layer in the middle which itself had appeared tiny this time or settled on top in their bulk phase.

Regarding the other emulsifiers SDDS and its action on 20-80% w/o of miri crude oil (A) emulsions, it was observed that at high concentration of 5%; foam had formed at first instead of expected emulsion, then settled to emulsion then water started to separate, it was not so stable hence most of water had separated from the first and second days as shown in figure 7.

The general observation in terms of water content and its effects on emulsion stability is that at low water content the percentage of water separation was lower than that of higher water content or 50-50%, thus for triton x-100 stabilized 20-80% water-in-miri oil emulsions the separation rate was 38%, 42% and 47% for 1%, 3% and 5% respectively this is strange actually to see the stability decreases with increasing emulsifiers concentration, but it was normal for SDDS stabilized emulsion and gave 38%, 32% and 28% separation rate for 1%, 3% and 5% respectively which in both cases the separation percentage was better than 50-50% emulsion means at low water content the emulsion was more stable than at 50% water content and that might be because at low water content the droplets are suspended far from each other within the bulk oil phase hence this long separating distance increase the repulsive force over the attractive force and that will hinder the aggregation and flocculation and retard the settling of the droplets and this lead to conclude that low water content emulsion is more stable than the higher water content emulsion, indeed the increase in the volume fraction of the dispersed phase also could increase the effective entropy of collision between the drops and that would lead to increase in the rate of coalescence and eventually leads to destabilization and water separation. similsr results were reported by Zaki, who investigated the effect anionic surfactants on crude-in-water emulsions prepared for pipeline transportation purposes (Nael N. Zaki., 1996). Sapan80 stabilized emulsions were always stable and no water separation was observed despite there were some oil separation.

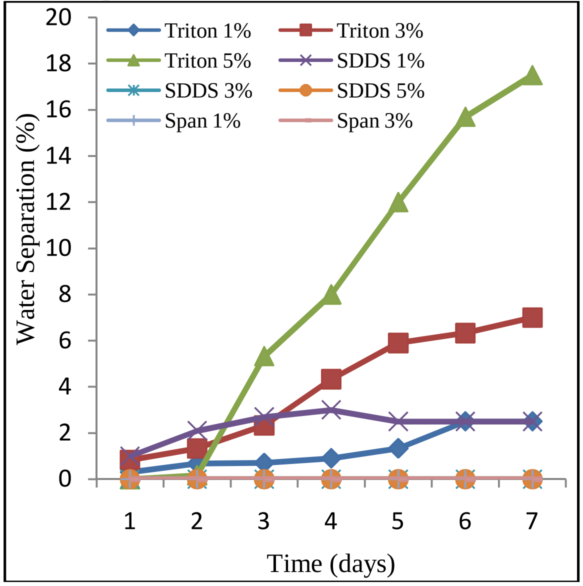

Figure 8: Effects of types of emulsifiers and their dosage on stabilizing 20-80% (w/o) emulsions from Kuwait crude oil (B)

Figure 8, shows the effectiveness of the types of emulsifiers and their dosage on 20-80% water-in-oil prepared from Kuwait crude oil (B), most emulsifiers has marked to possess a great effect with this formulation, thus all concentrations of Span80 had produced a very stable emulsion with zero water separation as usual, the water resolution from triton x-100 stabilized emulsions within their first 24hrs were 0.4%, 1% and 0.0% at 1%, 3% and 5% concentration respectively, seemingly it was 1%, 0% and 0% with SDDS stabilized emulsions, from personal perspective this is the only formulation in which all of the emulsifiers were effective and gave the most stable emulsions ever since the very beginning of this formulation. According to this result of 20-80% water-in-oil (B) crude oil; the most effective emulsifiers was Span80, followed by SDDS which gave the same result at its high concentrations of 3 and 5%, however at 1% SDDS concentration the emulsion could hold the separated levels to a very low quantity, hence the amount of water separated was less than 2% within 4 days and retained less than 4% for the whole week. The opposite was marked with the Tritonx-100 induced 20-80% Kuwait oil emulsion in which stability was observed to decrease with emulsifier's concentration as proved in Figure 4.4(8) and that might be attributed to the solubility of the emulsifiers (triton x-100).

From these experimental observations; emulsifiers were found to have paramount contribution on emulsion stability although they alone are not enough to produce stable emulsion. Other important parameters are internal phase volume fraction and viscosity as just discussed. Importantly Span80 gave very stable emulsions, therefore Span80 will be chosen for further investigations in terms of the emulsion characteristics such as rheolgy, emulsification temperature, emulsification (rpm) and droplet sizes analysis.

Conclusions

Based on the current experimental results the stbility of both crude oil samples were found to varies with emulsifiers' type concentration as well as water (droplets phase) volume fractions, for sample of 50-50% w/o emulsion of miri light crude oil for exemple, at concentration of 1%, Triton x-100 stabilized emulsion had lost around 70% of its water, and SDDS stabilised emulsion had lost around 60% of its water while Span80 Stabilised emulsion was stble water separation was zero within the first 24hours.

Similar observations were noticed with Kuwait oil, for 50-50% w/o Kuwait oil emulsions, at 1% emulsifiers' concentration, Triton x-100 stabilised emulsion had lost around 50% of the water contents, and SDDS stabilised emulsion had lost around 55% of the water contents, while span80 stabilised emulsion was stable and there there was no water resolution within the first 24 hours, anothe observation is that for tritonx-100, and SDDS stabilised emulsions, the stability decreases with time, thus by the day 7, most of the water is resolved, but this is not the case for span80 stabilised emulsion which had showed a great stability pattern and no water separation within the observation period of one week for both oils.

With respect to low water contained emulsions (20-80% w/o emulsions), the stability pattern had enhanced compared to the high water containd emulsions (50-50%).

In the case of 20-80% w/o emulsions of miri crude oil, the amount of water separated from the emulsions in first day were, 38% for triton x-100, 38% for SDDS, and 0% for Span80. But that was not the case for Kuwait crude oil, wherein the amount of water separated from 20-80% Kuwait oil emulsions within the first 24 hour were 0.4% for triton x-100 stabilised emulsions, 1% for SDDS stabilised emulsions, and 0% for the span 80 stabilised emulsion.

Therefore, from this experimental observation it was concluded that, Span 80 is the most suitable emulsifiers for producing experimental emulsions from miri light as well as Kuwait heavy crude oils.

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