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Demulsification of Crude Oil Emulsions Using Ethoxylated Aliphatic Amine Polyesters as Novel Demulsifiers

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Abstract: ***Twelve novel demulsifiers were prepared in two steps. In the first step, aliphatic fatty amines; octyl, decyl, dodecyl and tetradecyl amines were ethoxylated at different ethylene oxide units; 6, 12 and 18. In the second step, the prepared ethoxylated amines were used as a novel diol and then were polyesterified with maleic anhydride and poly propylene oxide - poly ethylene oxide (PPO-PEO) block copolymers. The prepared polyesters were abbreviated as $8E_6D$, $8E_{12}D$, $8E_{18}D$, $10E_6D$, $10E_{12}D$, $10E_{18}D$, $12E_6D$, $12E_{12}D$, $12E_{18}D$, $14E_6D$, $14E_{12}D$ and $14E_{18}D$. The demulsification efficiency of these polyesters was investigated using Sany glass. The effects of the molecular weight, concentration, asphaltene content, water content and temperature on the demulsification efficiency were studied. From the obtained results, it was found that; the $12E_{18}D$ exhibited the maximum demulsification efficiency at concentration 400 ppm and at 60 ^oC. The complete BSW "bottom sediment and water" was obtained within 15 minutes. The surface-active properties of the prepared demulsifiers were measured at 60 ^oC and these properties were discussed in relation to the demulsification efficiency.***

Keywords: Demulsification; nonionic polymeric surfactants; ethoxylated amines; polyesters

1. Introduction

Crude oil is produced as a persistent emulsion, which is resolved into two separate phases, before the crude oil can be accepted for pipelining. Water must be removed (down to a level of <1%), in a process that is usually called demulsification or dehydration. This consists of process forces coalescence of water droplets and producing their separation by settling. The droplets in emulsion are stabilized by the asphaltene and resin fractions of the crude oil. **(Wang, et al, 2012; Rondon, et al, 2006)**

Demulsifiers were organic molecules, when dissolve in emulsion at low concentration, they have the ability to adsorb and locate at the interfaces of droplets in emulsion; Thereby demulsifier alter significantly the physical properties of the interfaces. The adsorption and location behaviors can be attributed to the emulsion nature and the chemical structure of demulsifier combined both a polar and a non-polar group into a single molecule. To accommodate for dual nature, molecules of demulsifier adsorb and locate at interfaces so that the polar groups remain in the water while the non-polar groups in crude oil. It was known that any change in temperature causes changes of emulsion interfacial tension between the oil and the water phases, which leads to a change in the nature and viscosity of the interfacial film. Hence, also the relative solubility of the emulsifiying agents also was change in the two phases and in the thermal agitation of the dispersed droplets. Therefore, temperature changes usually cause considerable changes in the stability of the emulsion; they may invert the emulsion and cause breaking of emulsion. **(Wang, et al, 2012; EL-Ghazawy, et al, 2010; Al-Sabagh, et al, 2006; Al-Sabagh, et al, 2010; Al-Sabagh, et al, 2011; Al-Sabagh, et al, 2013; Wu, et al, 2003; Al-Sabagh, et al, Egyptian Journal of Petroleum, 2011; Al-Sabagh, et al, 2013, 996-1007)**

The present work focuses on preparing a new class of ethoxylated aliphatic amine polyester surfactants, in the presence of block polymer and dibasic acid and evaluating them as demulsifiers for crude oil emulsions, in different water content; 30, 50 and 70 and different asphaltene content; 1.6, 7.2 and 8.7%. The effect of demulsifier concentrations, temperature and demulsification time were studied. Our attention was extended to correlate the surface activity of the prepared non-ionic surfactants and their performance as demulsifiers.

2. Experimental

2.1. Materials Used

Chemicals Used: Aliphatic amines; octyl, decyl, dodecyl and tetradecy were supplied from Aldrich chemical company whereas maleic anhydride was obtained from Merck Chemical Company. Polyethylene oxide, polypropylene oxide block copolymer 5000 was supplied from Stepan Chemical Company. The other chemicals were of technical grade and used as received without further purification.

Formation Water Used: The sample of formation water was conducted from the Petro Gulf Company, Suez Gulf, Egypt and its physicochemical characterization was shown in **Table 1**.

Crude Oil Used: Two types of asphaltenic crude oils were submitted from Suez Oil Company (SUOCO), East Desert, Egypt and one waxy crude oil was submitted from Qarun Petroleum Company, West Desert, Egypt and their general physicochemical properties were shown in **Table**

2.2.2. Preparation of the aliphatic polyesters

2.2.1. Ethoxylation of aliphatic fatty amines

Four fatty amines; octyl, decyl, dodecyl and tetradecy were ethoxylated at 6, 12 and 18 ethylene oxide units, to get twelve ethoxylated fatty amines. Each fatty amine was charged into a closed reaction vessel individually with 0.5 gm Na-metal as a catalyst, it was heated from 150 to 180 ^{o} C with continuous stirring, while passing a stream of nitrogen gas through the system for 2 minutes before heating to flush the air. Then the nitrogen stream was, replaced by ethylene oxide at a rate, which was regulated by Monitoring Hg level of the manometer. The reaction was carried out in different intervals of time after which the apparatus was filled with nitrogen, cooled and the reaction vessel was weighed. The difference in weight indicated the amount of ethylene oxide consumed in the reaction, from which the number of moles of ethylene oxide can be calculated **(Hreczuch, et al, 2001, Al-Sabagh, et al, 2004)**. The total number, n, of ethylene oxide groups were = 6, 12 and 18. The product was then dissolved in isopropanol, then salted out with supersaturated NaCl solution. Then the organic layer was separated and the isopropanol was distilled off. The ethoxylated product obtained showed a brown viscous liquid appearance.

2.2.2. Polyesterification of the Ethoxylated Aliphatic Fatty Amines

The ethoxylated aliphatic amines (0.55 mol) were charged individually into the reaction vessel with (0.55 mol) block copolymer. The reaction mixture was heated in xylene as a solvent to 80 ◦C in N_2 atmosphere then 1 mol of maleic anhydride was added, and the temperature was raised to 190–200 ◦C for 4 h. The reaction vessel was connected to Dean Stark trap to removed water. The extent of the reaction was followed-up by monitoring the acid value. The reaction product was permitted to cool at room temperature and was stored in a dark reagent bottle. **(Al-Sabagh, 2000)**. The molecular weight and the polydispersity were determined by GPC and the nitrogen content was determined by the quartz method. **Table 3** shows the chemical designations and some physical properties. The scheme of reaction is shown in **Figure 1.**

IR spectra are recorded in a Fourier Transform Infrared Spectrophotometer (FT-IR 1615, Perkin Elmer, USA) with KBr pellets.

2.3. Preparation of the Water in Crude Oil Emulsions

In a 250 ml beaker, the crude-oil was stirred at 25^{o}C (200 rpm), while formation water was added gradually to the crude oil until the two phases became completely homogenized. **(Kim, et al, 1996)**. The emulsions were produced at different ratios of crude oil to water, namely 70:30 and 90:10 respectively. Emulsions were let 48 h at 60 ◦C, to make sure that no separation happened, before the treatment.

2.4. Hydrophile Lipophile Balance (HLB)

The HLB of the prepared demulsifiers were calculated according to the most commonly used formula for the nonionic surfactant; HLB = 20 x M_H / (M_H + M_L).

Where: M_H was the formula weight of the hydrophilic portion of the molecule and M_L was the formula weight of the lipophile (hydrophobic) portion of the molecule. **(Rosen, 2004)**

2.5. Surface and Interfacial Tension Measurements

The prepared polymeric water soluble surfactants were subjected to surface tension measurements. Different molar concentrations of each surfactant were prepared, and their surface tension was determined at 60 ^{o}C; the process temperature at petroleum fields with a Spinning Drop Tensiometer (SDT).

2.5.1. Surface Active Parameters

The surface active properties of the prepared surfactants, maximum surface pressure (π_{cmc}), maximum surface excess concentration at surface saturation (Effectiveness, Γ_{max}), the minimum surface area per adsorbate molecule of solute (A_{min}), the free energy of micellization (ΔG_{mic}) and the free energy of adsorption (ΔG_{ads}) were calculated using the following equations: **(Rosen, 2004)**

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \quad (1)$$

$$\Gamma_{max} = -10^{-7} [1/nRT] [d\gamma/d\ln C]_T \quad (2)$$

$$A_{min} = 10^{16} / [\Gamma_{max} . N_A] \quad (3)$$

$$\Delta G_{mic} = (2-\beta) R T \ln CMC \quad (4)$$

$$\Delta G_{ads} = \Delta G_{mic} – [\ 0.6022 \text{ x } \pi_{cmc} \text{ x } A_{min}\ ] \quad (5)$$

Where, γ_o is the surface tension measured for pure water at the appropriate temperature, γ_{cmc} is the surface tension at CMC, γ is the surface or interfacial tension (mN/m), C is the concentration of surfactant (mol/l), Γ was the surface excess concentration in mol / cm^2, R is the molar gas constant (R= 8.314 J/mol K), T is the absolute temperature = 333 K, A_{min} is the surface area per molecule of solute in square angstrom (A^{o2}/molecules), N_A is the Avogadro's number (6.023 x 10^{23} molecules / mol) and n is the number of solute species (The value of n is equal to 1 in the nonionic surfactants).

2.5.2. Interfacial Tension

The interfacial tension between the surfactant solutions and the crude oil was measured via spinning drop method on KRUSS spinning drop interfacial tension apparatus (Germany). The principle behind obtaining interfacial tensions using the spinning drop method is that oil (low density) forms long oval drops in the water phase (high density) when subjected to centrifugal force, gravity and interfacial tensions. Its major and minor axes are L and D, respectively.

The surfactant in distilled water solution as outer-phase was injected into the glass tube, and 3–4 μL crude oil as inner-phase was put into the middle of the tube. Then, the interfacial tension was measured applying a rotating velocity of 5000–6500 rpm in all cases as usual.

This technique relies on the fact that, gravitational acceleration has little effect on the shape of a less dense fluid drop suspended in a denser liquid, when the drop and the liquid are put in a horizontal tube spin about its longitudinal axis. At low rotational velocities, ω, the fluid drop will take an ellipsoidal shape, but when ω is sufficiently large, it will become cylindrical. The shape of the oil drop is controlled by a balance between centrifugal forces, which tends to elongate the drop, and interfacial forces, which consequently tend to oppose elongation as to reduce the interfacial area. This theory holds true only if, the fluids are in gyrostatic equilibrium (or rigid body rotation), i.e., if every element of the fluid inside the rotating tube is stationary relative to the wall of the tube. Gyrostatic equilibrium is only attained, at high enough rotation rates when gravitational forces perpendicular to the axis of rotation are negligible, compared with centrifugal forces. When $L/D \geq 4$, the measurements of interfacial tension is obtained based on Vonnegut's formula **(Vonnegut, 1942)**:

$$\gamma = \Delta \rho\, \omega^2 R^3 / 4 \quad (6)$$

where γ (mN m^{-1}) is the interfacial tension, $\Delta\rho$ (g cm^{-3}) is the density difference between the drop and the surrounding fluid, ω (rad s^{-1}) is the angular velocity and R (cm) is the drop radius. The formula was been shown to be valid within 0.1% accuracy, if the drop is in equilibrium and the length of the drop exceeds four times its diameter. In other words, this equation is only valid if the ratio of the drop length to diameter *(L/d)* is greater than 4. **(Venkataraman, et al, 2013; Martin, et al, 2008; Chan, et al, 2003)**

The spinning drop interfacial tensiometer yields the parameter *p*, which is the reciprocal of speed. Thus, the metrical drop diameter is not the actual size but an apparent diameter *d*. Therefore, the equation can be transformed into:

$$\gamma = 1.2336\, \Delta \rho\, (1/p)^2\, (d/n)^3 \quad (7)$$

where *d*, *p* and *n* are the drop apparent diameter, reciprocal of speed and solution refractive index, respectively. 1.2336 is the correction factor applicable when pure water is the outer fluid. **(Jiang, et al, 2014; Levy, et al, 2001)**. When L/d < 4, equation **(7)** should be modified as follows:

$$\gamma = 1.2336\, \Delta \rho\, (1/p)^2\, (d/n)^3\, f(L/d) \quad (8)$$

where ***f*(*L*/*d*)** is a correction factor related to L/d and has been tabulated elsewhere. **(Jiang, et al, 2014)**

A value for *n* of 1.33 was used in the calculations over the entire temperature range, since the refractive index of water is virtually invariant with temperature and this will introduce minimal errors to the calculation. **(Taylor, 2011)**

The spinning drop method is believed to be the most accurate method, to measure low interfacial tensions. So, it has been very successful in the measurement of ultralow interfacial tensions down to 10^{-6} *mN/m* for water surfactant system. **(Levy, et al, 2001)**

2.6. Demulsification Performance using the Bottle Test

The graduated bottle test (Sany glass) was used to estimate the efficiency of the demulsifiers toward resolving W/O emulsions. Each demulsifier was dissolved in xylene (20% active material) and then added to 100 ml of the previously prepared emulsion at different concentrations (ppm). The mixture was added to a 100-ml Sany glass and then was shaken vigorously for 1 min. The bottle was placed in a thermostated water bath at 50, 60 or 70 ^{o}C. Water separation (mls) was observed at different times depending on the efficiency of the undertaken surfactants (demulsifiers). A blank was considered in each set of experiments.

3. Results and Discussion

3.1 Synthesis and Spectral Characterization

Different aliphatic amines; octyl, decyl, dodecyl and tetradecyl amines were individually condensed with ethylene oxide gas, in nitrogen atmosphere in presence of triethylamine, as a catalyst at 80^{o}C, for different periods of time. The prepared ethoxylated amines at 6, 12 and 18 oxyethylene units were used as new diols in the preparation of the polyesters. Each ethoxylated amine (diol) was allowed to condense with dibasic acid and block polymer (diol) to get the corresponding polyester amine.

The structures of the ethoxylated amines were confirmed by FTIR. The FTIR spectra for $12E_{18}$ as a representative sample **(Figure 2.a)**, showed a characteristic broad band due to OH stretching at 3470 cm^{-1}. The peak at 1100 cm^{-1}, due to **C-O** stretching, indicated the formation of the ether bond in the ethylene oxide "$\mathbf{CH_2\ CH_2OCH_2\ CH_2}$". The absence of peaks in the range 3200-3400 cm^{-1} meant that the two hydrogen of the amine were replaced by ethylene oxide units.

Each ethoxylated amine (diol) was allowed to condense with dibasic acid and block polymer (diol) to get the corresponding polyester amine. The structure of the prepared polyesters was examined using the FTIR. The FTIR spectrum of $12E_{18}D$ as a representative sample was shown in **Figure 2.b**. The appearance of a broad band at 3490 cm^{-1} is due to **OH** stretching vibration and the strong band at 1730 cm^{-1} was due to the carbonyl **C=O** ester stretching vibration.

Nitrogen content in **Table 3** indicated that, the experimental and theoretical values were nearly close. This means that the synthesis and purification were performed successfully. The nitrogen content of the polyesters increased with the increase of the molecular weight. The generalized chemical structure for the prepared polyesters was formulated from consideration of nitrogen content and molecular weight of the different polyesters.

Also it was found that, the HLB generally increased with the number of the ethylene oxide content of the polymer. **(Table 3).**

Molecular weight determination **(Table 3)** clearly showed that, the increase of ethylene oxide units apparently caused a hindrance for the polyesterification reaction to form a high molecular weight polymer. The decrease in molecular weight with the increase in ethylene oxide units followed the order (41801 > 30538 > 26209) for $8E_6D$, $8E_{12}D$ and $8E_{18}D$ respectively. The polydispersity was found to equal unity or very near to unity which meant that the nonionic polymers were in ideal conformation.

3.2. Surface tension parameters

For all the investigated polyesters, the surface tension decreased with increasing the concentration until a certain concentration was reached; at which the surface tension remained constant ,even if the concentration of the surfactant was increased. This concentration was known as the critical micelle concentration (cmc), where saturation in the surface adsorbed layer was attained. At this concentration ,the surface-active molecules aggregated into clusters (micelles), with their hydrophobic groups directed towards the interior of the micelle and their hydrophilic groups directed towards the solvent (water). Micellization was therefore a mechanism alternative to adsorption at the interfaces for removing lyophobic groups from contact with the solvent, thereby reducing the free energy of the system. It has been shown previously that for polyoxyethylenated nonionics, the outer region included coils of the hydrated polyoxyethylene chains. Some bound water existed in the interior region of the micelle in the vicinity of the first few methylene groups adjacent to the hydrophilic head groups. The data presented in **Table 4** showed some of the surface-active properties for the prepared aliphatic polyester surfactants. It may be observed that the cmc for the prepared aliphatic polyesters, generally increased with increasing the number of ethylene oxide units per molecule. This behavior may be due to that increasing ethylene oxide increases hydrophilicity, which increases solubility of the surfactant in water. Such improved solubility lowers the tendency for surfactants to form micelles in water and increases the cmc. The CMC values can be considered as a measure of the efficiency of the surfactant to reduce surface tension.

Maximum surface tension reduction was effected in the polyesters which has ten oxyethylene units. For instance, the $\boldsymbol{\gamma_{CMC}}$ were 32.8, 31.5and 30.1 mN/m for tetradecylamine polyester ethoxylated with 6, 12 and 18 ethylene oxide units ,respectively. Thus, apparently a total of 12 ethylene oxide units were necessary to produce hydrophilic character contributing to the optimum reduction of surface tension of surfactant solutions.

The data included in **Table 4** indicated that the maximum surface pressure "$\boldsymbol{\pi_{cmc}}$" was slightly affected by the number of ethylene oxide units of the surfactant molecule. However, it may generally recognize that, the compounds containing ten ethylene oxide units were more capable of reducing the surface tension irrespective of the type of amine constituting the polyester surfactant.

Of prime importance, the maximum surface excess concentration at surface saturation "effectiveness" **"$\boldsymbol{\Gamma_{max}}$"** and the minimum area per molecule "$\boldsymbol{A_{min}}$" were calculated and illustrated in **Table 4**. The maximum surface excess concentration "$\boldsymbol{\Gamma_{max}}$" ranged from 1.10 x 10^{-10} to 1.70 x 10^{-10} mole/cm^2. The minimum area occupied per molecule "$\boldsymbol{A_{min}}$" was within the range 0.97 x 10^{-2} – 1.46 x 10^{-2} A^{o2}. $\boldsymbol{A_{min}}$ values tabulated in **Table 4** increased with increasing the total number of ethylene oxide units. This was because $\boldsymbol{A_{min}}$ depended mainly on the adsorption at interfaces, which in turn was affected by the total number of ethylene oxide units.

The free energy changes of micellization, ΔG_{mic}, ΔG_{ads} increased in negativity than ΔG_{mic}. That showed, the higher tendency of these amphiphiles towards adsorption rather than micellization. Then the adsorption will be accompanied with micellization at last. The tendency towards adsorption was referred to the interaction between the aqueous phases and the hydrophobic chains which pumped the amphiphile molecules to the interface. This means that, the micellization of these polymeric esters in the solution was inhibited more than the adsorption at the liquid / air interface, or the adsorption was facilitated more than micellization, such finding let us use thesis polymeric esters in the demulsification process, because the demulsification firstly depended on the efficiency of adsorption of the surfactant on the interface.

3.3. Interfacial Tension

The interfacial tension between crude oil and water depends on the composition of oil. The interfacial tension between the three investigated untreated crude oil phases and the formation water was measured using the Spinning Drop Tensiometer and the interfacial tension values were 19.0, 17.5 and 14 mN/m for Type I, Type II and Type III respectively. The addition of the prepared demulsifiers reduces the interfacial tension significantly. This was clear in Table 5. The data included in **Table 5 and 6** indicated that, the IFT of the untreated oil (without demulsifier) is higher than the treated one. The long time was taken for complete water separation of 10% water in oil emulsion (4weeks and 3 days) against type I crude oil, (4 weeks) against type II and 120 min against Type III. This is may be due to the presence of the asphaltene on the interface which makes hindrance of water droplet to coalescence with other to separate. By inspection of the data in **Table 5**, it was found that, the addition of demulsifier plays an important role to reduce the IFT on the interface farther the demulsification process occurs. The asphaltene content in the crude oil stabilizes the water-in-oil emulsion. The demulsification process was very sensitive to the demulsifier alkyl chain length and ethylene oxide units. The maximum demulsification efficiency was exhibited by $12E_{18}D$ (5.4 x10^{-2}, 1,9x 10^{-2} and 2x10^{-3} mNm^{-1}) against the used crude oil type I,II and III. The lowest demulsification efficiency was obtained by 8E18D (8.4, 5.6 and 5x10^{-1} mNm^{-1}) respectively. Also it was found that the IFT values for the demulsifier against waxy crude oil were more less than the values, which were obtained by the same demulsifier against the asphaltenic crude oil. This may be due to presence of asphaltene gives the highest values of the IFT, which associated with the highest emulsion stability during the demulsification process. The increasing of e.o units may increase the adsorption of surfactant molecules on the oil-in-water interface. The adsorption of surfactant molecules on the interface minimizes the interfacial tension between the water and oil, which leads to form un stable water in oil emulsion. Thus, apparently a total of 18 ethylene oxide units $12E_{18}D$ were necessary to produce hydrophilic character contributing to the optimum reduction of interfacial tension of surfactant solution.

3.4. Factors affecting the demulsification efficiency

The previous discussion was devoted to characterize the most fundamental physicochemical and performance properties of the prepared polymeric surfactants in an attempt to understand the mutual relationship between the structure of the surfactant and its interfacial and most important performance behavior. As a matter of fact, the polymeric surfactants might have varying demulsifying capabilities. Consequently, the following discussion will deal with the most important observations of the efficiency of the prepared surfactants as demulsifiers for water in crude oil emulsions. Several factors affect the demulsification process, some of them depend on the characteristics of the continuous phase, such as viscosity and asphaltene content in crude oil. However other factors depend on the structural modification of the demulsifier used.

3.4.1. Molecular weight effect

An increase in the molecular weight may lead to lower mobility of the demulsifier in the emulsion. Some investigators **(Schramm, 2000; Cooper, et al, 1980)** studied the relationship between the molecular weight of demulsifiers and their efficiency and they found a direct relation between the molecular weight and efficiency of demulsifiers. **(Al-Sabagh, et al, 2008)**. Careful inspection of **Tables 6-8 and Figure 3** showed that, the molecular weight of the polymeric surfactant had a pronounced effect on the demulsification of crude oil emulsions. Thus, the lowest molecular weight surfactants caused separation of the emulsion in much shorter times. This enhanced demulsification may be due to that; the high molecular weight polymeric demulsifiers cannot easily disperse in the viscous crude oil mass, which formed the continuous phase. Hence, they cannot penetrate the rigid film formed by the natural emulsion stabilizer (asphaltene) which protected the dispersed water droplets and prevented them from coalescence.

Polymeric surfactants comport onset as demulsifiers much more than the monomeric surfactants. This may be due to the fact that, the polymeric surfactants have a greater ability to displace the natural emulsifiers, forming the rigid film of the interface, around the dispersed water droplets. **(Graham, 1988)**. However these polymeric surfactants have an enhanced ability to trap the dispersed solid particles, which, due to their electrostatic repulsion they aid in the emulsion stability and consequently, they prevent the dispersed water droplets from coalescence. When these charged particles are trapped by the surfactant molecules the coalescence phenomenon can readily take place. The enhanced ability of polymeric surfactants, to trap the dispersed solid particles, is due to the large size of the surfactant molecule. This property causes the surfactant molecules, to sweep easily the dispersed solid particles, in the emulsion through their molecular mass.

3.4.2. Hydrophile Lipophile Balance “HLB” effect

The HLB was one of the most important characteristics of demulsifying agents which exerted an effective influence on the rate of coalescence of emulsions. In general, the demulsifiers with greater ethylene oxide content possessed a high hydrophilicity, and consequently higher solubility in the aqueous phase “dispersed phase”. When the demulsifier was initially introduced to the water-in-oil emulsion, it was more thermodynamically stable at the interface of the water droplets. Accordingly, the surfactants which had high HLB migrated faster to the interface than those having low HLB. As a result of such enhanced migration toward the interface, the surfactant formed a continuous hydrophilic pathway existing between the dispersed water droplets. This leads to a rupture of the interfacial oil film surrounding the water droplets. Another point of view, regarding the enhanced demulsification efficiency of the more hydrophilic surfactants, was based on the fact that, the destabilization of water-in-oil emulsions can be achieved by the addition of surface active agents, which promoted oil-in-water emulsions. It was known that, water soluble surfactants were more capable of stabilizing oil-in-water emulsions and vice versa. So, the higher the HLB, the higher the demulsification efficiency. The HLB was one of the most important factors determining the emulsion stability which was reflected on the demulsification process. **(Zaki, et al, 1996; Abdel-Azim, et al, 1998; Sjoblom, et al, 1990)**. The relationship between HLB, of the different polymeric amine surfactant and the time taken for water separation from crude oil emulsions, was illustrated in **Tables 6-8 and Figure 3**. The efficiency for surfactants as demulsifiers was correlated with HLB as indicated in **Tables 6-8 and Figure 3**. It was found that, all the studied surfactants had HLB values within the range of 8-11. Those surfactants with higher ethylene oxide units had higher HLB values and succeeded in separating water from the crude oil, in a small interval of time, whereas those with low ethylene oxide units and low HLB values failed to separate the emulsion in a small time interval. The time taken to separate the emulsion with 7.2 % asphaltene and 30% formation water at 60 ^{o}C using 400 ppm from $12E_6D$ (HLB = 7.77), $12E_{12}D$ (HLB= 9.45) and $12E_{18}D$ (HLB=10.18) was as follows 40 > 35 > 30 min, respectively. So, the data clearly showed that higher HLB of the surfactant resulted in enhanced demulsifying capability.

3.4.3. Effect of the Demulsifier Concentration

One of the most important parameters governing the adsorption of demulsifiers at the interface is the demulsifier concentration. **(Kim, et al, 1996)**. The effects of the investigated demulsifiers on the dewatering percentage were shown in **Tables 6-8**. Increasing the surfactant concentration, from 200 ppm to 400 ppm with respect to 10 and 30% water content and from 25 to

500ppm with respect to 50% water content, which greatly reduced the time required to complete water separation of the crude oil emulsions and thus fast demulsification could be achieved. These data indicated that, the increase of the demulsifier concentration led to an increase in the adsorption of the demulsifier molecules on the W/O interface, which replaces the native emulsifiers (asphaltene). This, decreased the mechanical stability of the interfacial film. The stability of this film continues to decrease until being thinner, and then collapsed totally with further adsorption of the demulsifier agent on the interface.

3.4.4. Effect of Water Content

From the data in **Tables 6-8** and the illustrations in **Figure 3**, it was obvious that, the demulsification efficiency increased with increasing water content from 30 to 70% for all the investigated demulsifiers. This may be due to, the internal pressure of water, which was lower than the external pressure of the oil at low water content. **(Kim, et al, 1996; Al-Sabagh, et al, 2007)**. This leads to an increase in the mechanical stability of the W/O interface and rigidity of the film. On the other hand, the rigidity of W/O films decreased with increasing water content in the bulk until the internal pressure became greater than the external pressure. At that moment, a rapid rupture of the W/O interface occurred and the coalescence of water droplets increased.

Several observations can be noticed by the inspection of **Tables 6-8**, which illustrated the data obtained for the demulsification of 7.2 % asphaltenic crude oil emulsions containing 30, 50 and 70 % formation water. It was obvious that, the separation of water from crude oil emulsions was directly proportional to the HLB of the demulsifier, and the number of ethylene oxide units in the molecule, irrespective of the length of the chain of the aliphatic amine, of the polymeric surfactant. The demulsification was improved by increasing the concentration of the demulsifier from 200 to 400 ppm. However, demulsifiers possessing aliphatic amine chain (14 carbons) exhibited the shortest time for complete emulsion breaking.

3.4.5. Temperature Effect

In the present study, the influence of temperature on the demulsification efficiency was investigated. In **Figure 4**, $8E_{18}D$ has been selected to show the effect of temperature on the demulsification efficiency. The results showed that, with raising the temperature from 50 ^{o}C to 70 ^{o}C, this cause improved demulsification efficiency towards the hard asphaltenic crude oil (8.7 % asphaltene content). These enhancements in efficiency led to the speculation that, emulsions commonly encountered, in producing crude oil were stabilized by films, which were formed at the water-oil interfaces and interfered with coalescence of the dispersed water droplets. These emulsion-stabilizing films composed of interfacially active materials from the asphaltene and resin fractions of the crude oil, combined with ions from the aqueous phase and insoluble fines in the crude oil-brine system. Emulsion stability can be decreased by conditions that reduced the film forming capacity of the crude oil. These films can be minimized or their physical altered by increasing the temperature via two routes **(Eow, et al, 2002)**. The first, by increasing the rate of coalescence by offering adequate energy for the bombardment of two droplets occurring prior to coalescence. The second, by causing reduction in the continuous phase viscosity; which facilitated the kinetic motion of the dispersed water droplets, hence, causing increased bombardment resulting in film relaxation, film rupture and coalescence. **(Bhardwaj, et al, 1994; Abdel-Azim, et al, 1998)**

In other words, increasing of the temperature appeared, primarily to reduce the viscosity of the continuous phase (oil) and increase the rate of collision between the emulsified droplets "water". As a result, the density difference between the aqueous and oil phase (usually) increases and hence induces separation of water droplets. Higher temperature might increase the solubility of emulsifiers, from interface, into oil phase, resulting in weaker film and greater degree of water droplet coalescence and separation. The interfacial turbulence that was frequently observed during heat or mass transfer across an interface, was commonly referred to Marangoni effect, and recognized as being due to surface tension variations **(Porter, 1994; Mosayebi, et al, 2013; Myers, et al, 2002; Strausz, et al, 1992)**. The rate of diffusion of the demulsifier molecules to the interface will increase with temperature and concentration of the demulsifier. Thus the interfacial tension decreases faster at high concentrations and temperatures as shown in **Figure 5**. It was clear that as the temperature increases while resolving the crude emulsion with 8.5 % asphaltene content from 50 to 70 ^{o}C using $8E_{18}D$, the time for demulsification decreases from 225min to 95min at 400 ppm.

3.4.6. Asphaltene Content Effect

Since asphaltene was recognized as the main chemical constituent of crude oil which acted as a natural emulsifier causing the production of water in oil emulsion in crude oil, it may be reasonable that, the presence of a great content of asphaltene will result in much stable W/O emulsions. Generally, in asphaltenic crude oil, the water / oil emulsion was stabilized by the high mechanical stability of asphaltene on the interface. **(Yan, et al, 2001; Yarranton, et al, 2000)**. The data presented in **Figures 3** illustrated the capabilities of the different prepared amine polyester surfactants in demulsifying water in crude oil emulsions containing 7.2 % asphaltene. However, in some particular cases, crude oil emulsions were formed by much less content of asphaltene. Thus, **Figure 4** illustrated the data obtained upon examination of some of the prepared amine polyester surfactants to separate the water / oil emulsions (1.6 % asphaltene). Evidently, it may be shown that, only smaller amounts of demulsifiers were sufficient to break such types of emulsions. The latter must be necessarily less stable than those formed by a great content of asphaltene. The break of emulsions took only 4-7 minutes at only 10 ppm of the tested demulsifiers used. It was noteworthy that, as the asphaltene content increases in the crude oil, the protecting film of the emulsion became denser. Moreover, the higher viscosity of the crude oil, with higher asphaltene content (9.6%) may be blamable for reducing the diffusion coefficient of the demulsifier molecules, thereby inhibiting the demulsification process. This was observed in **Figure 5**.

4. Conclusion

The conclusion of this work can be drawn in these following points:

- Twelve novel polyesters surfactants based on aliphatic amine ethoxylates, as a diol, were prepared.
- The prepared polyesters were performed as demulsifiers, to break down the W/O emulsions.
- The demulsification process was very sensitive to the molecular weight of the polyesters, HLB, concentration, alkyl group of fatty amine incorporating in the polyesters and ethylene oxide content.
- The asphaltene content in the crude oil composition and the temperature of the process were very important factors affecting the demulsifier efficiency toward complete separation of water from crude oil emulsions.

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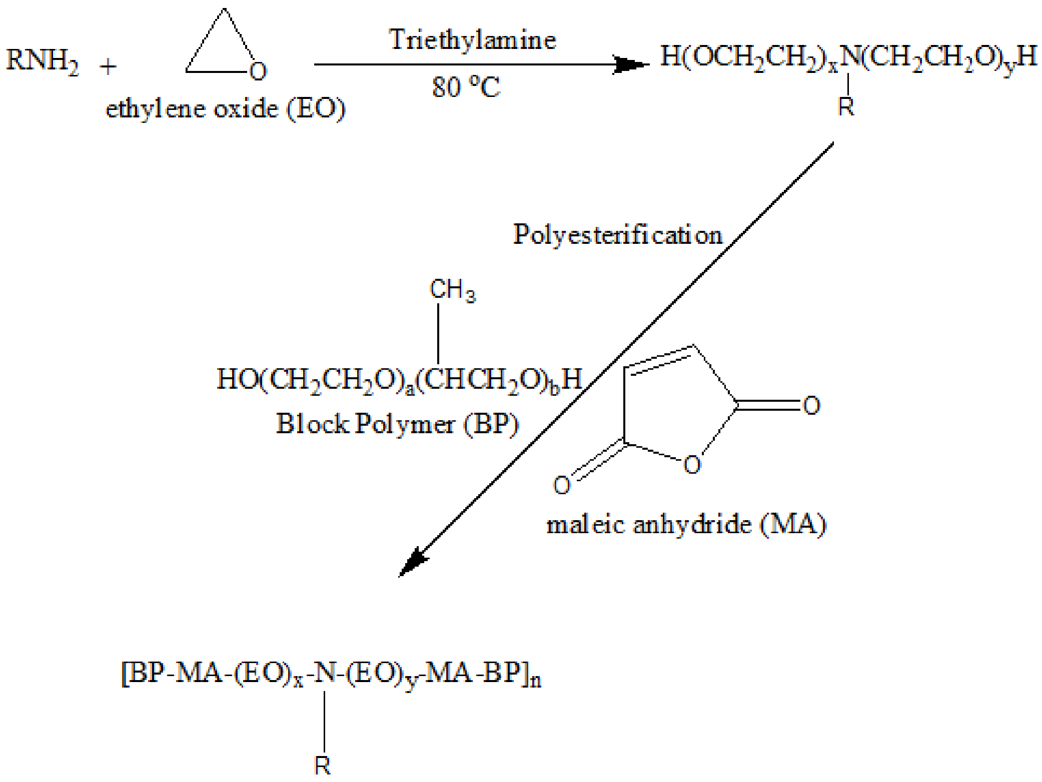

Wherein, 1) n = x + y = 6, 12, or 18 and
2) R = C_8H_{17}, $C_{10}H_{21}$, $C_{12}H_{25}$ or $C_{14}H_{29}$
3) a= 68 ethylene oxide and b= 34 propylene oxide, Block polymer (BP) Molecular Weight ≈5000

Figure 1: Scheme of reaction

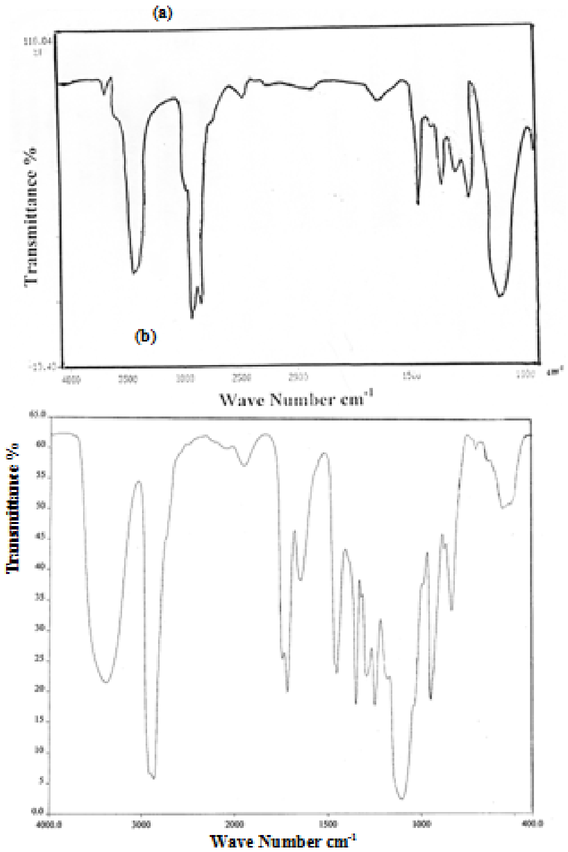

Figure 2: FTIR for (a) $12E_{18}$ and (b) $12E_{18}D$

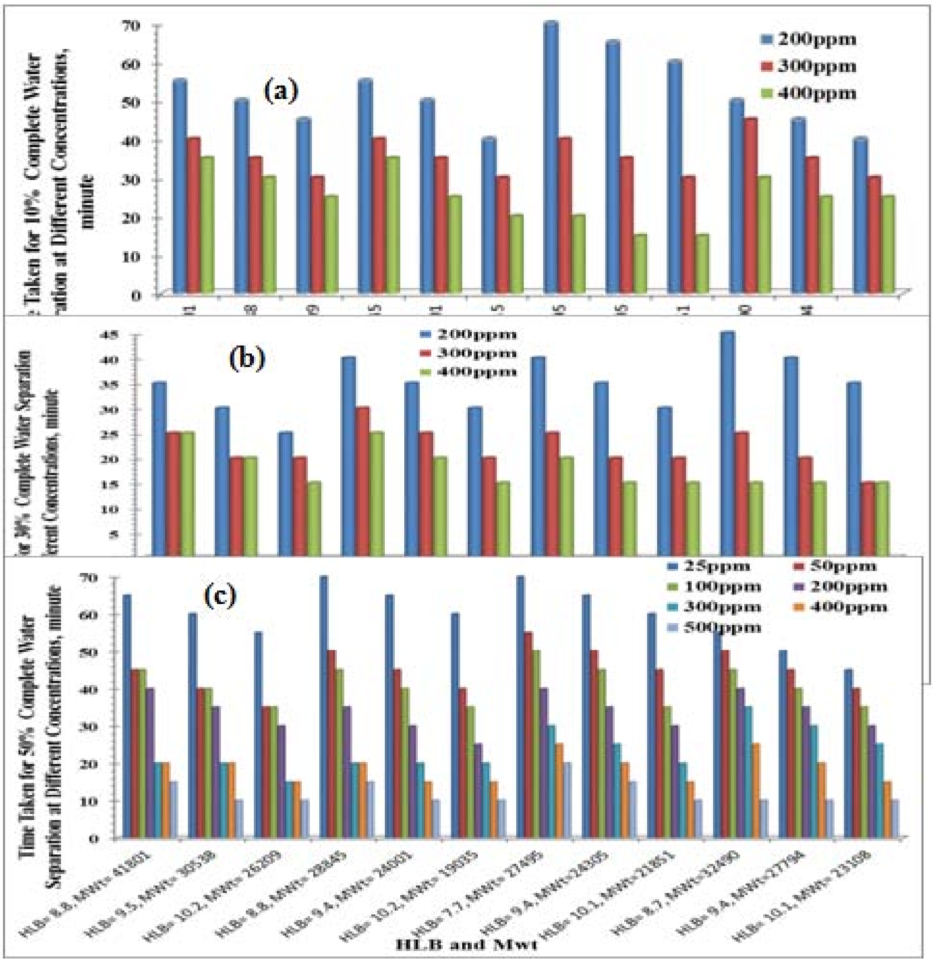

Figure 3: The Demulsification Efficiency for the Prepared Surfactants to Resolve Asphaltenic Crude Oil Emulsions (7.2% Asphaltene Content) with (a) 30%, (b) 50% and (c) 70% water content

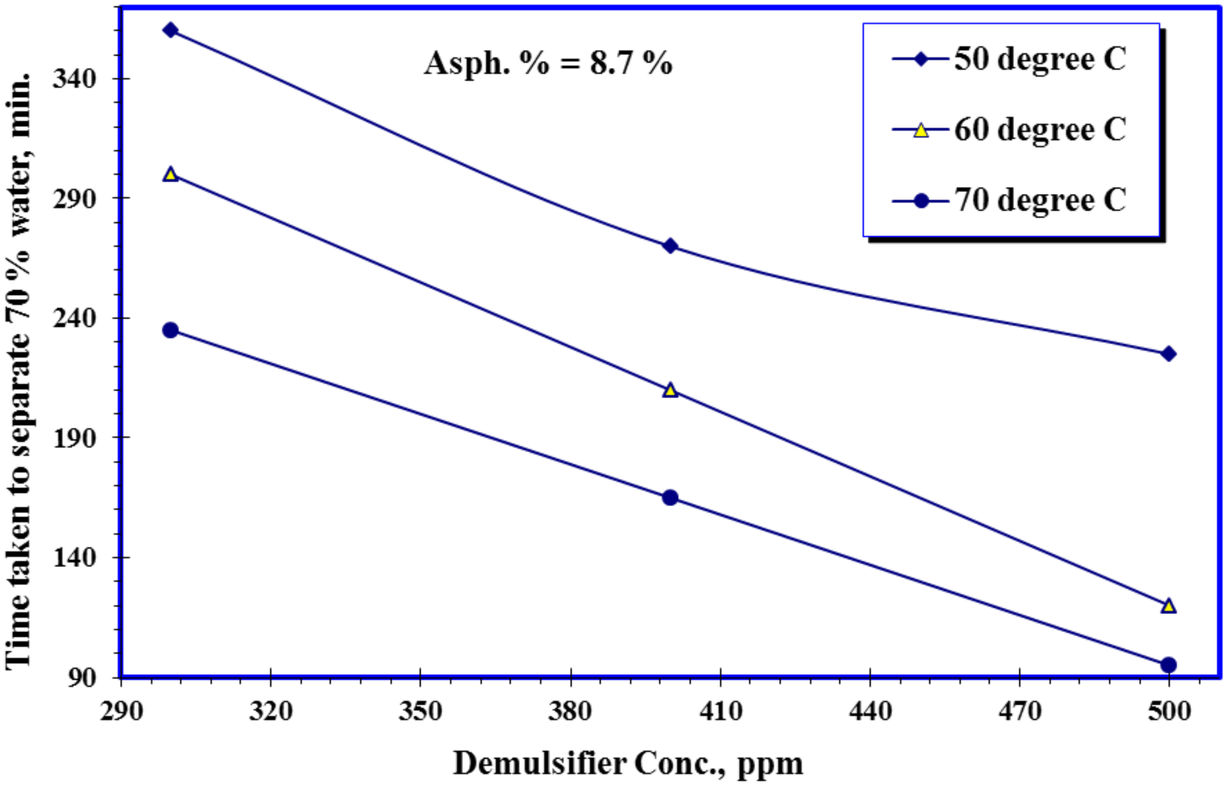

Figure 4: Effect of Temperature on the Demulsification Efficiency for $12E_{18}D$ to Resolve Hard Asphaltenic Crude Oil Emulsions

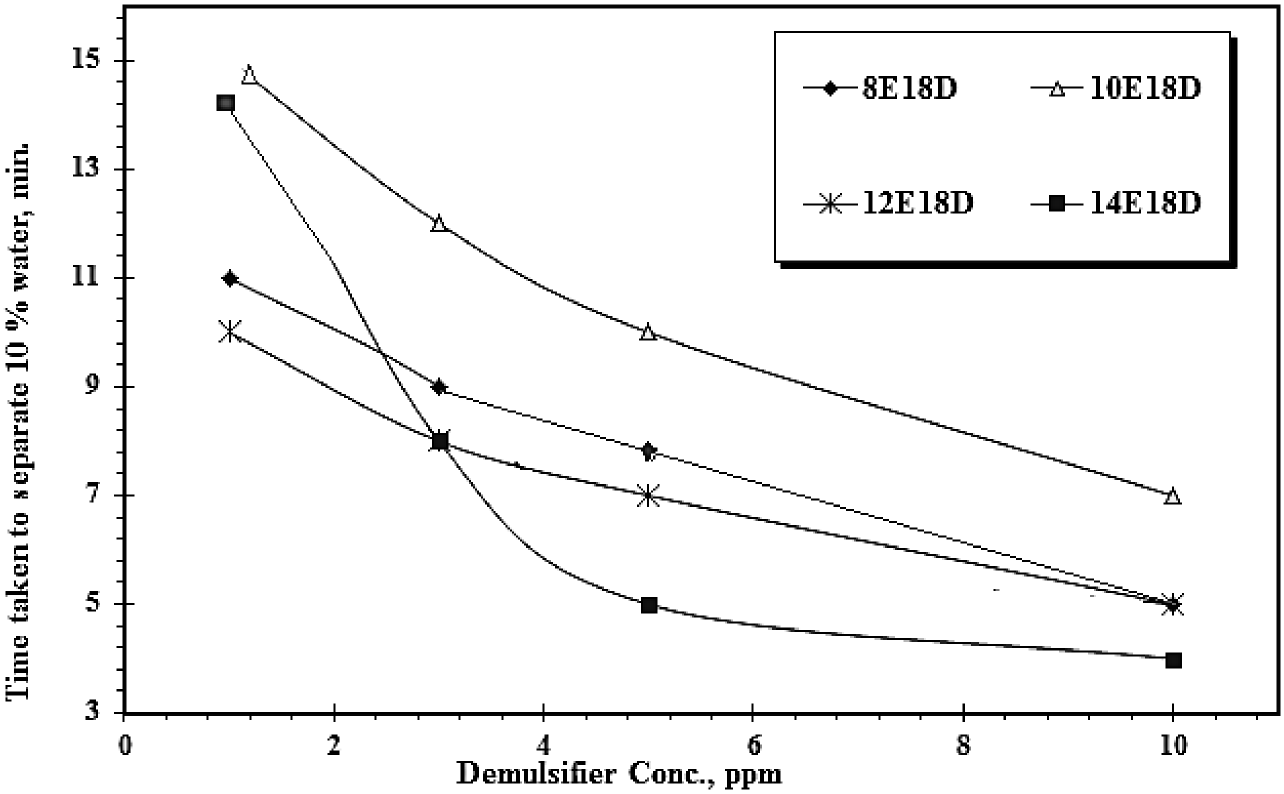

Figure 5: The Demulsification Efficiency for Some Selected Aliphatic Polyesters to Resolve Waxy Crude Oil Emulsions

Table 1: General Characterization of Formation Water

Total Dissolved Solids	44372 mg / L
Resistivity	0.01915 Ohm m at 19 ^{O}C
Conductivity	52.2 mS / M at 19 ^{O}C
Density	1.0322022 g / ml
pH	7.74 at 19 ^{O}C
Salinity	39996 mg / L
Specific Density	1.03304

Table 2: Physicochemical Properties of the used Untreated Crude Oils

Specification	*Method*	*Asphaltenic Crude Oil*		*Waxy Crude Oil*
		Type I	*Type II*	*Type III*
Specific Gravity (60 / 60 ^{O}F)	**IP 160**	0.973	0.874	0.8156
API Gravity At 60 ^{O}F	**IP 160**	26.29	40.955	43
Kinematic Viscosity at 60 ^{O}F (c. St)	**IP 71**	294.972	222.87	2.5
Asphaltene Content (wt. %)	**IP1 43**	8.7	7.2	1.6
Wax Content (wt.%)	**UOP 46**	2.5	2.9	15.4
Water content (vol %)	**ASTM, D - 4006**	0.5	0.5	0.5

Table 3: Name, Designation and Physical Characterization for the Prepared Aliphatic Polyesters

Demulsifier "Surfactant"	*Demulsifier Designation*	*M.wt.*	*Poly Dispersity*	*Repeating Unit*	*HLB*	*Alkylene Oxide*		*Nitrogen Content, ,%*	
						EO	*PO*	*Experimentally*	**Calculated**
Ethoxylated (6) Octyl amine polyester	$8E_6D$	41801	0.8999	7	8.8	490	238	0.27	0.26
Ethoxylated (12) Octyl amine polyester	$8E_{12}D$	30538	0.9897	5	9.5	390	170	0.23	0.24
Ethoxylated (18) octyl amine polyester	$8E_{18}D$	26209	1.2278	4	10.2	352	136	0.25	0.22
Ethoxylated (6) decyl amine polyester	$10E_6D$	28845	1.0023	5	8.8	350	170	0.25	0.26
Ethoxylated (12) decyl amine polyester	$10E_{12}D$	24001	0.9925	4	9.4	312	136	0.23	0.24
Ethoxylated (18) decyl amine polyester	$10E_{18}D$	19035	1.121	3	10.2	264	102	0.24	0.22
Ethoxylated (6) dodecyl amine polyester	$12E_6D$	27495	0.8998	4	7.7	280	136	0.25	0.23
Ethoxylated (12) dodecyl amine polyester	$12E_{12}D$	24305	0.9788	4	9.4	312	136	0.26	0.24
Ethoxylated (18) dodecyl amine polyester	$12E_{18}D$	21851	1.1671	3	10.1	264	102	0.25	0.22
Ethoxylated (6) tetradecyl amine polyester	$14E_6D$	32490	1.0143	5	8.7	350	170	0.27	0.25
Ethoxylated (12) tetradecyl amine polyester	$14E_{12}D$	27794	1.1679	4	9.4	312	136	0.25	0.24
Ethoxylated (18) tetradecyl amine polyester	$14E_{18}D$	23108	0.9981	3	10.1	264	102	0.24	0.22

Table 4: Surface Active Properties for the Prepared Aliphatic Polyesters at 60 °C

Polyesters, Demulsifier (Surfactant)	*CMC x10^5 mole/l*	*γ_{cmc} mN/m*	*Maximum surface pressure "π_{cmc}" mN/m*	*Effectiveness x 10^{10}, "Γ_{max}" mole/cm^2*	*A$_{min.}$ x 10^2 A^{o2}*	*Δ G$_{mic}$ (kJ mol^{-1})*	*ΔG$_{ad.}$ (kJ mol^{-1})*
8E$_6$D	2.4	32.5	33.74	1.70	0.97	-29.4	-31.5
8E$_{12}$D	1.2	31.1	35.14	1.39	1.20	-31.8	-34.4
8E$_{18}$D	1.1	30.1	36.14	1.14	1.46	-31.6	-34.0
10E$_6$D	1.2	32.4	33.84	1.49	1.11	-31.4	-33.6
10E$_{12}$D	5.6	31.2	35.04	1.34	1.24	-27.1	-29.7
10E$_{18}$D	7.6	30.7	35.54	1.14	1.45	-26.3	-29.4
12E$_6$D	4.7	32.6	33.64	1.69	0.98	-27.6	-29.6
12E$_{12}$D	5.5	31.4	34.84	1.44	1.15	-27.2	-29.6
12E$_{18}$D	6.3	30.5	35.74	1.10	1.51	-26.8	-29.8
14E$_6$D	3.6	32.8	33.44	1.38	1.21	-28.3	-30.8
14E$_{12}$D	4.6	31.5	34.74	1.23	1.35	-27.6	-30.3
14E$_{18}$D	4.9	30.1	36.14	1.23	1.35	-30.1	-32.8

Table 5: Interfacial Tension measured at 60 °C and 400 ppm

Demulsifier	Interfacial Tension, mN/m		
	Crude Oil Type I	Crude Oil Type II	Crude Oil Type III
Untreated	19.0	17.5	14
8E$_6$D	14.0	8.5	9 x 10^{-1}
8E$_{12}$D	11.5	6.4	6 x 10^{-1}
8E$_{18}$D	8.4	5.6	5 x 10^{-1}
10E$_6$D	12.5 x 10^{-1}	9.2 x 10^{-1}	8 x 10^{-2}
10E$_{12}$D	10.3 x 10^{-1}	8.1 x 10^{-1}	6 x 10^{-2}
10E$_{18}$D	7.5 x 10^{-1}	6.5 x 10^{-1}	4 x 10^{-2}
12E$_6$D	10.8 x 10^{-2}	5.5 x 10^{-2}	6 x 10^{-3}
12E$_{12}$D	7.6 x 10^{-2}	3.2 x 10^{-2}	4 x 10^{-3}
12E$_{18}$D	5.4 x 10^{-2}	1.9 x 10^{-2}	2 x 10^{-3}
14E$_6$D	8.5 x 10^{-1}	7.5 x 10^{-2}	9 x 10^{-3}
14E$_{12}$D	6.7 x 10^{-1}	6.9 x 10^{-2}	7 x 10^{-3}
14E$_{18}$D	5.6 x 10^{-1}	7.1 x 10^{-2}	5 x 10^{-3}

Table 6: Demulsification Efficiency for the Prepared Aliphatic Polyesters with Asphaltenic Crude Oil (7.2 %) Containing 10% formation water at 60 °C

Demulsifier	M.Wt.	HLB	Time Taken for 10 % Complete Water Separation at Different Concentrations*, minute		
			200ppm	300ppm	400ppm
8E$_6$D	41801	8.8	55	40	35
8E$_{12}$D	30538	9.5	50	35	30
8E$_{18}$D	26209	10.2	45	30	25
10E$_6$D	28845	8.8	55	40	35
10E$_{12}$D	24001	9.4	50	35	25
10E$_{18}$D	19035	10.2	40	30	20
12E$_6$D	27495	7.7	70	40	20
12E$_{12}$D	24305	9.4	65	35	15
12E$_{18}$D	21851	10.1	60	30	15
14E$_6$D	32490	8.7	50	45	30
14E$_{12}$D	27794	9.4	45	35	25
14E$_{18}$D	23108	10.1	40	30	25

*** Time taken, for 10 % water separation at 0 ppm (Blank Sample) = 4 weeks and 3 days against type I crude oil , 4 week against type II and 120 min against type III crude oil.**

Table 7: Demulsification Efficiency for the Prepared Aliphatic Polyesters with Asphaltenic Crude Oil (7.2 %) Containing 30% formation Water at 60 ^{O}C

Demulsifier	Time Taken for 30 % Complete Water Separation at Different Concentrations*, minute		
	200ppm	300ppm	400ppm
$8E_6D$	35	25	25
$8E_{12}D$	30	20	20
$8E_{18}D$	25	20	15
$10E_6D$	40	30	25
$10E_{12}D$	35	25	20
$10E_{18}D$	30	20	15
$12E_6D$	40	25	20
$12E_{12}D$	35	20	15
$12E_{18}D$	30	20	15
$14E_6D$	45	25	15
$14E_{12}D$	40	20	15
$14E_{18}D$	35	15	15

* **Time taken, for 30 % water separation at 0 ppm (Blank Sample) = 2 weeks and 5 days.**

Table 8: Demulsification Efficiency for the Prepared Aliphatic Polyesters with Asphaltenic Crude Oil (7.2 %) Containing 50% formation Water at 60 ^{O}C

Demulsifier "Surfactant"	Time Taken for 50 % Complete Water Separation at Different Concentrations*, minute						
	25ppm	50ppm	100ppm	200ppm	300ppm	400ppm	500ppm
$8E_6D$	65	45	45	40	20	20	15
$8E_{12}D$	60	40	40	35	20	20	10
$8E_{18}D$	55	35	35	30	15	15	10
$10E_6D$	70	50	45	35	20	20	15
$10E_{12}D$	65	45	40	30	20	15	10
$10E_{18}D$	60	40	35	25	20	15	10
$12E_6D$	70	55	50	40	30	25	20
$12E_{12}D$	65	50	45	35	25	20	15
$12E_{18}D$	60	45	35	30	20	15	10
$14E_6D$	55	50	45	40	35	25	10
$14E_{12}D$	50	45	40	35	30	20	10
$14E_{18}D$	45	40	35	30	25	15	10

*** Time taken, for 50 % water separation at 0 ppm (Blank Sample) = 1 weeks and 5 days**