Research Article

Influence of Surfactant Structure on the Stability of Water-in-Oil Emulsions under High-Temperature High-Salinity Conditions

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Emulsified water-in-oil (W/O) systems are extensively used in the oil industry for water control and acid stimulation. Emulsifiers are commonly utilized to emulsify a water-soluble material to form W/O emulsion. The selection of a particular surfactant for such jobs is critical and certainly expensive. In this work, the impact of surfactant structure on the stability of W/O emulsions is investigated using the hydrophilic-lipophilic balance (HLB) of the surfactant. Different commercial surfactants were evaluated for use as emulsifiers for W/O systems at high-temperature (up to 120°C) high-salinity (221,673 ppm) HTHS conditions. Diverse surfactants were examined including ethoxylates, polyethylene glycols, fluorinated surfactants, and amides. Both commercial Diesel and waste oil are used for the oleic phase to prepare the emulsified system. Waste oil has shown higher stability (less separation) in comparison with Diesel. This work has successfully identified stable emulsified W/O systems that can tolerate HTHS environments using HLB approach. Amine Acetate family shows higher stability in comparison with Glycol Ether family and at even lower concentration. New insights into structure-surfactant stability relationship, beyond the HLB approach, are provided for surfactant selection.

1. Introduction

Emulsions are broadly utilized in different industries such as pharmaceutical [1], hydraulic fluids [2], polymerization [3], paints [4], and food industries [5, 6]. Furthermore, emulsification technology has been extensively applied in the oilfields [7–10]. Usually, the emulsion contains two or more partially or completely immiscible liquids [11], where the dispersed phase exists as droplets suspended in the continuous phase. The interface between hydrophobic and hydrophilic molecules is intrinsically not stable [12]. When two immiscible liquids are stirred, the emulsion is formed [13, 14]. Emulsions are stabilized when a surfactant is added to a two-phase system due to the slowdown of emulsion breaking such as coalescences [15]. The interfacial tension is decreased with the adsorption of more surfactant at the interface, and consequently droplet coalescence is delayed [15, 16]. Stability of the emulsion is determined by different factors such as the nature of the interfacial film, continuous phase viscosity, oil-water-ratio, mixing time, and temperature [17].

2. Emulsification in the Oilfields

The emulsification technique is well documented in oil and gas production literature. For example, it has been employed in drilling fluid formulations [18, 19] and well stimulation

treatments [9, 20]. Also, it is used in well productivity enhancement via asphaltene deposition removal [21] drag reduction in multiphase flow [10] and for the control of excessive water production [8, 22]. Emulsification technique was introduced in the oil industry through the use of emulsified acids in 1933. Emulsified acids were invented to address corrosion problems rather than improving the stimulation job [23]. Thus, many researchers comprehensively studied this technique for further understanding of advantages and disadvantages of emulsified acids [20, 24–26]. Moreover, for emulsified acids, there are many reports on the effect of droplet size, water phase volume fraction, and the concentration of the emulsifier on their stability and rheology (see Al-Mutairi et al. [20] and references within). In addition to the well stimulation applications, a new application of emulsification technique in the oilfield is proposed recently as a method for water control with bullhead injection. In this case, the emulsion acts as a relative permeability modifier (RPM). The existence of RPM fluids is well known [27–30]. In a patent, Stavland and Nilsson suggested an injection of the gelant (crosslinked polymer) as an emulsion for RPM field application [22]. In work by Stavland et al. [8], an aqueous polymer gelant is emulsified into an oil and then injected as one component. Eventually, the solution separates into an oil phase and water phase upon reaching the reservoir. Afterward, the water phase gels up in a water-wet pathway of a pore space to reduce permeability to formation brine, and the oil phase remains mobile to secure a path for hydrocarbons to flow [8, 22]. The control of the gel fraction that occupies the porous media leads to the control of RPM, that is, the reduction in relative permeability of the hydrocarbons and formation brine; this is controlled by the water fraction in the emulsion [8]. In a recent publication, our group studied the gelation kinetics of emulsified PAM/PEI system using thermal analysis technique [31].

Undoubtedly, the type of emulsion is critical for those applications. Therefore, the emulsifier, which will be employed to accomplish the emulsification, must be cautiously selected to meet the requirements of those settings, so a fair rate of success could be seized. Nowadays, the biggest difficulty with surfactants, at least from the standpoint of those who have to choose them, is the staggering numbers that are available. Each manufacturer tries to provide one or more of his products that are suitable for every need, which makes the selection process difficult. The large numbers of surfactants available, coupled with the fact that application problems are becoming increasingly difficult, is making the need for a suitable process for the selection of surfactants more and more critical. Selection of surfactants is important for many applications in the oil field such as EOR, stimulation, and water shut-off. Our group has recently conducted a detailed surfactant screening study for chemical EOR purposes [32].

Forming stable emulsion is not straightforward routine. To emulsify two immiscible fluids, a particular emulsifier is necessary to form a specific type of emulsion. Consequently, selecting surfactant (emulsifier) to do the job is a critical subject, and it is certainly a very expensive exercise in terms of both cost and time. There is no systemic procedure in

the oil industry for selecting a suitable emulsifying agent for a specific application. The industry mainly relies on the experience and service providers' recommendations. Too often, a series of time-consuming laboratory measurements, such as phase behaviour and interfacial/surface tension, are performed at reservoir condition to select surfactant for an application. Commonly, the selection of an emulsifier is based on (a) the surfactant solubility, (b) controllable separation time (thermal stability), and (c) acceptable environmental consideration for a particular region [8]. This technique is founded on Bancroft's rule, which is an empirical rule grounded on the surfactant solubility [33, 34]; more details are given later. Interestingly, a more robust method such as hydrophobic-lipophilic balance (HLB), which is based on the surfactant chemical structure [35–37], is rarely used in the oilfields at least from surfactant selection point of view. Hence, the objective herein is to relate the surfactant structure to its performance in an attempt to ease the process of selecting a surfactant for emulsified W/O emulsions for applications in high-temperature high-salinity (HTHS) conditions. The performance of the different commercial emulsifiers is evaluated and correlated to their HLB. The usage of both Bancroft's rule and HLB as a selection criterion is investigated. Furthermore, the effects of surfactant chemistry and concentration, temperature, oleic phase composition, and water phase salinity on the emulsion stability are studied.

3. Experimental

In this section, details about materials, equipment, experimental procedures, emulsion preparation, and characterization are detailed.

3.1. Materials. The surfactants used in this study were supplied by Sigma-Aldrich®, AkzoNobel, and Capstone® as presented in Table 1. Sea water and brine formation are used as water phase. Water analysis is given in Table 2. Diesel from local gas stations and refinery waste oil are used for the oleic phase. The Diesel is representative of the oil utilized in the field by the industry for preparing emulsified acids. All salts used in this study are ACS grade.

3.2. Equipment. The emulsions were prepared in a high-performance dispersing instrument (Ultra-Turrax T 50 Basic) provided by VWR International. The homogenizer is equipped with a variable-speed drive with six different speeds in the range 500–10,000 rpm. All emulsions were prepared at room temperature at 2000 rpm mixing speed for 5 minutes. The mixing speed and time were selected following a separate investigation. A conductivity meter is provided by HACH (CDC401 model); the device can handle total dissolved solids in the range 0 to $50 \, mg \cdot L^{-1}$ as NaCl. The meter is used to classify the emulsion type whether it is W/O or O/W. GL-18 high-temperature disposable test tubes and soda-lime-glass ($18 \times 180 \, mm$) of approximate volume of 32 ml (operational temperature of 180°C) were used. The high-temperature tubes were sealed with a screw cap and a rubber seal case to prevent evaporation. The fact that no evaporation is taking place was assured by comparing the initial and final volumes of the

TABLE 1: Description of the surfactants used in this study.

Surfactant	Type	Mw (g·mol^{-1})	HLB	Weight ratio (%)
Glycolic Acid Ethoxylate-1 Ether ($C_{14}H_{24}O_6$)	AIS*	288.34	12	61.1
Glycolic Acid Ethoxylate-2 Ether ($CH_3(CH_2)_{11-13}(OCH_2\ CH_2)_nOCH_2CO_2H$ ($n = 6$))	AIS*	739.20	7.14	35.7
Glycolic Acid Ethoxylate-3 Ether ($C_{55}H_{112}O_8$)	AIS*	901.47	2	9.76
Ethylenediamine-Tetrol ($C_3H_6C_2H_8N_2C_2H_4O)_x$	N/A	3,600	7	35.7
Fluorosurfactant-1	N/A	N/A	N/A	N/A
Fluorosurfactant-2	N/A	N/A	N/A	N/A
Polyethylene Glycol-1 Ether ($C_{58}H_{109}KO_{24}S$)	AIS*	1260	14	69.8
Polyethylene Glycol-2 Ether ($C_{18}H_{35}(OCH_2CH_2)_nOH$, $n \sim 2$)	NIS**	356.58	4	20
Polyethylene Glycol-3 Ether ($C_{16}H_{33}(OCH_2CH_2)_nOH$, $n \sim 2$)	NIS**	330	5	25
Polyethylene Glycol-4 ($C_4H_{10}O_2$)	NIS**	90,12	N/A	N/A
Amine Acetates-1	IS***	N/A	6.8	34
Amine Acetates-2	IS***	200	10.5	52.5
Amine Acetates-3	IS***	263	6.8	34
Ethoxylated Amides-1 (Ethomid-1)	N/A	N/A	4.85	24.3
Ethoxylated Amides-2 (Ethomid-2)	N/A	340–360	5.1	25.5

*AIS = anionic surfactant; **NIS = nonionic surfactant; ***IS = ionic surfactant; Mw = molecular weight; N/A = data not available.

TABLE 2: Chemical analysis of water used in the study.

Ion, ppm	Water type concentration, mg·L^{-1}	
	Brine formation	Sea water
Na^+	59,300	18,300
Ca^{2+}	23,400	650
Mg^{2+}	1,510	2,083
SO_4^-	110	4,290
Cl^-	137,000	32,200
HCO_3^-	353	120
Total dissolved solids*	221,673	57,642

*Determined by addition.

FIGURE 1: Schematic diagram of surfactant (emulsifier) chemical structure.

sample at the end of the experiment. HAAKE FISONS hot oil bath Model N3 is used to study the emulsion separation (separated volume fraction of the phases versus time).

3.3. Experimental Setup and Procedure

3.3.1. Emulsion Preparation. Several emulsions were prepared systemically to ensure the reproducibility of the results. All emulsions were prepared at room temperature at a fixed mixing speed for 5 minutes. Enough time was given for the emulsifier to mix thoroughly in the external phase. Then, a desired volume of the dispersed phase was slowly added to the continuous (external) phase. It is important to control the addition of the dispersed phase droplets throughout the mixing. It is reported that both the addition rate of the dispersed phase and mixing intensity govern the type of emulsion; a coarse emulsion will be the result of adding the dispersed phase to the continuous phase in one step without intensive mixing. However, a fine emulsion can be produced by adding the dispersed phase in atomized form coupled with intensive mixing [20, 38].

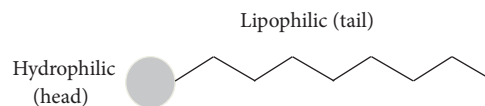*3.3.2. Emulsion Characterization.* Two methods are used for the surfactant selection, namely, Bancroft's rule and HLB

value of a surfactant. Different commercial surfactants with a broad range of properties are selected as shown in Table 1. Conductivity and dilution tests are used simultaneously to identify the type of emulsions.

Bancroft's Rule. The nature of the emulsifying agent controls the emulsion type rather than the oil-water-ratio or the method of emulsion preparation [16, 17, 34]. Bancroft developed one of the first empirical rules to describe the nature of emulsion that could be stabilized by a given emulsifier [33]. The continuous phase is the phase in which an emulsifier is more soluble as stated by Bancroft's rule. Hence, O/W emulsions are formed by the addition of a water-soluble emulsifier. On the other hand, W/O emulsions are formed when an oil-soluble emulsifier is used [33, 34].

Hydrophilic-Lipophilic Balance (HLB) Determination. HLB measures the degree to which a surfactant is hydrophilic or lipophilic. HLB offers an efficient way of picking the suitable surfactant for a specific application as suggested notably by Griffin [35, 36]. A scale of 0 to 20 is proposed. HLB value of 0 represents a completely lipophilic molecule, and a value of 20 accounts for a strongly hydrophilic molecule. The HLB values for W/O emulsifiers are in the range 3.5–6, while those of O/W are in the range 8–18. Wetting agents have HLB values in the range 7–9.

Surfactant HLB value is determined by calculating the contributions of different constituents of the molecular structure (see Figure 1) as described by Griffin [35, 36]. Another method was suggested in 1957 by Davies [37]. It is
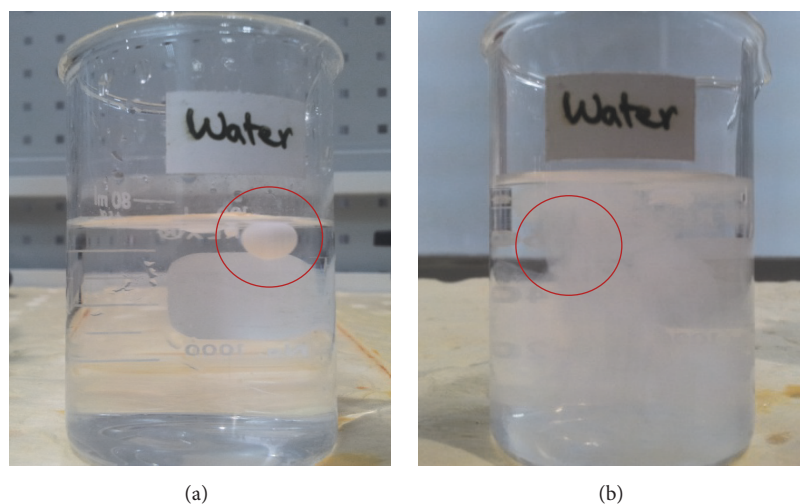
(a)

(b)

FIGURE 2: Dilution test, (a) Droplet sinking, (W/O) emulsion, and (b) Droplet dispersion, (O/W) emulsion.

based on the chemical groups of the molecule. This method considers the effect of strong and weak hydrophilic groups. However, it requires more information such as numbers of hydrophilic and lipophilic groups in the molecule and values of hydrophilic and lipophilic groups. Consequently, the value of HLB for a particular surfactant has been either provided by the supplier or calculated employing Griffin's method. Also, the weight ratio of the hydrophilic part to the hydrophobic (HLWR) is calculated as shown in Table 1.

Conductivity Test. The type of emulsion has been determined by measuring its conductivity; this is a quantitative method based on the electrical proprieties of the emulsion water phase, which is highly conductive, whereas the oleic phase is nonconductive. It should be pointed out that the external phase dominates the emulsion's conductivity [20, 39, 40]. Thus, O/W emulsion is conductive (i.e., $>0.00 \, \mu S \cdot cm^{-1}$), whereas W/O emulsion is nonconductive (i.e., $\sim 0.00 \, \mu S \cdot cm^{-1}$). Conductivity measurements for all the fluids used in this study were carried out to set a baseline for the conductivity test. The recorded conductance values at 28°C are as follows: standard NaCl buffer solution $950 \, \mu S \cdot cm^{-1}$, deionized water $6.71 \, \mu S \cdot cm^{-1}$, sea water $47.2 \times 10^3 \, \mu S \cdot cm^{-1}$, and field water $1078 \, \mu S \cdot cm^{-1}$.

Dilution Test. This test identifies the emulsion's external phase by dilution, in which water can be used to dilute O/W emulsion, whereas oil can be used to dilute W/O emulsion. In this test, a droplet of the formed emulsion is dispersed in water and Diesel to see if it spreads or sinks; if the placed droplet disperses, then the external phase is the same as the fluid used for the test. Conversely, if the droplet sinks in the medium, the external phase will be different from the fluid used for the test as shown in Figure 2 [39–41].

4. Surfactant Screening

In this section, two methods for the surfactant screening will be examined: (i) Bancroft's rule empirical based and

(ii) HLB founded on the physiochemical properties of the surfactant.

4.1. Results and Discussion. To investigate the validity of Bancroft's rule, emulsions were prepared using a number of surfactants with different solubility. Each surfactant was dissolved in sea water and Diesel at a time, wherein 2 vol% surfactant concentration was added to an external phase (28 vol%) and then mixed for a one minute at 500 rpm at room temperature. Afterward, the mixing speed was raised to 4000 rpm, and a dispersed phase was added to the solution of a surfactant and an external phase at a specific rate. Then the emulsions were characterized to identify the external and dispersed phases. The conductivity for each emulsion was measured periodically in parallel with the drop test in a span of one hour at room temperature (see Table 3), to make sure there was no inversion taking place.

When surfactants in Table 3 dissolved in sea water and Diesel separately to form the emulsion's continuous phase, various trends were noted. For instance, Fluorosurfactant-1 and Glycolic Acid Ethoxylate-2 Ether were dissolved in the Diesel (oleic phase) to form W/O emulsion, as Bancroft's concept explicitly theorizes. However, the conductivity and dilution tests showed that produced emulsions were O/W as shown in Table 3, which disagrees with Bancroft's rule. Conversely, Polyethylene Glycol-1 Ether did not dissolve in Diesel and formed O/W emulsion when dissolved in sea water, which is in complete agreement with Bancroft's rule. Furthermore, Ethylenediamine-Tetrol and Glycolic Acid Ethoxylate-3 Ether dissolved in Diesel and sea water equally, herein regardless in which phase the surfactants dissolved the resultant emulsions were O/W as in Table 3. Therefore, Bancroft's method for surfactant screening is found inconclusive. Consequently, another approach is proposed for use as a selection tool, which is based on the HLB value for the surfactant.

HLB values were calculated for all surfactants and were used to understand the surfactant behaviour as given in Table 1. The HLB values of most of the surfactants in

TABLE 3: Surfactant characterization based on conductivity and dilution tests.

Surfactant	Conductivity test (μS·cm^{-1})	Dilution test	Observations
*Fluorosurfactant-1	4.5	O/W	Disagrees with Bancroft's rule
*Fluorosurfactant-2	N/A	N/A	The surfactant is not oil-soluble
*Glycolic Acid Ethoxylate-1 Ether	N/A	N/A	The surfactant is not oil-soluble
**Glycolic Acid Ethoxylate-1 Ether	N/A	N/A	No stable emulsion formed
*Glycolic Acid Ethoxylate-2 Ether	1034	O/W	Disagrees with Bancroft's rule
*Glycolic Acid Ethoxylate-3 Ether	20.5×10^3	O/W	Disagrees with Bancroft's rule
**Glycolic Acid Ethoxylate-3 Ether	23.5×10^3	O/W	Agrees with Bancroft's rule
*Ethylenediamine-Tetrol	1072	O/W	Disagrees with Bancroft's rule
**Ethylenediamine-Tetrol	78.2×10^3	N/A	Agrees with Bancroft's rule
*Polyethylene Glycol-1 Ether	N/A	N/A	The surfactant is not oil-soluble
**Polyethylene Glycol-1 Ether	1078	N/A	Agrees with Bancroft's rule

*Surfactant dissolved in Diesel (oleic phase). **Surfactant dissolved in sea water (water phase); $1\,\mu$S·cm$^{-1} = 1E-3$ mS·cm$^{-1} = 1E-6$ mho·cm$^{-1} = 0.640$ ppm (TDS); N/A = data not available.

TABLE 4: New selected surfactant based on the HLB.

Surfactant	HLB	Application based on the HLB	Conductivity test (μS·cm^{-1})	Dilution test
Polyethylene Glycol-2 Ether	4	W/O emulsifier	0.02	W/O
Amine Acetates-2	10.5	O/W emulsifier	3.50×10^3	N/A*
Amine Acetates-3	6.8	W/O emulsifier	0.01	N/A*
Ethoxylated Amides-1	4.85	W/O emulsifier	0.02	W/O
Ethoxylated Amides-2	5.1	W/O emulsifier	0.02	W/O

*N/A = data not available.

Table 3 are in the recommended range for O/W, not W/O emulsion application, which explains why O/W emulsions were formed. Furthermore, HLB and HLWR can explain surfactants solubility as well. Surfactants with HLB values higher than 10 (or HLWR > 50%) are hydrophilic (water-soluble), while surfactants with HLB values less than 10 are lipophilic (oil-soluble). For example, Polyethylene Glycol-1 Ether HLB of 14 and HLWR of 69.8% signifies its affinity to be water-soluble and oil insoluble. Likewise, Glycolic Acid Ethoxylate-1 Ether with HLB of 12 and HLWR of 61.1% was observed earlier (see Table 3). For a surfactant, soluble in both oil and water, this behaviour can be explained by intermediate affinity as shown by HLB and HLWR, Ethylenediamine-Tetrol (HLB of 7 and HLWR of 35.7%). For Glycolic Acid Ethoxylate-3, HLB of 2 and HLWR of 9.76%, those values indicate a dominant lipophilic affinity. However, its solubility in water could be a product of its hydrophilic part strong ionic interaction (anionic surfactant) with sea water molecules.

To further investigate HLB approach, surfactants with HLB values inside the recommended range for W/O and O/W emulsion application were selected as shown in Table 4. The results of the conductivity and dilution tests (at ambient conditions) confirmed that the formed emulsions are in agreement with the predictions based on the HLB values. Thus, this approach is considered to be more reliable for surfactant selection.

4.2. Emulsion Thermal Stability. To investigate the thermal stability of the formed emulsion, a sealed case of high-temperature test tubes was used, by monitoring the separated volume fraction of the oleic and water phases versus time at constant temperature. Such a test can indicate emulsion quality.

In this paper, the possibility of employing commercial surfactants as an alternative emulsifier in forming stable W/O emulsion for HTHS applications in the oilfields is investigated. From an operational point of view, the thermal stability of the emulsified system plays a major role in the success of the placement job. For instance, in emulsified acid, no separation inside well during the injection operation is essential to preventing well tubular's corrosion, such as high bottom-hole static temperature reservoirs (e.g., Thunder Horse 138°C (280°F) and Ursa 121°C (250°F) in Gulf Mexico). The time required for treatment placement is reported around one hour. Thus, the emulsified system must be stable for the time period [9]; any separation will lead to well's metallic-parts corrosion.

Similarly, designed separation time is necessary for the water shut-off applications. For emulsified polymer gel, it is desired to have a controllable separation and gelation time [8, 22, 31]. The time needed for polymer gel placement at high-temperature (≥ 130°C) high-salinity with high Mg^{2+} and Ca^{2+} contents was reported to be about 55 minutes [42, 43] and around one and a half hours for the emulsified gel at similar conditions of high-temperature of 123°C [8]. Consequently, the emulsified gel system should be stable for at least one hour. Deemulsification and gelation should start afterwards. It is preferred that the gelation starts after a complete separation; if not, a weak gel will develop. In case of partial or complete separation during treatment placement, the emulsified gelant

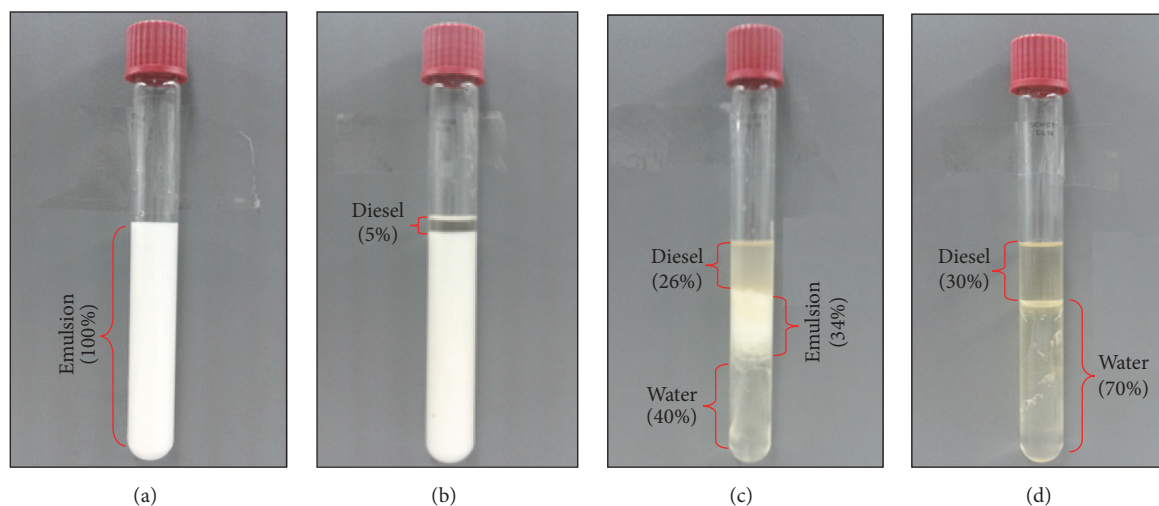|			
(a)	(b)	(c)	(d)

FIGURE 3: Water-in-oil emulsion separation, (a) no separation (100% emulsion), (b) separated volume fraction, zero water phase, and 0.05 oleic phase, (c) separated volume fraction, 0.4 water phase, and 0.26 oleic phase, and (d) complete separation (100%); separated volume fraction is 1 (0.7 water phase, 0.3 oleic phase).

will be exposed to high-temperature which will result in premature gelation inside the well tubular, which is highly undesirable [31]. For field applications, the high-temperature of the near wellbore area can be lowered using a preflush. Literature [41, 44] has shown that this method can reduce the temperature substantially; for example, the injection of 5,000 gallons of water can cool down the near well bore area from 150°C (302°F) to 116°C (240.8°F). Therefore, the thermal stability of all formed emulsions was investigated at 120°C.

In these experiments, no polymer or acid was used in the water phase. This is mainly because the current focus is to develop a surfactant selection criterion, for high-temperature high-salinity conditions, which can be utilized later for emulsified systems. At this phase of the research, the impact of several factors such as surfactant chemistry, temperature, water phase salinity and water-oil-ratio is quite significant. Hence, the focus was on those parameters. It is reported in the literature that the water phase significantly affects the thermal stability and the type of the emulsion. Addition of acid and corrosion inhibitors resulted in a less stable emulsion and, in some cases, lead to emulsion inversion from O/W to W/O [20]. However, addition of the gelant to the water phase slightly affected the stability [8, 31].

Moreover, an increase of salinity of the water phase from 5 to 20,000 ppm led to increase in the stability; increasing the salinity >20,000 ppm has significantly reduced the stability and resulted in emulsion inversion, and similar behaviour was noticed with water-oil ratio [39]. Since the emphasis of the manuscript is on the stability of the emulsion at salinity typical to those found in the oilfields, brine formation and sea water are used. Some of the surfactants screened in this study are successfully used to form stable emulsified PAM/PEI in a recent work by our group [31].

The emulsion stability is presented by using phase changes diagram (volume fraction versus time). This graph illustrates the percentage of the phases at a given time.

Initially, the emulsion is within the sample "homogeneous phase" before it starts to break. The single-phase water and oleic phases at the outset are 0% as the separation is yet to start as shown in Figure 3(a). However, macroemulsions are characteristically thermodynamically unstable; exposing the emulsion to a temperature over time leads to the separation of the emulsion. Then, the percentage of the water and the oleic phases increases as shown in Figures 3(b)–3(d). The volume proportion of the separated oleic and water phases keeps changing until it reaches a plateau or the emulsion is entirely separated. In all emulsions studied herein, the total volume was 30 ml, 70% of which is the water phase, and the rest 30% is the oleic phase (the mixture of emulsifier and the Diesel). Diesel percentage is in the range of 24–29.5%, while the emulsifier percentage is in the range 0.5%–6%. All emulsions were prepared at room temperature at 2000 rpm mixing speed for 5 minutes. Then, the thermal stability was examined in bulk at 120°C (248°F) for 12 hours using the oil heating bath.

4.3. Effect of Surfactant Type and Concentration. To study the influence of emulsifier type and concentration on the thermal stability, four surfactants were selected based on HLB criteria for W/O emulsions. Ethoxylated Amides-2, Amine Acetates-3, Polyethylene Glycol-2 Ether, and Polyethylene Glycol-3 Ether were used to emulsify the water phase, herein brine formation, into Diesel. To test the stability of the emulsion prepared using the surfactants mentioned above, each time three emulsions were prepared using one of the surfactants with different concentrations. The increase in the stability was noticed with the increase in the surfactant concentration. For instance, ~70% separation was observed at 8 and 120 minutes when Ethoxylated Amides-2 increased from 1 to 3 vol% as shown Figure 4, which signifies 93% (or a factor of 15) increase in the separation time. In the case where Amine Acetates-3 used 13% separation is noted at 2 and 330 minutes
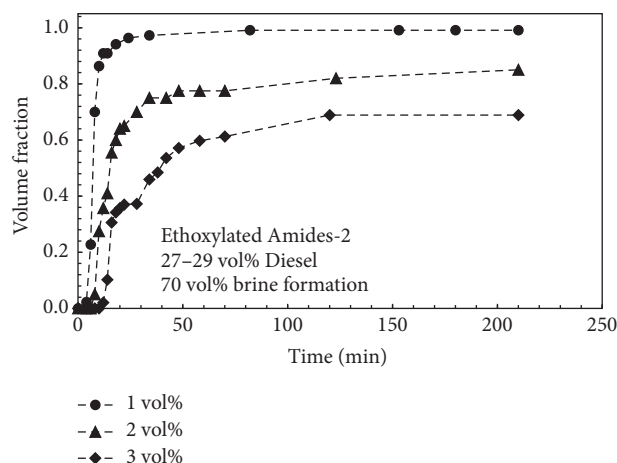
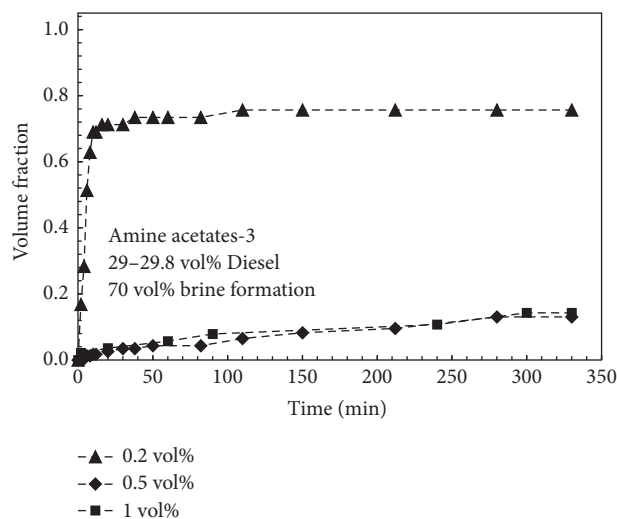FIGURE 4: Ethoxylated Amides-2 phase behaviour at 120°C (248°F).

FIGURE 6: Polyethylene Glycol-2 Ether phase behaviour at 120°C (248°F).

FIGURE 5: Amine Acetates-3 phase behaviour at 120°C (248°F).
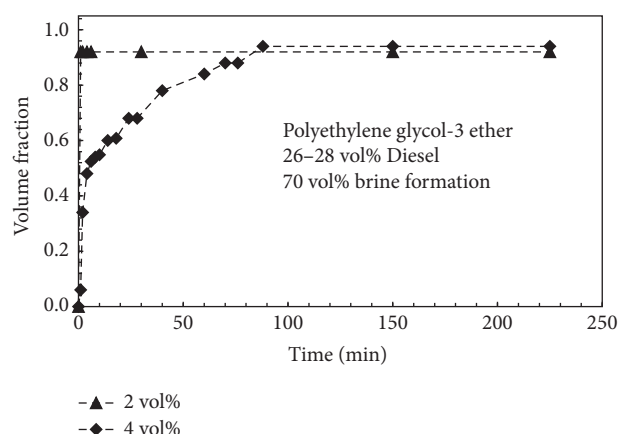
FIGURE 7: Polyethylene Glycol-3 Ether phase behaviour at 120°C (248°F).

when the concentration increased from 0.2 to 0.5 vol% (Figure 5). This indicates 99% increase in the separation time, while further increase in surfactant concentration (up to 1 vol%) did not result in a significant change. When Polyethylene Glycol-2 Ether was utilized, complete separation (100%) took place after 12, 22, and 109 minutes when used at 2, 4, and 6 vol%, respectively (see Figure 6); this represents 89% increase in the separation time (or a factor of 9.1). Also, ~90% separation occurred at 1 and 88 minutes (99% increase), when Polyethylene Glycol-3 Ether concentration increased from 2 to 4 vol% (see Figure 7). When comparing the performance of all the surfactants, three distinct trends were observed. Firstly, with a surfactant with a low concentration and high stability, the use of 0.5 vol% Amine Acetates-3 resulted in 13% separation at 330 minutes. Secondly, surfactants with a high concentration and a low stability, such as Polyethylene Glycol-2 Ether and Glycol-3 Ether, showed complete separation when both were used at a high concentration (~6 vol%). Finally, a surfactant with a moderate concentration and good stability, Ethoxylated Amides-2, showed a 69% separation
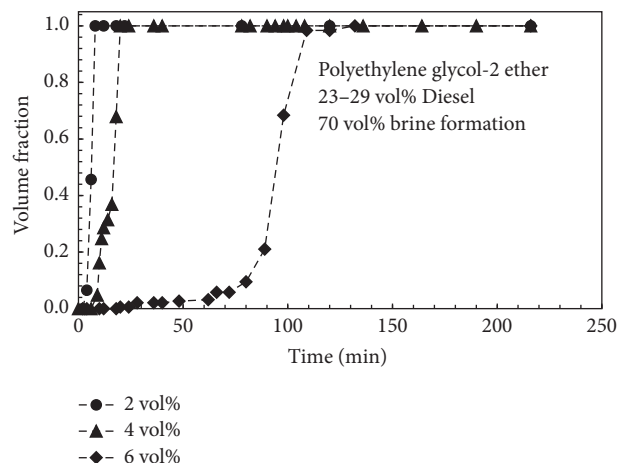
after 210 minutes when 3 vol% was used. Generally, with more surfactant adsorbed at the interface, more stability is achieved. Surfactant molecules reduce the interfacial tension and consequently retard droplets coalescence; this agrees with previous reports in the literature [16, 17, 41]. Moreover, surfactants with Amine functional group showed higher stability when compared to the Glycol Ether family group.

4.4. Effect of the Oleic Phase. To investigate the effect of the oleic phase on the emulsion stability, two emulsion samples were prepared, one with Diesel and the other with refinery waste oil. The composition of the waste oil and detailed analysis is given elsewhere (see Figure 5.1 of Sidaoui [45]). The phase separated volume (in Figures 8(a)–8(c)) is calculated as a percentage of the phase (i.e., emulsion, water, and oleic) total volume. For both samples, the water phase (formation brine) separation is almost identical as shown in Figure 8(a). However, the oleic phase separation is different, when waste oil is used instead of Diesel to prepare the emulsion. After 210 minutes in the oil bath, the separated oleic phase decreased from 100% to 9% (91% decrease or a
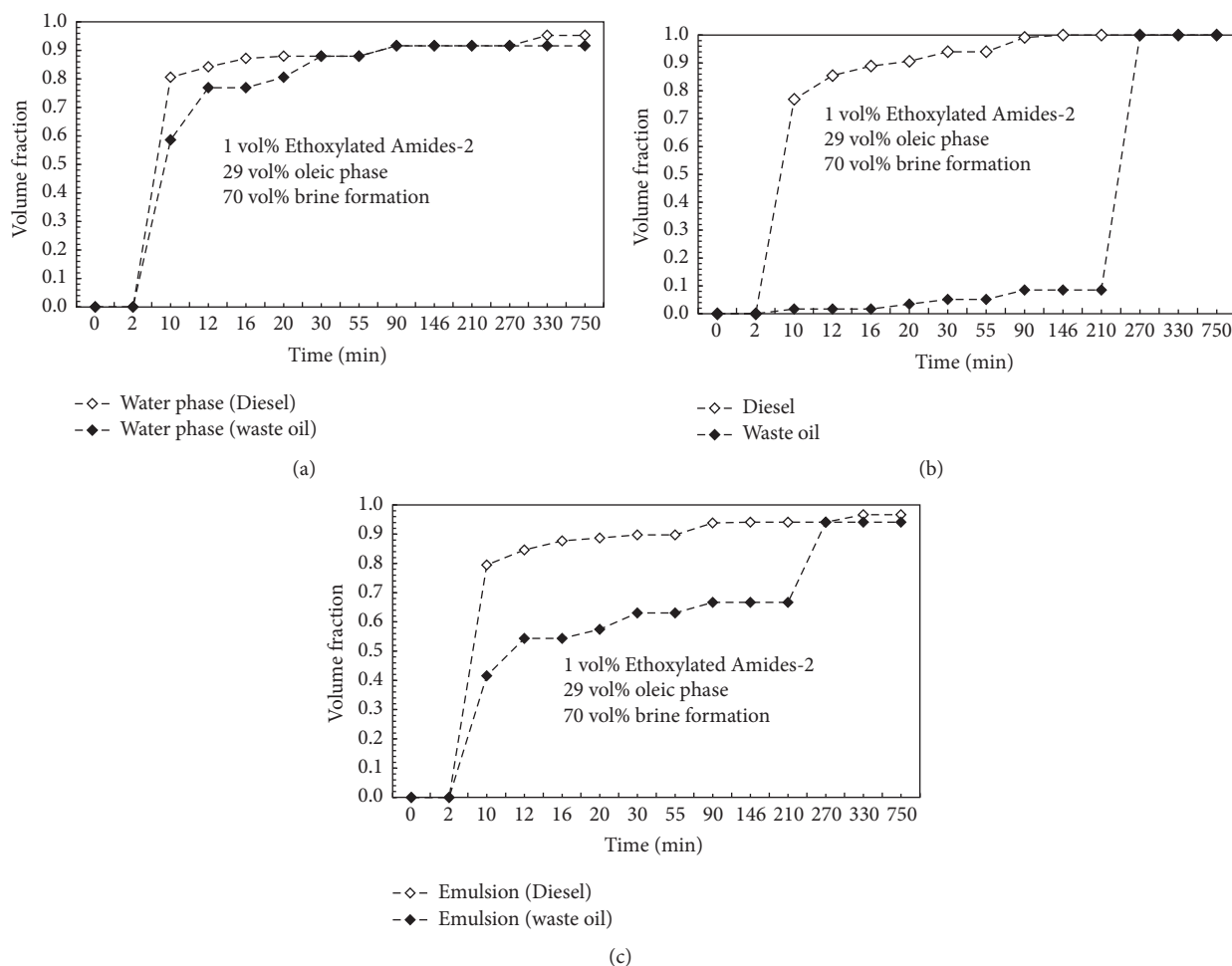
Figure 8: Emulsion phase behaviour at 120°C (248°F), (a) water phase, (b) oleic phase, and (c) emulsion phase.

factor of 11) as shown in Figure 8(b). Increase in the stability is noticed for the emulsion prepared with waste oil instead of Diesel with the separated volume decreased from 94% to 67% (28.7% decrease or a factor of 1.4) (see Figure 8(c)). The use of waste oil resulted in more stable emulsion (less separation). This may be because waste oil has resins or asphaltenes, which are natural emulsifiers. Commonly, Diesel and kerosene are used in the oilfields because of availability [8, 21, 40]. This work highlights the possibility of using waste oil as an alternative oleic phase for emulsification purposes, which will result in a reduction of associated cost of using mineral oils.

4.5. Reflections on HLB and Emulsion Stability. By definition, the HLB is a measure of the degree to which a surfactant is hydrophilic or lipophilic. Hence, authors reason that an ideal emulsifier has the hydrophilic part equivalent (equal) to lipophilic portion. This may allow for equal (balanced) distribution of the emulsifier in the water and the oleic phases, which may lead to a more stable emulsion. This hypothesis will be examined by correlating the emulsion stability to HLB and HLWR. It can be seen from Figure 9 that more stability of W/O emulsions is achieved at higher HLB and HLWR. For

instance, when an emulsifier with HLB of 6.8 and HLWR of 34% (Amine Acetate-3) was used at a very low concentration of 0.5 vol%, the emulsion took 310 minutes to break down completely. While in the case of the emulsifier with HLB of 4 and HLWR which equals 20%, the separation time was 20 minutes, although a higher concentration (6 vol%) was used. Also, in Figure 9, it has been noticed that the Polyethylene Glycol-3 Ether with HLB of 5 and HLWR of 25% formed more stable emulsion compared to Polyethylene Glycol-2 Ether with HLB of 4. By comparing the physiochemical properties of the two emulsifiers (see Table 1), the only difference is the H/C ratio which is higher in the case of Polyethylene Glycol-3 Ether (~2.1 for Glycol-3 Ether versus 2.0 for Glycol-2 Ether); this indicates the presence of more unsaturation in the Glycol-2 Ether chain. Here we like to postulate that this behaviour is likely related to the C/H in the surfactant. Higher C/H indicates the presence of more unsaturation, which will influence the polarity and the surfactant may favour one phase (i.e., water or oleic) over the other. Keeping in mind that the water phase contains ions, the oleic phase may contain heavy hydrocarbon/acidic components. Most likely, the reduced stability is due to the unbalanced distribution of the emulsifier molecules between the two phases, because of
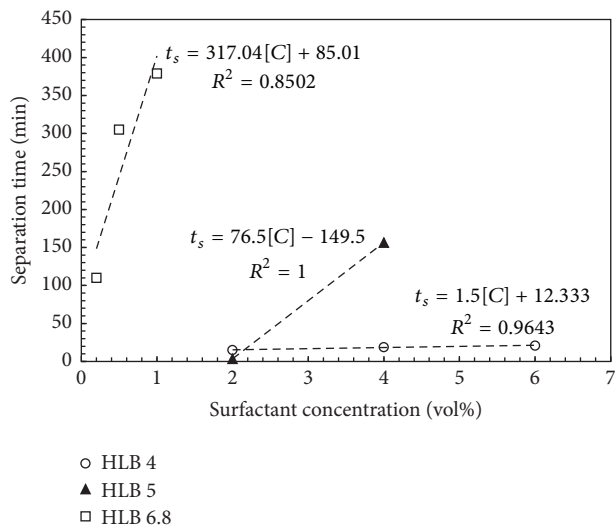
FIGURE 9: Separation time as function of surfactant concentration for different HLB (120°C).

FIGURE 10: Separation time as a function of HLB at 120°C.

the change in polarity. Furthermore, Amine Acetate-3 shows higher stability in comparison with Glycol Ether family and at a lower concentration. The dependency of the separation time to surfactant concentration at constant HLB value is correlated in the form of a linear relationship as follows:

$$t_s = a \times [C] + b, \tag{1}$$

where t_s is the separation time, $[C]$ is the surfactant concentration, and a and b are constants. Herein, the intercept b is thought to reflect the effect of the HLB as can be seen from Figure 9; the magnitude of b changes as HLB value changes.

Although the constituting functional group for the Amine Acetate is distinct from the two Glycols (i.e., Glycol-2 Ether and Glycol-3 Ether), a trend between the HLB and the stability is evident; the separation time increases with increase in HLB value as shown in Figure 10. The dependence of the separation time on HLB is correlated in linear form:

$$t_s = a \times \text{HLB} - b, \tag{2}$$

where t_s is the separation time, HLB is the surfactant hydrophilic-lipophilic balance, and a and b are constants. When HLB increased from 4 to 6.8 at a constant concentration, the separation time increased from 19 to 379 minutes (95% increases).

5. Conclusions

Here are the main findings of this article:

(1) Hydrophilic-lipophilic balance is used as a criterion for surfactant selection and was found to work well for many surfactants of different structures. This approach is expected to reduce the time and resources needed for selection of emulsifiers.

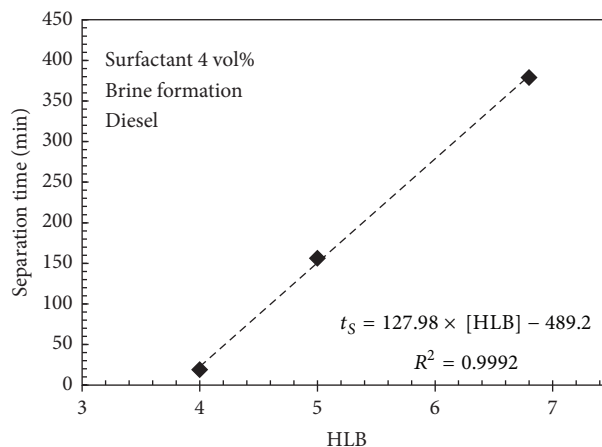(2) The solubility of the surfactant has been postulated to play a vital role in the type of the formed emulsion.

Bancroft's rule states "the phase in which an emulsifier is more soluble constitutes the continuous phase"; this argument was found to not necessarily hold true in all cases. For example, this work showed that when a set of surfactants were dissolved in Diesel W/O emulsions were expected to form as suggested by Bancroft's rule. However, the conductivity and dilution tests indicate that produced emulsions were O/W. To further investigate this observation, the same surfactants were dissolved in water; again, the type of the formed emulsion was O/W, which is not in agreement with Bancroft's rule.

(3) Surfactants with higher HLB values inside the recommended range for W/O emulsions resulted in more stable emulsions. A correlation is provided for the dependency of the emulsion thermal stability on HLB. For surfactants with similar structure and physical properties, this work shows that the surfactant with higher C/H ratio will likely form a less stable emulsion. The authors postulated that this result is probably due to the unbalanced distribution of surfactant because of the difference in polarity.

(4) Surfactants with Amine functional group were found to form more stable W/O emulsion when compared to the Glycol Ether family group.

(5) This work has identified a set of new cost effective emulsifiers, suitable for emulsified water phase (polymeric gels/acids) in the oleic phase. The formed W/O emulsion is very stable at HTHS conditions.

(6) The general trend is that the separation time increases with the increase in emulsifier concentration and vice versa. The increase in stability is likely due to the decrease in interfacial tension with the increase in emulsifier concentration and the consequent delay in the coalescence of the droplets.

(7) Oleic phase composition was found to affect the thermal stability. A higher emulsion stability is achieved when waste oil is used instead of Diesel to prepare the emulsion, and 91% decrease in the separated

oleic phase is recorded when waste oil used instead of Diesel. This behaviour is suggested to be due to the presence of resins or asphaltenes, which are natural emulsifiers, in the waste oil. Usage of waste oil will result in minimizing the associated cost of using mineral oils for the emulsification application in oilfields.

(8) Further investigation is required to understand the effect of the water phase in case of adding materials such as polymer gel and acid loading on the W/O emulsion system.

In general, this work was successful in developing stable emulsified water-in-oil systems that can tolerate high-temperature high-salinity environments using scientific approaches. Also, HLB approach was used for surfactant selection, and new insights into structure-emulsion stability relationships beyond the HLB approach were provided. The findings of this work would open more avenues for future research.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

References

[1] F. Nielloud and G. Marti-Mestres, *Pharmaceutical Emulsions and Suspensions*, Marcel Dekker Inc, New York, NY, USA, 1st edition, 2000.

[2] M. R. Greaves and J. C. Knoell, "A comparison of the performance of environmentally friendly anhydrous fire resistant hydraulic fluids," *Journal of ASTM International*, vol. 6, no. 10, 2009.

[3] C. D. Anderson and E. S. Daniels, *Emulsion Polymerization and Latex Applications*, Rapra Rev. Rep., Shawbury, England, 4th edition, 2003.

[4] S. A. Osemeahon, AJPAC 2011, 5, 204.

[5] D. J. McClements, "Biopolymers in Food Emulsions," *Modern Biopolymer Science*, pp. 129–166, 2009.

[6] S. Friberg, K. Larsson, and J. Sjoblom, *Food Emulsions*, Marcel Dekker, New York, NY, USA, 3rd edition, 2003.

[7] Q. A. Ahmed, A. Mohamed, R. Salah, and A. Bakhit, "Risk analysis and decision making in relative permeability modifier water shut-off treatment. society of petroleum engineers," *Society of Petroleum Engineers*, North Africa Technical Conference and Exhibition 2010, NATC 2010 - Energy Management in a Challenging Economy.

[8] A. Stavland, K. I. Andersen, B. Sandoey, T. Tjomsland, and A. A. Mebratu, "How to apply a blocking gel system for bullhead selective water shutoff: from laboratory to field," in *Proceedings of the SPE/DOE Symposium on Improved Oil Recovery*, Tulsa, Okla, USA.

[9] P. Nisha and W. Sushant, "A novel emulsified acid system for stimulation of very high-temperature carbonate reservoirs," in *Proceeding of the International Petroleum Technology Conference, IPTC*, Beijing, China, 2013.

[10] M. Al-Yaari, I. A. Hussein, and A. Al-Sarkhi, "Pressure drop reduction of stable water-in-oil emulsions using organoclays," *Applied Clay Science*, vol. 95, pp. 303–309, 2014.

[11] T. F. Tadros and B. Vincent, *Encyclopedia of Emulsion Technology*, Dekker, New York, NY, USA, 1983.

[12] J. Weiss, *Current Protocols in Food Analytical Chemistry*, John Wiley and Sons, 1st edition, 2002.

[13] M. M. Rieger, "Emulsions," in *The Theory and Practice of Industrial Pharmacy*, L. Lachman, H. A. Liberman, J. L. Kanig, and L. Fediger, Eds., pp. 502-503, Philadelphia, PA, USA, 3rd edition, 1986.

[14] S. Tamilvanan, S. R. Senthilkumar, R. Baskar, and T. R. Sekharan, "Manufacturing techniques and excipients used during the formulation of oil-in-water type nanosized emulsions for medical applications," *Journal of Excipients and Food Chemicals*, vol. 1, no. 1, 2010.

[15] P. Becher, *Encyclopedia of Emulsion Technology*, Dekker, New York, NY, USA, 0th edition, 1983.

[16] R. Navneet and I. P. Pandey, *Journal of Industrial Research Technology*, vol. 3, p. 12, 2013.

[17] H. C. Joshi, I. P. Pandey, A. Kumar, and N. Garg, APAC 2012,1, 2167.

[18] C. P. Lawhon, W. M. Evans, and J. P. Simpson, JPT 1967, 19, 943.

[19] A. D. Patel, *SPE Drilling and Completion*, vol. 14, p. 274, 1999.

[20] S. H. Al-Mutairi, H. A. Nasr-Ei-Din, A. D. Hill, and A. D. Al-Aamri, "Effect of droplet size on the reaction kinetics of emulsified acid with calcite," *SPE Journal*, vol. 14, no. 4, pp. 606–616, 2009.

[21] W. A. Fattah and H. A. Nasr-El-Din, *SPE Prod and Oper*, vol. 25, p. 151, 2010.

[22] Nor. 310581, (1999), invs.: A. Stavland, S. Nilsson.

[23] U.S. 1,922,154 (1933), invs.: De Groote.

[24] W. R. Dill, "Reaction times of hydrochloricacetic acid solutions on limestone," *Southwest Regional Meeting of the American Chemical Society, Society of Petroleum Engineers*, pp. 1–3, 1961, Oklahoma City.

[25] P. L. Crenshaw and F. F. Flippen, JPT 1968, 12, 1361.

[26] R. Navarrete, M. Miller, and J. Gordon, "Laboratory and Theoretical Studies for Acid Fracture Stimulation Optimization," in *Proceedings of the SPE Permian Basin Oil and Gas Recovery Conference*, Midland, Texas.

[27] F. N. Schneider and W. W. Owens, SPEJ 1982, 22, 79.

[28] D. D. Sparlin, JPT 1976, 28, 906.

[29] L. J. Kalfayan and J. C. Dawson, "Successful implementation of resurgent Relative Permeability Modifier (RPM) technology in well treatments requires realistic expectations," in *Proceedings of the SPE Annual Technical Conference and Exhibition, Society of Petroleum Engineers*, pp. 26–29, Houston, USA, September 2004.

[30] R. S. Seright, SPEJ 2009, 14, 5.

[31] A. I. A. Mohamed, I. A. Hussein, A. S. Sultan, K. S. M. El-Karsani, and G. A. Al-Muntasheri, "DSC investigation of the gelation kinetics of emulsified PAM/PEI system: Influence of surfactants and retarders," *Journal of Thermal Analysis and Calorimetry*, vol. 122, no. 3, pp. 1117–1123, 2015.

[32] M. S. Kamal, A. S. Sultan, and I. A. Hussein, "Screening of amphoteric and anionic surfactants for cEOR applications using a novel approach," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 476, pp. 17–23, 2015.

[33] E. Ruckenstein, "Microemulsions, macroemulsions, and the Bancroft rule," *Langmuir*, vol. 12, no. 26, pp. 6351–6353, 1996.

[34] D. J. McClements, "Lipid-Based Emulsions and Emulsifiers," in *Food Lipids: Chemistry, Nutrition, and Biotechnology*, C. A. Casimir and B. M. David, Eds., pp. 64–83, Taylor and Francis Group and CRC Press, New York, NY, USA, 3rd edition, 2008.

[35] W. C. Griffin, "Classification of surface-active agents by HLB," *Journal of the Society of Cosmetic Chemists*, vol. 1, p. 311, 1949.

[36] W. C. Griffin, "Calculation of HLB values of non-ionic surfactants," *Journal of the Society of Cosmetic Chemists*, vol. 5, p. 249, 1954.

[37] J. T. Davies, "A quantitative kinetic theory of emulsion type, I. Physical chemistry of the emulsifying agent: gas/liquid and liquid/liquid interface," in *Proceedings of the 2nd International Congress of Surface Activity*, pp. 426–438, Butterworths, London, UK, 1957.

[38] A. Sabhapondit, J. R. Vielma Guillen, and C. Prakash, "Laboratory optimization of an emulsified acid blend for stimulation of high-temperature carbonate reservoirs," in *Proceedings of the North Africa Technical Conference and Exhibition 2012: Managing Hydrocarbon Resources in a Changing Environment, NATC 2012*, pp. 352–358, egy, February 2012.

[39] M. Al-Yaari, I. A. Hussein, A. Al-Sarkhi, M. Abbad, and F. Chang, "Pressure drop reduction of stable emulsions: role of aqueous phase salinity," in *Proceedings of the SPE Saudi Arabia Section Technical Symposium and Exhibition 2013*, pp. 19–22, Al-Khobar, Saudi Arabia, May 2013.

[40] M. Al-Yaari, A. Al-Sarkhi, I. A. Hussein, F. Chang, and M. Abbad, "Flow characteristics of surfactant stabilized water-in-oil emulsions," *Chemical Engineering Research and Design*, vol. 92, no. 3, pp. 405–412, 2014.

[41] A. Mohamed, *Development of Emulsified gels for Water control in Oil and Gas Wells*, M.Sc., King Fhad University Petroleum Minerals, Al-Khobar, Saudi Arabia, 2014.

[42] P. Albonico, G. Burrafato, L. A. Di, and T. P. Lockhart, "Effective gelation-delaying additives for cr+3/polymer gels," in *Proceeding of the SPE International Symposium on Oilfield Chemistry, Society of Petroleum Engineers*, pp. 2–5, New Orleans, Louisiana, 1993.

[43] K. S. M. El-Karsani, G. A. Al-Muntasheri, A. S. Sultan, and I. A. Hussein, "Gelation of a water-shutoff gel at high pressure and high temperature: Rheological investigation," *SPE Journal*, vol. 20, no. 5, pp. 1103–1112, 2015.

[44] G. A. Al-Muntasheri, P. L. J. Zitha, and H. A. Nasr-Ei-Din, "A new organic gel system for water control: a computed tomography study," *SPE Journal*, vol. 15, no. 1, pp. 197–207, 2010.

[45] Z. Sidaoui, *A Novel Approach to Formulation of Emulsified Acid Using Waste Oil and Nano-Particles*, M.Sc., King Fhad University Petroleum Minerals, Al-Khobar, Saudi Arabia, 2016.

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