Surfactants as Integral Components of Chemical Demulsifiers

Abubakar A. Umar, Nobert I. Nnakenyi, Muhammad K. Abba, and I. H. Roy-Omeni

Abstract Emulsions are thermodynamically unstable systems, since they will separate to reduce the interfacial area between the oil phase and the water phase, as a function of time. As a metastable system, surfactant molecules, amphiphilic polymers or solid particles must be present before a stable emulsion system is formed. These components of an emulsion system are called emulsifiers. The relative balance of the hydrophilic and lipophilic properties of these emulsifiers is known to be the most important parameter dictating the emulsion type, whether an oil-in-water (o/w) or water-in-oil (w/o) emulsion. Irrespective of the emulsion type formed, demulsification is a costly exercise in the oil and gas industry. This chapter describes the fundamental role played by surface active agents (surfactants) as integral components of a chemical demulsifier.

Keywords Emulsions · Demulsification · Demulsifiers · Surfactants · Oil/water interface

1 Introduction

An exhaustive literature searches on emulsions during this study led to the understanding that there are certain universal rules that form the basic theory of emulsions formation and breaking. Firstly, crude oil emulsions are comprised essentially of immiscible liquids. Separation should be the normal susceptibility of these liquids in the presence of density difference between the immiscible liquids. Secondly, the rate of gravitational settling rate depends on the surface tension of the dispersed droplets. When these internal phase droplets are large, their surface tensions as a function of mass is smaller than when they are small. Therefore, any technique that would increase the sizes of the dispersed droplets (via coalescence mostly)

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will enhance water separation rate and subsequent demulsification. Thirdly, environmental influence on emulsion stability is also key. An emulsion that is stable in a given environment might separate instantly when a different environment is introduced to it. Lastly, a stable emulsion would form only in the presence of emulsifiers. Any technique that would alter, eliminate or neutralize the emulsifiers would lead to a successful separation of the water from oil.

2 The Emulsification Process—Surfactant Action

The formation of crude oil emulsion involves the commingling of crude oil and water (brine) when there is adequate mixing or agitation and in the presence of a surface-active agent (surfactant) that serves as an emulsifier.

How rigorous the two phases are being mixed as well as the amount or concentration of emulsifiers present is very critical in the formation of emulsions [1, 2]. There exist various mixing sources within reach during crude oil production. These sources provide what is called the amount of shear. These sources include; the flow of fluid through reservoir rock, fluid flow through tubing, bottom-hole perforations, flowlines, production headers (pipes connecting the wellhead to the manifold), chokes or orifices, several surface equipment as well as during the release of gas bubbles when there is change is fluid phase [3, 4]. Although a universal theory that has been hypothesized for all emulsions types and behaviors does not exist, several hypotheses have been suggested to explain variations in the processes of emulsions formation and stabilization [5]. Various researchers [6–15] have studied and identified several factors responsible for emulsions formation and stabilization, with variations in the significance of roles played by each factor.

The roles of surfactants in emulsion stabilization has been well established. Two major mechanisms have been identified, via which surfactants stabilize emulsions. These are: (a) by adsorption at the liquid–liquid interface, and (b) by altering the stability of solids at the interface.

2.1 Surfactants Adsorption at Liquid–Liquid Interface

The adsorption of surfactants at liquid interfaces can influence emulsion stability by lowering interfacial tension, increasing surface elasticity, increasing electric double layer repulsion (ionic surfactants), and possibly increasing surface viscosity [16]. Also, surfactant nature can control the arrangement of the phases in an emulsion, that is, which phase will form the dispersed versus continuous phase. As discussed earlier, several experimental predictive methods based on anticipated surfactant positioning at the interface exist [16–18]. These include the Bancroft's rule, the oriented wedge theory, the hydrophile–lipophile balance (HLB), and the volume balance value [17]. Among all the methods, the HLB has been the most widely used. The HLB

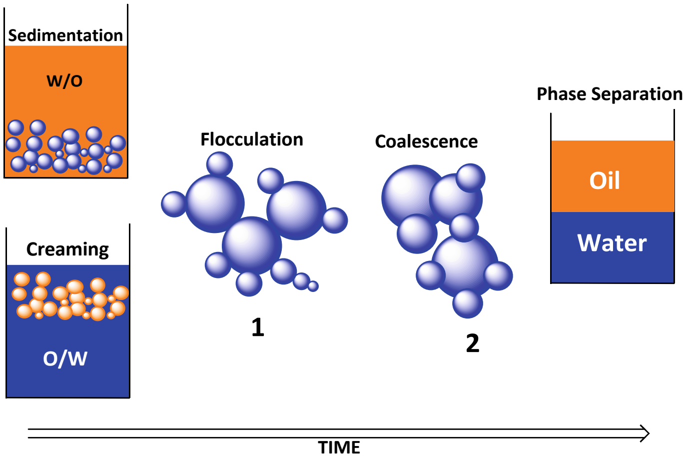


Fig. 1 Schematic representation of the various breakdown processes in emulsions. Modified from Alvarado et al. [22]

dimensionless scale ranges from 0 to 20 for non-ionic surfactants; a low HLB (<9) refers to a lipophilic surfactant (oil soluble) and a high HLB (>11) to a hydrophilic (water soluble) surfactant. Most ionic surfactants have HLB values greater than 20. Water-in-oil (w/o) surfactants show HLB values in the range 3–8 while oil-in-water (o/w) emulsifiers possess HLB values of about 8–18 [18–20]. Additionally, surfactant exchanges between the interface and the bulk can drastically lower interfacial visco-elasticities [21]. Figure 2 is a schematic surfactants types used to stabilize food emulsions (Fig. 1).

3 The Demulsification Process

Knowledge of the nature of emulsions and demulsification is important in resolving any emulsion [24, 25]. Nearly three-fourths of all crude oil produced must be treated. The percentage of crude needing treatment increases as fields become more mature and more water is produced. Demulsification most often is attained through the use of surfactants, heat and electric treaters. It is thought that over 75% of all oilfield emulsions are treated with chemicals usually containing alkylene oxide condensates. Although acids and bases are known to affect emulsion stability; they rarely are used in the oil field except in batch treatment when the stability of the emulsion is very severe [26, 27]. Separating produced water from crude oil is a problem that is as old as the oil and gas industry itself. In other words, this menace has existed since the advent of the oil industry. In the beginning of the Industry, the problem was managed by settling the free water from oil in open tanks or pits. The middle phase between clean water and clean oil, also known as "sludge," was disposed of normally by

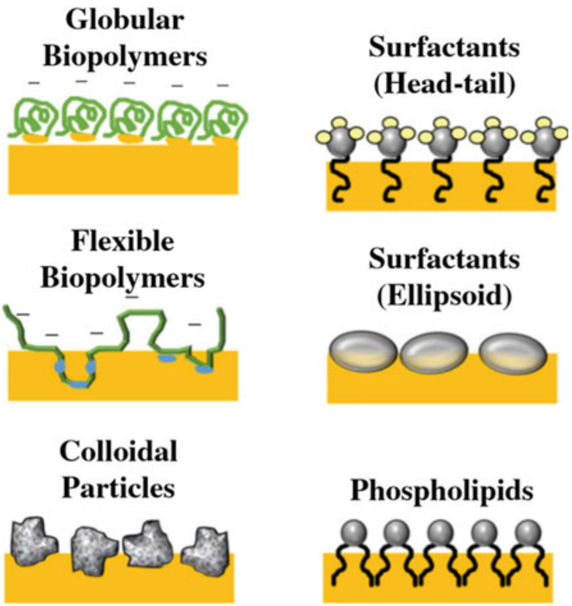


Fig. 2 Schematics of surfactants types used to stabilize food emulsions [23]

burning. It was not until the turn of the century that study and experience showed that, the “sludge” is an emulsion of crude oil and water and that large amounts of commercial oil can be recovered from this emulsion [28]. Several researchers have highlighted the necessity of demulsification for decades [29].

Kim [30] highlights the necessity of breaking emulsions in many practical applications such as the petroleum industry, coating, painting, and wastewater treatment in environmental technology. This is due to the occurrence of unwanted emulsions at many points within the process plant. These emulsions if not well treated can endanger the entire process or lead to added cost of operation.

Gafonava and Yarranton [31] in their work, pointed out the relevance of demulsification as the use of steam and caustic injection or combustion processes for in-situ recovery of heavy crude oils is complicated by the production of viscous emulsions of oil, water and clay. The demulsification of crude oil emulsions forms an integral part of crude oil production system. Even though demulsification of water-in-oil emulsions are conducted using either of four methods; chemical, mechanical, electrical and thermal, other methods such as pH adjustment, filtration, and membrane separation can also be used.

4 Demulsification Techniques

Although different types of techniques all aimed at; destroying the effects of the film surrounding the water droplets, bringing coalescence and providing an opportunity for undisturbed settling of water droplets through the oil- have been proposed and used at several applications [32], chemical demulsification is the most widely used and offers the advantage of completely preventing emulsions when injected at early stage of the treatment, and breaking emulsions at significantly lower temperatures, thus saving fuel and reducing crude oil volume and gravity losses [33, 34]. As a cost-effective and convenient method, chemical demulsification has been employed in the oil and gas industry to break up w/o emulsions. Chemical demulsifiers are amphiphilic compounds, which can destabilize emulsions by changing the interfacial film properties, such as interfacial tension, mechanical strength, elasticity and thickness of interfacial regions to promote coalescence, or through flocculation of water droplets [35]. Of all the methods of demulsification, the chemical method is the most widely used technique and it involves the use of chemical demulsifiers to accelerate the emulsion breaking process [30]. Figure 1 presents the detailed breakdown processes in an emulsion.

In emulsion treatment, the emulsion with large dispersed water percentage is less stable and easier to treat than one with a relatively small percentage of water [36]. This is largely because the presence of large dispersed water phase gives more opportunity for the droplets to join, collide, and subsequent coalescence into larger drops. This opportunity does not present itself for the few isolated drops in an emulsion with low water percentage. In an analogous way, a fresh emulsion is easier to treat than an aged emulsion. Among other reasons, this is because a prolonged ageing of emulsions in a tank permits the settling out of some of the water droplets (by gravity) leaving fewer droplets of water than if the emulsion is a fresh one. Again, less opportunity for the water droplets to collide and coalesce [30]. The breakdown of an emulsion process is majorly classified into five. These are: creaming and sedimentation, flocculation, Ostwald Ripening (Disproportionation), coalescence and phase inversion [9, 37]. Brief explanations with regards each of the demulsification step are provided in subsequent subsections.

4.1 Creaming and Sedimentation

This process is due to external forces; usually gravitational or centrifugal. When such forces surpass the thermal motion of the droplets (Brownian motion), a concentration gradient builds up in the system with the bigger droplets moving faster to the top (if their density is lower than that of the medium) or to the bottom (if their density is larger than that of the medium) of the container. In the limiting cases, the droplets may form a close-packed (random or ordered) array at the top or bottom of the system (as in points 1 and 2 in Fig. 1) with the remainder of the volume occupied by the continuous liquid phase [9, 37].

4.2 Flocculation

This breakdown process refers to the aggregation of the droplets into larger units (without any change in primary droplet size). This is due to the van der Waals attraction that is universal with all dispersed systems. Flocculation occurs when there is not enough repulsion to keep the droplets apart to distances where the Vander-Waals attraction is weak. Flocculation may be strong or weak, depending on the magnitude of the attractive energy involved [9, 37].

4.3 Ostwald Ripening (Disproportionation)

This process is consequent of the finite solubility of the liquid phases. Liquids that are referred to as being immiscible often have mutual solubilities that are not negligible. With emulsions, which are usually poly-disperse, the smaller droplets will have larger solubility when compared with the larger ones (due to curvature effects). With time, the smaller droplets disappear, and their molecules diffuse to the bulk and become deposited on the larger droplets. With time, the droplet size distribution shifts to larger values [9, 37].

4.4 Coalescence

This refers to the process of thinning and disruption of the liquid film between the droplets with the result of fusion of two or more droplets to form larger ones. The limiting case for coalescence is the complete separation of the emulsion into two distinct liquid phases. The driving force for coalescence is the surface or film fluctuations which results in close approach of the droplets whereby the van der Waals forces is strong thus preventing their separation [9, 37].

4.5 Phase Separation

This refers to the process whereby there will be an exchange between the disperse phase and the medium. For example, an o/w emulsion may with time or change of conditions invert to a w/o emulsion. In many cases, phase inversion passes through a transition state whereby multiple emulsions are produced [9, 37].

5 The Chemical Demulsification Technique

Chemical demulsifiers used in treating emulsions are similar to emulsifiers (they are also surface-active agents) [34]. The pioneer of the chemical method of treating emulsions was William S. Barnickel, a pharmaceutical chemist who, later became interested in this method of approach to treating oil fields in mid-continent [1]. The first chemical reagents used were of the inorganic type. This discovery was then followed by the discovery of the ability of soaps and soap variations to act as demulsifiers.

Monson [38] highlighted stages of demulsifier formulations prior to the knowledge of polyether condensates synthesis. That era witnessed the direct use of chemicals such as Turkey red oil, sulphuric acid, sulphated castor oil, mahogany soaps, polyamines and polyhydric alcohols as demulsifiers. The technology of alkylene oxide condensation then followed in the 1940s and opened a new phase of formulating demulsifiers with condensation products of ethylene, propylene and butylene oxides.

Post 1945, companies involved in surfactant technology had access to the whole branch of chemistry. This made possible the large-scale production of condensed polymer via ethylene and propylene oxides [39]. This led to the wide appearance of a new class of nonionic detergents in the oilfield markets. The condensation products of ethylene oxide were found to be water soluble, and the high reactivity of the Oxirane ring made it valuable in several chemical reactions. It was also found that the propylene oxide gave poly condensation products their tendency to be oil soluble.

The search for effective demulsifiers has continued since then, and the oil and gas industry and service providers have been tirelessly working towards solving this production menace [12, 40–46]. However, due to the complexity of an emulsion, and the variations in the nature and type of emulsifiers responsible for each emulsion type, a universal demulsifier that can solve all emulsion problems is far from being a reality. In fact, such attempt could amount to a work in futility.

Chemicals employed as demulsifiers may be ordinary surface-active agents (surfactants). These surfactants can be cationic or anionic. Cationic surfactants such as quaternary amines $(NR_1R_2R_3R4)^+$, where R can be any alkyl or aryl group have been used greatly in demulsifier formulation. Anionic surfactants such as sodium dodecybenzenesul-fonates ($RPhSO_3Na$), petroleum sulfonates ($RSO_3^-M^+$) and sodium di-iso-octylsulfonosuccinates [$ROOCC(CH_2COOR)H\ SO_3^-Na^+$, trade name Aerosol OT].

Apart from the ionic surfactants (cationic and anionic), nonionic surfactants have been used as well in the preparation of chemical demulsifiers. Surfactants such as fatty alcohol ethers [$CH_3(CH_2)_{10}CH_2O(C_2H_4O)_nH$], fatty esters [$(CH_3(CH_2)_{10}COO(C_2H_4O)_nH$], alkyl phenol ethers [$R\text{-}Ph\text{-}O\text{-}(C_2H_4O)_nH$], polyoxypropylene glycol ethers, and fatty amides. In the same vein, zwitterionic surfactants that are pH dependent, such as alkylbetaine derivatives [$RCH_2COO^-N^+(CH_3)_2$] have been used as demulsifiers too. There are situations where a more specific demulsifier is needed, and simple copolymers of ethylene oxide (EO) and propylene oxide (PO) may be used singly or as a blend in the presence of a surfactant to produce a good chemical demulsifier [47].

There has been an intricate classification of these surfactants in the literature (as shown in Fig. 2). There are several bases on which surfactants are classified, majorly; a classification that is based on usage and another classification based on their dissociation in water. Although they have largely been classified based on their usage, this classification is not as important as their classification based on their dissociation in water [48, 49]. In the Oil and Gas industry, for example, there is an increased deployment of surfactants during drilling fluids formulation. When formulating oil-based drilling fluid, for instance, surfactants are employed to serve as emulsifiers and/or wetting agents. However, the formulation of water-based drilling muds requires applications of diverse techniques that may involve oil in water (o/w) emulsification, prevention of wellbore instabilities using shell swelling inhibitors, and so on [13].

In this section, we will discuss surfactants classifications based on their dissociation in water.

5.1 Anionic Surfactants

Anionic surfactants are those surface-active agents that dissociate in water into an amphiphilic anion (such as $SO_4{}^{2-}$, COO^-, and $SO_3{}^-$) and a corresponding cation that is either an alkaline metal (Na+, K+) or quaternary ammonium. Anionic surfactants are the most extensively utilized surfactants in several industries largely due to its temperature stability and tolerance. They include the sulfonates of alkylbenzene (most common detergents), soaps (fatty acid), agents used in foam production (like lauryl sulfate), agents used to wet surfaces (wetting agents like di-alkyl sulfosuccinate), dispersants (like lignosulfonates), and so on [13]. It is believed that more than half of the world surfactants produced are Anionic surfactants [49]. This moiety bears a negative charge, as can be seen in a soap: $C_{17}H_{35}COO^- \ Na^+$, sodium stearate [50–52].

5.2 Cationic Surfactants

The second class of surfactants is the cationic surfactants. These surfactants are dissociated in water into an amphiphilic cation and an anion, most usually of the halide group. In general, cationic surfactants are more expensive than anionic surfactants, due to the high-pressure hydrogenation reaction involved during their synthesis process. Thus, cationic surfactants are exclusively used when cheaper substitutes are not available [48, 49, 51]. These moieties are positively charged, as can be seen in quaternary ammonium salts: $(C_{18}H_{37})_2\ N^+(CH_3)_2Cl^-$, dimethyl dioctadecyl ammonium chloride [8, 49, 53].

5.3 Zwitterionic Surfactants

There are circumstances where a surfactant molecule demonstrates both anionic and cationic dissociations. This class of surfactants is termed zwitterionic surfactants or amphoteric. Several natural substances exhibit this behavior; substances such as amino-acids and phospholipids, and other synthetic products like betaines or sulfobetaines [16, 49]. For these surfactants to solubilize, there must be positive and negative charge in the molecule, as can be seen in $C_{12}H_{35}N^{+}(CH_3)_2CH_2COO^{-}$, Ɓ-N-alkyl amino propionic acid [37, 50, 51].

5.4 Nonionic Surfactants

There is a class of surfactants that do not ionize in aqueous solutions and, thus, are called nonionic surfactants. This is because the hydrophilic group consists of a non-dissociated functional group. Exemplars of such functional groups include alcohol, phenol, ether, ester, or amide. By heavy usage, these surfactants come second with around 45% industrial production [16, 49]. The solubility of these surfactants is realized only when polyoxyethylene oxide groups solvate in water. Example of these surfactants are $C_9H_{19}C_6H_4(OCH_2CH_2)_9OH$ and nonyl phenol ethoxylate [37, 50, 51].

6 Surfactants as Demulsifiers

Due to their functionalities and several surface activities reported in many literatures [16, 49, 51], surfactants have been proven to be the integral parts of a chemical demulsifier. Chemicals (demulsifiers) are traditionally employed as interfacial tension (IFT) reducers. The effectiveness of such chemicals is enhanced by time, rate/strength of mixing, and temperature. Sufficient mixing and adequate time are required to achieve close contact of the chemical with the dispersed phase (either oil, in an oil-in-water emulsion, or water, in a water-in-oil emulsion). A specified minimum temperature is needed to guarantee the accomplishment of the functions of the chemical demulsifier. The reduction in viscosity as well as the effectiveness of chemical depends on fulfilling of a defined minimum temperature. The increase in chemical effectiveness may be a result of the decrease in viscosity of the oil phase [54]. One of the fundamental and principal reasons for the universal deployment of surfactants is their extraordinary ability to modify the properties of surfaces and interfaces, and thus, have an impact on technical processes and outcomes. The applicability of surfactants in the industry is quite distinct and covers a lot of areas. Surfactants are employed to advantage in the manufacturing industry, pharmaceuticals, agrochemicals, food processing, fuels, and adhesives, etc. Due to their surface activities, they

Table 1 Some examples of surfactant applications in the petroleum industry [50]

Gas/liquid systems	Producing oil well and well-head foams Oil flotation process froth Distillation and fractionation tower foams Fuel oil and jet fuel tank (truck) foams Foam drilling fluid Foam fracturing fluid Foam acidizing fluid Blocking and diverting foams Gas-mobility control foams
Liquid/liquid systems	Emulsion drilling fluids Enhanced oil recovery in situ emulsions Oil sand flotation process slurry Oil sand flotation process froths Well-head emulsions Heavy oil pipeline emulsion Fuel oil emulsions Asphalt emulsion Oil spill emulsions Tanker bilge emulsions
Liquid/solid systems	Reservoir wettability modifiers Reservoir fines stabilizers Tank/vessel sludge dispersants Drilling mud dispersants

have received a wide spectrum of applications in the oil and gas industry as well. Table 1 shows some of the applications of surfactants in the oil and gas industry.

The initial action in a well-organized emulsion breaking (demulsification) procedure is the characterization of the emulsion, whether it is an oil-in-water (O/W), water-in-oil (W/O) or multiple emulsion, the amount and type of immiscible phases, the existence of a protecting interfacial film round the dispersed droplets and the reactivity of the emulsifiers. The demulsification, therefore, involves two steps. Firstly, agglomeration or coagulation of the dispersed droplets must take place. Secondly, these agglomerated droplets must coalesce. Phase separation is only possible after two steps have occurred. It is worthy of note that, either of these two steps can determine the rate of demulsification of an emulsion. An emulsion can occasionally be broken by adjusting the temperature or by applying mechanical shear. More regularly, chemicals (demulsifiers) are applied to neutralize the impact of the emulsifier, accompanied by mechanical methods to conclude the phase separation [37, 55].

For this purpose, a wide range of chemical demulsifiers is available to effect this separation. These demulsifiers are classified based on their chemical structures, as discussed below.

6.1 Demulsifier Classifications and Selection

Generally, the chemicals employed in developing demulsifiers are classified according to their chemical structure, how they are applied, and the type of oil used in formulating them. Two major groups of chemicals are used: Non-ionic demulsifiers and Ionic demulsifiers. Although, classifying demulsifiers is not as easy as stated here, several w/o demulsifiers are polymeric nonionic chemicals, common with a complex comb or branched structures, having molecular weights (Mw) in the range of 2000–50,000 [56, 57]. Anionic and cationic polymers are used depending on the type of emulsifier that stabilized the emulsion, or as wetting agents. The most conventional classification of water-in-oil demulsifiers is summarized below.

- Polyalkoxylate block copolymers and ester derivatives
- Alkylphenol–aldehyde resin alkoxylates
- Polyalkoxylates of polyols or glycidyl ethers
- Polyamine polyalkoxylates and related cationic polymers (mainly for oil-in-water resolution)
- Polyurethanes (carbamates) and polyalkoxylate derivatives
- Hyperbranched polymers
- Vinyl polymers
- Polysilicones (also used as demulsifier boosters).

It is a fact that there is no universal demulsifier that can work for all emulsion problems. As the crude properties change over the life of a field, or from one reservoir to another, the efficiency of the demulsifier also change. Normally, at the beginning of a well's water production, the emulsions produced are tough to break. As the field matures and the amount of produced-water increases, the emulsion stability may change, so also the emulsifiers may change. Thus, it is conventional to examine demulsifier performance every 2–3 years [54]. Therefore, it is safe to say that demulsifiers are purpose-tailored, which means they are formulated with different primary active agents and precursors to serve the particular purpose they are designed for, depending on the type of emulsion (continuous phase) as well as the nature of emulsifiers. Some of the primary active agents in commercial demulsifiers include ethoxylated (either cross-linked or not) propylene oxide (PO)—ethylene oxide (EO) polymers or alkylphenol resins. The demulsifiers are formulated to give distinct properties, that includes including hydrophile-lipophile balance (HLB), solubility, the diffusion rate into the interface, and its efficacy at destabilizing the interface. Demulsifiers are normally added to the continuous phase, inside which they must then spread to the interface and interrupt the stabilizing film at the interface. The demulsifier should ordinarily be added adequately far, upstream to allow this process to take place, and so that droplet coalescence occurs before the emulsion get to the separating vessel [16, 53, 58].

There have been several studies with regards to how the structure of a demulsifier is related to its performance. For example, Zhang et al. [58] studied the demulsification of dendritic copolymers with the aim of establishing a correlation between their molecular structure and crude oil emulsions demulsifications. In a similar study, Wang et al. [59] studied the demulsification efficiency of six dendrimers with the same polyamidoamine (PAMAM) primary structure but distinct terminals. The dendrimers were investigated by surface tension estimation at the air–water interface. The results of the study showed that the dendrimers with proper structures have great potential for breaking crude oil emulsions.

Further in 2010, Wang et al. [60] further synthesized another set of six surfactants made of dendritic polyether using varying proportions of propylene oxide (PO) and ethylene oxide (EO) utilizing phenol-amine resin as a precursor. A study of surface tension and demulsification efficiency of these polyether surfactants shows that the six dendritic polyethers work like conventional surfactants. The findings from this study show that the structure of the polyethers can affect the demulsification efficiency, of which the principal determinant is the molecular block. Fink [61] expounded some of the common precursor chemicals that are used in the formulation of demulsifiers. Some of them are stated below, as outlined by Fink [61].

6.1.1 Polyalkylene Oxides

Polyalkylene oxides are precursor substances with the following general structure:

$$\mathrm{HO\text{-}(CH_2\text{-}CHR\text{-}O)_X\text{-}H}$$

The most essential precursors are the oxides of polyethylene polypropylene oxide, and polybutylene. These oxides are also called polyalkylene glycol (PAG), although this name is only suitable strictly for derivatives of 1,2-diols.

6.1.2 Polyamines

Polyamines are normally open-chain compounds that have primary, secondary, or tertiary amino groups. On the other hand, polyimines can be used.

7 Requirements of a Demulsifier

A triumphant breaking of emulsion requires an effective technique. In this work, a chemical demulsification technique is being considered. Both the processes involved in the emulsification and demulsification of emulsions are complex. Nevertheless, the process of demulsification is by no means the reverse of emulsification [62, 63]. This is particularly the case in the petroleum industry. An efficient demulsification of water-in-crude oil emulsions requires that a clear understanding of the characteristics of the emulsion in question should be achieved. Also, of paramount importance is the nature of the film at the oil/water interface, hence the causes of emulsion stability. Consequently, choosing a demulsification protocol requires that the key factors responsible for the emulsion stability be identified, identify those properties of these stabilizers and how they can be modified in order to achieve destabilization. Finally, a source of sufficient energy that will promote coalescence must be identified and introduced into the system as well as finding the most favourable conditions that allow phase separation [47].

Angle [64] made a comprehensive review in one of his works, from which it would appear that the fundamental requirements on demulsifiers are the abilities to possess one or more of the following properties:

(1) strong affinity to the oil/water interface with the capability to destabilize the protecting film that forms around the dispersed droplet and/or to alter the contact angle of the solids which may be a component of the interfacial film;
(2) ability to flocculate the droplets;
(3) ability to increase coalescence by creating pathways for water's natural attraction to water; and
(4) improvement of film drainage and thinning of the inter-droplet lamella by producing changes to the interfacial rheology such as lowered interfacial viscosity and improved compressibility.

7.1 Major Types of Demulsifier Chemicals

In the Oil industry, the most employed polymer in demulsification process is a surfactant that possesses both hydrophilic and hydrophobic groups [65]. The polymeric surfactant when added to the crude oil emulsion place itself in the interface between the water and oil molecules. While the hydrophilic groups orient themselves towards the water, the hydrophobic ends orient themselves towards the oil [66].

Nowadays, the best polymeric surfactants used world over, are derivatives of alkoxylated materials [65, 67].

Since these polymeric surfactants are alkoxylated, they are considered nonionic polymers. However, there are times when mixtures of nonionic, cationic, or anionic materials are used together. This depends on the characteristics of the crude oil. Etoxylated nonionic surfactants are effective multipurpose and versatile substances. Commercial products are obtained by reaction of ethylene oxide with a hydroprobe having an active hydrogen group (e.g. fatty acids, alkylphenols or fatty alcohols) in the presence of suitable catalysts. In Appendix C, a brief history of chemical demulsifiers used in breaking w/o emulsions since the work of Barnickel [68] is presented.

A lot of work has been done by different researchers from academia as well as the oil industry on the characteristics of the major types of demulsifiers that are employed in breaking w/o emulsions. Reported in Table 2 are some of the characterization of the major types of demulsifier chemicals. The actions of a chemical demulsifier are stated later in this section, and no single chemical can provide all the four required

Table 2 Class of water-in-oil demulsifiers

Demulsifier class	Functions/comments
Polyalkoxylate block copolymers	The hydroxyl groups on the edges of these polymers can be ethoxylated with EO to form EO/PO/EO block copolymers, which are linear demulsifiers. These copolymers are moderately poor demulsifiers by themselves [69, 70]
Alkylphenol–aldehyde resin alkoxylates	This class has been in existence for many decades, because they are easy to manufacture and have good performance. Contains phenol groups, and as such are not environmentally friendly, also considered as endocrine disrupters in marine species [61, 71]
Polyesteramines and related polymers	They are extremely surface active, can resolve emulsions at low dosage, produce sharp o/w interface [72, 73]
Polyurethanes and polyalkoxylate derivatives	A well-known class that contains carbamate functional groups. Prepared by condensing polyisocyanates and polyglycols with terminal hydroxyl groups. They perform well at moderate concentrations, but they delay coalescence at higher concentrations. Also, environmentally not friendly [74, 75]
Hyperbranched polymers	They include hyperbranches of polyesteramides, polyurethanes, polyurea, polyamides, polyethers, polyesters and so on [85]. Some can be reasonably biodegradable while some are not and can function as demulsifiers for both o/w and w/o emulsions [76–78]
Polysilicones (also as demulsifier boosters)	Some can be very good demulsifiers (e.g. block copolymers of polyoxyalkylene-polysiolxane), while others (like dimethyl siloxane) can function as demulsifier boosters [79, 80]
Oxyalkylated phenols	They are good wetting agents, used in blends, reduce interface pad build-up and are fair to poor demulsifiers [80, 81]

actions. Thus, commercial demulsifiers are exclusive mixtures of these compounds (i.e., surfactants and additives) [34, 62].

However, it is an acceptable practice to blend the selected mixtures (30–60%) of proprietary, solid chemicals with a suitable solvent such as heavy aromatic naphtha (HAN) or isopropyl alcohol (IPA) to obtain a liquid that pours at the lowest expected temperature. W/O demulsifiers are always very insoluble in water and highly soluble in oil so that they can diffuse rapidly through the continuous crude oil phase and reach the droplet interfaces [82–84]. Typically, these oil soluble demulsifiers are formulated in organic solvents alone such as toluene, xylene, tetrahydrofuran, dioxane, lower alcohols and light gasoline fractions having boiling limits from 50 to 200 °C.

Sometimes, they are formulated in co-solvents comprising organic solvents and water where in the organic solvents are usually C_3–C_{10} alkanols, ethylene diamine, diethyl triamine or ethanolamines including diethanol-amine [40].

However, using organic solvents in a demulsifier formulation has several disadvantages like increased cost, flammability, and toxicity. Thus, a demulsifier formulation, which does not include organic solvents would represent an improvement in the art of demulsification [65].

7.2 Functions of an Effective Demulsifier

An effective chemical demulsifier performs the following actions [34, 85]:

1. It must have a strong attraction to the water–oil interface. The demulsifier must displace and/or neutralize the action and/or position of the emulsifying agents already on the droplet surface.
2. Flocculation action: The demulsifier must neutralize any repulsive electrical charges between the dispersed water droplets and so allow the droplets to touch each other.
3. Coalescence action: The demulsifier must permit small droplets to combine and form large drops; large enough to settle. This requires that the film surrounding and stabilizing the droplets is being ruptured.
4. Wetting ability (solids wetting): Demulsifiers must prevent fines at the droplet interface from physically blocking coalescence. Clays, drilling muds, and iron sulfides fines can be water wet so that they leave the film interface and migrate into the water droplet. Asphaltenes and waxes can be dissolved or oil wet to disperse them into the continuous crude phase.

7.3 Mechanism of Chemical Demulsification

Theories of how demulsifiers perform are incomplete [34]. Their incompleteness is due to the failure of the theories to explain the extreme specificity of the various types of chemicals on any crude-water mixture. The wide variety of reagents needed for effective handling of different emulsions suggests that the mechanisms of performance of the chemical reagents on the film surrounding the water droplets are complex and cannot be adequately explained using a single theory [86]. However, two valid generalizations concerning the mechanism of the chemical demulsifiers hold. First, effective demulsifiers have high molecular weights that are comparable to those of the natural surfactants. Secondly, if used as emulsifying agents, they tend to cause emulsions opposite in type (i.e., o/w) to the produced w/o emulsions [48, 49].

Yang et al. [79] in their study found out that the demulsification process can occur via three mechanisms. (1) They can absorb at the w/o interface, displace indigenous surfactant into bulk phases and make interfacial film sufficiently weak and promote coalescence. (2) They also can act as flocculating agents, joining together small droplets, which then coalesce and grow. (3) Alternatively, or simultaneously, they can act as wetting agents and wet fine solids present in the crude oil, hence reduce their ability to stabilize emulsions.

However, other traditional theories as to why demulsifiers work also exist [26]. According to these theories, the demulsifier 'neutralizes' the emulsifying agent; in other words, breaking a w/o emulsion requires a chemical that would normally produce a reverse or o/w emulsion. Another explanation is that the demulsifying chemical makes the film surrounding the water droplet very rigid. When the oil drop expands on being heated, the film is ruptured. Alternatively, if the chemical makes the film to diminish, then heat is not required to burst the film [34, 42].

Nuraini et al. [81] in their study made a careful selection of four groups of demulsifiers; i.e. amine, natural, polyhydric, and alcohol demulsifier groups aiding in breaking of stable emulsions. They found out that amine demulsifier groups demonstrated the highest efficiency in breaking the emulsion, when compared to polyhydric, alcohol, and natural groups. They also found out that a demulsifier efficiency depends on two-factors; solubility of demulsifier (either in water or oil) and molecular weight of demulsifier. Figure 3 presents a chemical demulsification mechanism.

Krawczyk et al. [87] in a study of chemical demulsification of petroleum emulsions investigated the factors affecting the coalescence and interfacial behavior of w/o emulsions in the presence of oil soluble demulsifiers. They attributed the performance of a chemical demulsifier to the rupture of the thin film separating droplets,

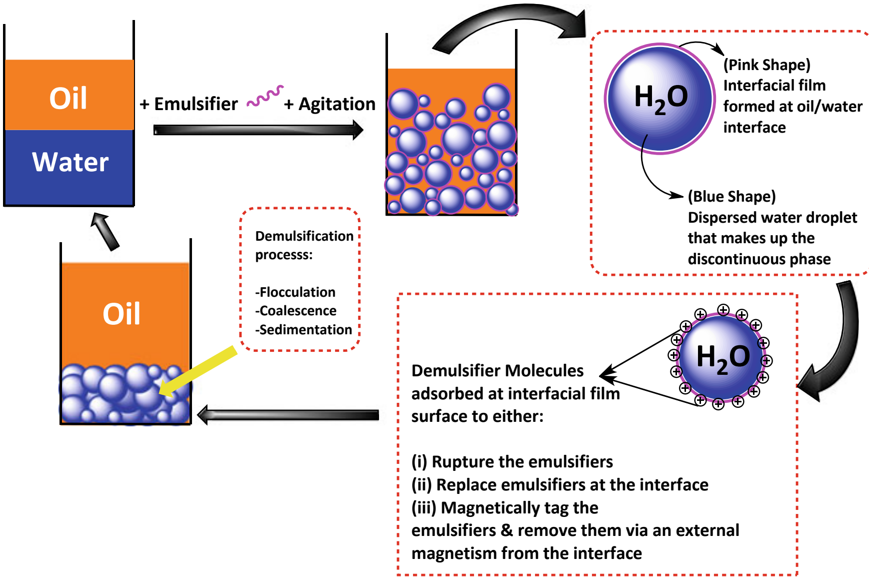


Fig. 3 Chemical demulsification mechanism

which affects the rate of coalescence of the droplets, and that the higher the rate of adsorption, the more effective the demulsifier is.

Kim [30] reported a novel procedure for measuring rheological properties of a water/oil/water film, characteristics of which actively determine whether demulsification occurs or not, and the mechanism of demulsification. Determinations of dynamic interfacial tension and activities with a standard drop-volume apparatus support the water/oil/water film results. Although the measurements of static interfacial tension could not correlate with the demulsifier performance data, the data, nonetheless, provide valuable insight into physicochemical mechanisms. The study shows that the rapidly dispersing, low molecular weight components of demulsifiers break emulsions by maintaining a low dynamic interfacial tension during film drainage.

In another study, Kang et al. [88] investigated the influence of demulsifier on interfacial film between oil and water and used that to explain the mechanism of demulsification. The study established that the mechanism exhibited by these demulsifiers is partial replacement of the emulsifiers, which led to the interfacial elasticity decrease.

The demulsification mechanism reported by Erica et al. [89] in a study of demulsification mechanism of asphaltene-stabilized w/o emulsions by a polymeric EO-PO demulsifier described gradual infiltration of the demulsifier into the asphaltene film. The demulsifier was more surface-active than asphaltenes and thus exhibited an effective competition with asphaltenes to occupy the interface, penetrating asphaltene films and softening them under shear and compression. The softness of asphaltenes films was found to increase with increasing demulsifier leading to faster kinetics of asphaltene film penetration at higher demulsifier dosages.

7.4 Formulation of a Chemical Demulsifier

Chemical demulsifiers are surfactants that can destabilize emulsions. For a demulsifier to perform effectively, it must counteract the emulsifying agent stabilizing the emulsion, and also promote aggregation and coalescence of the dispersed phase into large droplets that can settle out of the continuous phase [9, 47, 90]. Since chemical demulsifiers are surfactants; meaning they are surface active, they usually possess a reasonable degree of toxicity (EC50 < 10 mg/l) [57]. This is mostly applicable to cationic surfactants that are used in many production chemical products.

When formulating a demulsifier, certain properties must be put in mind. The demulsifier should have a strong attraction to the interface (good surfactant properties) and should be able to migrate rapidly through the continuous phase (in other words, should be oil-soluble) to reach the droplet interface [37, 50]. After the demulsifier concentrate at the oil/water interface, it counteracts the emulsifying agent and promotes flocculation of the dispersed phase. In the flocculated system, the emulsifier film is still continuous, thus it is a requirement that the demulsifier must neutralize the emulsifier and facilitate the rupture of the droplet interfacial film, leading to coalescence.

Addition of ethylene oxide and/or propylene oxide to formaldehyde resins and to diamines and higher functional amines (triamines, tetramines etc.) yields a variety of modified polymers that perform well at relatively low concentrations [50].

The low molecular weight demulsifiers can be transformed into high-molecular-weight products by reactions with diacids, diepoxides, di-isocynates, and aldehydes. This gives room for tailoring demulsifier chemistry to accommodate various oil gravities and surfactant properties, and to adjust surface activity and the rate at which demulsifiers move to the interface [37].

Fatty amine derivatives as surfactants have been studied for their biodegradability. Toxic surfactants would kill bacteria, which can affect the biodegradation results. (Biodegradation tests are usually carried out at 2–40 mg/l but toxicity tests are at µg/l). Generally, the longer the alkyl tail, the more toxic is the surfactant. Below a single tail of 8–10 carbon atoms (depending on the hydrophilic-lipophilic balance), the toxicity decreases significantly [57, 91].

8 Comparison Between Two Different Demulsifiers with Different Interfacial Properties (Interfacial Activity)

In order to describe how the surface activity of a demulsifier affects its performance, two different chemical demulsifiers were tested, after their interfacial tensions between oil and water were determined. An optical analyzer TURBISCAN was used to determine the performance of the demulsifiers and the result is shown below.

As discussed in Sect. 5, for a chemical to qualify as an effective chemical demulsifier, it must possess certain properties, one of which is its ability to exhibit surface activity. In a study of demulsification of water-in-crude oil emulsions, [92] found out that surfactants effective as demulsifiers reduced surface tension of water by more than 25 dynes-cm^{-1}. By exhibiting interfacial activity, it means that when the compound is added to a liquid at low concentration, it should be able to adsorb on the surface or interface of the system and reduce the surface or interfacial excess free energy, and a surface activity is achieved when the number of carbon atoms in the hydrophobic tail are higher than 8 [93]. There have been several efforts to establish a correlation between the performance of a demulsifier and other demulsifier properties like their molecular structures, hydrophilic-lipophilic balance (HLB), of the surfactants used as demulsifiers, interfacial tension, and so on. This work does not claim to achieve such, and only makes use of an established criterion of the ability of the demulsifier to reduce the surface tension of water by 25–30 dynes-cm^{-1} [93] as a good demulsifier.

The equilibrium interfacial tension measurements as well as the TURBISCAN procedure were carried out using the method described in our recent publication [29]. Two different commercial demulsifiers, DPG 144 and DTG 123 were used in the study. The result showed that DPG 144 reduced the water surface tension by 27 dynes cm^{-1} (27×10^{-4} mN/m) while DTG 123 reduced by surface tension of water by barely 10–11 dynes cm^{-1}. To further verify the performance of these two demulsifiers, the TURBISCAN test was run and the results are shown below.

Figure 4 shows the destabilization profile of a water-in-crude emulsion in the presence of DTG 123. The presence of wavy pattern at the bottom of the sample suggests that this part of the sample is inhomogeneous; and it is represented by 0–18 mm of the sample bottle. Beyond that point is an additional behavioral feature reported as the second wall effect as explained by Akther et al. 2007 [94], from 18 to 32 mm of the bottle length. The top of the sample is however characterized by “clarification”, where oil migrate from the bottom of the sample to the top, causing a fall in backscattering. It is believed that the phase separation caused a line pattern (striations to form on the wall of the cell). As there is no significant increase or decrease at the bottom of the sample, the water phase is mixed with a bit of oil, thus would require longer time to separate. This suggests that the demulsifier is not very effective.

Figures 5 shows the backscattering profiles of a water-in-crude oil. The same concentration of DTG 123 used in the first instance is used here for DPG 144. It can be seen from Fig. 5 that the emulsion ceases to be stable and a lot of water settles at the bottom of the bottle. From 0 mm to around 26 mm of the sample bottle witnesses settling of water (defined by increase in signal—sedimentation). Beyond this point, there is a drop in backscattering (from 26 to 40 mm of the sample bottle). This phase is the clarification zone, expressed by drop in signal due to the presence of oil phase absorbing the light. The ability of DPG 144 demulsifier to break more water than DTG 123 suggests that it is a better demulsifier.

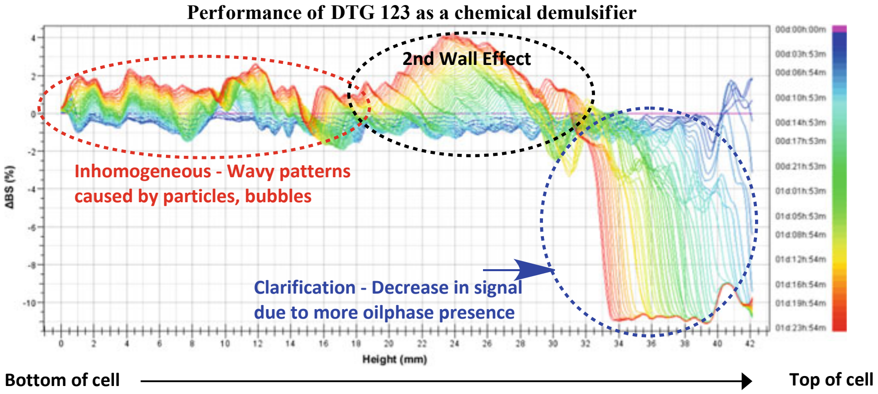
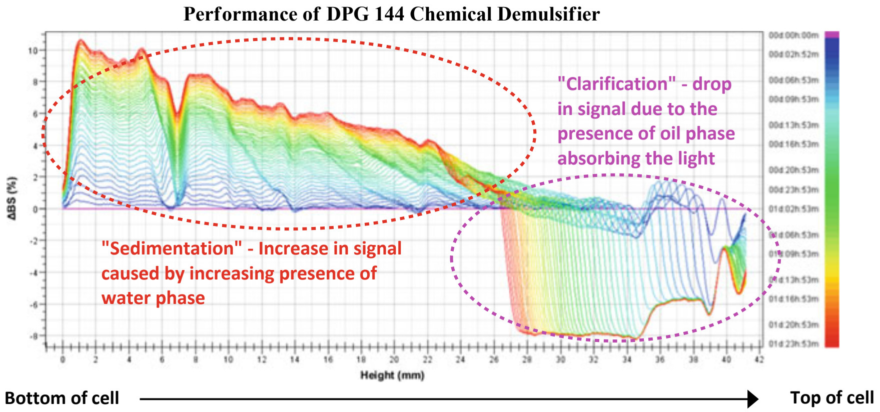


Fig. 4 Delta Backscattering profile for a stable water-in-crude emulsion evaluated by the Turbiscan Lab® AGS. Data are reported as a function of time (0–48 h) and sample height of the emulsion sample (0–42 mm)



"Clarification" - drop in signal due to the presence of oil phase absorbing the light

"Sedimentation" - Increase in signal caused by increasing presence of water phase

Fig. 5 Delta Backscattering profile for a stable water-in-crude emulsion evaluated by the Turbiscan Lab® AGS. Data are reported as a function of time (0–48 h) and sample height of the emulsion sample (0–42 mm)

9 Conclusion

As a conclusion, studies have shown that surfactants exhibit surface activity, which means their molecules will adsorb preferentially at the interfaces of air and water, oil and water, and solid/water. Surfactants are amphiphilic or amphipathic, and thus they can dissolve in nonpolar medium with the other part in the polar medium. Surfactant molecules form oriented monolayers at interfaces and show surface activity. Owing to their characteristic surface activity and tendency for molecular self-assembly, they can control and modify both the physical and chemical properties of the phase boundary between different phases of liquids encountered in almost all chemical reactions. This ability makes them the integral components in a demulsifier formulation. Although lowering in interfacial tension and adsorption of demulsifier at the crude oil/water interface is not the final and most important condition that determines a demulsifier efficiency, it has been shown in this study that the surface activity of a surfactant is a good condition for its efficiency as a demulsifier.

References

1. Kokal SL (2005) Crude oil emulsions: a state-of-the-art review. SPE Prod Fac 20(01):5–13
2. Kokal SL, Al Ghamdi A (2006) Oil/water separation experience from a large oil field. SPE Product Oper 21(03):365–371
3. Langevin D et al (2004) Crude oil emulsion properties and their application to heavy oil transportation. Oil Gas Sci Technol 59(5):511–521
4. Fingas M, Fieldhouse B (2009) Studies on crude oil and petroleum product emulsions: water resolution and rheology. Colloids Surf A 333(1):67–81

5. Fingas M, Fieldhouse B (2014) Water-in-oil emulsions: formation and prediction. Spill Sci Technol 225
6. Becher P (1988) Basic theory, measurement and applications. In: Encyclopedia of emulsion technology, vol 3. Dekker, New York
7. Sheu EY, Mullins OC (1998) Structures and dynamics of asphaltenes. Plenum Press, pp 337–423
8. Schramm LL (1992) Petroleum emulsions. ACS Publication
9. Sjoblom J (2005) Emulsions and emulsion stability: surfactant science series/61-Chp 14, vol 132. CRC Press
10. Clayton W (1923) The theory of emulsions and emulsification. J. & A. Churchill
11. Chevalier Y, Bolzinger M-A (2013) Emulsions stabilized with solid nanoparticles: pickering emulsions. Colloids Surf Physicochem Eng Aspects 439:23–34
12. Abdel-Raouf M (2012) Crude oil emulsions: composition stability and characterization. BoD–Books on Demand
13. Umar AA et al (2018) A review of petroleum emulsions and recent progress on water-in-crude oil emulsions stabilized by natural surfactants and solids. J Petrol Sci Eng 165:673–690
14. Umar A, Saaid I, Sulaimon A (2017) The roles of polar compounds in the stability and flow behavior of water-in-oil emulsions. ICIPEG 2016. Springer, pp 643–653
15. Urdahl O, Sjöblom J (1995) Water-in-crude oil emulsions from the Norwegian continental shelf. A stabilization and destabilization study. J Dispersion Sci Technol 16(7):557–574
16. Schramm LL (2000) Surfactants: fundamentals and applications in the petroleum industry. In: Surfactants in solutions. Cambridge University Press
17. Dingcong W (2002) A study of identifying the emulsion type of surfactant: volume balance value. J Colloid Interface Sci 247(2):389–396
18. Pasquali RC, Sacco N, Bregni C (2009) The studies on hydrophilic–lipophilic balance (HLB): sixty years after William C. Griffin's pioneer work (1949–2009). Lat Am J Pharm 28(2):313–317
19. Zafeiri I et al (2017) Emulsions co-stabilised by edible pickering particles and surfactants: the effect of HLB value. Colloid Interface Sci Commun 17:5–9
20. Surfluh J (1937) Prevention of oil-field emulsions. In: Drilling and production practice. American Petroleum Institute
21. Powell KC, Damitz R, Chauhan A (2017) Relating emulsion stability to interfacial properties for pharmaceutical emulsions stabilized by Pluronic F68 surfactant. Int J Pharm 521(1):8–18
22. Alvarado V, Wang X, Moradi M (2011) Stability proxies for water-in-oil emulsions and implications in aqueous-based enhanced oil recovery. Energies 4(7):1058–1086
23. McClements DJ, Jafari SM (2017) Improving emulsion formation, stability and performance using mixed emulsifiers: a review. Adv Colloid Interface Sci
24. Kokal S, Wingrove M (2000) Emulsion separation index: from laboratory to field case studies. In: SPE annual technical conference and exhibition. Society of Petroleum Engineers
25. Kokal S (2002) Crude oil emulsions: a state-of-the-art review. In: SPE annual technical conference and exhibition. Society of Petroleum Engineers
26. Jones T, Neustadter E, Whittingham K (1978) Water-in-crude oil emulsion stability and emulsion destabilization by chemical demulsifiers. J Can Petrol Technol 17(02)
27. Strassner J (1968) Effect of pH on interfacial films and stability of crude oil-water emulsions. J Petrol Technol 20(03):303–312
28. Moroney JR, Berg MD (1999) An integrated model of oil production. Energy J 20(1)
29. Umar AA et al (2020) Magnetic polyester bis-MPA dendron nanohybrid demulsifier can effectively break water-in-crude oil emulsions. J Market Res 9(6):13411–13424
30. Kim Y-H, Wasan D, Breen P (1995) A study of dynamic interfacial mechanisms for demulsification of water-in-oil emulsions. J Colloids Surf A Physicochem Eng Aspects 95(2–3):235–247
31. Gafonova OV, Yarranton HW (2001) The stabilization of water-in-hydrocarbon emulsions by asphaltenes and resins. J Colloid Interface Sci 241(2):469–478
32. Myers D (1990) Surfaces, interfaces and colloids. Wiley-Vch, New York etc.

33. Thompson D, Taylor A, Graham D (1985) Emulsification and demulsification related to crude oil production. Colloids Surf 15:175–189
34. Manning FS, Thompson RE (1991) Oilfield processing of petroleum: natural gas, vol 1. Pennwell books
35. Feng X et al (2009) Mechanistic study on demulsification of water-in-diluted bitumen emulsions by ethylcellulose. Langmuir 26(5):3050–3057
36. Meyer P (1964) Chemelectric treating a new phase in the electrical dehydration of oil emulsions. In: SPE production automation symposium. Society of Petroleum Engineers, Kansas
37. Schramm LL (2014) Emulsions, foams, suspensions, and aerosols: microscience and applications. Wiley
38. Monson T (1969) Chemical resolution of emulsions. In: Surface operations in petroleum production, II. Elsevier
39. Becker J (1997) Crude oil waxes, emulsions, and asphaltenes. Pennwell Books
40. Merchant Jr P, Lacy SM (1988) Water based demulsifier formulation and process for its use in dewatering and desalting crude hydrocarbon oils. Google Patents
41. Kim YH, Wasan DT (1996) Effect of demulsifier partitioning on the destabilization of water-in-oil emulsions. Ind Eng Chem Res 35(4):1141–1149
42. Abdel-Azim AAA , Zaki NN, Maysour NES (1998) Polyoxyalkylenated amines for breaking water-in-oil emulsions: effect of structural variations on the demulsification efficiency. Polym Adv Technol 9(2):159–166
43. Dalmazzone C, Noïk C (2001) Development of new” green” demulsifiers for oil production. In: SPE international symposium on oilfield chemistry. Society of Petroleum Engineers
44. Dalmazzone C, Noik C, Komunjer L (2005) Mechanism of crude-oil/water interface destabilization by silicone demulsifiers. SPE J 10(01):44–53
45. Darling DF (1982) Recent advances in the destabilization of dairy emulsions. J Dairy Res 49(4):695–712
46. Mat H et al (2005) Study on demulsifier formulation for treating Malaysian crude oil emulsion
47. Sjoblom J (2001) Encyclopedic handbook of emulsion technology. CRC Press
48. Salager J-L (1990) The fundamental basis for the action of a chemical dehydrant. Influence of the physical and chemical formulation on the stability of an emulsion. Int Chem Eng 30(1):103–116
49. Salager J-L (2002) Surfactants types and uses. FIRP booklet, (E300A)
50. Schramm LL, Stasiuk EN, Marangoni DG (2003) 2 Surfactants and their applications. Annu Rep Sect “C” (Phys Chem) 99:3–48
51. Migahed M, Al-Sabagh A (2009) Beneficial role of surfactants as corrosion inhibitors in petroleum industry: a review article. Chem Eng Commun 196(9):1054–1075
52. Fingas M (2014) Handbook of oil spill science and technology, vol 1. Wiley
53. Shehzad F, Hussein IA, Kamal MS, Ahmad W, Sultan AS, Nasser MS (2018) Polymeric surfactants and emerging alternatives used in the demulsification of produced water: a review. Polym Rev 58(1):63–101
54. Maurice S, Ken A (2008) Emulsions and oil treating equipment. Gulf Professional Publishing, Hardbound
55. Li Y et al (2017) A versatile and efficient approach to separate both surfactant-stabilized water-in-oil and oil-in-water emulsions. Sep Purif Technol 176:1–7
56. Bhardwaj A, Hartland S (1994) Kinetics of coalescence of water droplets in water-in-crude oil emulsions. J Dispers Sci Technol 15(2):133–146
57. Kelland MA (2014) Production chemicals for the oil and gas industry. CRC press
58. Zhang Z, Xu G, Wang F, Dong S, Chen Y (2005) Demulsification by amphiphilic dendrimer copolymers. J Colloid Interface Sci 282(1–4)
59. Wang J, Li C-Q, Li J, Yang J-Z (2007) Demulsification of crude oil emulsion using polyamidoamine dendrimers. Sep Sci Technol 42(9):2111–2120
60. Wang J, Hu F-L, Li C-Q, Li J, Yang Y (2010) Synthesis of dendritic polyether surfactants for demulsification. Sep Purif Technol 73(3):349–354

61. Fink J (2015) Petroleum engineer's guide to oil field chemicals and fluids Gulf Professional Publishing, Chp 23, p 705
62. Matijevic E, Good RJ (2012) Surface and colloid science, vol 12. Springer Science & Business Media
63. Sjöblom J (2012) Emulsions: a fundamental and practical approach, vol 363. Springer Science & Business Media
64. Angle CW (2001) Chemical demulsification of stable crude oil and bitumen emulsions in petroleum recovery—a review. Marcel Dekker, New York, pp 541–594
65. Hanapi B et al (2006) Study on demulsifier formulation for treating Malaysian crude oil emulsion. Internet website. http://eprints.utm.my/2768/1/74004.pdf
66. Fink J (2003) Oil field chemicals. Elsevier
67. Al-Sabagh AM et al (2013) Synthesis and evaluation of new demulsifiers incorporating linear alkyl benzene moiety for treating water-in-oil emulsion. J Dispers Sci Technol 34(7):996–1007
68. Barnickel WS (1922) Apparatus for treating natural emulsions of petroleum. Google Patents
69. Mansur CR et al (2004) PLURONIC× TETRONIC polyols: study of their properties and performance in the destabilization of emulsions formed in the petroleum industry. J Colloid Interface Sci 271(1):232–240
70. Alvarez F et al (2011) Dissipative particle dynamics (DPD) study of crude oil− water emulsions in the presence of a functionalized co-polymer. Energy Fuels 25(2):562–567
71. Beyer J et al (2001) Ecotoxicology of oilfield chemicals: the relevance of evaluating low-dose and long-term impact on fish and invertebrates in marine recipients. In: SPE international symposium on oilfield chemistry. Society of Petroleum Engineers
72. Al-Sabagh AM, Kandile NG, Noor El-Din MR (2011) Functions of demulsifiers in the petroleum industry. Sep Sci Technol 46(7):1144–1163
73. Ali N et al (2014) Synthesis of P (MMA-co-AA-co-DVB) Fe 3 O 4/magnetic composite nanoparticles. In: Proceedings of 2014 11th international Bhurban conference on applied sciences & technology (IBCAST). IEEE, Islamabad, Pakistan
74. Reeve PFD (2002) Method of inhibiting the formation of oil and water emulsions. Google Patents
75. Peña AA, Hirasaki GJ, Miller CA (2005) Chemically induced destabilization of water-in-crude oil emulsions. Ind Eng Chem Res 44(5):1139–1149
76. Feng X et al (2008) Biodegradable polymer for demulsification of water-in-bitumen emulsions. Energy Fuels 23(1):451–456
77. Killat GR, Conklin JR (1984) Use of quaternized polyamidoamines as demulsifiers. Google Patents
78. Conklin JR, Wilson LR (1984) Use of heterocyclic ammonium polyamidoamines as demulsifiers. Google Patent
79. Yang M, Stewart A, Davies G (1996) Interactions between chemical additives and their effects on emulsion separation. In: SPE annual technical conference and exhibition. Society of Petroleum Engineers
80. Pensini E et al (2014) Demulsification mechanism of asphaltene-stabilized water-in-oil emulsions by a polymeric ethylene oxide–propylene oxide demulsifier. J Energy Fuels 28(11):6760–6771
81. Nurainia M, Abdurahmanab H, Kholijaha A (2011) Effect of chemical breaking agents on water-in-crude oil emulsion system. Int J 2(4)
82. Madaan V et al (2014) Emulsion technology and recent trends in emulsion applications. Int Res J Pharm 5(7):533–542
83. McMahon AJ (1992) Interfacial aspects of water-in-crude oil emulsion stability. Emulsions—a fundamental and practical approach. Springer, pp 135–156
84. Manousakis M, Avranas A (2013) Dynamic surface tension studies of mixtures of hydroxypropylmethylcellulose with the double chain cationic surfactants didodecyldimethylammonium bromide and ditetradecyldimethylammonium bromide. J Colloid Interface Sci 402:237–245

85. Fink J (2015) Petroleum engineer's guide to oil field chemicals and fluids. Gulf Professional Publishing. GPP
86. Müller FH, Weiss A (2007) Emulsions, vol 63. Steinkopff
87. Krawczyk MA, Wasan DT, Shetty CJI (1991) Chemical demulsification of petroleum emulsions using oil-soluble demulsifiers. J Indus Eng Chem Res 30(2):367–375
88. Kang W et al (2006) Influence of demulsifier on interfacial film between oil and water. J Colloids Surf A Physicochem Eng Aspects 272(1–2):27–31
89. Pensini E et al (2014) Demulsification mechanism of asphaltene-stabilized water-in-oil emulsions by a polymeric ethylene oxide–propylene oxide demulsifier. Energy Fuels 28(11):6760–6771
90. Hunter TN et al (2008) The role of particles in stabilising foams and emulsions. Adv Coll Interface Sci 137(2):57–81
91. Kilpatrick PK (2012) Water-in-crude oil emulsion stabilization: review and unanswered questions. Energy Fuels 26(7):4017–4026
92. Bhardwaj A, Hartland S (1993) Study of demulsification of water-in-crude oil emulsion. J Dispers Sci Technol 14(5):541–557
93. Farn RJ (2008) Chemistry and technology of surfactants. Wiley
94. Akther S, Hwang J-Y, Lee H-M (2007) Effects of the water quality on the dispersion properties of bentonites used for drilling fluid. J Mineral Soc Korea 20(1):21–33