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# Surfactant for petroleum demulsification, structure, classification, and properties. A review

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**Abstract.** Crude oil as a complex fluid often consists of colloidal particles. These colloidal particles are made up of asphaltenes and resins diffused in a blend of aliphatic and aromatic solvents. At various stages of crude oil production, there is usually an occurrence a water-in-oil emulsion. The stability of the emulsion formed is dependent on the occurrence of the interfacial barrier which prevents the coalescence of the dispersed water droplets. Several operational difficulties are often encountered during crude oil processing as a result of the presence of water. These difficulties range from corrosion in equipment and pipelines as well as an increase in the production cost. Hence, to mitigate these economic and operational challenges, it is crucial to ensure that the water is separated from the crude oil prior to transporting or refining the oil. Demulsification using surfactant is one of the effective techniques used for the separation of crude oil from water. This paper presents a short review of the various application of surfactants for demulsification, their structure, classification as well as their properties. In addition, the mechanism and techniques for demulsification of crude oil were also presented.

## 1. Introduction

Crude oil is the most valued and traded source of energy which is highly demanded for various human activities. Studies have shown that over 65% of global power generation utilized fuel derived from crude oil. [1]. Due to increasing demand in energy resources, it has been projected that there will be a continuous increase in global crude oil as indicated by the U.S. Energy Information Administration [2]. The processing of crude oil is often associated with the formation of water-oil emulsions which constitute challenges when transporting in pipelines, due to pressure and shear forces [3]. Prior to the processing, the crude oil drilled from its reservoir is usually made of impurities like water, sediment as well as hydrocarbons in the form of asphaltenes, resins, carboxylic acids, waxes and solids from crude oil [4]. These hydrocarbon components often serve as natural emulsifiers [5]. However, these hydrocarbon components readily coagulate on the water-oil interface causing it to form a stable film around the droplets. The formation of these stable film droplets hinders the formation of coalescence water droplets which stabilize the water in oil emulsion [6]. Several challenges are often encountered as a result of co-production of water with crude oil. One of such major challenges is the cost associated with pumping or transporting the mixture of the crude oil and water through the pipeline or by tanker [7]. Moreover, problems associated with the corrosion of various processing facilities are also common



[8]. These have necessitated the installation of auxiliary equipment for the production of quality crude oil for export. Moreover, small dispersed water drops in crude oil could also result in the poisoning of downstream refinery catalysts and constraints in improving the crude oil viscosity [9]. Hence, it is expedient for complete separation of water from the crude oils prior to transporting or refining which will mitigate economic losses and operational difficulties [10].

It is essential to break down the formed emulsions in crude oil to minimize several challenges associated with crude oil production [11]. This can be achieved using demulsifiers. Demulsifiers which are usually surfactants help to facilitate the separation of crude oil from emulsified water during production. They display a unique ability to disrupt water-in-oil emulsions. also, the surfactant also helps in stimulating the aggregation and coalescence of the water droplets that lead to the separation of the water from the crude oil [7]. Demulsifier functions in such a way as to demulsify and prevent the repeated formation of emulsions as a result of the decrease in the mechanical strength of the protective shells formed on the surface of water drops [8]. The surfactants are often injected into the emulsion and thoroughly mixed. Subsequently followed by the removal of water from the oil via sedimentation. Several factors often influenced the performance of the Demulsifier [12]. These factors include the type of oil, the viscosity of the oil, presence and wettability of solids as well as the water phase size distribution [13]. There are similarities between demulsifiers and emulsifiers due to their surfactant nature. Hence, the role of the demulsifier in breaking the emulsion is to activate the influence of the intrinsic emulsifying agents. This process entails three stages namely creaming, sedimentation and coalescence [14]. An effective crude oil demulsification process involve the controlling of several parameters such as salinity, temperature, pH, water content, oil content, emulsifier/demulsifier concentration, agitation speed and duration, droplet size and distribution [15-16]. Each of these parameters can either be altered in favour of the emulsion stability. This short review presents an overview of various literature on petroleum surfactant, structure, types, and demulsification mechanism. The reviewed literature was also discussed as a function the different demulsifications techniques used for separating water from crude oil emulsion.

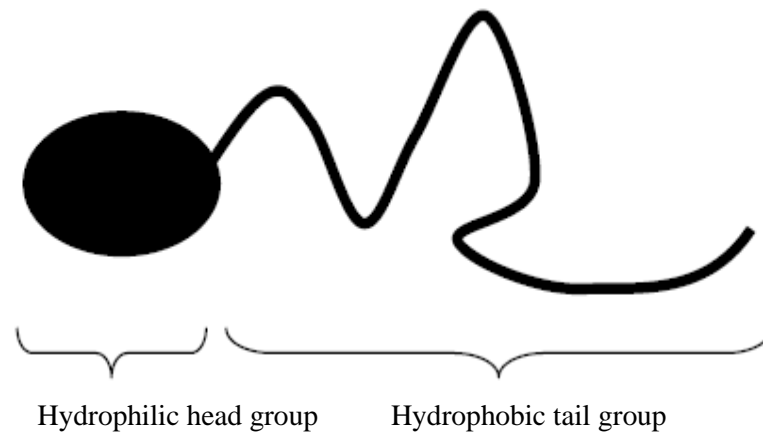
## **2. Surfactant**

Surfactants also are known as surface active agent consists of organic compounds that have the capability to drastically reduce interfacial tension. Each molecule of the surfactants is made up of a minimum of a hydrophobic and a hydrophilic group in the molecule. This implies that the hydrophobic component maintains a affinity for non-polar substances, but the preferred side of water converges with the polar region [17]

### *2.1. Surfactant Structure*

The surfactants consist of molecules that are of two types based on their chemical structure. Salomon reported that the surfactant comprised two distinct structures namely the polar hydrophilic (water-loving) and nonpolar lipophilic (oil-loving). These two structures plays enhanced the role of the surfactant as an amphipathic molecule [18].

Myers reported that is a variation between the chemical structure of surfactants in terms of their solubility properties, the conditions and the type of solvent system used. Based on the solubility properties, the surfactants can either be ahead or a tail. The head is often associated with the solubilizing group (lypophilic or hydrophilic) and the tail non-solubilizing group (hydrophobic or lipophobic) [19] as depicted in Figure 1.



**Figure 1.** Schematic illustration of a surfactant Source [20].

### 2.2. Hydrophilic-lipophilic balance

The idea of the Hydrophilic-Lipophilic Balance (HLB) was introduced in 1949 by Griffin in which he demonstrated the effect of weight for the structural property of a surfactant molecule using a specific scale and its relationship with the chemical components similar or incompatible to water [21]. Hydrophilic-Lipophilic Balance is a phenomenon whereby there is a state of equilibrium between the size and force of the hydrophilic (water-loving polar) and the lipophilic (oil-loving) groups of the emulsifier. The strength and size of the hydrophilic and lipophilic group of surfactant and demulsifier [22]. The HLB is usually scaled from 1 to 20, whereby a little HLB number implies a low solubility of water and a great number of HLB implies a high-water solubility. The application of surfactant can also be described using HLB as depicted in Table 1. [19]. Nevertheless, the stability of emulsion does not necessarily depend alone on producing an emulsion on the principle of HLB [23]. This quantification strengthens the principle propounded by Bancroft [24] which stipulated that the preferential solubilization of a surfactant in the oil phase promotes the formation of W/O emulsions. Also, the preferential solubilization of surfactant in the water phase promotes the development of O/W emulsions [25].

Although, the idea of the HLB is uncomplicated, however several weaknesses have been associated with it. One such instance is the non-consideration of the influences of temperature, salinity, co-surfactant concentration, and the nature of the hydrophilic group [26]. Studies have shown that HLB system changes with temperature, the oil types, the types and amount of additives in water and in oil and so on [27]. Moreover, it is inexact during the evaluation of various surfactant families and it is simply pertinent to nonionic surfactants [28].

**Table 1.** HLB ranges and their general areas of application [22].

Type of emulsion	HLB Range
W/O emulsifiers	4-6
Wetting agent	7-9
O/W emulsifiers	8-15
Detergent	13-15
Solubilizer	15-18

### 2.3. *Hydrophilic-lipophilic deviation (HLD)*

The shortcomings of the HBL in terms of not accounting for factors such as temperature, salinity, or the kind of the hydrophilic set has made it not feasible for comparing parameters between different families of surfactants. Hence, the need development of an equivalent process by considering all these parameters through a mathematical representation referred to as hydrophilic-lipophilic deviation (HLD). The HLD is often associated with positive or negative values in terms of O/W or W/O emulsion. The least stability of the emulsion happens when the HLD equals zero [29].

The concept of generalized physicochemical formulation known as surfactant affinity difference (SAD) was introduced by Salager, [30]. HLD can be expressed as the changes in the chemical potential,  $\mu$ , during the transfer of surfactant's molecule from oil to water. The expression representing the chemical reactivity of an optimal surfactant solution is described as  $\mu = \mu^* + RT \ln X$ , where  $\mu^*$  represents the surfactant's normal chemical potential in any reference state (superscript \*), X is the oil structure of the surfactant. At balance, where the surfactant allocates in the process of water and oil [28].

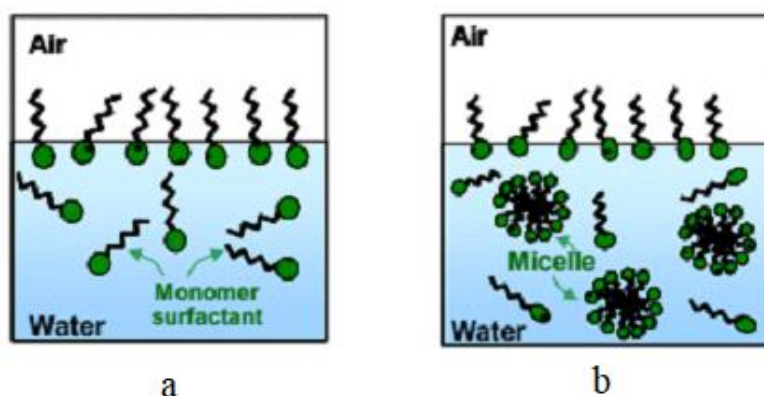
A non-stable emulsion usually occurs whenever a surfactant or combination of surfactants has a high hydrophilic or lipophilic affinity. The surfactant is immersed into the mixture and not on the surface to stabilize the emulsion. Furthermore, when there is the same affinity possesses by a surfactant both phases, there is usually a very unstable emulsion. The display of moderate lipophilicity by the surfactant (for the situation of a W/O emulsion) often result in high emulsion stability. Moreover, a moderate hydrophilic also occur (for O/W, which is related with a HLD of +3 or +4 but in the instance of a W/O emulsion or -3 to -4) [7]. The similarity of the surfactant by any of the phases can be controlled by the changes in various formulation parameters. For example the changes in the type of the components and the way they relate with the interface, the Changes in salinity (type and percentage of electrolyte), type of oil (number of carbon atoms in alkane), kind of alcohol, head and end of the surfactant, temperature and pressure [29].

### 2.4. *Relative solubility number (RSN)*

Another important term associated with analysis of surfactant is the relative solubility number. The RSN is among the properties of non - ionic surfactants that allows to calculate the combined tendency of the elements of a surfactant to the oil or aqueous system of the polar and the non-polar. RSN has been commonly used by producers of surfactants as it is challenging to calculate experimentally due to the simplicity and objectivity of its calculation relative to HLB. The surfactant's hydrophilicity is highly dependent on the RSN value [31-32].

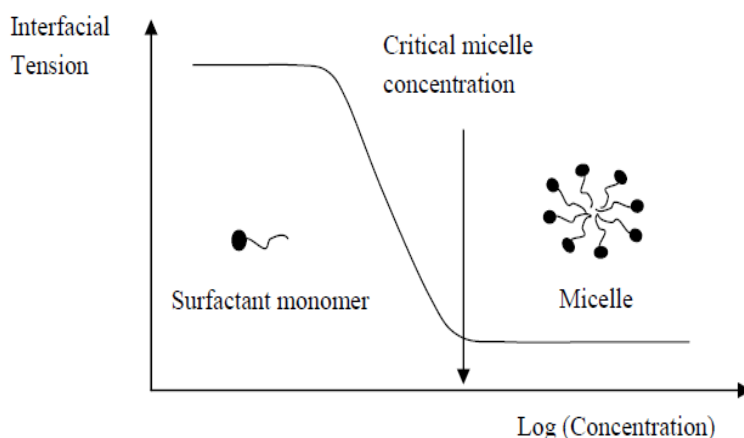
### 2.5. *Critical Micelle Concentration (CMC)*

Since the surfactant molecules have a certain concentration inside the emulsion, which leads to the formation of aggregates such as hydrocarbons that accumulate as the head is directed to the water side, causing the formation of a polar crust [33]. As shown in Figure 2, the head is directed toward the aqueous environment while the hydrophobic side of the tail is directed toward the organic part. This pattern reduces the energy used to break down the emulsion. These aggregates are known as micelles and the concentration at their formation is the critical micelle concentration (CMC) [12].



**Figure 2.** Aqueous surfactant solution a) below the cmc, b) up the cmc [33]

It has been reported that the surfactant's structural features often influenced the formation of the CMC. As a result of this surfactant structure, there will be a rise in CMC when there is the increase in the hydrophilic headset or a decrease when the hydrophobic end is reduced. A significant break in the interfacial tension versus concentration curve shown in Figure 3 is often found by the pure surfactant CMC. In addition, the break in the curve may not be sharp for the surfactants' mixture, [34].



**Figure 3.** Micellization of pure surfactant particles [35].

When the surfactant occurs upstairs the CMC, it can function as emulsifiers that will tolerate a formation of a compound that is usually unsolvable. The, dilution of the concentration of surfactant in the aqueous solution display the characteristic of a normal electrolytes whereas a higher concentration of surfactant result in very different behavior [36].

### 3. Classification of Surfactant

According to Myers, an emulsifier can be defined as a substance added to a mixture of two unmixed liquids to help form the emulsion and its stability.[19]. Whereas, demulsifier was depicted as a surfactant liable for the flocculation, coalescence or wetting agent. The negative charge might be caused by the hydrophilic group of the surfactant molecule. On the other hand, a positive charge, both positive and negative charges, or no charge at all can also be formed. These phenomena can be classified as anionic, cationic, amphoteric (or zwitterionic), and non-ionic surfactants.[22]. In general, the non-ionic surfactants have good properties such as they are not affected by the salinity of the water, have an

acceptable price, and have no unwanted residues that affect the properties of the oil [37-38]. Whereas, the cationic surfactants are often costlier than anionics, due to the high-pressure hydrogenation reaction performed during their synthesis. Consequentially, they are only employed in a situation where is lack of cheaper substitute [39]. Table 2 summarize the four class of the surfactants.

**Table 2.** List of surfactant [19]

Surfactant	Type Description
Ionic	A negatively charged surfactants present on the active surface components of the molecule.
Cationic	Surfactant which transfer a positive shipment on the active surface component of the molecule.
Amphoteric	A cationic or anionic based surfactant which are on the pH or other solution which include those that are zwitterionic that possessed repeated charges of each type.
Nonionic	Surfactants without electrical charges, in which their water solubility originated from the presence of polar functionalities with the ability of strong hydrogen bonding interaction with water

Surfactants can also be classified based on their commercial usage. There is an increasing used of surfactants in the manufacturing oil and gas for the creation of drilling liquids. Similarly, surfactants also find specific application in water-based muds [40]. There are series of other applications of surfactants Such as alkaline fluid formulations for emulsion of oil in water, as wellbore inhibitors, removing unwanted foam from some additives, as well as polymers as surfactants to improve fluid properties in low pressure tanks. [41].

#### 4. Surfactants as Demulsifiers

According to Fan et al., demulsification needs the breaking of emulsions to separate the water from oil. After demulsification, it is expedient to recover the emulsion in their original phase to achieving the right quality and specification of the crude oil for production facilities. Studies have shown that approximately 80% of crude oil produced globally are in the form of emulsion like such as w/o emulsions or o/w emulsions [42]. The formation of the emulsion is often caused by the co-production of water from the oil reservoir. During processing, sufficiently high mechanical energy input (shear forces) are introduced to the disperse water as droplets in the oil phase by the pressure gradients over chokes and valves [43].

There are wide practical applications of demulsification in the petroleum industry, coating, painting, and wastewater treatment. This demulsification process has attracted vital importance due to the complication of the existing technologies used for breaking emulsions. For instance, the steam and caustic injection or combustion process, for in-situ recovery of heavy crude oils, is complex leading to the production of viscous emulsions of oil, water, and clay. Crude oil demulsification is an integral part of crude oil production [44]. It is vital for the separation of water from oil to produce a fluid (typically less than 0.5% solids and water). By this economic loss and operational difficulties would be prevented and the fluid would be suitable for transportation via pipelines for further processing and refining. Un removed emulsions in crude oil often result in processing difficulties such as corrosion of pipes and equipment [45]. Certain qualities such as high separation rate, low residual water content in the crude oil, and a low oil concentration in the water to be disposed of are desirable, however difficult to attain [46]. Several approaches such as thermal, mechanical, electrical and chemical can be employed for demulsification of crude oil. Amongst all these techniques, chemical demulsification using a demulsifier is one of the commonly used in the industry to break emulsions [47]. The other techniques are used both with physical methods to assistance the demusification emulsion [48].

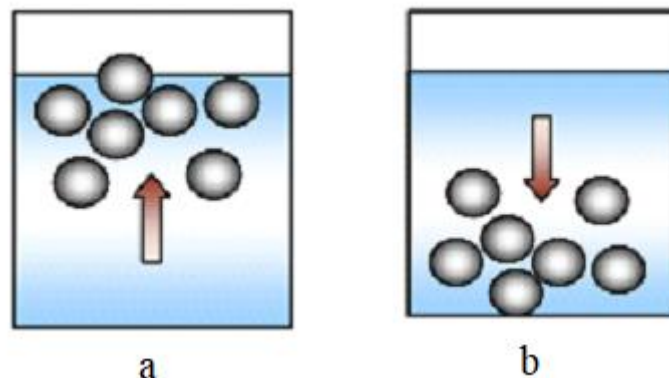
In the past decades, several demulsifiers have been developed. One of the oldest used demulsifier that has been used since the 1930s is the nonionic surfactants. Non-ionic surfactants are divided into two hydrophilic and hydrophobic groups, where the first group includes hydroxyl, carboxyl, ethoxyl, and amine group, while the other group consists of alkyl, alkyl phenol and oxypropylene. Hundreds of products can be created by changing the ratio and type of one of the two groups [49].

## 5. Demulsification Mechanism

Most emulsions are dynamically unstable, as they tend to separate into two phases over time due to the large surface area and system energy, and this leads to different emulsion properties such as dropping size distribution, average droplet size and other characteristics.[50]. Before the emulsion separates to its original stages, it goes through several stages. A mechanism such as creaming/sedimentation, flocculation, Oswald Ripening and coalescence are involved in the process. Figure (7) depicts the schematic representation of the destabilizing mechanism.

### 5.1. Creaming and Sedimentation

The term creaming means floating oil droplets in the crude oil emulsion as a result of the variation in the densities of the phases (Figure 4a). During water-in-oil emulsion, there is a settling of the water droplets at the bottom which is often referred to as sedimentation (Figure 4b). Creaming and sedimentation could be influenced by the decrease or rise in the density variation between the two phases leading to deceleration or speeding up the two processes [51].



**Figure 4.** Illustration of (a) creaming (b) sedimentation progressions [51].

Based on the report of [52], an emulsion with small drops ( $R < 1 \mu\text{m}$ ) are not sensitive to sedimentation or creaming as a result of Brownian motion which is dominated by gravitational forces. Sediment or cream drops resulted for a drop size larger than a few microns. Agreeing with Stoke's law, for an oil is the continuous phase, the creaming or sedimentation rate is depicted by Equation 1. [10, 53]

$$v_s = \frac{gD^2(\rho_w - \rho_o)}{18\mu_o} \quad (1)$$

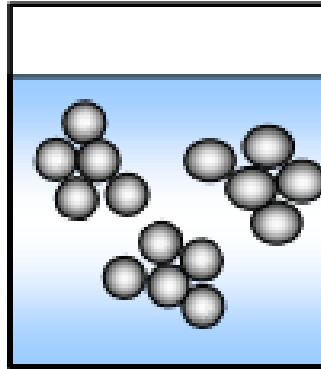
Where,  $g$  is representing the gravity constant and  $D$  is diameter of the droplets. While,  $\rho_w$  and  $\rho_o$  stand for density of water and oil, respectively. Whilst,  $\mu_o$  be a symbol of viscosity of oil phase.

### 5.2. Flocculation/Aggregation

The occurrence of aggregation is usually noticed when there is close droplets leading to the formation of flocs. This means during the flocculation process the droplets take the form of a cohesive group.



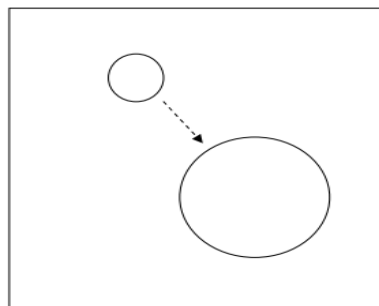
DLVO theory is the flocculation approach that is frequently employed in emulsion literature to explain emulsion interaction. DLVO theory is developed by Derjaquin [54], and independently applied by Verwey [55]. As reported by Hamnisdal, flocculation occurs when the Vander Waals' energy overrides the repulsive energy, causing strong or weak downward forces [56].



**Figure 5.** Representation of flocculation/aggregation [57].

### 5.3. 5.3. Ostwald ripening

Based on the work of Fernando et al. [58], Ostwald ripening depicts a phase that comprises of a diffusive change of the dispersed phase from smaller to larger droplets as shown in Figure 6. Ostwald ripening serves a key function in the stability of oil-in-water emulsion [59]. Gonzalez, and Paola, [60] reported that high Laplace pressure usually cause the surface concentration at a dispersed phase to be greater at the surface minor droplets. Hence, there is a diffusion of small materials that are present in the small droplets through the continuous phase leading to the formation of a larger drop. Previous study revealed that the presence of ionic micelles in a continuous phase usually give rise to a small effect on the ripening rate. This leads to a rise in the size of the droplets inside the emulsion [61].

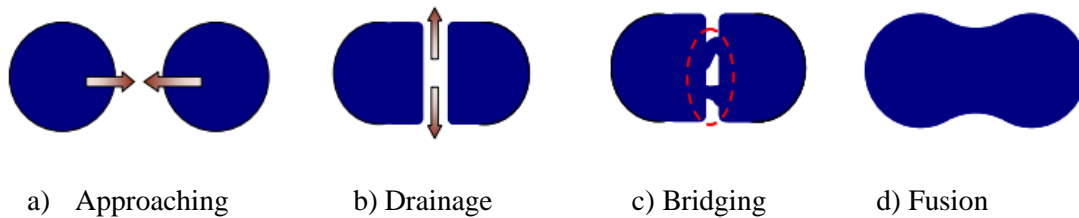


**Figure 6.** Mechanism of Ostwald ripening [22].

### 5.4. Coalescence

Coalescence is a phenomenon whereby two or several droplets are combined resulting in the formation of a large drop. Coalescence occurs when there is a breakage in the thin film between the two drops where they merge to obtain a one drop [62]. As shown in Figure 7 (a), a two drops close together during coalescence because convection effect of creaming. The coming together of these droplets might deform the surface and create a planar surface between the droplets. During the same period, there is a drain between the liquid in the two droplets enabling the droplets to approach even closer. When drainage

occurs, the surface material spreads and leads to the formation of gaps on the surface with less interfacial material. As shown in Figure 7 (c), the bridges between the droplets can originate from the gaps thereby resulting in the fusion of the two droplet as depicted in Figure 7 (d) [63].



**Figure 7.** Stage of Coalescence [22].

## 6. Demulsification systems

The demulsification process requires breaking or separating the emulsion into its basic stages. Crude oil demulsification is crucial in ensuring the appropriate specification and quality are attained during production and processing. In the downstream processing of crude oil, it is expedient to ensure the separation of water from the crude oil prior to refining. To achieve this, several techniques have been widely employed to separate water-in-oil emulsions. Studies published in the literature have shown that the resistance of emulsion to the fusion or breakage depends mainly on the type of oil and the physical and chemical composition from which it is formed, as well as on the emulsifying agents and aging. Which leads to different strategies and methods used in the demulsification process from one field to another [64]. Several approaches to separate emulsion from crude oil have been reported in literature. Chemical and physical techniques are the two vital approaches of demulsification that have been widely investigated. The chemical approach involves use of appropriate demulsifier as additives to emulsion while the physical techniques involve heating, electrical, or a mechanical method [65]. Sometimes the two techniques can be combined for effective demulsification. For instance, a thermo-chemical technique for demulsification involves the addition of a demulsifier and heat treatment and it is frequently used in the industry [66]. Other methods used in demulsifying emulsion include filtration, pH adjustment, and membrane separation [67].

## 7. Conclusions

The formation of emulsion is often caused by the mixture of water with crude oil in the well, during production or in the course of desalting process. The formation of these emulsions often results in significant operational and economic problems which justifies the quest to solving the challenges with these undesirable emulsions. To mitigate the challenges associated with the presence of emulsions in crude oil requires a thorough understanding of surfactant, structure and demulsification mechanism. Besides, there is a need to also go beyond just knowing the consequence of formation of emulsifier, but the factors that induce its formation as well as those that boost its stabilization. Hence, based on intense search of the literature, there are several studies conducted on the demulsification of emulsion using various techniques. Hence, this study presented a short review of crude oil emulsion, surfactant, construction, grouping, properties and demulsifiers mechanisms with the intention of building a primary database for researchers, to have a glance of information related research.

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