# A Review of Water-in-Crude Oil Emulsion Stability, Destabilization and Interfacial Rheology

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**Abstract:** Stable water-in-oil emulsions may form during the production and transportation of crude oil such as in highly turbulent nozzles and piping. Such emulsions introduce technical challenges as they must be resolved to provide the specified product quality. Emulsion behavior is largely controlled by the properties of the adsorbed layers that stabilize the water-oil surfaces. The complexity of petroleum emulsions comes from the oil composition in terms of surface-active molecules contained in the crude such as resin and asphaltenes. These molecules can interact and reorganize at water-oil interfaces. In order to successfully mitigate, the problems of stable emulsions, a thorough knowledge of component properties, behavior, interactions and effect on water-oil interfacial properties must be developed for pressures and temperatures ranging from ambient to high. Probably, more study on this area will reveal information concerning bulk viscosity, shear properties, mechanism and kinetics of film formation, surfactant adsorption and film rupture that ultimately govern emulsion behavior. The important stabilization mechanisms of emulsions have been identified but the difficulty still lies in the assessment of the relative level of influence that individual mechanisms and variables have over the final stability. This review seeks to bring to light recent findings related to emulsion stability, destabilization and interfacial properties.

**Key words:** Emulsions, stabilize, reorganize, viscosity, crude oil, interfacial properties

## INTRODUCTION

Crude oil is found in reservoirs along with water or brine and during oil removal, water is often co-produced. Water is also injected into the crude to remove salts or as steam to improve fractionation. An emulsion is a colloidal dispersion of one liquid (disperse phase) in another (continuous phase). Petroleum emulsions (typically water-in-oil) readily form with water in the highly turbulent nozzles and piping used for oil production. These emulsions can increase pumping and transportation expenses, corrosion of pipes, pumps, production equipment and distillation columns and the poisoning of downstream refinery catalysts. It is well recognized that emulsion stability arises from the formation of elastic interfacial film. Specker and Kilpatrick (2004) showed that soluble aggregates from the oleic phase adsorb at the oil-water interface and present a physical barrier to flocculation and coagulation of the dispersed phase droplets. Researchers have linked interfacial film and emulsion forming behavior of crude oil to petroleum asphaltenes and their interplay with resins as a solubilizing agent. The effect of asphaltenes solvency on the stability of water-in-crude oil emulsions have been

studied by McLean and Kilpatrick (1997) while the role of asphaltenes in the stability of water-in-bitumen emulsions has been reported by Yen et al. (1999). Mixing immiscible liquids such as oil and water with a surface active agent will often yield an emulsion of oil droplets in water (oil-water) or water droplets in oil (water-oil) according to Bancroft's rule. Bancroft's rule states that the liquid in which the surfactant is soluble becomes the continuous phase. Other factors such as oil-water volume fractions, surfactant concentration and hydrophile-lypophile balance will influence the type of emulsion formed. After droplets are completely dispersed within the continuous phase, surfactants migrate to the oil-water interface and can inhibit droplet rupture by steric, Marangoni-Gibbs or rigid-film forming interactions. Abdurahman et al. (2007a) reported that emulsions are characterized by the type of emulsion (w/o or o/w) nature of emulsifying agents present, bulk viscosity and interfacial viscosity.

## STABILIZATION OF EMULSION

Hannisdal et al. (2007a, b) reported that in order to understand the complex picture behind water-in-crude oil emulsion stability, a thorough knowledge at both ambient

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and high pressures should involve the structure and properties of the crude oil components, their association tendencies and accumulation at water-oil interfaces, their solubilities and sensitivity towards changes in pressure and temperature, the special features of acidic components and their association structures in water-oil systems and above all how these components by themselves or by an intricate interplay form highly elastic interfaces protecting the droplets against coalescence.

Mechanisms of emulsion stabilization have been discussed with steric, Marangoni-Gibbs and rigid-film forming interactions being the most common. Kloet (2000) elaborated on the mechanisms.

**Steric stabilization:** Surfactants containing a hydrophilic, polar head group and hydrophobic tail group will typically orient themselves at oil-water interfaces. The head group has a natural affinity for water while the tail group will preferentially remain in the oleic phase. Dispersed water droplets will thus be coated by surfactant material with hydrophobic tails protruding into the oil phase. When droplets approach each other, their adsorbed surfactant tails prevent droplet contact and coalescence.

**Marangoni-Gibbs effect:** The Marangoni-Gibbs effect can stabilize emulsions by preventing the drainage of continuous phase from between two opposing droplets. As droplets approach, their surfaces eventually become plane parallel and the film layer attempts to drain. This outward convection draws surfactants towards the droplet edges leaving a region of low surfactant concentration in the middle. This process sets up an unfavorable interfacial tension gradient along the interface. Surfactant diffusion thus proceeds in the direction opposing convection to eliminate the interfacial tension gradient. Stable emulsions can result from the balance of surface diffusion and film convection.

**Rigid film formation:** A third and most probable mechanism of petroleum emulsion stabilization comes from an adsorbed layer of material with high rigidity and elasticity. Asphaltenic aggregates in the oleic phase will adsorb to the oil-water interface and form a consolidated film or skin that resists droplet coalescence. This process can be quite complex and depends on asphaltene chemistry, solvency and the kinetics of diffusion and adsorption. Other factors leading to stable emulsions are high viscosity continuous phases, small-dispersed phase volume and droplet size and low interfacial tensions.

The appearance of other smaller surface-active molecules (different from wax and asphaltenes) at the oil-water interface has also been investigated by Kloet (2000). She reported that the composition at the interface is a combination of surface-active molecules in association with colloidal particles such as asphaltenes and possibly mineral solids. This interfacial composition leads to the formation of an interfacial skin which is easily seen upon carefully sucking a water droplet from the oil environment. The interfacial skin remains behind as a wrinkled phenomenon. Kloet (2000) further reported that these viscous interfacial films or skins contribute to water-in-crude oil stability by providing a barrier to droplet coalescence.

Other researchers have focused on the detailed effects of viscoelastic properties, interfacial tensions and shear viscosity. Hannisdal *et al.* (2006) reported that the coalescence of water droplets in a water-oil emulsion is accompanied by a reduction in surface area and hence, a compression of the adsorbed crude oil surfactant.

The viscoelasticity of an interfacial film can be readily demonstrated by slowly condensing a surfactant film and observing the resulting change in interfacial tension. Several studies on the compressibility of interfacial films were conducted and reported by Singh *et al.* (1999). It was found that the anionic component of fractionated crude oil could most effectively adjust to overcome the compressing barrier.

They concluded that the anionic oil fractions were best suited for emulsion stabilization. The effect of salts on film pressure was also investigated. Both anionic and cationic fractions exhibited enhanced compression in the presence of salts. The increased compressibility was attributed to the significant rise in concentration of the anionic polar molecules at the interface and in the film.

Abdurahman *et al.* (2007b) reported that the percentage of water separated is the best indicator of emulsion stability because it is a measure of the degree of aggregation or flocculation of individual emulsion water droplets and coalescence of aggregated water droplets. They reported that water phase pH has a strong influence on emulsion stability. Interfacial tension alone cannot be used as a gauge for emulsion stability in all cases. Interfacial tension values can however provide useful information on the amount of energy needed to create emulsions. Dynamic interfacial tensions of crude oil against water have also indicated that time-dependent surface adsorption may be due to the slow diffusion of crude oil natural surfactants to the oil-water interface followed by steric rearrangement at the interface. In general, the studies relating to the stability of water-in-crude oil emulsions are now focusing on the interfacial characteristics and composition of the film formed at the oil-water interface rather than on bulk fluid properties.

## DESTABILIZATION OF EMULSION

The destabilization of crude oil emulsions forms an integral part of crude oil production. Stable emulsions are typically broken using gravity or centrifugal settling, application of high electric fields and addition of destabilizing chemicals (demulsifiers). Other methods such as pH adjustment, filtration, membrane separation and heat treatment techniques may also be used.

The use of condensed $CO_2$ has also been suggested and studied by Zaki *et al.* (2003). Gravity settling tanks, cyclones, centrifugal separators and other kinds of mechanical separation tools are typical equipment used in the destabilization of crude oil emulsions. However, this hardware is of considerable volume as well as expensive to install on offshore platforms conditions. It is therefore of great economical benefit whenever the installations can be kept at a minimum in size and number. Chemical destabilization is therefore a very common method for destabilizing emulsions. Also, the capital cost of implementing or changing a chemical emulsion-breaking program is relatively small and can be accomplished without a shutdown.

The separation rate of a water-oil emulsion depends upon the matching of the demulsifier with the process residence time, the concentration and the stability of the emulsion, the temperature, the process vessel, the mixing energy and the type of stabilizing mechanisms. Through building up more fundamental knowledge concerning the processes involved in stabilizing and breaking the emulsions, the development and use of environmentally friendlier chemicals is facilitated.

Also, the optimization of type and amount of chemicals employed, contributes to reducing the oil content in the produced water offshore. Commercial demulsifiers are typically mixtures of several components which have various chemical structures and cover a wide molecular weight distribution. Some typical chemical structures used as demulsifiers are listed by Jones *et al.* (1978) and Djuve *et al.* (2001). Each component of the demulsifier typically possesses a different partitioning ability and a different interfacial activity and thus should provide a range of properties such as:

- Strong attraction to the oil-water interface with the ability to destabilize the protective film around the droplet
- The ability to function as a wetting agent, changing the contact angle of solids
- The ability to act as flocculants
- Promotion of film drainage and thinning of the interdroplet lamella by inducing changes to the interfacial rheological properties such as decreased interfacial viscosity and increased compressibility

Auflem (2002) reported that demulsifiers with equal partitioning between the aqueous and oil phase, gave the best destabilizing efficiency. This balance would lead to a maximum in the surface adsorption of demulsifier and a minimum in interfacial tension. However, partitioning would not be a dominant factor when other effects such as dissolution of the interfacial material or their flocculation by the demulsifier occur. Abdurahman *et al.* (2007b) reported that Amine demulsifiers group were more effective in emulsion breaking than polyhydric and acid demulsifiers. Decylamine demulsifiers are the best in terms of separation of both water and oil from emulsion. It separates 80% water and 87% oil from emulsion.

When two water droplets approach each other, the capillary pressure acting normal to the interface causes liquid to be squeezed out of the film into the bulk. This liquid flow results in a viscous drag on the surfactants in the sublayer and the adsorbed emulsifier are carried away towards the film periphery thereby creating a nonuniform concentration distribution. Demulsifier molecules may then occupy the empty spaces available for adsorption and due to the high interfacial activity of the demulsifier, the interfacial tension gradient is reduced.

This leads to a strong increase in the rate of film thinning and ultimately when the film thickness decreases below some critical value, the film ruptures and the droplets coalesce. Strong attraction to the oil-water interface is often dependent on diffusibility and interfacial activity of the demulsifier. For fast diffusion to the interface, the molecular weight of the demulsifier becomes important. The demulsifiers relative solubility in oil is also important for mass transport to the interface and where this is inadequate, carrier solvents (e.g., alcohols or benzene derivatives) are often used. At the interface, the demulsifier may influence the droplet interfacial film material by displacement, complexation, changing the solubility in the continuous phase, changing the viscosity of the interfacial film or through quick diffusivity and adsorption thus, inhibiting the Marangoni-Gibbs effect which counteracts film drainage.

In residual emulsions, the droplets are finely dispersed and widely distributed and the flocculating ability of the demulsifier is required to gather up the droplets. Then, high molecular weights highly branched demulsifiers with an affinity for the water droplet are necessary. For emulsions with particle-stabilized films, demulsifiers which act as wetting agents may prove effective. The demulsifier may adsorb on to the solids, causing them to be more oil or water wettable and thereby more easily transported into the continuous phase away from the interface. Auflem (2002) reported some situations demulsifiers have been used as inhibitors i.e., injected

before the emulsification process has taken place. This gives the demulsifier the chance to compete with the emulsifying agent in the process of covering the interface as the emulsifying process occurs and thereby hinder the formation of a stabilizing film. One should however not forget to clarify the effect of concentration of the injected chemicals on the emulsion stability as too much chemicals injected may result in an overtreat where the emulsion is actually stabilized or a new emulsion type is created. Also, the injected demulsifiers should be checked to be compatible with other chemicals (corrosion inhibitors, scale inhibitors and flow enhancers) used in the stream as well as the components in the produced stream itself.

The effect of increased temperature is the sum of changes in several parameters. For instance, changes in the solubility of the crude oil surfactants or injected treating chemicals may occur as a result of increasing temperature. The density of the oil is reduced faster than the density of water as temperature increases thereby accelerating the settling. Bulk viscosity of the crude oil decreases with increasing temperature hence facilitating an increased collision frequency between water droplets in addition to increasing the settling rate. Essential for the coalescence, especially in flocculated systems is the influence of the interfacial viscosity. Depending on the type of interface the interfacial viscosity may decrease, increase or remain unchanged with increased temperature. Jones *et al.* (1978) and Abdurahman and Yunus (2009) studied the coalescence of water droplets in water-in-crude oil emulsions and concluded that coalescence of water in the presence of a demulsifier is characterized by very short initial coalescence time. Electrical resolution of crude oil emulsions is possible since the systems are relatively non-conducting. Auflem (2002) mentioned the main behaviours of a drop or a pair of drops under an electric field. The mechanisms promoting separation are the result of either forces between particles resulting from induced dipoles charges (dipole coalescence) or forces that result from interactions between unidirectional field and particles having a net charge (electrofining). The principle behind the electrically induced coalescence is often divided into:

- Non interacting droplets approaching each other
- Deformation of droplets and formation of plane-parallel films
- Thinning of the films to a critical thickness at which the film becomes unstable, ruptures and the two drops unify and form a single large droplet

Important features of a typical electrocoalescer are the electric field (AC or DC), frequency and set up for electrodes. The electrocoalescers in the oil and petroleum industry use both AC and DC electric fields for the separation of water-in-oil emulsions. One problem is that most of the equipment in the market today are big and bulky and it would therefore be of interest to develop small portable devices, incorporating features such as an optimum applied field strength combined with centrifugal force to further enhance the separation. Nour *et al.* (2007) reported that microwave radiation can be an effective tool to separate emulsified water from oil mixtures.

Zaki *et al.* (2003) successfully used $CO_2$ to break water-in-crude oil emulsions and resolve bulk water. The process was found to be applicable to crude oils having different chemistries, asphaltene content and viscosities. The mechanism by which $CO_2$ destabilizes the emulsion was found to involve the precipitation of asphaltenes due to the antisolvent effect of $CO_2$. However, the use of $CO_2$ for destabilization of emulsions requires more study as literature on this subject is scanty.

## RHEOLOGY

Steinborn and Flock (1983) studied the rheology of crude oils and water-in-oil emulsions and they reported that emulsions with high proportions of water exhibited pseudo-plastic behaviour and were only slightly time dependent at higher shear rates. Omar *et al.* (1991) measured the rheological characteristics of Saudi Arabia crude oil emulsions and showed that Non-newtonian emulsions exhibit pseudo-plastic behaviour and followed a power-law model. Mohammed *et al.* (1993) studied crude oil emulsions using a biconical bob rheometer suspended at the interface and concluded that more stable emulsions displayed a viscoelastic behaviour and a solid-like interface. Demulsifiers changed the solid-like interface into a liquid one. Tadros (1994) summarized the fundamental principles of emulsion rheology. Emulsions stabilized by surfactant films (such as resins and asphaltenes) behave like hard sphere dispersions. These dispersions display viscoelastic behaviour. Water-in-oil emulsions show a transition from a predominantly viscous to a predominantly elastic response as the frequency of oscillation exceeds a critical value. Thus, a relaxation time can be determined for the system which increases with the volume fraction of the discontinuous phase. At the critical value, the system shows a transition from predominantly viscous to predominantly elastic response. This reflects the increasing steric interaction with increases in volume of the discontinuous phase. Pal (1996) studied the effect of droplet size and found it had a dramatic influence on emulsion rheology. Fine emulsions have much higher viscosity and storage moduli than the corresponding

coarse emulsions. The shear thinning effect is much stronger in the case of fine emulsions. Water-in-oil emulsions age much more rapidly than oil-in-water emulsions.

## INTERFACIAL PROPERTIES

Interfacial phenomena control the properties of emulsions and foams in the petroleum, food products, cosmetics and pharmaceutical industries. Studying the rheology of emulsions and foams can provide valuable information concerning bulk viscosity, shear properties and other end use issues.

The knowledge gained by investigating interfacial properties, however is considerably more revealing than the information available from bulk emulsions. From interfacial studies one can determine the fundamental mechanisms and kinetics of film formation, surfactant adsorption and film rupture that ultimately govern emulsion behavior.

Sjoblom *et al.* (1990) studied model emulsions stabilized by interfacially active fractions from crude oil and reported that a good correlation exists between interfacial pressure of the fractions as measured in a Langmuir trough and the stability of emulsions as measured by the amount of water separated with time. They also reported that surface tension as measured by the drop volume method did not show a surfactant like behaviour for the asphaltenes and resins.

Hartland and Jeelani (1994) performed a theoretical study of the effect of interfacial tension gradients on emulsion stability. Dispersion stability and instability were explained in terms of a surface mobility that is proportional to the surface velocity.

When the interfacial tension gradient is negative, the surface mobility is negative under some conditions which greatly reduces the drainage so that the dispersion is stable. This is a normal situation as surfactant is present at the interface. Demulsifier molecules penetrate the interface within the film thereby lowering the interfacial tension sufficiently and causing a positive interfacial tension gradient. Drainage is subsequently increased and the emulsion becomes unstable.

Ese *et al.* (1998) studied the film-forming properties of asphaltenes and resins using a Langmuir trough. Asphaltenes and resins were separated from different crude oils. It was found that the asphaltenes appear to pack closer at the water surface and form a more rigid surface than the resins.

The size of asphaltene aggregates appears to increase when the spreading solvent becomes more aliphatic and with increasing asphaltene bulk concentration. Resin films

show high compressibility which indicates a collapse of the monomolecular film. A comparison between asphaltenes and resins shows that resins are more polar and do not aggregate to the same extent as the asphaltenes. Resins also show a high degree of sensitivity to oxidation. When resins and asphaltenes are mixed, resins begin to dominate the film properties when resins exceed about 40% wt.

The interfacial mobility can be evaluated using several models, depending on whether the surfactant is initially located in the dispersed phase or the continuous phase. A drop collision causes a convective flux of continuous phase away from the contact zone. This may result in a tangential drag of surfactant molecules along the fluid flow.

The appearance of gradients of surfactant concentration (interfacial tension) is then opposed by the dynamics of surfactant molecules by interfacial diffusion, bulk diffusion, Gibbs elasticity or interfacial viscosity. Due to complex geometric considerations of the contact zone, the characteristics of the adsorbing unit, the mass transfer mechanism and rates, possibility for interfacial reactions or reorganization and considerations of the interfacial coverage, the attempts to seek mathematical equations for the interfacial mobility are confusing. Describing the lifetime of emulsions can be even more confusing.

## CONCLUSION

The emulsifying components of crude oil emulsions have been identified. However, the non-predictability and wild variation in the interfacial activity of these agents have frustrated many researchers. The important stabilization mechanisms have probably also been identified but the difficulty still lies in the assessment of the relative level of influence that individual mechanisms and variables have over the final stability.

Since, interfacial phenomenon controls the properties of emulsions, more study on this area will reveal information concerning bulk viscosity, shear properties, mechanism and kinetics of film formation, surfactant adsorption and film rupture that ultimately govern emulsion behavior. The use of more recent instruments in the measurement of interfacial tension of emulsion and the use of high pressure and high temperature rheometer to measure the viscosity and shear properties of emulsion is also recommended. This will enable the effect of various pressure and temperature range on the emulsion to be studied simultaneously and a correlation established. Since, properties of crude oil differ from place to place, interfacial study of Niger Delta crude oil as its counterpart in Saudi Arabia, Norway etc. is strongly needed as literature about its emulsion is lacking.

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