# CHAPTER II
# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Formation of Water-in-Crude Oil Emulsion

The oilfield emulsions can be classified into three broad groups:

- Water-in-oil (w/o) emulsions

- Oil-in-water (o/w) emulsions

- Multiple or complex emulsions

The w/o emulsions consist of water droplets in a continuous oil phase, and the o/w emulsions consist of oil droplets in a continuous water phase. The o/w emulsions are sometimes referred to as "reverse" emulsions. In the oil industry, the most oilfield emulsions are w/o emulsions. Multiple emulsions are more complex and consist of tiny droplets suspended in bigger droplets that are suspended in a continuous phase. For example, a water-in-oil-in-water (w/o/w) emulsion consists of water droplets suspended in larger oil droplets that in turn are suspended in a continuous water phase (Kokal, 2005).

Stable emulsions are characterized by properties that prevent the coalescence of the small water droplets, while in unstable emulsions, the larger water droplets quickly coalesce. Formation of water-in-crude oil emulsion is shown in Figure 1.
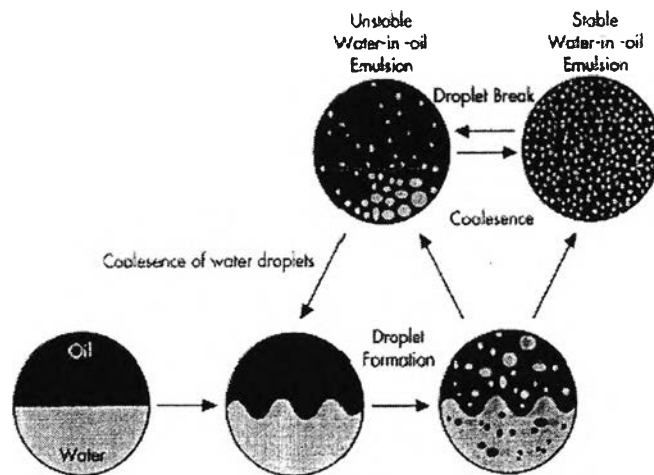


**Figure 2.1** Formation of water-in-oil emulsion (Lee, 1999)

## 2.2 Stability of Emulsions

The stable emulsion is composed of an aqueous phase, an oil phase and an emulsifying agent. Particles and surfactants found in crude oil can act as emulsifying agents, which promote and stabilize water-in-oil emulsions. If the concentrations of particles and surfactants are sufficiently high, then water droplet coalescence is prevented, leading to stable emulsions.

Emulsions are stabilized by emulsifiers (i.e., surface-active agents, or surfactants) that tend to concentrate at the oil/water interface where they form interfacial films. This generally leads to a reduction of interfacial tension (IFT) and promotes dispersion and emulsification of the droplets. Naturally occurring emulsifiers in the crude oil include higher boiling-point fractions such as waxes, asphaltenes and resins and can exist in both the dissolved and particulate form. Waxes are high-molecular-weight alkanes. Asphaltenes are defined as the solid material precipitating from crude oil after the addition of a low boiling liquid hydrocarbon such as heptane or pentane. The resins are defined as the pentane-soluble but methanol-insoluble fraction of crude oil. Resin particles are generally smaller than asphaltene particles and most of the metal porphyrins are in the asphaltene fraction. Asphaltenes have higher molecular weight and more polar than resins. Waxes cannot act as emulsifying agents by themselves but can act in combination with resins or asphaltenes to produce stable oil-in-water emulsions. Within the asphaltenes fraction, the nickel porphyrins appear to play an important role in emulsion formation by pervading at the oil-water interface forming a film, which prevent coalescence of water droplets (Lee, 1999).

Oilfield emulsions are characterized by a number of properties including appearance, basic sediment and water, droplet size, bulk and interfacial viscosities, and conductivities.

From a purely thermodynamic point of view, an emulsion is an unstable system. This is because there is a natural tendency for a liquid/liquid system to separate and reduce its interfacial area and its interfacial energy. However, most emulsions are stable over a period of time.

2.2.1 <u>Factors Affecting Stability</u> The important factors that affect emulsion stability include the following (Kokal, 2005).

*Heavy fraction in Crude Oil:* The naturally occurring stabilizers are concentrated in the higher-boiling-point, polar fraction of the crude oil. These include asphaltenes, resins, and oil soluble organic acids and bases. These compounds are the main constituents of the interfacial films surrounding the water droplets that give the emulsions their stability.

*Solid:* Fine-solid particles present in the crude oil are capable of effectively stabilizing emulsions. The effectiveness of these solids in stabilizing emulsions depends on such factors as the particle size, interparticle interaction, and the wettability of the solids. Solid particles stabilize emulsions by diffusing to the oil/water interface where they form rigid structures (films) that can sterically inhibit the coalescence of emulsion droplets. Furthermore, solid particles at the interface may be charged, which may also enhance the stability of the emulsion.

*Temperature:* Temperature can affect emulsion stability significantly. Temperature affects the physical properties of oil, water, interfacial films, and surfactant solubility in the oil and water phases. These, in turn, affect the stability of the emulsion.

*Droplet Size:* Generally, emulsions that have smaller-sized droplets will be more stable. For water separation, droplets have to coalesce, and the smaller droplets, the longer it will take to separate. The droplet-size distribution affects emulsion viscosity, it is higher when droplets are smaller.

*pH:* Water-phase pH has a strong influence on emulsion stability. The stabilizing, rigid-emulsion film contains organic acids and bases, asphaltenes with ionizable groups, and solids. Adding inorganic acids and bases strongly influence their ionization in the interfacial films and radically change the physical properties of the films. The pH of the water affects the rigidity of the interfacial films.

Xia *et al.* (2004) studied the influence of asphatenes and resins on the stability of emulsions. Emulsions were prepared by using distilled water, jet kerosene and varying concentrations of asphaltenes and resins. It was found that emulsions stability was related to the concentrations of the asphatenes and resins in crude oil. Adsorption of these components forms films with a certain extent of mechanical

strength at the droplet interface and renders the droplets stable to coalescence. The percentage of coalesced water droplets decreases with the concentration of the asphaltenes or resins in the range from 0.3 up to 0.5% or 1.0 up to 2.0%. However, after the concentration of the asphaltenes or resins is increased to 0.7% or 3.0%, the percentage of coalesced water droplets increases with the concentration of the asphaltenes or resins, with a subsequent decrease in the amount of droplets of the emulsion. The state of dispersion of the asphaltenes and resins (molecular versus colloidal) is critical to the strength or rigidity of the interfacial films and hence to the stability of the emulsions.

Schorling *et al.* (1999) suggested that asphaltenes consist mainly of polar hetero compounds and it is known that they decrease the interfacial tension between oil and water and form stable interfacial films. Both effects favor the formation and stabilization of emulsions. Crude oil resins consist mainly of hydrocarbons and their influence on the formation and stability of emulsions in the presence of asphaltenes is, however, not well understood. So they studied influence of the crude oil resin/asphaltene ratio on the stability of oil/water emulsions by investigating the influence of resins from different crude oils as well as of different resin/asphaltene ratios dissolved in decahydronaphthaline as a model system on colloidal stability of model oils, interfacial tension between model oil and distilled water, stability of emulsions formed from model oils and brine, effectiveness of demulsifiers, and viscosity and droplet size distribution of emulsions. It was found that the influence of resins in the presence of asphaltenes on the properties of emulsions is independent of the origin of the resins, i.e. of the oil, from which they are obtained, and high resin/asphaltene ratios decrease the emulsion stability.

## 2.3 Demulsification of Water-in-Crude Oil Emulsions

The demulsification is the breaking of a water-in-crude oil emulsion into oil and water phases. A key step in demulsification is the break-up of the emulsifying film (interface) surrounding the water or oil droplets so as to achieve coalescence of gravitational sedimentation.

**Destabilizing Emulsions**

The emulsion stability arises from the formation of interfacial films encapsulating the water droplets. To separate this emulsion into oil and water, the interfacial film must be destroyed and the droplets made to coalesce. Therefore, destabilizing or breaking emulsions is linked very intimately to the removal of this interfacial film. The factors that enhance or speed up the emulsion breaking include:

- Increasing temperature
- Reducing agitation or shear
- Increasing residence or retention time
- Solids removal
- Control of emulsifying agents

**Mechanisms Involved in Demulsification**

Demulsification is the separation of an emulsion into its component phases. It is a two-step process (Kokal, 2005).

*Flocculation or Aggregation:* The first step in the demulsification process is the flocculation of water droplets. During flocculation, the droplets clump together forming aggregates, or "flocs." The droplets are close to each other, even touching at certain points. The rate of flocculation depends on a number of factors including water cut, temperature, viscosity of the crude oil, and the density difference between the crude oil and water.

*Coalescence:* Coalescence is the second step in the demulsification process and follows flocculation. During coalescence, water droplets coalesce to form a larger droplet. This is an irreversible process that leads to a decrease in the number of water droplets, and eventually to complete demulsification. Coalescence is enhanced by a high rate of flocculation, absence of mechanically strong films, high IFTs, low oil and interfacial viscosities, high water cuts, and high temperature.

Demulsification can be divided into three main methods: mechanical, electrical, and chemical methods.

## 2.3.1 Mechanical Method

Mechanical method is the method that use mechanical devices for demulsification. Modern demulsification devices belong to two main classes: free water (brine) separators and demulsificators. A free water (brine) separator is typically a device for the separation of free water from the well-stream, before the actual start of demulsification. In a demulsification device, demulsification is facilitated by introduction of heat, use of electrostatic grids or mechanical devices to facilitate coalescence.

Kocherginsky *et al.* (2003) studied demulsification of water-in-oil emulsions via filtration through a hydrophilic polymer membrane. It is known that hydrophobic microfiltration membranes can be used for demulsification of oil-in-water (o/w) emulsion due to coalescence of oil droplets in membrane pores. This study demonstrated that a hydrophilic polymer membrane can be used for the demulsification of surfactant-stabilized water-in-oil (w/o) emulsions. Several factors were investigated and it was found that membrane material, membrane pore size and transmembrane pressure have the strong effects on demulsification. Not all types of membranes are effective in breaking water-in-oil emulsions. Demulsification is only possible with hydrophilic membrane having pore size smaller than the emulsion droplet diameter. The smaller the pore size, the better the demulsification efficiency. Lower transmembrane pressure also yields better separation. The membrane thickness and initial water content do not play essential role for demulsification performance. The separation process is not based on sieving effects due to a difference in membrane pore size, but is determined by droplets and membrane surface interactions.

Ezzati *et al.* (2005) studied separation of water in oil emulsions by using microfiltration. A hydrophobic PTFE membrane with 0.45 mm pore size was used. Gas oil, distilled water, and Span 80 were selected as continuous phase, dispersed phase and emulsifier, respectively. The prepared emulsions contained 5–20 %vol water and 0.2–0.8 %vol emulsifier for evaluated the effect of water and emulsifier content in feed, operating pressure, operating temperature and feed residence time in module on the response (permeate flux and water content in permeate). Preliminary experiments were carried out to identify critical feed conditions. It was shown that

increasing emulsifier content and decreasing water content feed decrease permeate flux and water content in permeate. Obviously, minimum and maximum permeate flux was observed when emulsifier and water content in feed were held at their maximum and minimum levels. It was found that decreasing residence time to its lower limit causes permeate flux to increase. Temperature is an effective factor on the response and increasing pressure decreases permeate flux. Analyzing of variance was finally applied to determine the optimum operating condition as well as contribution of each factor on the response.

### 2.3.2 Electrical Method

Electrical method is the use of electric field that has an effect on the surface tension of droplets, to provoke the rearrangement of polar molecules to enhance coalescence of aqueous droplets in crude oil and to improve phase separation. This method alone only rarely results complete demulsification, therefore it is frequently combined with the addition of chemicals, or the increase of the temperature.

Eow and Ghadiri (2002) suggested that the technology for electrostatic enhancement of coalescence of water droplets in oil emulsions is critically reviewed. Pulsed DC and AC fields are especially useful, when the aqueous phase content of the emulsion is high, to prevent short-circuiting between the pair of electrodes. Some workers indicated the existence of an optimum frequency, which depends on the electrode coating material, its thickness and the liquid emulsion composition. The characteristics and geometry of the electrode system (generally cylindrical or plate) influence the performance of the electrostatic coalescer, and are closely related to the type of the applied electric field and the emulsion used. There are basically two types of electrode: uninsulated electrode and insulated electrode. Combination of electrocoalescence and mechanical separation (e.g., centrifugal force) has also been introduced. Other methods that can be combined with the electrical treatment are filtration, methods employing high pressure and temperature, and mixing. Recent work showed that under a pulsed DC electric field, chains of water droplets are usually created during periods of high voltage, followed by rapid coalescence during periods of reduction or no voltage. Therefore, a further improvement in the electrostatic coalescence technology with respect to the applied electric field may be

achieved by operating t he coalescer at an optimum voltage and frequency with reference to the condition of the emulsion, as well as the design of the coalescer itself to give the best electric field configuration. In a water-in-oil emulsion with a high content of dispersed water, insulating the electrode may be necessary. This is because th e high water content tends to produce over-stressing of the electrical coalescer due to a direct conductive path between the electrodes.

### 2.3.3 Chemical Method

Chemical demulsification is a process in which the film thinning rate is enhanced, and stability of the film is reduced by a chemical demulsifier. The role of the demulsifier is to change the interfacial properties of the adsorbed layers on the droplet surfaces, destabilize the surfactant-stabilized emulsion films and increase the coalescence rate of dispersed droplets in order to facilitate phase separation.

Figure 2.2 shows the mechanism in chemical demulsification. Generally, crude oil contains natural surfactants. These natural surfactants stay at the interface between water and oil phase and stabilize the emulsion. Those natural surfactants found in petroleum crude are asphaltenes and resins. When demulsifiers or surfactants are added in order to break the emulsion, in this case, researchers use phenolic resins and polyurethanes as demulsifeirs. The demulsifiers have the properties to lower interfacial tension much more than the natural surfactants, and prefer to adsorb at the interface by replacing the natural surfactants. When a phenolic resin and a cross-linked polyurethane were dosed concomitantly, water separation took place at a much faster rate (seconds to a few minutes). In this case, both types of molecules acted synergistically. Once adsorbed at the interface, they made the film became unstable and the water droplets could be broken easily. Eventually coalescence occurred (Pena et al., 2005).
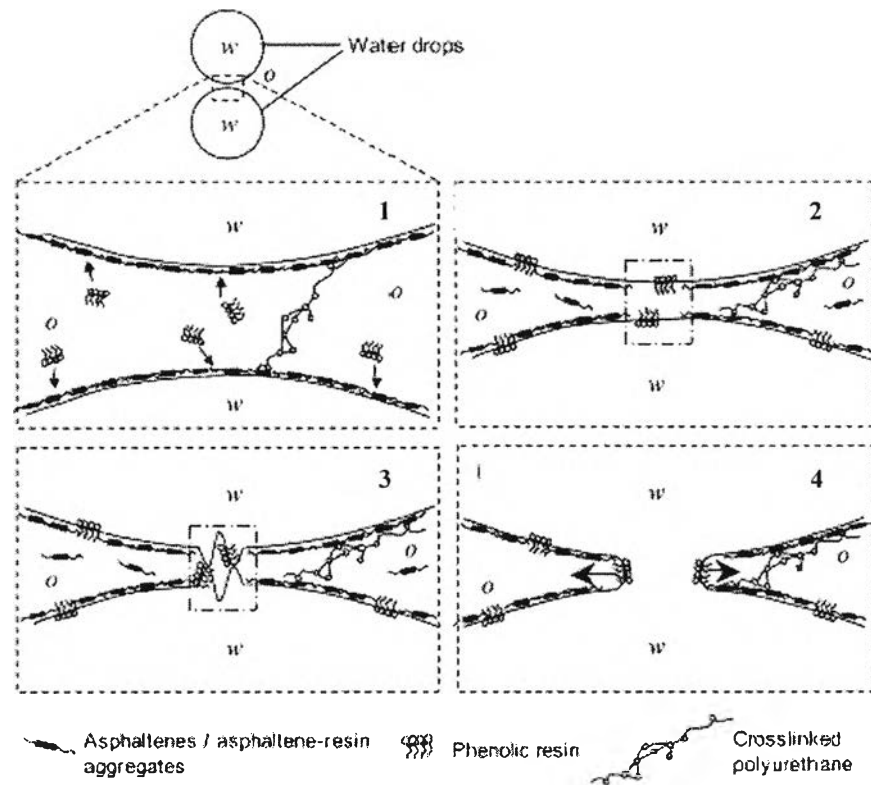
**Figure 2.2** Mechanism in chemical demulsification

Optimum emulsion breaking with a demulsifier requires,

- A properly selected chemical for the given emulsion

- Adequate quantity of this chemical

- Adequate mixing of the chemical in the emulsion

- Sufficient retention time in emulsion treaters to settle water droplets

- Addition of heat, electric grids, coalescers, or other methods to facilitate or completely resolve the emulsions

Surface-active agent or surfactant is a substance that, when present at low concentration in a system it has the property of absorbing onto the surfaces or interfaces of the system.

Nonionic surfactants have a characteristic molecule structure consist of the surface-active portion bears no apparent ionic charge. Nonionic surfactants are usually the reaction product of an alkylene oxide, typically ethylene oxide, with an

alcohol, alkylphenol, alkylamine, fatty acid or other appropriate compound having at least one active hydrogen atom.

Nonionic surfactants adsorb onto surfaces with either the hydrophilic or the hydrophobic group oriented toward the surface, depending upon the nature of the surface. If polar groups capable of H bonding with the hydrophilic group of the surfactant are present on the surface, then the surfactant will probably be adsorbed with its hydrophilic group oriented toward the surface, making the surface more hydrophobic; if such groups are absent from the surface, then the surfactant will probably be oriented with its hydrophobic group toward the surface, making it more hydrophilic.

*Hydrophile-lipophile Balance (HLB)*: is an important parameter characterizing a surfactant can indicate its appropriate applications. HLB value indicated the emulsification behavior and related to the balance between the hydrophilic and lipophilic (hydrophobic) portions of the molecule have been assigned to many commercial emulsifying agents.

*Cloud Point*: Aqueous solutions of amphipathic ethylene oxide derivatives become heterogeneous when the temperature is raised, as hydrogen bonds between the water and the ether oxygen atoms are broken. The temperature at which this phenomenon occurs is directly related to the number of molecules of ethylene oxide, and is called the cloud point. To conduct the test, an aqueous solution, or modified aqueous solution, containing the nonionic surfactant is heated until it clouds. The solution is then cooled slowly and the temperature at which it clarifies is recorded as the cloud point (Rosen, 2004).

Djuve *et al.* (2001) suggested that the investigation of the kinetics of the chemical demulsification is complicated by the interaction of three main effects: 1.The displacement of the asphatenic film from the oil-water interface by the demulsifier, 2. Flocculation, and 3. Coalescence of water droplets.

The efficiency of a surfactant acts as a demulsifier depends on many factors related to the structure of the surfactant. Such factors include the distribution of the demulsifier throughout the bulk volume of the emulsion, the partitioning of the demulsifier between the phases, and the temperature, pH, and salt content of the aqueous phase. Other factors of importance are the mode of injection of the

demulsifier, the concentration of the demulsifier, the type of solvent carrier, the amount of water in the emulsion, and the age of the emulsion.

### 2.3.3.1 Effect of Surfactant Structure

Wu et al. (2003) studied demulsification of water-in-bitumen emulsion by using 52 nonionic surfactants of different chemical families. Relative solubility number (RSN), which is similarly defined to HLB, a measure of the combined affinity of hydrophilic part and lipophilic part of nonionic surfactant to oil or aqueous phase, and molecular weight were determined for these demulsifiers. Their dewatering performance was evaluated by determining the rate of water separation during gravitational settling and centrifugation. The results indicated that there is no overall correlation between demulsification performance and RSN value. However, within a given surfactant family, such as polymerized polyols, oxyalkylated alkylphenol formadehyde resins, and oxyalkylated alkyl resins, the degree of demulsification was found to correlate with the RSN value. A maximum dewatering performance was observed in a specific RSN range. Molecular weight also showed a significant effect on demulsification performance. Surfactants with low molecular weight (<4000) did not break the emulsion in dosages of 300-400 ppm regardless of RSN value. For the water-in-bitumen emulsion studied in this work, the most effective demulsifiers are those with RSN values between 7.5 and 12.5 and molecular weights between 7500 and 15000.

Mansur et al. (2004) studied the properties and performance in the destabilization of emulsions of linear PLURONIC polyols compared with branched TETRONIC polyols. Additives have been employed as well in order to improve solubility of these materials in aqueous solution. The additives were the sodium p-toluene sulfonate (NaPTS) hydrotrope and concentrated hydrochloric acid. Solubility and surface tension were studied in term of aqueous solution, aqueous solution with hydrotrope, and aqueous solution with concentrate HCl. The solubility of such copolymers is increased by the presence of the hydrotrope. The presence of HCl caused increased solubility for the copolymer TETRONIC polyols only but less than that observed for the hydrotrope. For similar EO/PO ratios, TETRONIC polyols are

more water-soluble than PLURONIC polyols. This behavior has been attributed to the chemical structure: the TETRONIC owns the amine groups in its chains and present the more hydrophilicity. Moreover, the branched structure of TETRONIC polyols bears EO hydrophilic moieties distributed throughout the chain, making easier solubility. The performance evaluation of the polyols in w/o emulsions with Bottle Test method to assess the emulsion stability. It is concluded that for emulsion stabilization, TETRONIC polyols perform better due to the star-like structure of TETRONIC polyols which the EO and PO groups are better distributed in its chains and make easier their dispersion between the phases of water-oil emulsion.

Zhang *et al.* (2005) studied demulsification performance of crude oil emulsion by amphiphilic dendrimer copolymers, established a relationship between the molecule structure of dendrimers and demulsification. Five amphiphilic block copolymers with dendrimer structures were synthesized by anion polymerization. Five amphiphilic block copolymers were linear with one branch, linear with 2 branches, star structure, dendrimer block copolymer with 13 branches, and dendrimer block copolymer with 18 branches. Demulsification of water-in-crude oil was studied with the Bottle Test method at 60°C. The results showed that most of the water is separated by addition of dendrimer block copolymer with 13 branches and dendrimer block copolymer with 18 branches. In this study one must take in account that the structure of copolymers plays an important role in the demulsification process, the more branches the dendrimer copolymer has, the more effective it is in demulsification. Because the dendrimers have good penetrability, so they can quickly enter bulk solution and then pervade the oil/water interface. The interfacial activity of the dendrimers is higher than that of natural surfactants. So they can easily displace the natural surfactants.

Wu *et al.* (2005) studied effect of EO and PO positions in nonionic surfactants on surfactant properties and demulsification performance. The properties and the performance of 20 blocked copolymers from four surfactant families were investigated and three pair isomeric compounds were compared by using RSN determination, interfacial tension measurement, and demulsification test. The results showed that different positions of the ethylene oxide (EO) and propylene oxide (PO) in block copolymers lead to different hydrophile–lipophile balances (HLB) of

surfactant. The sequential block copolymer is more hydrophilic than the reverse-sequential one with similar chemical composition. The greater the molecular weight, the greater the difference between the hydrophile–lipophile balances of the two surfactant types. Generally, the demulsification performance of sequential copolymers is better than that of reverse-sequential copolymers. Position isomerism of the surfactant affects demulsification performance by changing the hydrophile–lipophile balance, surface and interfacial properties, and steric characteristics at the interface.

### 2.3.3.2  Effect of Partitioning of the Demulsifier between the Phases

Most commercial demulsifiers that are used to break up water-in-oil emulsions are oil-soluble. Some components of the oil-soluble demulsifier can be dissolved (partitioned) into the water drop phase (dispersed phase). This process is known as partitioning.

Kim and Wasan (1996) suggested that demulsifier partitioning have an effect on the destabilization of water-in-oil emulsions. They used both a model water-in-oil system and water-in-crude oil system with two types of demulsifiers ; A : dispersed mixtures of alkylaryl sulfonate, phenolic resins, and polyamines and B : ethylene oxide (EO)/propylene oxide (PO) copolymers and phenolic resins to study the effect of demulsifier partitioning on the interfacial and film rheological properties that relate to the demulsifier performance. There is one-to-one correlation between the performance of the demulsifier and the degree to which it partitions (partition coefficient). The partitioned demulsifier components exhibited an increased dynamic interfacial activity, high degree of static and dynamic interfacial activity, low interfacial shear viscosity, low film dilational modulus with a high adsorption rate and excellent demulsification performance.

Krawezyk et al. (1991) investigated factors affecting the coalescence and interfacial behavior of water-in-oil emulsions in the presence of oil-soluble demulsifiers. The variation of interfacial tension with demulsifier concentration for the model system was ascertained by measuring the interfacial tensions between the oil and water phase. Interfacial activity, adsorption kinetics, and partitioning were shown to be the most important parameters governing demulsifier performance. A

conceptual model of drop-drop coalescence process in demulsification was presented which indicates that the interfacial activity of the demulsifier must be high enough to suppress the interfacial tension gradient. This accelerates the rate of film drainage, thus promoting coalescence.

### 2.3.3.3 Effect of Temperature, pH-value, Salt Content (Salinity) of Aqueous Phase, contact time, and demulsifier concentration

Abdel-Azim *et al.* (2002) studied the effect of temperature, NaCl concentration (salinity), pH-value, and solvents on the demulsification efficiency of the demulsifiers synthesized from poly (ethylene terephthalate) waste [polyoxyethylenated glycolized product of PET (PO-GP)] in breaking synthetic water-in-benzene emulsions stabilized by petroleum asphaltenes. The results revealed that raising the temperature leads to an increase in the demulsification efficiency of the investigated PO-GP block copolymers. The demulsification efficiency decreases as the salinity of the emulsion's aqueous phase increases. The maximum demulsification efficiency is obtained when the pH-value of the emulsion's aqueous phase equals 7. Water and 1,2-propylene glycol were found to be the best solvents for the prepared demulsifiers. The solutions of the demulsifiers in these two solvents afford the highest demulsification efficiency.

Al-Sabagh *et al.* (2002) studied destabilization of naturally occurring water-in-oil emulsions by polyalkylphenol formaldehyde amine resins. Three polymeric surfactants were prepared and used as demulsifiers; polyalkylphenol formaldehyde monoethanol amine ethoxylate, polyalkylphenol formaldehyde diethanol amine ethoxylate, and polyalkylphenol formaldehyde triethanol amine ethoxylate. Their demulsification potency in breaking water-in-crude oil emulsions was investigated. In this study, two naturally occurring Egyptian water-in-oil (w/o) emulsions, waxy and asphaltenic crudes were used. The demulsification was performed by using demulsifier concentrations range 100-500 ppm, contacting times 30 mins to 24 hour and temperature range 50-70°C. The data revealed that, the resolution of water from waxy crude emulsion was easier than asphaltenic crude emulsion. The demulsification efficiency increases with increasing demulsifier concentration, contacting time and temperature. The interfacial tension (IFT) at the crude oil-water

interface was measured. It was found that the concentration of demulsifiers required to cause a minimum IFT are always less than these indicating a maximum demulsification efficiency.

Strom-Kristiansen *et al.* (1995) evaluated demulsification efficiency of heat or emulsion breaking alone and their combination in different crude oil residues w/o emulsions. The stability of a w/o emulsion and its response to heat and emulsion breaker is highly dependent on different characteristics of the oil from which it is formed. Stable w/o emulsions that can be slowly broken by heat alone were, in general, broken much more rapidly if emulsion breaker was added in addition to heat. The w/o emulsions formed from relatively paraffinic crude oil exhibit faster breaking rates than w/o emulsions formed from crude oils with high asphaltene content.

The demulsifiers act by total or partial displace the natural stabilizers present in the interfacial film around the water droplets. This displacement brings about by the adsorption of the demulsifier at the interface and change in properties such as interfacial viscosity or elasticity of the protecting film, thus enhancing destabilization.

Tambe *et al.* (1995) investigated the factors controlling the stability of colloid-stabilized emulsions. They used model emulsions that have the ratio of water to decane is 2 : 3 and demulsifiers are ethoxylated and/or propoxylated nonyl phenol formaldehyde resins (NPFRs) with varying percentages of EO and PO groups. Measurements of interfacial rheology are presented for demulsifiers at colloid/surfactant interfaces. The results indicated that effective demulsifiers exhibit short relaxation times and must lower the dilational viscoelasticity of the oil-water interfacial layers significantly. Rapid relaxation will ensure a quick supply of the demulsifier to the oil-water interface. Suppressing interfacial tension gradients thereby lead to faster film thinning during drop-drop coalescence. Film thinning will also be faster if the dilational elasticity and the dilational viscosity of the interfacial layers are reduced. By significantly reducing the dilational viscous and elastic properties of the interface (reducing interparticle interaction), effective demulsifiers also decrease the magnitude of steric hindrance.

Demulsification performance can be tested by the most common method, the Bottle Test method. The Bottle Test involves the adding of demulsifier into the emulsion, shaking to disperse the demulsifier, and observing the phase separation as a function of time. The tests are normally done at elevated temperatures and may involve centrifugation for enhancing the separation.

For the practical applications, mixtures of demulsifiers are used. In most cases, when different types of demulsifiers are purposely mixed, what is sought is *synergism*, the condition in which the properties of the mixture are better than those attainable with the individual components by themselves.

Pena *et al.* (2005) studied the effect of systematic changes in the structure of chemicals commonly used in demulsification operations (alkylphenol polyalkoxylated resins and polyurethanes) on the stability and properties of brine-on-crude oil emulsions via bottle test, interfacial tension, viscosity measurement, and nuclear magnetic resonance relaxometry. The phenolic resins promoted coalescence of droplets. The fastest rate for water separation was obtained when the emulsions were treated with resins exhibiting intermediate EO + PO content, in a fashion consistent with the optimum formulation for microemulsion formation in oil-water-surfactant systems. In contrast, cross-linked polyurethanes promoted flocculation and slow coalescence, and they were more effective with increase of molecular weight. When both types of molecules were added concomitantly, water separation rates were significantly higher than those observed when they were used individually. In this case, it seems that polyurethanes contributed to increase the water separation rate, but they retarded coalescence when added at high concentrations. These results can be explained in terms of a molecular mechanism that may involve the disruption of the asphaltenic film adsorbed at the water-oil interfaces by the phenolic resins, and the formation and expansion of holes between approaching droplets in regions depleted of asphaltenes. The action of the phenolic resins was supplemented by the cross-linked polyurethanes, which may act as bridges between droplets, thus increasing the probability for collisions leading to successful coalescence events.

Nanthakhetwong (2005) studied demulsification of water-in-crude oil emulsion from Phet crude oil. The demulsification efficiency was determined via Bottle Test method by using nonionic and anionic surfactants as demulsifiers. He

studied the effect of temperature, salinity, pH, and solvent and the demulsification of mixed crude oil from 6 wells. The results indicated that from the Bottle Test for screening the demulsifiers, Teric 61 was the best demulsifier, which represent for nonionic series. The optimum conditions of the best demulsifier were investigated and the results showed that raising the temperature leads to an increase in the demulsification efficiency. The demulsification efficiency for nonionic demulsifier decreased as the salinity concentration increased while the demulsification efficiency for ionic demulsifier decreased, the maximum demulsifier efficiency was obtained when pH-value of the water phase in the emulsion was 7. Xylene and Toluene were found to be the best solvent for the prepared demulsifier due to the solution from this solvent exhibited the highest demulsifier efficiency.