



PRESSURE DROP REDUCTION OF STABLE WATER-IN-OIL EMULSION FLOW IN PIPES

BY

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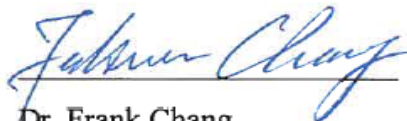
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*To my beloved parents,
wife,
brothers,
sisters,
and daughters: Aalaa, Rehab and Shadha*

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ABSTRACT

Full Name : Mohammed Abdullah Hussein Al-Yaari

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Emulsified acids provide significant benefits in stimulating oil and gas wells by slowing the reaction rate with carbonates and reducing corrosion in the tubular goods. However, high pressure drop, caused by friction losses, can be a problem while pumping emulsified acid. As a result, lower emulsified acid rates are pumped and thus limited job efficiency is achieved. Consequently, methods of pressure drop reduction are highly desired. Therefore, this experimental study aims to investigate a possible friction reduction at different pipe diameters through the control of water fraction, water salinity and the use of drag reducing polymers (DRP) and nanomaterials.

The results demonstrated a shear thinning behavior for the emulsions being investigated. In addition, at low water salinity, oil-in-water (O/W) emulsions were produced, and their stability decreased with increasing salinity. Increasing the aqueous phase salinity resulted in producing water-in-oil (W/O) emulsions. Moreover, as water fraction and salinity increased, W/O emulsion stability increased. Furthermore, a significant reduction in emulsion viscosity and pressure drop with decreasing water fraction and

salinity was observed. Moreover, for a given water fraction and salinity, the friction factor of stable W/O emulsions was found to be less in smaller pipe diameter.

As for the use of DRP, the results showed a significant increase in the emulsion stability with adding the proper DRP (which is soluble in the emulsion external phase) and this effect was enhanced as DRP molecular weight increased. In addition, injecting the right DRP resulted in a pressure drop reduction for all tested stable emulsions types and this effect increased as DRP concentration increased. However, injecting DRP which is soluble in the internal (dispersed) phase showed a drag reduction effect only for unstable emulsion but with less extent.

Furthermore, as for the nanomaterial use, the results showed a significant reduction in the emulsion viscosity with adding all the tested nano-additives and this effect was enhanced as nano-additives concentration increased. In addition, for the case of concentrated W/O emulsions, the addition of Cloisite 15A resulted in a clear reduction (about 25 %) in the emulsion pressure drop in both test sections. Also, for the stable W/O emulsion with only 0.3 water volume fraction, although no pressure drop reduction was observed in laminar region, it was detected in turbulent region and such effect became clearer as Reynolds number and Cloisite 15A concentration increased. Furthermore, for stable W/O emulsions with 0.3 volume fraction of the dispersed phase, although all laminar friction factor data were in good agreement with single phase theoretical values, they fell below the theoretical values of single phase flow in turbulent region.

Once well permeability has been recovered, all the attentions will be diverted to oil production. Oil is produced generally with water and methods that can facilitate separation between oil and water are highly desired. Therefore, water soluble polymer was tested in this regard for oil-water stratified horizontal flows. It has been reported that the injection of tiny amount of such polymer resulted in a reduction in the pressure drop. Such reduction was accompanied with stratification effect (more separation).

ملخص الرسالة

الاسم الكامل: محمد عبدالله حسين اليعري

عنوان الرسالة: تخفيض الهبوط في الضغط لمستحلبات الماء في الزيت الثابتة أثناء جريانها في الأنابيب

التخصص: هندسة كيميائية

تاريخ الدرجة العلمية: يونيو 2013

تستخدم المستحلبات الحامضية (حامض في زيت) في تحفيز آبار النفط والغاز لأنها تبطئ سرعة التفاعل بين الحامض و الصخور الكربونية و تقلل من التآكل في الأنابيب المعدنية مقارنةً بالحوامض المستخدمة. لكنه لا يمكن ضخها بسرعة عالية نظراً للزوجتها المرتفعة و هذا يقلل من كفاءتها. لذلك فهذه الدراسة العملية تهدف للبحث عن وسائل لتقليل إحتكاك المستحلبات أثناء جريانها في الأنابيب.

في هذه الدراسة تمت دراسة تأثير بعض العوامل على خصائص المستحلبات كثباتيتها، موصليتها، الخواص الريولوجية لها، حجم و توزيع قطرات الطور المتشتت (الداخلي) و الهبوط في الضغط أثناء جريانها في أنابيب مختلفة الأقطار. هذه العوامل تشمل نسبة الماء، ملوحة الماء، إستخدام المبلمرات الخافضة للضغط، و إستخدام بعض المواد النانوية (المتناهية الصغر).

فيما يخص تأثير الماء و ملوحته، فقد أظهرت الدراسة أن نقصان نسبة و ملوحة الماء تقلل من لزوجة و ثباتية المستحلبات و بالتالي إحتكاكها أثناء الجريان. و أظهرت أيضاً أن الإحتكاك يمكن تخفيضه و ذلك بالضغط في أنابيب صغيرة الأقطار. ويمكن التحكم في نوع المستحلب (ماء في زيت أو زيت في ماء) عن طريق التحكم في نسبة و ملوحة الماء.

كما أظهرت الدراسة أن إضافة المبلّمرات الخافضة للضغط والتي تذوب في الطور الخارجي للمستحلب تزيد من ثباتيته، و يزداد هذا التأثير بزيادة الوزن الجزيئي للمبلّمرات. و حقن هذه المبلّمرات (الذائبة في الطور الخارجي للمستحلب) لا إضافتها هو الأفضل لخفض الهبوط في الضغط أثناء جريان المستحلبات و يزداد التأثير الإيجابي بزيادة تركيزها. كما أظهرت الدراسة أنّه في غير المستحلبات (حالة الجريان الطبقي للماء والزيت) فإنّ حقن المبلّمرات التي تذوب في الماء تساهم في فصله عن الزيت.

و فيما يخص استخدام المواد النانوية المنتهية الصغر، فقد أظهرت الدراسة نجاح بعض الأطيّان المعدلة عضوياً" في تخفيض الهبوط في الضغط أثناء جريان المستحلبات المركزة و المخففة.

CHAPTER 1

INTRODUCTION

1.1 EMULSION FUNDAMENTALS

Emulsions can be encountered in everyday life. Especially, they can be found in all stages in the petroleum production and recovery and processing industry such as drilling fluids, production, process plant, and transportation. In each case, the presence and nature of emulsions, which have important desirable and undesirable properties, determine both the economic and technical successes of the concerned industrial process.

Some of the crude oil components can form films at oil surfaces, and others are surface active. As a result, the formation of stable and unstable emulsions varies greatly among different oils.

The widespread importance of emulsions, in general, and scientific interest in their formation, stability, and properties gave a wealth of published literature on this subject. However, all types of emulsions have the same basic principles of colloid science which governs the nature, stability, and other emulsions properties.

1.1.1 Interfacial Tension

When two immiscible liquids are mixed together in a container and then shaken, one of the two phases becomes a collection of dispersed droplets in the other phase. As a result, an emulsion is formed.

The inequality in the van der Waals forces, between molecules in the interfacial region and other molecules in droplet, pulls the interfacial molecules toward the interior of the droplet. Therefore, droplet tends to adopt a spherical shape, since this shape reduces the surface free energy.

Surface and interfacial tension can be defined as the free energy required creating new surface area or the force per unit length around a surface. Interfacial tension is frequently a value between the surface tensions values of the two liquids. When impure liquids are used to form emulsion, appreciable changes can take place with time at the interfaces.

Surfactants have dual solubility because they have one part that has an affinity for the oil and one part for water. Therefore, the energetically most favorable orientation for surfactants is at the oil-water interface to allow both parts to reside in the solvent for which it has the greatest affinity.

According to the nature of the polar (hydrophilic) part of the molecule, surfactants are classified as: anionic, cationic, nonionic and zwitterionic.

1.1.2 Definitions

Colloidal systems have at least one dimension between about 1 nm and 1 μm . Emulsions are a special type of colloidal system but emulsion droplets often exceed the size limit of colloidal system.

In petroleum emulsions, one of the liquid is aqueous, and the other is organic. Depending upon which kind of liquids forms the continuous phase, two types of emulsion are distinguished: *oil-in-water (O/W)* and *water-in-oil (W/O)* when water and oil forms the continuous phase respectively.

When the dispersion medium is water, colloid system is divided into lyophobic and lyophilic (Schramm, 1992). *Lyophilic colloids* are formed spontaneously when the two phases are brought together since the dispersion is thermodynamically more stable than the separated phases. On the other hand, *lyophobic colloids*, including all petroleum emulsions except microemulsions, are only formed by some means since they are thermodynamically unstable compared with the original separated phases.

Most petroleum emulsions contain oil, water and an emulsifying agent (*emulsifier*). The emulsifier could be: inorganic electrolytes, surfactants, macromolecules, or fine solids. Emulsifier is needed to reduce interfacial tension, increase the interfacial area with a minimum mechanical energy input, and/or to prevent droplets from coalescence by forming films around droplet surfaces.

When a co-surfactant is added to some systems containing oil, water and surfactant, the interfacial tension is reduced to a value near to zero (on the order of 10^{-3} to 10^{-4} mN/m).

The low interfacial tension allows spontaneous emulsification to very small droplet sizes (≤ 10 nm). As a result, *micro-emulsions* are formed. Microemulsions are usually thought to be stable, appear to be transparent and do not break on centrifuging.

Phase inversion is a less mechanical energy method used to change W/O emulsion to O/W emulsion and vice versa. For example, if a W/O emulsion is desired, then a coarse O/W emulsion is first prepared by mixing, and the oil content is gradually increased. At some volume fraction above 60-70 %, the emulsion will suddenly invert and produce a W/O emulsion of much smaller water droplet sizes than were the oil droplets in the original O/W emulsion.

1.1.3 Emulsions Physical Characteristics

Some physical characteristics of emulsions, reported by Schramm in 1992, are summarized as:

A. Appearance:

Depending upon the droplet sizes and the difference in refractive indices between the two phases, emulsion may show a wide range of appearance. For example, if refractive indices of the two phases are the same or if the droplets size is very small compared with the illuminating light, emulsion is transparent rather than milky. In addition, nature of an emulsion frequently reflects that of the external phase. Furthermore, the occurrence of multiple emulsions, of the types W/O/W and O/W/O is possible.

B. Droplet Sizes:

Characterizing an emulsion in terms of a given droplet size is very common but inappropriate since there is a size distribution which is usually represented by a histogram of sizes. The droplet size distribution has an important effect on viscosity.

If the droplet size is large enough, optical microscopy can be used to determine the size and size distribution. However, emulsions with smaller sizes can be characterized by scanning electron microscopy (SEM). For droplets in a non-concentrated emulsion, light scattering technique can be used.

C. Conductivity:

O/W and W/O emulsions can be distinguished from each other by conductivity measurements since emulsion conductivity reflects that of the continuous phase.

D. Rheology:

*a. **Bulk Viscosity.*** Viscosity is one of the most important properties of emulsion. A proper way to represent the emulsion flow properties is by plotting flow curves of shear stress versus shear rate. Emulsions are frequently pseudo-plastic (shear thinning): as shear rate increases, viscosity decreases. Also, an emulsion may exhibit a yield stress (the shear rate remains zero until a threshold shear stress is reached. If the internal phase has a sufficiently high volume fraction, the emulsion viscosity increases because of droplets crowding. The maximum possible internal volume fraction of

uniform and incompressible spheres is 74%, although emulsions with higher (99%) internal volume fraction are made (Griffin, 1995).

*b. **Interfacial Viscosity.*** It can be thought as bulk viscosity but operative in the oil-water interface region. As droplets become closer, the thinning the films between the droplets, and their resistance to rupture, are thought to be of great importance to the ultimate stability of the emulsion. Hence, a high interfacial viscosity can promote emulsion stability by retarding the rate of droplet coalescence.

1.2 EMULSION FORMATION

Stable emulsions contain: oil, water, an emulsifier to create small droplets by reducing the interfacial tension and another emulsifier to stabilize the created droplets. Casual mixing of these components can seldom produce stable emulsion for any length of time. However, in the classical method of emulsion preparation, emulsifier is dissolved in one phase, the second phase is added, and the whole mixture is vigorously agitated. The agitation is crucial to producing sufficiently small droplets, and frequently, after an initial mixing, a second mixing with very high applied mechanical shear forces is required which can be provided by a colloid mill or an ultrasound agitator.

The larger interfacial area will have a significant total free energy which is obtained by multiplying the total area by the interfacial tension. Such energy has to be added to the system to achieve the emulsification. If this amount of energy cannot be provided by

mechanical shear, then another alternative is to use surfactant to lower the interfacial tension and then the interfacial free energy.

The process of emulsification is governed by the surface forces. The free energy of formation of droplets from a bulk liquid (ΔG_{form}) is given by:

$$\Delta G_{form} = \Delta A \gamma_{12} - T \Delta S_{conf}$$

where: ΔA = the increase in interfacial area

γ_{12} = the interfacial tension between the two liquids

$T \Delta S_{conf}$ = the entropy contribution in configurational entropy when a large number of droplets is formed.

Emulsification is a non-spontaneous process since $\Delta A \gamma_{12} \gg T \Delta S_{conf}$. However, the energy required for emulsification process is orders of magnitudes larger than the thermodynamic energy ($\Delta A \gamma_{12}$) for creating a new surface. The presence of surfactant, which lowers the interfacial tension, lowers the energy required for emulsification.

The phenomenon of droplet breakup is of great importance in the preparation of emulsions. Any dispersion process is affected by the viscosity of each phase, the shear in the system and the interfacial energy. In tubular Poiseuille flow, where the shear is non-uniform, droplet breakup can be related to the bulk rheological properties of the dispersed and continuous phases and the critical Weber number (We_c) as shown in the figure below. We is a dimensionless group and is defined as

$$We = \frac{\eta_1 \dot{\gamma}_e R}{\gamma_{12}}$$

where:

η_1 and η_2 = the viscosities of the continuous and dispersed phases, respectively

$\dot{\gamma}_e$ = the rate of extension defined as the shear rate multiplied by deformation parameter

R = the radius of the particle

γ_{12} = the interfacial tension between the two liquids

At a given η_1/η_2 , lowering γ_{12} using surfactants lowers the energy, described by the We_c , required for droplet breakup. As shown in Figure 1.1, the greater the viscosity ratio (η_1/η_2), the easier it is to form the emulsion. Therefore, in heavy oil reservoirs, W/O emulsions are produced in preference to O/W emulsions.

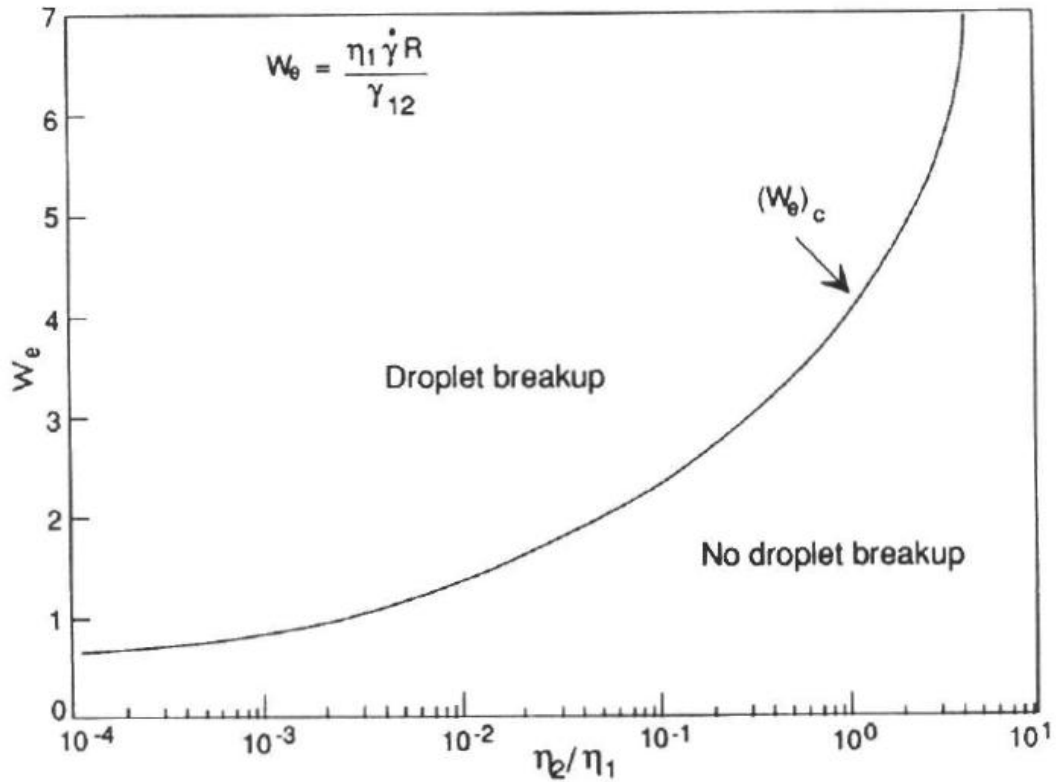


Figure 1.1 Droplet breakup as a function of viscosity ratio (Isaacs, E. and Chow, R. 1992)

While for O/W emulsions, the interfacial charge contributes the stability, in W/O emulsions, the strength of the interfacial film of oil that forms between the water droplets is of prime concern. Surfactants, asphaltenes, porphyrinic compounds and finely divided solids such as sand, wax crystals and clay particles can play a significant role in hindering the thinning and rupture of the liquid films and acts as a structural barrier to coalescence of water droplets. (Menon and Wasan, 1988)

1.3 EMULSION STABILITY

Encounters between particles in dispersion can occur frequently. The stability of the dispersion depends upon how the particles interact when these encounters happen. While the electrostatic repulsion between like-charge objects is the main cause of repulsion, the van der Waals forces are the main attractive forces.

Emulsion stability is considered against three different processes: creaming or sedimentation, aggregation and coalescence. Creaming and sedimentation, which are two opposite processes, result from a difference in the two liquids densities. Aggregation, referred sometimes as coagulation or flocculation occurs when two or droplets clump together and touching only at a certain points with almost no change in the total surface area. However, when two or more droplets fuse together to form a single large droplet with a reduced total surface area coalescence process occurs.

Determination of emulsion stability is one of the emulsion characterization features with which selection of the appropriate demulsification treatment and the cost of treatment cannot be achieved unless it is known. In addition, the effectiveness of any demulsifier depends upon the degree of stabilization.

It is simply involves monitoring the oil and water phase separation as a function of time. Bottle and centrifuge tests are the most common methods, to monitor phase separation with time. However, microscopic techniques can be utilized for the droplet coalescence monitoring.

In bottle and centrifuge tests, settling and separation of oil and water phases depends on the dispersed phase droplets size, density difference and the continuous phase viscosity as described by settling velocity (Stokes' law).

Emulsion stability can be determined simply by the simple bottle test. In this method, first emulsion viscosity is reduced, if required, by emulsion dilution with a proper solvent. Then, after shaking the emulsion sample to make it homogeneous, phase separation rate is monitored. Depending on the emulsion viscosity, phase separation can be enhanced by temperature or centrifugation. This test can give information about the clarity of the separated water.

In addition, centrifuge tests provide similar information to those obtained from the stability bottle tests at higher gravity or centrifugal force. Special centrifugal bottles are used in this technique and phase separation is monitored. Emulsion dilution is not necessary in this technique even for high viscous emulsion samples.

1.4 EMULSION CHARACTERIZATION

Complete characterization of an emulsion involved detailed chemical and physical analysis of all of the emulsion components: oil, water and surfactant. Also, it involves any bulk properties that might be of interest such as viscosity, density and etc. Therefore, emulsion characterization contains: quantification of the present phases, determination of the nature and size distribution of the dispersed phase, and measurements of the dispersed phase.

A fundamental understanding of the emulsion components interaction is usually valuable. In addition, interfacial properties, film rigidity or strength, and surface tension between the different emulsion phases are very important in stability determination of the dispersed phase.

For the emulsion characterization purpose, it is vital to determine the amount of each phase, the nature of the continuous and dispersed phases, and the size distribution of the dispersed phase. In addition, emulsion stability is another important property that can be measured (monitored) in terms of the phase separation over time. However, emulsion stability is directly related to the emulsion components' chemistry, physics and their interactions.

1.4.1 Bulk Properties

The bulk compositions or properties can be dealt as the index by which one can get an indication of the process efficiency. Therefore, accurate determination of the emulsion components is one of the important issues in emulsion characterization.

A. Continuous Phase Identification

Knowledge of the dispersed phase nature is critical in determining an effective treatment. The nature of the dispersed phase is quite clear in most emulsion systems. However, identification of the emulsion continuous phase, in some emulsions, cannot be achieved simply by naked eyes and in some cases it depends upon where in sample one looks.

Identification of dispersed phase nature cannot be achieved by knowing the oil to water ratio alone since the presence of emulsifier can dramatically affect the amount of the distributed dispersed phase in a given amount of the continuous phase.

Identification of the continuous phase nature can be achieved by different techniques.

These techniques include:

*a. **Dilution method.*** In this technique, one or two emulsion droplets are added to water. If the emulsion droplet remains as a droplet, oil is the continuous phase (W/O emulsion). However, if the emulsion droplet spreads and disperses, water is the continuous phase (O/W emulsion).

Emulsion phase inversion should be avoided while doing the dilution test. For example, W/O emulsion may invert to O/W emulsion because of the interaction of water dispersed phase with the dropper hydrophilic glass wall (Mikula, 1992).

*b. **Dyeing.*** Another way to identify the emulsion continuous phase nature is to dye the continuous phase by using suitable water or oil soluble dyes. This method is very useful for the microscope observations. If the oil soluble dye does not color the emulsion, water is the continuous phase (O/W emulsion). Unfortunately, the applicability of this method is limited because of the opaque oil field emulsions.

*c. **Emulsion capacitance or electrical conductivity.*** Since O/W emulsion is much higher conductive than a similar W/O emulsion, emulsion capacitance or

electrical conductivity technique can be used to indicate whether the continuous phase is oil or water (whether emulsion is W/O or O/W).

This method is the basis of many sensors and it can be used to monitor the emulsion phase inversion while changing concentration of any emulsion components (water, oil and/or surfactant). The presence of solids in emulsion may affect the accuracy of this method (Bhatnagar, 1920).

B. Emulsion Water Content

Several techniques can be used to measure emulsion water content (as well as emulsion oil content). These techniques include:

*a. **Centrifugation.*** A simple centrifuge test can be used to determine oil and water contents and it is one of the most commonly used technique for field evaluation of water contents since it is fast and reliable. In this test, first, emulsion is diluted with a given amount of solvent (Mikula, 1992). Then, it is centrifuged, in a centrifuge tube, for a fixed time. After that, the volume of water can be determined. Mikula also reported that this technique might not be useful for very high water content.

*b. **Karl Fischer Titration.*** This technique is reported as a fast and accurate method for water content determination (Mikula, 1992). In this method, the Karl Fischer reagent, which consists of mixture of iodine (I_2), SO_2 and pyridine dissolved in methanol, is used to titrate the emulsion sample since most substances are inert to this reagent.

In this method, in the presence of water, I_2 is reduced by SO_2 to form HI and SO_3 which are complex and neutralized by the pyridine. After reacting all of the water, the sample conductivity increases because of the appearance of highly conductive free I_2 . As a result, water content can be determined.

c. Electrical conductivity and dielectric constant. Since the electrical conductivity and dielectric constants of water and oil are quite different, these differences can be measured accurately by capacitance probe and correlated to the water content in oil pipeline.

d. Gamma-ray. The density of the emulsion, which can be correlated to the emulsion water content, can be measured by gamma-ray attenuation. This technique is quite common in process monitoring. Schweitzer and Ellis in 1988 reported that gamma-ray density meter is very useful to characterize emulsion especially when the solids content is zero or constant. This technique is applicable to field situations and on-line monitoring.

e. Microwave-based meters. Mikula in 1992 reported microwave-based meters can be used to monitor emulsion water content. In this technique, the microwave radiation due to the absorption of the water phase is measured. Also, capacitance or resonance changes in a microwave cavity are noted instead. Like the gamma-ray adsorption method, discussed earlier, this technique is sensitive to the solids content and it is applicable to field situation and on-line monitoring.

1.4.2 Emulsion Dispersed Phase Size Distribution

For emulsion characterization, determination of the dispersed phase chemical and physical properties is very important to measure most of the emulsion bulk properties. Different dispersed phase size distributions can result from various ways of emulsion formation from a fixed proportion of oil, water and surfactant. As a result, different emulsions, with different viscosities and stabilities, can be formed with the same compositions. Determination of the size distribution of the dispersed phase is an important requirement for the selection of the proper technique for specified purpose.

Determination of the emulsion dispersed phase size distribution can be achieved by different techniques which can be divided into three main groups: techniques that depend on the differences between the electrical properties of oil and water, techniques that result in a physical separation of the dispersed droplets, and techniques that depend on scattering phenomena due to the presence of the dispersed phase (Mikula, 1992).

Also, Mikula (1992) reported other techniques such as near-infrared spectroscopy (NIR) and differential scanning calorimetry (DSC) as techniques that can be used for emulsion characterization purposes.

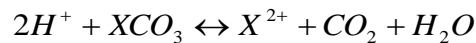
Azzopardi (1979) published an extensive study, which reviewed methods for the measurement of the size of drops in any system. Special review dealt with petroleum emulsion dispersed phase droplets size was reported by Mikula in 1992.

1.5 PROBLEM DEFINITION

Emulsion technology has been utilized to the acid treatment of reservoir rocks in the region near the well bore. Sometimes, the pore structure near the well bore is plugged either by particulates from drilling process or by production precipitation deposits caused by pressure or temperature changes. As a result, permeability is reduced as well as the well productivity.

To remove these unwanted deposits, acid stimulation is used. Wells in formations with naturally occurring low permeability can also be stimulated by using acid stimulation, but applied to the original rock matrix. This process is referred to as matrix stimulation.

The matrix acidizing process consists of injecting suitable acid, depending on the type of the formation, into the formation pore space. While hydrochloric acid is used for limestones, hydrochloric-hydrofluoric acid is used for sandstones. The acid reacts with and dissolves portions of rock matrix and hence permeability is increased. The effectiveness of the treatment depends on the depth that the acid penetrates into the formation. For carbonate matrix, acid consumption occurs very rapidly at elevated temperature according to the equation:



where X is mainly calcium or magnesium.

The rate of dissolution is limited by mass transfer (depends on the rate at which acid diffuses to the surface of the formation). Acid is consumed very quickly, since the rate

of mass transfer through the rock matrix is high, and it causes corrosion in the metal tubular goods. Therefore, deep penetration of the acid and corrosion rate reduction is a target.

Reservoir dominant flow channels or worm holes are randomly distributed through the formation. The longer the worm holes, the better will be the results. Therefore, loss of acid (leak-off) through the walls of the reservoir flow channels results in short worm holes and the effective stimulation requires retardation of the dissolution rate.

One method to achieve such retardation is the use of the emulsified acid where the hydrochloric acid is injected as a W/O emulsion. By doing so, the diffusion rate of the dispersed aqueous acid to the matrix formation is slower than that of acid from a totally aqueous system. As a result, the dissolution rate of limestone is retarded.

However, high pressure drop, caused by friction losses, can be a problem while pumping emulsified acid. As a result, lower emulsified acid rates are pumped and thus limited job efficiency is achieved. Consequently, methods of pressure drop reduction are highly desired.

1.6 DISSERTATION OBJECTIVES

The objectives of this experimental research can be summarized as follows:

1. Designing and constructing suitable flow loop facilities to be used for the study of unstable and surfactant-stabilized W/O as well as O/W emulsions.

2. Investigating the surfactant-stabilized W/O emulsion flow characteristics. This includes:
 - a) Emulsion stability
 - b) Emulsion rheology
 - c) Emulsion pressure drop
3. Studying the water fraction effect on stable W/O emulsion flow characteristics. In addition, investigating a possible friction reduction method by changing the dispersed phase fraction at different pipe diameters.
4. Investigating the aqueous phase salinity effect on stable emulsions flow characteristics. In addition, studying a possible friction reduction method through the control of water salinity at different pipe diameters.
5. Using the flow loop facilities to study the effect of polymer drag reducing agents (PDRA) on stable emulsions flow characteristics (stability, rheology and microscopy). Moreover, investigating a possible friction reduction method by adding and/or injecting PDRA at different pipe diameters.
6. Studying the effect of nano-additives on stable emulsions viscosities. Moreover, investigating a possible friction reduction method through the use of nano-additives.
7. Once well permeability has been recovered, all the attentions will be diverted to oil production. Oil is produced generally with water and methods that can facilitate separation between oil and water are highly desired. Therefore, water

soluble polymer is tested in this regard for oil-water stratified horizontal flows to seek for a possible stratification effect. In particular, investigating the effect of drag reducing polymers on water holdup for an oil-water horizontal flow has been conducted.

This thesis is divided into nine chapters. Chapter 1, the current one, is this introduction. The descriptions of the following eight chapters are as follows:

Chapter 2 presents a literature review on the unstable and surfactant-stabilized oil-water emulsions flow in horizontal pipes; especially the effect of water fraction on the pressure gradient. Chapter 3 gives a description of the experimental setup, the instrumentation used and testing procedures. The effect of the water fraction on the surfactant-stabilized W/O emulsions flow characteristics is reported in chapter 4. Chapter 5 is presenting the effect of the aqueous phase salinity on stable emulsions (W/O & O/W) flow characteristics. Moreover, effect of polymer drag reducing agents and some nano-additives on the surfactant-stabilized emulsions are given in chapter 6 and chapter 7, respectively. In addition, chapter 8 presents effect of drag reducing polymers on water holdup in an oil-water horizontal flow. Finally, based on the experimental findings, conclusions and some recommendations for future work are presented in chapter 9.

Each chapter of the main five chapters (4-8) is designed to stand for itself. Therefore, each chapter begins with introduction giving background about one specific objective and reviewing the previous related work done in the first section of each chapter. After that, the experimental setup and procedures for conducting the experiments are

described in the 2nd section. Then, results are presented and discussed in the 3rd section. Finally, in the 4th section of each chapter the main conclusions are highlighted.

CHAPTER 2

LITERATURE REVIEW

Under certain conditions, the injection of water into a crude oil pipeline results in a significant reduction of pressure loss, thereby facilitating oil transportation. Therefore, cocurrent flow of oil and water in pipelines has attracted the interest of researchers (Russel et al. (1959), Charles et al. (1961), Hasson et al. (1970), Oglesby et al. (1979), Arirachakaran et al. (1989), Valle and Kvandal (1995), Beretta et al. (1997), Angeli and Hewitt (2000), Soleimani et al. (2000) and Al-Yaari et al. (2008 & 2009)). However, the majority of studies reported in the literature, is mainly focused on either oil-water flow patterns or separated flows (annular and stratified flow of oil and water phases). The pipeline flow behavior of W/O and/or O/W emulsions has received less attention.

This chapter aims to highlight the flow characteristics of surfactant stabilized W/O emulsion. In particular, understanding the flow behavior of such emulsion in horizontal pipelines is targeted. Consequently, pressure drop reduction can be achieved. Therefore, in this chapter, works addressed the issue of horizontal pipeline flow behavior of unstable or stable emulsions are reviewed. Attention is not limited to W/O emulsion flow only but also works done to investigate the flow behavior of O/W emulsion is highlighted. Therefore, this chapter is divided into two sections. Horizontal pipeline flow behavior of unstable emulsions researches are reviewed in section 2.1 and

surfactant stabilized emulsion flow characteristics in horizontal pipeline works are summarized in section 2.2.

2.1 UNSTABLE EMULSIONS (DISPERSIONS)

This section is limited to review works which addressed flow behavior of unstable emulsions (without surfactant).

Baron et al. (1953) studied experimentally the turbulent flow behavior of unstable emulsions in pipelines. They used tap water and carbon tetrachloride to make O/W emulsions. They assumed that the emulsion is pseudo-homogenous to use simplified single phase flow equations using averaged fluid properties. They calculated the effective viscosities of emulsions from the single-phase friction factor vs. Reynolds number relation using the experimental data of pressure loss vs. flow rate.

In addition, laminar and turbulent flow behaviors of unstable O/W emulsions were studied by Cengel et al. (1962). They measured pressure drop and used Hagen-Poiseuille equation in laminar flow, and Blasius equation in turbulent flow to calculate the effective viscosities. They reported that emulsions exhibited drag reduction behavior in turbulent region since their friction factor fell below that for Blasius equation. Furthermore, they argued that such drag reduction increased as the dispersed phase fraction increased.

In 1987, the laminar and turbulent flow behaviors for unstable O/W emulsions studied by Pal. His flowloop had three different horizontal smooth pipes. Similarly, he used

Blasius equation to calculate the effective viscosities in the turbulent regime. Such calculated viscosities were found to be lower than those obtained in the laminar region using the Hagen-Poiseuille equation. As a result, he concluded that emulsions exhibited drag reduction behavior in turbulent flow. Finally, he reported that such difference in viscosities increased when dispersed phase volume fraction increased.

However, the laminar and turbulent pipeline flow behavior of unstable W/O emulsions was studied by Pal in 1993. Tap water and oil with 780 kg/m^3 density and viscosity of 2.41 mPa.s at 25°C were used. He used Hagen-Poiseuille equation to calculate the effective viscosities in the laminar regime and he reported that the emulsion viscosity was found to increase with an increase in the dispersed phase volume fraction. In addition, he found that at a water volume fraction of 41.7% volume, a sudden jump in the emulsion viscosity occurred and he attributed that to the phase inversion from W/O emulsion to O/W emulsion. Further increase in water volume fraction resulted in decreasing the viscosity due to dilution effect as he reported.

In addition, Pal (1993) reported that while the relative viscosities obtained from laminar data varied with dispersed phase volume fraction, they were a function of Reynolds number and the dispersed phase volume fraction, and pipe diameter in the turbulent region. Furthermore, he argued that unstable W/O emulsions exhibited strong drag reduction characteristics, as the measured friction factor fell well below the Blasius equation, in the turbulent flow and such drag reduction increased with the dispersed phase volume fraction increase. Moreover, he reported that smaller diameter pipe gave

larger drag reduction. The degree of drag reduction in O/W emulsions was reported to be less than that in the case of W/O emulsions at the same dispersed phase volume fraction. Finally, he argued that drag reduction in emulsions occurs due to turbulence modification of the continuous-phase liquid when droplets are introduced.

Angeli and Hewitt (1998) also studied the pipeline behavior of unstable W/O emulsions. Tap water and oil with a dynamic viscosity of 1.6 mPa.s were used. Their horizontal pipeline test sections were made from stainless steel and acrylic resin. They reported emulsions drag reduction behavior in both pipes and the degree of drag reduction was strongly influenced by the pipe material. The acrylic-resin pipe exhibited a higher degree of drag reduction as they argued.

Masalova et al. (2003) studied the pipeline flow behavior of W/O emulsions with water volume fraction of 0.9 in two different pipe diameters. They reported that the pressure drop data for pipe with smaller diameter fell lower than that for bigger pipe and they concluded that while that wall slip for pipes of large diameter can be neglected, wall slip must be considered for small diameter pipes.

Pal (2007) proposed another mechanism for drag reduction observed in the pipeline flow of unstable emulsions. He proposed that because of a significant decrease in emulsion viscosity when the flow regime is changed from laminar to turbulent, emulsions exhibit drag reduction. Also, in turbulent flow, viscosity reduction occurs because of stretching and elongation of droplets as he argued.

Al-Yaari et al. (2009) studied the effect of drag-reducing polymers on the horizontal

flow of unstable W/O and O/W emulsions in a 2.54 cm inside diameter acrylic pipe. Tap water and oil with a viscosity of 1.57 mPa.s and density of 780 kg/m³ were used. Such oil-water system was reported to have a phase inversion point at around 0.34 input water volume fraction.

Omer and Pal (2010) studied the effect of the water soluble polymer addition on the pipeline flow behavior of unstable W/O emulsions. They reported that unstable W/O emulsions were exhibited strong drag reduction behavior in turbulent flow and such reduction in the pressure drop decreased with the increase in the oil continuous phase viscosity.

2.2 SURFACTANT-STABILIZED EMULSIONS

The transport of emulsified acid through pipes requires the formation of stable emulsions in order to avoid corrosion, that may be faced in metallic tubular goods and to retard the reaction rate between HCl acid and the carbonate formations.

Generally W/O or O/W emulsions are unstable thermodynamically. As the water/oil droplets are hydrophilic/ hydrophobic they tend to separate from the oil/ water continuous phase. In order to form a stable emulsion, a surfactant (emulsifier) must be used to reduce the interfacial tension and this makes the formation of smaller droplets easier.

This section is limited to review works addressing flow behavior of surfactant stabilized emulsions (with surfactant or emulsifier).

Rose and Marsden (1970) studied experimentally the flow behavior of Triton X-14 surfactant stabilized O/W emulsions with 0.25-0.6 oil volume fraction. Brine and Prudhoe Bay oil, with 80 mPa.s viscosity at 65 °C, were used. Their test section was copper tubing with ID of 0.635 cm. They found that the created O/W emulsions had much lower viscosities than the oil itself and the emulsion viscosity increased exponentially with increasing the oil volume fraction.

The laminar and turbulent flow behaviors of surfactant stabilized O/W emulsions, with oil volume fraction between 0.5 and 0.75 were investigated by Zakin et al. (1979). They reported that the emulsions were non-Newtonian in laminar regime as indicated by rheological data and modified Hagen-Poiseuille equation (where Reynolds number is replaced by generalized Reynolds number) was used. They also observed drag reduction behavior in the turbulent regime, and they attributed it to be due to viscoelastic effects in emulsions, where individual droplets or a microstructure formed between the droplets can introduce viscoelastic effects in emulsions.

Pal (1993) also investigated the influence of surfactant on the pipeline flow behavior of W/O and O/W emulsions. Emulsions were prepared using Bayol-35 oil (refined mineral oil), with 780 kg/m³ density and 2.41 mPa.s viscosity at 25 °C, and tap water. Phase inversion point for the surfactant-stabilized W/O and O/W emulsions were reported at around 0.26 and 0.72 water and oil volume fractions respectively. Before those points, while W/O emulsions behaved like Newtonian fluids, O/W emulsions were Newtonian up to an oil volume fraction of 0.55 and non-Newtonian shear thinning up to 0.72, at

which emulsion showed the presence of a yield stress. In addition, he reported little or no drag reduction exhibited by the stabilized emulsions (in the laminar regime the friction factor data from various diameter pipes follows the Hagen-Poiseuille equation and in turbulent regime the friction data follows the Blasius equation as well).

Omer and Pal (2010) studied also the effect of surfactant concentration on the pipeline flow behavior of W/O emulsions. They reported that the presence of a surfactant in the oil phase results in the creation of stable water-in-oil emulsions with little or no drag reduction. In addition, they argued that the presence of a surfactant is expected to increase the rigidity of the droplets, leading to higher emulsion viscosity. Furthermore, they found that the relative viscosity of the stable emulsions increased with the increase in the dispersed-phase fraction. Finally, they reported that as the droplets of the stable W/O emulsions were small and stable with respect to coalescence, they behaved more like rigid particles and, therefore, no reduction in viscosity occurred upon a change in the flow regime from laminar to turbulent.

CHAPTER 3

EXPERIMENTAL SETUP & PROCEDURE

Experiments reported in this dissertation were performed to study the flow characteristics of surfactant stabilized W/O and O/W emulsions. Such study is mandatory to achieve the main goal of this research, to reduce the pressure drop of stable W/O emulsions. All experiments in this study were conducted using a flow loop described in section 3.1.

All flowloop experiments reported in this work were achieved by using water (with different NaCl concentration) as the aqueous phase and a type of kerosene known as SAFRA D60 (oil phase), produced in Saudi Arabia. Some physical properties of the oil phase are presented in Table 3.1.

Table 3.1 Properties of SAFRA D60

Product Name	SAFRA D60
Flash Point	67 °C
Density	780 kg/m ³
Viscosity	1.57 mPa.s at 25 °C
Interfacial Tension Oil-Water	0.017 N/m at 20 °C

3.1 DESCRIPTION OF THE FLOW LOOP

A photograph and schematic layout of the emulsion flow loop are shown in Figure 3.1 and Figure 3.2, respectively. As shown in these figures, the flow loop consists of the following:

1. Two small tanks made from PVC with a volume of 70 liters each. These tanks can be used together at the same time.
2. Two centrifugal pumps; one is produced by PEDROLLO with 1 HP power to be used for low pumping rates. The other one is produced by Semnan Co. with 2.5 HP to be used for high pumping rates.
3. Two OMEGA turbine flowmeters; one for the 1-in piping system and the other for the ½-in piping system. Both flowmeters cover the volumetric flowrates range between 0 gallon per minute (gpm) and 50 gpm. Flowrates can be read directly from flowmeter screen or can be read and stored in PC.
4. Two horizontal pipe test sections with inside diameter of 0.0254 m and 0.0127 m made from acrylic resin to allow visual observation. Each test section consists of 3 acrylic tubes with lengths of 1.5 m, 2 m and 1.5 m connected together in this order with flanges and fixed on a strong steel structure, giving a total length of 5 m. Other pipes were made from CPV with length of 6 m. Therefore, the total length of the flowloop is 11 m.

5. Two Smart Differential Pressure Transducers made by ROSEMOUNT Company. Both transducers have a built-in screen with four digits to monitor pressure difference between two points in the pipe 1 m apart from each other. They work with 24 V; Therefore they are connected firstly to a transformer and then to the main power supply. The pressure transducers are connected to test sections either as shown in Figure 3.1 and Figure 3.2 or as shown in Figure 3.3 and Figure 3.4. In order to avoid errors in the pressure drop measurements, the whole transducer system and its connecting lines should be filled with water and no burrs in the pipe wall of all connecting pipes. The first pressure tap is located 8 m apart from the entrance to be sure that the flow is fully developed. Both pressure transducers are connected to PC through a data acquisition (DAc) system to display and store all data.

6. Conductivity measurements cell, which is used to detect the emulsion type and to measure emulsion conductivity while flowing in the 1-in piping system. Such system is powered by AC power supply and conductivity measurements are monitored by PC through a data acquisition system.

7. Cooling system, to maintain temperature at the desired temperature (25 °C); It consists of a brass coiled tubing, placed in one of the tanks, connected to a Recirculator used to control the cooling fluid (water) temperature.



Figure 3.1 A photograph of the flowloop

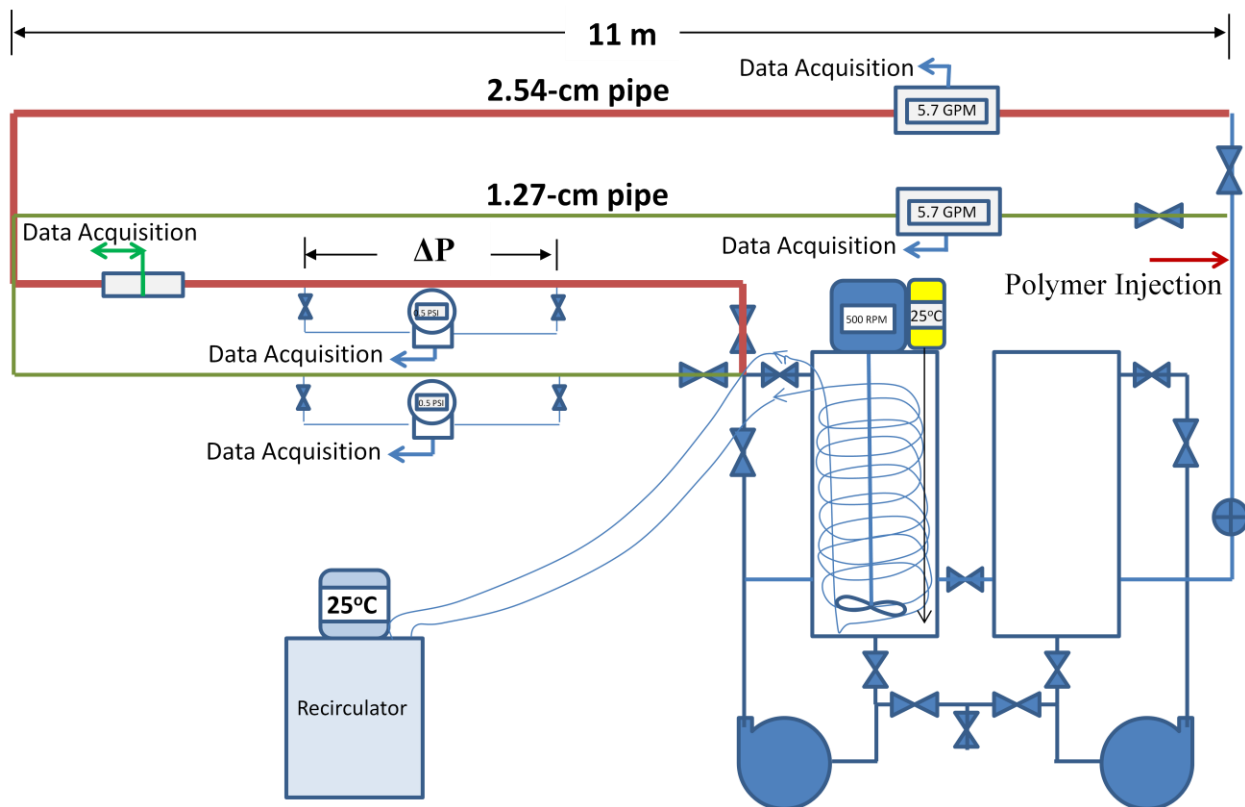


Figure 3.2 A Schematic layout of the flowloop

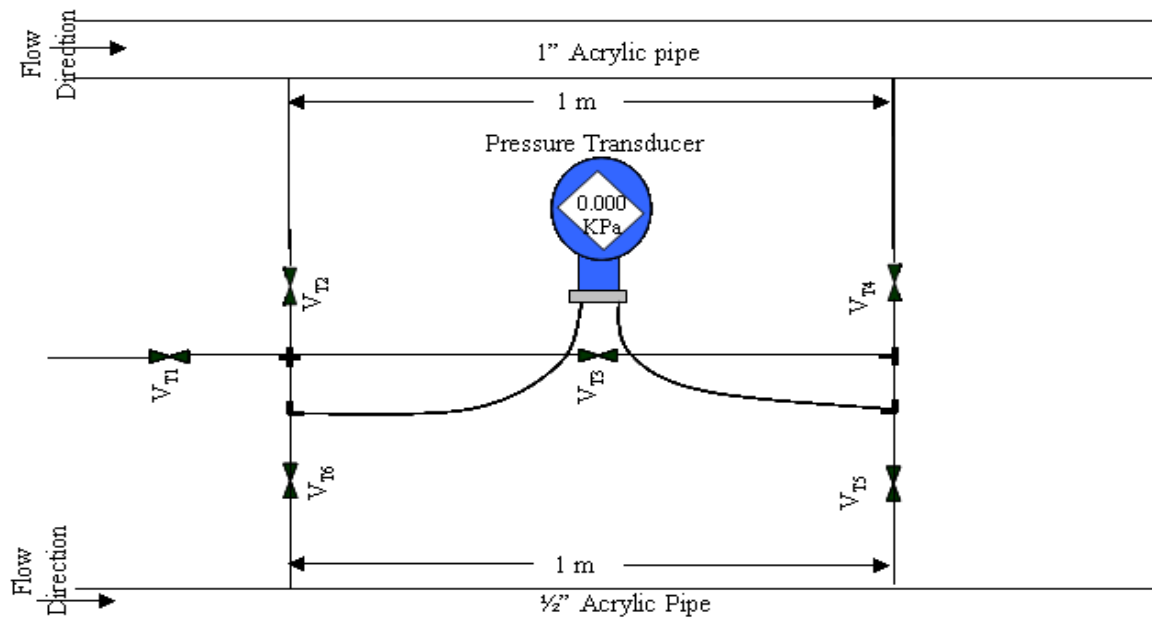


Figure 3.3 Schematic layout of one possible design of the pressure transducer system



Figure 3.4 A photograph of the pressure transducer systems

3.2 STABILITY TEST

Bottle test is used to achieve stability tests for all formed emulsions by monitoring percentage of separated oil and/or water layer with time. Such test can give an indication about emulsion quality. In other words, it can tell qualitatively about the average size of the dispersed phase droplets. The smaller the droplets average size, the more stable the emulsion.

3.3 EMULSION TYPE

Dilution test was used to identify the emulsion continuous (external) phase. In this test, one droplet of the formed emulsion is injected in an oil or water pure phase. If droplet disperses, emulsion continuous (external) phase is the same as the used fluid for the test and vice versa. For example, W/O emulsion droplet will disperse in oil rather than water.

Also, emulsion type can be detected by measuring its conductivity either statically by a conductivity meter or in-line (dynamically) by the designed conductivity measurements system as mentioned in section 3.6. This test is based on the fact that brine is conductive and oil is nonconductive and emulsion continuous phase is dominating emulsion conductivity.

3.4 DISPERSED PHASE DROPLET SIZE MEASUREMENTS

Such task is achieved using Leica-300 camera, connected to a Leica DM2000 microscope with 6 different lenses (5x, 10x, 20x, 40x, 50x, and 100x). Camera is also connected to a computer and all images can be produced by imaging software. This setup is illustrated in Figure 3.5.

3.5 RHEOLOGICAL TEST

All rheological measurements were conducted using the Rheologica StressTech rheometer, shown in Figure 3.6. The rheometer has a torque range from 3.0×10^{-8} to 2.0×10^{-1} N.m with a torque resolution of 1.0×10^{-10} N.m. The bob/cup set, where bob is

the rotating part, was used to conduct steady shear rate sweep tests. The tested emulsion volume is 15.9 cm^3 .



Figure 3.5 A photograph of the micrographic measurements setup



Figure 3.6 A photograph of the rheological test setup

3.6 CONDUCTIVITY MEASUREMENTS

Stability test is used to be conducted using bottle or centrifugal bottle tests, using naked eyes to monitor phase separation volume with time. However, some phase separation might occur without detection by naked eyes. Therefore, here, conductivity measurement system is proposed to be used to specify emulsion quality and to detect emulsion separation with time and to be used to identify the emulsion type (emulsion external phase). An AC power supply is used to supply 10 V. Current will pass through emulsion using a conductivity cell and measuring voltage across a resistor ($580\ \Omega$), placed in series with emulsion. Conductivity cell has two brass wires placed in the same x (direction of the flow) but perpendicular to the flow. Such setup is presented in Figure

3.7 and Figure 3.8. Also, in-line conductivity measurements of different tap water/oil compositions are illustrated in Figure 3.9.

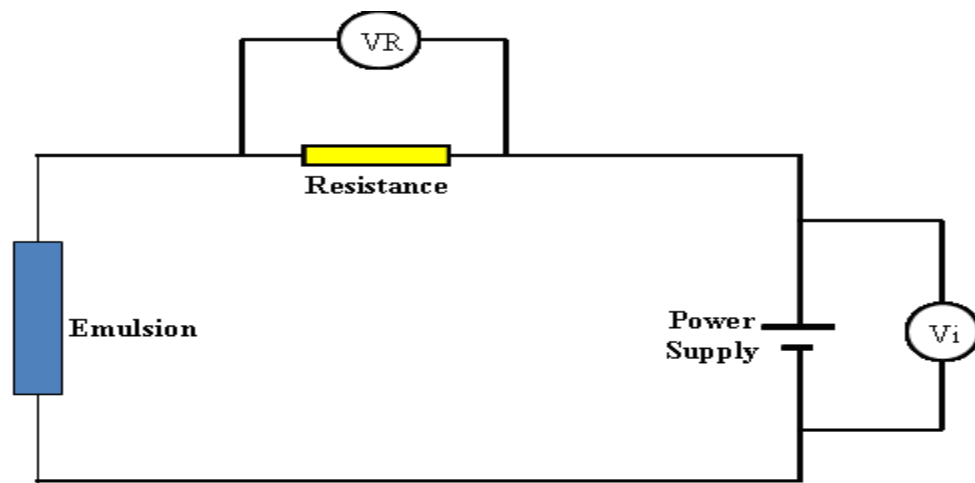


Figure 3.7 Schematic layout of the conductivity test setup

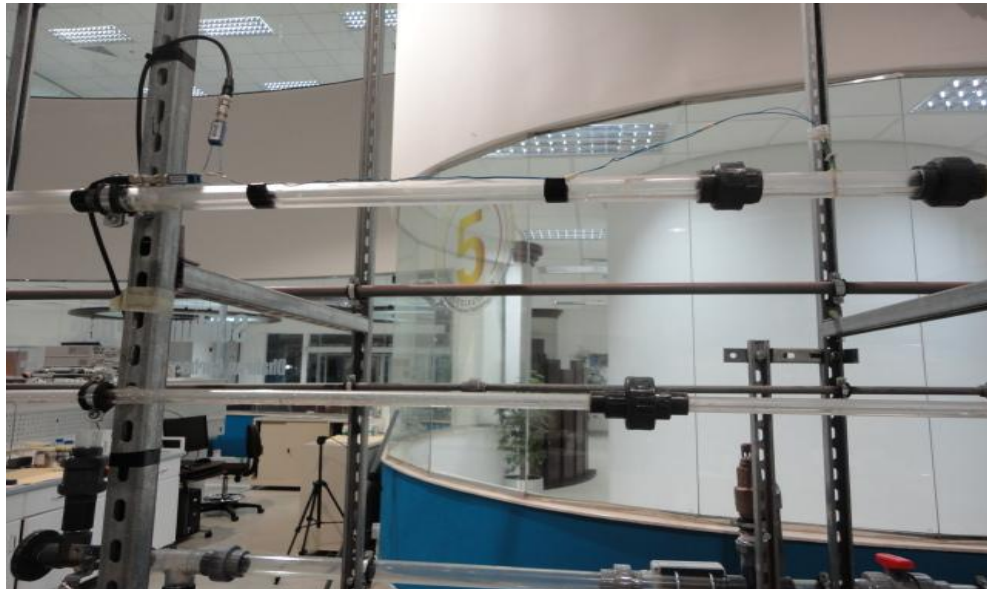


Figure 3.8 A photograph of the conductivity measurements setup

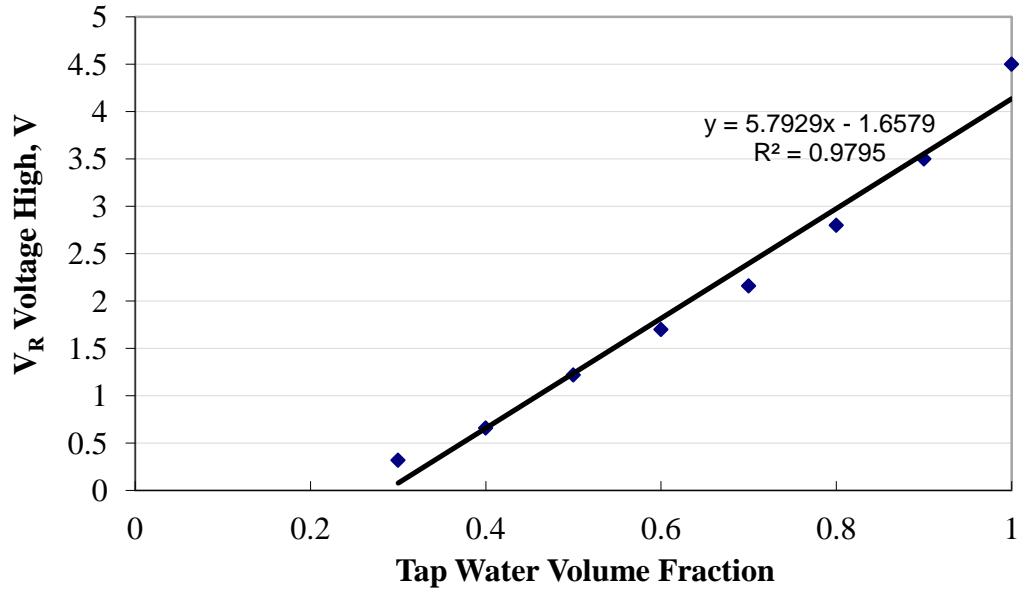


Figure 3.9 In-line conductivity measurements of water/oil system

3.7 EXPERIMENTAL PROCEDURE

3.7.1 Definitions

1. The *friction factor* (f) is a function of the Reynolds number of the flow and the relative roughness of the pipe (k/D). For a horizontal pipe flow, Darcy friction factor can be calculated from the following relation:

$$f = \frac{\Delta P}{L} \frac{2D}{\rho u^2} \quad (1)$$

where: ΔP : Pressure drop (Pa/m²)

L: The distance between the two pressure taps (m)

D: Inside diameter of the pipe (m)

ρ : Fluid density (kg/m³)

u : In-situ average velocity of the fluid (m/s)

However, for single phase laminar flow (Reynolds number less than 2300) in tubes, a well known correlation proposed by Hagen-Poiseuille can be used:

$$f = 64 / \text{Re} \quad (2)$$

In addition, for single phase turbulent flow (Reynolds number up to 10^5) in smooth pipes, a very widely used empirical equation, giving a very good approximation of the friction factor, is a correlation proposed by Blasius:

$$f = 0.316 \text{Re}^{-0.25} \quad (3)$$

In addition, the turbulent friction factor can be determined using other correlations, such as the Zigrang & Sylvester (1985) correlation defined in equation (4), or by using a Moody's chart.

$$\frac{1}{\sqrt{f}} = -2 \log \left[\frac{k/D}{3.7} - \frac{4.518}{\text{Re}} \log \left[\frac{6.9}{\text{Re}} + \left(\frac{k}{3.71D} \right)^{1.11} \right] \right] \quad (4)$$

2. The *wall shear stress* (τ) can be estimated as follows:

$$\tau = \frac{\Delta P}{L} \frac{D}{4} \quad (5)$$

3. At a given flow rate, the *pressure drop reduction percentage* (*PDR %*) resulted from any change can be calculated in terms of friction factor, shear stress or pressure drop as follows:

$$PDR\% = \left(\frac{f_{\text{before}} - f_{\text{after}}}{f_{\text{before}}} \right) \times 100 \quad (6)$$

$$PDR\% = \left(\frac{\tau_{\text{before}} - \tau_{\text{after}}}{\tau_{\text{before}}} \right) \times 100 \quad (7)$$

$$PDR\% = \left(\frac{\Delta P_{before} - \Delta P_{after}}{\Delta P_{before}} \right) \times 100 \quad (8)$$

3.7.2 Calibration

After finishing building the emulsion flow loop, all required calibrations were conducted as follows:

1. Both flowmeters were calibrated. The calibration curves of the flowmeter of the one inch piping system are shown in Figure 3.10 and Figure 3.11. However, the calibration curves of that used in the half inch piping system are shown in Figure 3.12 and 3.13. While the first curves represent the flowrate calibration, the second ones represent the flowmeters signals calibration. In Figure 3.10 and Figure 3.12, manual measurements of the flowrates were conducted by measuring the average time required to collect specific water volume.

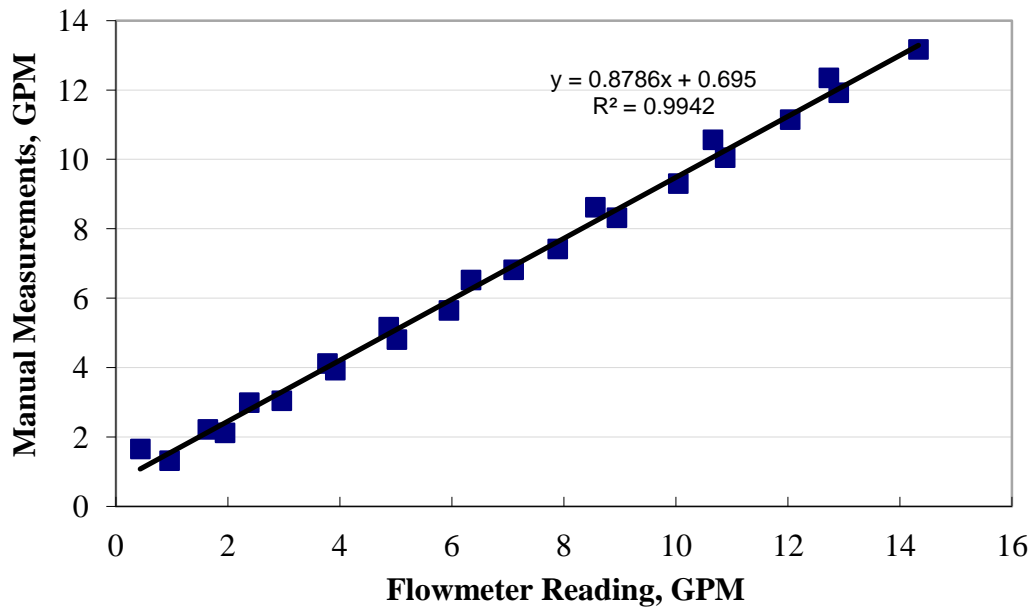


Figure 3.10 The one inch pipe flowmeter calibration

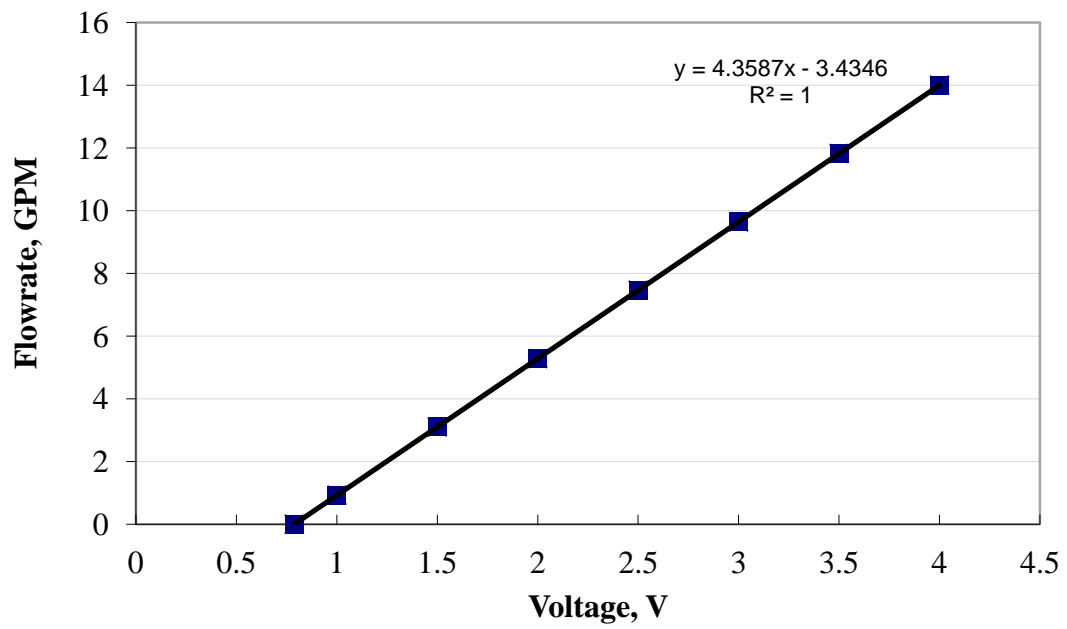


Figure 3.11 The one inch pipe flowmeter signal calibration

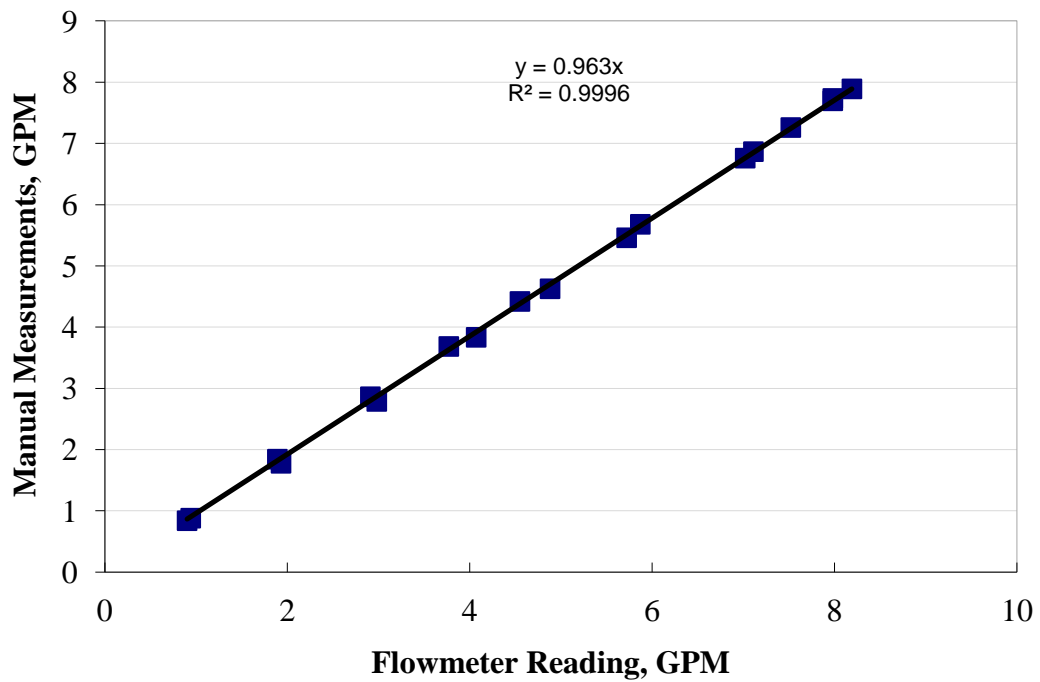


Figure 3.12 The half inch pipe flowmeter calibration

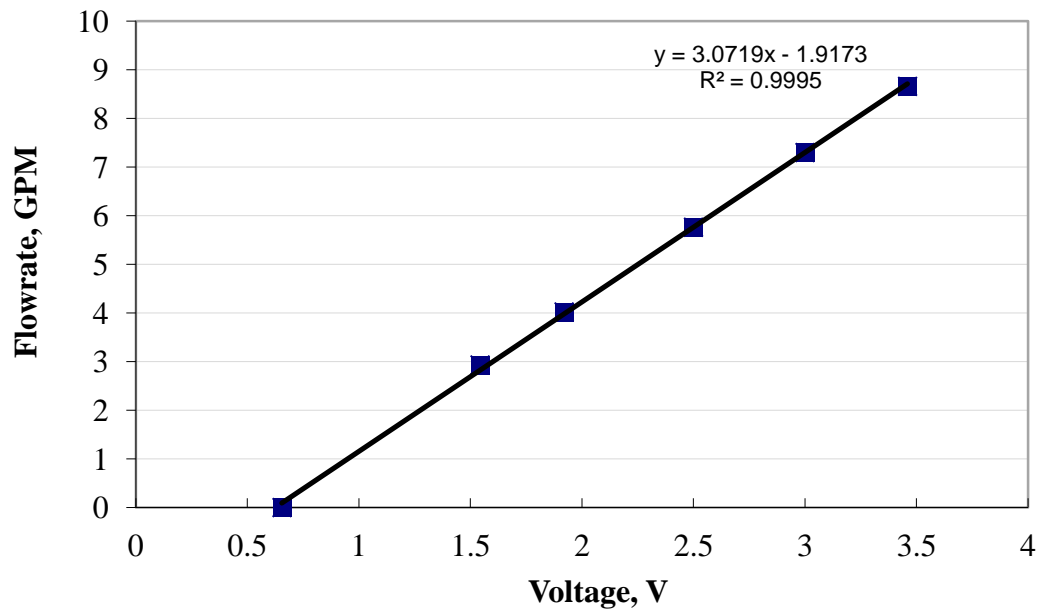


Figure 3.13 The half inch pipe flowmeter signal calibration

2. Pressure transducers were calibrated by using a calibrator. The pressure transducer, connected to the one inch piping system, has a range of 0 – 0.8 PSI and its calibration curve is shown in Figure 3.14. However, the pressure transducer, used for the half inch piping system, is ranging from 0 to 1.8 PSI and its calibration curves are shown in Figure 3.15 and Figure 3.16.

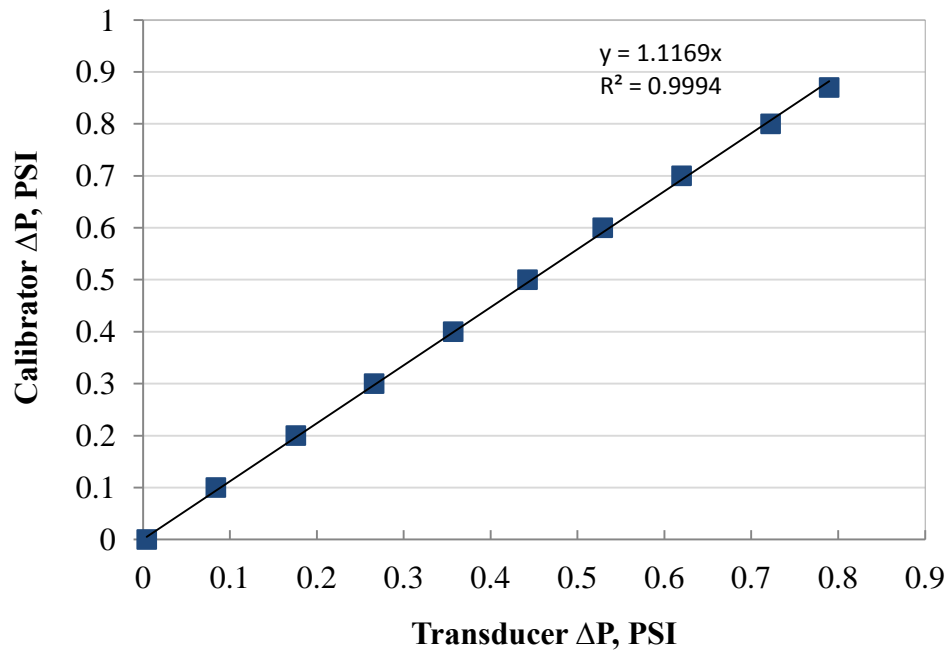


Figure 3.14 Calibration of the pressure transducer used for the one inch piping system

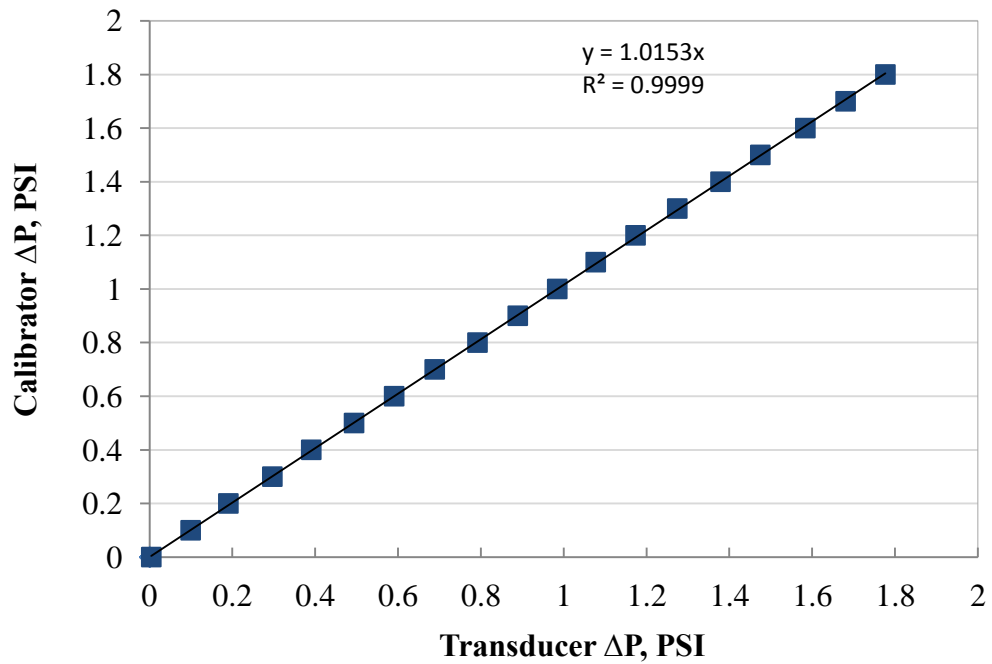


Figure 3.15 Calibration of the pressure transducer used for the half inch piping system

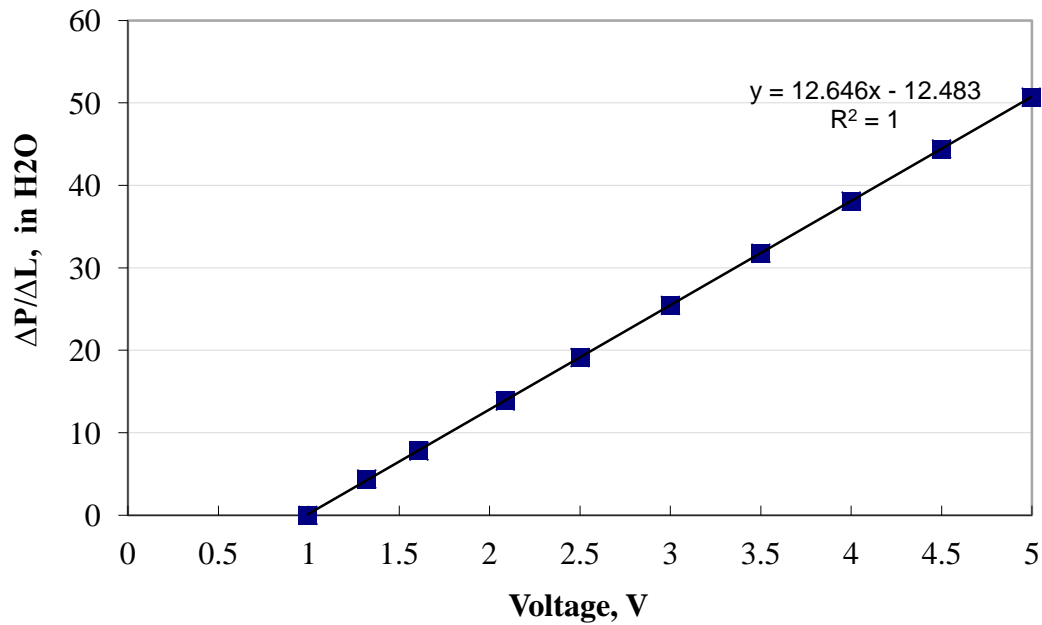


Figure 3.16 Signal calibration of the pressure transducer used for the half inch piping system

The roughness of the acrylic test section was estimated using water single phase pressure drop measurements. Pressure drops were measured and then friction factor was calculated using equation (1). The measured friction factor was then compared with the friction factor calculated from Blasius equation (3) and the Zigrang & Sylvester correlation (equation (4)) for different roughness (see Table 3.2). A log-log figure of Reynolds number against the measured and calculated friction factor was plotted as shown in Figure 3.17. From this figure, the roughness of the acrylic pipe, used as the test sections, was estimated. Blasius and Zigrang & Sylvester correlation (when $k=10^{-5}$ m) gave a good approximation to the friction factor with a deviation of 2.48 % and 2.7 %

from the measured values. Therefore, the roughness of the pipe was 1×10^{-5} m which can be considered as a smooth pipe.

For checking, experimental single phase data of water and oil in both pipes with those from Blasius form were compared. Results showed a close agreement between experimental data and Blasius data (see Figure 3.18 and Figure 3.19) and that means that pipes are smooth.

Table 3.2 Single phase water friction factors

Water flowrate (m ³ /s)	Reynolds Number	Experimental friction factor (Eq. 1)	Blasius friction factor (Eq. 3)	Zigrang & Sylvester friction factor (Eq. 4)		
				k=0.1mm	k=0.01mm	k=1μm
1.26E-04	6262	0.0372	0.0355	0.0396	0.0356	0.0351
2.52E-04	12524	0.0301	0.0299	0.0351	0.0298	0.0292
3.79E-04	18786	0.0272	0.027	0.0332	0.0271	0.0264
5.05E-04	25047	0.0259	0.0251	0.0321	0.0255	0.0246
6.31E-04	31309	0.0235	0.0238	0.0315	0.0243	0.0234
7.57E-04	37571	0.0225	0.0227	0.031	0.0235	0.0224
8.83E-04	43833	0.022	0.0218	0.0306	0.0228	0.0217
1.01E-03	50095	0.0207	0.0211	0.0304	0.0223	0.0211

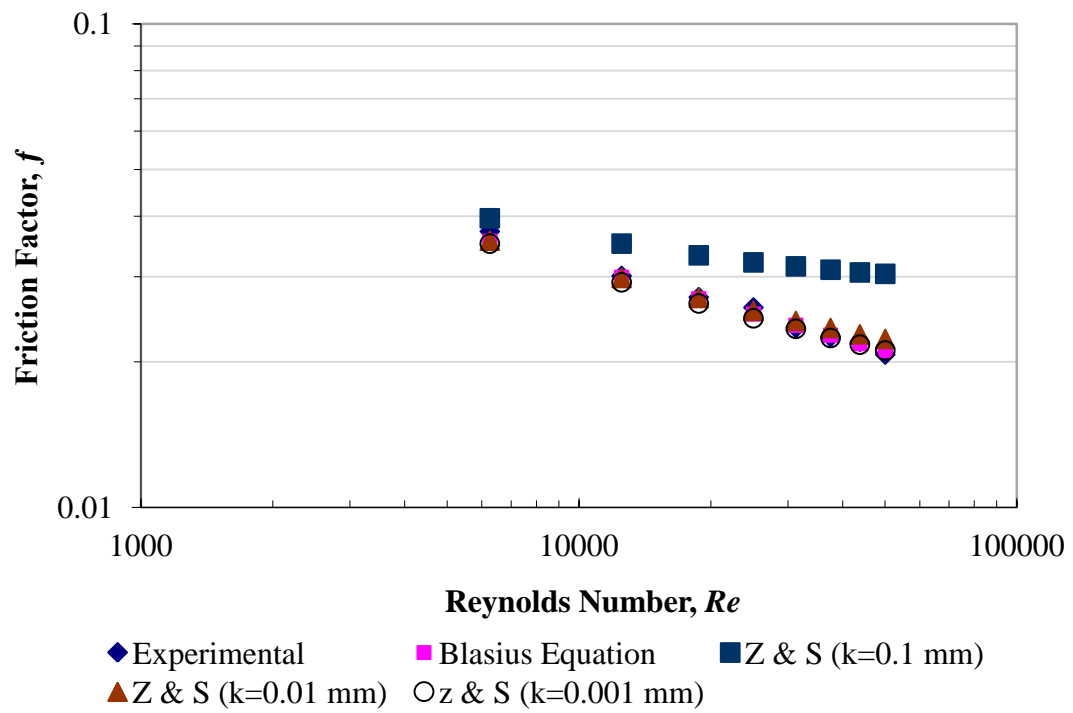


Figure 3.17 Friction factors vs. Reynolds number of water flow

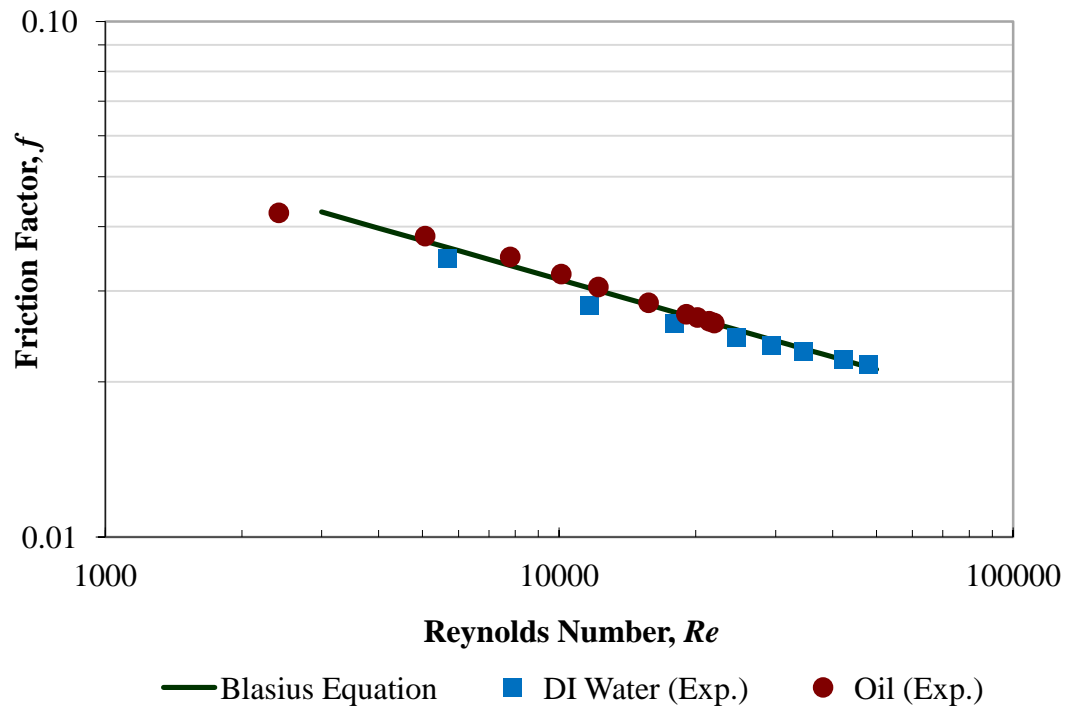


Figure 3.18 Friction factor vs. Reynolds number of single phase flow in 1-in pipe

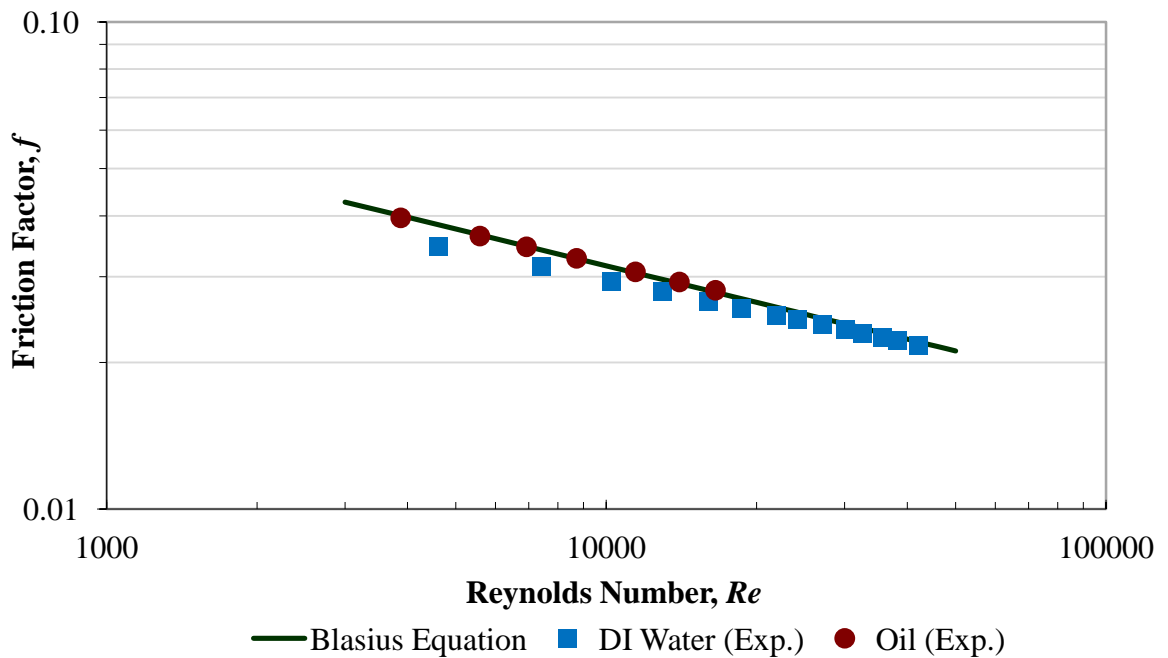


Figure 3.19 Friction factor vs. Reynolds number of single phase flow in 0.5-in pipe

3.7.3 Emulsion Preparation

Surfactant stabilized W/O and O/W emulsions were made as follows:

The dispersed phase (either Bine (with specific wt% NaCl) or oil) was added at 1 L/min to the emulsified external phase. Stable emulsions were prepared as follows:

1. Specific volume of the external phase is put in a 36 L container.
2. 0.6 volume % of emulsifier is then added.
3. After that, specific volume % of dispersed phase was added at 1 L/min while mixing at 8000 RPM by using high power homogenizer. This homogenizer was produced by IKA in Germany and it has a power of 1100 W.
4. Emulsion quality is then tested by dilution and conductivity measurements tests as discussed earlier.

3.7.4 Operation of the Flow Loop

Once emulsion is already made, before any experiments, the followings should be checked:

1. All lines in the pressure transducer systems, illustrated in Figure 3.3 and Figure 3.4, are filled with water and no vacuum pressure exists in the flowloop pipes, pumps and tanks.
1. When measuring pressure drop, all valves should be checked.
2. No air bubbles exist in all connection lines in the pressure transducer systems

since air bubbles will affect pressure drop measurements.

3. When using only one differential pressure transducer, as shown in Figure 3.3, during pressure drop measurements through the 1-in pipe, the valves V_{T2} and V_{T4} are open while the remaining valves are closed. However, when emulsion is flowing inside 0.5-in pipe, V_{T5} and V_{T6} are open while the remaining valves are closed. The emulsion pump is turned on and the volumetric flowrate is controlled via a control valve.

A fully developed flow must be achieved before all experiments reported in this dissertation. Theoretically, Coulson et al. (1980) reported that a single-phase fully developed flow can be reached at the distance of 50-100 pipe diameters at the low Reynolds number of 2500. Therefore, for these particular test sections with 0.0254 m and 0.0127 m inside diameter, a fully developed single phase flow could be achieved at less than 2.54 m and 1.27 m from the entrance for both pipes respectively. However, a fully developed turbulent flow could be obtained at a pipe length smaller than 1.27 m from the entrance section. Therefore, since the distance between the tee-section and the first pressure tap is about 8 m, there is no problem to achieve a fully developed flow before pressure drop measurements.

Once stabilized pressure transducer readings and flowrates are achieved, pressure drop is recorded. Then, three emulsion samples are taken for stability, droplet size measurements and rheological tests.

3.8 UNCERTAINTY ANALYSIS

Error limits and the experimental data quality can be described by a technique known as uncertainty analysis. Each measurement is associated with error which can be defined as the difference between the true and measured values. Errors can be divided into two groups: random and systematic. While random uncertainty was calculated based on the data standard deviation, systematic uncertainty was calculated based on the equipment calibration errors. Therefore, the combination of the random and systematic uncertainties is known as the combined uncertainty. More details of this technique are explained extensively by Dieck (2007).

The flowmeters and differential pressure transmitters and viscometer information and accuracies are presented in Table 3.3. All uncertainties were calculated within the 95 % confidence level using method described by Dieck (2007).

Table 3.3 Instruments information and accuracies

					Measurements Uncertainty for 95% Confidence					
					Low Re			High Re		
Parameter	Test Section	Instrument	Supplier	Range	Random Uncertainty	Systematic Uncertainty	Combined Uncertainty	Random Uncertainty	Systematic Uncertainty	Combined Uncertainty
Flowrate	1.27-cm pipe	Digital Flowmeter	OMEGA	0 - 50 gal/min	0.151%	0.04%	0.305%	0.117%	0.04%	0.237%
	2.54-cm pipe				0.046%	0.58%	0.587%	0.010%	0.58%	0.580%
Pressure Drop	1.27-cm pipe	Smart Rosemount Pressure Transmitter	Emerson	0 - 1.8 PSI	0.172%	0.01%	0.344%	0.219%	0.01%	0.438%
	2.54-cm pipe			0 - 0.8 PSI	0.675%	0.06%	1.351%	0.047%	0.06%	0.112%
Viscosity	N/A	Rheometer	Rheologica StressTech	3.0×10^{-8} to 2.0×10^{-1} N.m	0.00007%	0.099%	0.099%	0.00002%	0.099%	0.099%

CHAPTER 4

EFFECT OF WATER FRACTION ON SURFACTANT-STABILIZED WATER-IN-OIL EMULSION FLOW CHARACTERISTICS

4.1 INTRODUCTION

One of the common occurrences in the petroleum industry during transportation and production is oil-water flow in pipes. Moreover, two-phase liquid-liquid flow is common in the process and petrochemical industries. Although the accurate prediction of oil-water flow is essential, oil-water flow in pipes has not been explored as much as gas-liquid flow. The majority of studies reported in literature, have mainly focused on oil-water segregated flow patterns (annular and stratified flow). The pipeline flow behavior of water-in-oil (W/O) and/or oil-in-water (O/W) emulsions has received less attention.

Emulsion technology has been utilized in the acid treatment of reservoir rocks in the region near well bore. Sometimes, the pore structure near the well bore is plugged either by particulates from drilling process or by production precipitation deposits caused by pressure or temperature changes. As a result, permeability is reduced as well as the well productivity. To remove these unwanted deposits, acid stimulation is used. The carbonate matrix acidizing process consists of injecting hydrochloric acid into the formation pore space. The acid reacts with and dissolves portions of rock matrix and hence permeability

is increased. The effectiveness of the treatment depends on the penetration depth of the acid into the formation.

Acid is consumed very quickly and it causes corrosion in the metallic tubular goods. Therefore, deep penetration of the acid as well as corrosion rate reduction is the target. One method to achieve such retardation and to avoid corrosion is the use of the emulsified acid where the hydrochloric acid is injected as a W/O emulsion. To maintain hydrochloric acid as the dispersed phase, it is necessary to use a composition that sits near the oil apex of the pseudo ternary diagram as reported by Hoefner and Fogler (1985) to form stable emulsion.

Generally, water-in-oil (W/O) or oil-in-water (O/W) emulsions are unstable thermodynamically. As the water/oil droplets are hydrophilic/ hydrophobic they tend to separate from the oil/ water continuous phase. In order to form a stable emulsion, a surfactant (emulsifier) must be used to reduce the interfacial tension and promote the formation of smaller droplets. High pressure drop, caused by friction losses, can be a problem while pumping emulsified acid. As a result, emulsified acid is pumped at low flowrates and thus limited job efficiency is achieved. Consequently, methods of pressure drop reduction are highly desired.

Laminar and turbulent flow behaviors of unstable O/W and W/O emulsions in pipes have received a considerable attention (Baron et al. (1953), Cengel et al. (1962), Pal (1987), Pal (1993), Angeli and Hewitt (1998), Masalova et al. (2003), Pal (2007), Al-Yaari et al. (2009) and Omer and Pal (2010)). The emulsion effective viscosities were calculated

form single phase Hagen-Poiseuille equation and Blasius equation for laminar and turbulent flow, respectively. Since emulsion effective viscosity calculated for turbulent flow is lower than that for laminar flow or since the measured turbulent pressure drop is lower than that calculated from Blasius equation, drag reduction was claimed (Cengel et al. (1962), Pal (1987), Pal (1993), and Omer and Pal (2010)). In addition, it was reported that such drag reduction increases with: the increase in the dispersed phase fraction (Pal (1987) and Pal (1993)); the decrease in pipe diameter (Pal (1993) and Masalova et al. (2003)) and the decrease in the viscosity of oil continuum (Omer and Pal (2010)). Moreover, drag reduction is a function of emulsion type (Pal 1993) and pipe material (Angeli and Hewitt (1998)). Droplets stretching and elongation, in turbulent regime, is proposed as a mechanism of the reported drag reduction of studied unstable emulsions (Pal (2007)). Furthermore, phase inversion of unstable emulsions was also reported (Pal (1993) and Al-Yaari et al. (2009)).

However, pipeline flow behaviors of stable O/W and W/O emulsions have received less attention. While drag reduction was reported for surfactant stabilized O/W emulsions (Rose and Marsden (1970) and Zakin et al. (1979)), little or no drag reduction was addressed for surfactant stabilized W/O emulsions (Pal (1993) and Omer and Pal (2010)). In addition, as dispersed phase fraction increased, phase inversion and an increase in emulsion effective viscosities, calculated from the single phase equations, were reported (Pal (1993) and Omer and Pal (2010)).

This chapter aims at studying the flow characteristics of surfactant stabilized W/O emulsions. The influence of water (dispersed phase) fraction on emulsion stability,

droplet size, viscosity and pressure drop is investigated. Also, it aims to examine a possible friction reduction through the control of water fraction. In addition, stable W/O emulsions dependency on pipe diameter is studied.

4.2 EXPERIMENTAL SETUP & PROCEDURE

Surfactant-stabilized W/O emulsions were prepared using brine (with 50 kppm NaCl) as the aqueous phase and a type of kerosene known as SAFRA D60 produced in Saudi Arabia as the oil phase. Some physical properties of the oil are presented in Table 3.1.

ARMAC T, from Akzo Nobel, was used as the emulsifying agent and some of its physical properties are presented in Table 4.1. 40 wt % of the emulsifying agent (solid) was dissolved in naphtha to form the liquid phase.

Table 4.1 Emulsifying agent properties

Commercial Name	ARMAC T
Common Name	Tallowalkylamine acetates
Appearance at 25 °C	Solid
Hydropile- Lipophile Balance (HLB)	6.8

A schematic layout of the flow loop is shown in Figure 3.2. The flow loop consists of two small 70-L PVC tanks. Two centrifugal pumps are used for low and high pump rates. The test sections are two acrylic resin horizontal pipes (2.54-cm and 1.27-cm ID) that allow visual observation. Flow rate is measured by two OMEGA turbine flowmeters.

The total length of the flowloop test sections is 11 m. Emulsion pressure drop is measured by two smart differential pressure transmitters manufactured by the Rosemount, Inc. A fully developed flow must be achieved before all experiments reported in this chapter. Theoretically, Coulson et al. (1980) reported that a single-phase fully developed flow can be reached at the distance of 50-100 pipe diameters at the low Reynolds number of 2500. Therefore, for this particular test sections with 0.0254 m and 0.0127 m inside diameters, a fully developed single phase flow could be achieved at less than 2.54 m and 1.27 m from the entrance for both pipes respectively. However, a fully developed turbulent flow could be obtained at a pipe length smaller than 1.27 m from the entrance section. Therefore, since the distance between the tee-section and the first pressure tap is about 8 m, there is no problem to achieve a fully developed flow before pressure drop measurements. In addition, the flow loop contains a conductivity measurements cell that is used to detect the emulsion type and to measure emulsion conductivity while flow takes place in the 2.54-cm piping system. The conductivity measurements are monitored by PC through a data-acquisition system. Furthermore, emulsion temperature was maintained at 25 °C by the cooling system illustrated in Figure 3.2.

Emulsion Preparation

36 liters of surfactant-stabilized W/O emulsions were made by adding the required volume % of brine at 1 L/min to the emulsified oil (oil with 0.6 volume % emulsifier) while mixing at 8,000 rev/min (RPM) using high power homogenizer (Ultra Turrax T 50

basic, WERKE IKA, Germany). Emulsion quality was tested by dilution and conductivity measurements. Emulsions were then transferred to one of the flow loop tanks. This procedure was used in preparing all the emulsions but with different brine-volume fractions.

Stability Test

A bottle test was used to achieve stability tests for all formed emulsions by monitoring the percentage of separated oil and/or water layer with time. Such a test can give an indication about emulsion quality. In other words, it can determine qualitatively the average size of the dispersed phase (brine) droplets. As a rule of thumb, the smaller the droplets, the more stable the emulsion if other conditions are same.

Emulsion Type

A dilution test was used to identify the emulsion continuous (external) phase. In this test, a droplet of the formed emulsion was injected into an oil or water sample. If the injected droplet was found to disperse, the emulsion continuous (external) phase is the same as the fluid used for the test. For example, W/O emulsion droplets will disperse in an oil sample rather than a water sample. Also, the emulsion type was detected by measuring its conductivity. This test is based on the fact that a brine solution is conductive, oil is nonconductive, and the emulsion continuous phase dominates the emulsion conductivity.

Rheological Test

All rheological measurements were conducted using the Rheologica StressTech rheometer. The rheometer has a torque range from 3.0×10^{-8} to 2.0×10^{-1} N.m with a

torque resolution of 1.0×10^{-10} N.m. The bob and cup set where the bob is the rotating part was used to conduct steady shear-rate sweep tests. The tested emulsion volume was 15.9 cm^3 .

Once W/O emulsions have been produced, steady shear rate sweep tests were conducted to produce emulsion viscosity curves at different water fractions. In this test, 15.9 cm^3 of the emulsion sample, containing specific water composition, was sheared gradually with increasing the bob rotating speed till a level where the emulsion sample started spelling out of the cup. The shear rate at this point (upper shear rate), for all the tested emulsions, was $\geq 1000 \text{ s}^{-1}$. The upper shear rate increases as emulsion viscosity increases.

4.3 RESULTS AND DISCUSSIONS

Emulsion Stability

To investigate the effect of water fraction on emulsion stability, emulsions with different water to oil volume % (10/90 (a), 40/60 (b), 50/50 (c), 60/40 (d) and 70/30 (e)) were used. Brine with 5 wt% NaCl (50 kppm) was used as an aqueous phase. After preparing such emulsions, stability tests were carried out using bottle test, by monitoring phase separation with time. These results are presented in Figures 4.1 and 4.2. Although the emulsion preparation procedure is the same (including the emulsification time and intensity and the adding rate of brine), an increase in the volume fraction of the dispersed phase (water) resulted in more concentrated emulsion. In addition, the chance for the

dispersed phase droplets to sediment was lower and the separation occurred only from the oil side.

As shown in these figures, increasing water fraction resulted in more stable emulsion. As water fraction increased, the dispersed phase droplets size became smaller (see Figure 4.3). This is acceptable because when diluted system is mixed, the probability of the dispersed phase droplets to break is lower than that for concentrated systems. Thus, stable W/O emulsion with water of 70 volume % was the most stable one compared with the other emulsions covered in this chapter.

Emulsion Type and Conductivity

Emulsion type and conductivity tests were conducted by performing dilution tests and conductivity measurement, respectively. The emulsion conductivity test was conducted under static conditions after preparing the emulsion by using a conductivity meter. All of the tested emulsions were W/O with a conductivity of 0 $\mu\text{S}/\text{cm}$ (static test), which was confirmed by dilution tests.

Emulsion Droplet Size Distribution

Some microscopic photos were taken for all tested emulsions. Since all emulsions were milky, careful use of cover slips were mandatory to get representative micrographs. These photos are shown in Figure 4.3. As shown in this figure, increasing the water (dispersed phase) fraction resulted in tight emulsion with smaller droplet size distribution which enhances emulsion stability.

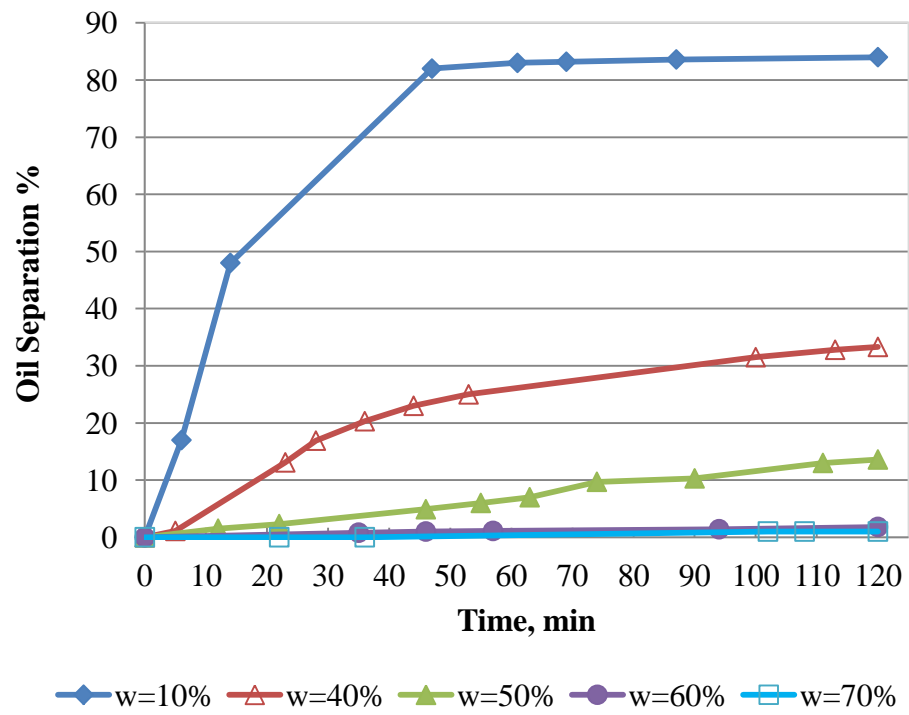


Figure 4.1 Effect of water volume fraction on water-in-oil emulsion stability

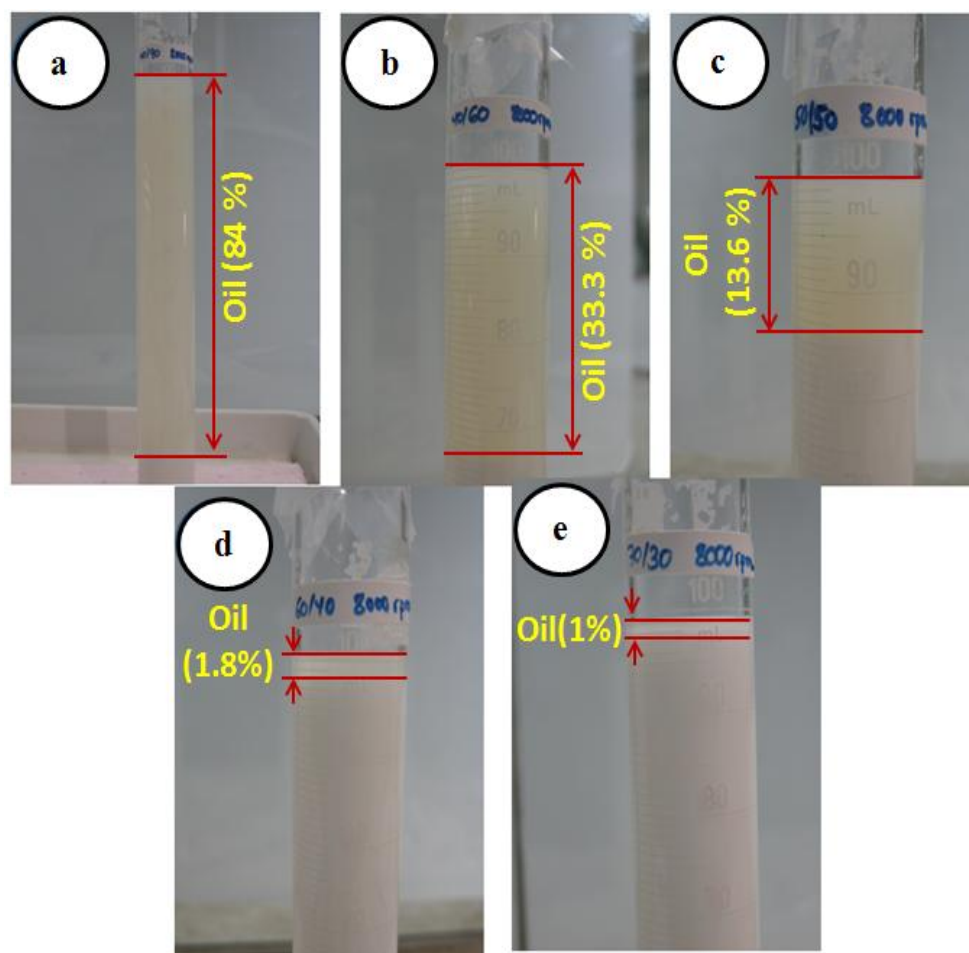


Figure 4.2 Water-in-oil emulsion stability (after 2 hours) at different water volume fractions; (a) 0.1, (b) 0.4, (c) 0.5, (d) 0.6 and (e) 0.7

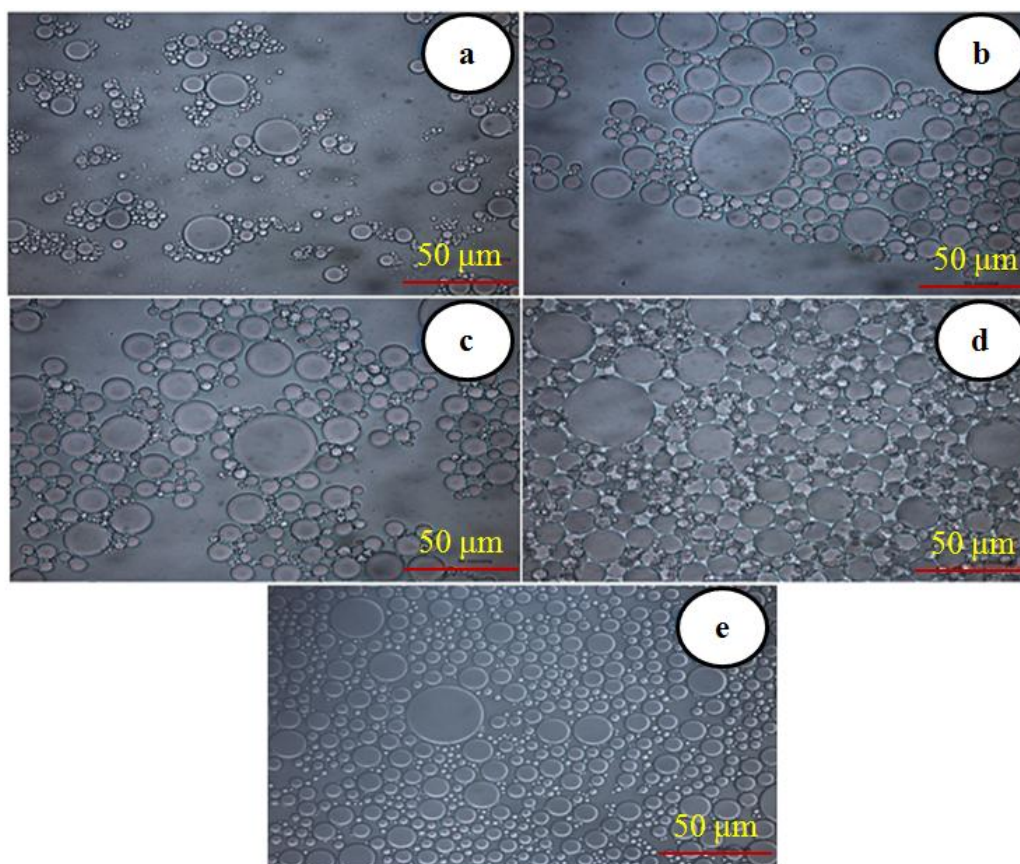


Figure 4.3 Water-in-oil emulsion droplets size and distribution at different water volume fractions; (a) 0.1, (b) 0.4, (c) 0.5, (d) 0.6 and (e) 0.7

Emulsion Rheology

Viscosity curves for all surfactant-stabilized W/O emulsions were obtained using a bob and cup viscometer. As shown in Figure 4.4, almost all emulsions showed a shear thinning behavior. Shear-rate dependency of the viscosity increases as brine (dispersed phase) volume fraction increases. Steady shear rate viscosities were used to calculate emulsion Reynolds numbers (Re) at different shear rates (flowrates).

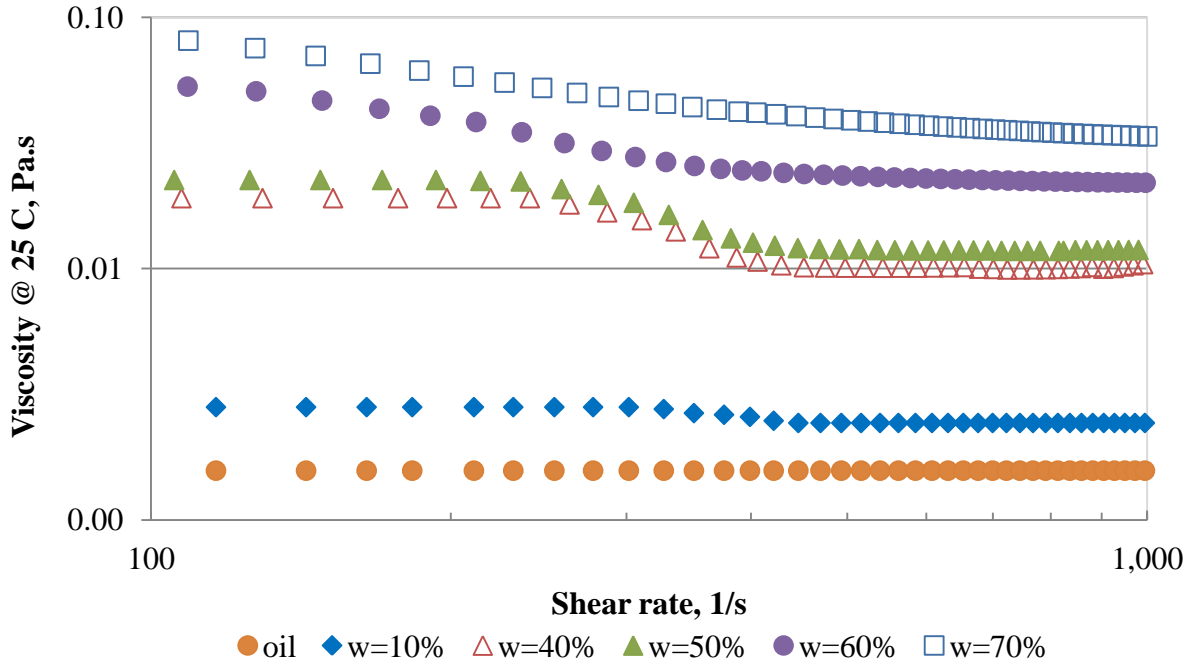


Figure 4.4 Effect of water fraction on water-in-oil emulsion viscosity

Power-law or Ostwald-de Waele model represents the fluid viscosity as a function of shear rate ($\dot{\gamma}$) as shown in equation (1) where k and n are the consistency and the power-law index, respectively. It can be used for shear thinning fluids for the shear rate range within which viscosity decreases as shear rate increases. W/O emulsions behaved as shear thinning fluids when water volume fraction was ≥ 0.4 (see Table 4.2).

$$\eta = k \dot{\gamma}^{n-1} \quad (1)$$

The true wall shear rate and the behavior index (n) were calculated using equations (2) and (3), respectively (Wilkes, 2010). However, n' and k' are related to the power-law constants

as shown in equations (4) and (5), respectively (Wilkes, 2010). In addition, zero-shear rate viscosity (η_o) as well as infinite-shear rate viscosity (η_∞) of all emulsions were calculated from data fittings using Cross model ($R^2 \geq 0.99$), expressed by equation (6). Behavior index (n, n'), consistency index (k, k'), η_o and η_∞ shear rate viscosities are reported in Table 4.2.

$$\dot{\gamma}_w = \frac{4 Q}{\pi R^3} \left[\frac{3}{4} + \frac{1}{4} \frac{d(\ln Q)}{d(\ln \tau_w)} \right] \quad (2)$$

where $\dot{\gamma}_w$ = True wall shear rate

Q = Volumetric flowrate

R = Pipe radius

τ_w = Wall shear stress

The term in brackets in equation (2) is the Robinowitsch correction for non-Newtonian fluids.

$$\frac{d(\ln Q)}{d(\ln \tau_w)} = 1/n \quad (3)$$

$$n' = n \quad (4)$$

$$k' = k \left(\frac{1 + 3n}{4n} \right)^n \quad (5)$$

$$\frac{\eta - \eta_{\infty}}{\eta_o - \eta_{\infty}} = \frac{1}{1 + (\lambda \dot{\gamma})^m} \quad (6)$$

where

η = Emulsion viscosity

η_o = Emulsion zero shear rate viscosity

η_{∞} = Emulsion infinite shear rate viscosity

$\dot{\gamma}$ = Shear rate

λ, m = constants

By fitting data presented in Figure 4.5, η_o and η_{∞} for stable W/O emulsion can be related to water volume fraction (x_w) as shown in equations (7) and (8), respectively.

$$\eta_o = \eta_{oil} * e^{5.8344 x_w} \quad (7)$$

$$\eta_{\infty} = \eta_{oil} * e^{4.3504 x_w} \quad (8)$$

where

η_o = Emulsion zero shear rate viscosity

η_{∞} = Emulsion infinite shear rate viscosity

η_{oil} = Oil viscosity

x_w = Water volume fraction

The mixture viscosity (η) of immiscible liquids can be expressed by the Fluidity-Additivity equation (Equation (9)) as reported by Bingham (1922). Lin (1979) introduced slip factor (λ) to account for slippage effect in polymer liquids (Equation (10)). However, those equations did not account for the presence of emulsifier and hence underestimate W/O emulsion viscosities at different water fraction. Therefore, a viscosity enhancement factor (β) is introduced (Equation (11)). This factor, expressed by equation (12), is a strong function of water fraction and at low shear rates (flowrates) it depends on shear rate as well. Figure 4.6 shows a comparison between the Fluidity-Additivity model and the proposed model to predict stable W/O emulsion viscosities. The proposed model fits the experimental data very well.

$$\frac{1}{\eta} = \left[\frac{x_w}{\eta_w} + \frac{x_o}{\eta_o} \right] \quad (9)$$

where η = Emulsion or mixture viscosity

x_w = Water volume fraction

x_o = Oil volume fraction

η_w = Water viscosity

η_o = Oil viscosity

$$\frac{1}{\eta} = [1 + \lambda (x_w x_o)^{0.5}] \left[\frac{x_w}{\eta_w} + \frac{x_o}{\eta_o} \right] \quad (10)$$

$$\frac{1}{\eta} = [1 - \beta (x_w x_o)^{0.5}] \left[\frac{x_w}{\eta_w} + \frac{x_o}{\eta_o} \right] \quad (11)$$

$$\beta = 1.2381 e^{0.7721 x_w} \quad (12)$$

The majority of the proposed models to predict emulsion viscosities are for low capillary numbers ($N_{ca} \rightarrow 0$), where the emulsion droplets are almost spherical and under creeping flow conditions ($Re \rightarrow 0$) (Hatschek (1911), Richardson (1933), Broughton and Squires (1938), Eilers (1941) and Pal and Rhodes (1989)). Therefore, their models are not function of shear rate.

$$N_{ca} = \frac{\dot{\gamma}_c R_d}{\sigma} \quad (13)$$

where $\dot{\gamma}_c$ = Viscosity of the continuous phase

R_d = Droplet radius

σ = Interfacial tension

However, in our proposed model the shear rate effect is considered. In addition, other proposed models such as that proposed by Pal (2003); although it is not for zero capillary No., it is more complicated and additional information such as interfacial tension, droplet radius, etc are required to be used.

Table 4.2 Rheological parameters of water-in-oil emulsions at 25 °C

Water Volume Fraction (x_w)	Behavior Index		Consistency Index		Zero-Shear Rate Viscosity, Pa.s	Infinite- Shear Rate Viscosity, Pa.s
	n	n'	k	k'	η_o	η_∞
0.7	0.614	0.614	0.4502	0.27052	0.09515	0.0336
0.6	0.586	0.586	0.3302	0.19415	0.05642	0.022
0.5	0.403	0.403	0.703	0.38561	0.02246	0.0118
0.4	0.346	0.346	0.4437	0.24216	0.019071	0.0101
0.1	N/A	N/A	N/A	N/A	0.00281	0.00243

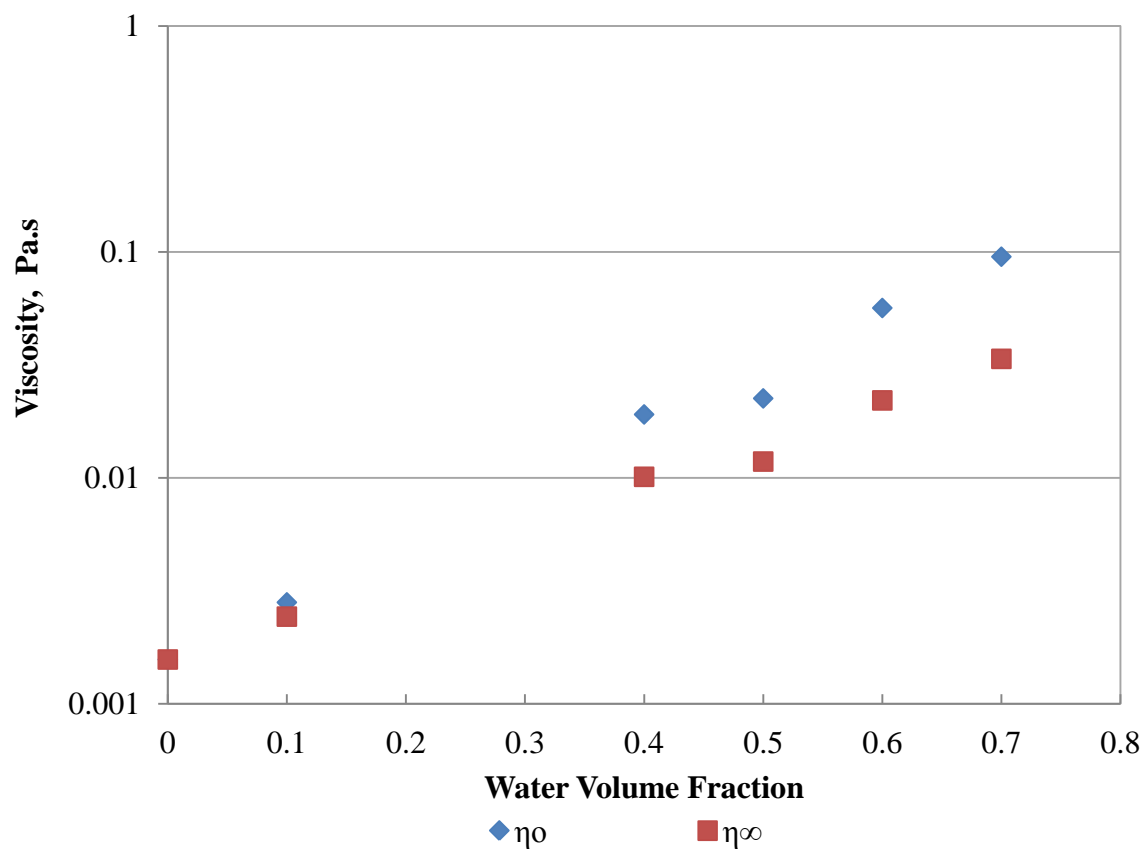


Figure 4.5 Effect of water fraction on emulsion zero and infinite shear-rate viscosities at 25 °C

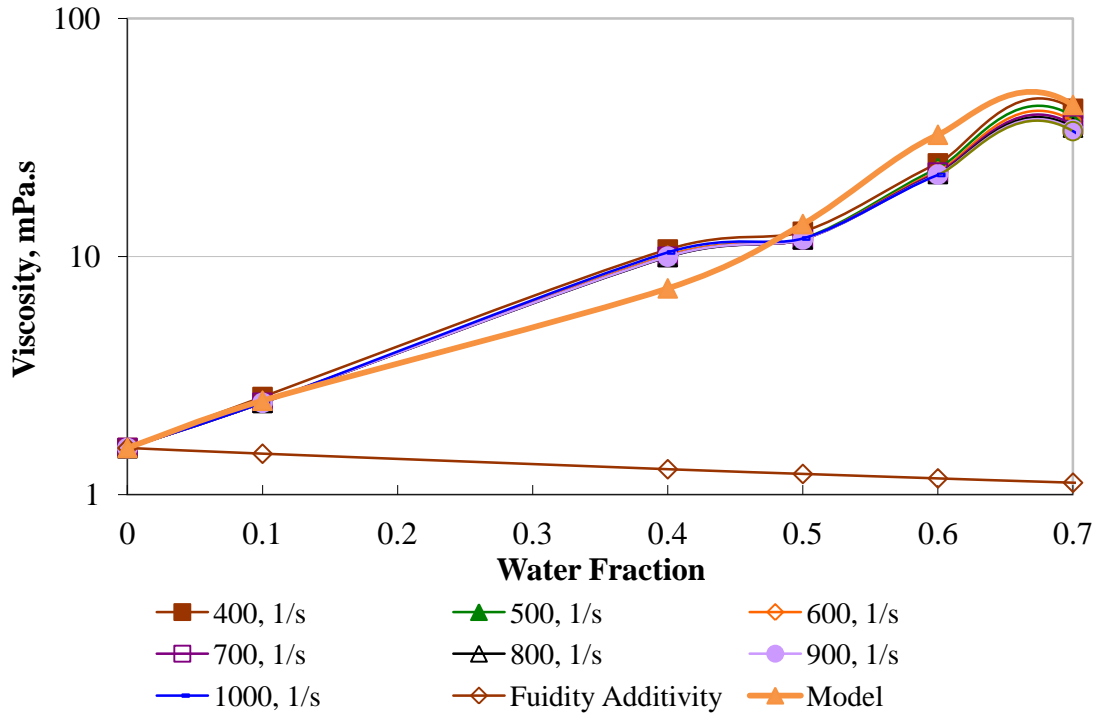


Figure 4.6 Comparison of experimental data of stable water-in-oil emulsion viscosities with predictions using Fluidity Additivity and the proposed model

Emulsion Pressure Drop

The pressure drop of all prepared surfactant-stabilized W/O emulsions were measured at different flow rates in both pipes test sections. All measurements were conducted at steady-state conditions. The emulsion temperature was maintained at 25 °C. Based on the pipe flow shear rate (Eq. (1)), the emulsion viscosity was extracted from rheological measurements and used to calculate Re for the emulsion flow. Reynolds number (Re) and friction factor (f) were defined as shown in equations (13) and (14), respectively.

$$Re = \frac{\rho u D}{\eta} \quad (14)$$

$$f = \frac{\frac{\Delta P}{\Delta L} D}{0.5 \rho u^2} \quad (15)$$

where ρ = Emulsion density at 25 °C

u = Emulsion average velocity

D = Pipe diameter

η = Emulsion viscosity extracted from the steady shear rate sweep test data at the flow corresponding shear calculated by equation (1) at 25 °C

$\frac{\Delta P}{\Delta L}$ = Fully developed pressure gradient

Pressure drop measurement results for emulsion flow in the 2.54-cm pipe are presented in Figure 4.7 and Figure 4.8. However, the pressure drop results for emulsion flow in the 1.27-cm pipe are shown in Figure 4.9.

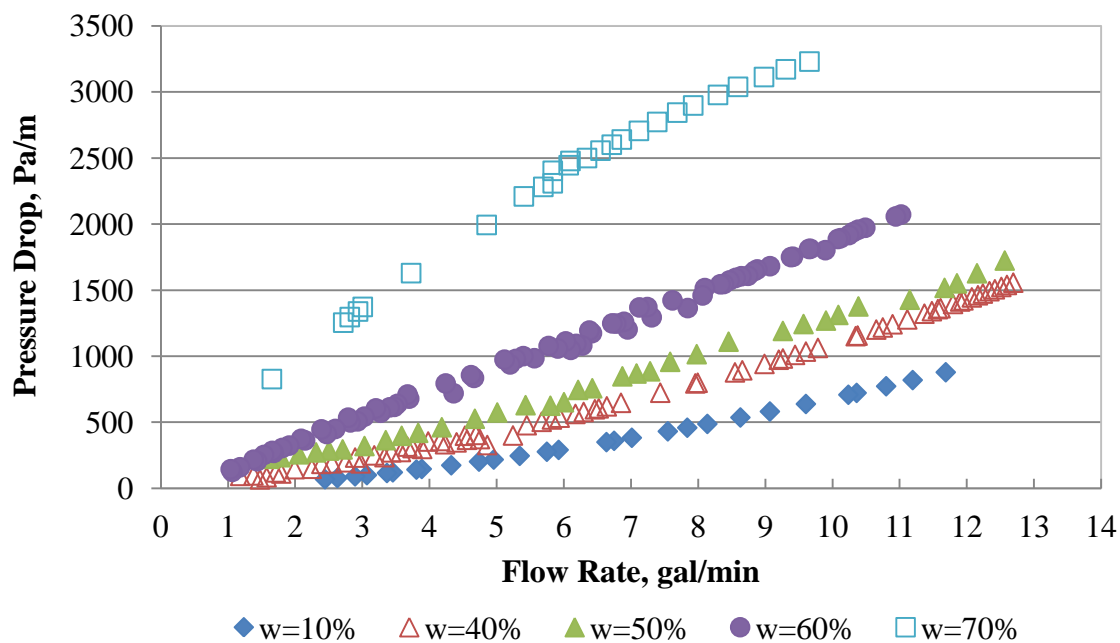


Figure 4.7 Effect of water fraction on water-in-oil emulsion pressure drop in the 2.54-cm pipe

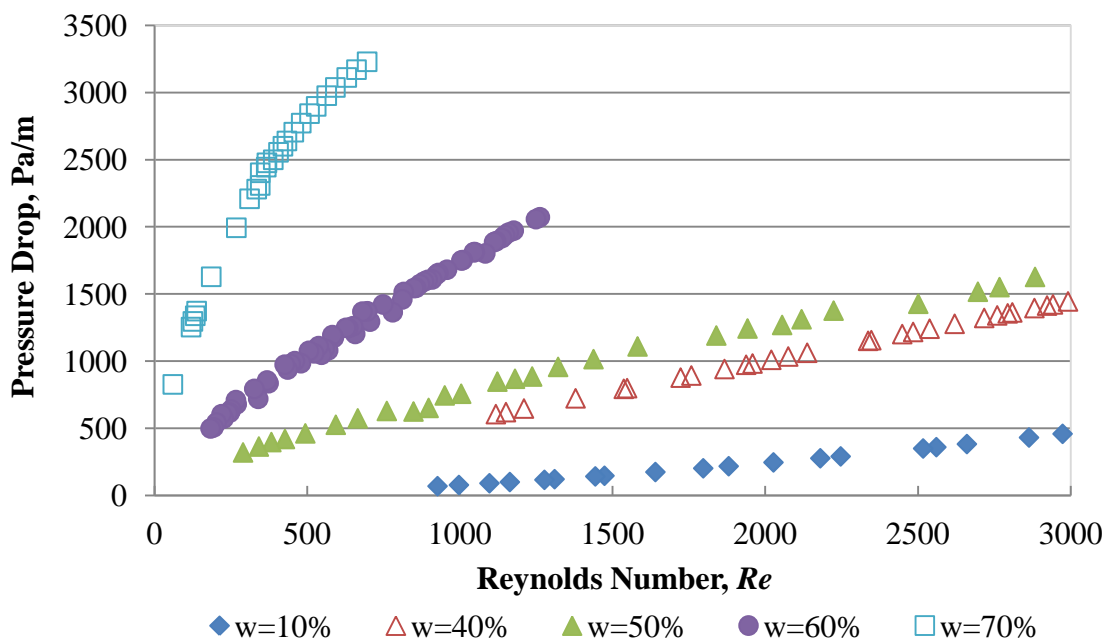


Figure 4.8 Effect of water fraction on water-in-oil emulsion pressure drop in the 2.54-cm pipe

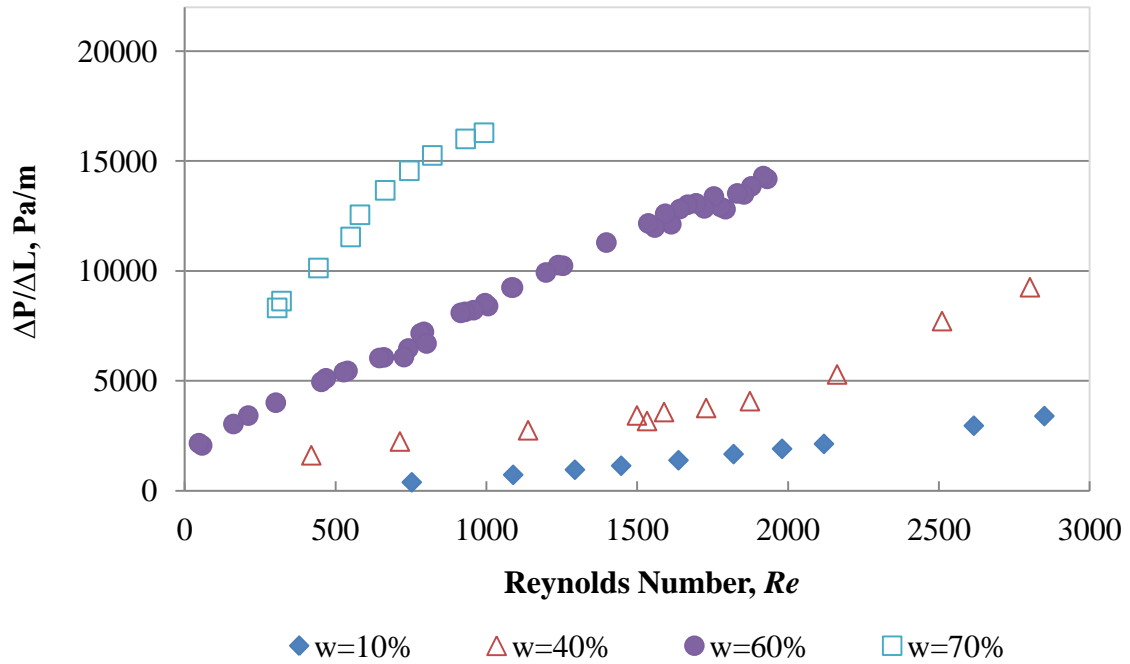


Figure 4.9 Effect of water fraction on water-in-oil emulsion pressure drop in the 1.27-cm pipe

As water (dispersed phase) fraction increased, the emulsion frictional pressure drop in both test sections increased. This increase is due to emulsion crowding at high-dispersed phase-volume fractions. In addition, surfactant-stabilized dispersed phase droplets have strong interfaces; therefore, emulsion viscosity as well as stability was enhanced with increasing water fraction.

Understanding surfactant-stabilized W/O emulsions will help to achieve one of the important goals, which is pressure-drop reduction of such stable emulsions. Based on the results presented in this chapter, pressure-drop reduction of surfactant-stabilized W/O emulsions can be achieved by controlling the water fraction and pipe diameter.

Initially, the pressure drop reduction of stable W/O emulsions can be achieved by decreasing the water fraction (at least for the studied range of Re values). As an example, for acidizing purposes, emulsified acid contains 70 volume % aqueous phase. Therefore, if the water fraction is reduced to 60 volume %, pressure drop could be reduced by (78% to 48%) in the 2.54-cm pipe and by (63% to 41%) in the 1.27-cm pipe for Re ranges of 100 to 1000.

If water volume fraction was reduced from 0.7 to lesser values, the percentages of emulsion pressure drop reduction in both test sections are shown in Figure 4.10 and Figure 4.11. The pressure drop reduction relative to the 70 volume % case (water) is defined as follows:

$$\text{Pressure Drop Reduction} = \frac{\Delta P_{70\% \text{ brine}} - \Delta P_{x\% \text{ brine}}}{\Delta P_{70\% \text{ brine}}} \quad (16)$$

where

$\Delta P_{70\% \text{ brine}}$ = Pressure drop of Emulsion containing 70 volume % water

$\Delta P_{x\% \text{ brine}}$ = Pressure drop of Emulsion containing x volume % water

In the carbonate acidizing process, a higher acid volume fraction is preferable to successfully perform the job. Therefore, emulsified acid with only 10 % volume fraction of acid cannot be used although the pressure drop is very low.

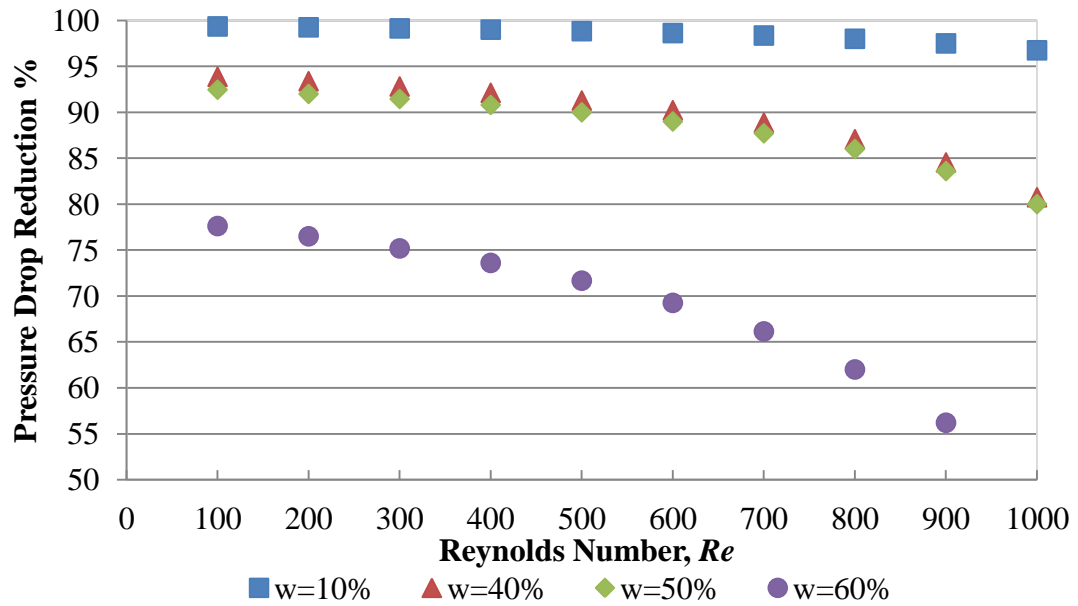


Figure 4.10 Emulsion pressure drop reduction in the 2.54-cm pipe by changing the water volume fraction from 0.7 to lesser values

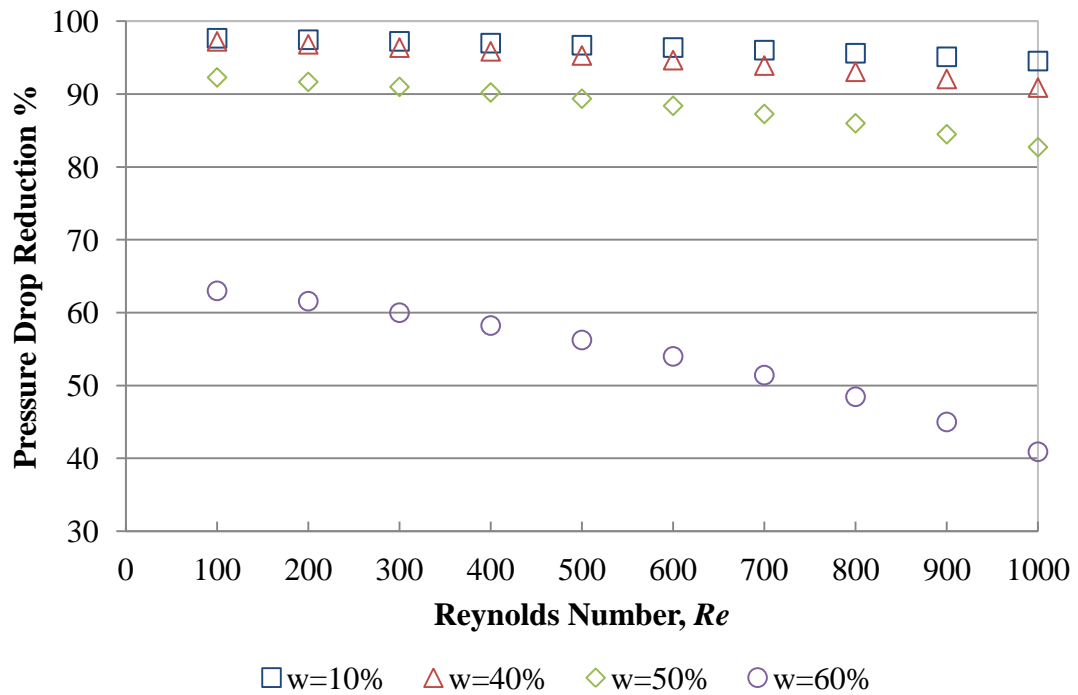


Figure 4.11 Emulsion pressure drop reduction in the 1.27-cm pipe by changing the water volume fraction from 0.7 to lesser values

Secondly, as presented in Figures 4.12-4.14, surfactant-stabilized W/O emulsions showed emulsion friction factor reduction with decreasing pipe diameter. Also, this effect increases with increasing water fraction. This result can be attributed to the shear thinning effect of highly concentrated emulsions. At the same Re , the calculated shear rate for emulsion flow in the 1.27-cm pipe was almost four times that calculated for emulsion flow in the 2.54-cm pipe. As a result, droplets elongation and breakup are more pronounced in the 1.27-cm pipe test section and thus viscosity is smaller.

Finally, if the initial point is intended to be used, surfactant-stabilized W/O emulsions pressure drop reduction increases for emulsion flow in large diameter pipe as shown in Figure 4.15.

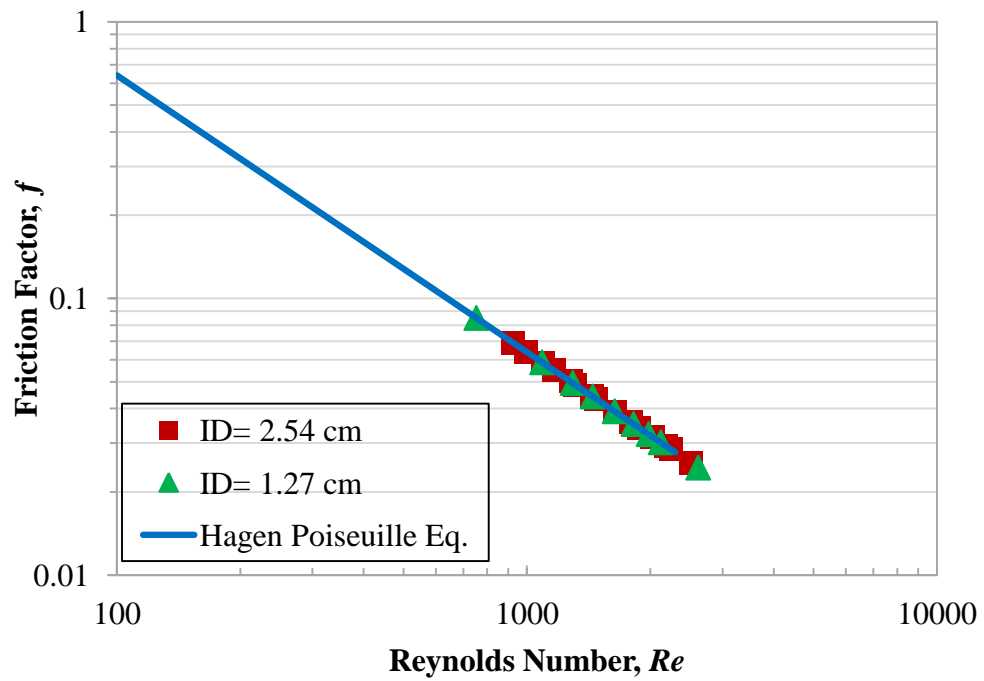


Figure 4.12 Friction factor of stable W/O emulsion with 0.1 water volume fraction

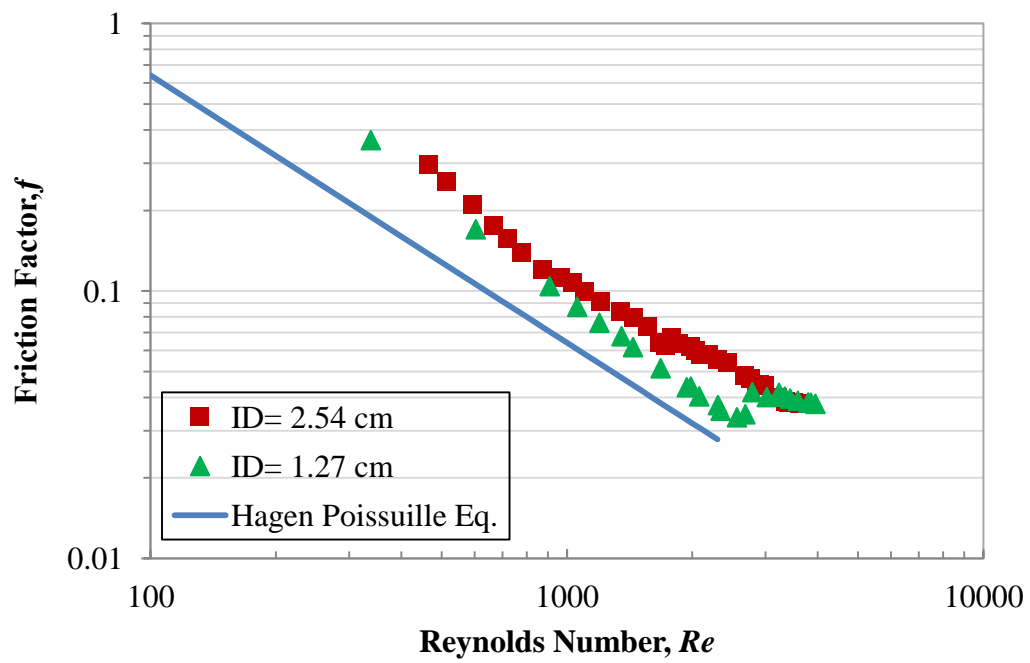


Figure 4.13 Friction factor of stable W/O emulsion with 0.5 water volume fraction

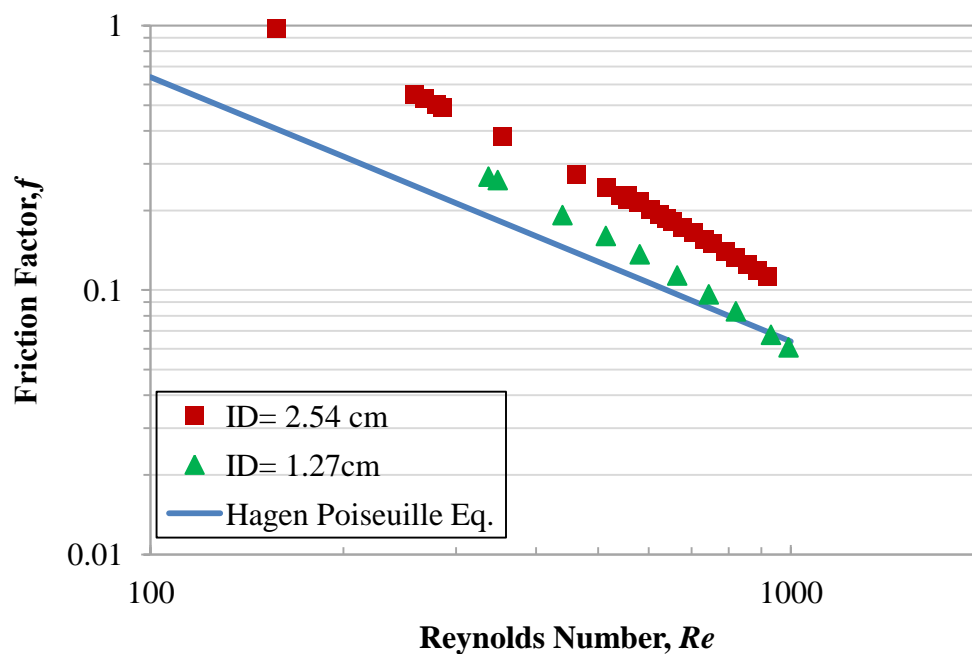


Figure 4.14 Friction factor of stable W/O emulsion with 0.7 water volume fraction

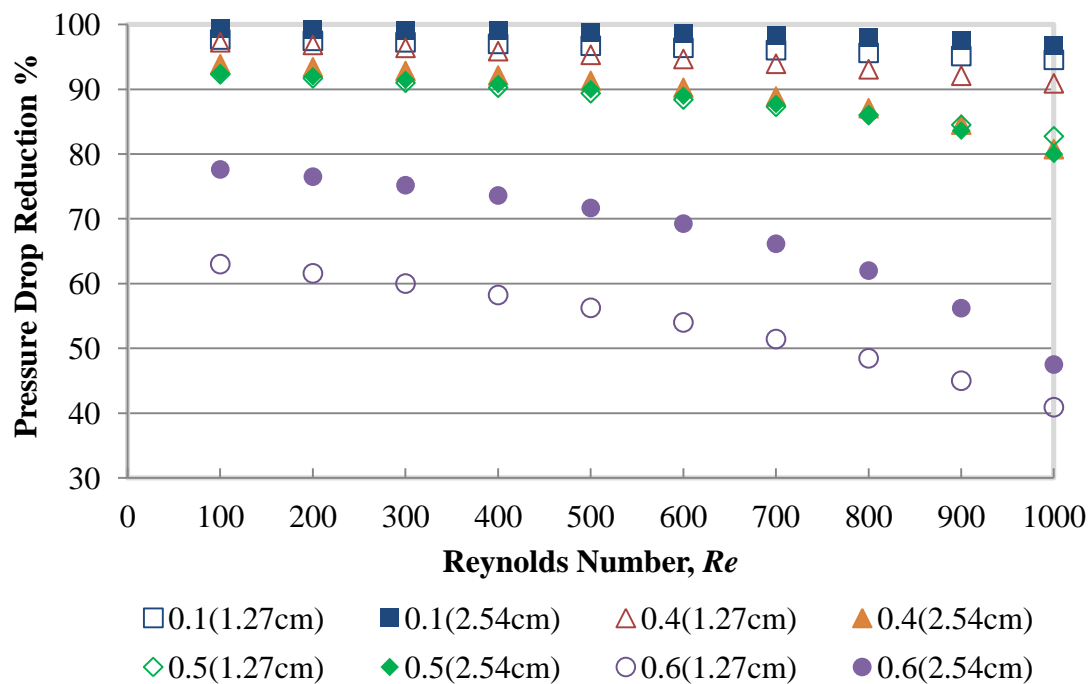


Figure 4.15 Emulsion pressure drop reduction as a function of pipe diameter

4.4 CONCLUSIONS

Emulsion flow characteristics of surfactant-stabilized water-in-oil (W/O) emulsions at different water fractions and pipe diameters have been studied. Such emulsion features include stability, type, conductivity, viscosity, and pressure drop. At different pipe diameters, as the dispersed phase (water) fraction decreases, emulsion stability and viscosity as well as pressure drop decreases for all emulsions reported in this chapter. Stable W/O emulsions pressure drop can be reduced by reducing the brine (dispersed phase) volume fraction. In addition, friction factor of stable W/O emulsion can be reduced by pumping fluids in small pipe diameters due to the shear effect of the highly concentrated stable emulsions. To complete the picture, it is highly recommended to investigate such effects at high Reynolds number. The stable W/O emulsion with 70 volume % of brine is the most stable compared with the other tested emulsions. The rheology of surfactant-stabilized W/O emulsions was modeled with a modified Fluidity-Additivity model as shown in Eq. 11 and 12. Additional studies are continuing to characterize and predict this behavior at actual field conditions.

CHAPTER 5

EFFECT OF WATER SALINITY ON SURFACTANT-STABILIZED EMULSIONS FLOW CHARACTERISTICS

5.1 INTRODUCTION

When two immiscible liquids are mixed together, the droplet formation of one phase (dispersed or internal phase) in the continuous (or external phase) of the other, is known as a dispersion (unstable emulsion) process.

Generally, water-in-oil (W/O) or oil-in-water (O/W) emulsions are unstable thermodynamically. As the water-oil droplets are hydrophilic or hydrophobic, they tend to separate from the oil-water continuous phase. To create stable emulsion, showing stability for a certain period of time, an emulsifier (surface active agent) is used to reduce the interfacial tension and promote the formation of smaller droplets (Binks and Rocher (2009), Guo, et al. (2006)).

Emulsifiers are believed to be able to create a viscoelastic barrier to droplets coalescence by creating a cross linked three dimensional networks of aggregates on the droplet surface (Binks and Rocher (2009), Guo, et al. (2006)). Emulsions rigid interfacial films on the dispersed droplets surface are reported to have the ability to prevent the coalescence process (Kokal (2005)). These interfacial films consist of some surface active species such as fine solids (Mclean and Kilpatrick (1997)). W/O and O/W emulsions represent the dispersion of water droplets in oil and the dispersion of oil

droplets in water, respectively. Each emulsion type has its own morphology and characteristics and they can be converted to each other by changing some parameters through a phase inversion process.

W/O emulsions phase separation is preceded by three steps: flocculation, sedimentation and coalescence. When water droplets aggregate, they sediment because of gravity effect. Then, the aggregated droplets coalesce to form larger droplets which will result in a phase separation. (Graham, et al. (2008)) However, the coalescence process might be delayed by fine solid particles acting as stabilizing agent (Graham, et al. (2008), Sjoblom, et al. (2003)).

Emulsion technology has been used in the acid treatment of reservoir rocks in the region near the wellbore. Occasionally, the pore structure near the wellbore is plugged either by particulates from the drilling process or by deposits from precipitation caused by pressure or temperature changes. As a result, permeability is reduced in addition to the well productivity. To remove these unwanted deposits, acid stimulation is used. The acid reacts with and dissolves portions of the rock matrix; hence, permeability is increased. The effectiveness of the treatment depends on the penetration depth of the acid into the formation. The rate of dissolution is limited by mass transfer and acid is consumed very quickly; therefore, deep penetration of the acid and reduction in the corrosion rate are process goals. One method to achieve such retardation and to avoid corrosion is the use of the emulsified acid where the hydrochloric acid is injected as a W/O emulsion. A high-pressure drop caused by friction losses can be a problem when pumping emulsified acid.

Hence, lower emulsified acid rates are pumped; and thus, limited job efficiency is achieved. Consequently, methods that reduce pressure losses are highly desired.

In addition, stable W/O emulsions, produced naturally from water and oil mixtures, are targeted to be treated to avoid the related operational issues during crude oil production. Therefore, this problem has to be resolved in the field and before crude oil transportation to refineries. This goal is attempted to be achieved by different operational procedures and equipment. These techniques involve the use of chemical demulsifier (Jones et al. (1978), Staiss et al. (1991), and Mikula and Munoz (2000)), centrifugation (Lissant (1983) and Leopold (1992)), large vessels (Manning and Thompson (1995)), electrical effect (Eow et al (2001)) and filtration (Lissant (1983) and Manning and Thompson (1995)). Therefore, investigating an inexpensive, easy to implement and widely applicable method to demulsify water is highly desirable.

Pipeline laminar and turbulent flow behaviors of unstable O/W and W/O emulsions have received considerable attention over the years (Baron et al. (1953), Cengel et al. (1962), Pal (1987), Pal (1993), Angeli and Hewitt (1998), Masalova et al. (2003), Pal (2007), Al-Yaari et al. (2009) and Omer and Pal (2010)). Furthermore, phase inversion of unstable emulsions was also reported (Pal (1993) and Al-Yaari et al. (2009)). However, pipeline flow behavior of stable O/W and W/O emulsions has received less attention. Some of these works aimed to explore the drag reduction phenomenon of stable O/W emulsions (Rose and Marsden (1970) and Zakin et al. (1979)) and stable W/O emulsions (Pal (1993) and Omer and Pal (2010)). Furthermore, effect of the dispersed phase fraction of stable

W/O emulsion on its flow characteristics was studied (Pal (1993), Omer and Pal (2010) and Al-Yaari et al (2013a, 2013b)).

This chapter presents results of the flow characteristics of surfactant-stabilized W/O and O/W emulsions. In particular, the influence of the aqueous phase salinity on emulsion stability, type, droplet size, viscosity, and pressure drop is investigated. Furthermore, a possible friction reduction through the control of water salinity is examined.

5.2 EXPERIMENTAL SETUP & PROCEDURE

Surfactant-stabilized emulsions were prepared using brine (with 0, 5, 20, 50 and 200 kppm NaCl) as the aqueous phase and a type of kerosene known as SAFRA D60 (oil phase) produced in Saudi Arabia. Some physical properties of the oil were presented in Table 3.1. ARMAC T, from Akzo Nobel, was used as the emulsifying agent and some of its physical properties are presented in Table 4.1. A schematic layout of the flow loop is shown in Figure 3.2 and its description is explained in details in Chapter 3.

Emulsion Preparation

36 liters of surfactant-stabilized (W/O and O/W) emulsions were prepared by adding 70 volume % of brine at 0.5 L/min to the emulsified oil (oil with 0.6 volume % emulsifier) while mixing at 8,000 rev/min using a high-power homogenizer (Ultra Turrax T 50 Basic, IKA WERKE, GERMANY) for 40 minutes. Emulsion quality was tested by dilution and conductivity measurements. Emulsions were then transferred to one of the

flow loop tanks. This procedure was used in preparing all of the emulsions with different brine salinity.

Emulsion Type

A dilution test (or emulsion drop test) was used to identify the emulsion's continuous (external) phase. In this test, a droplet of the formed emulsion was placed on water or oil sample. If the placed droplet was found to disperse, then the external phase is the same as the fluid used for the test. For example, W/O emulsion droplets dispersed in oil sample rather than water sample. Also, the emulsion type was detected by measuring its conductivity which increased with increasing water fraction of the external phase (see Figure 5.1). This test is based on the fact that brine solution is conductive, oil is nonconductive, and the emulsion's continuous phase dominates the emulsion conductivity.

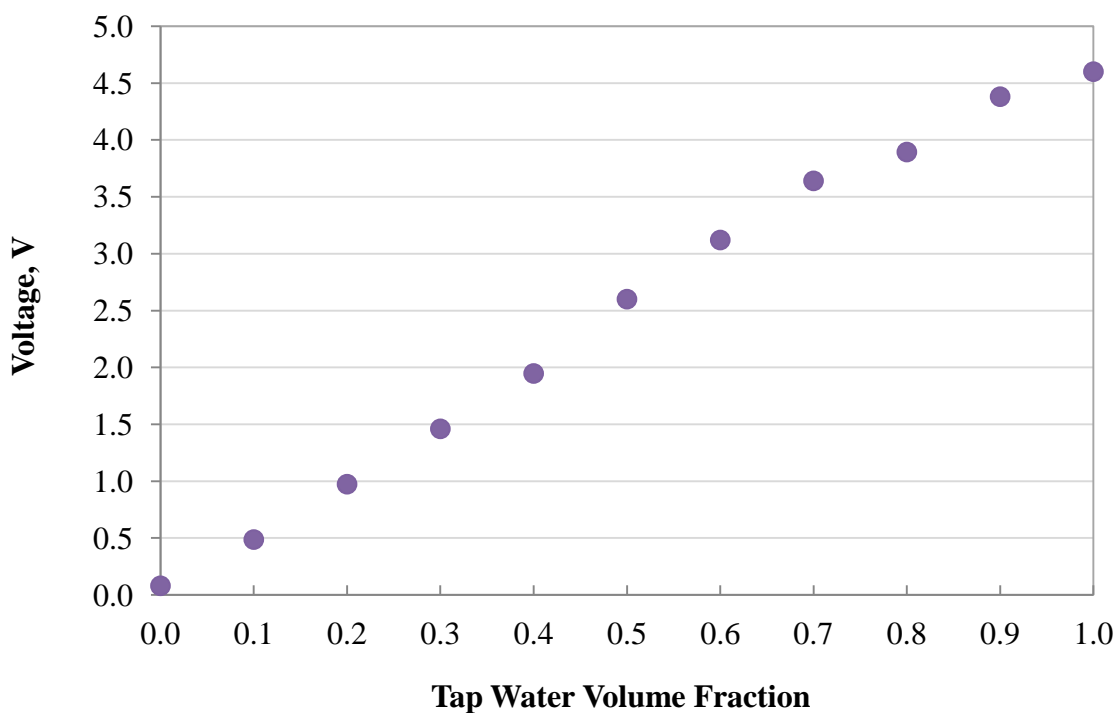


Figure 5.1 Oil-water conductivity measurements at different water fractions

Stability Test

A bottle test was used to achieve stability tests for all formed emulsions by monitoring the percentage of separated oil and/or water layer with time. Such a test can give an indication about emulsion quality.

Rheological Test

All rheological measurements were conducted at 25 °C using Rheologica StressTech rheometer. The rheometer has a torque range from 3.0×10^{-8} to 2.0×10^{-1} N.m with a torque resolution of 1.0×10^{-10} N.m. The bob and cup set where the bob is the rotating part was used to conduct steady shear-rate sweep tests. The tested emulsion volume was 15.9 cm^3 .

5.3 RESULTS AND DISCUSSIONS

Emulsion Type

Emulsified acid used in the carbonate acid fracturing and matrix acidizing is formed with aqueous to oil volume ratio of 70/30, in order to pump the highest acid rate, and stabilized with an emulsifier. Therefore, in this chapter, all emulsions were prepared with 70/30 water to oil volume ratio. All formed emulsions were tested using dilution test (or emulsion drop test). As shown in Figure 5.2, at low water salinity (≤ 5 kppm), O/W surfactant-stabilized emulsions were formed [see Figure 5.2 (a and b)]. The formed emulsion did not disperse in oil but dispersed in water, as shown in Figures 5.2a and 5.2b, respectively. This observation suggest that the external phase was water (i.e. O/W emulsions, O/W). Conversely, emulsions of high aqueous phase salinity (≥ 20 kppm) did not disperse in water; hence, surfactant-stabilized W/O emulsions were obtained (see Figure 5.2 (c-e)).

At low water salinity (≤ 5 kppm), it is acceptable to have O/W emulsion since water phase represents 70 % of the emulsion volume. For low water salinity, when water droplets were added to the emulsified oil (oil + emulsifier) W/O emulsion began to form. With the increase in water fraction, water droplets coalesced and formed a continuous phase and established O/W system. The formation of O/W emulsion was likely due to the absence of the electrostatic charges that maintain stable droplets.

On the other hand, at high enough water salinity (≥ 20 kppm), added water droplets were dispersed and stabilized in the oil continuous phase and their stability enhanced with increasing salt concentration as discussed in the emulsion stability section.

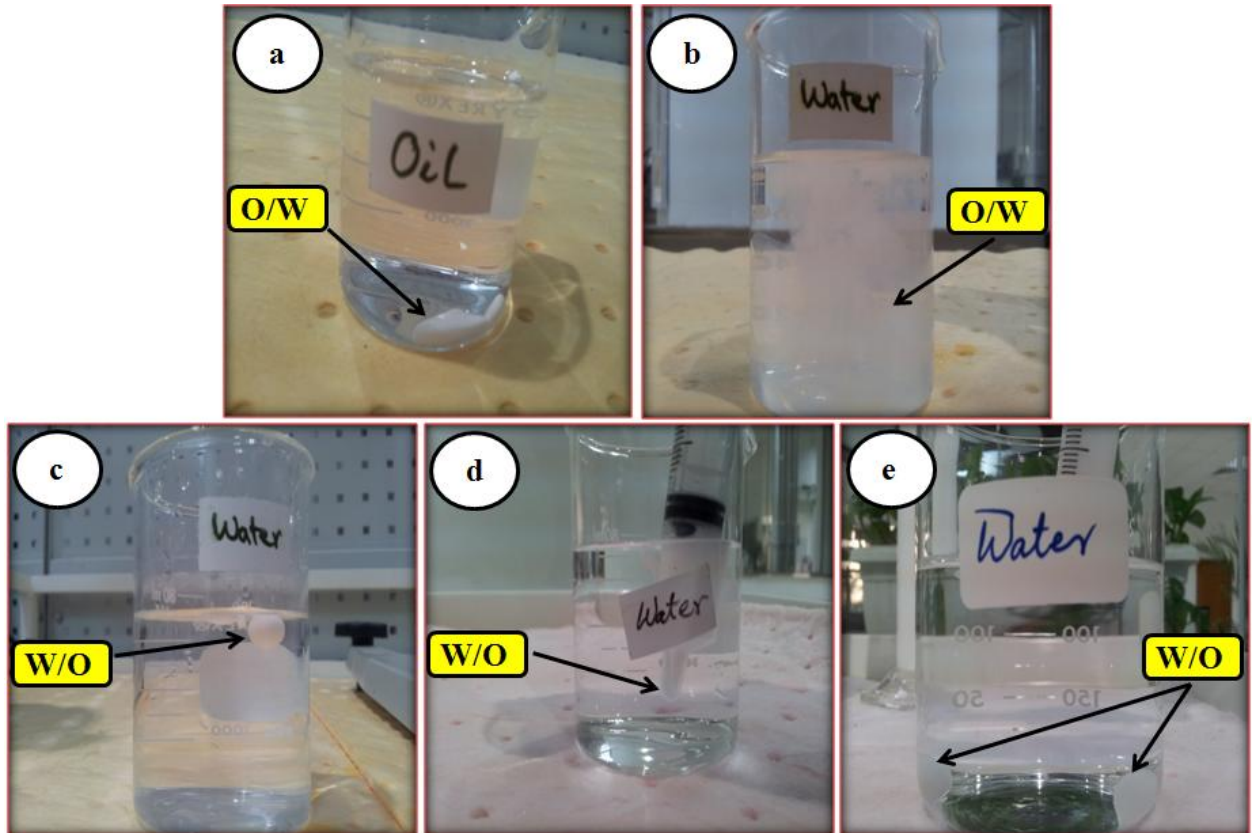


Figure 5.2 Surfactant-stabilized emulsion types at different water salinity; (a) (O/W) Emulsion with DI water, (b) (O/W) Emulsion with 5 kppm brine, (c) (W/O) Emulsion with 20 kppm brine, (d) (W/O) Emulsion with 50 kppm brine and (e) (W/O) Emulsion with 200 kppm brine

Emulsion Stability

To investigate the effect of water salinity on emulsion stability, emulsions with different water salinities (0 kppm (a), 5 kppm (b), 20 kppm (c), 50 kppm (d) and 200 kppm (e)), but with fixed water volume fraction of 0.7, were tested. After preparing such emulsions, stability tests were carried out using the bottle test by monitoring phase separation with time. These results were presented in Figure 5.3. After one hour, results of bottle test for all emulsions were shown in Figure 5.4. Separated oil layer was shown between two redlines. The volume of the oil separated layer was 1 %, 17.4 %, 1 %, 0.2 % and 0 % of the emulsion total volume for systems (a), (b), (c), (d) and (e), respectively.

At low water salinity (≤ 5 kppm), an increase in the external phase (water) salinity resulted in smaller double layer indicated by a lower interfacial tension (Aveyard, et al. (1989)). Further increase in water salinity resulted in phase inversion from O/W to W/O (Winsor (1948)). Therefore, increasing the water salinity from 0 to 5 kppm salinity resulted in less stable O/W emulsions. This could be attributed to the late phase inversion occurrence (from W/O to O/W) and then to the negative interaction between the charges available in the external phase (brine) and the used emulsifier. As a result, a non-uniform distribution of the oil dispersed droplets were observed when water salinity increased from 0 ppm to 5 kppm as shown in Figure 5.5 (a and b).

However, at high enough water salinity (≥ 20 kppm), as the water salinity increased, W/O emulsion viscosity as well as film rigidity of the dispersed phase (brine) droplets were enhanced; as a result, water droplets double layer increased, which can be indicated by an increase in the interfacial tension (Aveyard, et al. (1989)) and hence droplet size

increased with increasing salt concentration of W/O emulsions (see Figure 5.5 (c, d and e)). In addition, in stable (W/O) emulsions, emulsifier is more soluble in oil (external phase); therefore, an increase in water salinity decreases the medium hydrophilicity and then emulsion stability increases (Strassner, (1968) and Fortuny, et al. (2007)). It is likely that increasing the aqueous phase salinity increases the water dispersed droplets film rigidity (McLean and Kilpatrick (1997)) which can be indicated by increase in the emulsion stability as shown in Figures 5.3 and 5.4 (c-e).

Emulsion Rheology

Viscosity curves for all surfactant-stabilized O/W and W/O emulsions were obtained using a bob and cup viscometer. As shown in Figure 5.6, generally, as water salinity increased emulsion viscosity increased and this could be due to the increase in droplet size with salinity as shown in Figure 5.5. However, the emulsion phase inversion (from O/W to W/O) due to the aqueous phase salinity increase resulted in a dramatic increase in emulsion viscosity. This is a direct result of having the more viscous component of the emulsion (oil) as the external phase. Therefore, the matrix phase viscosity and droplets size contribute to the viscosity enhancement as a result of phase inversion. Salt type and concentration strongly influence the interfacial tension; hence, the stability of the droplets. Therefore, their impact would be better assessed through the measurement of the interfacial tension.

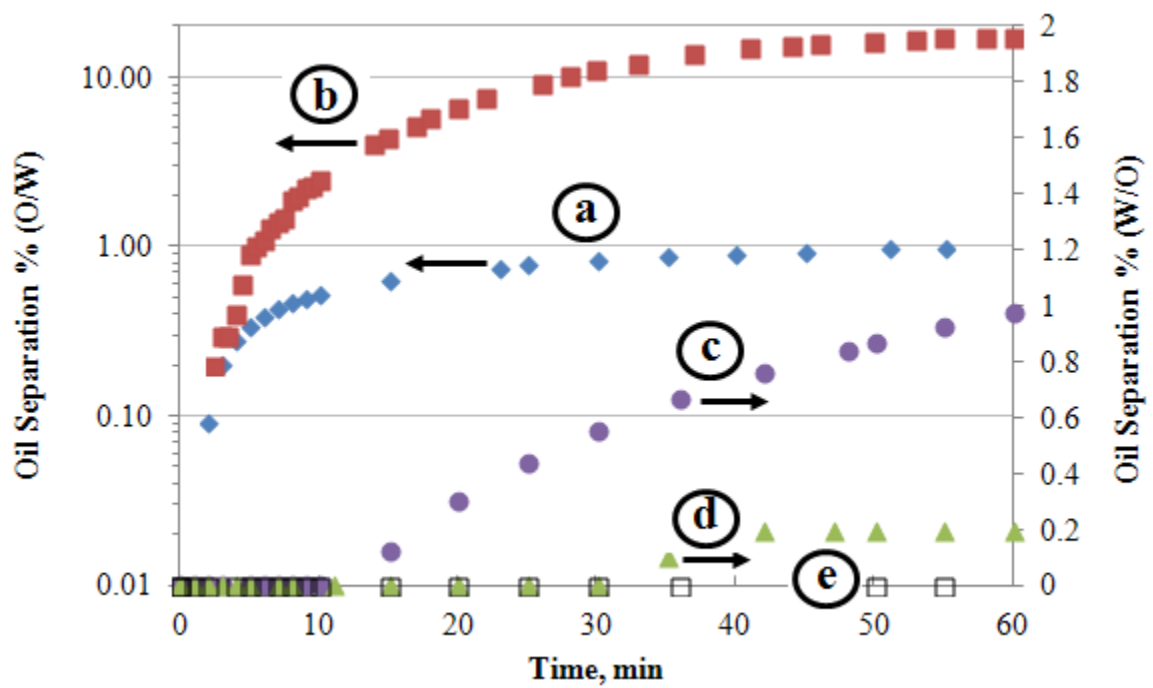


Figure 5.3 Effect of water salinity on surfactant-stabilized emulsion stability; (a) (O/W) Emulsion with DI water, (b) (O/W) Emulsion with 5 kppm brine, (c) (W/O) Emulsion with 20 kppm brine, (d) (W/O) Emulsion with 50 kppm brine and (e) (W/O) Emulsion with 200 kppm brine

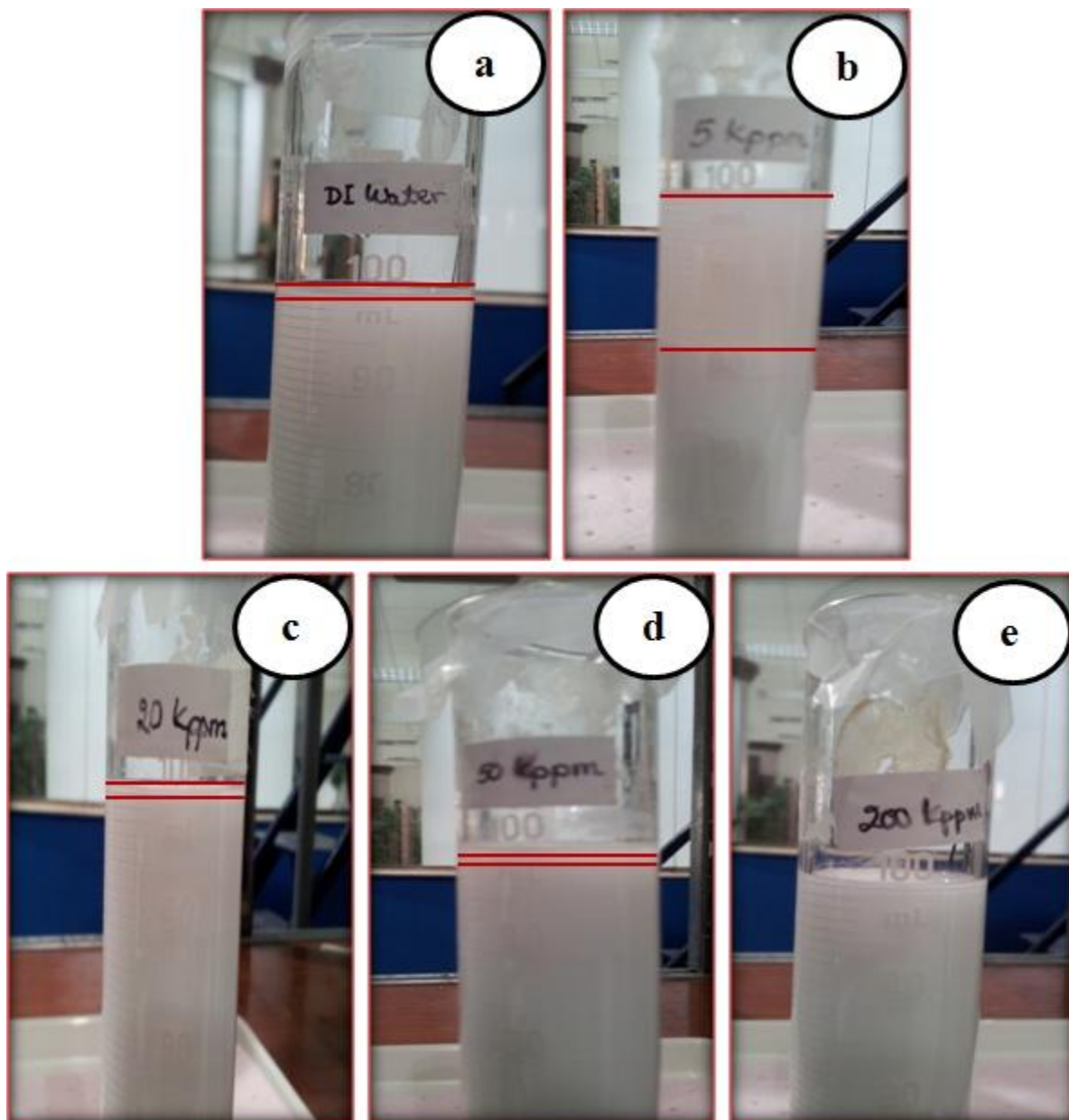


Figure 5.4 Effect of water salinity on surfactant-stabilized emulsion stability (after 1 hr); (a) (O/W) Emulsion with DI water, (b) (O/W) Emulsion with 5 kppm brine, (c) (W/O) Emulsion with 20 kppm brine, (d) (W/O) Emulsion with 50 kppm brine and (e) (W/O) Emulsion with 200 kppm brine

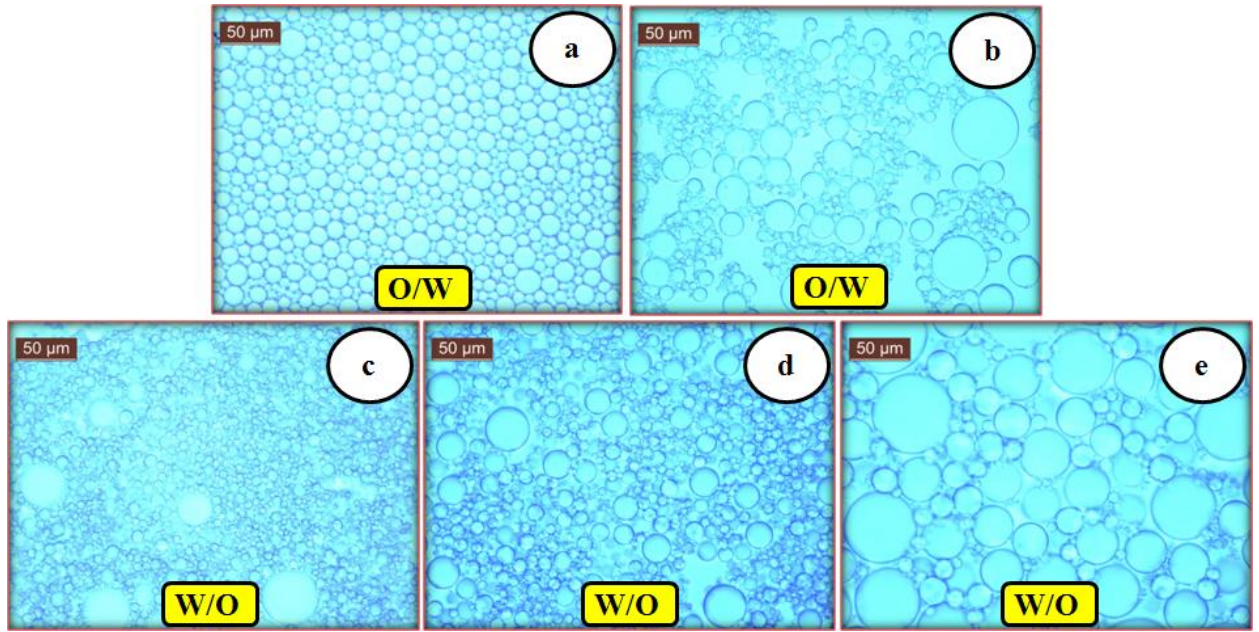


Figure 5.5 Effect of water salinity on surfactant-stabilized emulsion droplet size and distribution; (a) (O/W) Emulsion with DI water, (b) (O/W) Emulsion with 5 kppm brine, (c) (W/O) Emulsion with 20 kppm brine, (d) (W/O) Emulsion with 50 kppm brine and (e) (W/O) Emulsion with 200 kppm brine

Furthermore, while W/O emulsions showed a shear thinning behavior, almost over the whole shear rate covered in this study; O/W emulsions showed two distinct shear-independent viscosities. The shear dependent viscosity is limited to the range $300\text{-}400\text{ s}^{-1}$. For a salinity of less than 20 kppm, the viscosity results at low shear rates suggest two distinct and stable morphologies in the range $100\text{-}300\text{ s}^{-1}$ while a different morphology is depicted in the range $400\text{-}1000\text{ s}^{-1}$. However, for salinities higher than 20 kppm the stability of the emulsion and the large droplet size resulted into more shear thinning which is likely due to the breakup of droplets due to shear.

The behavior index (n) and the consistency index (k) were calculated using the power law model fittings represented by Eq. (1) with fitting accuracy ≥ 0.997 . In Eqs. (2) and (3), n'

and k' are related to the power-law constants (n and k). In addition, zero shear-rate viscosity (η_o) as well as infinite shear-rate viscosity (η_∞) for all emulsions were calculated by data fitting using Cross model ($R^2 \geq 0.99$) expressed by Eq. (4). The behavior index (n, n'), consistency index (k, k'), and η_o and η_∞ shear-rate viscosities were presented in Table 5.1.

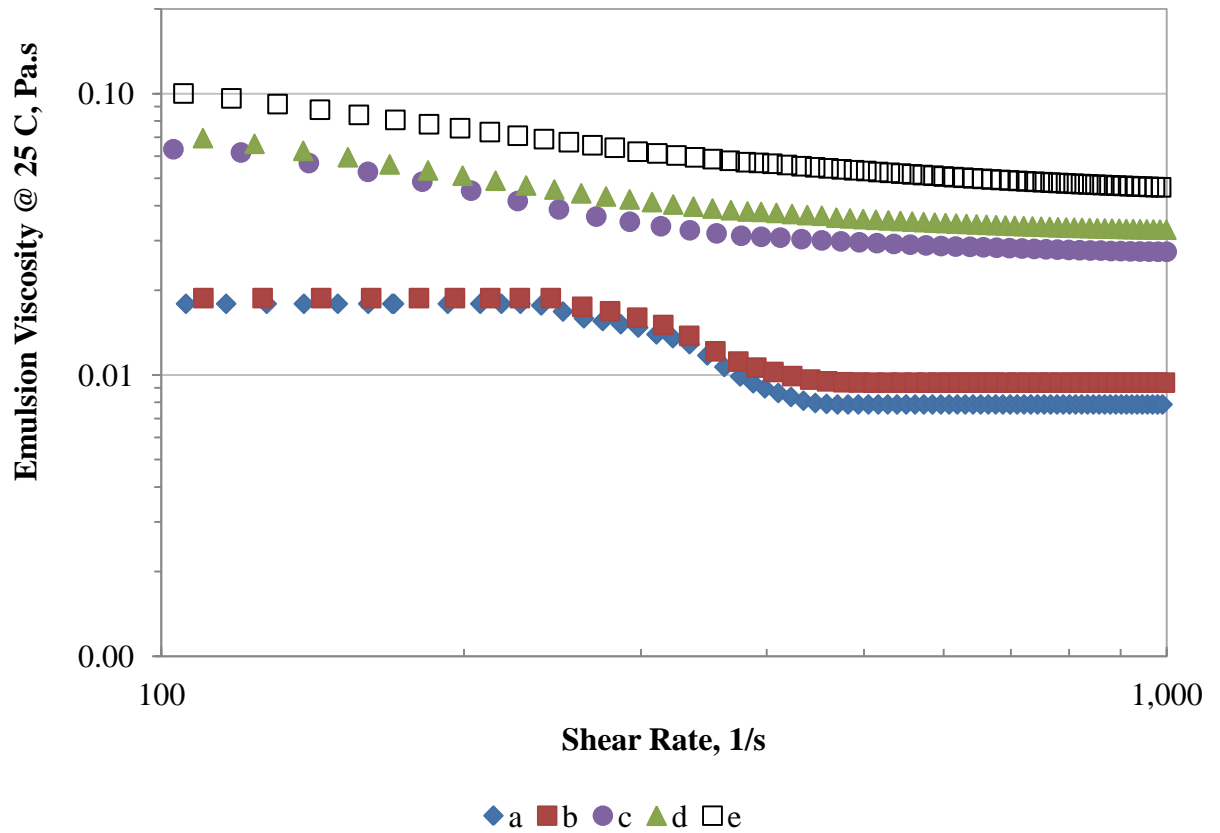


Figure 5.6 Effect of water salinity on surfactant-stabilized emulsion viscosity; (a) (O/W) Emulsion with DI water, (b) (O/W) Emulsion with 5 kppm brine, (c) (W/O) Emulsion with 20 kppm brine, (d) (W/O) Emulsion with 50 kppm brine and (e) (W/O) Emulsion with 200 kppm brine

$$\eta = k \dot{\gamma}^{n-1} \quad (1)$$

where η = emulsion viscosity

$\dot{\gamma}$ = shear rate

$$n' = n \quad (2)$$

$$k' = k \left(\frac{1+3n}{4n} \right)^n \quad (3)$$

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + (\lambda \dot{\gamma})^m} \quad (4)$$

The term in brackets in Eq. (3) is the Robinowitsch correction for non-Newtonian fluids.

Table 5.1 Rheological parameters of surfactant-stabilized emulsions at 25 °C

Water Salinity (kppm)	Behavior Index		Consistency Index		η_o , Pa.s	η_{∞} ,
	n	n'	k	k'	η_o	η_{∞}
200	0.5451	0.5451	0.83884	0.93	N/A	N/A
50	0.4767	0.4767	0.82204	0.922	N/A	N/A
20	0.3513	0.3513	1.40371	1.604	0.0635	0.0274
5	N/A	N/A	N/A	N/A	0.0188	0.0094
0	N/A	N/A	N/A	N/A	0.0179	0.00786

Emulsion Pressure Drop

The pressure drop of all prepared surfactant-stabilized O/W and W/O emulsions was measured at different flow rates in the 2.54-cm and 1.27-cm pipes. All measurements

were conducted at steady-state conditions. The emulsion temperature was maintained at 25 °C.

The results of the pressure drop measurement for emulsions in the 2.54-cm pipe and the 1.27-cm pipe were given in Figures 5.7 and 5.8, respectively. As shown in these figures, increasing the aqueous phase salinity resulted in an increase in the emulsion flow pressure drop regardless of the identity of the emulsion (O/W or W/O). This observation was a direct result of the increase in the viscosity and the dispersed phase droplet size as discussed earlier.

At low water salinity (≤ 5 kppm), a slight increase in the salinity (before the phase inversion) resulted in a slight increase in the pressure drop. This is could be due to the slight increase in the emulsion viscosity as a result of the increase in droplet size. However, a large enough increase in the aqueous phase salinity (≥ 20 kppm) resulted in phase inversion from O/W to W/O emulsion. In this case, because of the phase inversion phenomenon, a sharp increase in the emulsion flow pressure drop was observed.

Friction factor (f) for W/O emulsion was calculated using equation (5). The results (Figure 5.9) showed dependency of f on pipe diameter. A decrease in pipe diameter resulted in a decrease in the emulsion friction factor and such effect increased with increasing Reynolds number (Re). This effect can be attributed to the fact that at the same Re , although the flowrate in 1.27-cm pipe is almost half of that in the 2.54-cm pipe, the shear rate in 1.27-cm pipe is almost four times that in the 2.54-cm pipe. Consequently, the average droplet size of the emulsion in the 1.27-cm pipe is smaller (around 4.7 μm)

compared with that for 2.54-cm pipe flow (around $9.9 \mu\text{m}$). For example, for the same Re of 1000, the corresponding shear in 2.54-cm and 1.27-cm pipes were 442 s^{-1} and 1553 s^{-1} , respectively. The corresponding micrographs were presented in Figure 5.10. Thus reducing the pipe diameter from 2.54-cm ID to 1.27-cm ID resulted in up to 36.4% reduction in the friction factor at low Re (≤ 2000). If higher Re could be reached, we anticipate such reduction in friction factor to increase as a result of the formation of smaller and stable droplets. However, this anticipation needs to be verified.

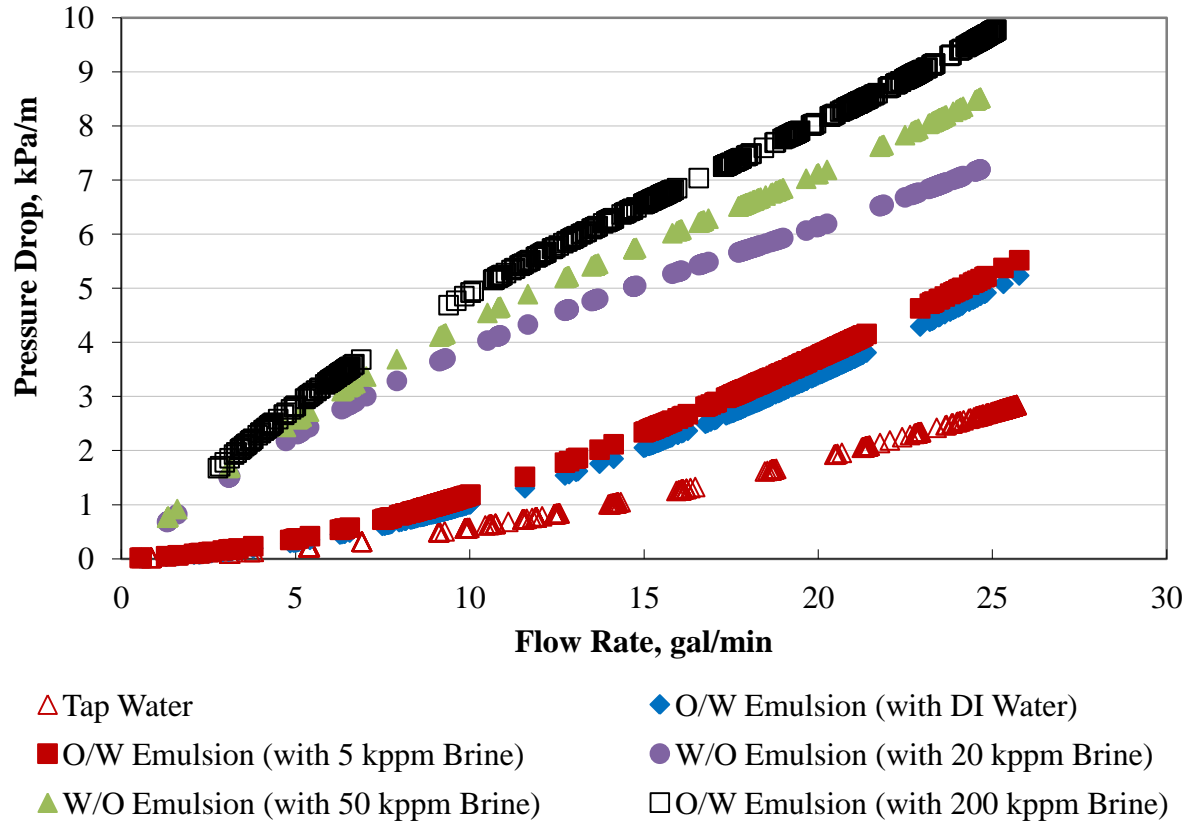


Figure 5.7 Effect of water salinity on surfactant-stabilized emulsions pressure drop in the 2.54-cm pipe

$$f = \frac{\frac{\Delta P}{\Delta L} \times 2 D}{\rho u^2} \quad (5)$$

where

f = Darcy friction factor

$\frac{\Delta P}{\Delta L}$ = Pressure gradient (Pa/m)

D = Pipe diameter (m)

ρ = Emulsion density (kg/m³)

u = Emulsion average velocity (m/s)

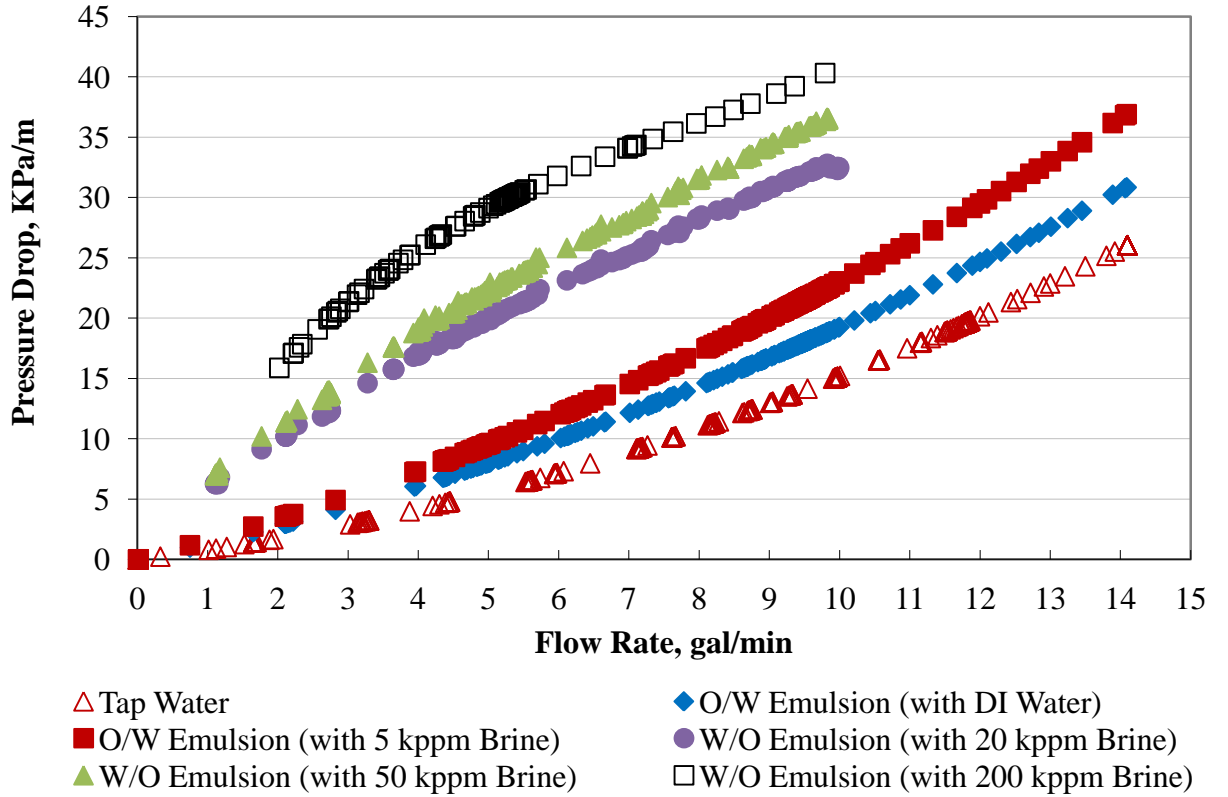


Figure 5.8 Effect of water salinity on surfactant-stabilized emulsions pressure drop in the 1.27-cm pipe

This finding might help a lot while dealing with some of the petroleum processes. For example, adding fresh water to control salinity can be a key solution if there is a need for phase inversion to decrease the W/O emulsion viscosity. Conversely, changing O/W emulsions to W/O emulsions and/or the need to increase the emulsion viscosity for any purpose, could be met using smart water (salty water) and proper types of surfactants. Also, adding fresh water to stable W/O emulsions could help in phase inversion. In particular, this smart water could be used as an inexpensive, easy to implement technique for W/O emulsion separation or for converting O/W to W/O or vice versa. In addition, further increase in the aqueous phase salinity resulted in an increase in the W/O emulsion pressure drop. Therefore, based on the results presented in this chapter, pressure-drop reduction of surfactant-stabilized W/O emulsions can be achieved by controlling water salinity.

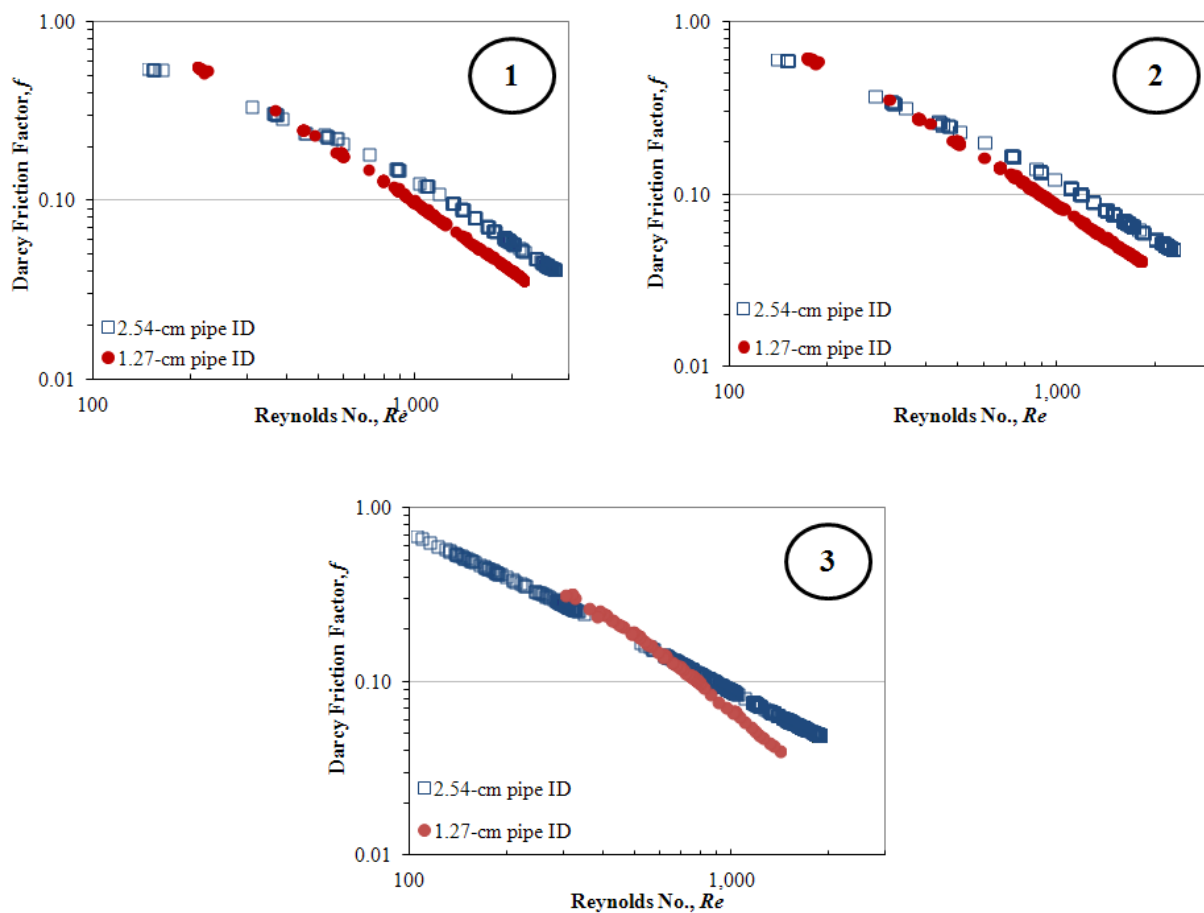


Figure 5.9 Effect of pipe diameter on W/O emulsion friction factor at different water salinity; (1) using 20 kppm brine, (2) using 50 kppm brine, (3) using 200 kppm brine

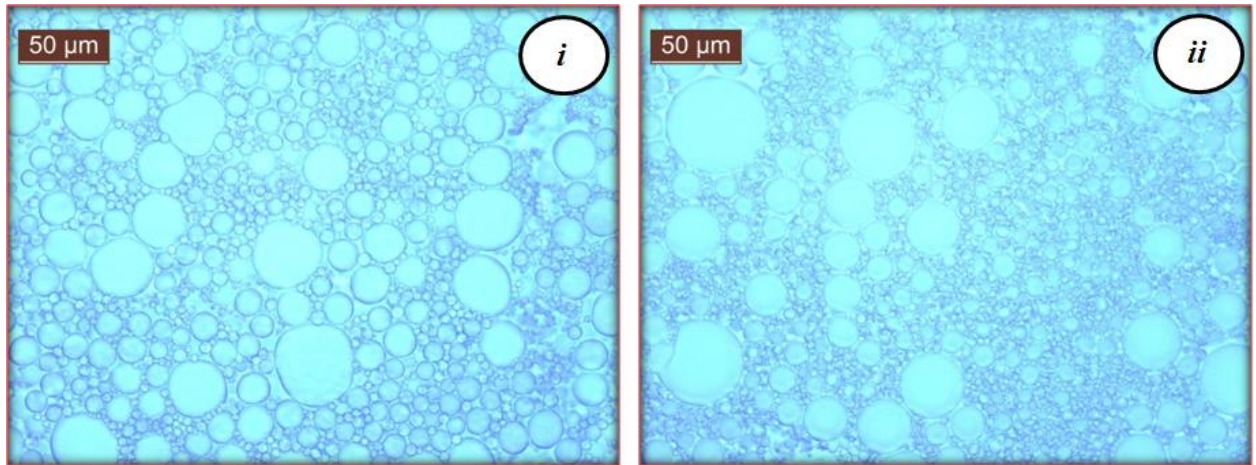


Figure 5.10 Effect of pipe diameter on W/O emulsion dispersed phase droplet size at 1000 Reynolds no.; (i) sheared at 442 s^{-1} , and (ii) sheared at 1553 s^{-1}

5.4 CONCLUSIONS

The role of the aqueous phase salinity on surfactant-stabilized water-in-oil (W/O) as well as oil-in-water (O/W) emulsions flow characteristics was investigated experimentally in this study. In particular, dependency of emulsions type, stability, average droplet size of the dispersed phase, viscosity and pressure drop dependency on water salinity was studied in 2.54-cm and 1.27-cm pipes.

Surfactant-stabilized emulsions of 70/30 water to oil volume ratio were prepared. For low water salinity range (≤ 5 kppm), W/O emulsion was produced and its stability decreased as water salinity increased. However, emulsion viscosity as well as the average droplet size of the oil dispersed phase increased as the aqueous phase salinity increased. For high water salinity range (≥ 20 kppm), W/O emulsion was formed and its stability, viscosity as well as the average droplet size of the water dispersed phase increased with the increase in aqueous phase salinity. Also, the increase in water salinity resulted in an increase in

the pressure drop. In particular, phase inversion from O/W to W/O resulted in a sharp increase in the pressure drop. In addition, surfactant stabilized W/O emulsion friction factor showed a pipe diameter dependency and smaller diameter gave lower friction factor as a result of smaller droplet size.

Therefore, based on the results presented in this chapter, pressure-drop reduction of surfactant-stabilized W/O emulsions can be achieved by controlling water salinity as well as droplet size through the use of pipes of smaller diameters. In addition, controlling water salinity could be used as an inexpensive, easy to implement technique for phase inversion of W/O or O/W emulsions.

CHAPTER 6

EFFECT OF DRAG REDUCING POLYMERS ON SURFACTANT-STABILIZED WATER-OIL EMULSIONS FLOW CHARACTERISTICS

6.1 INTRODUCTION

Friction reducing agents, or drag reducing additives, have been used to increase the through put of oil and gas pipelines. Typically a dilute polymer solution is continuously injected into the pipe lines resulting in a drag reduction of up to 70 % (Al-Yaari et al, 2008 and 2009).

The phenomenon of drag reduction by polymer additives, whereby dilute solutions of linear, flexible, high molecular-weight polymers exhibit frictional resistance to flow much lower than that of the pure solvent, has almost exclusively been studied within the context of turbulent flows since the pioneering work of Toms in 1948. A broader discussion of the single phase drag reduction literature can be found in the survey by Manfield et al. (1999).

Compared to the huge amount of work on the drag reduction phenomenon by polymer additives in single phase flow, there is comparatively less published literatures on the subject of drag reduction in multiphase flow.

Greskovich et al. (1971) were the first who studied the effect of drag reducing polymers (DRP) in gas-liquid flow. A 50 wppm polymer solution of Polyox was used in an air-water and a 50 wppm solution of Visanex L-200 was used in a mixture of nitrogen-

kerosene to study slug flow in an acrylic pipe with inside diameter of 0.038 m. They reported that during the air-water slug flow, the percentage of drag reduction was approximately 40 %. However, only one data point was reported for the nitrogen-kerosene slug flow and the drag reduction percentage was between 25 % and 29 %.

Sylvester and Brill (1976) studied the effect of DRP on annular gas-liquid flow for air-water in a horizontal pipe with a diameter of 0.0127 m and a length of 6.1 m. A polymer solution with 100 wppm of polyethylene oxide was used. The percent change in the pressure gradient from what was observed in the absence of polymer varied from zero to about 37 without explanation of these changes.

Al-Sarkhi & Hanratty (2001a) studied the effect of DRP on annular air-water flow in a horizontal pipe with a diameter of 0.0953 m and 23 m long. Their polymer solution was a co-polymer of polyacrylamide and sodium-acrylate (Percol 727) in water. The injection of polymer solution (without using a pump) produced drag reduction of 48 % with concentrations of only 10-15 wppm in water. Also, they found that annular flow regime is changed to a stratified pattern at large drag reductions. Al-Sarkhi & Hanratty (2001b) studied the effect of pipe diameter on the performance of DRP in annular air-water flows by varying the diameter of the pipe from 0.0953 m to 0.0254 m. Up to 63 % drag reductions were observed in the 0.0254 m pipe compared with 48 % previously achieved in the 0.0953 m pipe.

Soleimani et al. (2002) injected a co-polymer of polyacrylamide and sodium acrylate solution into a stratified flow of air and water in a horizontal 0.0254 m pipe. A damping of waves and an increase in the liquid holdup were observed. Those changes, in turn,

caused an increase in the gas velocity and a decrease of the interfacial drag. Transition to slug flow was found to occur at larger liquid flows.

Baik and Hanratty (2003) studied how the addition of polymers can influence wave structure of stratified flow. Their experiments of air-water system were conducted in a horizontal Plexiglas pipe that had a diameter of 0.0953 m and a length of 23 m. Magnafloc 1011 was mixed with water. The concentration of the master polymer solution was 1000 wppm. It was injected into the flow loop through a hole with a diameter of 10 mm that was located at the bottom of the pipe, 2.9 m downstream of the tee section. The mixed concentration in the flow loop was 50 wppm. They found that the wave amplitude decreased dramatically when a 50 wppm polymer solution was used (superficial liquid velocity (U_{sl}) = 0.15 m/s) at low superficial gas velocity (U_{sg}) and the addition of polymers also delayed the transition to slug flow. However, no effect of polymers on the critical U_{sl} for the transition to slugging was observed for U_{sg} = 5 m/s (high superficial gas velocity).

Al-Sarkhi and Soleimani (2004) studied the effect of the addition of DRP on air-water flow patterns in a horizontal pipe of 0.0254 m diameter and 17 m long. The additive was a copolymer of polyacrylamide and sodium acrylate (formally sold under the trade named Percol 727 but now called Magnafloc 1011). They used the same mixing technique that first used by Warholic (1999). They described the characteristics of two phase flow with and without DRP. They reported that the addition of DRP is accompanied by changes in the flow pattern map and pressure drop reduction occurs in almost all flow pattern

configurations. Their study indicated that maximum drag reduction usually occurs when a slug, pseudo-slug or annular flow changes to stratified flow by adding DRP.

Fernandes et al. (2004) achieved experimental measurements of drag reduction of a horizontal annular two phase flow. The experiments were conducted in a high-pressure (10 bar) two-phase flow of methane (CH_4) and a condensate sample with thermo-physical properties close to that of decane ($\text{C}_{10}\text{H}_{22}$) in 0.019 m inside diameter pipe. The drag reducers were high molecular weight poly-alpha-olefin polymers. They argued that the reduction of frictional drag in an annular flow was primarily due to the modification of the flow regime or flow pattern. Also, they noticed that, in annular flow regime, for a fixed superficial gas velocity, the magnitude of drag reduction increased with increasing superficial liquid velocity (U_{SL}). Beyond a threshold U_{SL} (approximately $U_{\text{SL}} = 0.2$ m/s) the drag reduction reached a maximum and remained constant for increasing U_{SL} for all the examined U_{SL} (up to 0.7 m/s). However, for superficial gas velocities which result in an annular flow, the maximum drag reduction decreased with increasing superficial gas velocity (U_{SG}) (as the U_{SG} increased from 10.4 to 21.3 m/s the maximum drag reduction decreased from 62% to 44%). Finally, they concluded that for low superficial liquid velocities, the overall drag reduction is generally dominated by the reduction of interfacial friction.

Al-Sarkhi and Abu-Nada (2005) studied the effect of DRP on an annular air-water flow in a horizontal pipe. Pipe with inside diameter of 0.0127 m and a length of 7 m was used. Magnafloc 1011 (polyacrylamide) was mixed with water in a 150-liter tank with a concentration of 1000 wppm. The injection of polymer solution (without using a pump)

produced drag reduction of 47 % with concentrations of only 40 wppm in water. Also, they found that annular flow pattern was changed to a stratified pattern at large drag reductions and the effectiveness of the drag-reducing polymer was sensitive to the gas and liquid flow rates.

Mowla and Naderi (2005) studied the effect of the presence of a polymer drag reducing agent (PDRA) on the pressure drop in co-current horizontal pipes carrying slug two phase flow of air and crude oil. Their test section of the experimental set-up was consisted of: a smooth pipe of polycarbonate with 10.3 m long and 0.0254 m ID (inside diameter), a rough pipe of galvanized iron with 8.8 m long and 0.0254 m ID and a rough pipe of galvanized iron with 8.8 m long and 0.0127 m ID. The employed PDRA was a Polyalpha-olefin (Polyisobutylene). Their results showed that the addition of PDRA could be effective up to some doses of PDRA after which the pressure drop was kept constant. A drag reduction percentage of about 40 was obtained for some experimental conditions. Also, they reported that PDRA are more effective in rough pipe than in smooth pipe and the drag reduction in 0.0127 m inside diameter pipe was more.

Dass and Bleyle (2006) did experimental work in 0.1 m ID horizontal pipes utilizing carbon dioxide as the gas phase and two types of oil with different viscosities; namely 2.5 mPa.s (density = 800 kg/m^3) and 50 mPa.s (density = 830 kg/m^3), as the liquid phase. They studied the influence of oil viscosity on the magnitude of total pressure drop and the effectiveness of PDRA in decreasing the pressure in two-phase oil–gas slug flow. They concluded that the PDRA was more effective in reducing the total pressure drop and its

components in the 2.5 mPa.s oil, but the magnitude of drag reduction was higher in the 50 mPa.s oil.

Al-Yaari et al (2008, 2009) studied the effect of PDRA on oil water flow characteristics in a horizontal acrylic pipe with inside diameter of 0.0254 m and a length of 11 m. SAFRA D60 (known type of kerosene produced in Saudi Arabia) with a density of 780 Kg/m³ and a viscosity of 1.57 mPa.s and tap water were used. He used Magnafloc 1011 (partially hydrolyzed polyacrylamide) and polyethylene oxide with different molecular weights and concentrations. The effect of the polymer concentration and molecular weight, mixture velocity, water fraction and salt on the performance of polymers as drag reducing agents was experimentally investigated.

Emulsified acids provide significant benefits in stimulating oil and gas wells by slowing the reaction rate with carbonates and reducing corrosion in the tubular goods. However, pumping emulsified acids can result in high friction losses. Stimulation treatments thus require lower pumping rates hence reducing stimulation efficiency. Therefore, reducing friction pressure loss is an important factor in expanding the application of emulsified acids.

For stimulations, water based gels or oil based gels are used not only to increase viscosity for fracture width creation, leak-off prevention, proppant suspension, and diversion, but also are used because of their friction reduction capability. The macro-structure of the polymers dampens the development of turbulence at high pumping rate such that the friction loss is reduced and the Reynolds stresses at the wall goes to zero or close to zero.

This chapter aimed at studying the effect of DRP on flow characteristics of stable and unstable water-in-oil (W/O) and oil-in-water (O/W) emulsions in different pipe diameters. The influence of polymer type, concentration and molecular weight on emulsion stability, viscosity and pressure drop was investigated.

6.2 EXPERIMENTAL SETUP & PROCEDURE

All tested surfactant stabilized W/O and O/W were prepared using brine (with 20 kppm NaCl) as the aqueous phase and a type of kerosene, known as SAFRA D60 produced in Saudi Arabia, as the oil phase. Some physical properties of the oil are presented in Table 3.1. ARMAC T, from Akzo Nobel, was used as the emulsifying agent and some of its physical properties are presented in Table 4.1.

In addition, Polyacrylamide (PAM) and Polyethylene oxide (PEO) were used as water soluble DRP and some of their physical properties are presented in Table 6.1 and Table 6.2, respectively. Also, Polyisobutylene, with physical properties reported in Table 6.3, was used as oil soluble DRP. A schematic layout of the flow loop is shown in Figure 3.2 and its description is explained in details in chapter 3.

Table 6.1 Physical properties of polyacrylamide (PAM)

Product name	MAGNAFLOC 1011
Supplier	Ciba Specialty chemicals
Molecular Weight	7×10^6 g/mol
Description	Anionic polyacrylamide flocculant ; white granular powder
Specific Gravity	0.7
Solubility	Water soluble

Table 6.2 Physical properties of polyethylene oxied (PEO)

Product name	Poly(ethylene oxide)
Supplier	Polysciences, Inc.
Molecular Weight	5×10^6 g/mol
Description	white granular powder
Specific Gravity	1.2
Solubility	Water soluble

Table 6.3 Physical properties of polyisobutylene (PIB)

Product name	Polyisobutylene
Supplier	Scientific Polymer Products, Inc.
Molecular Weight	0.85×10^6 g/mol, 2.8×10^6 g/mol and 4.7×10^6 g/mol
Description	Odorless clear slab
Specific Gravity	0.92 at 20 °C
Solubility	Oil soluble

36 liters of surfactant stabilized W/O emulsions with 70/30 water to oil volume ratio were made by adding the internal phase (in this case water) at 1 L/min to the emulsified external phase (here oil with 0.6 volume % emulsifier) while *mixing* at 8000 RPM (for 30 minutes) by using high power homogenizer (Ultra Turrax T 50 basic, WERKE IKA, Germany). Emulsion quality was tested by dilution and conductivity measurements tests. Emulsions were then transferred to one of the flowloop tanks. Same procedure was followed for stable W/O and O/W with 0.3 dispersed phase volume fraction.

Dilution test was used to identify the emulsion external phase. Also, emulsion type was detected by measuring its conductivity. In addition, bottle test was used to achieve stability tests by monitoring percentage of separated oil and/or separated water layers with time at 22 °C, 44 °C and 60 °C. Also, all rheological measurements were conducted using Rheologica StressTech rheometer.

Polymer solutions were prepared and then transferred to stainless steel tanks (pressurized tanks). Then, the pressurized tank is compressed with air till reaching the sufficient pressure required to get a maximum flowrate of polymer solution injection for that experiment. A pressure of 4×10^5 Pa is sufficient for all experiments reported in this work. After that, polymer solution was injected into the test section, as shown in Figure 3.2. This method for transferring the concentrated polymer solution (master solution) is used in order to avoid the degradation that would have occurred if a pump is used (Al-Sarkhi and Hanratty (2001a) and Al-Sarkhi and Abu-Nada (2005)). To check the possible polymer degradation when using centrifugal pumps, oil with 200 ppm PIB was re-circulated in the flowloop using one of the centrifugal pumps. As illustrated in Figure 6.1,

with continuous shear, pressure drop increased to the level of that for pure oil which proves the degradation of the DRP if a centrifugal pump was used. Therefore, polymer solution was recommended to be injected rather than added.

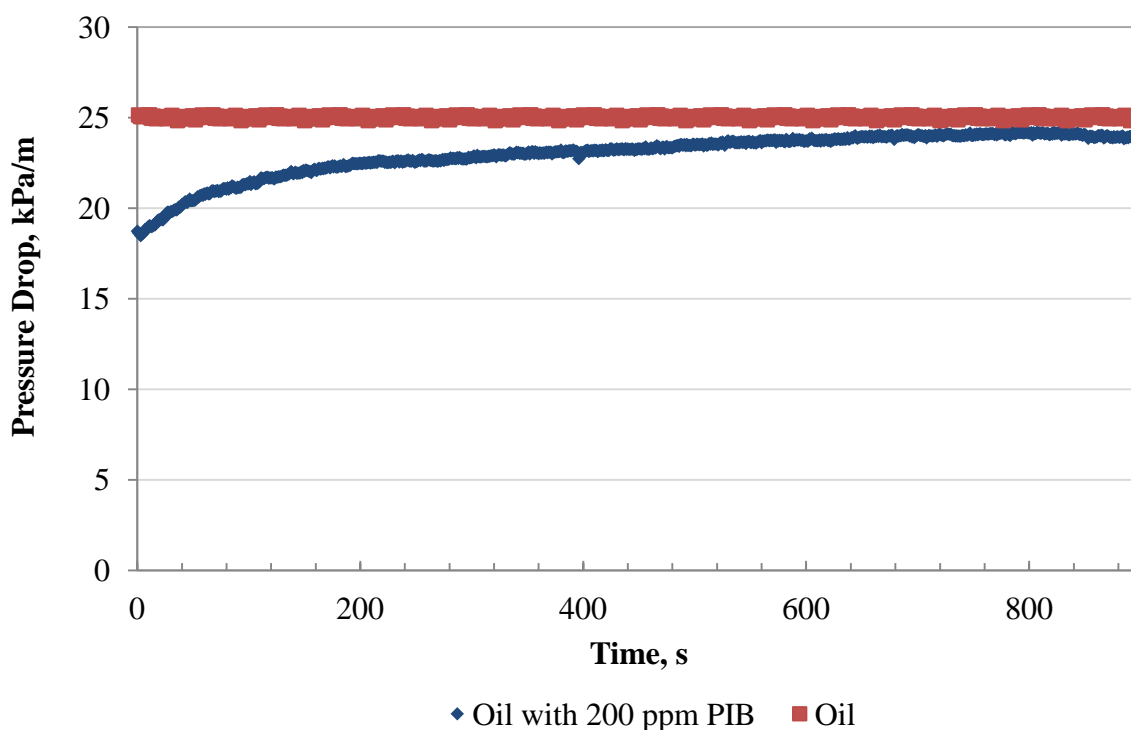


Figure 6.1 Polymer degradation by mechanical shear (centrifugal pump)

Pressure drop of all prepared emulsions were measured at different flowrates in both 2.54-cm and 1.27-cm pipes. All measurements were conducted at steady state conditions. Emulsion temperature was maintained at 25 °C. Based on the pipe flow shear rate Eq. (1), emulsion viscosity were extracted from rheological measurements and used to calculate Reynolds number (Re) for emulsion. The term in brackets in equation (1) is the Robinowitsch correction for non-Newtonian fluids. The pressure drop reduction percentage (DR %) was defined as presented in Eq. (2).

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3} \left[\frac{3}{4} + \frac{1}{4} \frac{d(\ln Q)}{d(\ln \tau_w)} \right] \quad (1)$$

where

$\dot{\gamma}_w$ = True wall shear rate

Q = Volumetric flowrate

R = Pipe radius

τ_w = Wall shear stress

$$DR\% = \left(\frac{\Delta P_{without\ DRP} - \Delta P_{with\ DRP}}{\Delta P_{without\ DRP}} \right) \times 100 \quad (2)$$

where

$\Delta P_{without\ DRP}$ = Emulsion pressure drop before drag reducing polymer injection

$\Delta P_{with\ DRP}$ = Emulsion pressure drop after drag reducing polymer injection

6.3 RESULTS AND DISCUSSIONS

Emulsion stability

Stability of surfactant-stabilized W/O emulsions, with 0.7 water volume fraction, without and with 50 ppm of different DRP types and molecular weights was tested using bottle test at 22 °C, 44 °C and 60 °C. Two ovens were used for the tests at 44 °C and 60 °C. Five samples, at each temperature, were used for the test. These samples contains: (a) no polymer, (b) 50 ppm of PIB with 4.7×10^6 g/mol molecular weight, (c) 50 ppm of PIB with 2.8×10^6 g/mol molecular weight, (d) 50 ppm of PIB with 0.85×10^6 g/mol molecular weight and (e) 50 ppm of PEO with 5×10^6 g/mol molecular weight.

As shown in Figure 6.2 and 6.3, although adding PIB polymers enhanced W/O emulsion stability, added PEO DRP sedimented to form a water layer. It is worthy to recall that oil constitutes the emulsion external layer and adding PIB DRP, which is oil soluble polymer, increased oil viscosity and hence emulsion stability. However, adding PEO DRP, which is soluble in the emulsion internal phase (water), to the emulsion sample had no chance to interact with the emulsion dispersed phase droplets and because of its higher density it settled down to form water separated layer (see Figure 6.3).

In addition, increasing PIB DRP molecular weight enhanced the W/O emulsion stability and this is could be attributed to the increase of oil viscosity as well as emulsion elasticity with increasing PIB DRP molecular weight.

At higher temperatures (44 °C and 60 °C), as presented in Figures 6.4 – 6.7, as PIB DRP molecular weight increased, emulsion stability was improved but with a less extent compared with that at 22 °C. This is can be explained in terms of oil viscosity drop with temperature increase.

Furthermore, as temperature increased emulsion stability decreased because of the viscosity drop of both phases and the surfactant solubility reduction in either phase (Ghannam, M. (2005)) and due to the loss modulus drop (Andre, et al (2003)). This effect is illustrated in Figure 6.8.

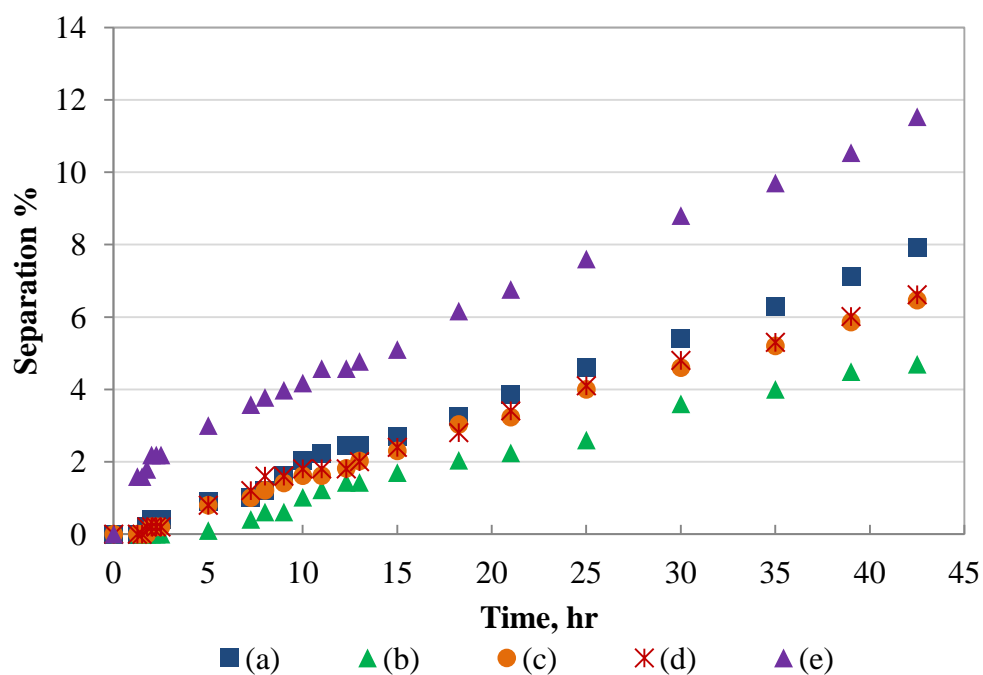


Figure 6.2 Effect of 50 ppm polymer additives on W/O emulsion stability at 22 °C; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), (d) with PIB (0.85×10^6 g/mol) and (e) with PEO (5×10^6 g/mol)

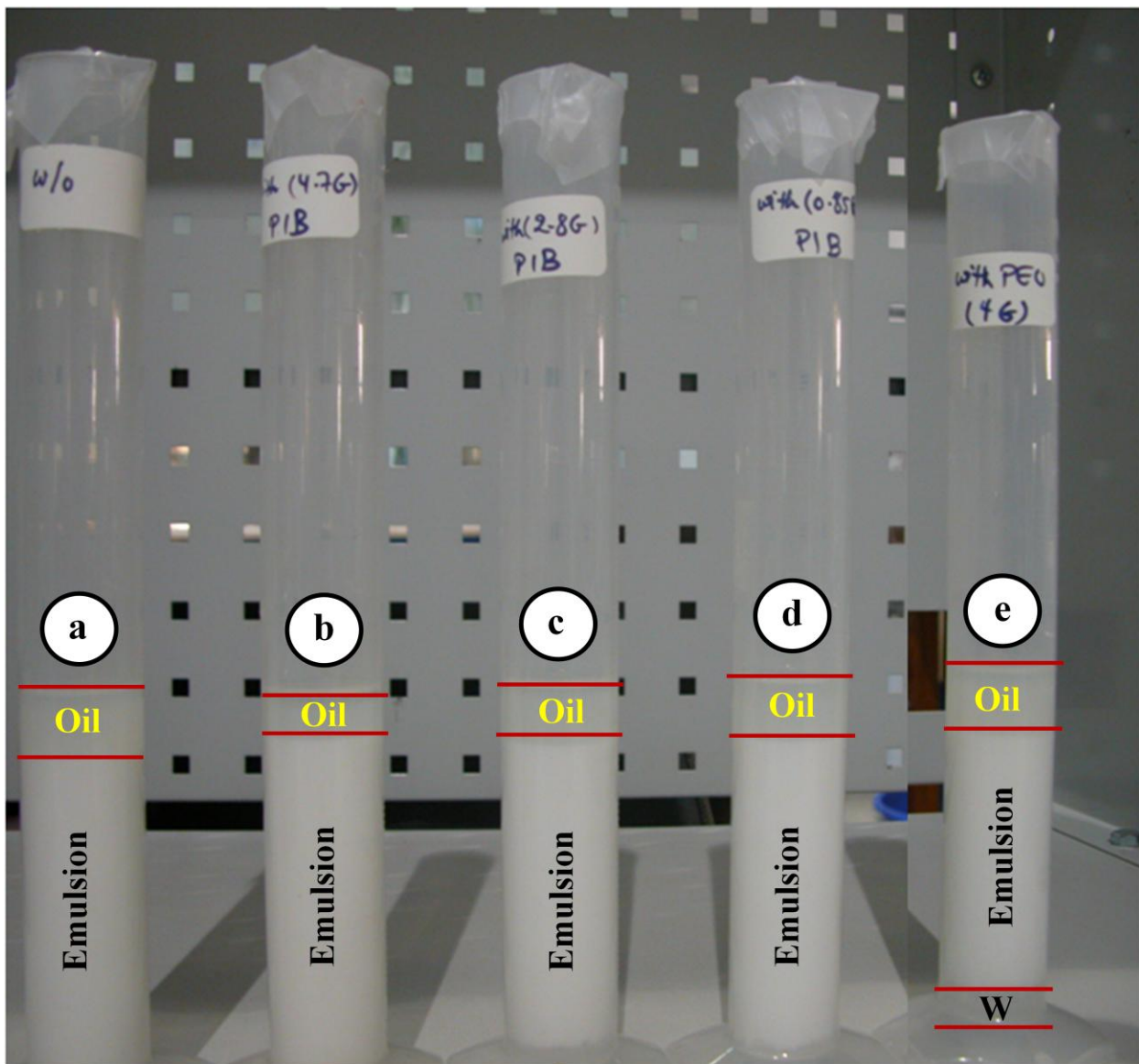


Figure 6.3 W/O emulsion stability test after 110 hrs at 22 °C with 50 ppm of different polymers; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), (d) with PIB (0.85×10^6 g/mol) and (e) with PEO (5×10^6 g/mol)

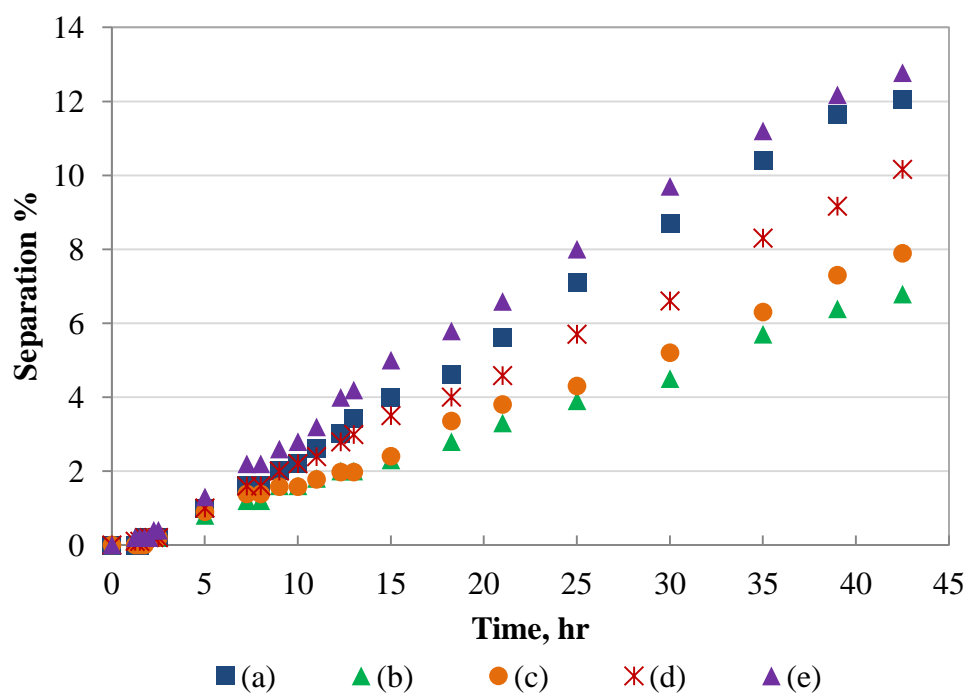


Figure 6.4 Effect of 50 ppm polymer additives on W/O emulsion stability at 44 °C; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), (d) with PIB (0.85×10^6 g/mol) and (e) with PEO (5×10^6 g/mol)

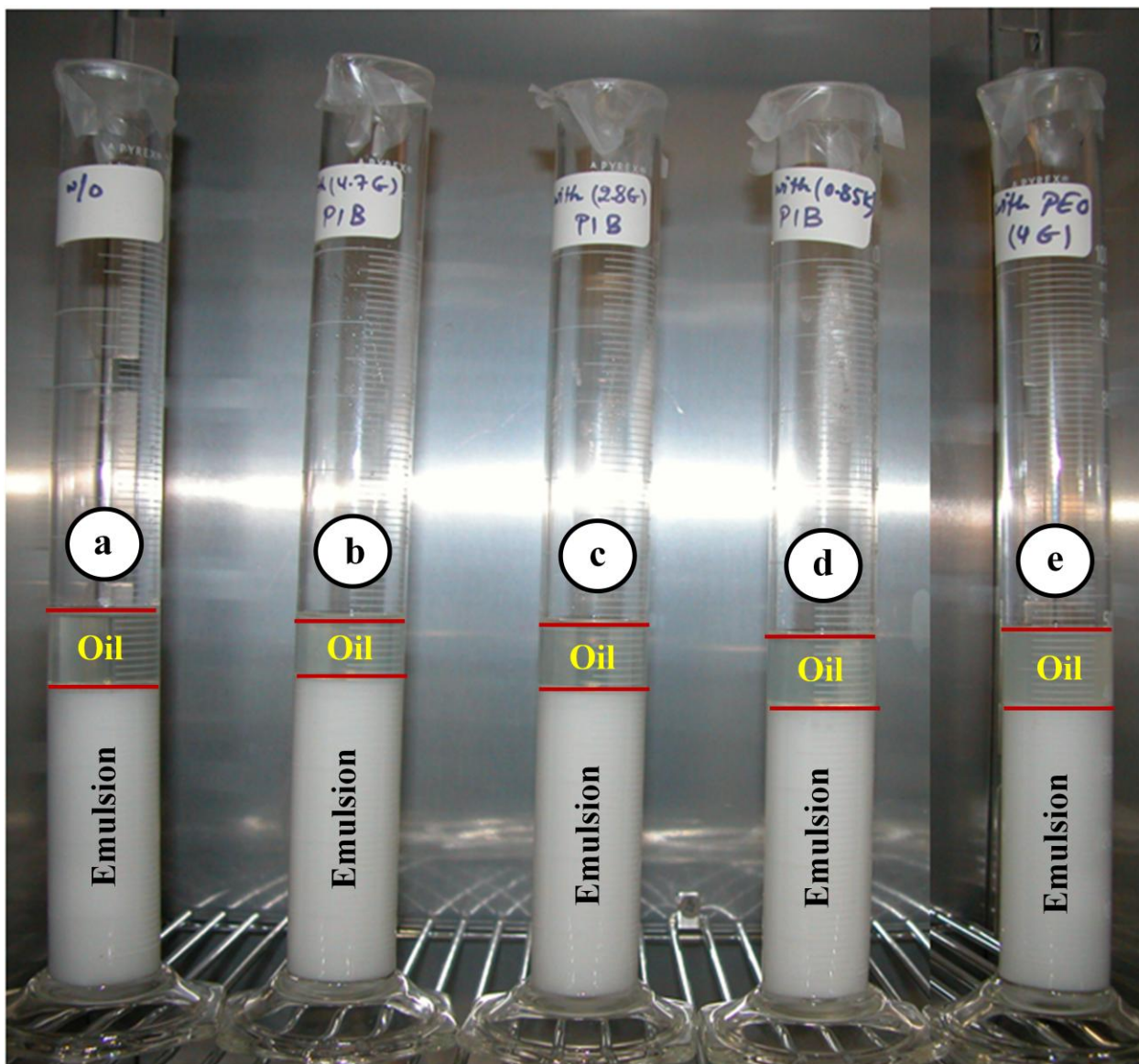


Figure 6.5 W/O emulsion stability test after 110 hrs at 44 °C with 50 ppm of different polymers; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), (d) with PIB (0.85×10^6 g/mol) and (e) with PEO (4.7×10^6 g/mol)

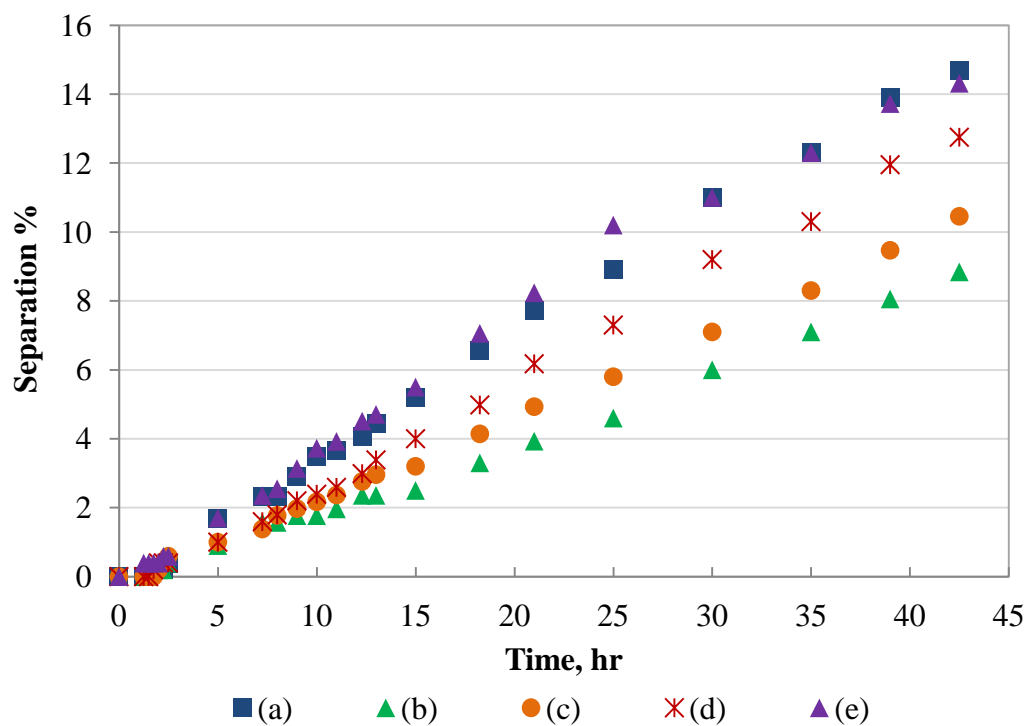


Figure 6.6 Effect of 50 ppm polymer additives on W/O emulsion stability at 60 °C; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), (d) with PIB (0.85×10^6 g/mol) and (e) with PEO (5×10^6 g/mol)



Figure 6.7 W/O emulsion stability test after 110 hrs at 60 °C with 50 ppm of different polymers; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), (d) with PIB (0.85×10^6 g/mol) and (e) with PEO (4.7×10^6 g/mol)

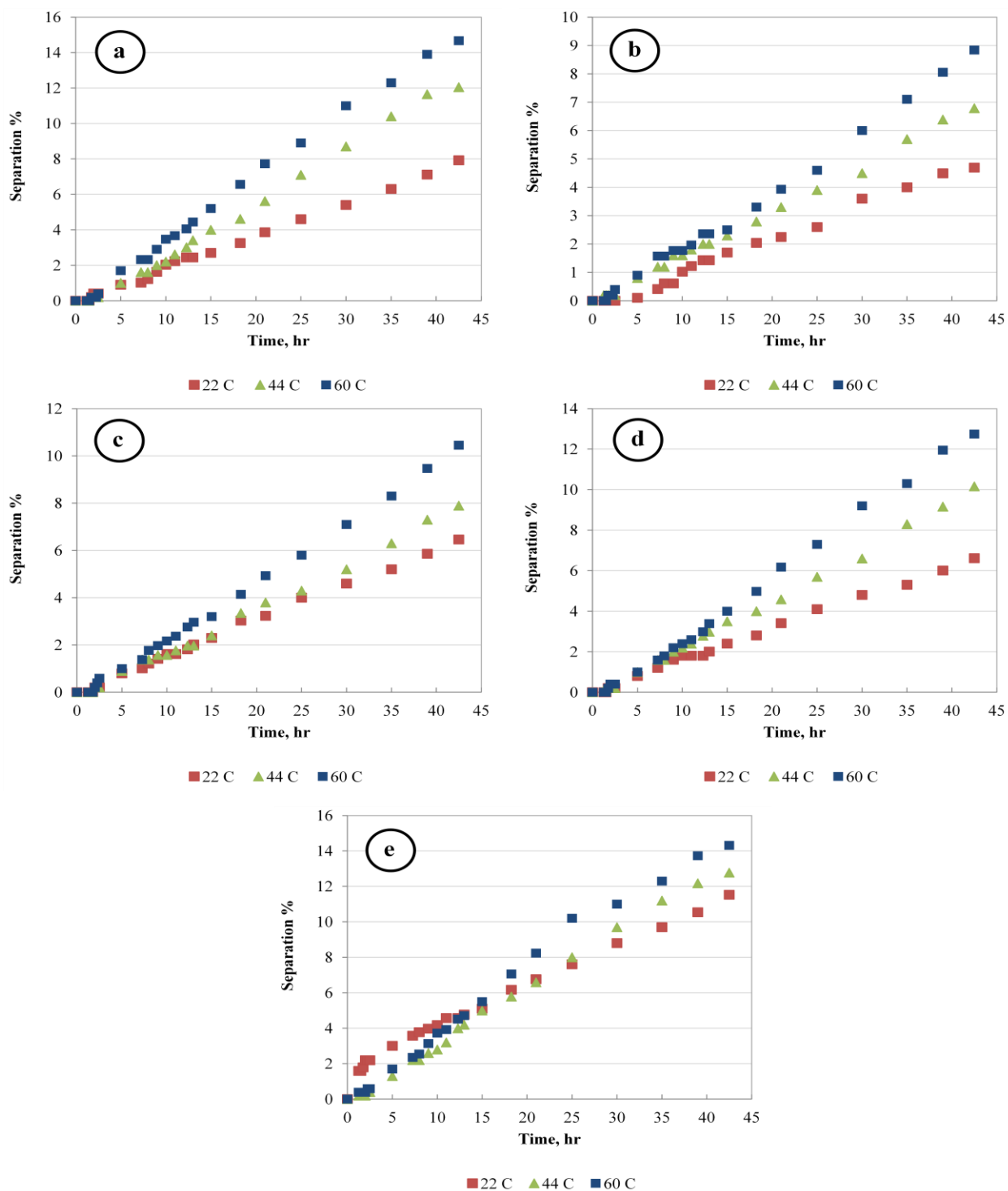


Figure 6.8 Effect of temperature on W/O emulsion stability with 50 ppm of different polymers; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), (d) with PIB (0.85×10^6 g/mol) and (e) with PEO (4.7×10^6 g/mol)

Emulsion Rheology

Effect of polymer concentration and molecular weight on W/O emulsion viscosity was studied using a Bob and Cup viscometer. PIB DRP with different concentrations (50, 200 and 400 ppm) and molecular weights (0.85×10^6 g/mol, 2.8×10^6 g/mol and 4.7×10^6 g/mol) was added to the formed W/O emulsion having 0.7 water volume fraction. These results are illustrated in Figures 6.9 - 6.11.

As shown in these figures, at low DRP concentration (50 ppm) emulsion viscosity increased after adding PIB polymers with different molecular weights. In addition, although low concentration DRP with high molecular weights (2.8×10^6 g/mol and 4.7×10^6 g/mol) showed shear thinning effect, DRP with low molecular weight might be dispersed instead of showing a drag reducing effect.

However, as DRP concentration increased shear thinning effect became clearer and this effect was enhanced as DRP molecular weight increased. At steady shear rate sweep test, emulsion sample (without PIB additives) was spilled off of the viscometer cup at 1012 s^{-1} shear rate. However, adding 200 ppm of DRP facilitated the shearing in the viscometer cup as emulsion viscosity was reduced; thus emulsion sample was thrown out earlier (at low shear rate). In addition, as DRP concentration as well as molecular weight increased, shear thinning effect increased. This impact is illustrated in Figure 6.12, where y-axis represents the shear rate required to push emulsion sample out of the viscometer cup. Also, this effect was confirmed by microscopic test (see Figure 6.13). While emulsion sample without DRP showed a fixed droplets micrograph, addition of 100 ppm of PIB

DRP (with 4.7×10^6 g/mol molecular weight) resulted in a significant movement of the dispersed phase droplets.

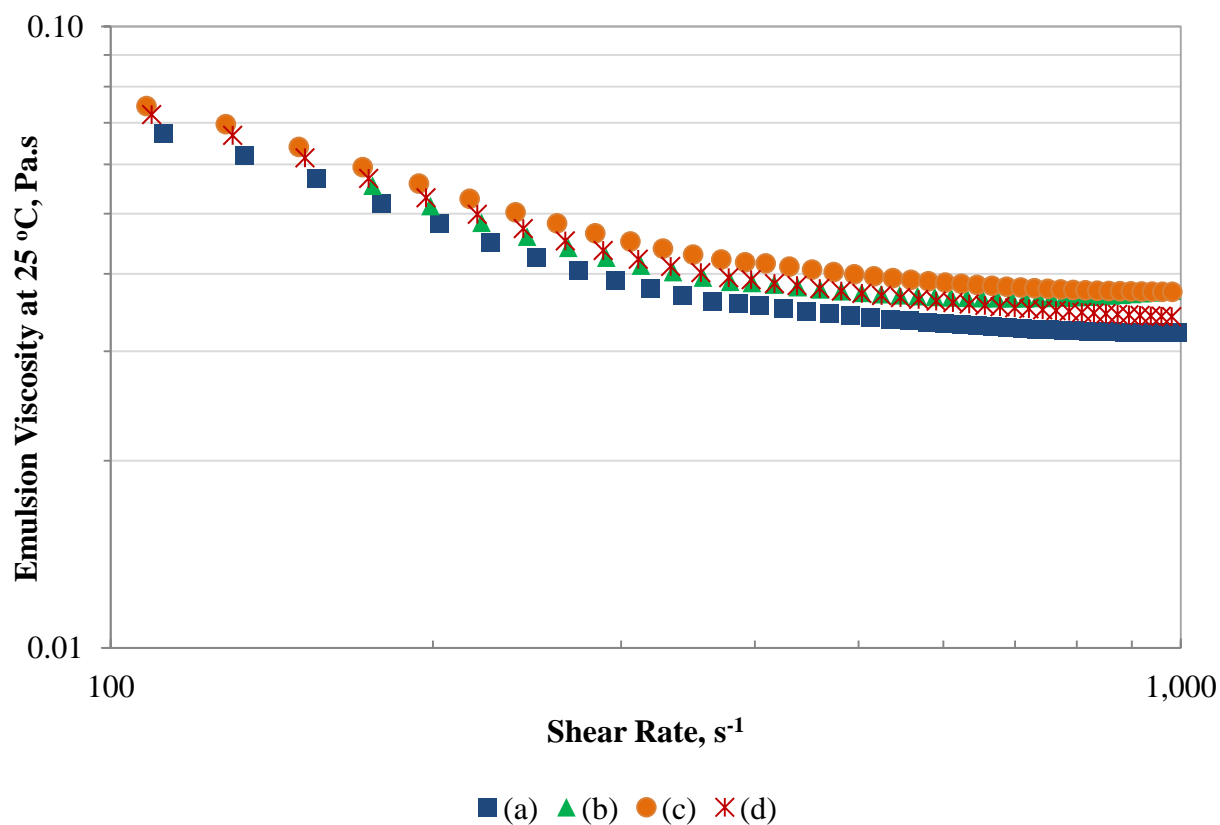


Figure 6.9 Effect of 50 ppm of PIB on concentrated W/O emulsion viscosity at different molecular weights; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), and (d) with PIB (0.85×10^6 g/mol)

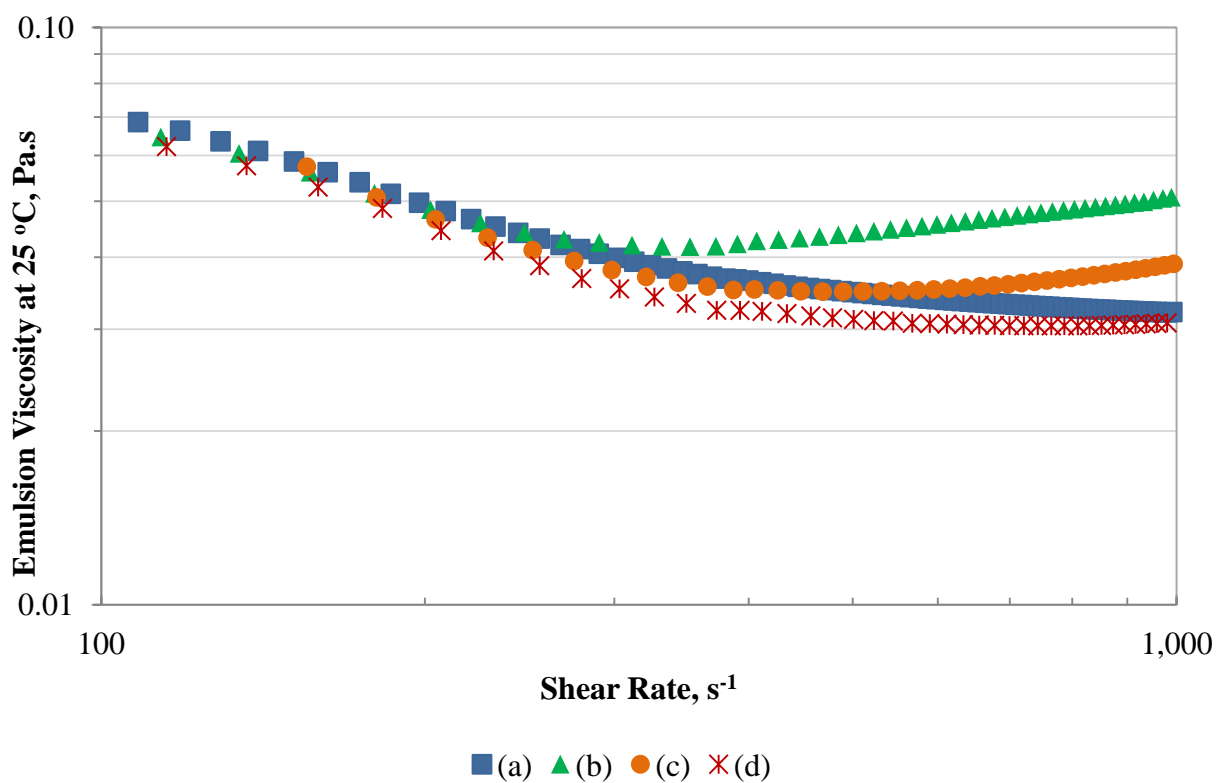


Figure 6.10 Effect of 200 ppm of PIB on concentrated W/O emulsion viscosity at different molecular weights; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), and (d) with PIB (0.85×10^6 g/mol)

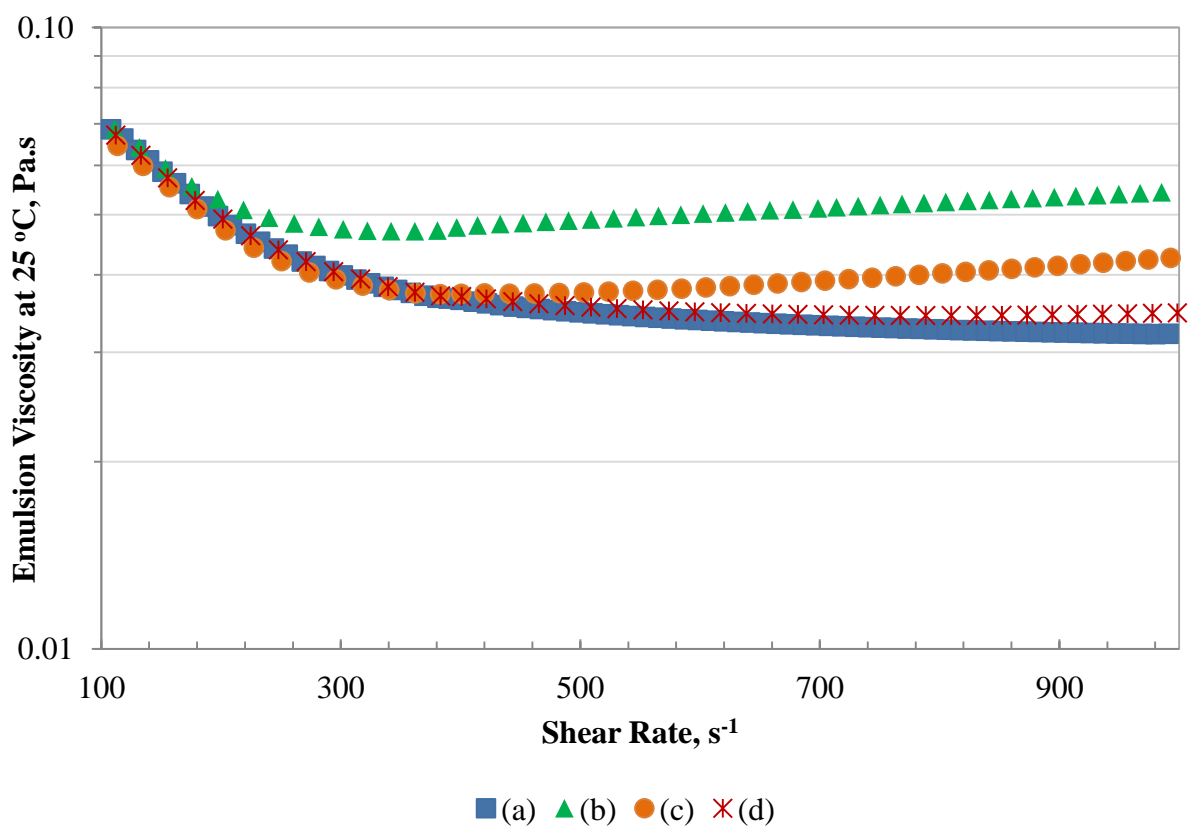


Figure 6.11 Effect of 400 ppm of PIB on concentrated W/O emulsion viscosity at different molecular weights; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), and (d) with PIB (0.85×10^6 g/mol)

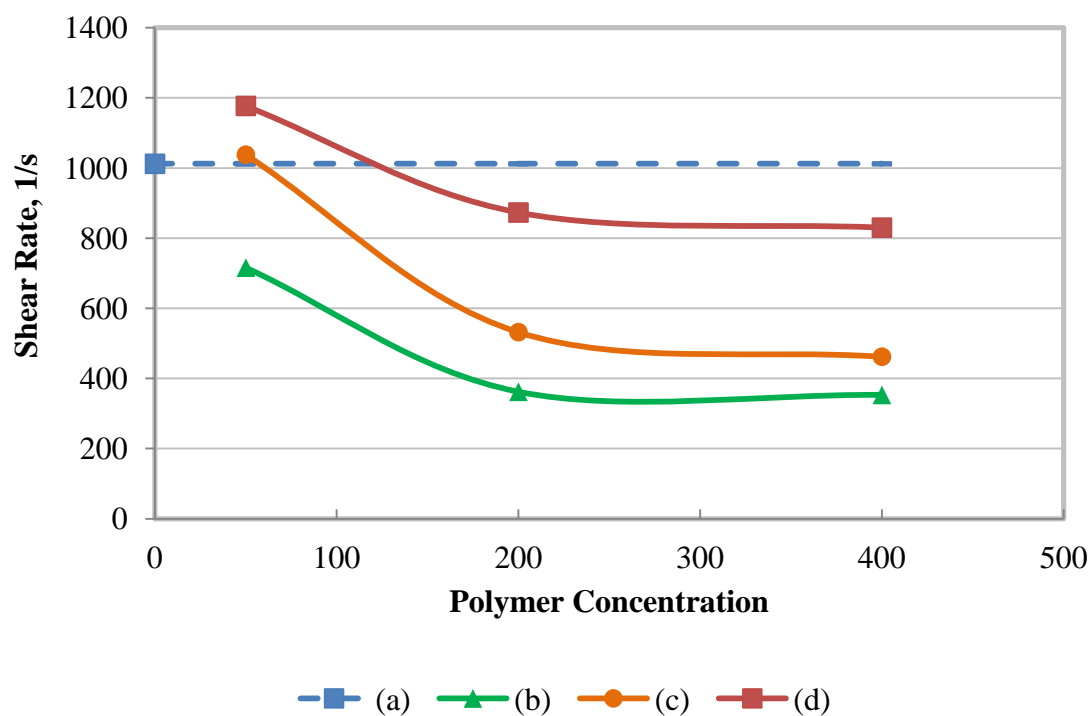


Figure 6.12 Polymer shear thinning effect on W/O emulsion at different PIB molecular weights; (a) no polymer, (b) with PIB (4.7×10^6 g/mol), (c) with PIB (2.8×10^6 g/mol), and (d) with PIB (0.85×10^6 g/mol)

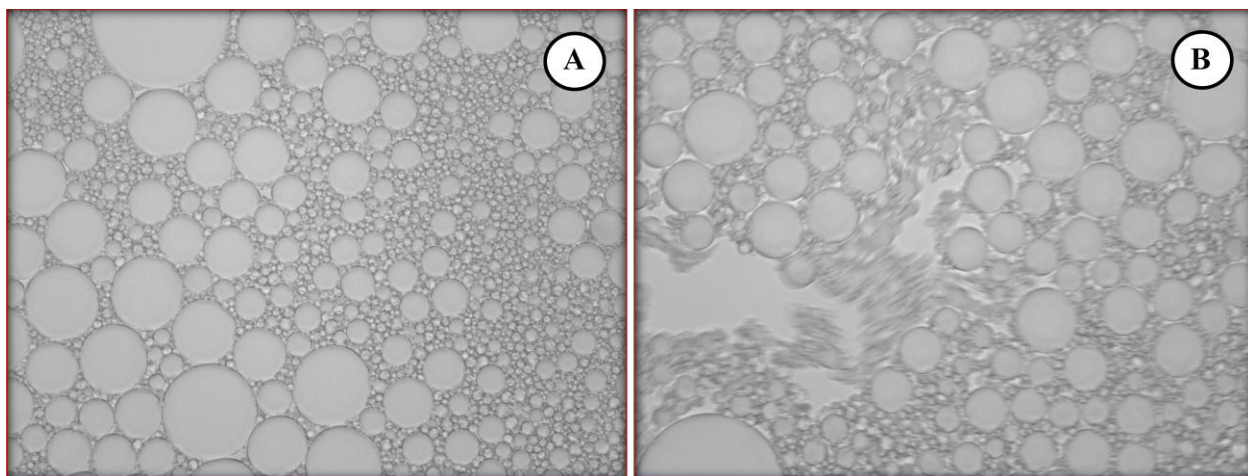


Figure 6.13 Effect of polymer shear thinning on W/O emulsion; (A) without polymer and (B) with 100 ppm PIB (with 4.7×10^6 g/mol)

Pressure Drop Measurements

Single phase flow

The performance of both oil soluble polymer (PIB with 4.7×10^6 g/mol molecular weight) and water soluble polymer (PAM with 7×10^6 g/mol molecular weight) was checked by injecting 200 ppm of PIB and PAM in oil and water single phase flow in 1.27-cm pipe, respectively.

As shown in Figure 6.14, at the same Reynolds number of 41000, while injecting 200 ppm of PAM reduced water pressure drop by 33.3 % (A), injecting 200 ppm of PIB resulted in 50 % oil pressure drop reduction (B). These values are lower than those reported in the literature. For example, Al-Yaari (2008) reported more 70 % drag reduction due to the use of only 100 ppm PAM for the same Reynolds number but for fresh water. This could be attributed to the polymer injection point location as well as water salinity. Since PAM is partially anionic, as water salinity increases, its performance as a drag reducing agent decreases (Al-Yaari et al (2008 and 2009)).

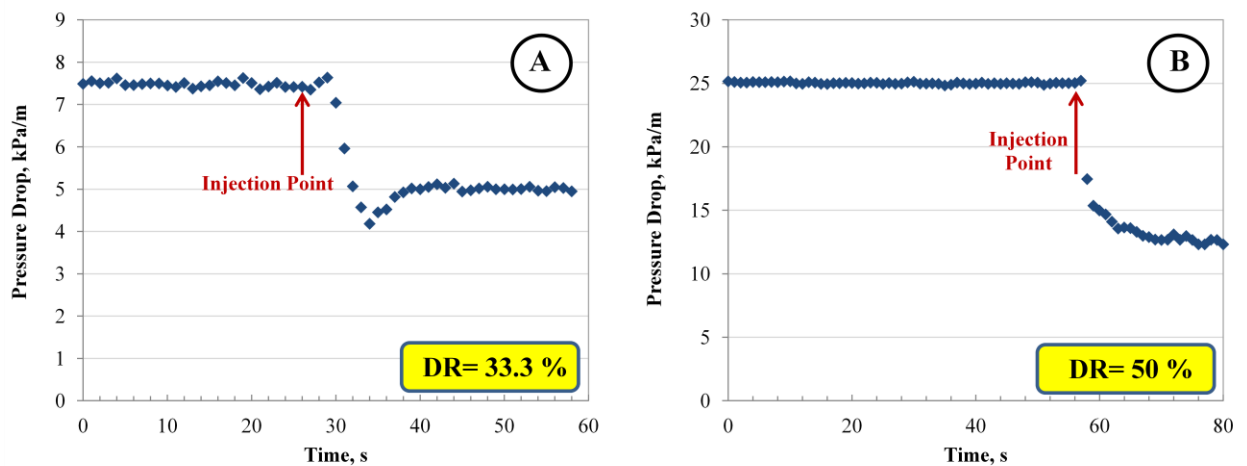


Figure 6.14 Performance of injected DRP for single phase flow in 1.27-cm pipe; (A) water with 200 ppm of PAM and (B) oil with 200 ppm PIB

Stable W/O emulsion with 0.7 water volume fraction

Pressure drop measurements of surfactant-stabilized W/O emulsion were conducted in both flowloop pipe test sections (See Figure 6.15). For each flowrate, true shear rate was calculated by Eq. (1) and then the corresponding apparent viscosity was used to calculate Re. As shown in Figure 6.15, because of the emulsion viscosity, pump power and flowloop design, the maximum Re reached was about 2100 and 2700 for emulsion flow in the 1.27-cm and 2.54-cm pipe test sections, respectively.

Since oil is the external phase of the W/O emulsions, PIB DRP with 4.7×10^6 g/mol molecular weight was injected to investigate any possible drag reduction of such concentrated emulsion at low Re. PIB DRP at different pipeline concentration (50, 100 and 200 ppm) was tested as drag reducing polymer for such emulsion flows in both test sections at 25 °C.

As shown in Figures 6.16 and 6.17, for the same Re (Re = 1800), although injection of PIB DRP with low concentration (50 & 100 ppm) showed no drag reducing effect in both pipes, injection of PIB DRP with 200 ppm concentration resulted in 12 ± 2 % pressure drop reduction. This is could be because of some reasons including the shear thinning effect at higher concentration as mentioned earlier.

Since DRP are believed to work fine at high Re (high turbulent flow), W/O as well as O/W emulsions with low dispersed phase fraction were made and DRP performance for such dilute system was then tested as shown in the following sections.

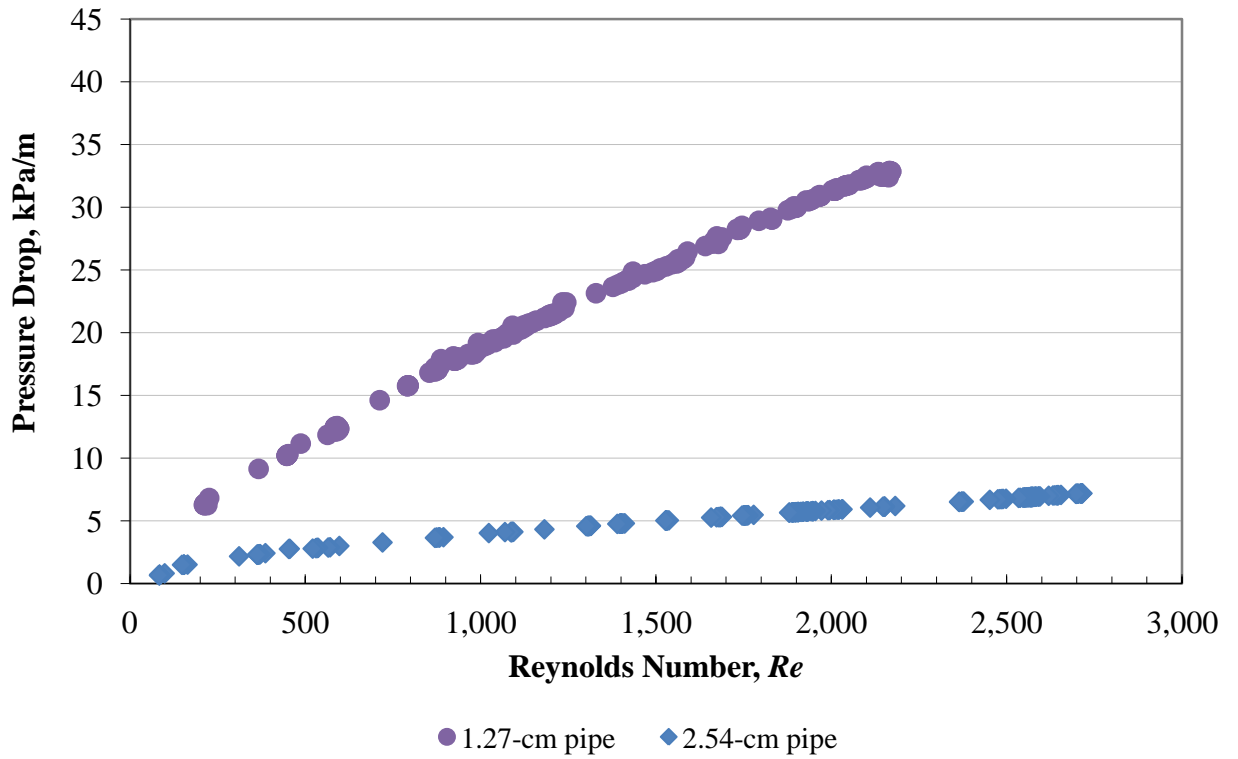


Figure 6.15 Pressure drop measurements of stable W/O emulsion with 0.7 water volume fraction

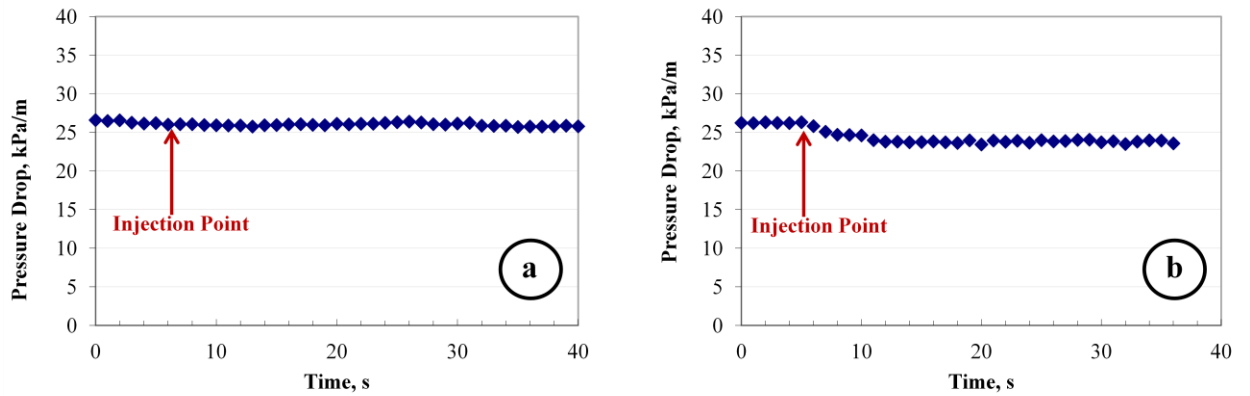


Figure 6.16 Effect of injected PIB (oil soluble) on concentrated W/O emulsion pressure drop in 1.27-cm pipe ($Re = 1800$) at different concentrations; (a) 100 ppm, and (b) 200 ppm

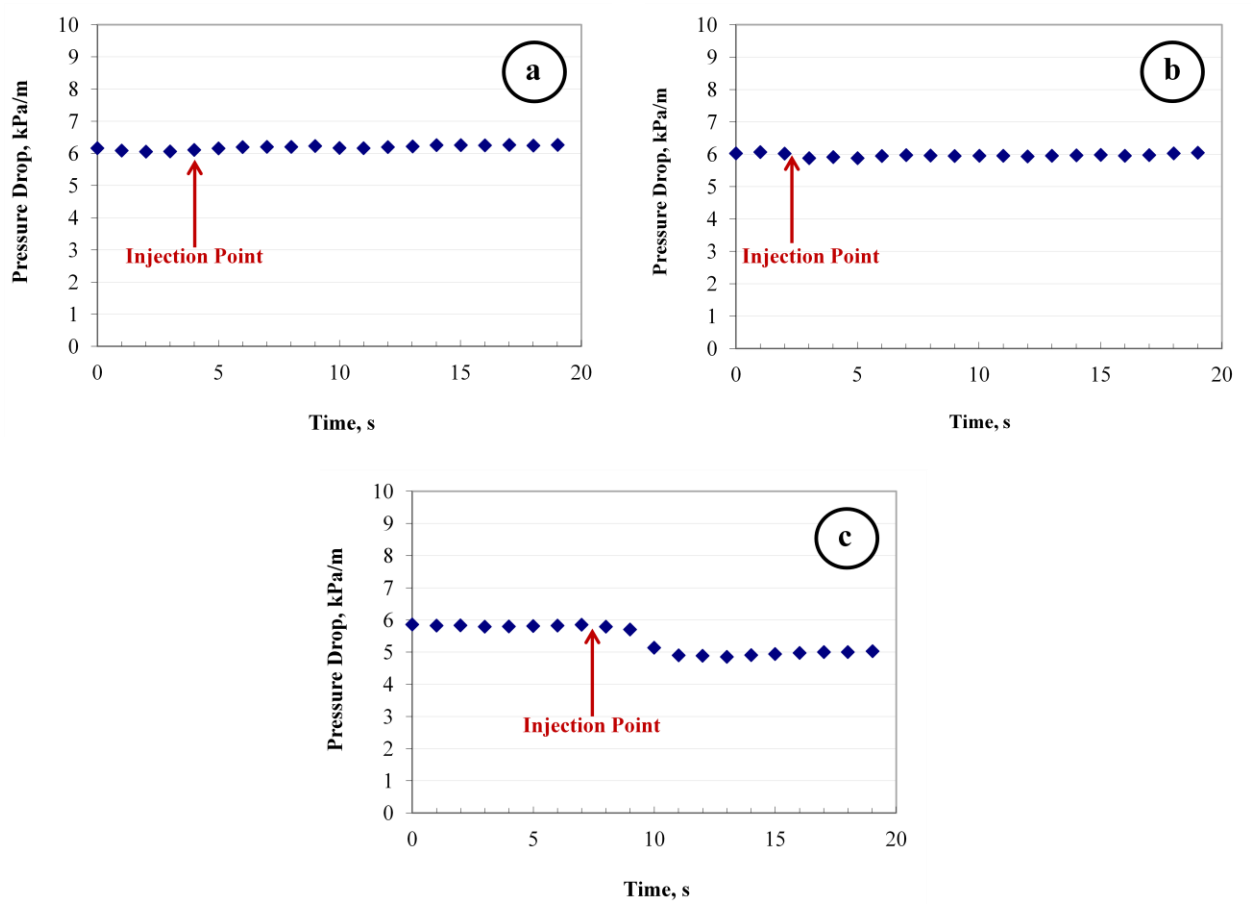


Figure 6.17 Effect of injected PIB (oil soluble) on concentrated W/O emulsion pressure drop in 2.54-cm ($Re = 1800$) pipe at different concentrations; (a) 50 ppm, (b) 100 ppm, and (c) 200 ppm

Stable W/O emulsion with 0.3 water volume fraction

W/O emulsion with 0.3 water (brine with 20 kppm NaCl) volume fraction was made with the same procedure mentioned earlier. Its pressure drop measurements in both pipe test sections are illustrated in Figure 6.18. Since oil is the external phase and constituting 70 % of the emulsion volume, PIB DRP with 4.7×10^6 g/mol molecular weight was used. DRP was injected at different concentrations (50, 100, 200 and 400 ppm) while emulsion flow in both test sections (with pipe ID of 1.27-cm and 2.54-cm) at the same Re of 8500. DRP performance in both pipes is presented in Figure 6.19 and Figure 6.20. As shown in these figures, as DRP concentration increased, its performance as a drag reducing agent increased in both pipes.

Summary of the PIB DRP performance when used for stable W/O emulsion with 0.3 water volume fraction is presented in Figure 6.21. While high shear may cause high dispersion at low DRP concentration, high shear is required for the polymer to be in its expanded form which is the preferable form to work as drag reducing agent; therefore, as DRP concentration increased, its efficiency increased. In addition, as shown in Figure 6.21, almost there was no significant effect on the DRP performance due to the pipe diameter for the flow at the same Re.

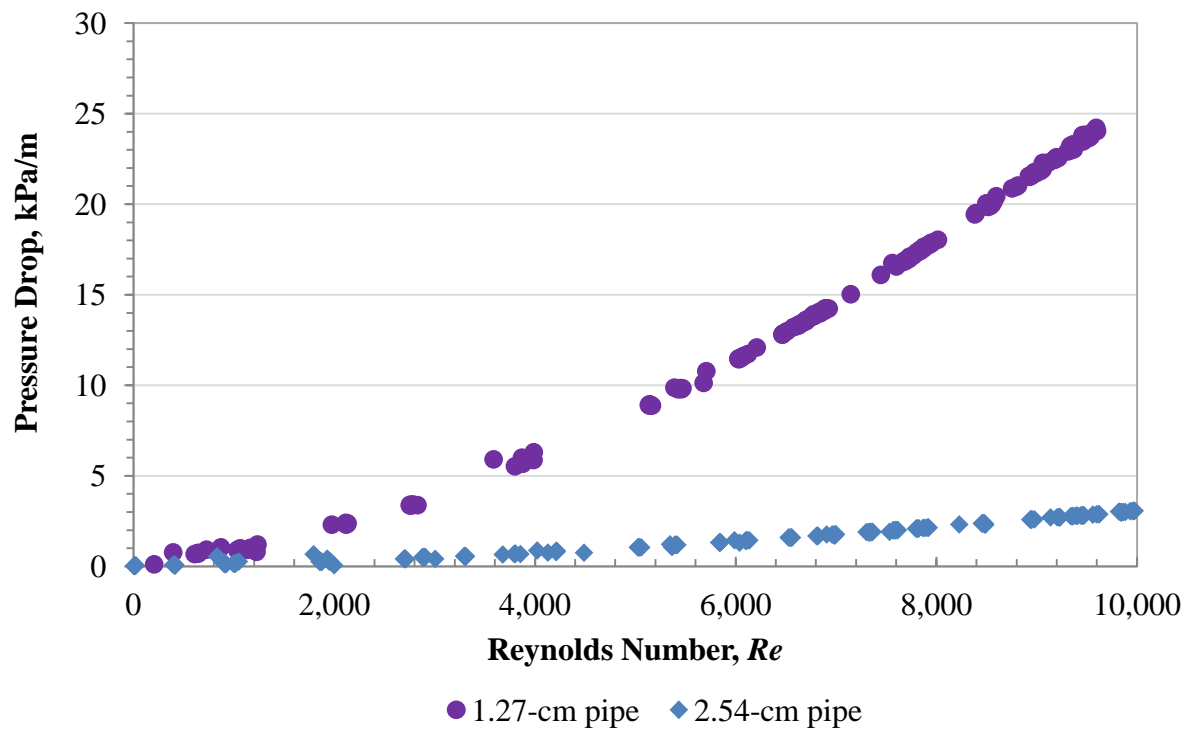


Figure 6.18 Pressure drop measurements of stable W/O emulsion with 0.3 water volume fraction

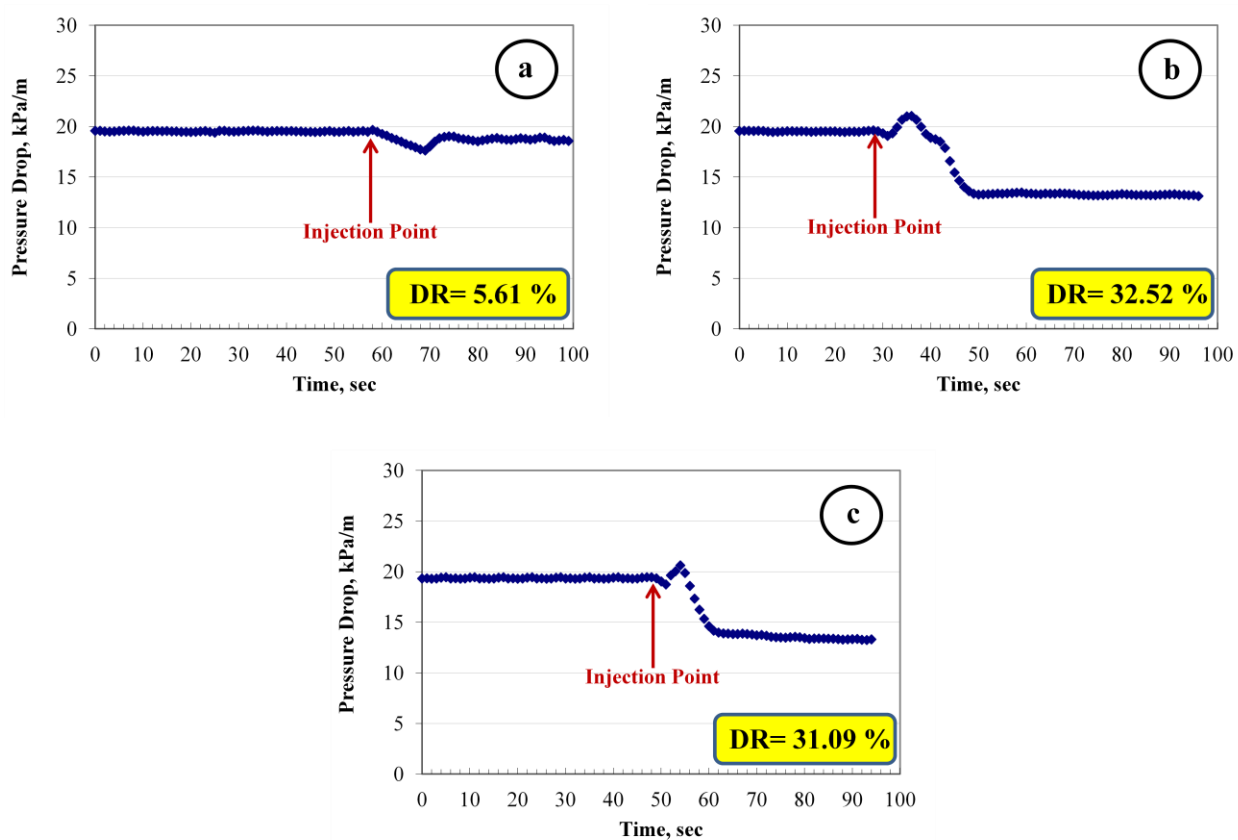


Figure 6.19 Effect of injected PIB (oil soluble) on W/O emulsion pressure drop in 1.27-cm pipe at different concentrations; (a) 100 ppm, (b) 200 ppm and (c) 400 ppm

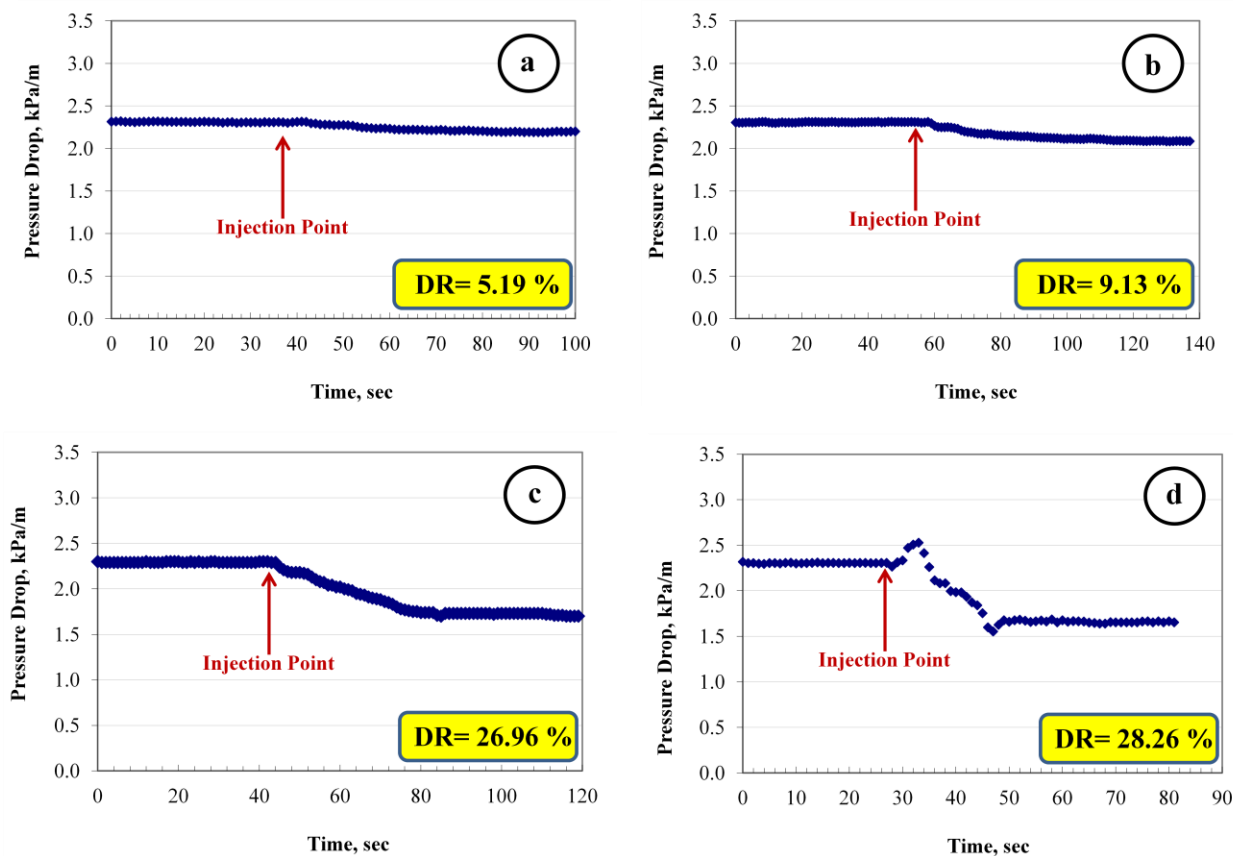


Figure 6.20 Effect of injected PIB (oil soluble) on W/O emulsion pressure drop in 2.54-cm pipe at different concentrations; (a) 50 ppm, (b) 100 ppm, (c) 200 ppm and (d) 400 ppm

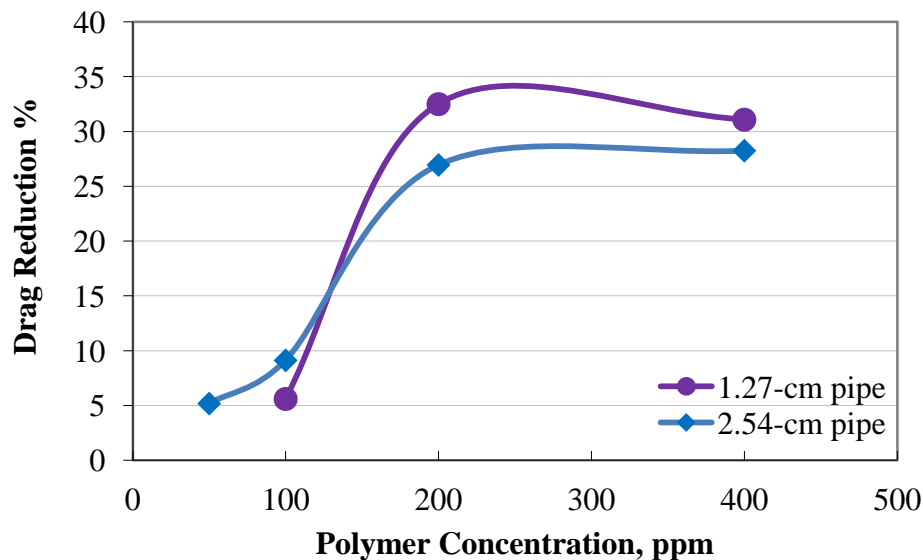


Figure 6.21 PIB DRP performance when used for W/O emulsion with 0.3 water volume fraction

Stable O/W emulsion with 0.3 oil volume fraction

O/W emulsion with 0.3 oil volume fraction was made with the same procedure mentioned earlier. Its pressure drop measurements in both pipe test sections are illustrated in Figure 6.22. Since water, constituting 70 % of the emulsion volume, is the external phase, PAM DRP was used. DRP was injected at different concentrations (50, 100, 200 and 400 ppm) while emulsion flow in both test sections (with pipe ID of 1.27-cm and 2.54-cm) at the same Re of 16700.

DRP performance in both pipes is presented in Figure 6.23 and Figure 6.24. As shown in these figures, at low DRP concentration (≤ 200 ppm), although slight drag reduction was observed in the 1.27-cm pipe test section, there was no effect in the 2.54-cm pipe test section. However, maintaining higher DRP concentration (400 ppm) in both test sections, emulsion pressure drop was reduced by almost 39 %.

In addition, although the external phase was water, PIB DRP (oil soluble) performance was checked in the 1.27-cm pipe test section to check for any possible interaction between the DRP and the internal phase (oil). As shown in Figure 6.25, no effect was detected (see Figure 6.25 a-c) and at high concentration (400 ppm) negative effect was monitored (see Figure 6.25 d). This is acceptable since PIB DRP is insoluble in the external phase (water) and its preferable phase is dispersed. Therefore, no enough space for such long molecules to interact with the turbulence eddies at the high shear rate region (near the wall) and at high concentration such molecules were dispersed and created additional energy loss.

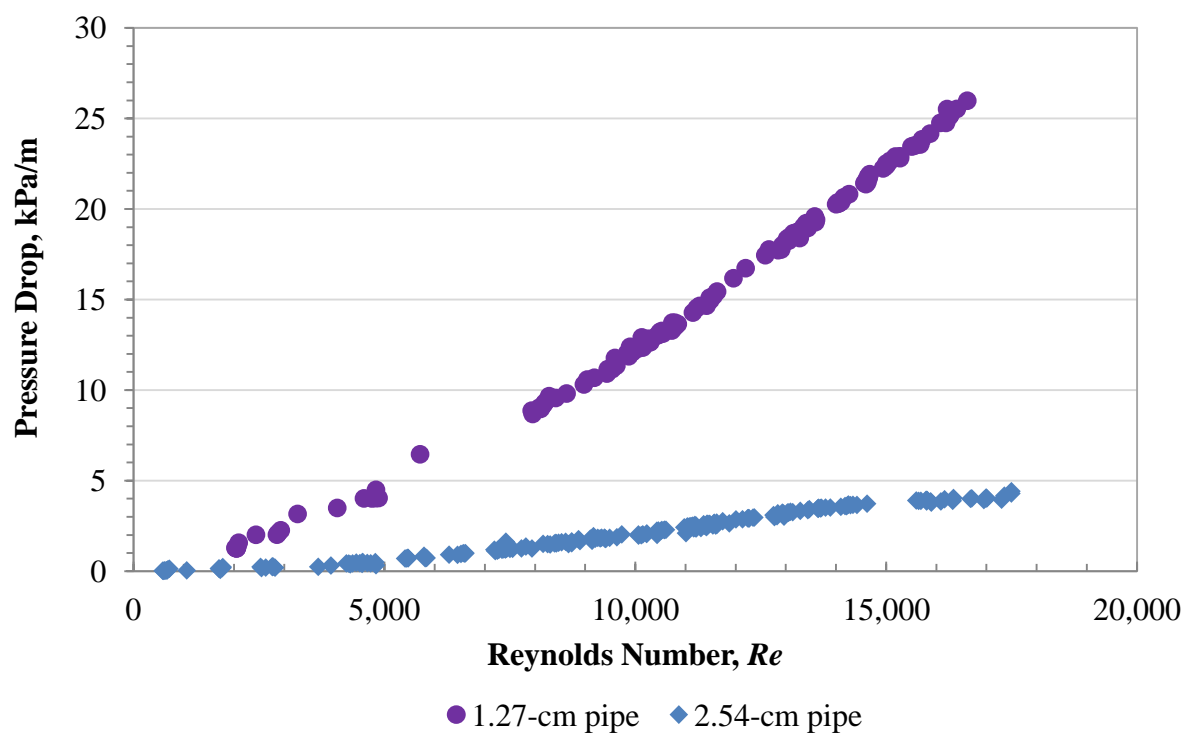


Figure 6.22 Pressure drop measurements of stable O/W emulsion with 0.3 oil volume fraction

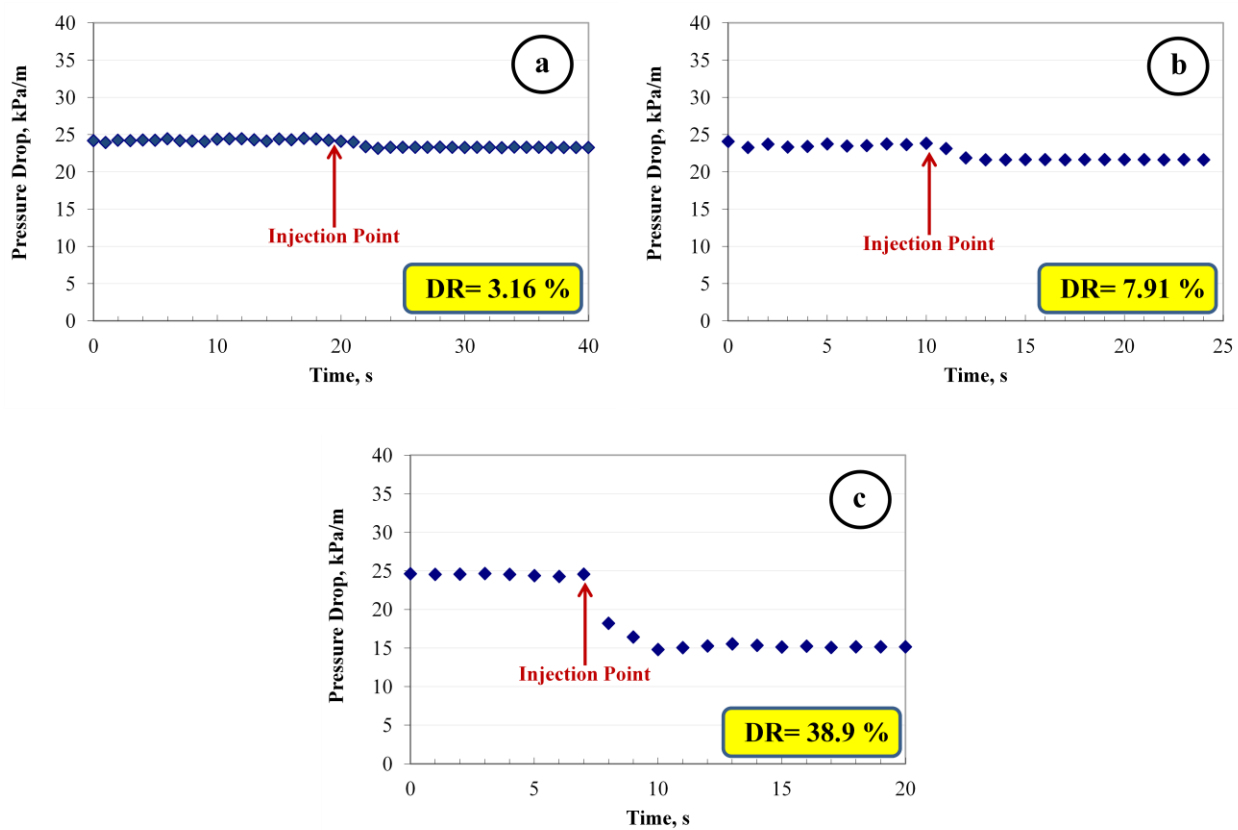


Figure 6.23 Effect of injected PAM (water soluble) on O/W emulsion pressure drop in 1.27-cm pipe at different concentrations; (a) 100 ppm, (b) 200 ppm and (c) 400 ppm

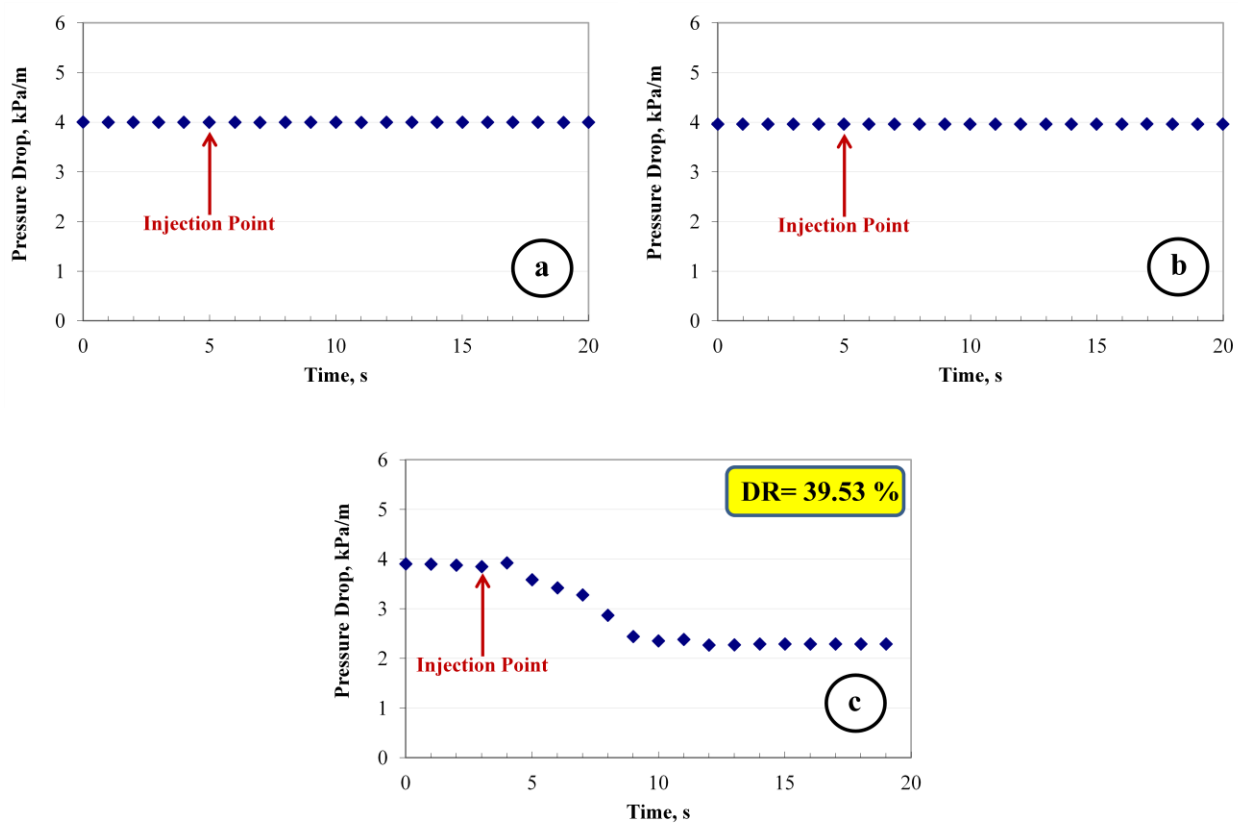


Figure 6.24 Effect of injected PAM (water soluble) on O/W emulsion pressure drop in 2.54-cm pipe at different concentrations; (a) 100 ppm, (b) 200 ppm and (c) 400 ppm

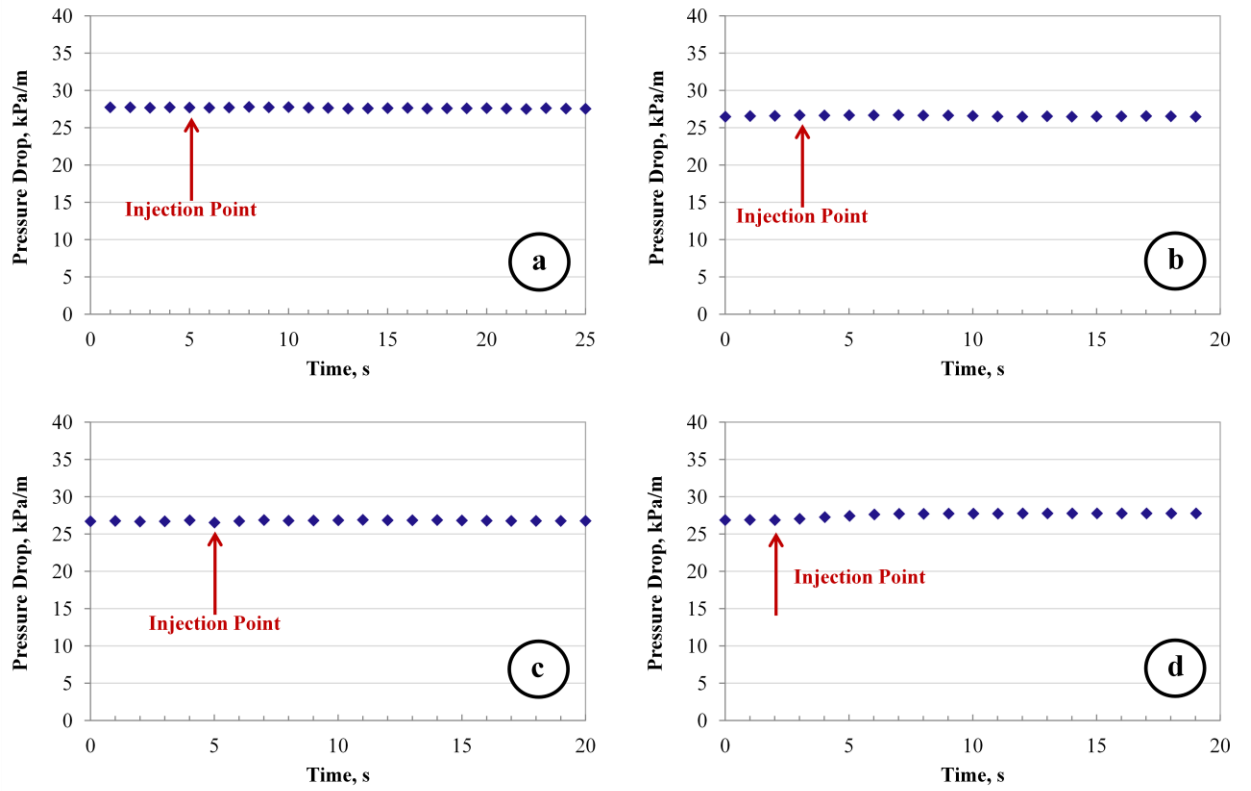


Figure 6.25 Effect of injected PIB (oil soluble) on O/W emulsion pressure drop in 1.27-cm pipe at different concentrations; (a) 50 ppm, (b) 100 ppm, (c) 200 ppm and (d) 400 ppm

Unstable W/O emulsion with 0.3 water volume fraction

Stable W/O emulsion with 0.7 water (brine with 20 kppm NaCl) volume fraction was left till the initiation of the emulsion separation occurrence. This separation was detected by the inline conductivity cell through a sharp drop in the emulsion resistance and by static conductivity measurements through a sharp increase in emulsion conductivity from 0 $\mu\text{S}/\text{cm}$ to 8 mS/cm . Because of that, this emulsion was considered as unstable emulsion. Then, PIB DRP with pipeline concentration of 400 ppm was injected while emulsion turbulent flow ($\text{Re} = 16700$) in both test sections separately and its performance is illustrated in Figure 6.26. Emulsion pressure drop was reduced by almost 22 % in both pipes compared with no effect in the case of stable O/W emulsion (see Figure 6.25). This is could be attributed to the formation of the preferable phase (oil) at the high shear rate region (near the wall) for the case of unstable emulsion flow.

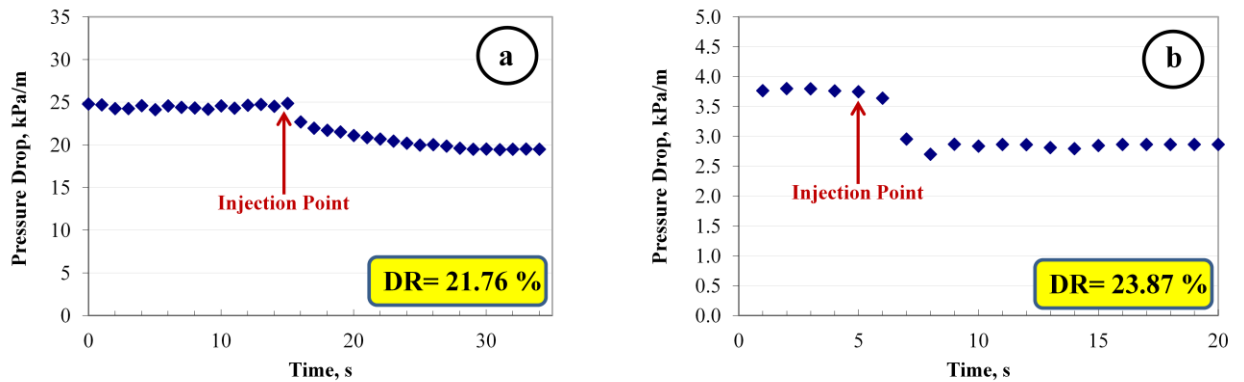


Figure 6.26 Effect of 400 ppm injected PIB (oil soluble) on unstable O/W emulsion pressure drop at different pipe diameters; (a) 1.27-cm pipe, and (b) 2.54-cm pipe

6.4 CONCLUSIONS

The effect of DRP on the flow characteristics of surfactant stabilized water-oil emulsions was investigated experimentally. Oil soluble polymers as well as water soluble polymers were tested as drag reducing agents for stable and unstable water-in-oil (W/O) and oil-in-water (O/W) emulsions. Pressure drop measurements were conducted in 2.54-cm and 1.27-cm horizontal pipes. The influence of DRP type, concentration and molecular weights on emulsion stability, viscosity and pressure drop were reported.

The results showed a significant increase in the emulsion stability with adding the proper DRP (DRP) and this effect was enhanced as DRP molecular weight increased at ambient temperature. In addition, emulsion stability as well as DRP effect on emulsion stability was reduced as temperature increased. Furthermore, DRP showed shear thinning effect and this effect becomes more dominant as DRP molecular weight increased. Injecting the right DRP (DRP which is soluble in emulsion external phase) resulted in a pressure drop reduction for all tested emulsion types (stable concentrated W/O, stable O/W and stable W/O) and this effect increased as DRP concentration increased. However, injecting DRP which is soluble in the internal phase showed a drag reduction effect for unstable emulsion only but with less extent. Moreover, injecting all types of DRP for emulsion flow with the same turbulence intensity (same Re) showed almost no dependency on the pipe diameter.

CHAPTER 7

PRESSURE DROP REDUCTION OF STABLE EMULSIONS BY ORGANO-CLAYS

7.1 INTRODUCTION

Emulsified acids provide significant benefits in stimulating oil and gas wells by slowing the reaction rate with carbonates and reducing corrosion in the tubular goods. The emulsified acid is essentially a mixture of up to 70 % acid emulsified in a 30 % continuous diesel phase. However, pumping emulsified acids can result in high friction losses. Such losses limit the matrix acidizing job efficiency by reducing the penetration depth. Therefore, reducing friction pressure loss is an important factor in extending the application of emulsified acids to deeper targets.

Friction reducing agents, or drag reducing additives, have been used to increase the through put of oil and gas pipelines. Typically a dilute polymer solution is continuously injected into the pipe lines resulting in a drag reduction of up to 70 % (Al-Yaari, et al., 2008; 2009 and 2012). For stimulations, water based gels or oil based gels are used not only to increase viscosity for fracture width creation, leak-off prevention, proppant suspension, and diversion, but also are used because of their friction reduction capability. The macro-structure of the polymers dampens the development of turbulence at high pumping rate such that the friction loss is reduced and Reynolds stresses at the wall goes to zero or close to zero.

It is known that the addition of drag reducing polymers (DRP); such as polyethylene oxide (PEO), or others, reduces eddies viscosity; hence reduces turbulence, at high water flowrate (typical to those used in firefighting). Addition of less than 0.5 % of PEO to water under turbulent conditions could result in a significant reduction in friction factor. In addition, the use of DRPs is a well-known practice in oil transportation.

New nanomaterials showed high performance in polymer nano-composites due to their high aspect ratio and the high surface area of the dispersed nano-sized particles. Various nanomaterials are currently being developed; however, layered silicate clay minerals are the most popular due to their availability (natural source), low cost and more importantly environmentally friendly . Of particular interest, organically modified layered silicate showed significant enhancement of a large number of physical properties (Sinha Ray, et al. (2005a), and Sinha-Ray and Bousmina (2005b)). The main reason for these improved properties in polymer/layered silicate nano-composites is the high surface area of the organically modified layered silicate particles as opposed to conventional fillers (Chen et al. (2002)). Layered silicates generally have layer thickness in the order of 1 nm and very high aspect ratios (length over thickness) in the range 10–1000.

Most of the polymer literature has focused mainly on improvement in mechanical properties of nano-composites. However, in polymer literature, known instabilities associated with polymer flow such as sharkskin and melt fracture (Boger (1987), White et al. (1987), Binding and Walters (1988) and Binding (1991)) have been significantly reduced and flow rates have increased by the addition of nano-clays.

The impact of nanomaterials on polymer flow was limited to rheological tests. However, Hatzikiriakos et al. (2005) found that nano-clay additives had a significant effect on the

extrudate appearance of polyethylene. It eliminated surface instabilities and postponed the critical shear rate for the onset of gross melt fracture to significantly higher values depending on resin type, temperature, and additive concentration (typically 0.05 to 0.5 wt %). The authors observed that the presence of nano-clays suppressed the development of extensional stresses to such high levels that can cause a shift in melt fracture phenomenon. Also, it was reported that the combination of nano-clays with traditional processing aids such as fluoro-polymers produce an enhanced processing aid that can increase the critical shear rates for the onset of melt fracture to levels much higher than the individual constituents when they are used independently.

Adesina and Hussein (2012) studied the effect of organoclay on high density polyethylene (HDPE) rheology and extrusion. It was reported that the addition of ≤ 0.1 wt % of clay resulted in reduction in extensional strain and stress growth of HDPE. Also, the addition of such small amount of organoclay eliminated the gross melt fracture in HDPE and reduced the extrusion pressure; hence more throughputs were reported. Therefore, they concluded that the addition of platy-like organoclay can result in melt flow streamlining. They reported that the transient stress overshoot, normal stress difference, zero shear viscosity, onset of shear thinning, and extrusion pressure of polyethylene was reduced by the addition of only 0.05 wt % of the organoclay and such reduction was for both shear and extensional flows.

Research and experimentation into the application of nano-additives for emulsified acid system may result in a cost-effective solution for reduction of surface treating pressures. Potential applications extend from stimulation treatments to downhole or surface chemical injection wherever emulsified oil-water solutions can exist. For example, in

downhole electric submersible pumps or gas lifted well applications the additional fluid flow friction from emulsion causes excessive back pressure to the system. It is known that the addition of a long molecule reduces single phase turbulence in the flow of a small molecule. Therefore, the use of organoclays is expected to behave like the classical DRPs.

This chapter aims at exploring the possibility of using organoclays, for the first time, as drag reducing agents. Here, we look for reduction of pressure drop in stable W/O emulsions using different pipe diameters. The influence of organoclay type and concentration on emulsion viscosity and frictional losses was investigated.

7.2 EXPERIMENTAL SETUP & PROCEDURE

All tested surfactant stabilized W/O and O/W emulsions were prepared using brine (with 20 kppm NaCl) as the aqueous phase and a type of kerosene, known as SAFRA D60 produced in Saudi Arabia, as the oil phase. Some physical properties of the oil are presented in Table 3.1. ARMAC T, from Akzo Nobel, was used as the emulsifying agent and some of its physical properties are presented in Table 4.1. In addition, Cloisite 15A (OC1) and Cloisite 30B (OC2) were used as surface active organoclays and their physical properties are given in Table 7.1 and Table 7.2, respectively. A schematic layout of the flow loop is shown in Figure 3.2 and its description is explained in details in chapter 3.

The flowmeters, differential pressure transmitters and rheometer information and accuracies are presented in Table 7.3. All uncertainties were calculated within the 95 % confidence level using method described by Dieck (2007). Summarized uncertainty

values in Table 7.3 are representing the combined uncertainties of random and systematic uncertainties.

Table 7.1 Physical properties of Cloisite 15A (OC1)

Product name	Ditallowdimethylammonium Salts with Bentonite
Supplier	Southern Clay Products, Inc.
Description	Cream powder
Specific Gravity	1.6 – 1.8
Solubility	Oil soluble

Table 7.2 Physical properties of Cloisite 30B (OC2)

Product name	Alkyl Quaternary Ammonium Salts with Bentonite
Supplier	Southern Clay Products, Inc.
Description	Cream powder
Specific Gravity	1.9 – 2.1
Solubility	Oil soluble

Table 7.3 Some instruments information and accuracies

Parameter	Test Section	Instrument	Supplier	Range	Uncertainty
Flowrate	1.27-cm pipe	Magnetic Flowmeter	OMEGA	0 - 50 gal/min	0.001%
	2.54-cm pipe				0.584%
Pressure Drop	1.27-cm pipe	Smart Rosemount Pressure Transmitter	Emerson	0 - 1.8 PSI	0.391%
	2.54-cm pipe			0 - 0.8 PSI	0.732%
Viscosity	N/A	Rheometer	Rheologica	3.0×10^{-8} - 0.2 N·m	0.099%

36 liters of surfactant stabilized W/O emulsions with 70/30 water to oil volume ratio were prepared by adding the internal phase (in this case water) to the emulsified external phase (here oil with 0.6 volume % emulsifier) at a rate of 1 L/min while mixing at 8000 RPM (for 30 minutes) by using high power homogenizer (Ultra Turrax T 50 basic, WERKE IKA, Germany). Emulsion type was tested by stability drop test where emulsion droplets were injected in a pure phase. If emulsion droplets disperse, the emulsion external phase is the same as the used phase for the test and such results were confirmed by conductivity measurements. Emulsions were then transferred to one of the flowloop tanks. The same procedure was followed for stable W/O with 0.3 dispersed phase (water) volume fraction.

All rheological measurements were conducted using Rheologica Stress Tech rheometer. Pressure drop measurements of the prepared emulsion were performed first in both 1.27-cm pipe and 2.54-cm pipe test sections. Then, organo-clays were added to the prepared emulsion in one of the flowloop tanks to produce a specific concentration. After that, emulsion with nano-additives was remixed to get a homogeneous distribution of the nano-additives within the emulsion system. Finally, pressure drop measurements of the emulsion with organo-clays were conducted in both test sections.

Pressure drop for all emulsions was measured at different flow rates in both test sections. All measurements were conducted at steady state conditions. Emulsion temperature was maintained at 25 °C. Based on the pipe flow shear rate (equation (1)), emulsion viscosity (η) was extracted from rheological measurements and used to calculate Reynolds number (Re) for emulsion. The term in brackets in equation (1) is the Robinowitsch correction for

non-Newtonian fluids. In addition, emulsion friction factor (f) was calculated using equation (2) and the pressure drop reduction (PDR) was defined by equation (3).

$$\dot{\gamma}_w = \frac{4Q}{\pi R^3} \left[\frac{3}{4} + \frac{1}{4} \frac{d(\ln Q)}{d(\ln \tau_w)} \right] \quad (1)$$

where $\dot{\gamma}_w$ = True wall shear rate (s^{-1})

Q = Volumetric flowrate (m^3/s)

R = Pipe radius (m)

τ_w = Wall shear stress (Pa); $\eta = \tau_w / \dot{\gamma}_w$

$$f = \frac{\frac{\Delta P}{\Delta L} \times 2D}{\rho u^2} \quad (2)$$

where f = Darcy friction factor

$\frac{\Delta P}{\Delta L}$ = Pressure gradient (Pa/m)

D = Pipe diameter (m)

ρ = Emulsion density (kg/m^3)

u = Emulsion average velocity (m/s)

$$PDR \% = \frac{\Delta P_{\text{without additives}} - \Delta P_{\text{with additives}}}{\Delta P_{\text{without additives}}} \quad (3)$$

where

$\Delta P_{\text{without additives}}$ = Emulsion pressure drop before the addition of organo-clays

$\Delta P_{\text{with additives}}$ = Emulsion pressure drop after the addition of organo-clays

7.3 RESULTS AND DISCUSSIONS

Emulsion Rheology

Effect of nano-additives (organoclays) on W/O emulsion viscosity was studied using a Bob and Cup viscometer. OC1 and OC2 with different concentrations (50, 200 and 400 wppm) were added to the emulsion containing 70 volume % water. This test was performed to determine the optimum loading that can produce a pressure drop reduction in the flowloop experiments and results are given in Figures 7.1 and 7.2.

As shown in these figures, adding 0.005 wt % of all nano-additives showed no effect on emulsion viscosity (see Figures 7.1 and 7.2 (b)). However, as the loading increased, emulsion viscosity decreased for all nano-additives as illustrated in Figures 7.1 and 7.2 (c and d). To explain these observations, we should recall that all used nano-additives (organoclays) are soluble in both phases. Therefore, they behave like surfactants. As a result, they may reduce the interfacial tension more to end up with smaller droplets (see next section) and hence lower viscosity. Also, they may reduce transverse flow (Hatzikiriakos, et al. (2005), Arumugam, et al. (2011), Adesina and Hussein (2012), and Adesina, et al. (2012)). Based on these results, 400 wppm concentration was the minimum loading to be tested for the flowloop emulsion flow. In addition, although OC1

and OC2 showed almost the same performance in terms of emulsion viscosity reduction, OC1 showed better dispersion in oil and thus it was recommended for the flowloop tests.

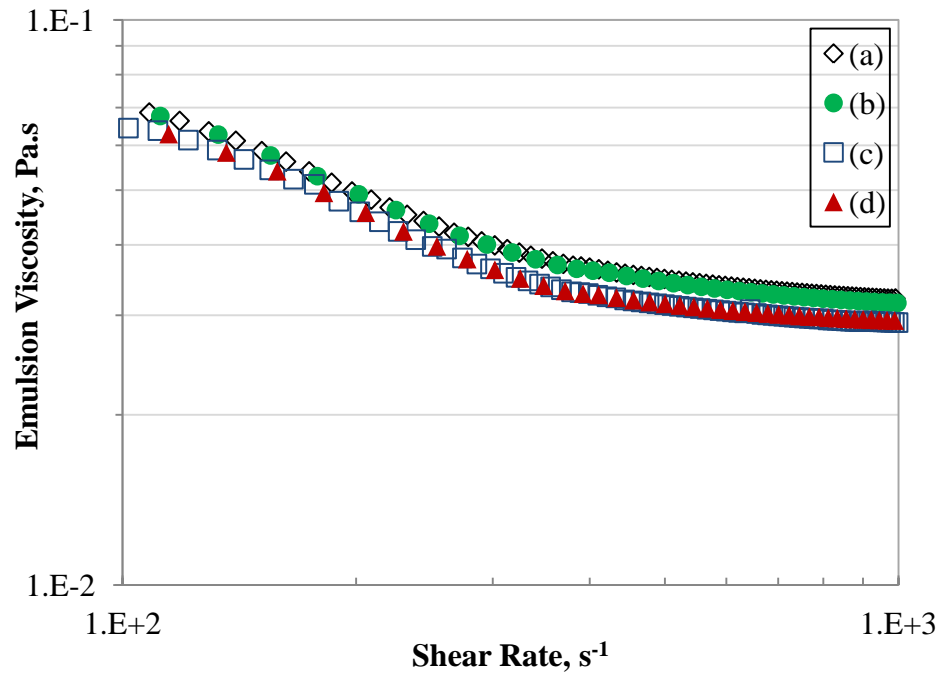


Figure 7.1 Viscosity curve of stable W/O emulsion at 25 °C with Cloisite 15A (OC1) at different loadings; (a) 0, (b) 50 wppm, (c) 200 wppm and (d) 400 wppm

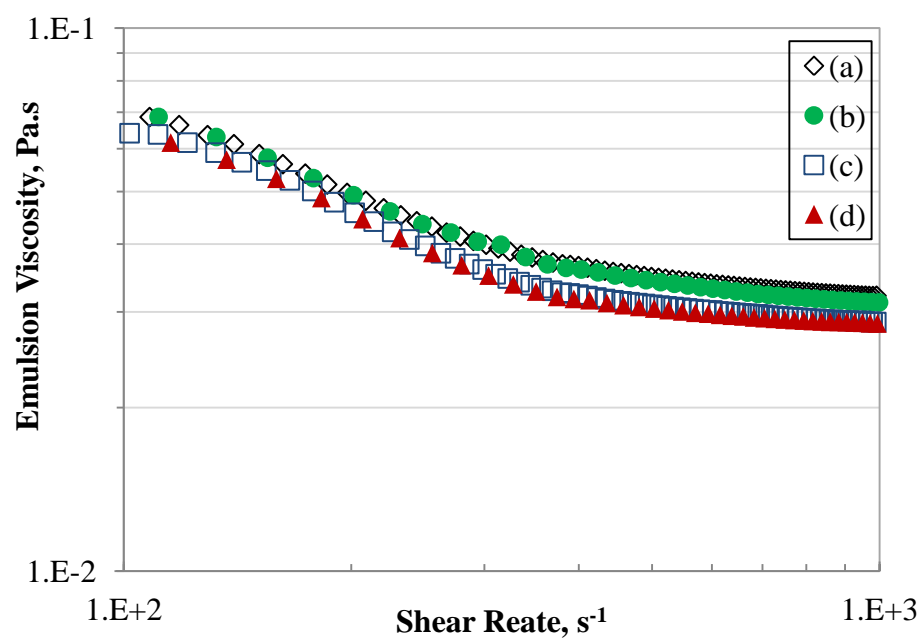


Figure 7.2 Viscosity curve of stable W/O emulsion at 25°C with Cloisite 30B (OC2) at different loadings; (a) 0, (b) 50 wppm, (c) 200 wppm and (d) 400 wppm

Pressure Drop Measurements

Stable O/W emulsion with 0.7 water volume fraction

Pressure drop measurements of surfactant-stabilized W/O emulsion were conducted in the two flowloop test sections. The internal phase (water) constitutes 70 % of the emulsion volume. For each flow rate, true shear rate was calculated by equation (1) and then the corresponding apparent viscosity was used to calculate Re . However, Darcy friction factor was calculated using equation (2).

Since oil is the external phase of the produced W/O emulsions, 0.04 wt % of OC1 (organoclay Cloisite 15A) was added to the emulsion and mixed outside the flowloop tank. Then, the nanofluid sample was mixed with the emulsion in the flowloop tank. Pressure drop in both test sections was measured for the concentrated emulsion flow at 25 °C. The relationship between Re and the true shear rate for the emulsion flow in both test sections before and after the addition of 400 wppm of OC1 is illustrated in Figures 7.3 and 7.4, respectively. As shown in these figures, at the same shear rate, Re number in the 2.54-cm pipe test section is almost 4 times that for the flow in the 1.27-cm pipe test section. In other words, at the same Re number, the shear rate in the 1.27-cm pipe test section is about 4 times that in the 2.54-cm pipe test section. Pressure drop measurements of this concentrated W/O emulsion before and after the addition of 400 wppm of OC1 in the flowloop are illustrated in Figures 7.5 and 7.6. Due to emulsion viscosity, pump power and flowloop design, the maximum Re reached was about 1800 and 2000 for the flow in the 1.27-cm and 2.54-cm pipes, respectively.

In addition, as presented in these figures, introducing 400 wppm of OC1 resulted in a reduction of 25 % in emulsion friction factor. Most likely, organoclay has worked as a surfactant where the organoclay part is expected to be in the oil phase and the clay part in water. Thus, the organoclay emulsifier has the capability to reduce the interfacial tension; and hence reduces the average droplet size as shown in Figure 7.7. As a result, emulsion friction factor was reduced due to the addition of only 400 wppm of OC1 and a better performance is believed to be achieved when an optimum concentration is used.

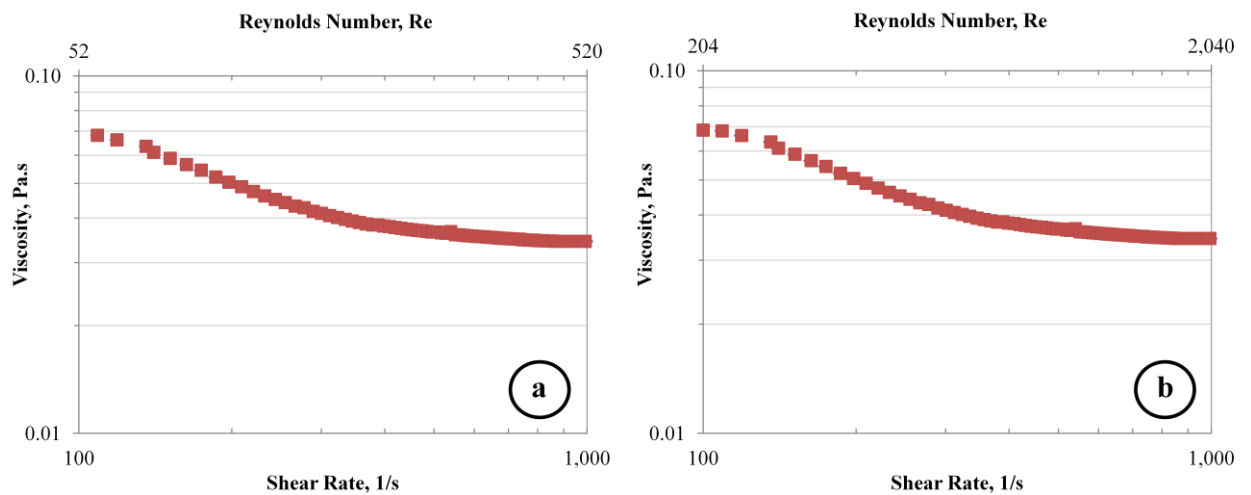


Figure 7.3 Viscosity curve of concentrated W/O emulsion without organo-clays and the corresponding Re at both test sections: (a) 1.27-cm pipe and (b) 2.54-cm pipe

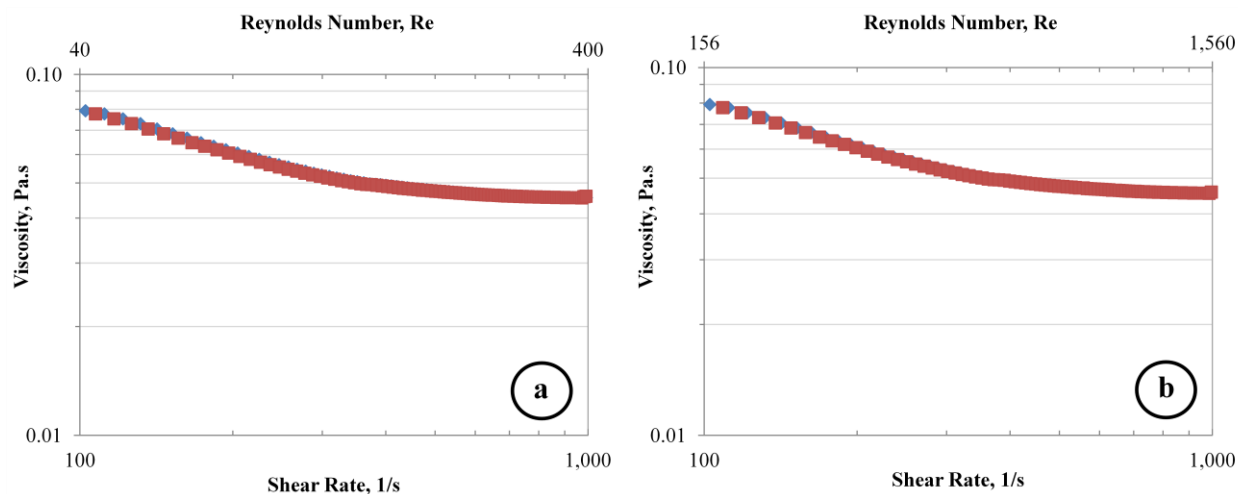


Figure 7.4 Viscosity curve of concentrated W/O emulsion with 400 ppm of Cloisite 15A and the corresponding Re at both test sections: (a) 1.27-cm pipe and (b) 2.54-cm pipe

Furthermore, stable W/O emulsions showed a decrease in the emulsion friction factor (f) with decreasing pipe diameter (see Figure 7.8). As shown earlier in Figures 7.3 and 7.4, at the same Re number, the true shear rate in the 1.27-cm pipe is almost four times that in the 2.54-cm; as a result the emulsion dispersed phase droplets are smaller in the smaller diameter pipe as proved by microscopic images shown in Figure 7.9.

Although our results are limited to laminar flow regime (as per the criterion for single phase), it is believed that at high Re organoclay may orient in the direction of flow leading to more reduction in fluid friction. In multiphase flow, the organoclay is expected to work as a surfactant to reduce emulsion droplet size. In addition, the platy-like surface of the clay part will help in reducing drag at high Re.

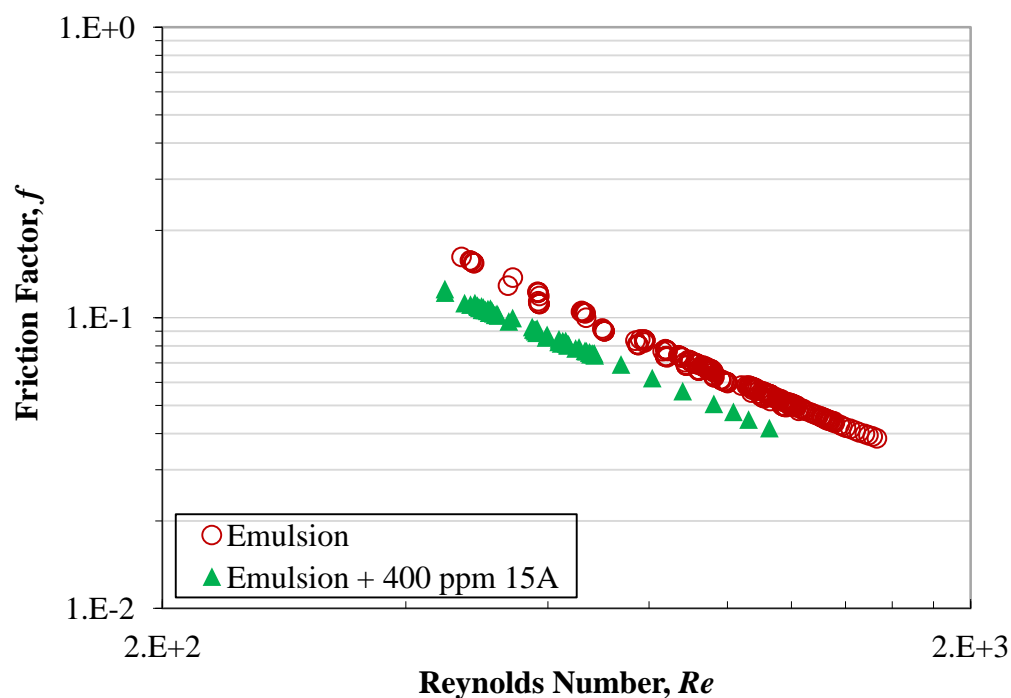


Figure 7.5 Effect of OC1 (Cloisite 15A) on the W/O emulsion friction factor while flowing in the 1.27-cm pipe test section

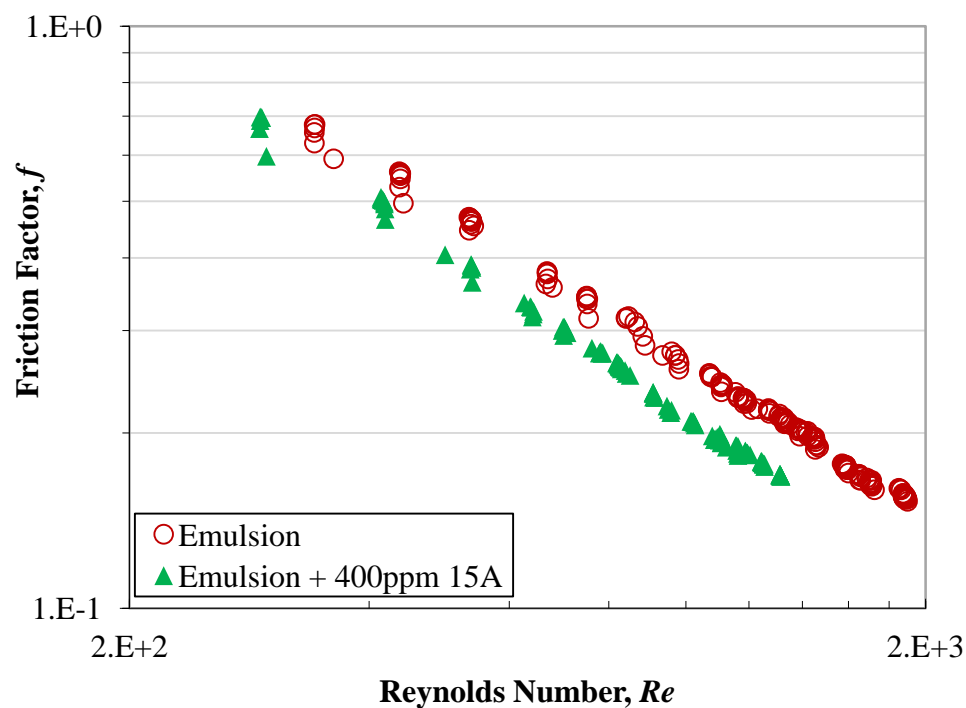


Figure 7.6 Effect of OC1 (Cloisite 15A) on the W/O emulsion friction factor while flowing in the 2.54-cm pipe test section

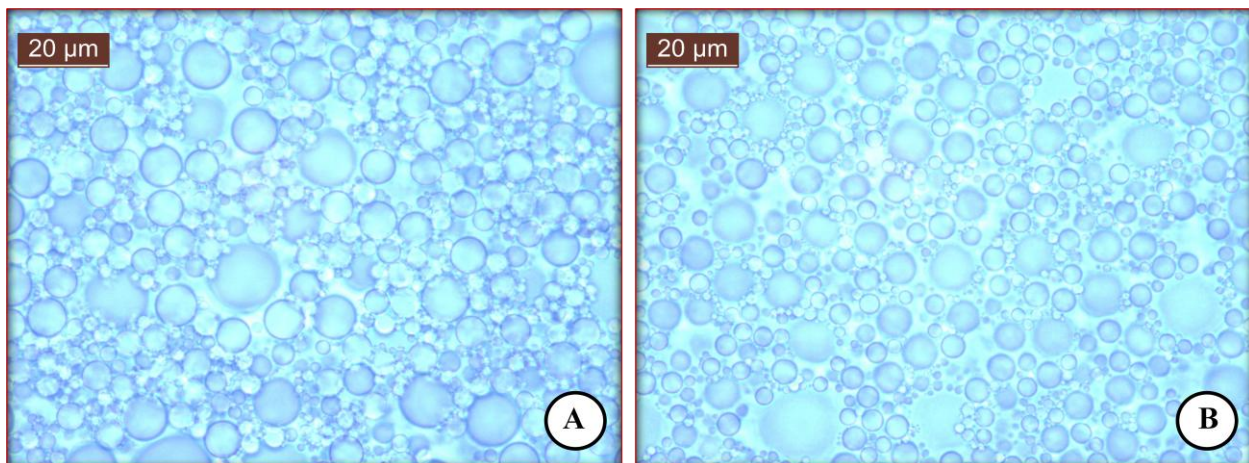


Figure 7.7 Droplet size distribution of W/O emulsion with 0.7 water volume fraction; (A): without organoclays and (B): with 400 wppm Cloisite 15A

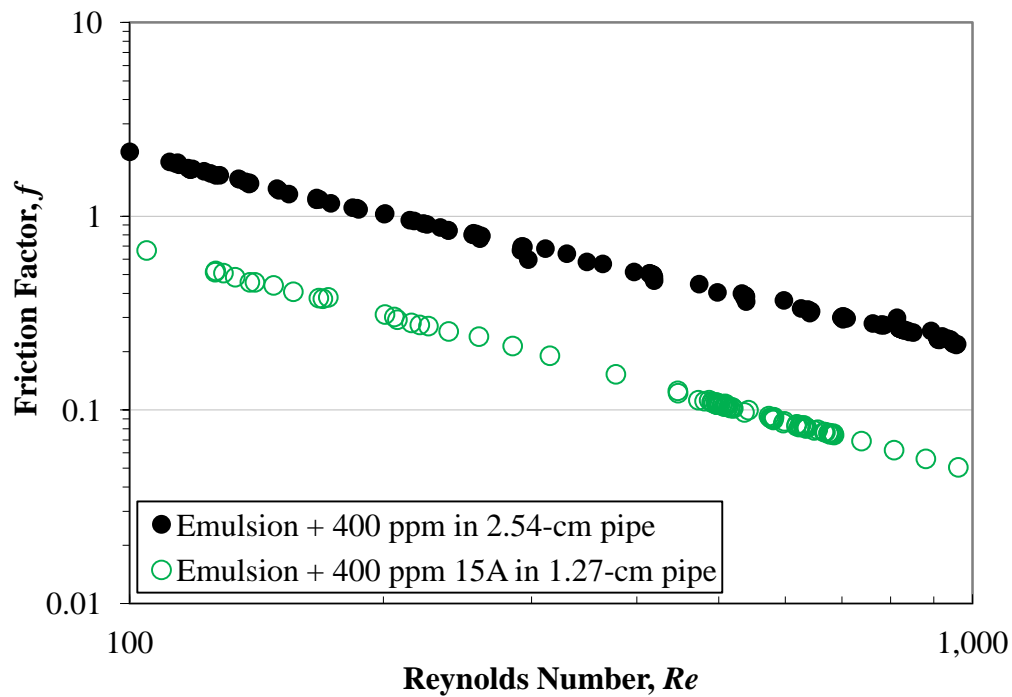


Figure 7.8 Effect of pipe diameter on the W/O emulsion friction factor

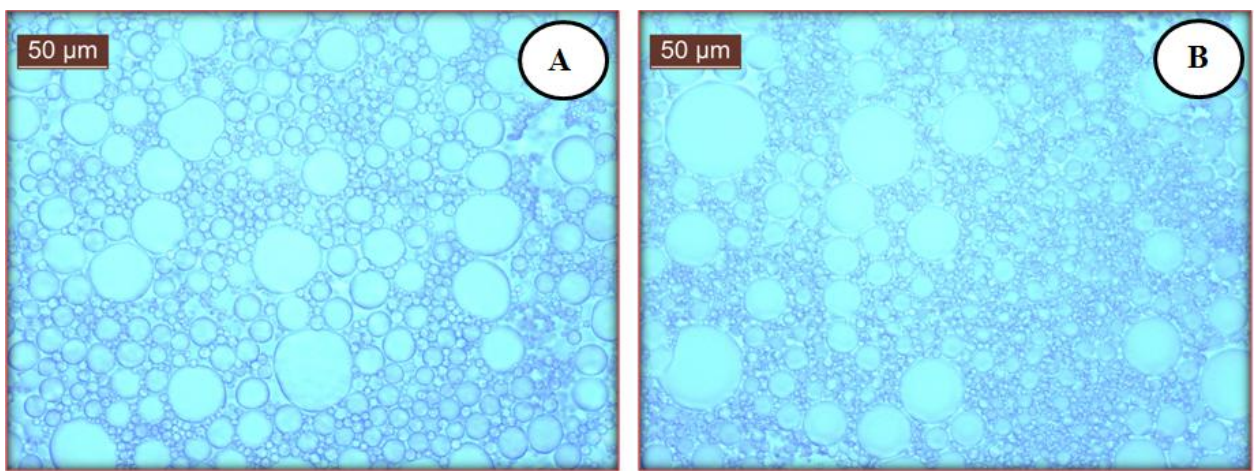


Figure 7.9 Droplet size distribution of W/O emulsion with 0.7 water volume fraction while flowing at the same Re number ($Re = 1000$) at different pipe diameters; (A) flow in 2.54-cm pipe and (B) flow in 1.27-cm pipe

Stable W/O emulsion with 0.3 water volume fraction

W/O emulsion with 0.3 volume fraction of water (brine with 20 kppm NaCl) was prepared following the same procedure mentioned earlier. OC1 performance, as a pressure drop reducing agent for this multiphase system, at different concentrations (400, 600, 800 and 1000 wppm) was measured. The required mass of OC1 was mixed with the prepared emulsion which is available in one of the flowloop tanks.

Emulsion pressure drop measurements, before and after the addition of OC1, in both pipe test sections are illustrated in Figures 7.10-7.13. As shown in Figures 7.10 and 7.11, slight reduction in the emulsion pressure drop was observed after the addition of 400 and 600 wppm of OC1 and such reduction became clearer as OC1 concentration increased. At low concentrations, the effect of the nano-additives was so small and difficult to detect. However, at high concentrations such molecules might work as emulsifiers leading to a decrease in the droplet size and the pressure drop.

In addition, as shown in Figures 7.11 and 7.13, it is interesting to observe that the measured friction factors of stable emulsions, in laminar region, with and without organoclays are in a good agreement with the single phase theoretical friction factor calculated from Hagen-Poiseuille equation (equation (4)). However, in turbulent region, the emulsion friction factors, with and without nano-additives, fell below the single phase theoretical values calculated from Blasius equation (equation (5)). For unstable emulsions (oil/water mixtures without surfactant), different mechanisms were proposed. Omer and Pal (2010) claimed that the size of the droplets were bigger than the length scale of

turbulence. Furthermore, it was attributed to the turbulent viscosity reduction due to the stretching and elongation of droplets (Pal (2007)) or due to the dispersed phase droplets effect on the turbulence characteristics of the single external phase when droplets are introduced (Pal (1993)). However, for stable emulsion, in some literatures Re numbers were calculated based on the laminar flow viscosity using equation (4) and thus it was reported that emulsion friction factor (in laminar and turbulent regions) could be predicted reasonably well by the usual single phase equation (Pal (1993), and Omer and Pal (2010)). It is believed that such approach was not correct since viscosity is changing with flow rate (shear rate or Re) rather than constant.

$$f = \frac{64}{Re} \quad (4)$$

$$f = \frac{0.316}{Re^{0.25}} \quad (5)$$

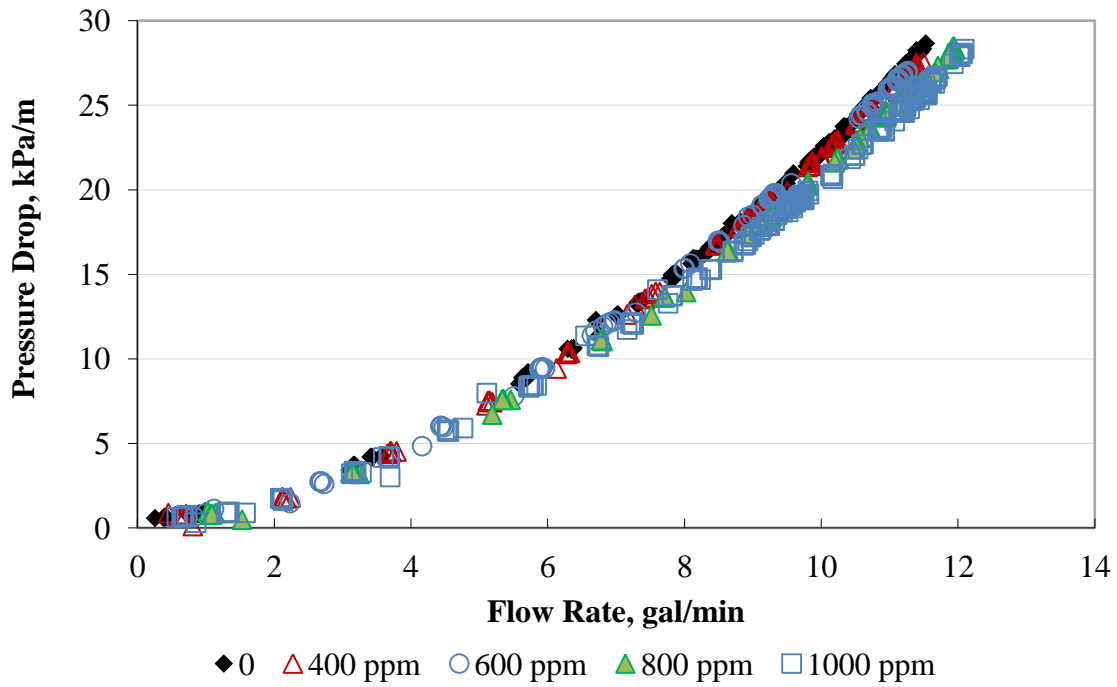


Figure 7.10 Pressure drop measurements of stable W/O emulsion (with 0.3 water volume fraction) in the 1.27-cm pipe test section at different OC1 loadings

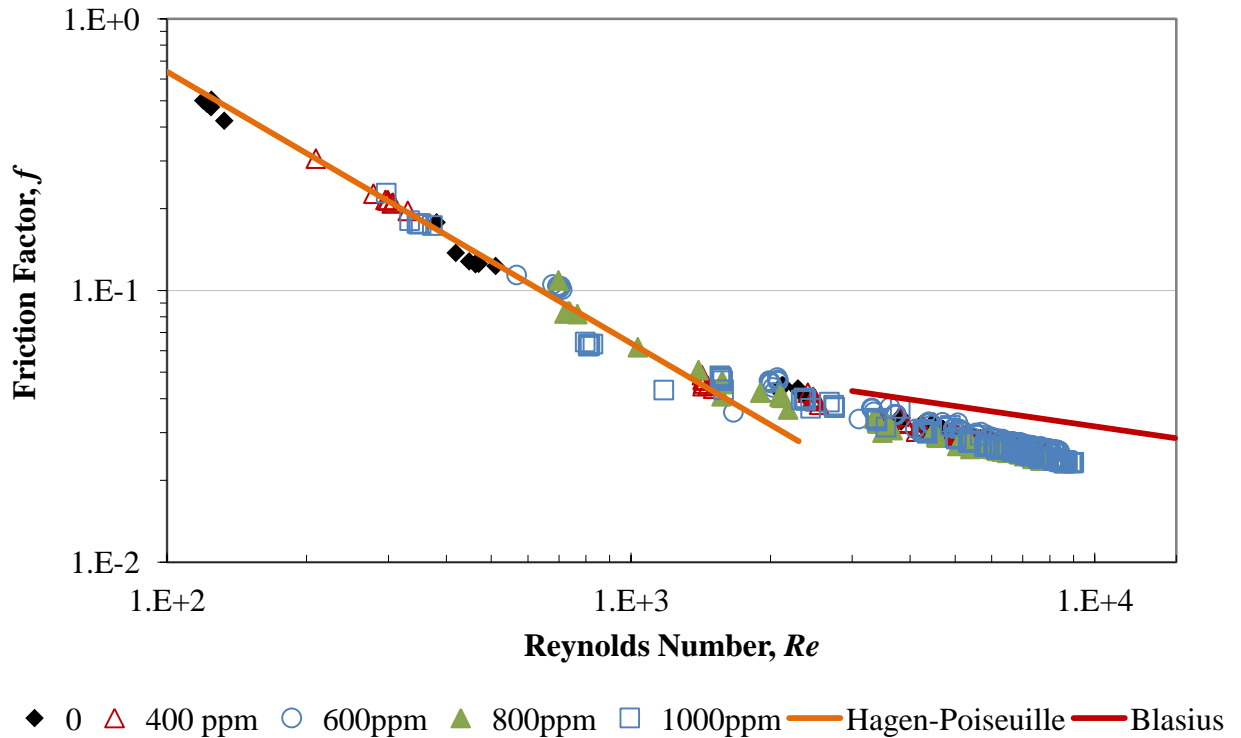


Figure 7.11 Stable W/O emulsion (with 0.3 water volume fraction) friction factor in the 1.27-cm pipe test section at different OC1 loadings

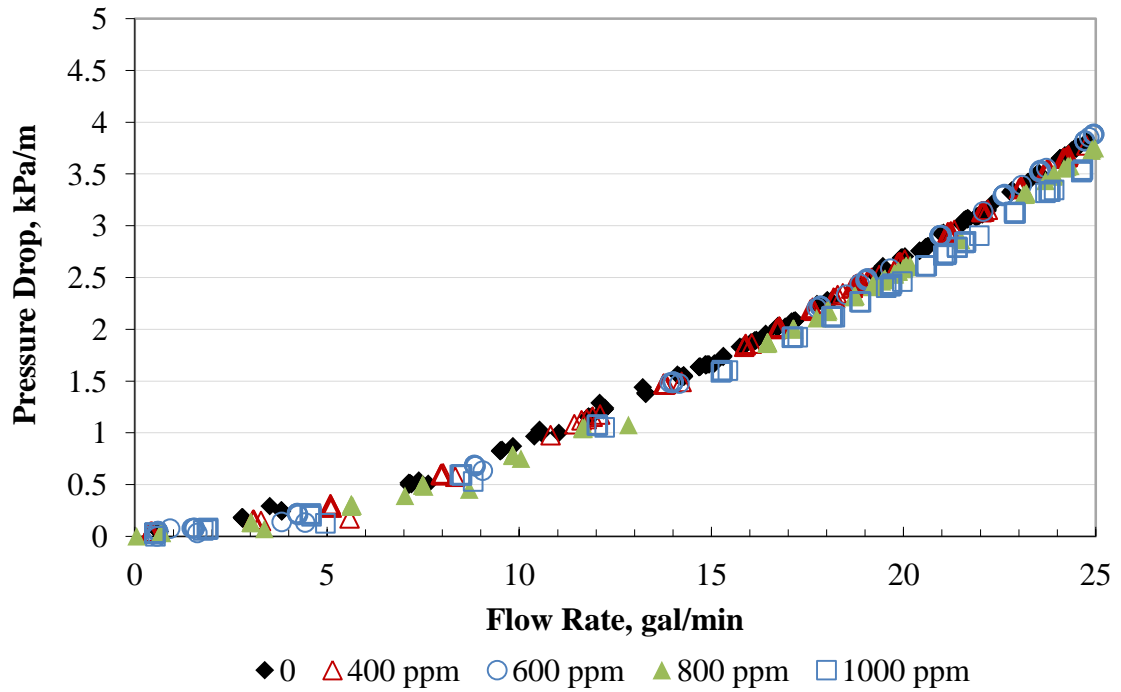


Figure 7.12 Pressure drop measurements of stable W/O emulsion (with 0.3 water volume fraction) in the 2.54-cm pipe test section at different OC1 loadings

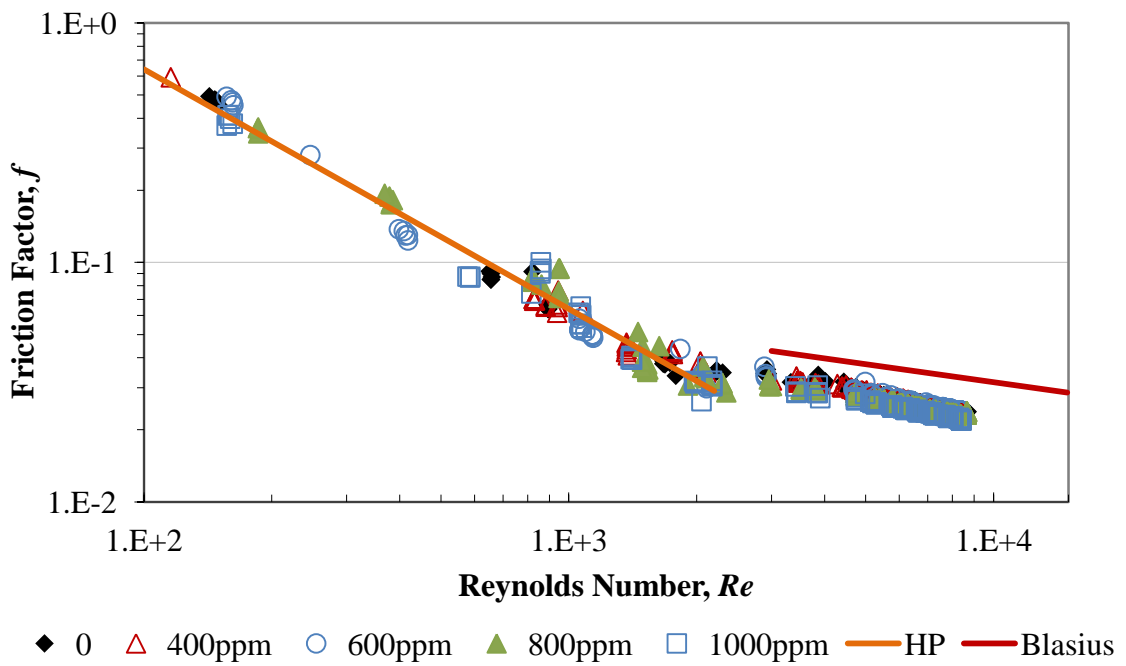


Figure 7.13 Stable W/O emulsion (with 0.3 water volume fraction) friction factor in the 2.54-cm pipe test section at different OC1 loadings

7.4 CONCLUSIONS

The potential application of nanomaterials for friction reduction and particularly in emulsified acid solutions has a potential in extending the capabilities of stimulation treatment applications. This chapter aimed mainly to investigate a possible pressure drop reduction of stable water-in-oil (W/O) emulsion using nano-additives. The influence of nano-additives type and concentration on emulsion viscosity was reported. Organoclays were tested as pressure drop reducing agents for stable W/O emulsions with 0.7 and 0.3 water volume fractions. Pressure drop measurements were conducted in 2.54-cm and 1.27-cm horizontal pipes.

The results showed a significant reduction in the emulsion viscosity with adding all the tested nano-additives and this effect was enhanced as the nano-additives concentration was increased. In addition, for the case of concentrated W/O emulsions, the addition of organoclays resulted in a reduction of ~ 25 % in the emulsion pressure drop. Also, for the stable W/O emulsion with only 0.3 water volume fraction, although no pressure drop reduction was observed in the laminar region, it was detected in the turbulent region and such effect became pronounced at high Re number and organoclay concentration. Such results were explained in terms of emulsion dispersed phase droplet size.

In addition, for stable W/O emulsions with 0.3 volume water fraction, all laminar friction factor data (with and without nano-additives) was in a good agreement with single phase predictions. However, the measured emulsion friction factors fell below the single phase predictions in the turbulent regime. Finally, organo-clays proved to work as drag

reducing agents. However, further research is needed to explain such observation in detail and highlight the mechanisms of drag reduction in multiphase flow.

CHAPTER 8

EFFECT OF DRAG REDUCING POLYMERS ON WATER HOLDUP IN AN OIL-WATER HORIZONTAL FLOW

8.1 INTRODUCTION

Since the fascinating discovery of Toms (1948) of drag reduction by polymers, extensive research works have been done on the influence of high molecular weight polymers on the frictional drag in single phase liquid flows. The effect of such drag-reducing additives on gas–liquid flow has received more attention than liquid-liquid flow. A summary of work in this area is presented in a literature review by Al-Sarkhi (2010).

Al-Sarkhi and Hanratty (2001 and 2002) showed that the injection of solution of DRP into a horizontal flow of air and water causes a change from an annular flow to a stratified flow by destroying the disturbance waves on the liquid film. Drag reductions of up to 48 % were realized for a 9.53-cm pipe and up to 63 % for a 2.54-cm pipe. Recent studies on gas-liquid flows (Al-Sarkhi et al. (2006), Al-Sarkhi and Soleimani (2004), Soleimani et al. (2002), Fernandes, et al. (2004), Baik and Hanratty (2003)) have revealed how the flow patterns and pressure drop of air-water flows differ after adding water soluble drag-reducing polymers to the flow.

Recent studies from this laboratory (Al-Yaari et al. (2009)) showed that the injection of water soluble polymer solution into oil-water flows in a 2.54-cm horizontal pipe in

some cases produced drag reduction of about 65 % with concentration of only 10–15 wppm (weight basis). The results showed a significant reduction in frictional pressure loss due to DRP especially at high mixture velocity which was accompanied by a clear change in the flow pattern. Phase inversion point, indicated by its pressure drop peak, in the dispersed flow regime disappeared by injecting only 5 wppm of the used drag reducing polymer (DRP). Effect of DRP concentration and molecular weight on flow patterns and pressure drops were also presented in this study.

Al-Wahaibi et al. (2007) studied the effect of DRP on oil–water flow in a relatively small 1.4-cm diameter horizontal pipe. Oil (5.5 mPa s, 828 kg/m³) and a co-polymer (Magnafloc 1011) of polyacrylamide and sodium acrylate were used. The results showed a strong effect of DRP on flow patterns. The presence of DRP extended the region of stratified flow and delayed transition to slug flow. The addition of the polymer clearly damped interfacial waves. The DRP caused a decrease in pressure gradient and a maximum drag reduction of about 50 % was found when the polymer was introduced into an annular flow.

Sifferman and Greenkorn (1981) studied drag reduction of three types of polymers (carboxymethyl cellulose, polyethylene oxide, and guar gum) in three different fluid flow systems: single-phase dilute polymer-water solutions, two-phase liquid-solid, and three-phase immiscible liquid-liquid-solid solutions. Drag reduction was observed for all three flow systems studied.

The present chapter focuses on the effect of DRP on the liquid holdup in a horizontal pipe. All experiments were conducted at the same mixture velocity with varying the oil-water volumetric flow rate ratio. Significant difference between the water holdup

before and after the injection of DRP was observed. This variation is linked to the flow pattern changes due to the injection of DRP. In particular, it aims to seek for a possible method facilitating oil-water separation through the use of water soluble drag reducing polymers.

8.2 EXPERIMENTAL SETUP & PROCEDURE

The experiments were conducted in a horizontal Plexiglas pipe that has a diameter of 2.54-cm and a length of 10 m. The schematic of the flowloop is shown in Figure 8.1 and polymer injection system setup and procedure details used in this study is explained in a paper by Al-Yaari et al. (2009). Tap water and oil, with average properties given in Table 3.1, were the test fluids. The specification of the DRP used in this experiment is given in Table 8.1. Each phase is transferred with a pump from the respective storage tank to the test section via variable area flowmeters. The test section consists of a 10 m long acrylic horizontal pipe with 2.54-cm ID. The conductivity probe (for water holdup measurement) was located 8.2 m apart from the mixing point and its calibration is shown in Figure 8.2. The mixture returns via a PVC pipe to a separator tank, which allows the phases to separate and the dispersed drops to coalesce. Within each run the fluids are not recycled. At the end of a run the separated oil returns to its storage tank, while fresh water is used for each run more details can be found in Al-Yaari et al. (2009). Some specifications of the used pressure transducer and flowmeters were tabulated in Table 8.2.

All experiments conducted at same mixture velocity of 1 m/s (the mixture velocity is the summation of the superficial water (U_{sw}) and the superficial oil (U_{so}) velocities at different volumetric flow ratio of water and oil. The test matrix and the flow patterns of the water-oil flow without DRP and after injecting the DRP are shown in Table 8.3 and Figure 8.3.

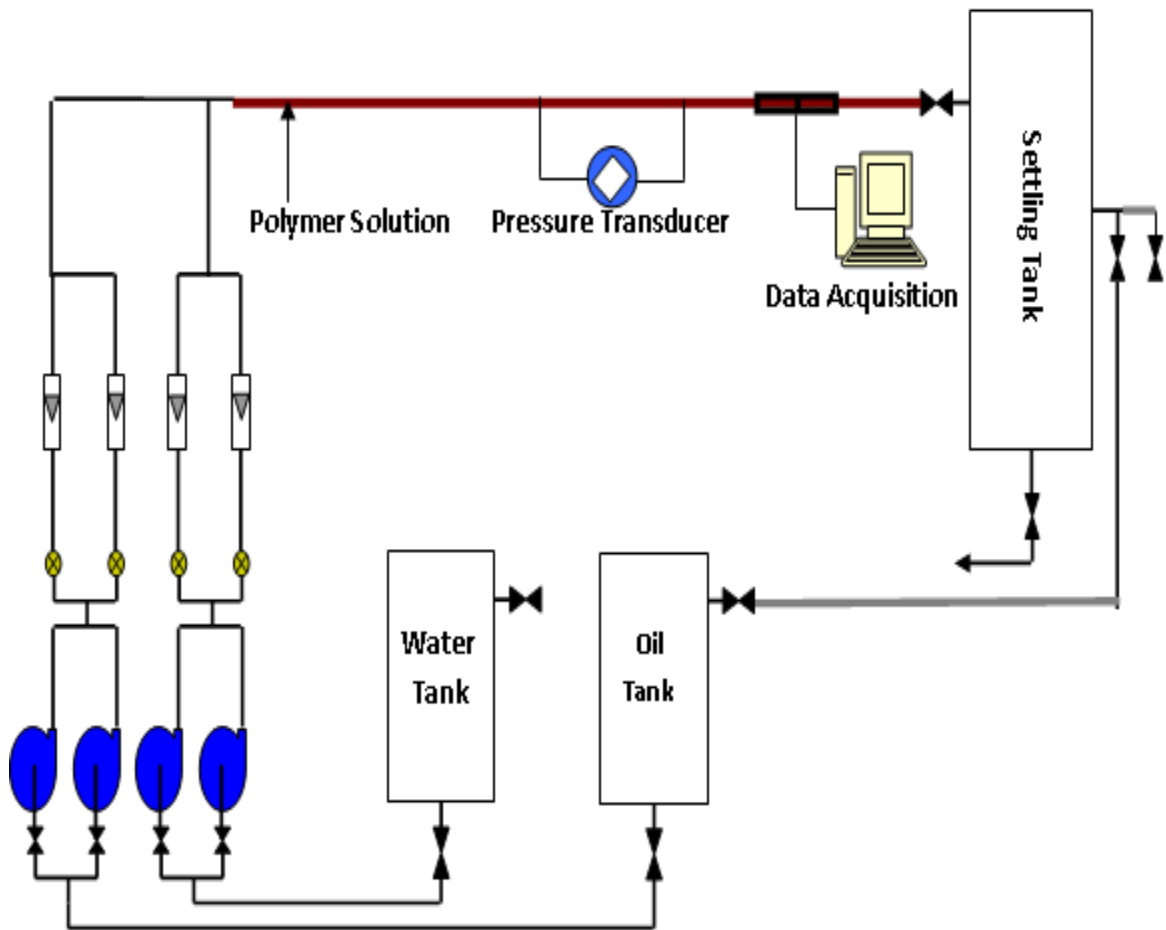


Figure 8.1 Schematic layout of the flow loop

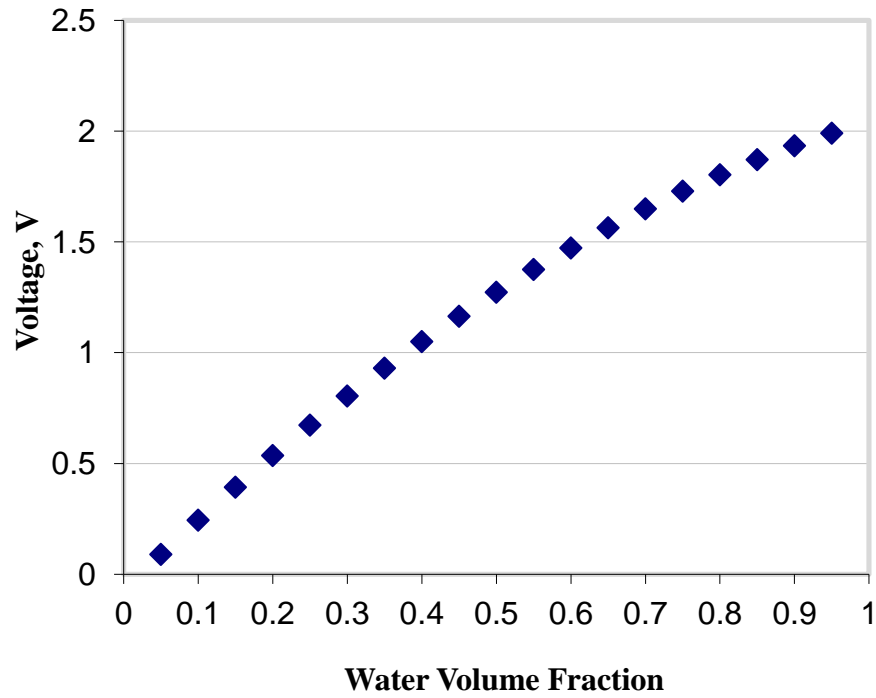


Figure 8.2 Conductivity probe calibration

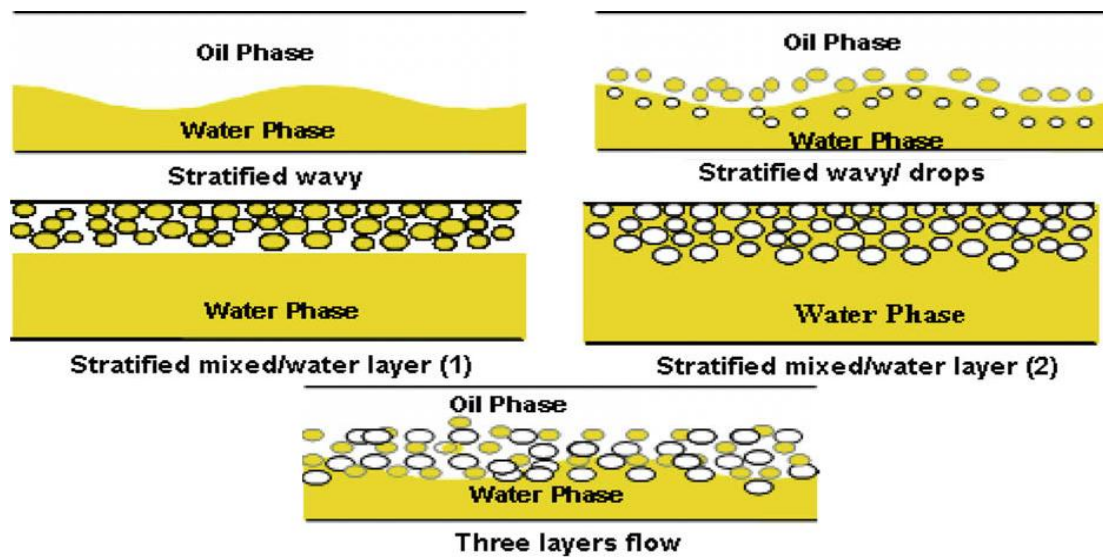


Figure 8.3 Oil-water flow patterns in a horizontal pipe with 2.54-c m ID at mixture velocity of 1 m/s

Table 8.1 Physical properties of drag reducing polymer MAGNAFLOC 1011

Product name	Ciba MAGNAFLOC 1011
Molecular Weight	10^7 g/mol
Description	Anionic polyacrylamide flocculant ; white granular powder
Bulk density	0.7 g/cm^3

Table 8.2 Specifications of the used pressure transducer and flowmeters

Item	Pressure Transducer	Flow Meters
Producer	ROSEMOUNT	KING Instrument Co.
Model	3051S	7510-6A
Full Scale	0 – 0.8 PSI	0-11.4 GPM
Uncertainty	0.0001 PSI	0.2 GPM

Table 8.3 Experimental matrix and flow patterns

U_{SW}, m/s	U_{SO}, m/s	Flow pattern without DRP	Flow pattern with DRP
0.15	0.85	SW	S
0.2	0.8	SW	S
0.25	0.75	SW	SW
0.3	0.7	SW	SW
0.35	0.65	SWD	SW
0.4	0.6	SWD	SW
0.45	0.55	SWD	SW
0.5	0.5	SWD	SW
0.55	0.45	3L	SW
0.6	0.4	3L	SWD
0.65	0.35	3L	SWD
0.7	0.3	3L	SWD
0.75	0.25	SMW	SWD
0.8	0.2	SMW	SWD
0.85	0.15	SMW	SWD
0.9	0.1	SMW	SWD

S: Smooth Stratified flow

SW: Stratified Wavy flow

SWD: Stratified Wavy flow with some droplets in the interface region

SMW: Stratified flow (mixed layer in the upper part of the tube and separated water layer in the bottom part)

3L: Three layers flow. There are clear oil and water layers at the top and bottom of the pipe respectively with a dispersed layer between them.

8.3 RESULTS AND DISCUSSION

Figure 8.4 and Figure 8.5 show the real time water hold up signal with the observed flow patterns before and after the DRP addition. All the 16 cases studied are for one mixture velocity equal to 1 m/s. The volumetric flow rate of water was increased and the volumetric flow rate of oil was decreased to get the total mixture velocity of 1 m/s for all runs. It can be seen from this figure that the fluctuating value over the mean for the case of oil-water with DRP is relatively less than that for the case of oil-water only (without DRP) specially for the cases of low U_{sw} ($U_{sw} < 0.4$ m/s). The water holdup for these cases in the presence of water soluble DRP is always larger than that for oil-water without DRP. For U_{sw} between 0.4 m/s and less or equal 0.5 m/s almost both holdups are the same. This means that there are no differences in the velocity of water for the case with DRP and the corresponding one without DRP. However, for the cases when the U_{sw} is larger than U_{so} ($U_{sw} > 0.5$ m/s), the water holdup of oil-water with DRP is less than that without DRP. Recall that this is a water soluble DRP and for large superficial water velocity the DRP damped the high amplitude waves and the water moved faster than before.

The water holdup is presented as the time average water height measured by the conductivity probe to the pipe diameter hw/D . Understanding this figure should be connected to the flow pattern changes before and after the injection of the DRP presented in Table 8.3.

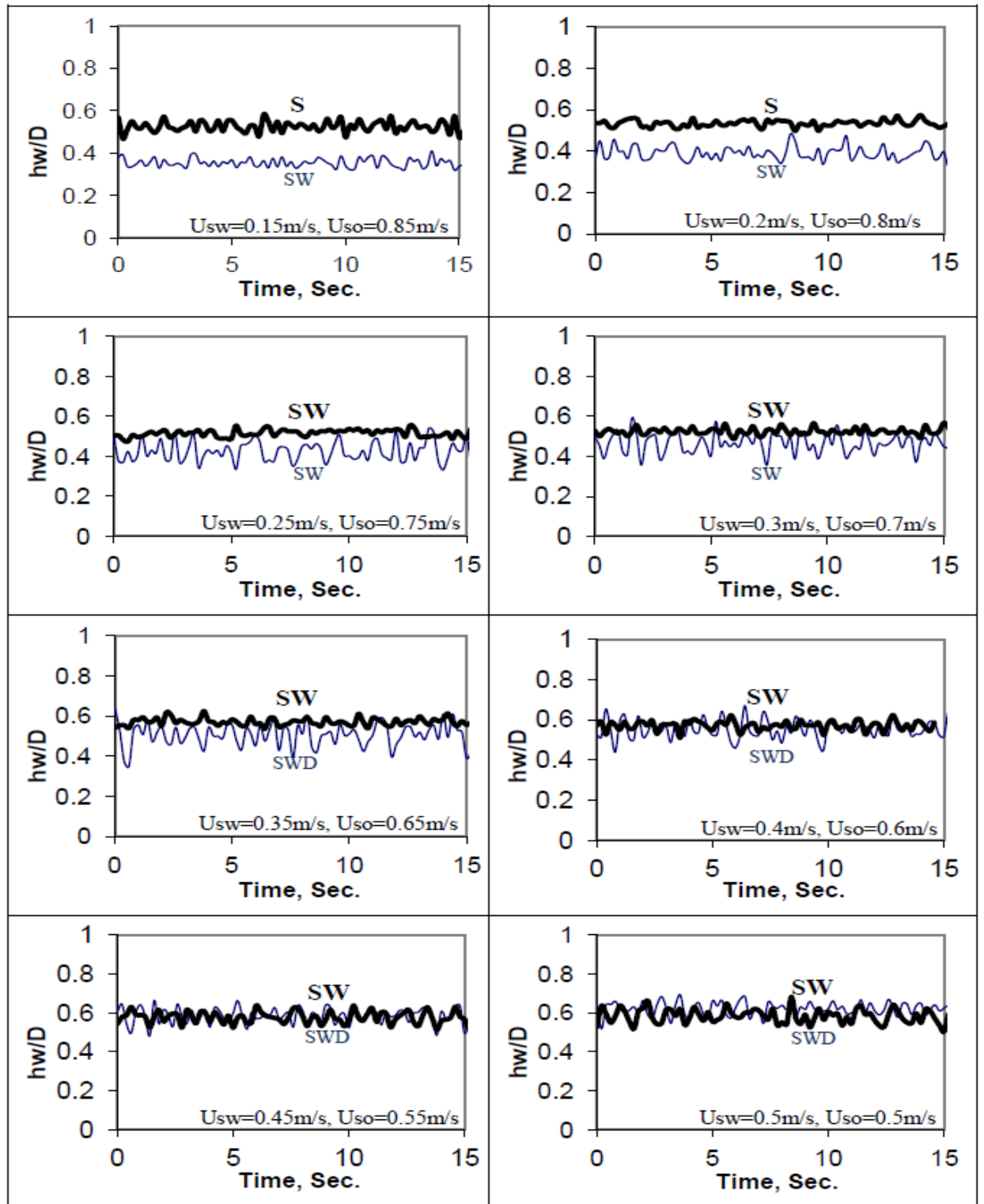


Figure 8.4 Water holdup signal measurement (Thick line: with DRP; thin line without DRP; $U_{sw} \leq U_{so}$)

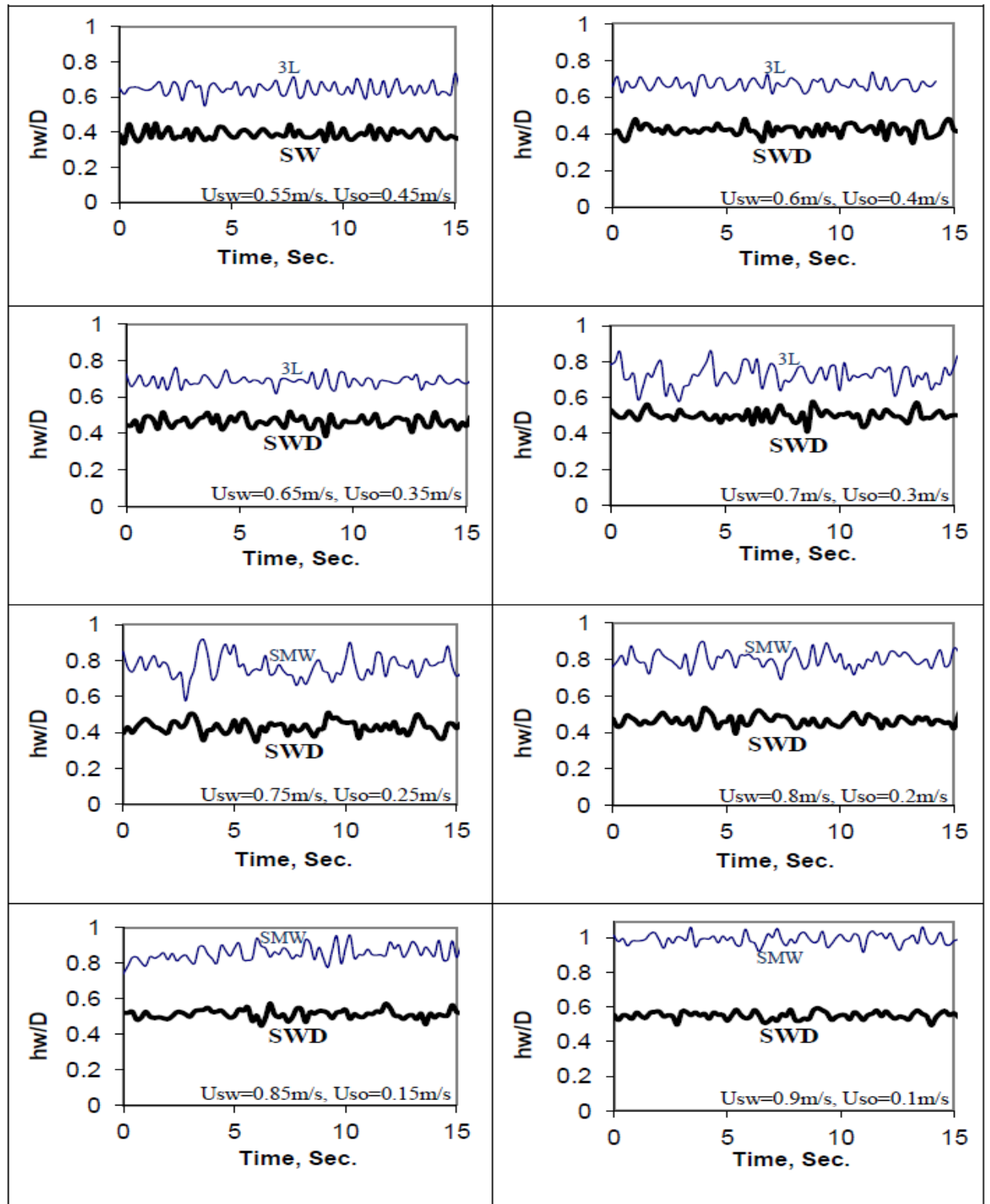


Figure 8.5 Water holdup signal measurement (Thick line: with DRP; thin line without DRP; $U_{sw} > U_{so}$)

Figure 8.6 shows clearly the relation between the water holdup before and after the injection of DRP and the percentage of drag reduction achieved.

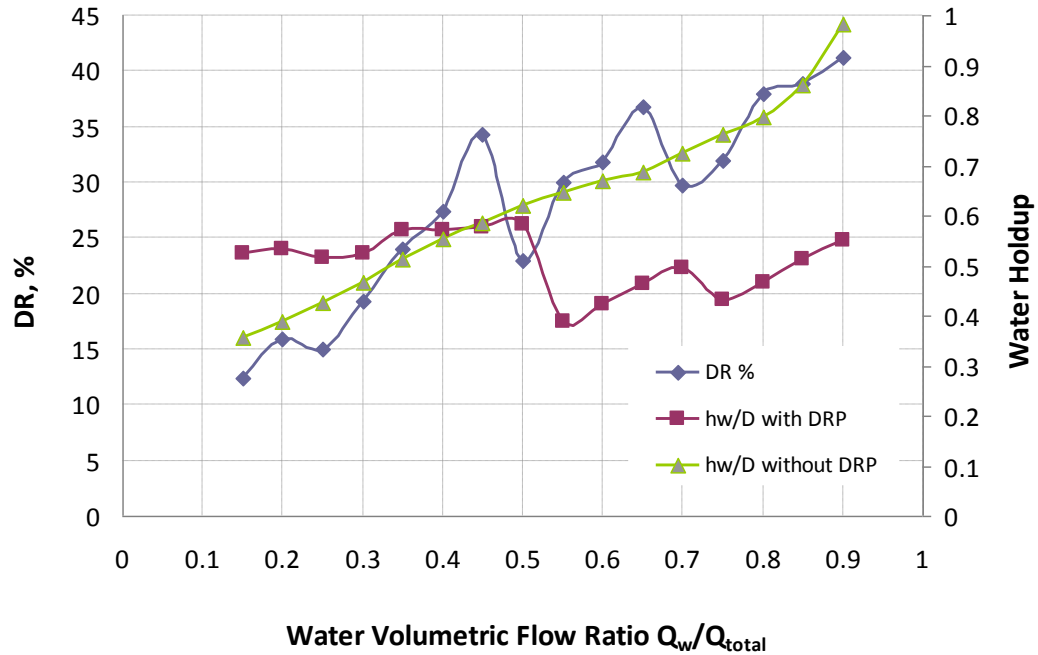


Figure 8.6 Average water holdup in oil-water flow with and without DRP

For the low values of U_{sw} (< 0.5 m/s) without DRP the flow pattern was either stratified wavy (SW) or stratified wavy flow with some droplets in the interface region (SWD) and the final flow pattern after the injection was either smooth stratified or stratified with some waves. The final water holdup after the injection of DRP was larger than before. This leads to a conclusion that the DRP damped some waves and then the water holdup seen by the conductivity probe became larger than before and also killed the turbulence at the interface. Finally, in the case of oil-water with DRP there was not enough turbulence at the interface to form water droplets in the interface region then these droplets coalesced and contributed to the water phase and as a result the water holdup increased.

The second case when both oil and water holdups are about the same, the changes in the flow pattern are not significant. The flow pattern was stratified wavy with droplets in the interface region (SWD) and after the injection becomes stratified wavy (SW) which means that droplets could be oil droplets and because of the smoother interface, caused by the addition of the DRP, oil droplets were not created. As a result, holdup is still almost the same.

For the large values of U_{sw} (> 0.5 m/s) case, without DRP the flow pattern was either stratified flow with mixed layer in the upper part of the pipe and separated water layer in the bottom part (SMW) or three layers flow with clear oil and water layers at the top and bottom of the pipe respectively with a dispersed layer between them (3L). After the injection of the DRP, the flow became stratified wavy flow with some droplets in the interface region (SWD). That means with this high reduction in pressure drop the water was flowing faster than before and most of the oil droplets contributed to oil holdup and at the end few droplets of both oil and water exist at the interface region and as a result the water holdup was less. The results promote the idea that DRP effects is also contributing to oil water separation by reducing the turbulence activities in the interface layer between the oil and water enhancing the droplet coalescence due to the lack of enough mixing turbulent energy.

8.4 CONCLUSIONS

Holdup measurements in oil-water flow with and without DRP polymers were conducted using conductivity probe technique. The set of experiments performed at

same mixture velocity by varying the water volumetric flow rate to the total liquid flow rate ratio. Water holdup is not the same for both cases with and without DRP for the same inlet conditions. Drag reduction accompanied with changing in the flow patterns by damping the high amplitude waves and reducing the turbulence activities which control the droplets formation mechanism. The results showed that the water holdup for the case of oil water with DRP is larger than that for the case of without DRP for $U_{sw} < 0.5$ and less for $U_{sw} > 0.5$ m/s. The results showed the possibility of using DRP for separating and changing the distributions of oil-water droplets mixture.

An explanation of how polymers affect interfacial waves and, in particular, affecting the droplets of oil-water mixture formation-deformation process is introduced. It emerges as a fundamental problem in understanding how drag reducing polymers influence oil–water stratified flows. The main rheological property of the dilute polymer solution, linked with drag reduction in single phase flow, is that it exhibits large elongational viscosities is playing a significant part in the drag reduction process too. However, wave growth and structure could also be affected by shear thinning (Khomami (1990)) and by the injection technique (Al-sarkhi and Hanratty (2001)) which creates coherent entanglements polymer threads.

CHAPTER 9

CONCLUSIONS & RECOMMENDATIONS

Emulsions can be encountered in everyday life. Especially, they can be found in all stages in the petroleum production, recovery and processing industry. In each case, the presence and nature of emulsions, which have important desirable and undesirable properties, determine both the economic and technical successes of the concerned industrial process.

Emulsion technology has been utilized to the acid treatment of reservoir rocks in the region near well bore. Sometimes, the pore structure near the well bore is plugged either by particulates from drilling process or by production precipitation deposits caused by pressure or temperature changes. As a result, permeability is reduced as well as the well productivity. To remove these unwanted deposits, acid stimulation is used.

Emulsified acid is essentially a mixture of up to 70 volume % acid emulsified in a 30 volume % continuous diesel phase. They provide significant benefits in stimulating oil and gas wells by slowing the reaction rate with carbonates and reducing corrosion in the tubular goods. However, pumping emulsified acids can result in high friction losses. Such losses limit the matrix acidizing job efficiency. Therefore, reducing friction pressure loss is an important factor in expanding the application of emulsified acids. Therefore, this experimental investigation aims to study possible friction reduction methods for stable emulsions at different pipe diameters through the control of water

fraction and salinity, the injection of drag reducing polymers (DRP) and the addition of nanomaterials.

For this purpose, a multiphase flow loop with two test sections (with 1.27-cm and 2.54-cm pipe ID), polymer injection systems and pressure transducer systems were constructed to investigate the effect of water fraction and salinity, the injection of drag reducing polymers (DRP) and the addition of nanomaterials on water-in-oil (W/O) flow characteristics. Such features include emulsion stability, conductivity, type, viscosity, dispersed phase average droplet size and pressure drop measurements.

As for the water fraction effect, surfactant-stabilized W/O emulsions, with different water volume fractions (0.1, 0.4, 0.5, 0.6 and 0.7), were examined. In addition, to investigate the possibility of pressure drop reduction of stable emulsions via the aqueous phase salinity control, stable emulsions with different water salinities (0, 5, 20, 50, 100 and 200 wkppm) were studied. Moreover, oil soluble polymers as well as water soluble polymers with different concentrations and molecular weights were tested as drag reducing agents for stable W/O and O/W at different internal phase volume fractions. Furthermore, some organo-clays, with specific distinguished features at different loadings, were tested to explore any possible friction reduction findings for W/O emulsions at different dispersed phase (water) volume fractions.

This chapter is divided into two sections. Section 9.1 presents the main conclusions of the work described in this dissertation. Some recommendations for future work are given in section 9.2.

9.1 CONCLUSIONS

Based on experimental findings, the following conclusions can be concluded.

9.1.1 Influence of Water Fraction

Emulsion flow characteristics of surfactant stabilized W/O emulsions at different water fractions and pipe diameters have been studied. Such emulsion features include: stability, type, conductivity, viscosity and pressure drop. Stable W/O emulsion with 70 volume % of brine was the most stable one compared with the other tested emulsions and showed the highest pressure drop at the same flowrate. As the dispersed phase (water) fraction decreased, emulsion stability, viscosity as well as pressure drop decreased for all emulsions reported in this study at different pipe diameters. Therefore, surfactant stabilized W/O emulsions pressure drop can be reduced by reducing brine (dispersed phase) fraction. In addition, decreasing pipe inside diameter from 2.54-cm to 1.27-cm resulted in up to 74% reduction in emulsion friction factor and such dependency was clearer as water fraction increased. Therefore, stable W/O emulsions friction factor can be reduced by pumping fluids in small pipe diameters due to the shear thinning effect of the high concentrated stable emulsions. Furthermore, stable W/O emulsions viscosity was modeled with a modified Fluidity-Additivity model.

9.1.2 Influence of Water Salinity

The role of the aqueous phase salinity on surfactant-stabilized W/O as well as O/W emulsions flow characteristics has been investigated. In particular, stable emulsions type, stability, average droplet size of their dispersed phase, viscosity and pressure drop, in 2.54-cm and 1.27-cm pipes, dependency on water salinity has been studied.

Based on the present results, which conducted for surfactant-stabilized emulsions with 70/30 water to oil volume ratio, some findings can be summarized. First, for low water salinity range (≤ 5 kppm), O/W emulsion was produced and its stability decreased with increasing water salinity. However, emulsion viscosity as well as the average droplet size of the oil dispersed phase increased as the aqueous phase salinity increased. Second, for high water salinity range (≥ 20 kppm), W/O emulsion was produced and its stability, viscosity as well as the average droplet size of the water dispersed phase increased as the aqueous phase salinity increased. Third, an increase in the water salinity resulted in an increase in the emulsion pressure drop measurements. In particular, changing from O/W to W/O emulsions through phase inversion resulted in a dramatic increase in the pressure drop measurements due to the change in the dispersed phase volume fraction from 0.3 to 0.7 and due to the increase of the external phase viscosity. In addition, stable W/O emulsion friction factor showed a pipe diameter dependency and smaller diameter gave lower friction factor.

Therefore, based on the results presented for this objective, pressure-drop reduction of surfactant-stabilized W/O emulsions can be achieved by controlling the water salinity as well as pipe diameter. In addition, controlling water salinity could be used as an inexpensive, easy to implement technique for W/O emulsion separation or changing to O/W emulsion.

9.1.3 Influence of Drag Reducing Polymers

The effect of DRP on the flow characteristics of stable W/O emulsions was investigated experimentally. Oil soluble polymers as well as water soluble polymers were tested as

drag reducing polymers (DRP) for stable and unstable W/O and O/W emulsions. The influence of DRP type, concentration and molecular weights on emulsion stability, viscosity and pressure drop were reported.

The results showed a significant increase in the emulsion stability with adding the proper DRP and this effect was enhanced as DRP molecular weight increased at ambient temperature. In addition, emulsion stability as well as DRP effect on emulsion stability was reduced as temperature increased. Furthermore, DRP showed shear thinning effect and this effect becomes more dominant as DRP molecular weight increased. Injecting the right DRP (DRP which is soluble in emulsion external phase) resulted in a pressure drop reduction for all tested emulsion types (stable concentrated W/O, stable O/W and stable W/O) and this effect increased as DRP concentration increased. However, injecting DRP which is soluble in the internal phase showed a drag reduction effect for unstable emulsion only but with less extent. Moreover, injecting all types of DRP for emulsion flow with the same turbulence intensity (same Re) showed almost no dependency on the pipe diameter.

9.1.4 Influence of Organoclays

The potential application of nanomaterials for friction reduction in particularly to emulsified acid solutions has a potential in extending the capabilities of stimulation treatment applications. This objective aimed mainly to investigate a possible pressure drop reduction of stable W/O emulsion using organoclays. The influence of organoclays type and concentration on emulsion viscosity was reported. Cloisite 15A was tested as a

pressure drop reducing agent for stable W/O emulsions (with 0.7 and 0.3 water volume fractions).

The results showed a significant reduction in the emulsion viscosity with adding all the tested nano-additives and this effect was enhanced as organoclays concentration increased at ambient temperature. In addition, for the case of concentrated W/O emulsions, the addition of Cloisite 15A resulted in a clear reduction (about 25 %) in the emulsion pressure drop in both test sections. Also, for the stable W/O emulsion with only 0.3 water volume fraction, although no pressure drop reduction was observed in laminar region, it was detected in turbulent region and such effect became clearer as Re number and Cloisite 15A concentration increased. Such results were explained in terms of emulsion dispersed phase droplet size.

In addition, for stable W/O emulsions with 0.3 volume fraction of the dispersed phase, all laminar friction factor data (with and without nano-additives) were in a good agreement with single phase theoretical values. However, the measured emulsion friction factors fell below the theoretical values of single phase flow in turbulent region. Further research is needed to explain such behavior.

9.1.5 Influence of Drag Reducing Polymers on Water Holdup

Holdup measurements in oil-water flow with and without DRP polymers were conducted using conductivity probe technique. The set of experiments performed at same mixture velocity by varying the water volumetric flow rate to the total liquid flow rate ratio. Water holdup is not the same for both cases with and without DRP for the same inlet conditions. Drag reduction accompanied with changing in the flow patterns by damping

the high amplitude waves and reducing the turbulence activities which control the droplets formation mechanism. The results showed that the water holdup for the case of oil water with DRP is larger than that for the case of without DRP for $U_{sw} < 0.5$ and less for $U_{sw} > 0.5$ m/s. The results showed the possibility of using DRP for separating and changing the distributions of oil-water droplets mixture. In particular, DRP can be used as a means to facilitate oil-water separation.

9.2 RECOMMENDATIONS

Based on the results presented in this study, the following recommendations are made to improve the quality of the data and to extend the scope of the research area:

1. Collecting all the data presented in this study to end up with a useful model to predict emulsion friction factors for pipe flow at different compositions and conditions.
2. Correlating all reported results, in this dissertation, to the emulsion dispersed phase droplets size and distribution using a suitable laser particle analyzer.
3. Implementing all the findings to the real emulsified acid.
4. Exploring the influence of the recommended results on emulsified acid reactivity.
5. Modifying the flow loop and using higher power pumps to reach high Reynolds number. Then, all studied parameters (water fraction, water salinity, drag reducing polymers performance and nanomaterials performance) can be investigated in the turbulent regime.
6. Performing inline measurements of the true emulsion dispersed phase droplet size while emulsion flow in pipes.
7. Investigating the effect of droplets interaction on emulsion pressure drop.

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