

# Prediction and Experimental Measurements of Water-in-Oil Emulsion Viscosities During Alkaline/Surfactant Injections

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## Summary

Oil production is generally a complicated multiphase flow inside pipelines, with possible water-in-oil (W/O) emulsions present with other usual phases such as free water and free oil. The W/O emulsions formed can present significant hurdles in production facilities for pumping fluids and during pipeline transport. It is well known that high shear rates provided by pumps, chokes, or valves result in stable emulsion behavior for a field in primary production. Several field tests are under way to test the potential of surfactant flooding as a tertiary-recovery mechanism. The effect of addition of surfactants on the emulsion rheology of production fluids, as in alkaline/surfactant/polymer (ASP) flooding, is not very well understood. This understanding of W/O-emulsion rheology in ASP-injection oil recovery is essential for design of pumps and pipelines as well as for handling flow-assurance issues.

In this paper, we report results from experiments as well as modeling of W/O-emulsion rheology that can form during ASP injections. We focus here only on the alkaline/surfactant (AS) part of these injections in order to clearly understand the impact of surfactants, removing the uncertainties that come with large rheology changes with polymer addition. The effect of surfactants on the rheology of W/O emulsions was studied by making two different types of emulsions: (1) native-brine W/O emulsions without surfactants to provide a baseline and (2) brine W/O emulsions with surfactants used in ASP injections. This way, the impact of ASP injections on emulsion rheology can easily be quantified. A new correlation is developed, based on in-house historical experimental data, to describe rheology of emulsions without surfactants. This correlation should assist in managing the uncertainties that come from extrapolating emulsion rheology measured in the laboratory to actual field conditions. Further, to understand the effect of ASP injections, new experimental measurements were made by adding surfactants to brine solutions. The addition of surfactants resulted in different rheology as compared with emulsions formed by brine solutions. These differences have been attributed to the W/O interfacial tension (IFT), and IFT was added to modify the original correlation. To our knowledge, this is the first study that explicitly relates emulsion rheology with IFT.

## Introduction

Some of the predictions regarding oil production using primary depletion and secondary waterfloods point to a significantly large fraction of original oil in place. The capillary trapping of oil in the pores and inefficient sweep during secondary waterflooding are factors primarily responsible for poor oil recoveries. Enhanced-oil-recovery techniques using chemicals reduce capillary trapping and increase oil recovered from reservoirs. Among the chemicals in-

jected, the ASP-injection technique that includes a mix of an alkali, surfactant, and polymer addresses both volumetric sweep efficiency (polymer part) and capillary trapping (surfactant part).

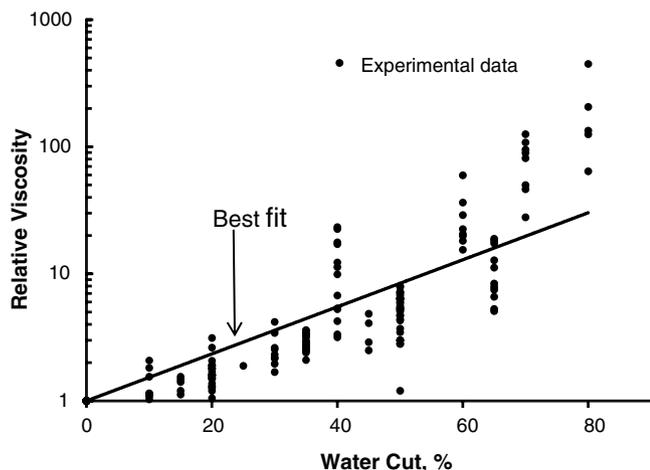
The surfactants injected as part of ASP floods alter the IFT between the oil and water. Depending on the nature of surfactants injected, a significant portion of these surfactants may adsorb on the rock material. However, some portion of these surfactants will mix into the connate water and/or aquifer water from the injection stream. Along with the injected water, some portion of this connate or aquifer water will eventually be produced and may form stable W/O emulsions. Eventually, roughly 10–50% of the injected chemicals are produced back. As a result, the surfactant molecules will end up being at the interface of water droplets and the oil continuous phase in W/O emulsions. The goal of this work is to provide model correlations for predicting W/O-emulsion viscosity for oil production, with or without ASP injections, as well as report experiments to understand the effect of surfactants on W/O-emulsion rheology. These correlations will be particularly important in situations where surfactant-containing emulsions are transported over long distances to producing facilities (for example, from subsea wells to offshore platforms).

**Modeling of W/O Emulsions Using First Principles.** Einstein (1906) used a simple model to explain the rheology of small solid spheres suspended in solution. This model was later modified by researchers for suspended particles that were flattened and elongated as solids. Taylor (1932) extended Einstein's approach to model viscosity of liquid drops suspended in another liquid. There have been several attempts to model emulsion viscosity from first principles, such as Oldroyd (1955). A good review of rheology of emulsions, classifying them into different types, based on volume fraction of suspension, and discussing the advantages and disadvantages of different models is provided by Derkach (2009).

Past studies for prediction of emulsion viscosities have been based on correlations [refer to Derkach (2009) and Johnsen and Rønningsen (2003)], while some are also derived from theoretical foundations such as those postulated by Richardson (1933). Lopez and Hirsra (1998) explain an experimental technique to directly measure the surface shear and dilatational viscosities of a Newtonian interface as functions of the surfactant surface concentration. Danov (2001) developed an analytical formula for viscosity of emulsions in the presence of surfactants by averaging stress-tensor flux at an arbitrary surface of the dilute emulsion and then further explained its relationship to the well-known Einstein formula. The challenge in such first-principles approaches is the need of parameters that are not easily measured in the laboratory. For example, Lopez and Hirsra (1998) and Danov (2001) introduced the concept of dilatational viscosity; however, measurement of such quantities is very difficult. Typically, the available laboratory measurements involving emulsion rheology include quantities such as  $T$ ,  $P$ , shear rate, and density and occasionally droplet-size distribution. Our goal is to predict emulsion viscosities on the basis of such readily available or easily measured quantities.

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**Fig. 1—Raw data of relative viscosities vs. water cuts measured in Shell laboratories and belonging to various fields. Other variables such as temperature, shear rate, and oil type are not added as extra dimensions in this graph for simplicity. These variables, as added later in the paper, will reduce the scatter. At high water cuts (>50%), viscosity of W/O emulsions could be as much as two orders of magnitude higher compared with base oil. The black line is a best fit (exponential fit) to the raw data to signify a general trend.**

**Correlations and Semiempirical Approaches.** W/O-emulsion rheology is traditionally expressed relative to the base-oil viscosity as

$$\eta_{\text{relative}} = \frac{\eta_{\text{emulsion}}}{\eta_{\text{baseoil}}} \quad \dots \dots \dots (1)$$

(i.e., in terms of the factor of increase or decrease in viscosity of emulsions relative to base oil). The “base oil” is the reference oil, without any water. This reference oil could be, in principle, dead oil or oil saturated with gas or undersaturated oil, depending on conditions (pressure, temperature, and fluid compositions). For the purpose of this work, we attempt to model relative viscosities for emulsions and rely on literature or pressure/volume/temperature reports for an estimation of viscosity of the base oil [for example, Bergman and Sutton (2007), and Dindoruk and Christman (2004)]. The experimental and modeling results presented in this paper pertain to W/O emulsions made from dead oil.

Previous studies [such as Dan and Jing (2006) and Arhuoma et al. (2009)] on correlations for predicting viscosities of emulsions are mainly an extension of correlations developed by either Pal and Rhodes (1989) or Richardson (1933).

**Pal and Rhodes (1989) Correlation.** Pal and Rhodes (1989) proposed viscosity/concentration behavior of Newtonian and non-Newtonian emulsions having dispersed-phase volume less than 74% by volume. Eq. 2 was proposed for relative viscosity:

$$\eta_{\text{relative}} = \frac{\eta_{\text{emulsion}}}{\eta_{\text{baseoil}}} = \left[ 1 + \frac{\left( \frac{\phi}{K_2} \right)^{2.5}}{1.1884 - \left( \frac{\phi}{K_2} \right)} \right], \quad \dots \dots \dots (2)$$

where  $K_2$  is the dispersed-phase concentration at which relative viscosity is equal to 100 and  $f$  is the water cut. In this approach, an experimental measurement is required to get an estimate of  $K_2$ . Therefore, this is a tunable model and, in cases where experimental measurements are possible, researchers have used it and proved that this correlation is strong.

TABLE 1—OIL SAMPLES AND RANGE OF CONDITIONS USED IN VISCOSITY MEASUREMENTS TO GENERATE THE RAW DATA USED IN THIS REPORT AS A BASIS FOR CORRELATION FITTING	
Range of experimental data used during parameter fitting	
Water cut	0–80%
Temperature	4–90°C
Shear Rate	1–2490 s <sup>-1</sup>
Range recommended during use of prediction correlation	
Water cut	0–50%
Temperature	20–80°C
Shear rate	10–2500 s <sup>-1</sup>

**Derivatives of Richardson (1933) Original Model.** Richardson (1933) proposed a very simple model for emulsion rheology where an exponential increase in relative viscosity is observed as a function of water cut. Eq. 3 was proposed:

$$\eta_{\text{relative}} = \frac{\eta_{\text{emulsion}}}{\eta_{\text{baseoil}}} = \exp(k \cdot \phi), \quad \dots \dots \dots (3)$$

where  $k$  is a constant and  $f$  is the water cut. This exponential dependency of relative viscosity has been verified and used by many researchers, such as Johnsen and Rønningesen (2003), following Richardson’s original work. A number of modifications were made to this correlation, such as adding temperature dependency for  $k$ .

**Factors Impacting Emulsion Rheology.** In a review paper, Derkach (2009) indicated that viscosity of W/O emulsions depends on a variety of factors such as viscosity of the continuous phase (base oil), viscosity of the dispersed phase (brine), temperature, volume fraction of the dispersed phase, shear rate, droplet radius, pressure, and presence of solids. Farah et al. (2005) studied the effect of varying temperature and water volume fraction in predicting the viscosity of W/O emulsions. Bullard et al. (2009) proposed an equation for shear viscosity based on differential-effective-medium theory that extends the dilute limit to higher volume fractions in emulsions. Basma (2003) developed equations for rheology of O/W emulsions containing fine particles. The effect of specific solid particles (asphaltene, carbonate, and clay minerals) on the stability of W/O emulsions has been addressed by El Gamal et al. (2005). Further studies on W/O-emulsion rheology by Poindexter et al. (2005) and Sjöblom et al. (2003) have also shown how solid content dominates emulsion stability properties and emulsion rheology.

Derkach (2009) explained that the presence of surfactants provides repulsive forces between the droplets of an emulsion, thereby stabilizing the emulsion. In addition, a relationship between the rheology of interfacial surfactant layers and the stability of emulsions is discussed. Zaki (1997) showed that the stability of O/W emulsions is increased by adding anionic surfactant and that the viscosity decreases by lowering the oil content. In addition to such experimental work, there have also been some theoretical studies on the effect of surfactants on emulsion stability and rheology. A detailed theoretical framework on rheology of diluted emulsion with surfactant-covered spherical drops was formulated by Blawdziewicz et al. (2000). The study reported that the presence of small quantities of surfactants significantly affects the rheology of emulsions.

Except for very few sources in literature such as the three papers mentioned in the preceding paragraph, IFT between the oil and water phase is generally not considered as an input parameter to model the prediction of emulsion viscosities. As a result, the implications of surfactant addition on W/O-emulsion rheology during ASP-assisted oil production are not well understood. In such ASP injections where IFT is reduced by orders of magnitude from typ-

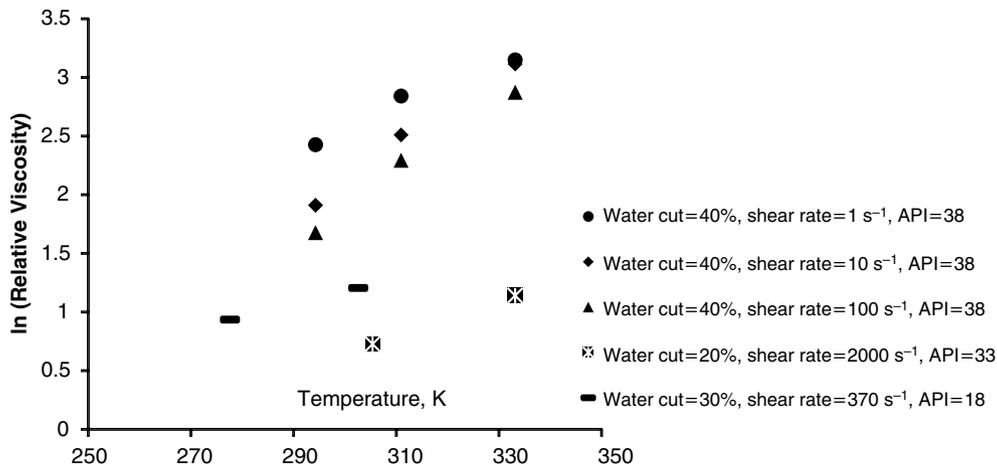


Fig. 2—Temperature dependence of relative viscosity for three different types of oils and at a variety of shear rates and water cuts.

ical oil/brine values seen in primary production, IFT should become an important factor; as such, it is investigated in this paper.

### Correlation for Predicting Native W/O-Emulsion Rheology

W/O emulsions can lead to a significant increase in viscosity of the production fluid. It is also well known that emulsion stability is quite transient—there may exist just the right conditions for emulsion formation or water may exist as a second liquid phase along with hydrocarbons. There is uncertainty not just in emulsion formation during production but also concerning the extent to which the viscosity of the fluids increases as a result of emulsion formation. An example of an increase in viscosity of W/O emulsions is shown in Fig. 1. Clearly, the relative viscosity of W/O emulsions, at higher water cuts, could be one or two orders of magnitude higher when compared with the viscosity of the relevant base oil. Pump designs and pipeline transport systems have to account for this variation in viscosity. Hence, there is a strong need for a predictive correlation for viscosities of emulsions where an engineer can vary important factors contributing to emulsion formation and see subsequent effects on viscosity. A sound correlation for predicting viscosities of emulsions adds value in the exploratory phase of hydrocarbon production.

In summary, Table 1 shows the ranges of temperature, water cut, and shear rates that were available in the raw data for development of predictive correlations. It also shows the recommended ranges for use of the correlation proposed in this section.

The laboratory measurements for W/O-emulsion viscosities reported in Fig. 1 were performed on samples prepared with varying water cuts. A temperature and shear-rate sweep measurement of the sample was taken with a rheometer. Typically, all these emulsions were uniformly made using a constant shear rate (2000 rev/min) and mixing for 2 minutes with the same mixer, similar to the method described in ASTM D-1401. Thus, most of the data on emulsion viscosity have three variables: water cut, temperature, and shear rate. Indeed, these are the three most important variables that can effectively capture the rheology of native W/O emulsions—that is, not looking at the effect of ASP injections or decreasing IFT for the purpose of this section. Fig. 1 shows the raw data that were quality checked and picked for further fitting of the correlation. In total, roughly 195 data points (where each data point corresponds to at least a different water cut, temperature, shear rate, or oil type) were finally used to develop the correlation. Six different oil types were used. It is important to note that these oils are very different in nature [American Petroleum Institute (API) oil gravity, paraffin/aromatic ratio]. The proposed correlation is developed in a stepwise manner by including the key variables one at a time: (1) effect of water, (2) effect of temperature, (3) type of oil, and (4) shear rate.

**Development of Correlation.** In this section, we discuss the development of the correlation for emulsions. We begin with the early correlation proposed by Richardson (1933) and show its development to include other factors influencing emulsion rheology. We extend this correlation and propose to include several other factors and demonstrate a fit of those parameters for the data set obtained from Shell's laboratories.

Richardson (1933) proposed a simple exponential increase in relative viscosity as a function of water cut in Eq. 3, where  $k$  is a constant. In the following years, many researchers modified the variable  $k$ . For example, Broughton and Squires (1937) incorporated a system dependent parameter  $A$  and modified the equation to

$$\eta_{\text{relative}} = A \cdot \exp(k \cdot \phi) \quad (4)$$

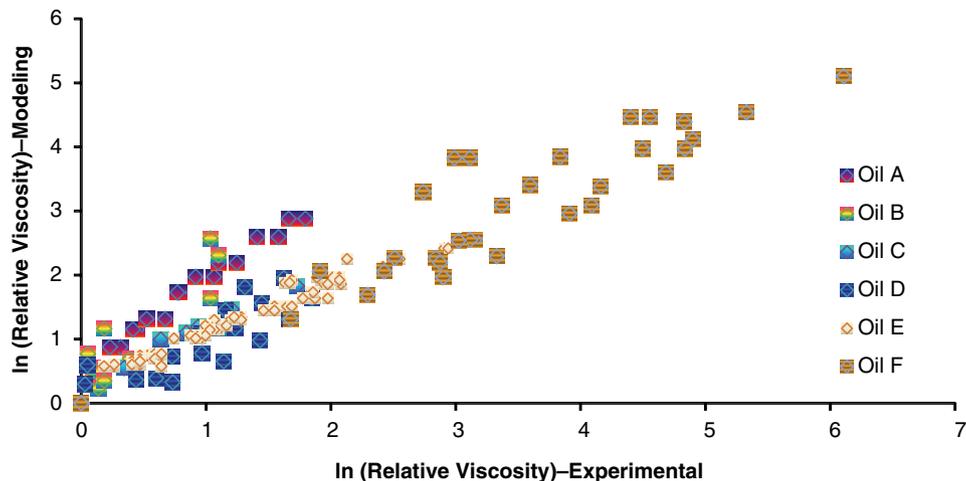
where  $k$  is a constant and  $A$  is a system dependent parameter.

Rønningsen (1995) used Richardson's correlation and added temperature-dependent terms to both  $A$  and  $k$  to study several North Sea crude oils. It is very important to realize that the base oil (or the continuous phase) has its own temperature dependency. A sound argument to capture temperature dependency of viscosity of emulsions exists by assuming that it will be identical to temperature dependency of the base oil. However, that is not the case as observed in our experimental data. Fig. 2 shows the relative viscosity of three different types of oil at a variety of shear rates and water cuts as a function of temperature. These data sets portray a strong temperature dependence for relative viscosity. If the temperature dependency of emulsion rheology would be originating solely from that of base oil, the curves shown in Fig. 2 should have been essentially flat. As a result, it was concluded that there is a need to have temperature in the relative-viscosity term.

Rønningsen (1995) proposed the following modified form of Richardson's equation by including the temperature-dependent term ( $k_1, k_2, k_3, k_4$  are shear-rate-dependent coefficients):

$$\ln(\eta_{\text{relative}}) = k_1 + k_2 T + k_3 \phi + k_4 T \phi \quad (5)$$

**Proposed Development To Include Nature of Oil and Effect of Shear Rate.** In the correlation proposed by Rønningsen (1995) (Eq. 5), it should be observed that at  $\phi=0$ , for a reference temperature, the left-hand term should in principle become zero. Without any water, viscosity of emulsion should be identical to that of base oil. However, the term  $k_1 + k_2 T$  remains in the right-hand side of Eq. 5 at  $\phi=0$ . At a particular temperature, it may be possible to choose  $k_1$  and  $k_2$  such that the left-hand term also goes to zero. However, in reality, the correlation either loses the intended temperature dependency or does not converge to a value of unity at  $\phi=0$ .



**Fig. 3—Comparison of relative viscosities obtained from experiments with model prediction by fitting to Eq. 6.**

To include the temperature dependency, as a first step, we propose the following simple modification of the original Richardson equation:

$$\eta_{\text{relative}} = A \cdot \exp(k_{\text{proposed}} \cdot \phi), \dots\dots\dots (6)$$

where  $k_{\text{proposed}}$  is a temperature-dependent term given by  $c_1 + c_2T$ , where  $c_1$  and  $c_2$  are constants.

The correlation proposed in Eq. 6 led to a good fit to the data within one field. However, while attempting to fit data from six different oil fields, it was difficult to capture the variability in the oil type by the simplicity of this equation. **Fig. 3** shows the best fit of experimental data using Eq. 6, and it is clear that there are separate slopes depending on the oil type. In the literature, this problem is usually addressed by proposing correlations for a particular geography (for example, North Sea or Gulf of Mexico). We investigated several parameters to include the oil type, such as API gravity, molecular weight, sulfur content, total acid number, paraffin/aromatic ratio. After performing this background work, the following correlation is proposed to include the effects of oil type:

$$\ln\left(\frac{\eta_{\text{emulsion}}}{\eta_{\text{baseoil}}}\right) = \phi \cdot (c_1 + c_2T) \cdot [\ln(\text{API})]^{c_3 + c_4T} \dots\dots\dots (7)$$

The emulsion-rheology data used for fitting the correlation were made at varying shear rates, along with different temperatures, water cuts, and oil types. In general, the viscosity of emulsion decreases as the shear rate is increased (shear-thinning behavior). However, depending on the oil type or temperature, this trend is not always consistent. Indeed, the data showed that, in some cases, the change could be any one of the following:

- (a) Monotonic decrease in viscosity with an increase in shear rate.
- (b) Constant viscosity until a specific shear rate, followed by a decrease in viscosity with increasing shear rate.
- (c) No significant change in viscosity as a function of shear rate.

In addition, there are significant amounts of data where the shear rate during measurement has not been reported. As a result, it was a difficult exercise to include any shear-rate effects based on all available data.

We also observed that behavior of emulsion viscosity was, in general, different for low shear rates (defined as shear rates  $< 100 \text{ s}^{-1}$ ) as compared with data obtained at higher shear rates (defined as shear rates  $> 100 \text{ s}^{-1}$ ). As a simple approximation and because of limitations of available data, the shear-rate effects in the correlation were accounted for by two separate fittings: (a) all data  $< 100 \text{ s}^{-1}$  and (b) all data  $> 100 \text{ s}^{-1}$ . As a result, two sets of coefficients  $c_1 - c_4$  were developed, one set for low ( $< 100 \text{ s}^{-1}$ ) and the other set for high ( $> 100 \text{ s}^{-1}$ ) shear rates. This way, the shear-rate effects on

W/O-emulsion viscosity were captured by grouping the data into low ( $< 100 \text{ s}^{-1}$ ) and high ( $> 100 \text{ s}^{-1}$ ) shear rates.

**Final Correlation.** The final correlation, taking into account all parameters mentioned in the preceding section, takes the following form:

$$\ln\left(\frac{\eta_{\text{emulsion}}}{\eta_{\text{baseoil}}}\right) = \phi \cdot (c_1 + c_2T) \cdot [\ln(\text{API})]^{c_3 + c_4T} \dots\dots\dots (8)$$

where we define two sets of coefficients ( $c_1 - c_4$ ) based on: (1) low shear rates ( $< 100 \text{ s}^{-1}$ ), and (2) high shear rates ( $> 100 \text{ s}^{-1}$ ).

A simple scatter plot showing the values predicted from the proposed correlation vs. the experimental data at a given temperature, API oil gravity, water cut, and shear rate is shown in **Fig. 4**. The reasoning behind using the steps explained in this paper in arriving at the proposed correlation was to minimize the scatter shown in this plot. The level of scatter obtained by using the four previously mentioned variables is reasonable, as seen in Fig. 4.

The coefficients and units for  $\phi$  and  $T$  are given in **Table 2**. The user can easily enter this formula into an Excel™ sheet and predict the increase in relative viscosity of a W/O emulsion as a function of water cut, temperature, API gravity, and shear rate.

**Graphical Representation of the Correlation.** The correlation proposed in this work, shown in Eq. 8, has been presented graphically in **Figs. 5 and 6**. The following are the main observations regarding dependency of W/O-emulsion viscosity on important variables:

1. Shear rate: Comparing differences between Figs. 5 and 6 for a given water cut, temperature, and API gravity of the oil, it is observed that the viscosity of emulsion at high shear rates is generally lower than the same at low shear rates. This illustrates the shear-thinning behavior of W/O emulsions formed from produced oils from six different fields. As mentioned earlier, emulsions may show Newtonian or non-Newtonian or mixed behavior. The shear-thinning prediction of the model is a result of average of data showing all these three different types of behavior, although the majority of data is shear thinning. We recommend that if it is known that the W/O emulsion in a project is non-Newtonian or if nothing is known about rheology type of W/O emulsions, then the model-prediction results for both low and high shear rates should be used. On the contrary, if it is known that the emulsion in a project is Newtonian, then the model predictions at low shear rates across the entire range of shear rates should be used.

2. API gravity of oil: Comparing the difference between dashed (light oil) and solid (heavy oil) in Figs. 5 and 6, it is clear that the increase in viscosity of W/O emulsion is more pronounced for a lighter oil compared for a heavier oil. This may sound counterintuitive. To clarify it further: It is obvious that absolute value of base-oil

Experimental Data vs. Proposed Correlation

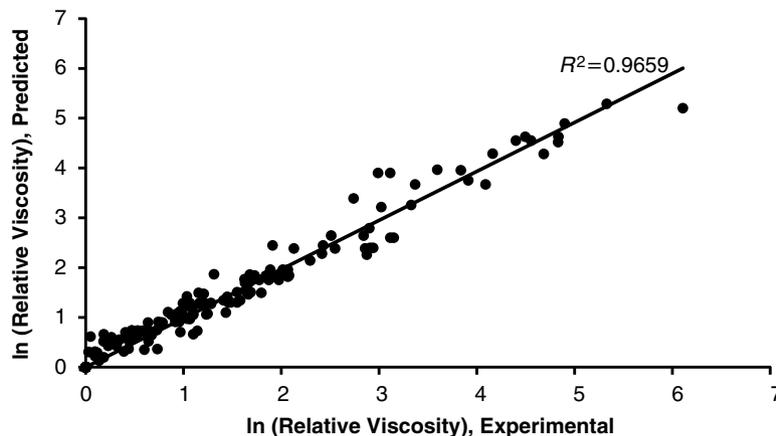


Fig. 4—A scatter plot showing the predictions from the proposed correlation in this paper (y-axis) and the experimental values (x-axis) at varying temperature, shear rates, oil type, and water contents.

TABLE 2—COEFFICIENTS FOR THE CORRELATION PROPOSED IN THIS WORK FOR PREDICTING W/O-EMULSION VISCOSITIES\*

Coefficients	Low shear (>100 s <sup>-1</sup> )	High shear (>100 s <sup>-1</sup> )
c <sub>1</sub>	-1.31E-02	-7.05E-03
c <sub>2</sub>	5.20E-05	2.77E-05
c <sub>3</sub>	5.96E+00	5.76E+00
c <sub>4</sub>	-1.16E-02	-9.74E-03

\*For these coefficients, the units of input variables should be  $\phi$  (in % water cut) and  $T$  (in Kelvin). Ln refers to the natural log in the correlation.

viscosity for heavy oil is much greater than that of light oil. The correlation proposed in this work (Eq. 8) predicts that the relative viscosity increase, as a result of W/O emulsions, is higher for light oil compared with heavy oil. As an end result, the absolute viscosity of W/O emulsion, which is relative viscosity multiplied by the base-oil viscosity, may still be higher for heavy oil compared with light oil.

3. Temperature: Comparing different lines in Figs. 5 and 6, the effect of temperature on W/O-emulsion viscosity can be observed. As the temperature is increased, the relative viscosity of W/O emulsion, at a given water cut, shear rate, and oil API gravity, also increases. This observation is consistent with two earlier works [Johnsen and Rønningsen (2003) and Farah et al. (2005)]. One must admit that it is really difficult to understand the trend of this temperature-dependent behavior; this aspect was not well explained by the previous studies. However, the raw data used in this paper for the correlation development show a strong dependence of relative viscosity of W/O emulsions with temperature, analogous to (and consistent with) the light-oil behavior shown in Figs. 5 and 6.

4. Water cut: As is evident in Figs. 5 and 6, the relative viscosity of W/O emulsions increases sharply as a function of water cut. At conditions shown in the two plots, the increase in viscosity could be as high as a factor of 28. This illustrates the strong need to include the changes in viscosity because of formation of emulsion for design of pipelines and pumps. One note of caution: These correlations are meant for W/O emulsions only. At some point, the oil-continuous phase may convert to water-continuous phase, resulting in oil-in-water (O/W) emulsions. This is called the inversion point. After the inversion point, the viscosity of the emulsion will drop sharply and the correlation proposed in Eq. 8 will no longer hold. So, the user should be absolutely sure that the water cut is below the inversion point. Indeed, either below or above inversion point, water or oil may

also be present as a free phase or in microemulsion form; therefore, those uncertainties should also be considered before application of this correlation. The W/O emulsion is just one of the many phase regimes possible in oil production with water.

### Experimental Measurements of Emulsion Rheology for IFT Variability

Further in this paper, we investigate and report experimental results on W/O-emulsion rheology in the presence of surfactants used in ASP flooding. We develop a relation between changes in IFT and the rheology of emulsions formed during ASP-injection field oil production, based on the experimental results. To our knowledge, this is first time such a possible relation has been postulated and addressed by experimental measurements.

**Native and ASP W/O Emulsions.** To remove the complexities in viscosity measurements attributed to the presence of water-soluble polymer, as a first step, only AS solutions without the polymer were used to make the emulsions. With this approach, the effects of surfactants on W/O-emulsion rheology should be identified more clearly. In addition to added surfactants, surface-active soaps are present because of conversion of organic acids in the crude oil by alkali. W/O emulsions with varying water cuts (20 and 40%) were formulated in the laboratory at a constant salt concentration (2.8 wt%) and made with the following two solutions: (1) oil with brine and (2) oil with ASP/brine solution.

A prototype ASP solution currently being considered for a field study was used for these experimental measurements. The experiments were performed by diluting the original ASP solution with brine solution to reflect the mixing of ASP solution with connate water and, thereby, the production of water with a variety of dilutions of injected ASP solution at different production times. As an example, an  $x\%$  ASP solution here implies an  $x$  wt% of the original ASP solution mixed with  $(100-x)\%$  brine solution. A 100% ASP solution represents the original injected AS solution.

We illustrate the difference between native emulsions and surfactant W/O emulsions with an experiment and show the results in Fig. 7. This figure shows that the presence of surfactants decreases the relative viscosity of W/O emulsions compared with emulsion formed by brine solution (native emulsion). These viscosities have been measured at 20°C and at a shear rate of 10 s<sup>-1</sup>. As the ASP solution strength (i.e., surfactant concentration) increases, the relative viscosity decreases further compared with emulsions made with brine solutions. We now systematically investigate the effect of surfactants on W/O-emulsion rheology and will also update the correlation proposed in Eq. 8. With this approach, we assume that the quantitative nature of the impact of water cut, temperature, shear rate, and API gravity of the oil is the same for native and ASP W/O

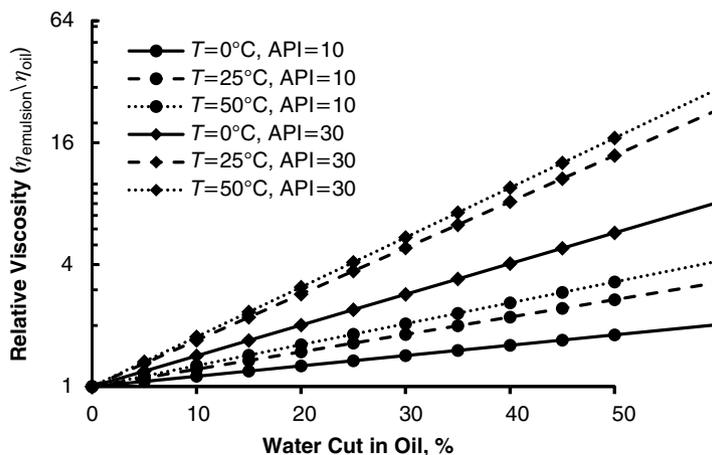


Fig. 5—For low ( $<100 \text{ s}^{-1}$ ) shear rates. Values of relative viscosities generated from the correlation proposed in this paper, varying with water cut, temperature, and API gravity of oil.

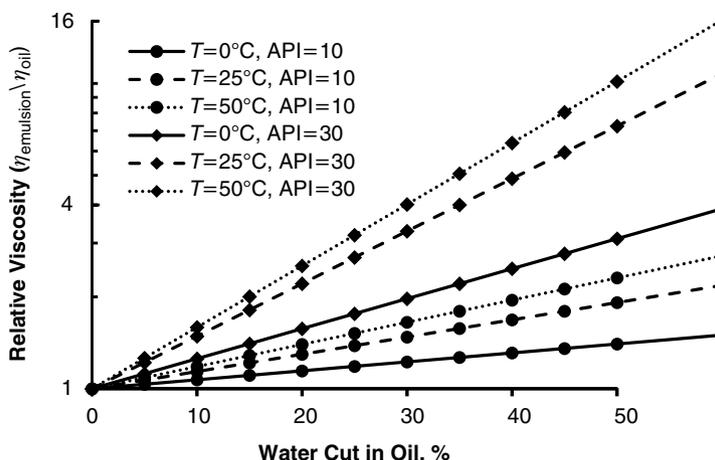


Fig. 6—For high ( $>100 \text{ s}^{-1}$ ) shear rates. Values of relative viscosities generated from the correlation proposed in this paper, varying with water cut, temperature, and API gravity of oil.

emulsions and that the difference between the two types of emulsions can be explained by IFT.

**Design of Experiments.** The reservoir connate water was represented as brine having 2% NaCl. As mentioned earlier, varying concentrations of ASP in brine (4, 20, and 50%) represent the varying percentages of the ASP solution mixed into the production fluid as chemicals are injected over the life cycle of the enhanced-recovery project. The details of oil, brine, and ASP used for emulsion preparation are given in Table 3. Two different oil samples (taken at different times) from the oil field were used in these studies. All emulsions were formed by mixing the three fluids in different proportions in a laboratory paddle mixer for up to 2 minutes at approximately 2,000 rev/min. All samples were made in a similar way for consistency in the applied shear rate.

Two separate instruments were used to measure IFTs because the entire breadth of the range of IFT in this work could not be measured accurately by a single instrument. The higher values of IFT (15–30 dynes/cm) were measured using the pendant-drop instrument (manufactured by TECLIS Tracker™). The relatively low IFT measurements (0.1–5 dynes/cm) were made using the spinning-drop tensiometer manufactured by the University of Texas at Austin. The two instruments can provide measurements outside their intended IFT ranges but are prone to large errors and hence unreliable. Therefore, it is important to use one of these two instruments, depending on the expected range of IFT.

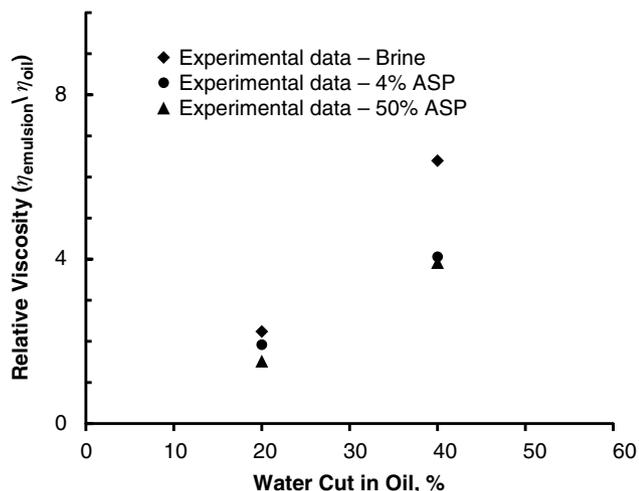
Viscosity was measured using a double concentric cylinder viscometer (manufactured by Anton Parr, Model number MCR 301).

It is an automated instrument having the capability of a pressure cell (for high-pressure measurements). The instrument can perform both temperature sweep and shear-rate sweep for rheology measurements. Because we used dead oils, the measurements were performed in an open cell (at atmospheric pressure).

**Experimental Conditions.** A shear sweep (between 10 and  $100 \text{ s}^{-1}$ ) and a temperature sweep (between 20 and  $50^\circ\text{C}$ ) were made in the rheometer on Oil Sample A to measure viscosities of W/O emulsions, with both brine and surfactant solutions. A key observation made during these sweeps is that there is a significant difference in rheology for emulsions made by brine and by ASP solutions. We observed that this difference is most pronounced at the lowest temperature of the sweep ( $20^\circ\text{C}$ ) and lowest shear rate ( $10 \text{ s}^{-1}$ ). It is not clear whether these differences are because of IFT effects pronounced at low temperatures and shear rates or because of other factors such as wax crystals making emulsions more stable. Nevertheless, all further experiments were conducted at these temperature and shear-rate conditions where the overall rheology difference between emulsions made by brine and those made with ASP solutions was the largest.

## Experimental Results

**IFT Measurements.** The IFT between brine water and oil was measured using a pendant-drop tensiometer. However, after adding ASP solutions, it was found that the lower IFTs were not being accurately measured with the same instrument. In case of surfactant additions, the resulting pendant drop was unstable, and its dimensions were



**Fig. 7—Comparison of relative viscosity of W/O emulsions formed by brine solution (native emulsions) and AS solutions (surfactant emulsions).**

difficult to measure because of the lack of color contrast between the oil and water drop in the presence of surfactants. Therefore, the spinning-drop tensiometer was used to help distinguish IFTs for varying concentration of ASP solutions.

We use the pendant-drop instrument to measure brine-W/O-emulsion IFT value (approximately 20 dynes/cm). It is very difficult to distinguish the IFT of surfactant W/O at varying level of ASP concentrations (the IFT drops below 5 dynes/cm). For those measurements, we instead used results from the spinning-drop tensiometer (Fig. 8). As the ASP concentration increases from 4% to 20% and to 50%, the equilibrium IFT value decreases to 4.7, 1.9, and 0.18 dynes/cm, respectively.

A variety of W/O emulsions was formed at 20°C using the paddle mixer, and their viscosities were measured at a shear rate of 10 s<sup>-1</sup>. Fig. 9 shows the emulsion-sample pictures. In general, more small drops were formed in the presence of surfactant.

The water cuts and level of surfactants were varied to form different data points shown in Figs. 10 and 11. Results are shown for Samples A and B, respectively, to verify the repeatability of the observations.

**Emulsion-Rheology Measurements for Sample A.** The viscosity of the pure-oil sample (Sample A) was measured (indicated as the black horizontal line in Fig. 10) as a reference for base oil. The data points lying on the y-axis (ASP concentration=0%) in the plot show the rheology measurement made for brine W/O emulsion (i.e., without any surfactant solution). As seen in Fig. 10, with increasing ASP concentration, the viscosity of W/O emulsion increases slightly initially (for 4% ASP solution) and then decreases very dramatically. Indeed, at higher ASP concentrations (20 and 50%), the viscosity of W/O emulsions is less than the viscosity of base oil. One likely explanation is that there may be an inversion in phases where the oil is not the continuous phase at the higher surfactant concentrations. In such a scenario, water present earlier as a dispersion in the oil phase now reverses to a continuous phase with oil droplets dispersed in water (O/W emulsions). In support of this hypothesis, we did visually observe some free water in the 20%-ASP=20% and 50%-ASP cases. This inversion at higher water cuts did not occur in the case of brine W/O emulsion, indicating that presence of surfactants may have facilitated the inversion or the formation of free water. There is a need to verify these observations with other samples of oil. This should help establish the inversion phenomenon's dependence on a number of factors such as the phase behavior of surfactants, nature of the oil, nature and concentration of surfactant, and shear mixing.

**Emulsion-Rheology Measurements for Sample B.** Rheology tests on emulsions from Oil Sample B were also performed, and the measurements are plotted in Fig. 11. The absolute viscosity of

**TABLE 3—DETAILS ON SAMPLES USED FOR DESIGN OF EXPERIMENTS REPORTED IN THIS PAPER**

Sample Type	Description	Sample Received Date
Sample A	Oil sample from Shell oilfield. Dehydrated and demulsified	4/12/2004
Sample B	Oil sample from the same oilfield as sample A but at different production time. Dehydrated and demulsified	7/7/201
Brine (wt%)	2% NaCl and 98% DI water	Prepared
ASP (wt%)	0.6% proprietary cocktail of anionic surfactant	Prepared

W/O emulsions decreases with increase in surfactant concentration (similar to observation made on Sample A). However, the inversion of W/O emulsions is not observed and the value of absolute viscosity always remain higher than that of the base oil.

It can be concluded from Figs. 10 and 11 that the presence of surfactants decreases the W/O-emulsion viscosity and, in some cases, may even facilitate the W/O inversion that is helpful for pipeline flow because inversion to oil-in-water (O/W) emulsions will result in much lower viscosity for the production fluids. The stark variance in results from the two oil samples is unexplained at this time, but it could result from the presence of differing levels of production chemicals in the two samples or variation in the compositions of the oils themselves. There is a need to verify these trends with more oil samples.

### Modification of Correlation To Explain IFT Effects

We now modify the correlation proposed earlier in this paper (Eq. 8) for native emulsions to include the effect of IFT. The experimental results reported earlier indicate that a decrease in IFT between oil and water typically results in a decrease in viscosity of W/O emulsions.

The experimental data also provided us some data points for changes in viscosity as a function of IFT. These data points are quite limited; we have a total of only 8 data measurements (four on each sample) that relate W/O-emulsion viscosity with IFT. As a first step, we propose a preliminary modified correlation for W/O-emulsion viscosity prediction, to include the IFT effects observed in experiments reported here.

The following relation accounts for the effect of IFT on emulsion rheology:

$$\ln\left(\frac{\eta_{\text{emulsion with ASP}}}{\eta_{\text{baseoil}}}\right) = \ln\left(\frac{\eta_{\text{emulsion with ASP}}}{\eta_{\text{emulsion with brine}}}\right) + \ln\left(\frac{\eta_{\text{emulsion with brine}}}{\eta_{\text{baseoil}}}\right) \dots \dots \dots (9)$$

The B-term accounts for the effect of surfactant on the rheology of emulsions. The C-term represents the correlation developed earlier in the paper for native emulsions, as shown in Eq. 8.

The following modified correlation is proposed for predicting the W/O-emulsion rheology including the effect of IFT:

$$\ln\left(\frac{\eta_{\text{emulsion with ASP}}}{\eta_{\text{baseoil}}}\right) = \phi \cdot \left\{ (c_1 + c_2 T) \cdot [\ln(API)]^{c_3 + c_4 T} + \frac{3}{2} \left( \frac{IFT_{\text{with brine}}}{IFT_{\text{with ASP}}} - 1 \right) \right\} \dots \dots \dots (10)$$

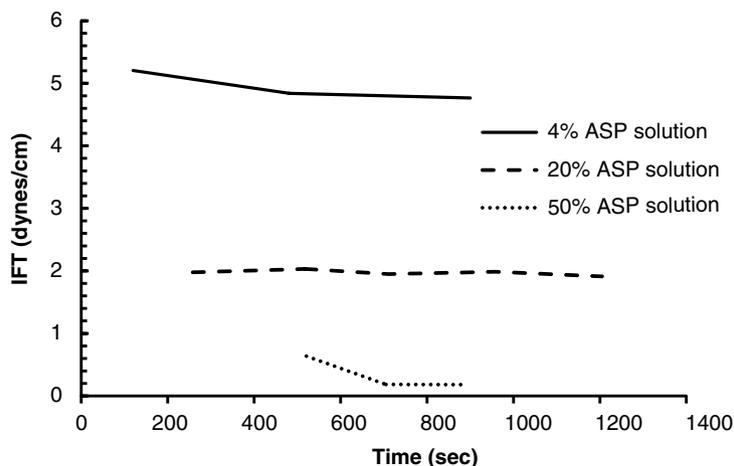


Fig. 8—IFT measurements for ASP water/brine at different levels of surfactant concentrations using the spinning-drop tensiometer.

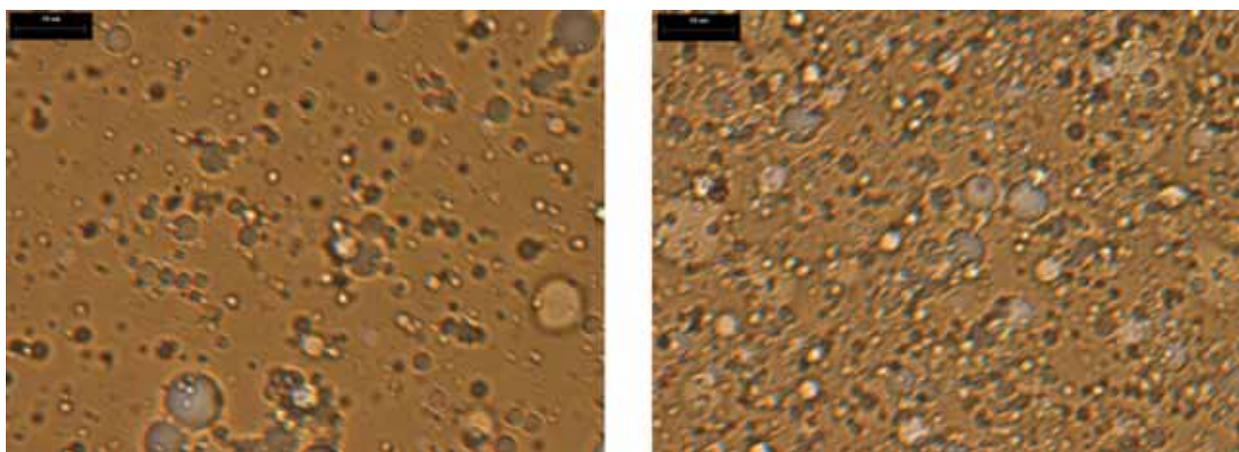


Fig. 9—W/O emulsions for 20% water cut (left: brine only, right: 4% ASP solution) (black bar=10  $\mu$ m).

The coefficient  $3/2$  is an approximate value found after regressing the experimental data and lends itself to further modification by matching more data when available.

The experimental values and the predictions of the correlation modified for IFT effects (Eq. 10) are shown in Fig. 12. The modified correlation shown in Eq. 10 offers a prediction of W/O-emulsion rheology in the presence of ASP surfactants.

A reasonable explanation for the decrease in relative viscosity on addition of surfactants is that the water droplets are more prone to shape deformation upon adding surfactants because of the low IFT. This causes reduction in the relative friction that the water drops would impose on fluid flow in pipelines. Also, upon surfactant addition, the likelihood of forming a free-water phase decreases and the likelihood of forming a reverse O/W emulsion increases.

### Conclusions

A new correlation for prediction of W/O-emulsion viscosity has been developed. Furthermore, a modification of this correlation is proposed to include the effect of IFT. This modification was based on experimental data obtained to correlate the relation between viscosity of the W/O emulsion and the IFT changes incurred because of the addition of surfactants.

The correlation developed for emulsions made of brine solution (Eq. 8) is very robust and is correlated with an extensive set of raw data. On the other hand, the correlation proposed to include the effect of surfactants (Eq. 10) should be considered limited in nature

because of the number of data sets used in training the regression coefficients. The proposed correlation with modification of IFT should be fine tuned with more oils. Such samples should be available for testing as more ASP pilot tests in various parts of the world are undertaken.

The proposed viscosity correlations (Eqs. 8 and 10) shall be extremely useful for production-facilities design in projects where there is high probability of W/O-emulsion formation and in the absence of experimental data or when no fluid sampling is possible. Eqs. 9 and 10 will at least form a basis for screening of possible emulsions.

The experiments reported here help us to understand the relation between W/O-emulsion rheology and the IFT decrease caused by the addition of surfactants. The experiments clearly demonstrate that, by adding surfactants, the effective viscosity of W/O emulsion decreases and potentially a lower water-cut inversion point could develop for W/O emulsions. These two observations should indeed favor ASP injections with respect to pumping requirements as well as any needed demulsification.

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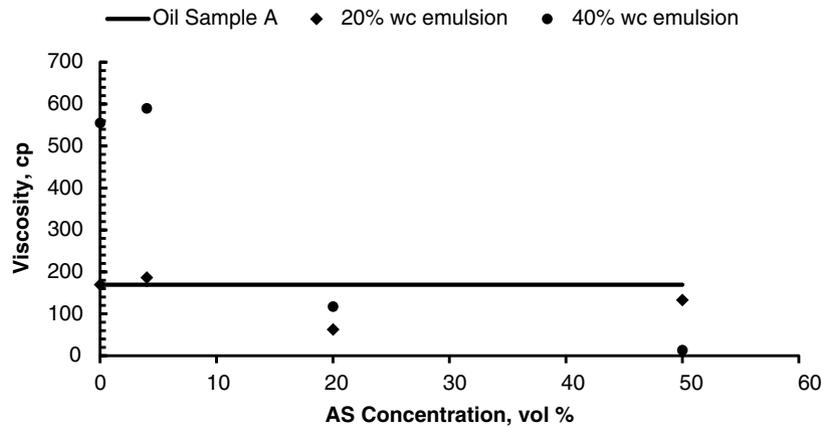


Fig. 10—Absolute viscosities of W/O emulsions formed with Oil Sample A, at different water cuts (shown by different symbols) and varying ASP concentration (x-axis). X-value=0 shows the emulsion viscosity for brine W/O case.

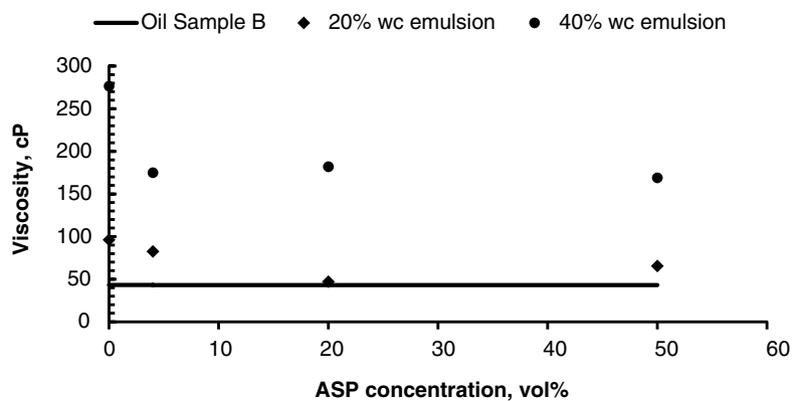


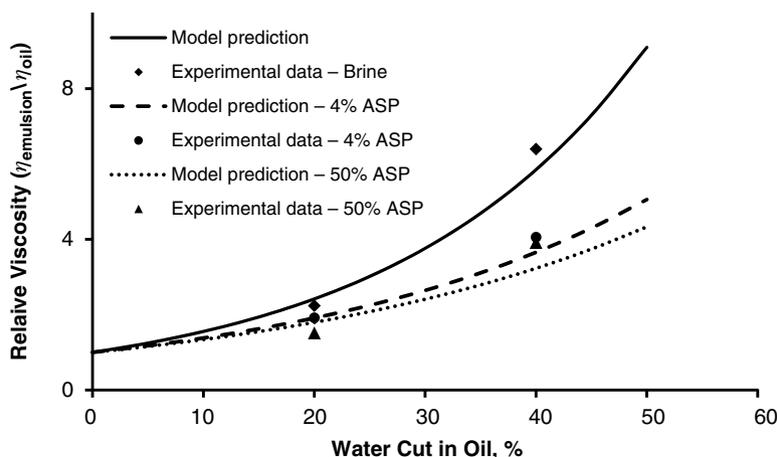
Fig. 11—Absolute viscosities of W/O emulsions formed with Oil Sample B, at different water cuts (shown by different colors) and varying ASP concentration (x-axis). x-value=0 shows the emulsion viscosity for brine-W/O-emulsions case.

## Nomenclature

- $\eta$  = viscosity
- $P$  = pressure
- $T$  = temperature
- $\phi$  = water cut
- $k$  = constant

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**Fig. 12—Experimental data and the model results from the modified correlation (Eq. 10) to include the IFT effects. The decrease in IFT results in decrease in W/O-emulsion viscosity.**

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