USING LOW FIELD NMR TO PREDICT VISCOSITIES OF CRUDE OILS AND CRUDE OIL EMULSIONS

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ABSTRACT

Knowledge of oil viscosity is vital to most areas of the petroleum industry, and is especially important in the production of heavy oil and bitumen. Stable crude oil emulsions are also prevalent in many stages of the production and transport of heavy oil and bitumen. These emulsions contain water as a dispersed phase, which makes them even more viscous than their constituent oil. Knowledge of emulsion viscosity is necessary for determining energy requirements for transport and upgrading of the produced crude. As viscosity increases, conventional measurements become less accurate and more difficult to obtain. An alternate method of predicting viscosities would be extremely beneficial to the industry.

Low field nuclear magnetic resonance is examined in this work for its potential to predict viscosity of crude oil and crude oil emulsions. NMR is an attractive alternative to conventional measurements because it provides fast, unbiased and non-destructive data even for high viscosity oils. A correlation was developed which predicts the viscosity of heavy oils and bitumens over a wider range of viscosities than any other published NMR viscosity correlation. Viscosity is increased further by the emulsified water fraction, which can also be measured with NMR. Emulsion NMR models were also developed that provide order of magnitude viscosity predictions over a wide range of emulsion viscosities by incorporating the effect of the suspended water and the size of the water droplets. Data for these correlations have been obtained at different temperatures, proving that NMR can be used to predict viscosity changes with temperature as well.

INTRODUCTION

Knowledge of oil viscosity is vital to most areas of the petroleum industry, from reservoir engineering and consideration of potential recovery schemes to production and refining of the reservoir oil. In heavy oil and bitumen, oil viscosity is often correlated directly to the reserves estimate[1], and can determine the success or failure of a chosen enhanced oil recovery scheme. Water-in-oil emulsions, also known as crude oil emulsions, are also prevalent in many stages of the production and transport of heavy oil and bitumen. These emulsions may form during steam assisted heavy oil recovery, offshore oil production or during transport of oil due to shear forces in the pipe[2]. Knowledge of emulsion viscosity is necessary for determining energy requirements in transport and upgrading of the produced oil.

As viscosity increases, conventional laboratory measurements become progressively less accurate and more difficult to obtain. As well, oil samples extracted and measured in the lab may not be representative of actual field conditions[1]. An alternate method of determining oil and emulsion viscosities would therefore be extremely beneficial to the petroleum industry. Low field nuclear magnetic resonance (NMR) is examined in this work as an attractive alternative to conventional viscosity measurements. NMR experiments are fast, non destructive, and not sensitive to technician error. NMR is already an accepted technology in conventional oil sandstone reservoirs, but there has only been limited success so far in extending the previously developed NMR models to heavy oil and bitumen formations. This work demonstrates that NMR does in fact have great potential as an analysis tool for heavy oil and bitumen formations as well.

THEORY

The development of low field NMR models for viscosity predictions requires a fundamental understanding of NMR and viscosity principles. More detailed explanations are given by Pal[3] and Coates *et al.*[4]

Viscosity of Crude Oil and Crude Oil Emulsions

The viscosity of a liquid is simply the relationship between the shear stress applied to the liquid and the resulting shear rate that occurs. Newton's law of viscosity is given as[3]:

$$\tau = \eta\dot{\gamma} \tag{1}$$

Where τ = shear stress (Pa)
$\dot{\gamma}$ = shear rate (s^{-1})
η = viscosity.

If the liquid is non-Newtonian, viscosity is no longer a constant. Many emulsions are shear thinning, meaning that viscosity decreases with increasing shear rate[5].

The viscosity of an emulsion is directly proportional to the continuous phase viscosity, which is oil in the case of crude oil emulsions. When emulsified drops of water are introduced into a given flow field, the flow field becomes distorted and the rate of energy dissipation increases due to increased hydrodynamic interactions between the molecules[3,5]. This leads to an increase in the viscosity of the system. In other words, the effect of emulsified water is to create barriers to flow of oil molecules, so a change in shear stress will correspond to a smaller change in shear rate, which is shown as higher viscosity. As a result, the volume fraction of the dispersed water phase in a crude oil emulsion in the most important factor that leads to a viscosity increase[3].

Einstein's theory of viscosity for emulsions is given as[3,5]:

$$\eta_r = 1 + 2.5\phi \tag{2}$$

Where η_r = the relative viscosity; emulsion viscosity divided by oil viscosity
ϕ = the dispersed water volume fraction.

This model was developed assuming that the emulsion is dilute, meaning that the suspended particles are far apart, and that the particles are "hard spheres"[5]. In practice, particles are not really hard spheres, and when emulsions contain a significant volume fraction of emulsified water, the system is no longer dilute either. Most oilfield emulsions are outside of the range where Einstein's equation holds true[3]. Many empirical correlations have been developed to correct Einstein's equation for more concentrated emulsions. Pal[3] presents a comprehensive overview of many of the most common empirical emulsion viscosity fits.

The effect of emulsion droplet size can also affect the emulsion viscosity. In a dilute emulsion where the droplets are not hard spheres, the droplets will deform under shear, leading to non-Newtonian effects. Smaller droplets tend to behave more like rigid spheres, so their deformation will be less and viscosity will be higher[5]. For a constant emulsion volume fraction, smaller particles will also be closer together so the forces between the molecules will be greater and the viscosity will be higher as a result[6].

Many of the emulsion viscosity models present in the literature do not include the size of the droplets, based on the assumption that the volume fraction of the emulsified phase is the main contributing factor to the increase in viscosity over the oil viscosity. It should be noted, however, that droplet size can play a role in increasing viscosity as well.

NMR Fundamentals

Low field NMR measures the response of hydrogen protons in magnetic fields. Hydrogen protons have a property known as spin[4], which causes the protons to act as small bar magnets. In the presence of an external magnetic field, the protons will therefore tend to line up either parallel or anti-parallel to the external field lines. A pulse sequence is then applied to the protons, giving them energy and causing them to tip onto another plane, called the transverse plane. The protons precess about this plane and give off energy to the walls and to other protons. As they give off their energy, they return back to their equilibrium position. A low field NMR experiment measures two properties[7]: the strength of the signal, and a characteristic relaxation time. This characteristic time could either be the time for the signal to reappear in the direction of the external field lines (T_1) or the time for the signal to disappear in the transverse plane (T_2). T_2 measurements tend to be faster and are used in this paper.

The strength of the magnetic signal is directly proportional to the number of hydrogen protons in the fluid[4], which is a measure of fluid volume. In the lab, mass measurements can be taken more accurately than volume measurements and are directly comparable to volume measurements. An NMR parameter called *amplitude index* was defined to relate NMR amplitude to amount of fluid:

$$\mathrm{AI} = \frac{\mathrm{A_t}}{\mathrm{mass}} \tag{3}$$

Where A_t = the total amplitude of the measured sample
mass = mass of the sample.

In order to compare different molecular composition oils with one another, relative hydrogen index is also defined:

$$\mathrm{RHI} = \frac{\mathrm{AI_{bitumen}}}{\mathrm{AI_{water}}} \tag{4}$$

For a heavy oil or bitumen made of complex molecules containing branches and rings, the number of hydrogen protons present in a given mass will tend to be less than in the same mass of conventional oil. Conventional oils, with viscosities not significantly higher than water, have RHI values close to one. As viscosity increases, the general trend is for RHI values to decrease[8], although there is some scattering in this relationship. RHI can therefore be used as a loose indicator of viscosity.

As the excited protons in the transverse plane give off energy, they return to their equilibrium direction and the signal in the transverse plane decays. This process is known as relaxation. Three types of relaxation exist in porous media[4,7]: bulk relaxation, surface relaxation, and relaxation due to diffusion in the presence of magnetic field gradients. In the experiments performed for this paper, no magnetic field gradients were present so there were no diffusional effects leading to additional T_2 relaxation. Only bulk and surface relaxation of fluids were measured.

Bulk relaxation is a fluid property, and is a measure of how easily the protons give off energy to one another. Bulk relaxation can be expressed in the following form[7]:

$$\frac{1}{T_{2B}} \propto \frac{\eta}{T} \tag{5}$$

Where $1/T_{2B}$ = the rate of bulk relaxation (s^{-1})
T = absolute temperature of the sample.

Oil contains many components, and each component has its own characteristic time constant T_{2B}. The geometric mean T_2 for the components is therefore used in equation 5 to relate relaxation time to oil viscosity.

From equation 5 it can be seen that samples with higher viscosity will relax faster than samples with lower viscosity. This is because after the protons are tipped onto the transverse plane, they must give off energy to other protons in order to return to their equilibrium direction. Eyring's theory of viscosity states that in order for molecules to flow by one another after shear is applied, other molecules must give way in order for movement to occur[9]. Samples with higher viscosity have molecules that cannot move by one another as easily as samples with lower viscosity[9]. This lack of mobility in higher viscosity samples leads to more frequent exchange of energy between protons of these samples, allowing energy to be dissipated more rapidly. In this manner, an NMR experiment reproduces microscopically the phenomenon observed macroscopically in viscosity measurements.

Surface relaxation occurs when fluids are present in confined volumes, such as in small pores or emulsion droplets. This relaxation has the following form[4,7]:

$$\frac{1}{T_{2S}} = \rho \frac{S}{V} \tag{6}$$

Where ρ = surface relaxivity
S/V = surface to volume ratio.

Fluid in an emulsion, therefore, will relax due to bulk processes (a property of the fluid) and surface processes (a property of the fluid interface). The total relaxation rate is the sum of the two individual rates[4,7].

S/V for a spherical emulsion droplet corresponds to the droplet size. In order to determine what value of T_2 corresponds to a particular droplet size, however, the surface relaxivity of the oil-water interface must be known.

EXPERIMENTAL PROCEDURE

Around twenty-five heavy oil and bitumen samples were originally measured at 30° - 50°C. Viscosity measurements were performed using a Brookfield cone and plate viscometer, and NMR measurements were obtained using a Corespec 1000^{TM} relaxometer at a frequency of 1 MHz with TE = 0.3 ms and 5000 pulses. The results of this work were presented in a previous paper[8]. The correlation developed has been improved with the addition of more bitumen samples at very high viscosities, and an additional set of five bitumen samples of varying viscosity were measured from 25° - 80°C. For bitumen samples outside of the range of the Brookfield viscometer, viscosity measurements were performed using a Haake control stress cone and plate rheometer.

The oil samples measured had water fractions ranging from 0 – 11% water as a dispersed phase, although most of the samples contained under 5% water. To further investigate the effect of emulsified water on viscosity, six emulsions with dispersed water fractions ranging from 15 – 52% were measured from 25° - 80° C. Another twenty-four emulsions with water fractions ranging from 12 – 50% emulsified water were also measured at

30°C. All of these samples appeared to be a single oil phase to the naked eye. The viscosity measurements for these emulsions were performed using the Haake rheometer, and the NMR measurements were taken using the same parameters as for the oils. These NMR parameters provide 1.5 seconds of measurement time, which was seen to be long enough to capture the water signal even for large emulsion droplets where most of the relaxation occurs through bulk processes. In these droplets, there is still some surface effect to reduce the overall T_2 value of the water.

RESULTS AND DISCUSSION

Conventional oil NMR viscosity models[7,10] relate the oil viscosity to the geometric mean T_2, following the form of equation 5. These models were developed using conventional oils, which have very similar proton mobility to water. As a result, it was shown in a previous study[8] that these models grossly underestimate viscosity of heavy oil and bitumen mixtures. By correlating only T_{2gm} to viscosity, the conventional models have an upper limit in their viscosity predictions, so the models consistently underestimate bitumen viscosity. Other models avoid this problem by correlating viscosity to RHI, but the relationship between viscosity and RHI is not very strong[8]. An NMR viscosity model was previously developed[8] that relates both oil T_{2gm} and RHI to oil viscosity. This model can provide order of magnitude viscosity estimations for oils ranging from under 10 cP to 90 000 cP with an R^2 statistical fit of 0.95, but it did not predict viscosity very accurately for low viscosity conventional oils, and did not include bitumens over 100 000 cP. Higher viscosity oils have since been added, and the model has been tested over a wider temperature range. Based on 112 samples, the new NMR oil viscosity model is:

$$\eta = \frac{1.15}{(RHI)^{4.55} T_{2gm\_oil}} \tag{7}$$

This model collapses to a form very similar to the Kleinberg model[10] when measuring conventional oils. The results of this model are shown in Figure 1. This model provides an R^2 fit of 0.97 for samples ranging from just under 1 cP to over 3 000 000 cP, which is a larger range of viscosities than any other NMR viscosity model in the literature. This model was developed over temperatures ranging from 25° - 80°C. Temperature is not a required input parameter, as viscosity changes with temperature are incorporated in the NMR parameters RHI and T_{2gm_oil}, which also change with temperature for any given oil.

A representative emulsion NMR spectrum is shown in Figure 2. For all the samples analyzed in this paper, the first peak is taken to be oil and all subsequent peaks are taken to be water. The sample is liquid in a glass vial, so the first peak which has a T_{2gm} under 10 ms is viscous oil, relaxing through mainly bulk relaxation. The large peak at above 1000 ms is water in a large emulsion droplet, where relaxation is occurring mainly through surface processes. It should be noted that even for water in large droplets, there is some effect of surface relaxation, so the last peak still occurs faster than the bulk relaxation value for water (around 2.5 seconds). The other peaks between 10 – 300 ms are water in smaller emulsion droplets, where the surface effects are leading to faster relaxation. By taking the first peak as oil and all other peaks as water, NMR is able to predict the water fraction of a crude oil sample. This procedure has been proven elsewhere for water cut measurements[11]. As can be seen from Figure 4, there is significant water suspended in the oil even though the sample appears to be one continuous phase to the naked eye.

When this model is applied for emulsions with significant suspended water, the NMR oil viscosity model considers only the information from the first peak, and hence consistently underestimates the emulsion viscosity. This is shown in Figure 3. From 0 – 11% emulsified water, as measured by NMR, the emulsion viscosity prediction is still within an order of magnitude fit. Figure 3 shows that samples in this group have predicted viscosities that fall near the 45° line of equal NMR and measured viscosity. As the water fraction increases, however, predictions made using only the oil peak data consistently underestimate viscosity. The grouping of samples into 0 – 11%, 12 – 35% and >35% water was made simply by observing that within these ranges, the NMR oil viscosity model tends to underestimate viscosity by the same fraction.

It should be noted that even for samples with emulsified water, no shear thinning behavior was observed in the measurements of viscosity. An example shear stress vs. shear rate plot is shown in Figure 4. This data was gathered using the Haake rheometer. The slope of the line, indicating the measured viscosity is straight, indicating no shear thinning in the range measured. The maximum shear rate was kept low in order to ensure that no sample would leak out of the cone and plate assembly. It is possible that at higher shear rates some shear thinning may occur, but since NMR measurements do not apply changing shear to a sample, no shear thinning would be seen with NMR. As a result, non-Newtonian behavior was not of interest in these measurements.

In crude oil emulsions, the emulsified water fraction is generally thought to be the factor that contributes most to the increased viscosity of the emulsion[3]. This water leads to an increase in viscosity, and should be considered in the NMR estimation of viscosity. An NMR emulsion model was therefore developed to include the effect of the dispersed water fraction. This model computes oil viscosity using the first peak of the NMR spectrum (Equation 7) but then multiplies this viscosity by a polynomial involving the emulsified water fraction. The model is shown as:

$$\eta = \left[\frac{1.15}{(RHI)^{4.55} T_{2gm\_oil}} \right] \cdot \left[\frac{1}{(1 - x_w)^{4.46}} \right] \tag{8}$$

Where T_{2gm_oil} = geometric mean T_2 of the first peak, representing pure oil (s)
x_w = the dispersed water fraction.

This NMR water cut model has a similar form to many of the emulsion viscosity models presented in the literature[3], in that the emulsion viscosity is simply the oil viscosity multiplied by a polynomial of $(1 - x_w)$. As in the oil viscosity model, the power for the water fraction term was determined empirically. When this new NMR model was applied to the tested emulsions, Figure 5 was obtained. As can be seen, including the water fraction in the viscosity prediction brings all the samples back to the 45° line of equal NMR viscosity and measured viscosity.

The overall fit for the emulsions is shown in Figure 6, which is simply Figure 5 with a single trend line fitted through all the data. The NMR water cut model has slightly more scatter than the fit in Figure 1, which only contained oils with less than 12% water. The R^2 fit of the emulsion water cut viscosity model is 0.92, as opposed to 0.97 for the oils. This could be in part to the fact that if the emulsion was not homogeneous then the sample measured in NMR may not have identical water content to the sample measured using the rheometer. It is also possible that some very small water emulsion droplets may be hidden in the first peak of the spectrum that was attributed to oil, which would be another cause of scatter. The oil peak has also shifted due to the presence of the significant oil-water interface, and this has not been considered when determining oil viscosity for the emulsion model. Despite these difficulties, however, it can be concluded that NMR is capable of making order of magnitude viscosity predictions even for emulsions with 50% suspended water over a wide range of viscosities and temperatures.

Theoretically, the size of the emulsified water droplets should also impact the viscosity of the emulsion[3,5]. Figure 2 shows that different sized emulsion droplets have different T_2 values, so the NMR water spectrum can indicate the relative fraction of large vs. small droplets. Without having an independent measure of either surface relaxivity or droplet size, however, these T_2 values cannot be directly correlated to actual droplet sizes. Peña and Hirasaki[12] present a method of using NMR to predict both surface relaxivity and droplet size, but these findings have not yet been tested by our group. In spite of this limitation, the water fraction is the major cause of increased emulsion viscosity[3], and the NMR emulsion viscosity model uses this with good success.

CONCLUSIONS

An NMR based oil viscosity model has been developed that can provide order of magnitude viscosity predictions for oils ranging from under 10 cP to 3 000 000 cP, over a temperature range of 25° - 80°C. This model predicts oil viscosity with an R^2 fit of 0.97 over a wider range of oil viscosities than any other NMR model in the literature.

When the emulsified water fraction exceeds 12%, the NMR oil viscosity model begins to underestimate viscosity. As the water fraction increases, the NMR estimate gets progressively worse. This is because the model only considers the oil signal, and emulsion viscosity is higher than its constituent oil viscosity due to the presence of water. An NMR emulsion model was developed that incorporates the water fraction of the emulsion as well, and can predict emulsion viscosity with order of magnitude accuracy and an R^2 fit of 0.92. The NMR model does not include the effects of emulsion droplet size, but the water fraction is the main contributor to increased viscosity and this is included in the model.

If these results could be applied *in-situ*, the oil viscosity correlation could be applied on a logging tool or as a laboratory analysis for ore, to give order of magnitude estimates of viscosity change in different heavy oil and bitumen bearing formations. The emulsion viscosity model could be applied online in a pipe or process stream or again as a laboratory analysis tool, to estimate changes in viscosity due to the presence of emulsified water at different fractions and droplet sizes. These measurements can be performed quickly and easily, without technician bias or error, even for very high viscosity oils and oil emulsions.

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NOMENCLATURE

AI	Amplitude index; the measured NMR amplitude / g of sample
A_t	Total NMR amplitude
RHI	Relative hydrogen index; sample AI / water AI
S/V	Surface to volume ratio for fluid in a confined space
T	Absolute temperature
T_2	Transverse relaxation time constant (s)
T_{2gm}	Geometric mean T_2 value of a distribution of components (s)
x_w	Water fraction in an emulsion
ϕ	Dispersed water volume fraction in Eintein's theory of emulsion viscosity
$\dot{\gamma}$	Shear rate (s^{-1})
η	Viscosity (Pa s)
ρ	Surface relaxivity
τ	Shear stress (Pa)

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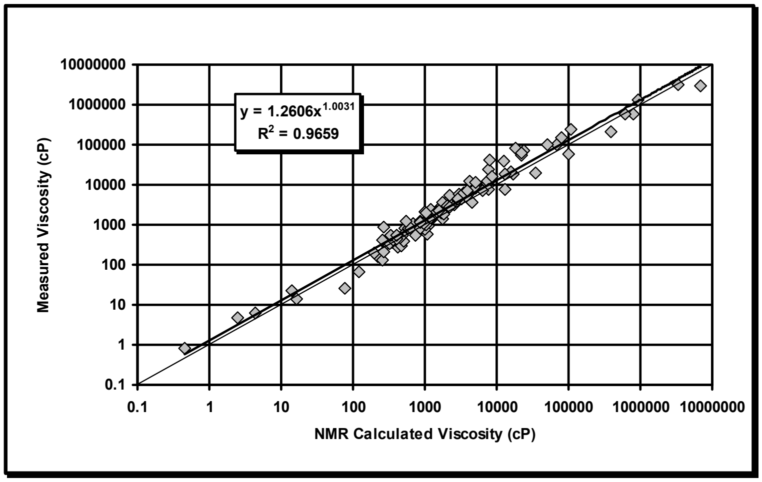

Figure 1. Oil Viscosity Model Results

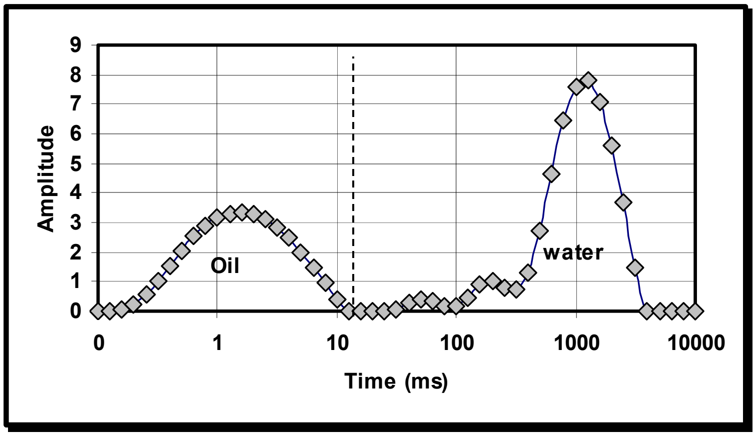

Figure 2. Representative Emulsion NMR Spectrum

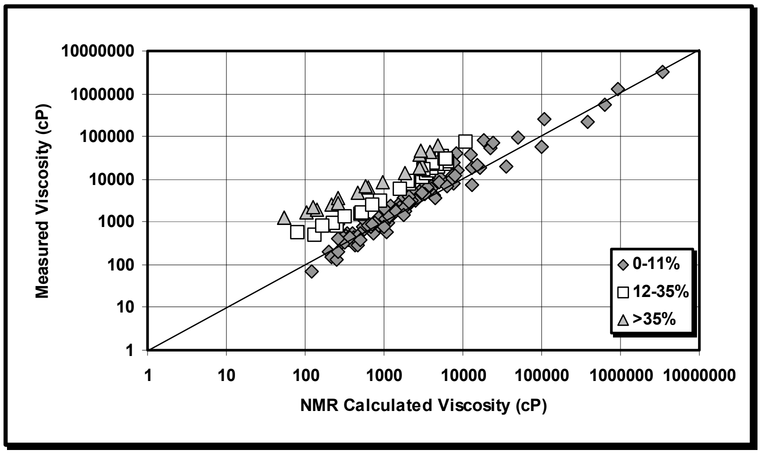

Figure 3. Emulsion Viscosities Predicted Using NMR Oil Viscosity Model

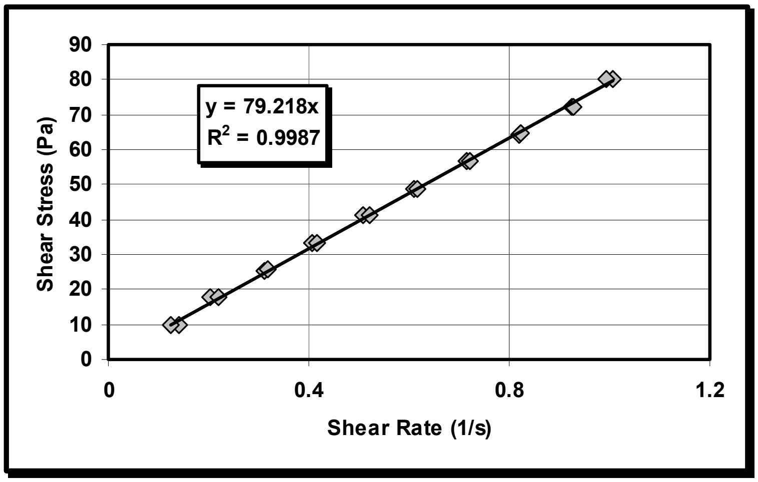

Figure 4. Measured Viscosity of a Crude Oil Emulsion

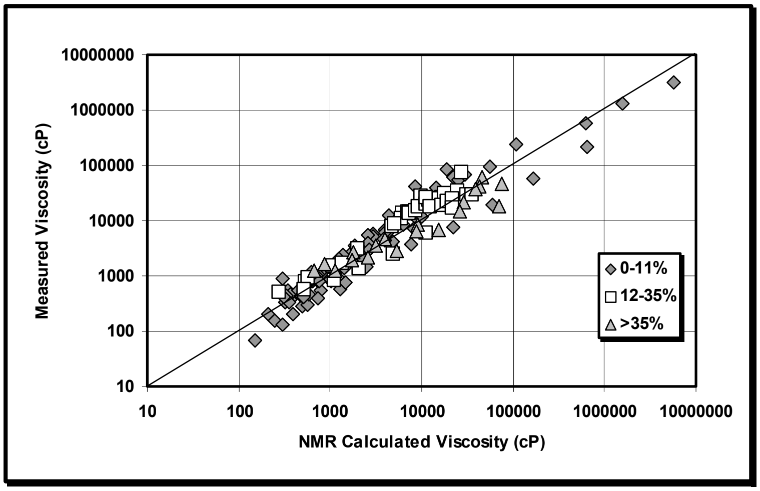

Figure 5. Emulsion Viscosities Using the NMR Emulsion Viscosity Model

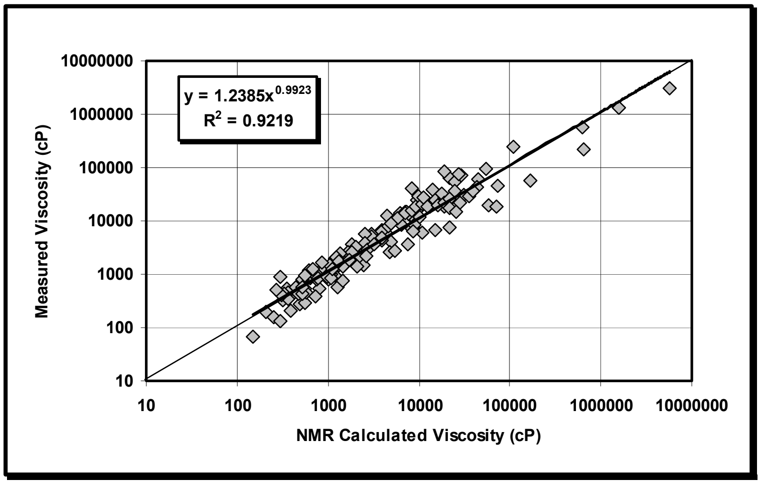

Figure 6. NMR Water Cut Emulsion Viscosity Model Fit