

# IMPROVEMENT OF VISCOSITY PREDICTION USING NMR RELAXATION

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## ABSTRACT

In a previous paper, we proposed to build the  $T_2$ -viscosity relationship using the Bloembergen theory based on the dipole-dipole interaction of neighboring spins modulated by Brownian motions. This theory was extended to a distribution of correlation times to predict medium and high viscosity from  $T_2$  measurements. For very high viscosity, the deviation from the theory was explained essentially by the problem of short component detection. A methodology was proposed for generating the  $T_2$ -viscosity relationship taking into account the fluid and spectrometer properties. In this work we take into account additional effects occurring at low and medium viscosity: the effect of the inter proton effective distance and the change of slope of the  $T_2$ -viscosity relationship near the minimum value of  $T_1$ .

The variation of the effective inter proton distance  $b$  between different oils is an important source of uncertainty. It can be deduced from measurements of  $T_2$  at 2 frequencies (in our case 2 and 23 MHz). For oils containing different amounts of saturated components, we show that the data collapse on a single curve when taking into account the measured  $b$  value.

For medium viscosity oils, a change of slope in the  $T_2$ -viscosity relationship around 1000 cP can be explained by the Bloembergen theory extended to a distribution of correlation times. When taking into account this effect in the above mentioned methodology, a good agreement between theory and data is obtained.

## INTRODUCTION

The link between NMR relaxation and fluid viscosity has been established since the early days of NMR by the pioneering work of Bloembergen (1961). For petroleum application, Brown (1961) studied longitudinal relaxation ( $T_1$ ) of some crude oils over a wide range of temperature and viscosity. Using the initial slope of the magnetisation decay curve as a

measure of the relaxation time, he found a global correlation between viscosity and relaxation time. Much later, Morris (1994) measured the distribution of transversal relaxation times ( $T_2$ ) on several crude oils. In contrary to refined oils that exhibit narrow  $T_2$  distributions, crude oils have generally wide  $T_2$  distributions spanning over several decades. In addition, as viscosity increases, the  $T_2$  distribution are always very large while the short time components becoming more and more important. To avoid unnecessary complications a representative parameter, the logarithmic mean of the distribution  $T_{2ml}$ , has been chosen by many authors. It is defined as:

$$T_{2ml} = \exp(\overline{\log(T_2)}) \quad (1)$$

Numerous empirical correlations can be found in the literature to relate  $T_{2ml}$  to the macroscopic viscosity. Very simple equations have been proposed (Straley et al. (1994) and Kleinberg and Vinegar (1996)). Some author proposed more complex equations, taking into account the effect of dissolved oxygen (Zega et al. (1990), Zhang et al. (1998) and Lo et al. (1998, 2000)) or the lack of detection of the short  $T_2$  components (Bryan et al. (2002a, 2002b) and LaTorraca et al. (1998, 1999))

If numerous correlations can be found to link NMR relaxation times to viscosity, these works raises three main issues:

- the problem of short component detection. For viscous oils, the short components are underestimated or not detected resulting in an signal loss,
- the exact origin of the change of curvature in the  $T_2$ - $\eta$  relationship,
- the dependence of the correlation with the characteristics of the NMR instrument

In a previous paper (Nicot et al. 2006) we proposed a new methodology to predict the relationship between relaxation time and viscosity. We used the theory proposed by Bloembergen (1961) valid for small molecules with nearly a single relaxation time and extended it to large molecules with a distribution of relaxation times. In addition, we simulate the lack of

detection of the shortest  $T_2$  components for heavy oils to predict the change of curvature.

In this paper, we first propose a way to improve the accuracy of the viscosity prediction, by taking into account the variations in the inter proton distance, a key parameter in the theory. We propose a method to estimate its effective value based on a two frequency NMR measurement (Part 1). Then we propose a way to improve our previous methodology by taking into account the inflexion point in the theoretical curve  $T_2=f(\tau_c)$  yielding an additional change of curvature of the  $T_2$ -viscosity relationship.

## THEORY

In order to relate NMR relaxation times to the macroscopic viscosity, one need to understand the theoretical relationship between NMR relaxation and Brownian molecular motions, and the underlying assumptions. The theoretical model for NMR relaxation developed by Bloembergen (1961), considers two protons on the same molecule. The relaxation of these protons is linked to the characteristic time  $\tau_c$  of reorientation of the proton-proton vector, called correlation time. If one considers that these protons undergo rotational Brownian motions, one can express the NMR relaxation times  $T_1$  and  $T_2$  as a function of the correlation time  $\tau_c$  and of the inter proton distance  $b$ :

$$\begin{aligned} \frac{1}{T_1} &= C \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right) \\ \frac{1}{T_2} &= C \left( \frac{3}{2} \tau_c + \frac{5}{2} \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right) \quad (2) \\ C &= \frac{3}{10} \left( \frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma^4}{b^6} \end{aligned}$$

where  $\gamma$  is the proton magnetogyric constant,  $\omega_0$  is the Larmor frequency and  $\mu_0$  is the magnetic permittivity of free space. Note that  $b$  is at the power 6 in the above formulae.

The reorientation of the proton bearing molecule subjected to rotational Brownian motions can be described in a macroscopic way using the Debye model, and the Stokes Einstein equation, leading to:

$$\begin{aligned} \tau_c &= \frac{1}{6D_{rot}} \\ D_{rot} &= \frac{kT}{8\pi\eta a^3} \quad (3) \end{aligned}$$

where  $D_{rot}$  is the rotational diffusion coefficient of a hard sphere of radius  $a$  in a uniform media of viscosity  $\eta$ .

As a result, knowing the values of the inter proton distance  $b$  and of the Stokes Einstein radius  $a$ , one is able to plot the theoretical relationship between the NMR relaxation times  $T_1$  and  $T_2$  and the viscosity.

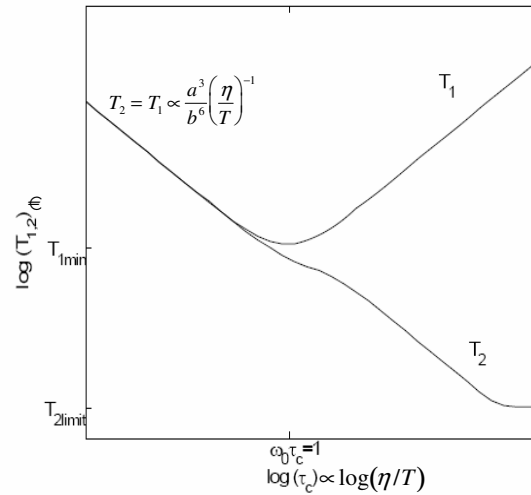


Figure 1 :  $T_1$  and  $T_2$  versus viscosity, as predicted by the theory.

When studying different fluids, different crude oils with different compositions, one can easily imagine that the parameters  $a$  and  $b$  can change.  $a$  can a-priori be linked to the molecular size, and variations in  $b$  can arise from different compositions in saturates and aromatics. In fact, as shown in Figure 2, the effective inter proton distance in the presence of a carbon-carbon double bond is bigger than the one on saturated oils.

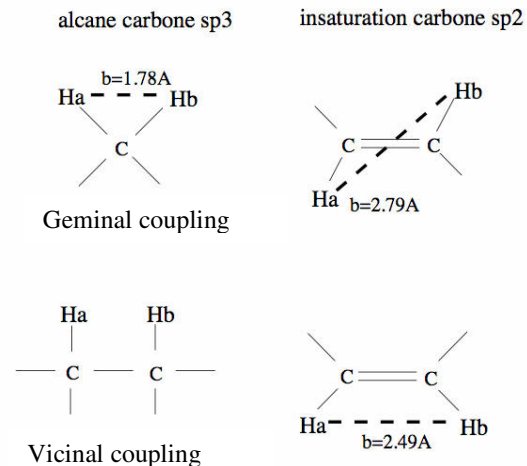


Figure 2 : inter proton distances calculated in methane (left) and in ethylene (right)

## EXPERIMENTS

### Samples

In order to study the effect of molecular size we studied different mineral oils of different viscosities: durasyn, albelf, marcol\_172, Squalane and Marcol\_52. Some non saturated oils were also studied, like sunflower and olive oil. For Part 1 we also studied two oils of similar molecular size and chemical formula, but one is saturated (Squalane) and the other exhibit unsaturated parts (Squalene). The chemical formulas of these products are given in Figure 3. For Part 2, we studied also crude oils, including a heavy oil from Venezuela.

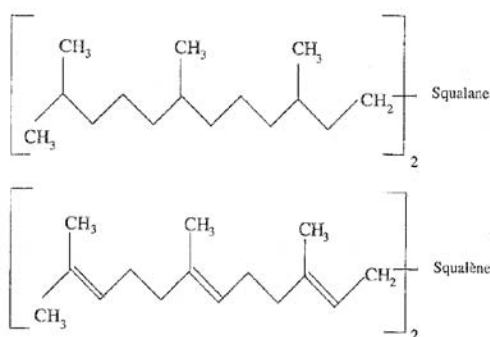


Figure 3 : Chemical formulas of Squalane and Squalene

### NMR measurements

We measured the NMR relaxation times  $T_1$  and  $T_2$  using a 23MHz and a 2 MHz MARAN Ultra proton spectrometer from Oxford instrument. The  $T_2$  relaxation times were measured using the classical CPMG sequence using an inter echo time of 100  $\mu\text{s}$ . The  $T_1$  relaxation times were measured using the Inversion Recovery sequence using 80 points. The number of scans is set such as to obtain a signal to noise ratio of the order of 200. The data were then treated by inverse Laplace transform to obtain the  $T_2$  and  $T_1$  distributions. The results presented here are the log mean values  $T_{2ml}$  and  $T_{1ml}$  of these distributions.

Control and variation of temperature were performed using a heated air flow system on the 23 MHz, a heating cell on the 2MHz instrument. The temperature of the magnets is stabilized at 30°C.

### Viscosity measurements

The samples viscosity was measured using a cone-plate rheometer AR1000 from TA Instruments. For each sample, the Newtonian behavior was verified. The temperature was controlled by a Pelletier system in the plane.

## PART 1:

In this section, we study the effects of the two parameters  $a$  and  $b$  on the  $T_2$ -viscosity relationship.

### T2-VISCOSITY RELATIONSHIP

When presented on a  $T_{2ml}$ -viscosity cross plot (Figure 4) the results of this study show clearly a systematic shift between the saturated and non saturated oils as the result of different inter proton distances. However, within the saturated oils, we did not observe any significant effect of the molecular size.

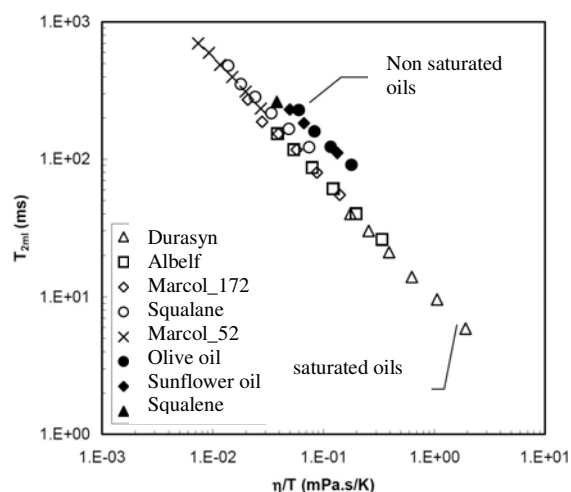


Figure 4 : log mean relaxation time  $T_2$  measured at 2MHz versus viscosity/temperature ratio.

### INTER PROTON DISTANCE CALCULATION

We propose an approach to estimate the effective inter-proton distance. By effective inter-proton distance we mean the inter proton distance that counts for the relaxation process, which can be different from the real one. One obvious reason for this distance to be different is the occurrence of a third interacting proton in the relaxation process for example.

The effective inter proton distance is estimated using measurements of relaxation time  $T_2$  at two different frequencies. The frequencies available in our laboratory are 2.2 MHz and 23.7 MHz. For each frequency, the average relaxation time  $T_2$  is given by the BPP model:

$$\frac{1}{T_2} = C \left( \frac{3}{2} \tau_c + \frac{5}{2} \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right) \quad (4)$$

In this equation the unknowns are the average correlation time  $\tau_c$  and the inter proton distance  $b$ . By measuring  $T_{2ml}$  at two different frequencies ( $\omega_h$ ) we

obtain two equations, enabling us to determine the two unknowns.

### EXAMPLE

We applied the two frequency technique on two different fluids, Squalane and Squalene. These fluids have been chosen for having similar chemical formula and therefore similar molecular sizes. By measuring  $T_{2ML}$  on Squalane at 2.2 and 23.7 MHz we found  $b=2.34\text{\AA}$  ( $1\text{\AA}=10^{-10}\text{m}$ ) and  $\tau_c=1.6 \cdot 10^{-9}\text{s}$ . For Squalene we found  $b=2.50\text{\AA}$  ( $1\text{\AA}=10^{-10}\text{m}$ ) and  $\tau_c=1 \cdot 10^{-9}\text{s}$ . The compound that exhibits the largest inter proton distance (Squalene) is the non saturated one. As expected, the effect of the presence of non saturated carbons, is to increase the effective inter proton distance. Moreover, we found the longest correlation time for the most viscous fluid (Squalane  $\eta=22.5\text{cP}$  at  $30^\circ\text{C}$ ) and the shortest correlation time for the less viscous fluid (Squalene  $\eta=11.5\text{cP}$  at  $30^\circ\text{C}$ ).

As the parameter  $b$  appears to the power 6 in the theory, any small error in the determination of this parameter may have important effects. Hence, we rely on the accuracy of the  $T_{2ml}$  measurements. To estimate the uncertainties, we used a Monte Carlo approach. We generated 200 NMR synthetic magnetization decays representative of the signals of Squalane and Squalene. For each of them, a different random noise representative of the measurements was added. Then, we applied the inverse Laplace transform to obtain the  $T_2$  distributions, and then extracted the log mean value  $T_{2ml}$ . A histogram of the 200  $T_{2ml}$  values gives an estimation of the errors (about  $\pm 1\text{ms}$ ). Errors on the estimation of the effective inter proton distance  $b$  follows:

$$\begin{aligned} 2.33\text{\AA} < b_{\text{Squalane}} < 2.36\text{\AA} \\ 2.48\text{\AA} < b_{\text{Squalene}} < 2.56\text{\AA} \end{aligned} \quad (5)$$

Therefore, the measured differences are significant and we can approximate the results to the first digit:  $b_{\text{Squalane}}=2.3\text{\AA}$  and  $b_{\text{Squalene}}=2.5\text{\AA}$

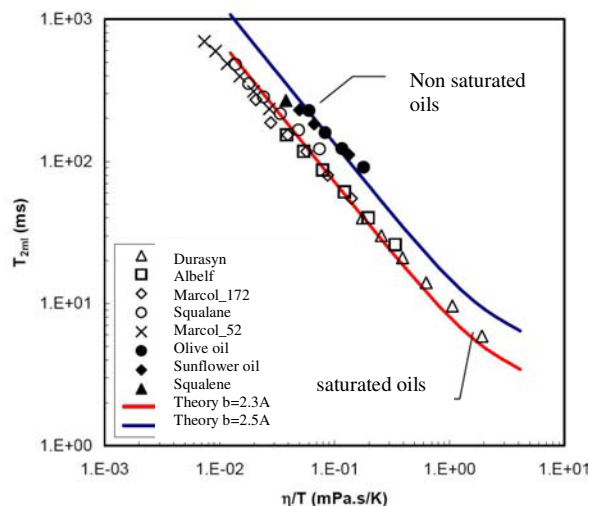
### COMPARISON WITH THE THEORY

We used the values of  $b$  found previously with our two frequency approach and adjusted the parameter  $a$  to fit the experimental data (Figure 5). For the saturated oils we used the  $b$  value found on Squalane and for the non saturated oils the  $b$  value found on Squalene.

In addition, when the effective inter proton distance  $b$  is known, we can obtain the parameter  $a$ . For both data set, we used the same value for the Stokes Einstein radius  $a=4.3\text{\AA}$ . Such a small value means that NMR relaxation in large molecules is sensitive to very local motions, concerning only small segments of molecules. An order of magnitude of the size of these segments is

found to be  $8\text{\AA}$ . This explains why the Bloembergen theory, valid on small molecules, can be used on complex oils.

In conclusion, the accuracy of viscosity prediction can greatly be improved by including the possible fluctuations of the inter proton distance  $b$  due to a change of oil composition within a given field. The present study suggests that the parameter  $a$  plays a minor role in the scatter of experimental  $T_2$ -viscosity correlations.



**Figure 5 : Comparison between experimental results and theory. The theoretical results were calculated using the  $b$  values found for Squalane and Squalene and  $a=4.3\text{\AA}$ .**

## PART 2

In this section, we study the effects of the inflexion point that appears in the  $T_2$  curve in Figure 1.

### PRINCIPLE

In a previous paper (Nicot et al. 2006) we presented a novel approach to predict heavy oil viscosities using NMR Relaxation. This approach consisted in several steps, aiming at taking into account the presence of distributions of relaxation times and measurement limitations. In fact, when the relaxation time becomes small compared to the inter echo time of the CPMG sequence, the shortest part of the  $T_2$  distribution is not well resolved, resulting in a decrease of the apparent hydrogen index. We performed a quantitative study to assess these effects.

The principle was to calculate the viscosity from a  $T_2$  distribution considered fully resolved. From this distribution, we simulated the  $T_2$  distribution that would be really measured, and extracted its log mean value

$T_{2mlexp}$ . This workflow enabled us to build  $T_2$ -viscosity relationships.

The calculation of viscosity, called “step 2” in this previous paper, was performed using a correlation between the log mean  $T_2$  of the fully resolved distribution and the viscosity;

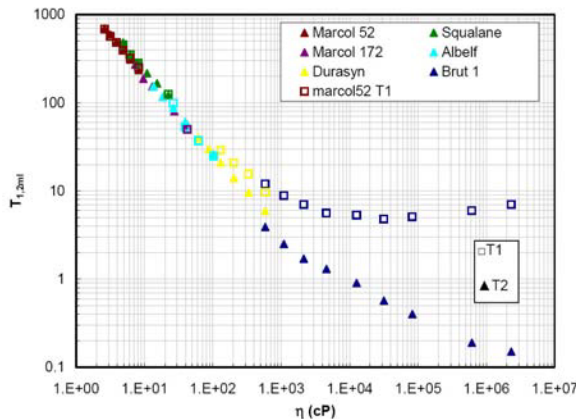
$$T_{2ml} = A\eta^{-n} \quad (6)$$

where  $A$  and  $n$  can be chosen from literature (e.g.  $A=1200$ ,  $n=0.9$ , [Straley, 1994]) or derived from a set of experimental data.

Although this empirical correlation gave good results for heavy oils, it may not be the case around about 1000 cP. Indeed, the theory predicts a power law between  $T_2$  and viscosity only below  $\omega\tau_c$  (Figure 1). At  $\omega\tau_c=1$ , there is an inflection point in the curve. For crude oils with large  $T_2$  distributions, this inflection point will be smoother and less obvious. In order to take into account this effect, we modified “step 2” in our methodology in order to calculate the viscosity not directly from  $T_2$ , but from the log mean value  $\tau_{cml}$  of the correlation time distribution:

$$\eta = A\tau_{cml}^{1/n} \quad (7)$$

In the domain where  $\omega\tau_c \ll 1$  (non viscous liquids), one can approximate  $1/T_2 = 5C\tau_c$  and then determine the parameters  $A$  and  $n$  from a set of experimental data. From our set of experimental data (Figure 6) we found  $n=0.9$  and  $A=1.656*5C$ , giving  $\eta$  in cP if  $\tau_{cml}$  is in s.



**Figure 6 : Measured log mean relaxation times  $T_1$  and  $T_2$  as a function of viscosity on a set of mineral and crude oils.**

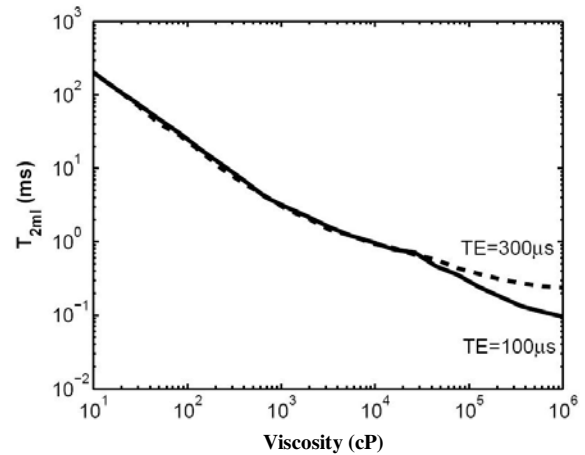
In the domain where  $\omega\tau_c \gg 1$  (very viscous liquids), the use of this relationship enable us to take into account the existence of the inflection point in the  $\log(T_2)$ - $\log(\tau_c)$  by calculating  $\tau_{cml}$  from  $T_{2ml}$  using the BPP model.

## RESULTS

Using our improved methodology, we were able to create different NMR-viscosity relationships, depending on the width of the  $T_2$  distribution and on the inter echo time of the CPMG sequence. On Figure 7 we present the results on this procedure for two different values of the inter echo time: 100 and 300  $\mu$ s.

For low viscosity ( $\eta < 1.000$  cP), we obtain the classical linear relationship between  $\log(T_2)$  and  $\log(\eta)$ . For very high viscosity ( $\eta > 10.000$  cP) we obtain different results depending on the inter echo time. In this domain, the viscosity is very high such as the shortest components of the  $T_2$  distribution are not detected. As a result, the log mean  $T_{2ml}$  is overestimated, and the curve is very sensitive to the inter echo time; for a larger inter echo time,  $T_{2ml}$  is more overestimated.

For intermediate viscosity ( $1.000 \text{ cP} < \eta < 10.000 \text{ cP}$ ), one can observe a deviation of the curve from linearity not due to measurement problems. This deviation is due to the theoretical inflection point in the  $T_2 = f(\tau_c)$  theoretical curve (Figure 1).

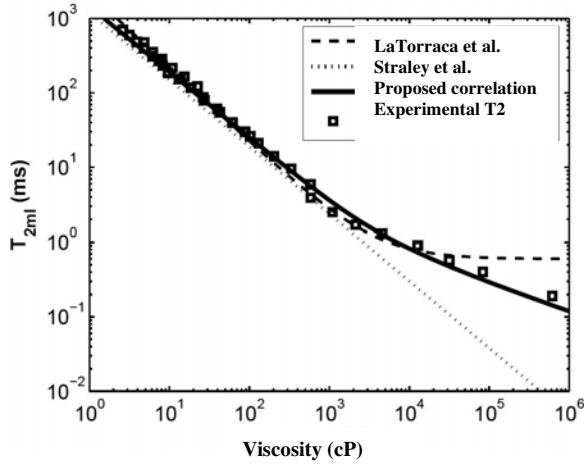


**Figure 7 :  $T_2$  versus viscosity curves obtain for two different values of the inter echo time  $TE$**

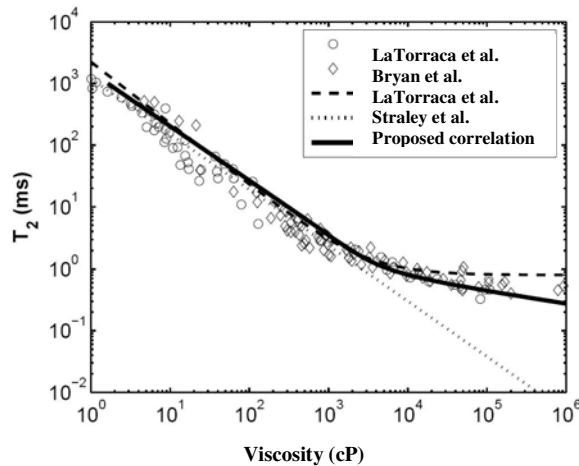
For practical application, it is convenient to have an analytical formula. As proposed by Nicot and al. 2006, we fitted our results to the following equation :

$$\eta = KT_{2ml}^{-n_1} \frac{1 + CT_{2ml}^{-n_2}}{1 + C} \quad (8)$$

We then compared the obtained analytical equation to the equations proposed by Straley et al. and LaTorraca et al. on two different data sets. The first data set has been acquired in our laboratory, using an inter echo time  $TE=100 \mu$ s (Figure 8) and the second dataset is from the literature, using an inter echo time  $TE=300 \mu$ s (Figure 9).



**Figure 8 : Comparison between our viscosity prediction and different correlation proposed in the literature on a dataset from our laboratory (2MHz,  $TE=100\mu s$ )**



**Figure 9 : Comparison between our viscosity prediction and different correlation proposed in the literature on a dataset from the literature (2MHz,  $TE=300\mu s$ )**

In both cases, a clear improvement in viscosity prediction is obtained, particularly for viscous oils ( $\eta > 1000\text{cP}$ ).

## CONCLUSION

In PART 1, on the basis of the Bloembergen theory, we show that a key parameter in the NMR-viscosity relationship is the inter proton distance. The fluctuations of the Stokes Einstein radius  $a$  between different oils may be less important. We propose a simple NMR method to measure the effective inter proton distance. Using this method, we proved that the differences observed in the  $T_2=f(\eta)$  graph between saturated and non saturated oils are due to small variations in the effective inter proton distance. As this parameter appears to the power 6 in the equations, these small variations have a non negligible effect on the relaxation time values. We showed that the NMR relaxation is sensitive to very local molecular motions. The size of the molecular segment that reorients during the relaxation process is of the order of 8 Å ( $1\text{Å}=10^{-10}\text{m}$ ).

In PART 2, we improved the previously proposed methodology to predict viscosity using NMR relaxation. On the basis of a theoretical study, we propose a way to take into account the inflection point in the  $T_2=f(\tau_c)$  curve. This enables us to explain the early departure from linearity observed on the experimental  $T_2=f(\eta)$  curves in log-log scale. This methodology has been tested on a data set from our laboratory and on data from the literature, showing in both cases a clear improvement of the viscosity prediction, particularly for viscous oils ( $\eta > 1000\text{cP}$ ).

## ACKNOWLEDGEMENTS

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