

Power-law Relationship between the Viscosity of Heavy Oils and NMR Relaxation

Yuesheng Cheng¹, Abdel M. Kharrat¹, Rob Badry² and Robert L. Kleinberg³

1. Schlumberger-DBR, Edmonton AB

2. Schlumberger of Canada, Calgary AB

3. Schlumberger-Doll Research, Cambridge MA

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ABSTRACT

Knowledge of viscosity is required to develop and manage heavy oil reservoirs. There are good correlations between viscosity and NMR relaxation time for relatively light oils. However, highly viscous (heavy) oils fail to follow these correlations. Numerous papers discuss the use of NMR for estimating the viscosity of heavy oils. All these correlations are based on the assumption that the oils are Debye fluids, i.e., that the molecular correlation function decays exponentially. Conventional correlations fail for heavy oils because the exponential decay approach is conceptually inappropriate.

In this paper, we present a new relationship between NMR relaxation time and viscosity based on the Kohlrausch-Williams-Watts (KWW) molecular correlation function for inhomogeneous fluids. The new relationship has been validated by measurements on a substantial sampling of Canadian and international dead oils, and on a wide range of recombined live oils.

INTRODUCTION

Viscosity measurements are needed to determine if cold production of heavy oil will give economic rates of production, or if thermal processes will be required. If cold production is selected, viscosity is again used to help determine whether vertical or horizontal wells should be used. Viscosity data are also used to adjust cold production exploitation strategies if the production rates are significantly lower than expected.

The NMR relaxation times of bulk fluids are sensitive to molecular rotational and translational correlation times, which are controlled by viscosity and temperature. Although there is a good correlation between viscosity and NMR relaxation time for relatively light oils, a generally accepted correlation for

heavy oils has been lacking. In this paper, we present a new approach to this problem.

Literature Review

Presently there are three widely-used correlations between oil viscosity and NMR relaxation time [Zega et al., 1990; Kleinberg and Vinegar, 1996; Zhang et al., 1998]. These three correlations have some physical foundation and work well for conventional oils. However, they break down for oil viscosities greater than 1000 cP, see Figure 1.

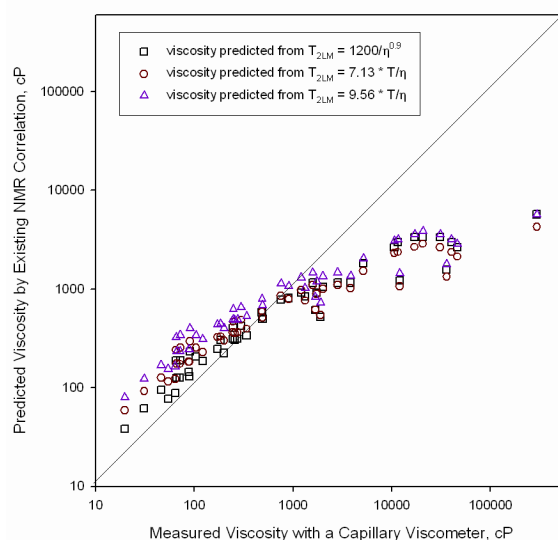


Fig. 1 Laboratory-measured viscosity versus viscosity estimated from three conventional correlations. The data represent fourteen Canadian and international heavy oil samples, with temperature ranging from 10°C to 110°C.

To deal with the heavy oil problem, LaTorraca et al. [1999], Bryan et al. [2002], and Burcaw et al. [2008] utilized the apparent hydrogen index concept. Looking into fundamental NMR relaxation mechanism, Nicot et al. [2006] proposed a method combining the classic

BPP approach [Bloembergen et al., 1948] with a distribution of correlation times.

Experiments

The fourteen heavy oil samples for this study were collected from various regions of the world. Three of the oils were charged with varying amounts of a gas mixture, the composition of which is listed in Table 1. Nine live oils with gas oil ratios ranging from 8 to 28 m³/m³ were produced. Laboratory values of viscosity, determined with a capillary viscometer, ranged from 20 cP to 900,000 cP at temperatures from 10°C to 150°C.

Table 1. The composition of the gas mixture

Component	mol%
Carbon Dioxide	10.11
Methane	77.72
Ethane	4.32
Propane	3.00
i-Butane	0.85
n-Butane	1.45
i-Pentane	0.60
n-Pentane	0.48
Hexane	1.47

For the NMR measurements, heavy oils were loaded into a ceramic tube (1.59 cm i.d. x 5.09 cm long) inside a high temperature, high pressure sample holder supplied by Temco. Fluorinert was used to control temperature and to balance the pressure of live fluids. Sample temperatures between 10°C and 110°C were achieved by circulating Fluorinert. The desired temperature was maintained to within ±1°C with a Temco temperature control unit.

Measurements were made at 2 MHz using an Oxford Big 2 NMR instrument. The proton spin-lattice relaxation time (T_1) was measured by the saturation recovery technique. Proton spin-spin relaxation time (T_2) was determined by a modified Carr-Purcell-Gill-Meiboom (CPMG) pulse sequence with $2\tau = TE = 200 \mu s$ and a cycle time greater than 5 times T_1 . The T_2 distribution was recovered by a numerical inverse Laplace transform of time domain CPMG echo signals. The logarithmic mean of the T_2 distribution is defined by

$$T_{2LM} = \left(\prod_{i=1}^n T_{2i}^{n_i} \right)^{1/\sum_i n_i}$$

or

$$\ln(T_{2LM}) = \frac{\sum_i n_i \ln(T_{2i})}{\sum_i n_i} \quad (1)$$

where n_i is proportional to the number of protons corresponding to the i^{th} component in the T_2 distribution spectrum.

Relaxation Theory

Nuclear spin relaxation is a consequence of the coupling of the spin system to its surroundings. Atoms and molecules are in a constant state of thermally activated rotation and translation, which in turn generate rapidly fluctuating magnetic and electric fields. It is these oscillating fields which provide relaxation mechanisms.

Relaxation times depend on the nature of the coupling, of which there are many forms including dipole-dipole coupling, quadrupolar coupling (nuclear spin $> 1/2$), chemical shift coupling, scalar coupling and spin-rotation interactions. For nuclei like hydrogen, for which $I = 1/2$, dipole-dipole coupling is usually the dominant source of relaxation mechanism.

To quantify the effect of the molecular motion on relaxation, we define the autocorrelation function,

$$G(\tau) = \langle F(t)F(t+\tau) \rangle, \quad (2)$$

where $F(t)$ is the time dependent function of molecular position and orientation. $G(\tau)$ is the correlation between the function at a time t and a later time $t + \tau$, i.e. it describes how the value of the function depends on its previous values. The Fourier transformation of the auto correlation function gives the spectral density, which describes the relative contributions of the Fourier components of the motion:

$$J(\omega) = \int_{-\infty}^{\infty} G(\tau) e^{i\omega\tau} d\tau. \quad (3)$$

Typically if the motional correlation time is τ_c , the motions contain a spectrum of frequencies up to $\omega \sim 1/\tau_c$.

The relaxation rates $1/T_1$ and $1/T_2$ for two identical spins are related to the spectral density function by:

$$\frac{1}{T_1} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} I(I+1) [J(\omega_0) + J(2\omega_0)] \quad (4)$$

$$\frac{1}{T_2} = \frac{3}{8} \frac{\gamma^4 \hbar^2}{r^6} I(I+1) [J(0) + J(\omega_0) + J(2\omega_0)]. \quad (5)$$

Here, I is the spin quantum number and r is the distance between two spins of gyromagnetic ratio γ . \hbar is Plank constant divided by 2π . ω_0 is the Larmor frequency [Abragam, 1960].

According to Debye's theory, the autocorrelation function is normally expressed in terms of a single exponential decay

$$G(\tau) = \langle F(0)^2 \rangle e^{-|\tau|/\tau_c} \quad (6)$$

Then the relaxation rates become the following popular BPP expressions [Bloembergen et al., 1948]:

$$\frac{1}{T_1} = \frac{3}{10} \frac{\gamma^4 \hbar^2}{r^6} \left[\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right] \quad (7)$$

$$\frac{1}{T_2} = \frac{3}{20} \frac{\gamma^4 \hbar^2}{r^6} \left[3\tau_c + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right]. \quad (8)$$

However it is well known that the correlation of molecular motion in many complex liquids cannot be expressed as a single exponential decay. This has been shown to be true in a wide variety of organic liquids and solutions, polymers, and glass-forming materials. For glasses, correlation times range from microsecond time scale of the segmental motions to minute or hour time scale of the entire chain motions. Similar molecular dynamic behaviors have been observed by dielectric relaxation, photon correlation spectroscopy and mechanical relaxation experiments.

Generally, one can write the correlation function

$$G(\tau) = \int \rho(\tau_c) f(\tau, \tau_c) d\tau_c \quad (9)$$

where $\rho(\tau)$ is the distribution of correlation times and $f(\tau, \tau_c)$ is the general expression of the decaying function.

Two limiting scenarios have been discussed. The first scenario is that non-exponential molecular dynamic behavior is due to a spatial distribution of simple molecular processes, each governed by an autocorrelation function which decays exponentially,

$f(\tau, \tau_c) = e^{-\tau/\tau_c}$. This corresponds to the fully heterogeneous limit, which is the underlying physics for all previous correlations.

At the other extreme, all molecular processes are assumed to be characterized by the same autocorrelation function, but one with an inherently nonexponential decay. An empirical stretched-exponential function, also known as the Kohlusch-Williams-Watts (KWW) function, has found widespread acceptance. In this model, the autocorrelation has the form

$$G(\tau) = \langle F(0)^2 \rangle e^{-(\tau/\tau_c)^\gamma} \quad (10)$$

For the intermediate case between these two extremes, the correlation function can be expressed as

$$G(\tau) = \int \rho_{\gamma_{in}}(\tau_c) \exp[-(\tau/\tau_c)^{\gamma_{in}}] d\tau_c \quad (11)$$

One may define a degree of heterogeneity $h = (\gamma_{in} - \gamma) / (1 - \gamma)$. This quantity vanishes in the homogeneous limit and it is unity in the heterogeneous limit [Bohmer et al., 1998].

Theory of Viscosity Estimation

Molecular motion in liquids is often compared to the prediction of the Debye-Stokes-Einstein (DSE) equation, which describes the rotational motion of a sphere of radius r in a hydrodynamic continuum with viscosity η and temperature T . The DSE rotational correlation time τ_c is

$$\tau_c = \frac{4\pi\eta r^3}{3kT} \quad (12)$$

Although this theory was not designed for complex liquids, experimental observation follows the temperature dependence of the DSE equation as the

viscosity is changed by twelve orders of magnitude [Blackburn et al., 1996].

To link T_1 and T_2 to viscosity, we first need to link them to the correlation time, τ_c . As the T_2 distribution is widely used in well logging, T_{2LM} will be used here. According to BPP theory [Bloembergen et al., 1948], in the extreme narrow limit ($\omega\tau_c \ll 1$) and for longer correlation times ($\omega\tau_c \gg 1$), T_2 is inversely proportional to the correlation time, τ_c .

$$T_2 \sim \frac{1}{\tau_c}. \quad (13)$$

In the rigid lattice regime, $\omega\tau_c \gg 1$, T_2 is independent of the correlation time [Bloembergen et al., 1948].

Recalling the definition of the T_{2LM} (Equation 1), we can write the following relationship for an n-component mixture

$$T_{2LM} \sim \left(\prod_{i=1}^n \tau_{c,i}^{-n_i} \right)^{1/\sum_i n_i}, \quad (14)$$

where $\tau_{c,i}$ is the correlation time corresponding to $T_{2,i}$ of the i-th molecular constituent.

The constituent correlation times, $\tau_{c,i}$, can be expressed as the following linear relationship in terms of the characteristic correlation time, τ_c , of the mixture:

$$\tau_{c,1} = k_1 \tau_c, \tau_{c,2} = k_2 \tau_c, \tau_{c,3} = k_3 \tau_c, \dots, \tau_{c,n} = k_n \tau_c. \quad (15)$$

Substituting Equation 15 into Equation 14, we find that

$$T_{2LM} \sim \left(\prod_{i=1}^n (k_i \tau_c)^{-n_i} \right)^{1/\sum_i n_i} = \frac{1}{\tau_c} \prod_{i=1}^n (k_i)^{-n_i/\sum_i n_i}. \quad (16)$$

From Equation 16 and Equation 12, it is found that $T_{2LM} \sim T/\eta$, in agreement with early viscosity estimators. While this relationship is adequate for light oils it is not useful for heavy oils, as shown in Figure 1. The main reason for breakdown at high viscosity is that the link between T_{2LM} and rotational correlation time is based on the Debye single exponential decay correlation function.

From Figure 2, we show that the viscosity-temperature relationship for heavy oils does not follow Arrhenius behavior [Williams et al., 1955]. This indicates that heavy oils share some properties with supercooled liquids. Therefore, we propose the use of the stretched-exponential form of the correlation function (Equation 11).

There is no analytical expression for the Fourier transform of the KWW function. However, the Cole-Davidson (CD) function has been extensively used to describe the frequency dependence of the complex dielectric constant. Although the CD and KWW functions are not exactly a Fourier transform pair, previous researchers have analyzed the close similarity of the KWW and CD functions [Lindsey and Patterson, 1980; Meier et al., 1991]. Therefore, we express the spectral density in the Cole – Davidson form

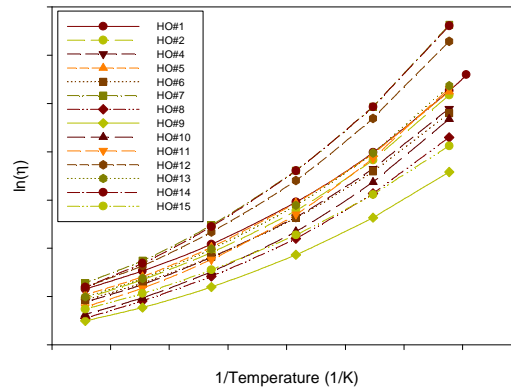


Figure 2 Relationship of viscosities and temperature for fourteen heavy oils.

$$J(\omega) = \frac{1}{\omega} \frac{\sin[\beta_{CD} \arctan(\omega\tau_c)]}{(1 + \omega^2 \tau_c^2)^{\beta_{CD}/2}} \quad (17)$$

In the extreme narrowing limit, we again recover Eqn (13). However, in the slow motion limit ($\omega\tau_c \gg 1$) [Beckman, 1988]

$$T_2 \sim \tau_c^{\beta_{CD}}. \quad (18)$$

Without loss of generality, let's assume that there are L components of the mixture in the extreme narrowing limit and (n-L) components in the long correlation time limit. Then Eqn (16) becomes

$$\begin{aligned}
 T_{2LM} &\sim \left[\left(\prod_{i=1}^L (k_i \tau_c)^{-n_i} \right) \left(\prod_{i=L+1}^n (k_i \tau_c)^{\beta_i n_i} \right) \right]^{1/\sum_i n_i} \\
 &= \tau_c^\Delta \left[\left(\prod_{i=1}^L (k_i)^{-n_i} \right) \left(\prod_{i=L+1}^n (k_i^{\beta_i n_i}) \right) \right]^{1/\sum_i n_i} \quad (19)
 \end{aligned}$$

$$\text{where } \Delta = \frac{\sum_{i=L+1}^n \beta_i n_i - \sum_{i=1}^L n_i}{\sum_i n_i} .$$

Considering the instrument dead time and Equations 19 and 12, T_{2LM} and η/T can be linked according to the following equation:

$$T_{2LM} = a + b \left(\frac{\eta}{T} \right)^c \quad (20)$$

Here, a is the instrument dead time effect on the T_2 distribution, and b and c are fitting parameters characterizing the molecular motion of a heavy oil. When $c = -1$, Equation 20 becomes similar to equations in Figure 1.

Results

The viscosities of three randomly selected heavy oil samples, HO#2, HO#7 and HO#8, were fit to Equation 20. The results are listed in Table 2. The average values of a , b and c were chosen and substituted into Equation 20 to predict the viscosities of all 14 heavy oil samples from their corresponding T_{2LM} (Figures 3 and 4).

Table 2. Parameters of Eqn (20) for three heavy oils

HO Samples	a	b	c	R ²
HO#2	0.4070	6.2053	-0.6160	0.998
HO#7	0.3426	5.4494	-0.6063	0.998
HO#8	0.3550	5.8159	-0.6193	0.998
Average	0.3682	5.8235	-0.6139	-

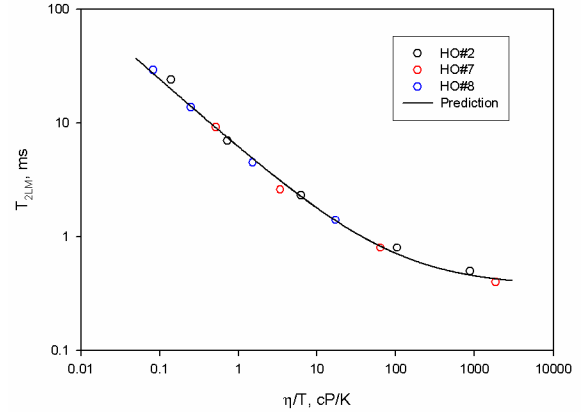


Figure 3 Double logarithmic plot of T_{2LM} and η/T . The solid line represents the correlation according to Eqn (20), with the average values of a , b and c from Table 2.

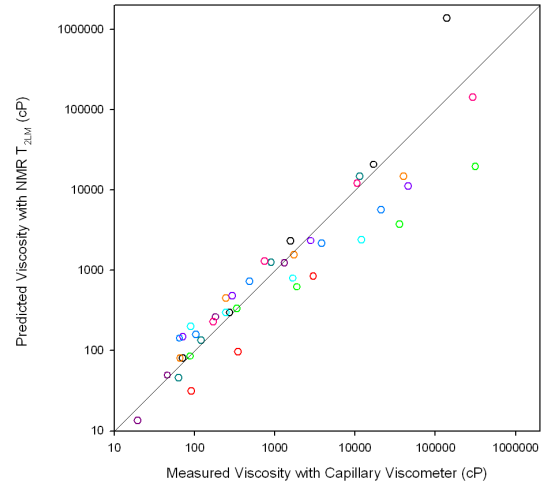


Figure 4 Estimated viscosity from NMR using Eqn (20), plotted against capillary viscometer results. The parameters of Eqn (20) were determined from HO #2, #7 and #8 experimental data, $a=0.3682$, $b=5.8235$ and $c=-0.6139$. Open circles represent data from eleven samples, not including HO#2, #7 and #8.

Eqn (20), with the average parameters derived from HO#2, 7 and 8, was also validated with recombined live heavy oil samples. Figure 5 is the comparison between capillary viscometer measurements and NMR predictions. The log standard deviation is 2.5.

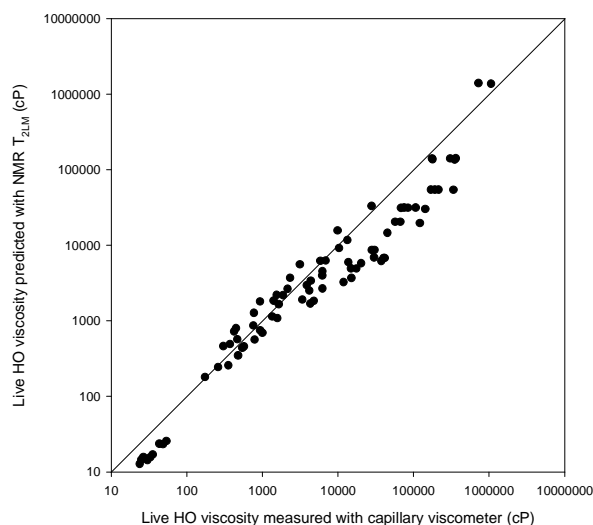


Figure 5 Plot of lab measured and estimated live heavy oil viscosity using Eqn (20) with $a=0.3682$, $b=5.8235$ and $c=-0.6139$.

Conclusions

Based on the observed non-Arrhenius relationship between the heavy oil viscosity and temperature, we propose a model using a stretched exponential decay of the molecular correlation. Our model for the heavy oil system assumes a spatial distribution of simple molecular processes, each governed by a stretched exponential decay function (KWW). This approach leads to a power law relationship between T_{2LM} and η/T . Coefficients of the power-law function determined from three heavy oil samples work well for eleven other dead and nine live heavy oil samples.

Based upon the method presented in this paper, the accuracy of the correlations is the log standard deviation of 2.5.

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ABOUT THE AUTHORS

Yuesheng Cheng is a senior research scientist at Schlumberger DBR Technology center. Dr. Cheng received a Ph.D. degree in chemistry from the University of New Brunswick, Canada, in 2006. He joined Schlumberger DBR in 2005. His present main research interests include reservoir fluids characterization and monitoring with NMR, and oil recovery and production processes.

Abdel Kharrat is Principal Scientist at the Schlumberger DBR Technology Center. Dr. Kharrat was research associate and lecturer at the University of Alberta, Edmonton, for eight years before moving to the Alberta Research Council as a senior research scientist in 1994. In 2003, he joined Schlumberger at DBR as senior analytical and process chemist and moved to his current position in January 2006. He has B.S., M.S., and Ph.D. degrees in chemistry from the Université Bordeaux I, France.

Rob Badry is Petrophysics Advisor for Schlumberger Canada Ltd. in Calgary, Alberta. He started his career with Schlumberger in 1978 as a field engineer after obtaining his B.S. degree in electrical engineering from the University of Calgary. He held several field and sales assignments before working as a senior log analyst in the Calgary Log Interpretation Center. Badry joined the interpretation development group in 1988 and has been actively involved with the introduction, and the training and interpretation support of advanced wireline services, including the Combinable Magnetic Resonance and Sonic Scanner services. Badry has been actively working on the application of magnetic resonance measurements in reservoirs containing very heavy oil and bitumen. He is a member of APEGGA, and an active member of the Canadian Well Logging Society (CWLS).

Robert Kleinberg is technical lead of Unconventional Resources at Schlumberger-Doll Research in Cambridge, Massachusetts. Dr. Kleinberg was educated at the University of California, Berkeley (B.S. Chemistry, 1971) and the University of California, San Diego (Ph.D. Physics, 1978). He was a post-doctoral scientist at the Exxon Corporate Research Laboratory in Linden, New Jersey before joining Schlumberger in 1980. His present research interests include heavy oil, oil shale, gas hydrate, and carbon dioxide sequestration. He has published more than 90 academic and professional papers, holds 30 U.S. patents, and is the inventor of several well logging tools that have been commercialized on a worldwide basis.