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The NMR T_2 Response of Crude Oils at Elevated Temperatures

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Abstract

Until recently, most nuclear magnetic resonance (NMR) measurements in support of lab petrophysics and well logging were conducted at room temperature. However, the T_2 relaxation of bulk crude oils strongly depends on temperature. Measurement of the crude oil relaxation response at reservoir temperatures is needed for optimal interpretation of log data.

This work used a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence to measure the NMR T_2 relaxation at 2 MHz. Four stock tank crude oils were studied over the temperature range 30-100°C at a constant pressure of 300 psig. For comparison, the T_2 temperature response of five viscosity standards was measured over the same range and compared to the crude oil data. A two-component exponential decay described all the data. As expected from the temperature dependence of translational diffusion, there is not a universal curve that fits all hydrocarbon mixtures. The standards and the crudes did not fit a single curve.

The observed oil T_2 varied directly with absolute temperature and inversely with the viscosity. For the crude oils, the log mean T_2 was related to a viscosity value calculated from the stock tank oil viscosity correlation as developed by Beggs and Robinson and modified by Egbogah (EBR). This T_2 relation did not agree with a T_2 correlation (SRVTM, 1994) developed at room temperature from oil samples of differing viscosity (0.7 to1000 cp). When the viscosity of one of the crude oils was measured as a function of temperature, that data then fit the SRVTM room temperature T_2 correlation. Viscosity values derived from correlations based only on API gravity are evidently insufficient to make close estimates of crude oil T_2 relaxation at elevated temperatures.

One of the crudes was a distinct outlier from the others. The composition of this sample suggests further investigations into the T_2 relaxation of oil-based mud filtrate and mixtures of crude and oil-based mud filtrate.

Introduction

There are many reasons why a reservoir engineer may prefer in-situ measurement of reservoir fluid properties if they are available.[1] In fact, quantitative NMR logging of fluid properties are under development.[1,2] In addition, downhole fluid properties aid in general NMR log interpretation.[3]

NMR background. The text by Fukushima and Roeder provides a good introduction to the practice of NMR.[4] The text edited by Delpuech provides a modern review of how NMR is used to discern dynamical information on liquids at the molecular level.[5]

T_2 relaxation measurement. The process in which the spins return to equilibrium is termed relaxation. The so-called T_1 (longitudinal or spin-lattice) relaxation describes energy loss by the spins to their environment. The T_2 (transverse or spin-spin) relaxation describes an entropy gain, the decay of observed signal as the transverse spin components becomes randomly distributed with time due to spin-spin interactions. In a water or oil-based liquid, the ^1H spin-spin interaction is a dipole-dipole interaction occurring as two molecules (containing the hydrogen atoms, the protons) pass close to one another. This contributes an additional signal loss mechanism that is not present in a T_1 energy-loss measurement.

In a liquid, the diffusion of a molecule containing proton spins will expose the spins to a time-varying magnetic field. The time-varying magnetic field is due to nearby dipolar fields from the ^1H spins of closely approaching molecules. The CPMG pulse sequence can correct for the varying precessional frequencies impressed upon the ensemble of spins by a time-varying field only if the time between spin echo refocusing, the inter-pulse spacing τ, is much shorter than the correlation time, the characteristic rate of change of these fields. Otherwise the spins lose coherency, the net magnetization decays, and the observed signal decays. Thus a CPMG sequence with short τ can correct for the small field inhomogeneities of the NMR magnet. However, this sequence cannot affect the intrinsic T_2 relaxation occurring in the liquid at the molecular level, because the correlation time for this interaction is on the order of the collision time, the time for a molecule to diffuse a molecular diameter.[6]

Thus with proper NMR technique, the observed relaxation of a bulk liquid is an intrinsic property of the liquid. As can be seen from the above discussion, the T_2 relaxation for a liquid is mediated by the translational diffusion.[6,7] Self-diffusivity is a relatively difficult thing to measure accurately and is prone to systematic errors.[8] Diffusivity D and viscosity μ are inversely related. Since viscosity data is abundant, and since there are theoretical reasons why the translational transport properties D and μ should behave similarly, T_2 is usually related to viscosity.[8] T_2 has been observed to depend approximately linearly on μ/T.[6,7] In the fast-motion correlation time regime, at room temperature and above for all but the most viscous crudes, $T_1 \approx T_2$, and they have an identical temperature dependence.[6] Although T_1 measurements involve fewer additional relaxation mechanisms and complications, it takes more time to perform; thus there is more interest in T_2 measurement for downhole.

Relation of diffusivity to viscosity for liquids. The diffusivity and viscosity are not simply inversely related for most situations. For non-associating, non-aqueous systems, the infinite-dilution diffusivity for solute species A into solvent species B is best expressed as

$$D_{AB} = Q\,\mu_B^{q}, \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where Q and q are constants of the power law relation.[8] Over a wide range of solute-solvent pairs, the constant q can vary from –0.5 to –1.

Various correlations for D_{AB} assume that $D_{AB}\mu_B/T_K$ is a constant.[8] The Hayduk-Minhas method for calculating D_{AB} assumes an exponentially increasing form with respect to temperature. In brief, a simple universal relationship of diffusivity with viscosity or temperature is not possible. Since relaxation and diffusivity are so closely linked, and given the added complexity of crude oils, the relation of NMR relaxation to viscosity and temperature is best determined in the lab.

Available T_2-μ crude oil data sets. The simplest form for describing the T_1 and T_2 relationship with viscosity is[9]

$$T_1 \approx T_2 = \frac{1.2T_K}{298\mu}\,. \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Over an extended range, the relationship is noticeably more complex. T_1 measurements at room temperature for light and medium crudes (0.5-200 cp) and alkanes could not fit a simple power law relationship with viscosity over more than a decade of viscosity values before deviations could be noticed.[10] The declining T_1 has little slope with respect to μ at viscosity values above 100 cp.

Room temperature T_2 measurements, however, exhibit a power law relation over three decades, up to viscosities of over 1000 cp.[11] This can be explained by the fact that medium-to-heavy crude oils at room temperature are near the minimum in T_1 for the relaxation-correlation time curve; for slower (more viscous) internal motions, the values of T_1 and T_2 increasingly diverge. Fortuitously for NMR logging, as temperatures rise above room temperature, crudes move into the less complex behavior evident for the fast-motion regime.

Egbogah (modified Beggs and Robinson) correlation. Viscosity measurements at temperature and pressure are relatively expensive in terms of time and money and traditional rolling ball viscometers require more sample than may be available. So we investigated the use of viscosity correlations. The Egbogah correlation, also known as the modified Beggs and Robinson equation, (EBR in this work) relates dead oil viscosity to API gravity and temperature, which is minimal information available for most situations.[12] No compositional information is required.

$$\log_{10}(\log_{10}(\mu_{od} + 1)) = 1.8653 - 0.025086\,\rho_{o,API}$$

$$- 0.5644\,\log_{10}(T_F), \quad \ldots\ldots\ldots\ldots\ldots(3)$$

where μ_{od} is the dead oil viscosity, γ_o is the API gravity of the crude, and T_F is the temperature in °F. This correlation was developed using 394 oil systems over an API gravity range of 5-58° and temperature range of 59-176^{o}F. The relative error between the measured and calculated viscosity values was quoted 5.13%. We observed larger systematic variations.

Experimental Setup and Procedure

A Resonance Instruments' Maran-2 tabletop spectrometer supplied the 2 MHz NMR data for this study. The basic experimental pulse sequence and hardware parameters for the spectrometer are provided in Table 1. The multi-exponential T_2 values were obtained from the fitting program included with the spectrometer. The data of this study were optimally described by a two component relaxation model.

The samples were pumped into a Peek plastic liquid chromatography cell of 2.2 ml volume. The cell was rated at 4000 psig and 100°C. All measurements were made at a constant pressure of 300 psig to prevent any evolution of light hydrocarbons upon heating. A computer-controlled positive displacement pump, Quizix QL-700-5K operated in constant pressure mode to maintain the 300 psig. To maintain a stable pressure in the very small volume of the sample cell, the pump needed a small cylinder, 7.25 ml in this case.

The Peek cell was surrounded by a double-helical heat exchanger immersed in a cylindrical bath in the bore of the Maran spectrometer. The temperature of the sample was controlled by a heat transfer fluid circulated through the helical heat exchanger by a standard laboratory circulating hot bath. To prevent interference with the NMR measurements, the heat transfer fluid and the bath fluid were a non-hydrogen perfluoropolyether, Galden HT-270, from Ausimont. This particular fluid was chosen for its combination of low viscosity at room temperature, low vapor pressure at elevated temperatures and very low water solubility (14 ppm).

The temperature of the bath fluid surrounding the sample cell could be measured to ± 0.1°C using a Luxtron Fluoroptic thermometer, which uses a very small fluoroptic sensor at the end of a glass fiber light pipe. This thermometer probe is minimally invasive, non-conductive electrically, and remains accurate in high magnetic fields and in high RF fields. The bath temperature was monitored and allowed to stabilize before the data acquisition at each temperature. In short, each measurement was performed at constant temperature and pressure. The maximum variation in temperature and pressure was approximately, ±0.8% and ±0.05% respectively. The temperature of the magnet remained stabilized at 30°C throughout the experiment.

Effect of dissolved oxygen. Early relaxation measurements in light hydrocarbons with long T_1 (~1-20s) were often reduced due to the presence of dissolved (paramagnetic) oxygen.[6] All four crude oil samples were measured native state and degassed by a standard helium sparging technique. No difference was noted. This is not unexpected, since none of the four crude samples had room temperature T_1 over about one second.

Experimental Data

The two-component T_2 data are provided in Tables 3 and 4 for the Cannon viscosity standards and the dead crude oil samples, respectively.

For calibration and as a test of the equipment, T_2 was measured for a suite of Cannon viscosity standards at different temperatures. The viscosity standards used were N350, N100, S60, N35, and S20. The viscosity ranged from 4 to 600 cp for the range of temperatures at which the T_2 was measured. These standards consist of a set of homologous aliphatic oils with viscosities measured over a specified temperature range.[10]

The logarithmic mean T_2, T_{2ML}[4], was calculated as

$$T_{2ML} = \exp(\log T_2) = \exp\left(\frac{\sum f_i \log T_{2i}}{\sum f_i}\right). \quad \ldots\ldots\ldots\ldots\ldots(4)$$

T_{2ML} was plotted against absolute temperature and viscosity, a form equivalent to equation 2. As expected, T_{2ML} varied linearly with the temperature and inversely with the viscosity. The best-fit power law did not explicitly involve the temperature.

$$T_{2ML} = \frac{1.32}{\mu^{0.84}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

The T_2 was then measured for four crude oils (Sample 1, 2, 4, and 29) and T_{2ML} was calculated. The viscosity of the crudes at the various temperatures were calculated using the EBR correlation. Table 2 shows the crude oil analysis and SARA analysis for samples 2, 4 and 29.

T_{2ML} vs Viscosity

For the sample crude oils, the T_{2ML} was plotted against their viscosities calculated from the EBR correlation (**Fig. 1**). Sample 2 was found to be an outlier. The best fit for the rest of the data was

$$T_{2ML} = \frac{5.89}{\mu^{1.47}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

For the crude Sample 2, this was

$$T_{2ML} = \frac{8.78}{\mu^{1.11}}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

The GC crude oil analysis of Sample 2 shows a higher percentage of intermediates compared to the other crude samples. The SARA analysis shows a much higher percentage of saturates. We believe that this appreciable compositional difference from samples 4 and 29, makes this sample atypical. This could be due to a physically different T_2 process or merely due to the failure of the EBR viscosity correlation. Why this sample is compositionally unique is another question. Sample 2 could have an unusual composition, or it could have been possibly contaminated with distillates used in oil based muds.

For Sample 1, the viscosities at the various elevated temperatures were measured using a Ruska rolling ball viscometer. The viscometer was first calibrated using the Cannon standards. The measured viscosity was found to differ systematically significantly from the viscosities calculated using the EBR correlation. **Fig. 2** shows the crossplot of the measured viscosities versus the viscosities calculated using the EBR correlation. The figure also shows the difference in the actual viscosities from EBR viscosities for the Cannon Viscosity standards. The measured viscosities of Sample 1 for different temperatures were plotted against their corresponding logarithmic mean T_2 values (**Fig. 3**). Also shown in this figure is the relation of T_{2ML} to the quoted viscosities for the Cannon standards. For Sample 1 the fit is described by

$$T_{2ML} = \frac{1.2}{\mu^{0.88}} . \qquad \text{……..……………………………(8)}$$

This regression is equivalent to the regression correlation (SRVTM) by Straley et al. This work correlated T_{2ML} to the measured viscosities of 64 dead oil samples at a fixed (ambient) temperature.[11] That relation was

$$T_{2ML} = 1.2 / \mu^{0.9} . \qquad \text{….…………………………..……(9)}$$

The average errors in the T_2 measurements at 30°C and 100°C were both 8%. The data points for the Sample 1 crude at elevated temperatures is overlain on the SRVTM correlation of equation (8) in **Fig. 4**. The data of one crude whose viscosity varied as a result of temperature fits the span of many crudes of differing viscosity at one fixed temperature.

Conclusions

The SRVTM, T_2 relaxation versus viscosity correlation, developed using several crudes at a single temperature, was upheld when the viscosity range was spanned by a single crude with viscosity varying with temperature. Dead oil non-compositional viscosity correlations should not be used to predict T_2 at elevated temperatures. The available data suggests investigating the behaviour of OBM filtrate and its mixtures with crude oils as a possible source of compositional unconformity to the SRVTM relaxation correlation.

Nomenclature

f_i = fractional spin signal intensity of ith component
D = self-diffusivity, cm^2/s
D_{AB} = infinite dilution diffusivity, solute A into solvent B, cm^2/s
Q, q = constants in a power law relation
T_1 = longitudinal relaxation time constant, s
T_2 = transverse relaxation time constant, s
T_{2i} = ith component of transverse relaxation time constant, s
T_{2ML} = logarithmic mean of multi-component T_{2i}, s
T_F = temperature, °F
T_K = absolute temperature, °K
$\rho_{o,API}$ = API gravity
μ = viscosity, cp
μ_{od} = dead oil viscosity, cp
τ = inter-pulse spacing time of CPMG sequence, μs

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TABLE 1 – SPECTROMETER SETTINGS

Acquisition:	
Nucleus	$^1H_1$
Spectrometer Frequency	2.03 MHz
Filter Width	100 kHz
Number of Echoes	100 – 8000
Number of Repetitions	64
Timing:	
90° Pulse Length	24.6 µs
180° Pulse Length	48.3 µs
Inter-Pulse Spacing, τ	400 µs
Experiment Recycle Delay	8 s

TABLE 2 - CRUDE OIL ANALYSIS

	Sample 2	Sample 29	Sample 4	Sample 1
Wt %				
Saturate	61.3	45.6	38.3	-
Aromatic	34.5	31.0	35.3	-
Resin	4.2	19.1	18.5	-
Asphaltene	0.0	4.6	8.6	-
C1-4	0.009	0.286	0.023	-
C5-7	1.931	4.908	1.828	-
C8-10	12.039	9.181	7.447	-
C11-14	29.473	11.323	10.712	-
C15+	56.548	74.302	79.99	-
T_{2ML} @ 87° F	0.739 s	0.102 s	0.040 s	0.009 s
API Gravity	29.68	28.03	23.35	19.52

TABLE 3 - CRUDE OIL RELAXATION DATA

sample	temp (°C)	T_{21} (µ s)	f_1 (%)	T_{22} (µ s)	f_2 (%)	T_{2ML} (s)	EBR µ (cp)
# 2	31.2	1106716	67.4	320759	32.6	0.739	10.32
	40.0	1098475	70.8	335727	29.2	0.777	8.12
	50.8	1507529	74.5	425459	25.5	1.092	6.45
	64.2	1837887	75.2	553523	24.8	1.365	5.14
	83.4	2379945	78.2	766795	21.8	1.859	4.01
	97.5	3003042	76.6	941086	23.4	2.289	3.47
	103.3	3156056	80.5	830017	19.5	2.432	3.29
# 29	29.0	170019	64.6	25537	35.4	0.087	14.48
	31.0	174421	69.0	31291	31.0	0.102	13.52
	40.4	236054	69.2	38485	30.8	0.135	10.27
	50.3	306359	72.4	36525	27.7	0.170	8.18
	64.6	418893	71.0	39974	29.0	0.212	6.32
	85.0	678327	71.7	83102	28.3	0.374	4.79
	100.0	940290	72.6	140548	27.4	0.559	4.09
#4	29.3	72735	65.5	7709	34.5	0.034	34.77
	31.4	80922	62.1	12796	38.0	0.040	31.79
	41.2	109806	65.6	10644	34.4	0.049	22.34
	50.1	156548	66.2	19092	33.8	0.077	17.35
	64.7	217156	68.2	19492	31.8	0.101	12.56
	85.0	382148	70.8	41627	29.2	0.200	9.00
	100.0	543350	69.1	74324	30.9	0.294	7.43
# 1	31.4	25392	30.3	5600	69.7	0.009	76.82
	39.6	36338	51.9	7869	48.1	0.017	53.13
	50.0	49707	57.4	7367	42.6	0.022	36.84
	65.0	98731	57.3	15733	42.7	0.045	24.68
	84.9	111516	49.9	33253	50.1	0.061	16.71
	100.0	284660	73.7	47087	26.3	0.177	13.29

TABLE 4 – CANNON VISCOSITY STANDARDS RELAXATION DATA

	Temp (^{o}C)	T_{21} (μ s)	f_1 (%)	T_{22} (μ s)	f_2 (%)	T_{2ML} (s)	μ (cp)
N 350	28.6	11999	56.0	3759	44.0	0.007	587.70
	40.2	35929	25.4	8883	74.6	0.013	268.30
	49.9	48728	28.9	14318	71.1	0.020	160.20
	50.4	39677	46.7	12680	53.3	0.022	156.00
	64.8	63474	57.3	12874	42.7	0.032	72.90
	85.1	113027	64.9	25374	35.1	0.067	34.20
	100.0	185221	71.9	37758	28.1	0.118	19.90
N 100	31.0	36360	43.8	10368	56.2	0.018	140.47
	40.1	55791	50.8	17322	49.2	0.031	82.87
	50.5	79005	59.8	20297	40.2	0.046	51.85
	65.0	124432	64.3	30261	35.7	0.075	26.97
	85.0	216224	70.4	49685	29.6	0.140	14.38
	100.0	297734	78.2	62198	21.8	0.211	9.03
S 60	31.0	59067	51.8	18752	48.2	0.034	73.59
	50.0	108709	74.6	30437	25.4	0.079	30.64
	65.0	184236	67.3	59253	32.7	0.127	16.70
	85.0	276776	85.3	68152	14.7	0.225	9.48
	100.0	388272	86.5	104159	13.5	0.325	6.23
N 35	31.0	73762	68.7	20765	31.3	0.050	41.45
	50.0	144399	74.3	53329	25.7	0.112	18.71
	65.0	228407	82.6	72568	17.5	0.187	10.80
	85.0	351704	87.9	121470	12.1	0.309	6.47
	100.0	558579	24.5	409423	75.5	0.442	4.44
S 20	29.0	100072	73.1	32501	26.9	0.074	24.11
	31.1	103398	79.7	33490	20.3	0.082	22.01
	50.0	197129	86.8	57326	13.2	0.167	10.92
	66.4	290696	92.0	71302	8.0	0.260	6.50
	85.0	422571	93.0	28253	7.0	0.350	4.25

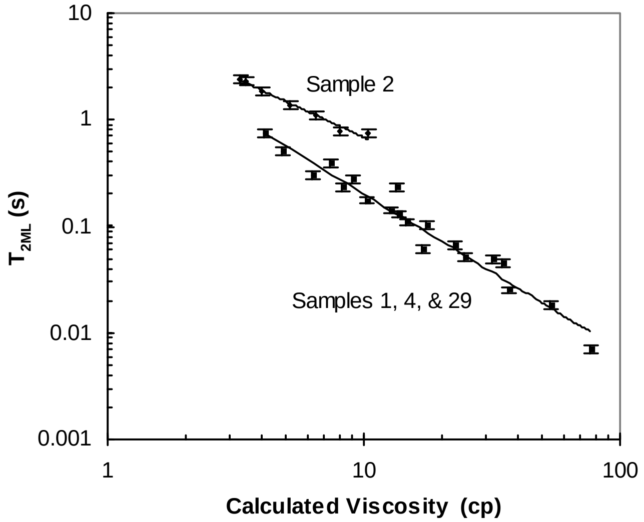

Fig. 1 – Logarithmic plot of T_{2ML} of the Crude Samples against the EBR Viscosities. The data points of Sample 2 do not follow the same trend as the other samples.

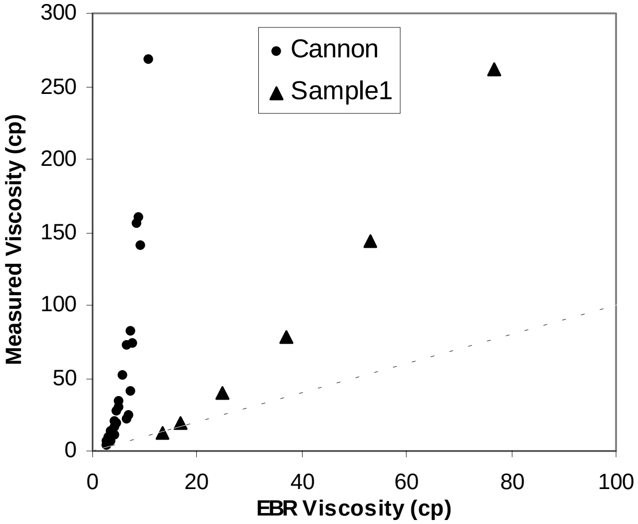

Fig. 2 – Crossplot of Actual versus Calculated Viscosity values for Sample 1 and Cannon Standards. The Measured Viscosities differ significantly from the EBR Viscosities.

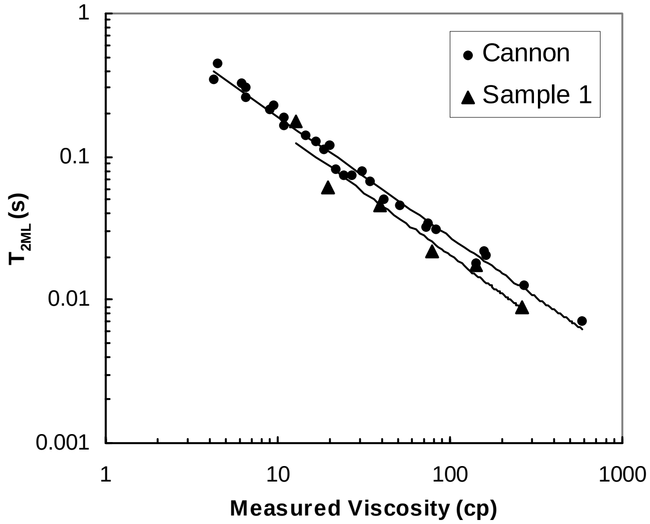

Fig. 3 – Logarithmic plot of T_{2ML} of Sample 1 versus corresponding Viscosities, measured using a Rolling Ball Viscometer. Also shown is T_{2ML} versus Actual Quoted Viscosity for the Cannon Viscosity Standards.

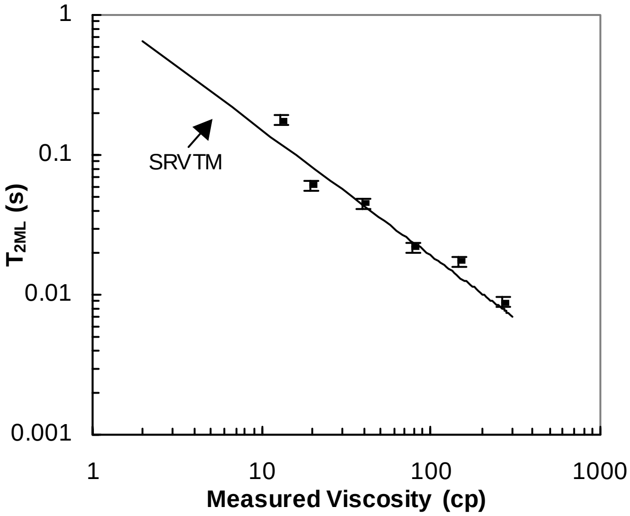

Fig. 4 – Comparison of Sample 1 Elevated Temperature Data with SRVTM Correlation. The data points of Sample 1 fits the SRVTM Correlation.