NMR Properties of Petroleum Reservoir Fluids

George J. Hirasaki, *Rice University*

Sho-Wei Lo, *Shell International E&P Co.*

Ying Zhang, *Bechtel*

Paper presented at the 6th International Conference on Magnetic Resonance in Porous Media, Ulm, Germany, September 8-12, 2002.

ABSTRACT

NMR well logging of petroleum reservoir require the measurement of the NMR response of water, oil, and gas in the pore space of rocks at elevated temperatures and pressures. The viscosity of the oil may range from less than 1 cp to greater than 10,000 cp. Also, the oil and gas are not a single component but rather a broad distribution of components. The log mean T_1 and T_2 relaxation time of dead (gas free) crude oils are correlated with viscosity/temperature and Larmor frequency. The relaxation time of live oils deviate from the correlation for dead crude oils. This deviation can be correlated with the methane content of the oil. Natural gas in the reservoir has components other than methane. Mixing rules are developed to accommodate components such as ethane, propane, carbon dioxide, and nitrogen.

Interpretation of NMR logs uses both relaxation and diffusion to distinguish the different fluids present in the formation. Crude oils have a broad spectrum of components but the relaxation time distribution and diffusion coefficient distribution are correlated. This correlation is used to distinguish crude oil from

the response of water in the pores of the rock. This correlation can also be used to estimate viscosity of the crude oil.

KEYWORDS: well logging, crude oil, natural gas, relaxation time, diffusivity

INTRODUCTION

NMR well logging has been commercially available since the early 1990s [1,2]. More recently, NMR has been used for real-time analysis of bottom-hole sampling of reservoir fluids [3,4]. Interpretation of these measurements require an understanding of the relationship between NMR dependent parameters, hydrogen index, T_1 and T_2 relaxation time, and diffusion coefficient with the composition, density, pressure, temperature, and viscosity of the fluids. With this understanding, it is possible to estimate from the well log, the formation porosity and permeability, irreducible water saturation, saturation of water, oil, and gas, and the oil viscosity.

RESULTS

Correlation of Relaxation Time with Viscosity/Temperature and Larmor Frequency

The correlation of the T_2 relaxation time with crude oil viscosity was developed by Morriss et al. [5] from 31 Belridge oil samples, 35 samples from international fields and viscosity standards. The crude oil samples had a broad distribution of relaxation times and the correlation was based on the geometric-mean or log-mean relaxation time, $T_{2,\mathrm{LM}}$.

$$T_{2,LM} = \frac{1200}{\eta^{0.9}} \tag{1}$$

The correlation is compared with experimental data of T_1 and T_2 relaxation times of crude oils and *n*-alkanes on Fig. 1, [5-14]. The low viscosity and long relaxation time portion of the correlation show a systematic deviation from the data for *n*-alkanes. The *n*-alkanes data reported here were deoxygenated. The crude oil systems were not deoxygenated. Air saturated *n*-alkanes have a relaxation time that corresponds to that of the correlation for crude oils and viscosity standards [12]. The T_2 relaxation time data deviate from the correlation as the relaxation time approaches 1 ms. This is because information about the relaxation times much smaller than the echo spacing is lost in the CPMG measurement. The T_1 relaxation time has crude oil data for 2 MHz [8,13,14] and 80 MHz [6]. There is no difference between T_1 and T_2 at low viscosity and Larmor frequency. However, the T_1 has a plateau with increasing viscosity with the level of the plateau dependent on the Larmor frequency. Additional measurements were made at 7.5 MHz and 20 MHz [13,14] to verify this trend.

The dependence of the T_1 relaxation time on viscosity and Larmor frequency was examined by comparing with the model for a spherical molecule. The relation between the relaxation times and the rotational correlation time for intra-molecular, dipole-dipole interactions is as follows [15].

$$\begin{aligned}
\frac{1}{T_1} &= M_2\,\tau_c\left[\frac{2/3}{1+(\omega_o\,\tau_c)^2}+\frac{8/3}{1+(2\omega_o\,\tau_c)^2}\right]\\
\frac{1}{T_2} &= M_2\,\tau_c\left[1+\frac{5/3}{1+(\omega_o\,\tau_c)^2}+\frac{2/3}{1+(2\omega_o\,\tau_c)^2}\right] \qquad (2)\\
M_2 &= \frac{9}{20}\left(\frac{\mu_o}{4\pi}\right)^2\frac{\hbar^2\,\gamma^4}{r^6},\quad \text{for a diatomic molecule}
\end{aligned}$$

where ω_o is the Larmor frequency, μ_o is the magnetic permeability of free space, $\hbar$ is Planck's constant divided by 2π, γ is the gyromagnetic ratio for the ^{1}H proton, and r is the distance between the nearest protons in the molecule. Only the nearest neighbors are considered because the coefficient, M_2, is a function of distance to the inverse sixth power.

It is helpful to express the rotational correlation time in terms of measurable variables. This can be done by assuming that the molecule is a sphere undergoing rotation by Brownian motion [15].

$$\begin{aligned}
&\tau_c = \frac{1}{6D_r} \\
&D_r = \frac{kT}{8\pi a^3 \eta}, \qquad \text{spherical molecule} \\
&\tau_c = \frac{4\pi a^3 \eta}{3kT}, \qquad \text{spherical molecule} \\
&\frac{1}{T_1} = \frac{1}{T_2} = \frac{40\pi M_2 a^3 \eta}{9kT}, \qquad \omega_o \tau_c \ll 1, \quad \text{spherical molecule}
\end{aligned} \tag{3}$$

where a is the radius, η is the viscosity, k is the Boltzmann constant, and T is the absolute temperature. The significant result here is that liquids of spherical molecules in the fast motion limit ('motional narrowing') have T_1 and T_2 equal to each other and inversely proportional to viscosity/temperature.

The dependence of the relaxation times on viscosity/temperature can be visualized by expressing the equation for relaxation by intramolecular dipole-dipole mechanisms in dimensionless variables.

$$T_{1,2\,D} = \frac{M_2}{\omega_o} T_{1,2}$$
$$\omega_o\,\tau_c = \frac{4\pi\,\omega_o\,a^3\,\eta}{3k\,T}, \qquad \text{spherical molecule} \tag{4}$$

The results are shown in Fig. 2. The relaxation times, T_{1D} and T_{2D} are equal to each other for short correlation times compared to the Larmor period, e.g., for low viscosity/temperature. When the correlation time is long compared to the Larmor period, e.g., for high viscosity fluids, T_{1D} is larger than T_{2D}.

The dependence of the T_1 on Larmor frequency can be correlated by normalizing the relaxation time and viscosity with the Larmor frequency in the manner suggested by the section on intramolecular dipole-dipole interactions.

$$T_{1,2\mathrm{N}} = \frac{2(\mathrm{MHz})}{\omega_0} T_{1,2}$$
$$\left(\frac{\eta}{T}\right)_{\mathrm{N}} = \frac{\omega_0}{2(\mathrm{MHz})}\left(\frac{\eta}{T}\right) \tag{5}$$

The normalized $T_{1,\mathrm{LM}}$ relaxation time as a function of the normalized viscosity is shown in Fig. 3. This normalization to 2 MHz collapses all $T_{1,\mathrm{LM}}$ data of crude oils to a single curve. For low viscosities, the measured $T_{1,\mathrm{LM}}$ data agree well with the correlation between viscosity and $T_{2,\mathrm{LM}}$ derived for gas-free crude oils, and therefore illustrate the validity of the fast motion approximation for this viscosity range. At higher viscosities, the measured $T_{1,\mathrm{LM}}$ values depart from the $T_{2,\mathrm{LM}}$ correlation. Furthermore, the experimental $T_{1,\mathrm{LM}}$ show a lower plateau value instead of the theoretically expected increase of T_1. In Fig. 3, a dashed line shows the theoretical prediction for T_1 of a system with a single molecular correlation time. Given that T_1 will reach its minimum when the inverse of the

Larmor frequency is equal to the molecular correlation time, the observed lower plateau of the T_1 data suggests that crude oils need to be characterized by a spectrum of molecular correlation times.

The viscosity and thus the relaxation time of heavy oils are very strongly dependent on the temperature. Thus measurements at different temperature is a good test of the correlation of $T_{2,\mathrm{LM}}$ with the ratio of viscosity and temperature. Fig. 4 shows a plot of $T_{2,\mathrm{LM}}$ as a function of the ratio of viscosity and temperature for measurements at 40°, 70°, and 100° C. These results show that the correlations which were developed for alkanes at close to ambient conditions apply to viscous, heated oils until $T_{2,\mathrm{LM}}$ becomes close to the echo spacing of the measurement. It was mentioned earlier that short relaxation times are truncated by lack of data shorter than the echo spacing.

Live Crude Oils

Live oils differ from dead oils in that they contain dissolved gas components. Methane is the primary, but not the only, dissolved component. Supercritical methane and methane vapour relax by the spin-rotation mechanism. Cryogenic liquid methane relaxes by intermolecular dipolar coupling. With decreasing viscosity, the contribution from spin rotation to the relaxation process of methane successively increases and leads to an opposite trend for the relaxation time-viscosity relation compared to higher alkanes.

For formation fluids with a significant amount of solution gas, the relaxation behaviour will be governed by both dipolar interactions and spin rotation. The contribution from spin rotation increases with increasing gas-oil ratio and increasing hydrogen index of the gas phase. This is illustrated in Fig. 5, which includes methane-alkane mixtures, in addition to pure methane and pure higher alkanes [16].

Because of the opposite dependencies on the ratio of viscosity/temperature between dipolar interactions and spin rotation, prediction of the NMR relaxation times from PVT data for live oils is complicated. Generally speaking, live fluids will have shorter relaxation times than gas-free fluids of similar viscosity because of the additional contributions to the relaxation from spin rotation.

Lo *et al*. [16] have shown that the relaxation times of methane-alkane mixtures show a significant deviation from the straight-line correlation for pure liquid alkanes. This departure is not exclusively due to the system being a mixture, since the log-mean relaxation of n-hexane and n-hexadecane mixtures followed the correlation for pure liquid alkanes. The deviation of the methane-alkane mixtures from the correlation for the liquid alkanes correlates with the methane content of the mixture or the gas/oil ratio, *GOR*, (in m^3/m^3) [16]. The correlation of the measurements resulted in the following expression:

$$\begin{aligned} deviation &= \mathrm{Log}_{10}\left(T_{1,linear}/T_1\right) = \mathrm{Log}_{10}\left[f\left(GOR\right)\right] \\ \mathrm{Log}_{10}\left(deviation\right) &= \mathrm{Log}_{10}\left\{\mathrm{Log}_{10}\left[f\left(GOR\right)\right]\right\} \\ &= -0.127\left[\mathrm{Log}_{10}\left(GOR\right)\right]^2 + 1.25\,\mathrm{Log}_{10}\left(GOR\right) - 2.80 \end{aligned} \tag{6}$$

The relaxation of the live oil can thus be estimated from the correlation in the absence of methane, denoted $T_{1,linear}$, and the function of the *GOR*:

$$T_1 = \frac{T_{1,linear}}{f(GOR)} \tag{7}$$

The correlation of the relaxation time as a function of viscosity/temperature and *GOR* is shown in Fig. 6. The contour lines of constant *GOR* are straight lines that are parallel to the line for dead oils.

Reservoir Gas

The primary component of natural gas is methane. Supercritical methane relaxes by the spin rotation mechanism and the relaxation time can be correlated with density and temperature. Although methane is usually the primary component of natural gas, other light hydrocarbons and non-hydrocarbons are usually present. Pure ethane and propane gas have relaxation times that are longer than that of methane [13], especially when correlated with molar density (Fig. 7).

Carbon dioxide and nitrogen do not have protons but their presence in mixtures with methane results in a reduction of the relaxation time of methane compared to the correlation for pure methane based on mass density [17]. However, if the molar density rather than the mass density is used in the correlation, the methane relaxation in mixtures with CO_2 or nitrogen will approximately correlate with that of pure methane. The symbols in Fig. 8 are the relaxation times of methane in mixtures with either CO_2 or nitrogen compared with the correlation for pure methane. The departure is apparently due to the collision cross-section of methane with these other gases being different from the methane-methane collision cross-section.

Relationship between Relaxation Time and Diffusivity

NMR well logs need to distinguish between water, oil, and gas in the pore space of the rock. Water usually has a broad relaxation time in rocks because of surface relaxation on the pore wall of pores of different sizes. The fluids are distinguished by the difference of the diffusivity. Crude oil is a mixture of many components and thus usually has broad relaxation time and diffusivity distributions. Crude oil has been distinguished from water and the viscosity of the crude oil estimated through the use of the *constituent viscosity model* [18]. “In the CVM, each hydrocarbon molecule in the mixture is assumed to relax and diffuse like it would in the pure-state liquid except the macroscopic pure-state viscosity is replaced by the microscopic constituent viscosity.” This implies that the relaxation time distribution and diffusivity distribution are coupled through a common “constituent viscosity.” The expressions for the mixture’s and the constituent’s relaxation time, diffusivity, and viscosity are as follows.

$$
\begin{aligned}
&T_{2,LM} = \frac{aT}{\eta}, \qquad T_{2,k} = \frac{aT}{\eta_k}, \qquad T_{2,LM} = \prod_{k=1}^{N} T_{2,k}^{f_k} \\
&D_{LM} = \frac{bT}{\eta}, \qquad D_k = \frac{bT}{\eta_k}, \qquad D_{LM} = \prod_{k=1}^{N} D_k^{f_k} \\
&\frac{D_{LM}}{T_{2,LM}} = \frac{D_k}{T_{2,k}} = \frac{b}{a} \\
&\eta = \prod_{k=1}^{N} \eta_k^{f_k} = \frac{aT}{T_{2,LM}} = \frac{bT}{D_{LM}} \\
&\sum_{k=1}^{N} f_k = 1
\end{aligned}
\tag{8}
$$

The parameter, f_k, is the proton fraction of the *k*-th molecular constituent. The parameters, $a \text{ and } b$, were determined from the measurements of the relaxation time and diffusivity of pure components and the mean value of the mixture. It has been established that for the alkanes the ratio of b/a is equal to 5.28×10^{-6} (cm^2/s^2) while for dead crude oils b/a is approximately 1.26×10^{-5} (cm^2/s^2). This model assumes that relaxation time and diffusivity distributions are coupled with each constituent having a common proportionality constant, b/a. A correction for the GOR should be made for live oils [18].

Freedman *et al*. [18] studied mixtures of *n*-hexane (C_6H_{14}) and squalene ($C_{30}H_{50}$) and demonstrated the relation between the relaxation time and diffusivity distributions for these mixtures. The relaxation time and diffusivity distributions are shown in Figs. 9 and 10, respectively. The light vertical line on each plot is the relaxation time estimated by fitting the CPMG response to a bi-exponential model. H(C6) is the proton fraction of hexane in the mixture. A(C6) is the fraction of the area attributed to hexane. There is good agreement between H(C6) and A(C6). The peaks of the diffusivity distributions are broader than those of the T_2 distributions. This can be explained by the difference in signal/noise for the two measurements. Figure 11 is the correlation between the pure and constituent diffusivity and relaxation time for the *n*-hexane and squalene systems. The measured points compare well with the correlation that was independently developed from pure alkanes and mixture of alkanes.

CONCLUSIONS

1. Crude oils have equal T_1 and T_2 at low viscosity and can be correlated with the ratio of viscosity /temperature. The T_1 of high viscosity crude oils approach a plateau valued that is a function of the Larmor frequency. The

measured T_2 of high viscosity crude oils continue to follow the viscosity/temperature correlation until the loss of information due to finite echo spacing limits the accuracy of the measurements.

2. Methane saturated oils have a relaxation time that departs for the correlation based on methane-free alkanes. These systems can be correlated with the gas/oil ratio in addition to the ratio of viscosity/temperature.
3. Natural gas often has in addition to methane, a significant amount of ethane, propane, CO_2 and nitrogen. Ethane and propane has significantly higher relaxation time for the same molar density compared to methane. Nitrogen and CO_2 have only a small effect on the methane relaxation when the relaxation time is correlated with the total molar density.
4. The relaxation time and diffusivity distributions in hydrocarbon mixtures are correlated through the 'constituent viscosity model.'

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of NSF, USDOE, and the industrial consortium on Processes in Porous Media at Rice University. Also, the contributions of Kelly McCann, Abby Vinegar, Waylon House and Riki Kobayashi are acknowledged. The advice of Harold Vinegar is gratefully acknowledged.

REFERENCES

[1] G.R. Coates, L. Xiao, and M.G. Prammer, NMR Well Logging, Principles & Applications, Halliburton Energy Services, Houston (1999).

[2] K.-J. Dunn, D.J. Bergman, and G.A. Latorraca, Nuclear Magnetic Resonance Petrophysical and Logging Applications, Pergamon, New York, (2002).

[3] J. Bouton, M.G. Prammer, P. Masak, and S. Menger, Assessment of Sample Contamination by Down- Hole NMR Fluid Analysis, Paper SPE-71714, Society of Petroleum Engineers, presented at the 76 th Annual Technical Conference and Exhibition, New Orleans, LA, Sept. 30-Oct. 3, (2001).

[4] P.C. Masak, J. Bouton, M.G. Prammer, S. Menger, E. Drack, B. Sun, K-J. Dunn, M. Sullivan, Field Test Results And Applications Of The Downhole Magnetic Resonance Fluid Analyzer, SPWLA 43rd Annual Logging Symposium, Oiso, Japan, June 2-5, (2002).

[5] C.E. Morriss, R. Freedman, C. Straley, M. Johnston, H.J. Vinegar, and P.N. Tutunjian, Hydrocarbon Saturation and Viscosity Estimation from NMR Logging in the Belridge Diatomite, *The Log Analyst*, March-April (1997), 44-59.

[6] H.J. Vinegar, P.N. Tutunjian, W.A. Edelstein, and P.B. Roemer, Whole-Core Analysis by ^{13}C NMR, *SPE Formation Evaluation*, June (1991), 183-189.

[7] C. Straley, D. Rossini, H. J. Vinegar, P. Tutunjian, C. Morriss, Core Analysis by Low-Field NMR, *The Log Analyst*, March-April (1997), 84-94.

[8] G.A. LaTorraca, K.J. Dunn, P.R. Webber, and R.M. Carlson, Low-Field NMR Determination of the Properties of Heavy Oils and Water-in-Oil Emulsions, *Magnetic Resonance Imaging*, **16**, Nos. 5/6 (1998), 659-662.

[9] S.Kh.G. Kashaev, B. Le, and M.Z. Zinyatov, Proton Spin-Lattice Relaxation, Viscosity, and Vibration of Molecules in the Series of n- Paraffins, translated from *Doklady Akademii Nauk SSSR*, **157**.6, 1438-1440 (August, 1964) 846-848.

[10] J.A. Zaga, Spin-Lattice Relaxation in Pure and Mixed Alkanes and Their Correlation with Thermodynamic and Macroscopic Transport Properties, M.S. Thesis, Rice University, (1987).

[11] J.A. Zaga, Spin-Lattice Relaxation in Normal Alkanes at Elevated Pressures, Ph. D. Thesis, Rice University, (1990).

[12] S.W. Lo, Correlations of NMR Relaxation Time with Viscosity/Temperature, Diffusion Coefficient and Gas/Oil Ratio of Methane-Hydrocarbon Mixtures, Ph.D. Thesis, Rice University (1999).

[13] Y. Zhang, G.J. Hirasaki, W.V. House, and R. Kobayashi, Oil and Gas NMR Properties: The Light and Heavy Ends, paper HHH prepared for presentation at the 43rd SPWLA Annual Logging Symposium, (June 2–5, 2002), Oiso, Japan.

[14] Y. Zhang, NMR Relaxation and Diffusion Characterization of Hydrocarbon Gases and Liquids, Ph.D. Thesis, Rice University (2002).

[15] B. Cowan, Nuclear Magnetic Resonance and Relaxation, Cambridge, New York (1997).

[16] S.-W. Lo, G.J. Hirasaki, W.V. House, and R. Kobayashi, Mixing Rules and Correlations of NMR Relaxation Time with Viscosity, Diffusivity, and Gas/Oil Ratio of Methane/Hydrocarbon Mixtures, *SPEJ*, (March, 2002), 24-34.

[17] S. Rajan, K. Lalita, and S.V. Babu, Intermolecular Potentials from NMR Data: I. CH_4-N_2 and CH_4-CO_2, *Can. J. Phys.* (1975), **53**, 1624-1634.

[18] R. Freedman, S.-W. Lo, M. Flaum, G.J. Hirasaki, A. Matteson, and A. Sezginer, A New NMR Method of Fluid Characterization in Reservoir Rocks: Experimental Confirmation and Simulation Results, *SPEJ* (December, 2001) 452-464.

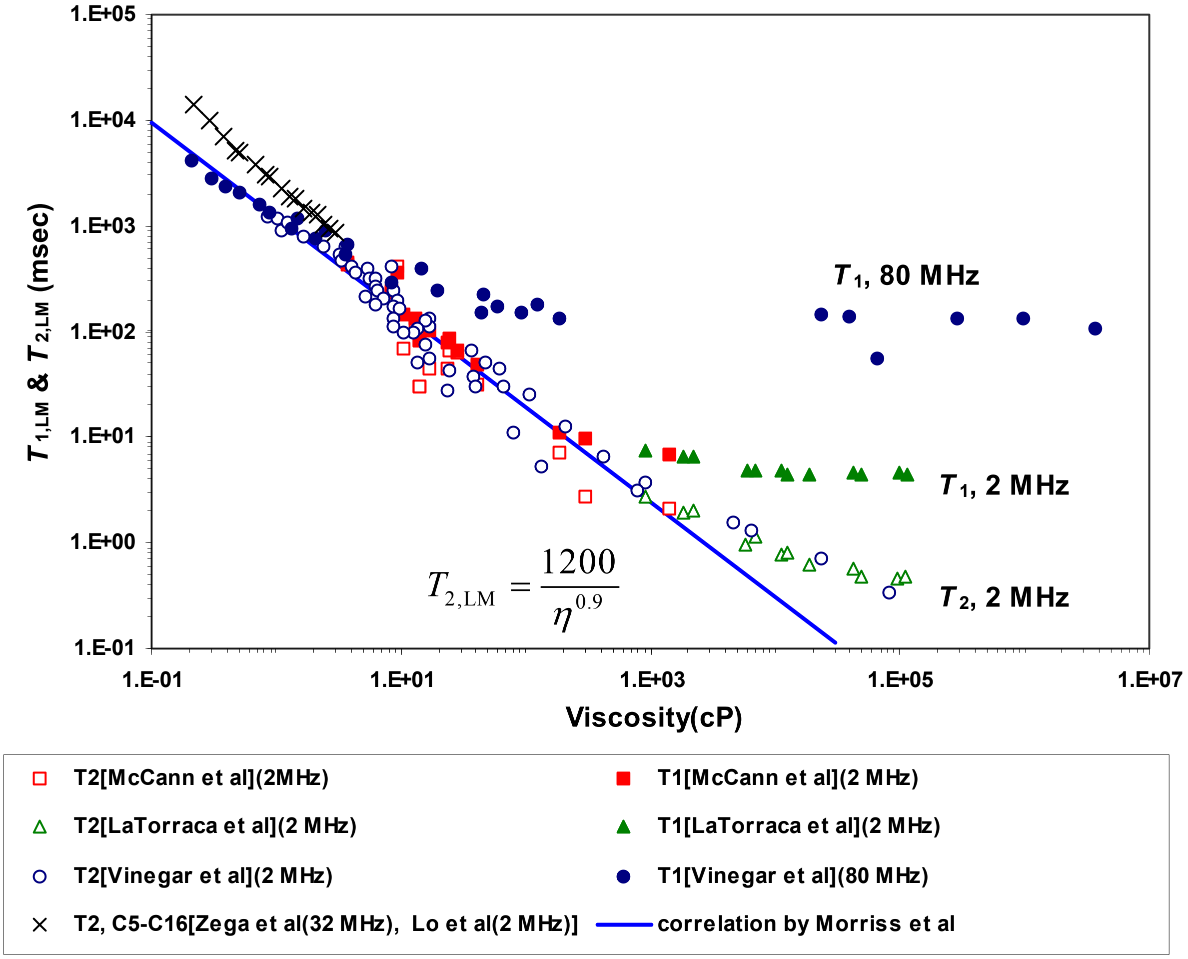

Fig. 1 T_1 and T_2 relaxation times of alkanes, crude oils, and viscosity standards at a Larmor frequency of 2 and 80 MHz. (Zhang et al. [13])

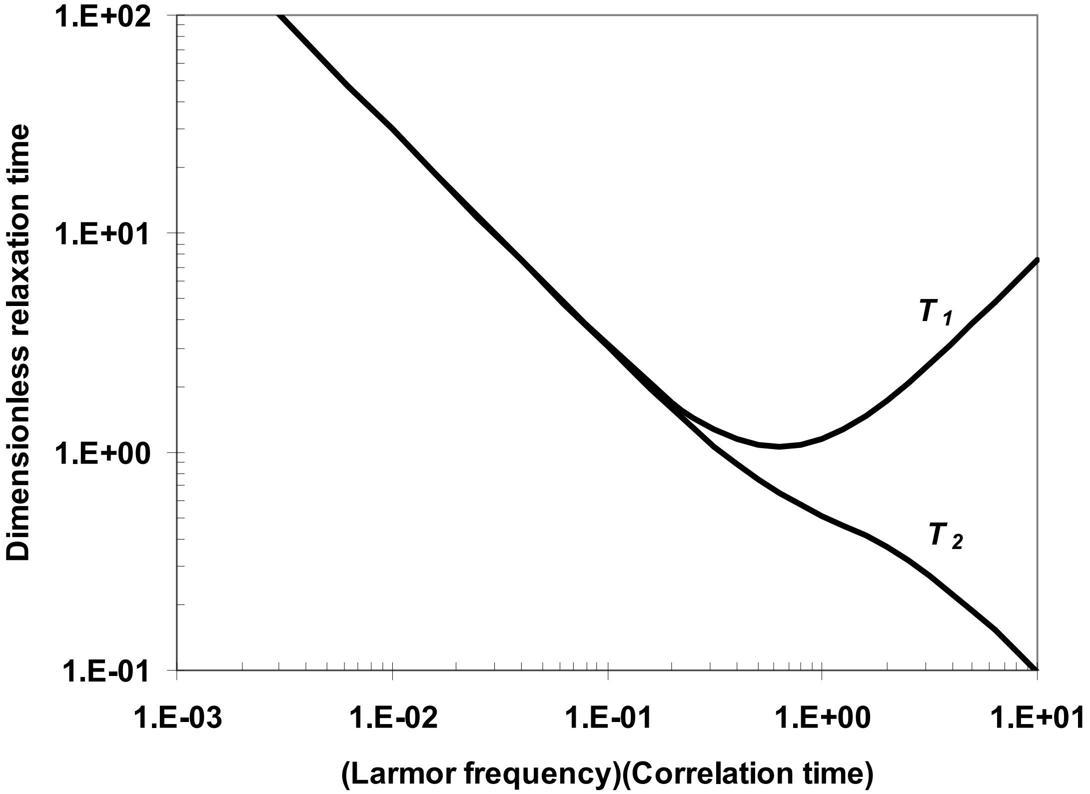

Fig. 2 Dimensionless T_1 and T_2 relaxation times (Zhang et al. [13])

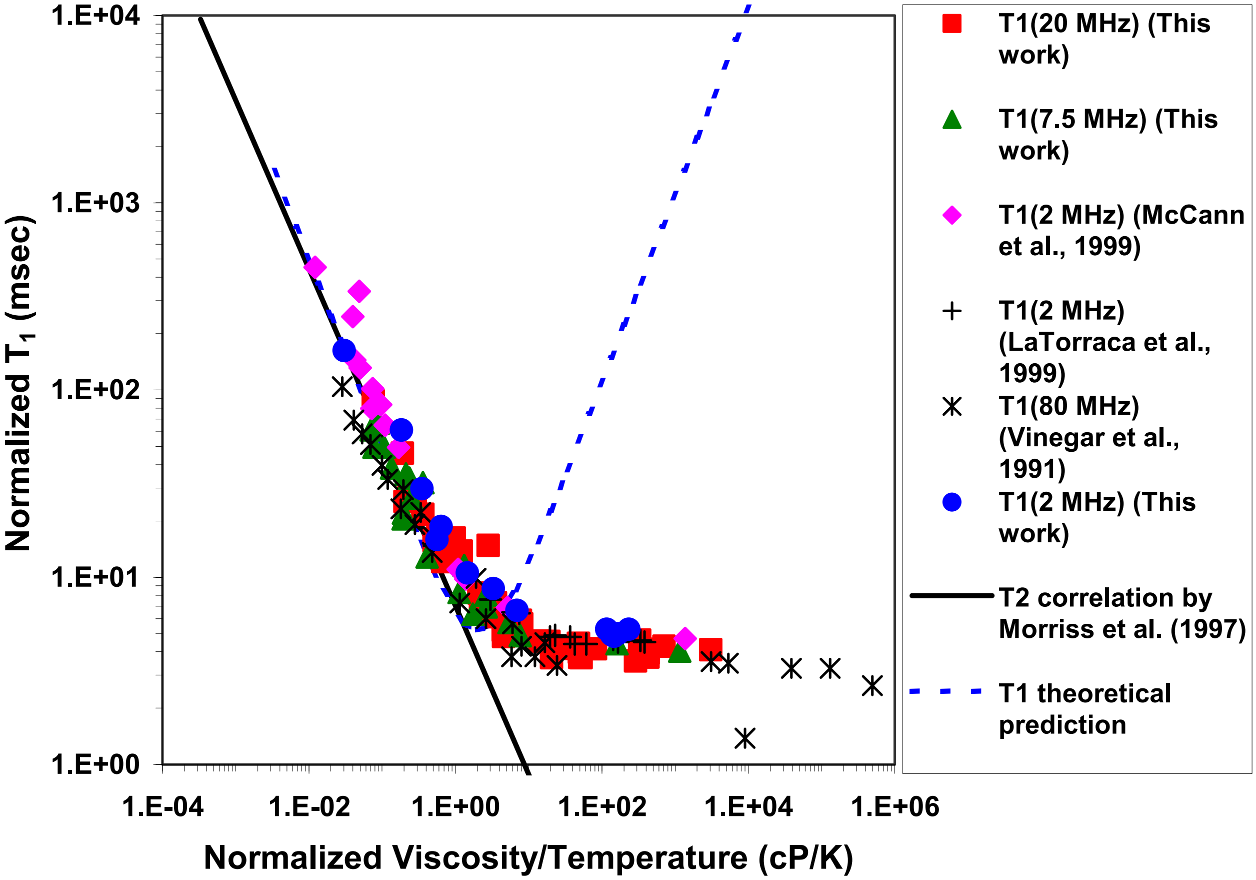

Fig. 3 T_1 and T_2 relaxation times and viscosity/temperature normalized with respect to Larmor frequency (Zhang, et al [13]).

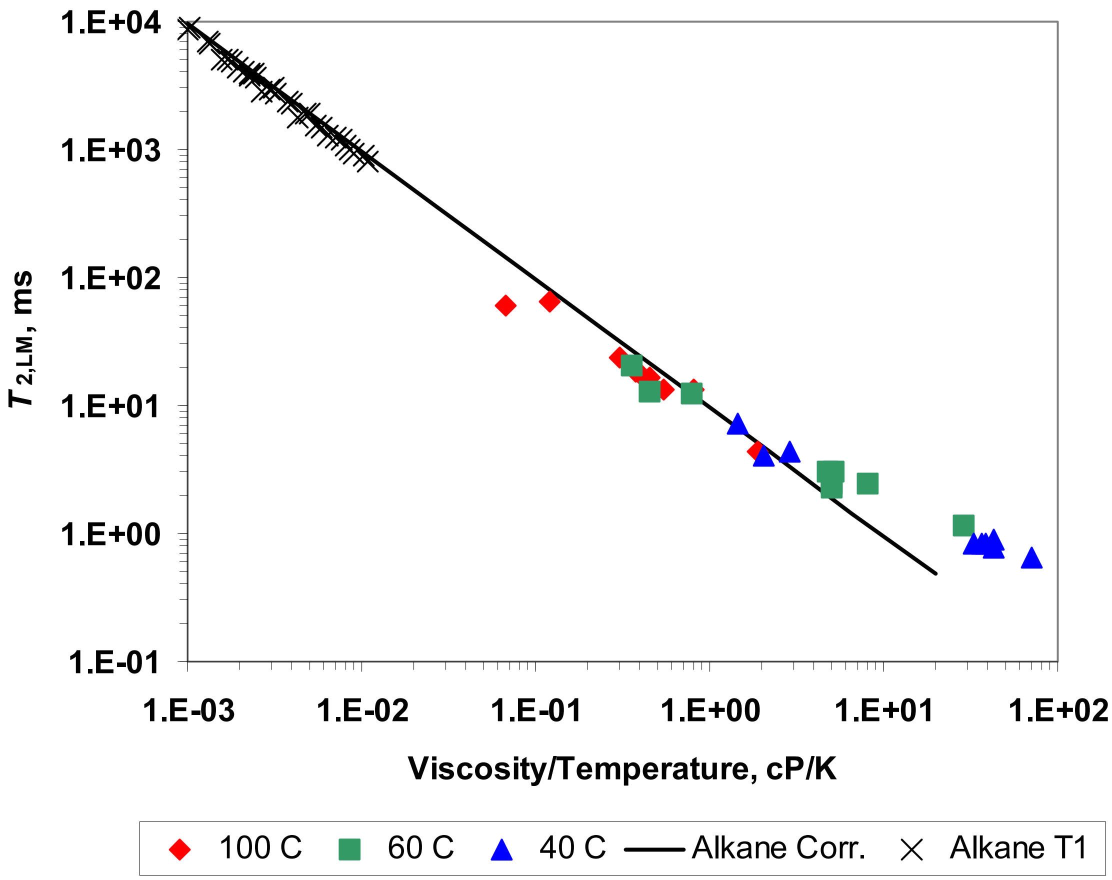

Fig. 4 $T_{2,LM}$ at elevated temperatures are represented by the correlation derived for alkanes. Measurements were made at 20 MHz with 0.2 ms echo spacing.

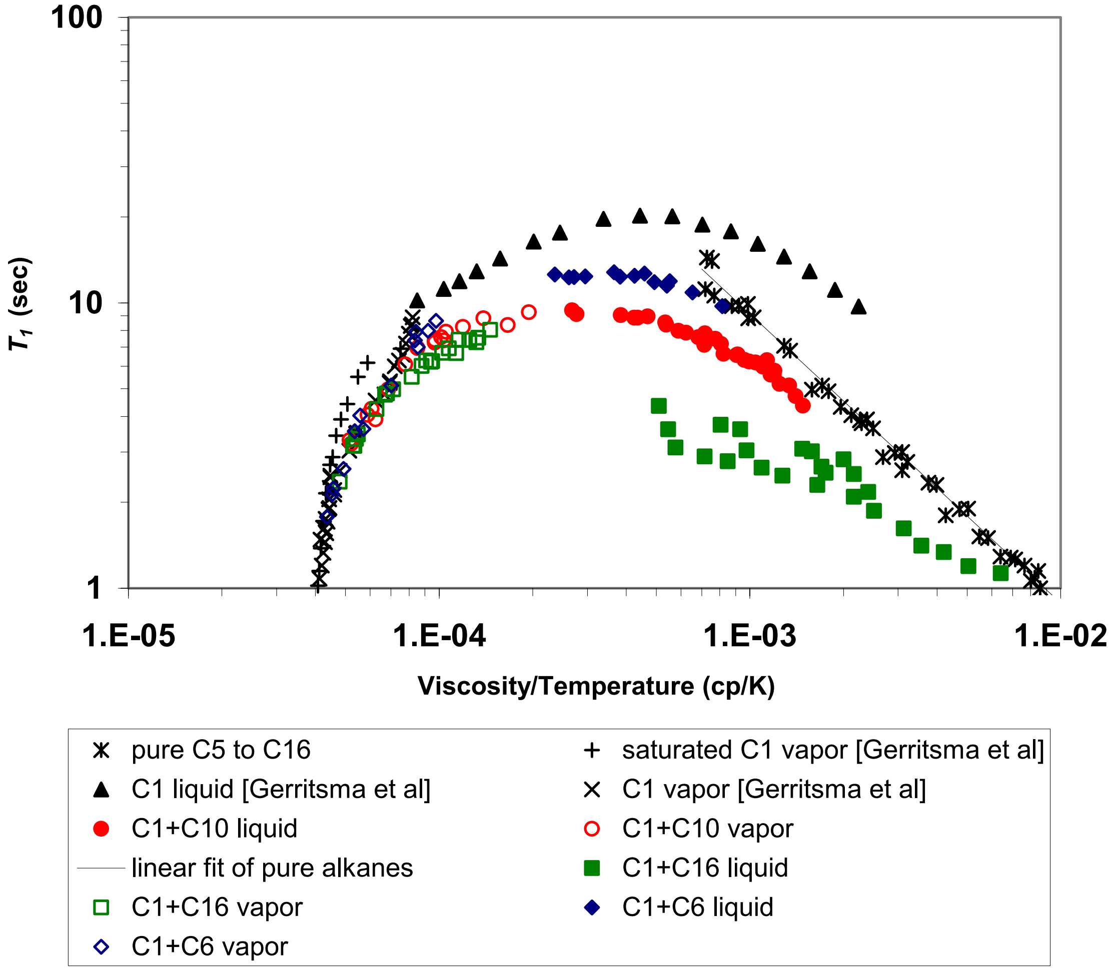

Fig. 5 Relaxation time for methane and methane-higher alkane mixtures do not correlate with that for the pure higher alkanes (Lo et al. [16]).

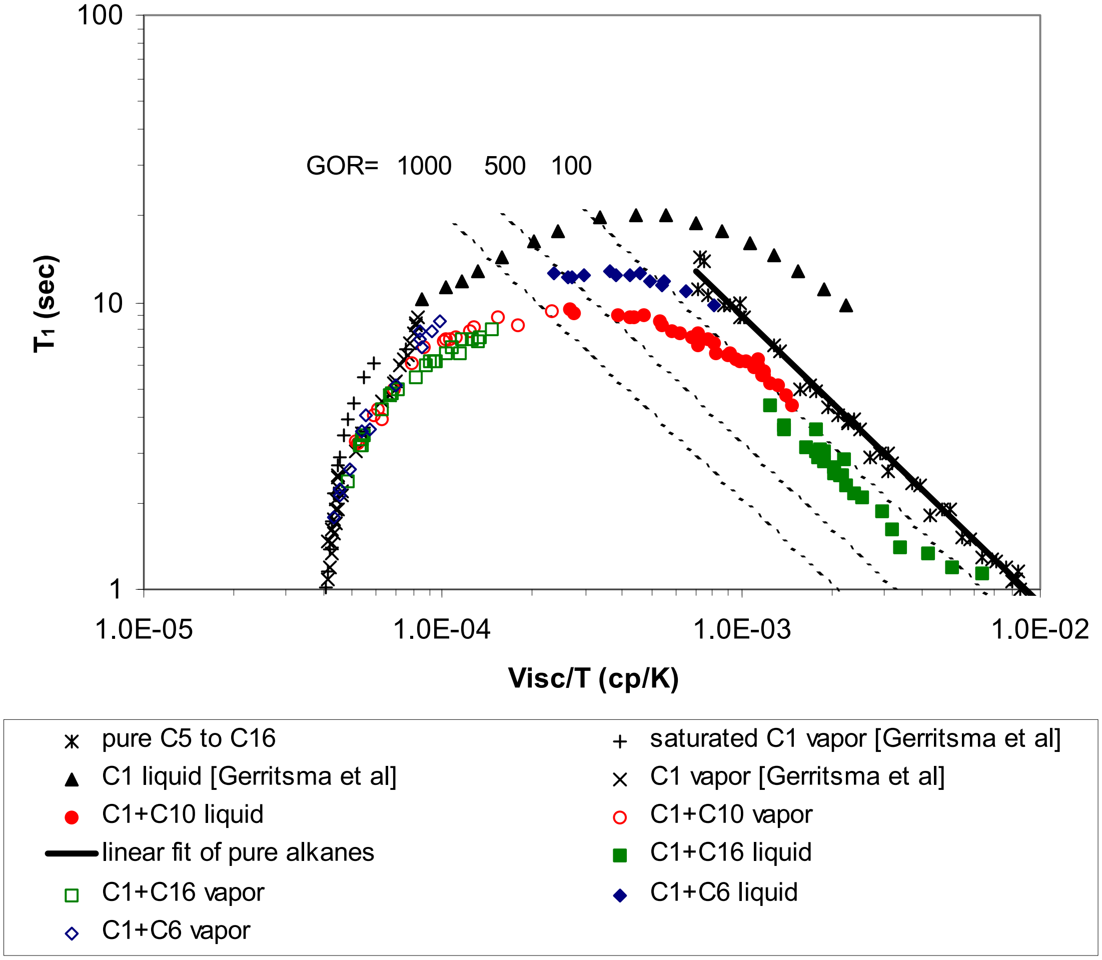

Fig. 6 Relaxation time of live oils correlate with the gas/oil ratio (Lo et al [16]).

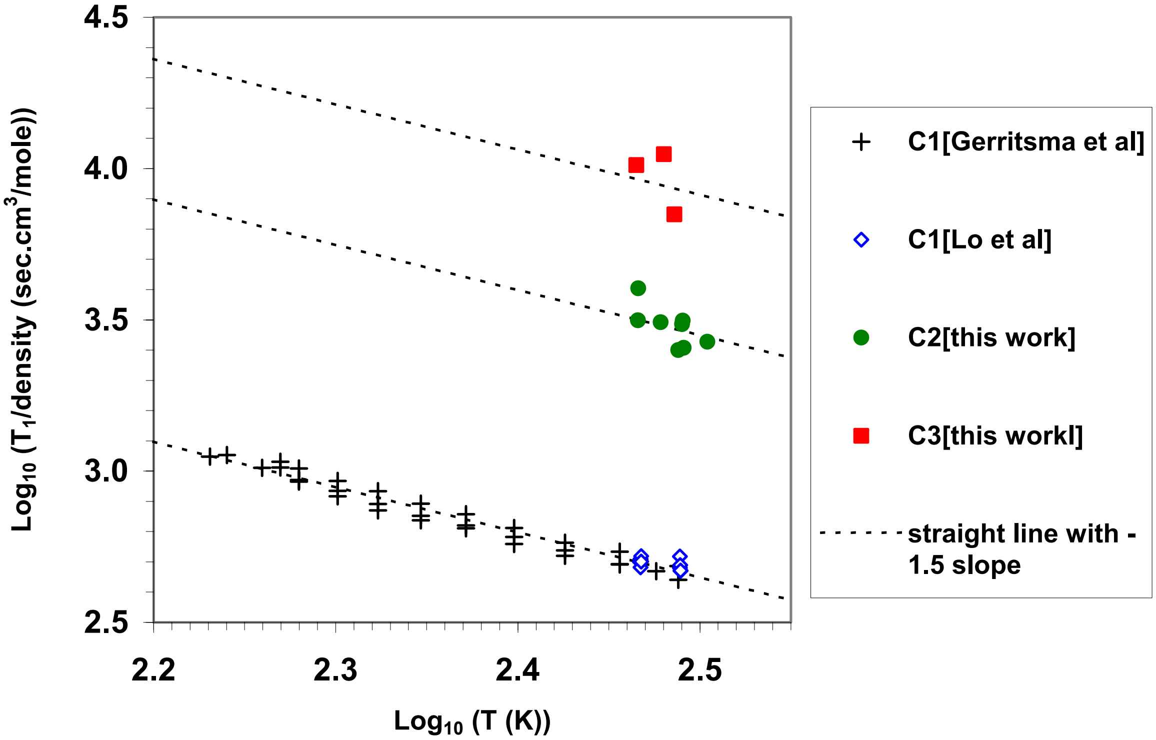

Fig. 7 Relaxation time of methane, ethane, and propane (Zhang et al. [13]).

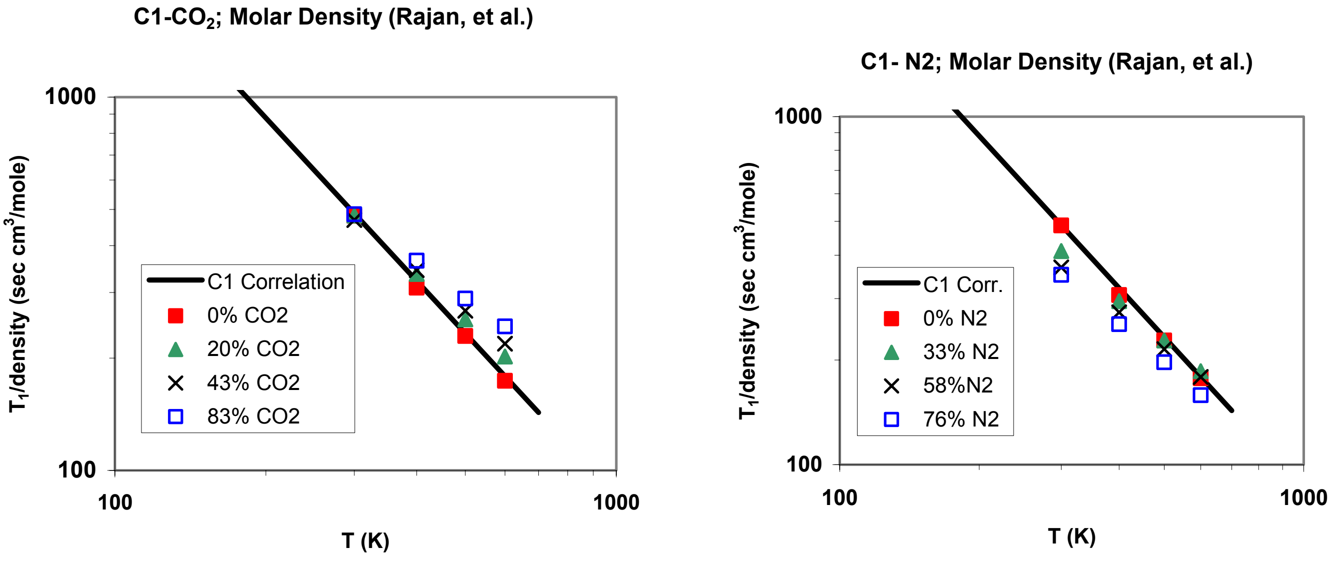

Fig. 8 Relaxation time of methane in the presence of CO_2 or nitrogen (Zhang et al. [13])

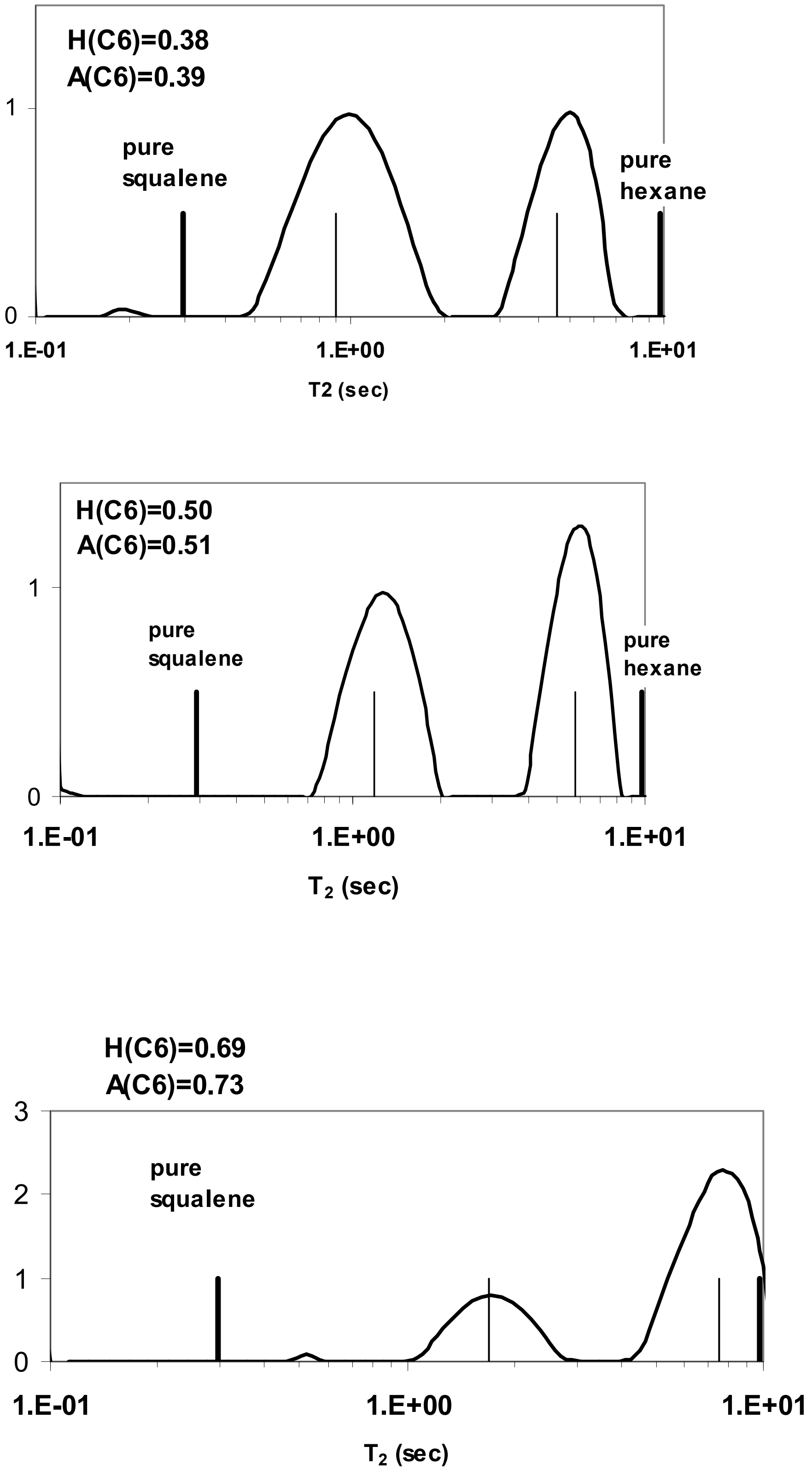

Fig. 9 Relaxation time distributions of squalene – *n*-hexane mixtures (Freedman et al. [18]).

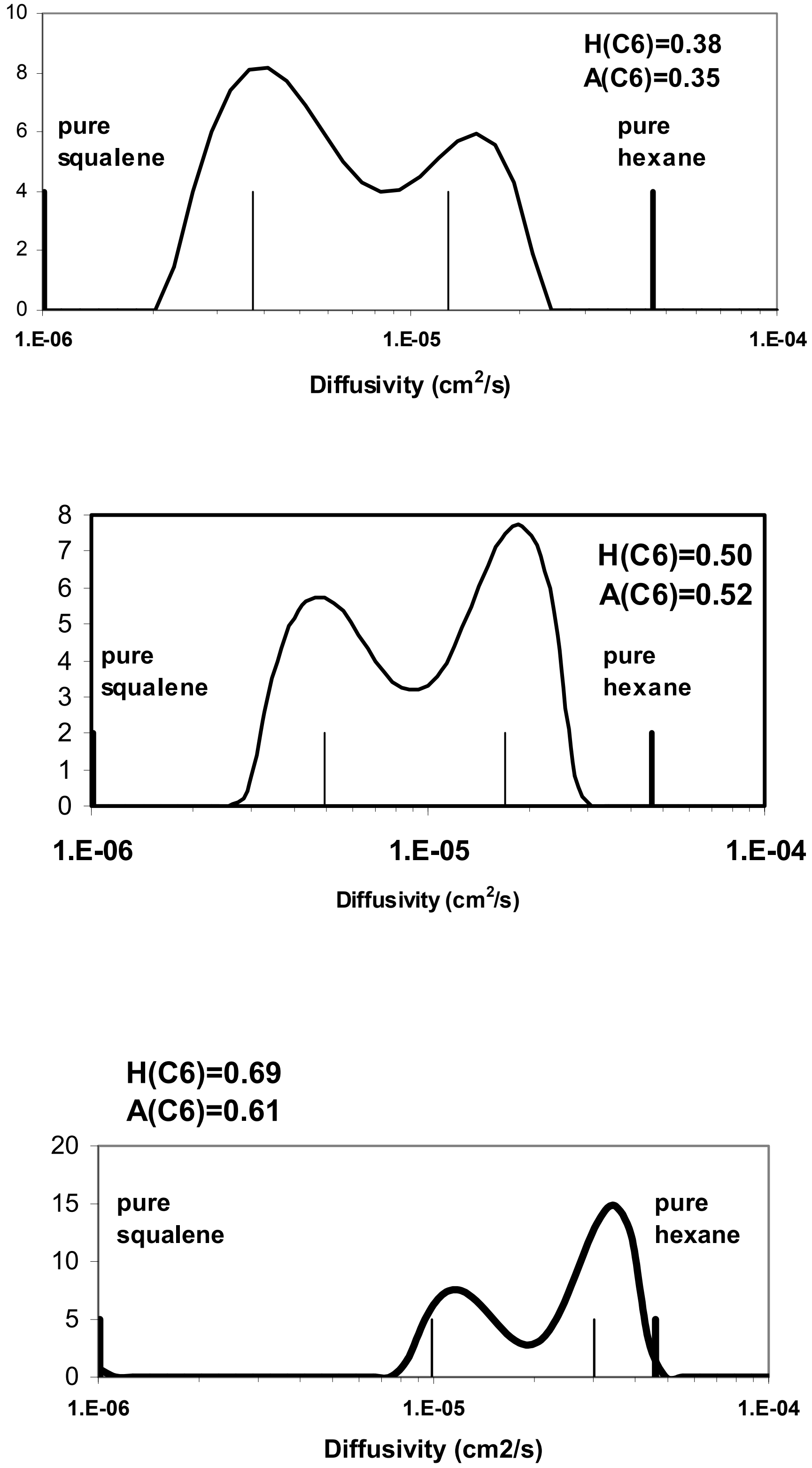

Fig. 10 Diffusivity distributions of squalene – *n*-hexane mixtures (Freedman et al. [18]).

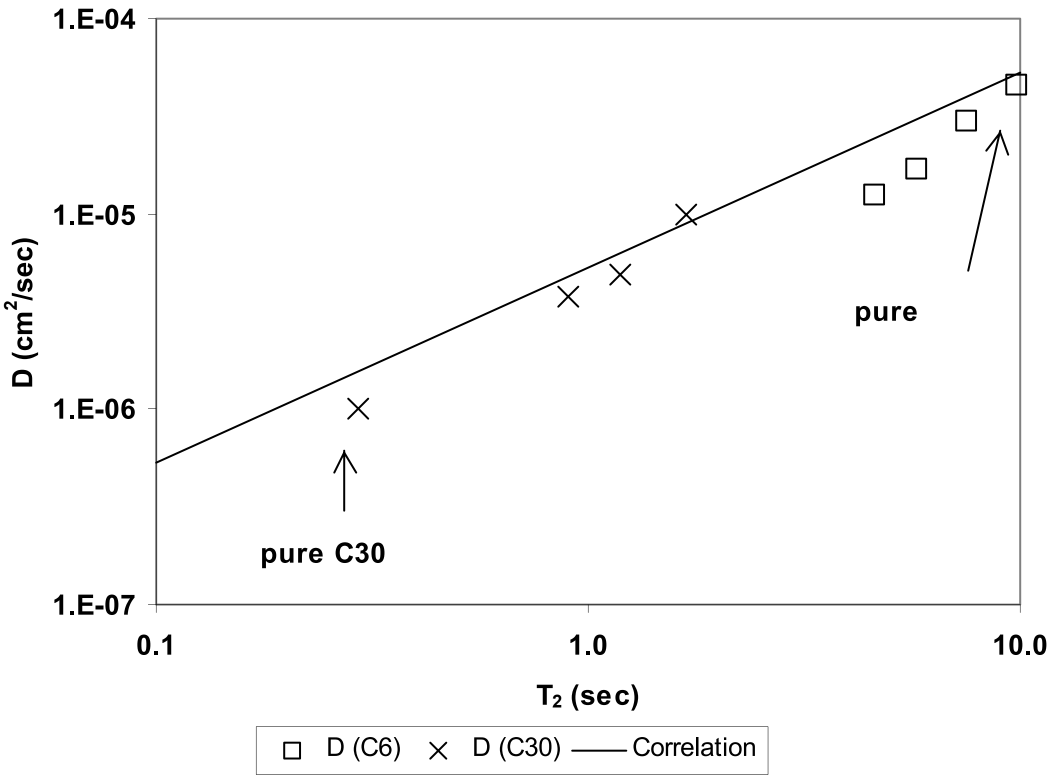

Fig. 11 Correlation between diffusivity and relaxation of pure components and mixtures (Freedman et al. [18]).