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**NMR Response of Liquids and
of Natural Gas Mixtures**

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ABSTRACT

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This research relates T_1 and T_2 to thermodynamic and transport properties, such as composition and possibly density and viscosity, for types of reservoir fluids that have not previously been systematically studied using nuclear magnetic resonance (NMR). NMR measurements, which provide quantitative values including relaxation times T_1 and T_2 , assist in detecting and characterizing formation oils and gases. This work involves NMR laboratory experiments at a ^1H frequency of 2 MHz. Thermodynamic and transport properties are established by sample preparation or are obtained by measurement or are based on available data. Then, the connection between these properties and NMR data is developed or assessed. These relationships are the basis of NMR correlations. Previous correlations have been developed for linear alkanes, for oil mixtures containing methane, and individually for methane and ethane. A theoretical model exists for natural gas mixtures.

The current work addresses three situations that existing correlations do not treat. First, results appear for NMR estimation of crude oil contamination by base oils. The presence of base oils interferes with NMR assessments of crude oils. Relating T_2 measurements to the level of contamination provides the answer, shown for three separate crude oils mixtures with a base oil

contaminant. This work develops two novel evaluative parameters, namely selective contamination index (SCI) and distribution parameter index (DPI), to interpret the effect of contamination of crude oil with base oils. The SCI and DPI surpass standard methods in the precise determination of the degree of contamination. The second topic is assessing T_1 and T_2 for cyclic molecules and base oils. Though monocyclic aromatic and aliphatic molecules deviate from alkane correlations, it is found that bicyclic compounds and base oils do not. Another situation this work addresses is the determination of T_1 and T_2 for gaseous mixtures of methane and other natural gas components. The measurements illustrate the effect of density and composition on NMR assessments. Methane and ethane measurements are presented, as are measurements and interpretation for gas mixtures. The latter measurements show good agreement with NMR gas mixing rules.

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Chapter 1: Introduction

This research relates nuclear magnetic resonance (NMR) measurements of relaxation to viscosity and (where appropriate) composition of oils and gases in situations where standard interpretations are problematic. NMR measurements are increasingly being used in oil exploration and production (Stambaugh 2004). In the oilfield setting, these measurements occur in a phase called well logging. Well logging is an integral step in the oil exploration and production development process. A readable account of well logging is provided by Clark and Kleinberg (2002). Logging occurs in formations where wells are drilled and formation information is desired. This information may refer to either the fluids in the formation and/or the characteristics of the formation itself.

However, this work deals only with the fluid aspects of NMR measurements. The fluids in oil or gas reservoirs are mixtures of components. In particular, crude oils may contain alkanes, aromatics, asphaltenes, and other components containing the heteroatoms sulfur, oxygen, and nitrogen (Rudzinski and Aminabhavi 2000). A gross accounting of these components is done through a measurement with the acronym SARA. SARA stands for Saturates-Aromatics-Resins-Asphaltenes, where saturates are equivalent to alkanes and resins contain functional groups including carboxylates, sulfoxides, amides, thiophenes, and pyridines (Rudzinski and Aminabhavi 2000), which contain heteroatoms such as oxygen, nitrogen, and sulfur. Although the SARA analysis identifies classes of molecules in crude oils, more intensive methods are needed for determining components within the SARA classes (Rudzinski and Aminabhavi

2000). In addition, crude oils often contain dissolved gases like methane, ethane, and carbon dioxide (McCain Jr., 1990). All this serves to illustrate that hydrocarbons in formations are themselves complex, irrespective of the formation properties. This complexity contributes to the observed NMR response.

In NMR well logging, data can appear as relaxation information, in the form of the relaxation times T_1 and T_2 , or diffusivities. Methods to simultaneously obtain T_2 relaxation times and diffusivities have especially received strong attention (Coates *et al.* 1995, Hürlimann *et al.* 2002). The simultaneous obtainment of T_2 and diffusivity is facilitated by so-called diffusion editing measurements (Hürlimann and Venkataramanan 2002). In diffusion editing, a “suite” of measurements is made, each at a different magnetic field gradient. The addition of these gradients slightly modifies typical T_2 measurements to attain responsiveness to diffusion. The combined attainment of T_2 and diffusion yields diffusivity- T_2 (D - T_2) maps, which are contour plots of the combined distributions of T_2 relaxation times and of diffusivities of the sample measured (Hürlimann and Venkataramanan 2002). Methods for measuring relaxation times will be given in Chapter 3.

The previous paragraph provides a brief overview of what is measured in NMR well logging. Here, the discussion shifts to how the measurements occur. In a typical well-logging situation, operators send tools, possibly including NMR tools, into the drilled borehole for measurements as a function of depth. This

mode of operation is called “wireline” operation, referring to the use of logging tools in wells that have already been drilled.

Fig. 1.1 (Stambaugh 2004) shows a sketch of a typical logging tool, manufactured by Halliburton. Logging tools are long (15 to 50 ft) and slim (approximately 6 inches in diameter) (Stambaugh 2004). The diameter is such that the tool can fit into drilled well bores. Housed within the tools themselves is a permanent magnet, which provides the magnetic field for the measurements. The RF pulses generated also originate from the within the tools. One important result of housing the permanent magnet within the tools is that the magnetic field is inhomogeneous (Kleinberg 1996). That is, different portions of the surrounding formation experience different magnetic fields. Hence, the magnetic field gradients necessary for measuring diffusion exist solely as a result of the design of the NMR logging tools (Kleinberg 1996).

Modern tools also have another important feature. The operating frequency of the logging tool can be changed, which allows multiple depths of investigation (Coates *et al.* 1999). This is illustrated in Fig. 1.2 (Stambaugh 2004). The three annuli shown in red are three regions in the formation brought into resonance as a result of three different operating frequencies of the tool. Although some tools measure entire annuli as shown in Fig. 1.2, others investigate different distances from the borehole via small sideward-looking sections of the formation, as depicted by the cartoon in Fig. 1.3 (Stambaugh 2004).

Up to this point, only the wireline mode of NMR well-logging has been mentioned. However, some NMR logging tools make fluid measurements in two other modes of operation. They are logging-while-drilling (LWD) and fluid sampling.

LWD is treated first. It has become more practical to log wells while they are being drilled because of improvements in NMR technology (Prammer *et al.* 2000, Horkowitz *et al.* 2002). In wireline operation, the relaxation times measured are usually T_2 relaxation times because the longer duration of time required to measure T_1 limits its practical use (Kleinberg 1996). However, because the drilling process is slower than wireline logging, measurement of T_1 during drilling has become more practical (Prammer *et al.* 2000). In fact, T_2 measurements are more problematic due to the rugged motions experienced by a drilling tool. Unlike T_2 measurements, T_1 logging is not sensitive to tool motion (Prammer *et al.* 2002).

Fluid sampling provides another avenue where T_1 measurements can be done, but with wireline tools. Fluid sampling refers to the acquisition of a quantity of fluid from the formation. The following describes the features of a fluid sampler used by Masak and co-workers (Masak *et al.* 2002). In the fluid sampler, both T_1 and T_2 can be measured on the sample, with a flow-through cell within the tool proving particularly convenient for T_1 . This flow-through cell allows a fluid to flow while T_1 measurements are made. Flow can also be stopped for T_2 measurements.

Relaxation times and diffusivity from NMR measurements can be related to other fluid properties. Important fluid information obtained via NMR includes hydrogen index; oil viscosity; and discernment between oil, water, and gas (Kleinberg and Vinegar 1996, Freedman *et al.* 2001). Although it will not be treated here, NMR can also provide information about the formation containing these fluids (Coates *et al.* 1999).

One current interpretation of NMR measurements regards linear alkane liquids (without their dissolved gases) as an appropriate model for NMR relaxation of crude oils (Lo 1999). In the presence of dissolved gases, linear alkanes with dissolved methane serve as the model for crude oils (Lo 1999). That is, linear alkanes (with or without methane) were used to develop some of the current correlations for crude oils, where the correlations relate NMR relaxation times to viscosities and diffusivities (Lo 1999). Correlations based on alkanes and methane, as well as others will be expanded upon in Chapter 2. This research is intended to address those situations, however, that require treatment outside the jurisdiction of these correlations.

The specific issues in the studies below are now introduced. The topics are three in number. The first topic is relating NMR relaxation measurements to the level of contamination of crude oils with base oils. Base oils are a kind of refined oil added to aid in the drilling process. The second topic regards the behavior of liquid molecules that are not linear alkanes, which may be present down hole. Finally, this work verifies a recently developed model for relaxation behavior in gas mixtures.

The topics mentioned above address a common need. They all elucidate the relationship of NMR parameters— T_1 and T_2 —to composition and viscosity. Furthermore, they address compounds or mixtures that are known to exist in particular formations but whose contribution to measured NMR data has not been explained in previous work. Thus, this work attempts to form a bridge between circumstances observed in actual practice and the available capabilities of earlier NMR fluid correlations.

The contents of this thesis will provide the framework for appreciating the issues involved in relating fluid properties such as viscosity, diffusivity, and composition to NMR relaxation times. Chapter 2 provides a theoretical background, which is the basis for relating NMR to hydrodynamic properties. Correlations for various fluids are also expressed in this chapter. Chapter 3 provides the experimental procedures used for this work. Chapters 4 and 5 treat two of the topics mentioned above, namely crude oil contamination by base oils and the relationship of relaxation time to viscosity for compounds that are not linear alkanes. Chapter 6 treats NMR measurements of natural gas components and mixtures. The natural gas mixture data match the NMR mixing rule for natural gases.

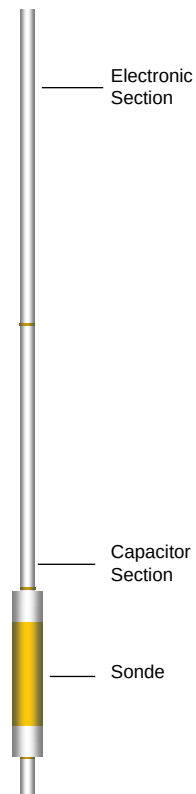


Figure 1.1: Illustration of a typical well-logging tool. The particular tool shown is a Halliburton/NUMAR tool called the MRIL-D. (Figure courtesy of Brian Stambaugh, NMR Petrophysics, Inc.)

MRIL Sensitive Volume

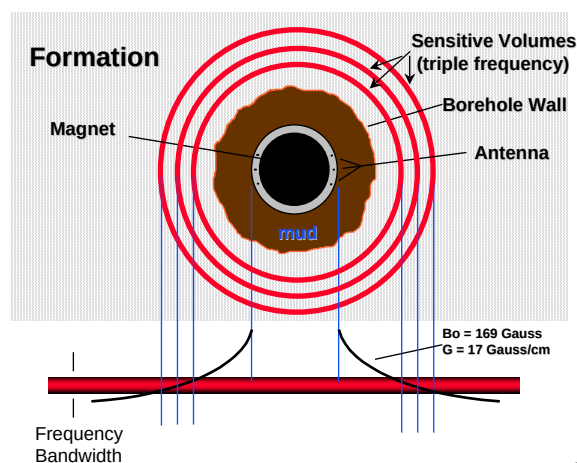


Figure 1.2: Cross-sectional view of sensitive regions for current NMR tools. In particular, sensitive regions for a Halliburton/NUMAR tool with three depths of investigation are shown. (Figure developed by NUMAR and obtained courtesy of Brian Stambaugh, NMR Petrophysics, Inc.)

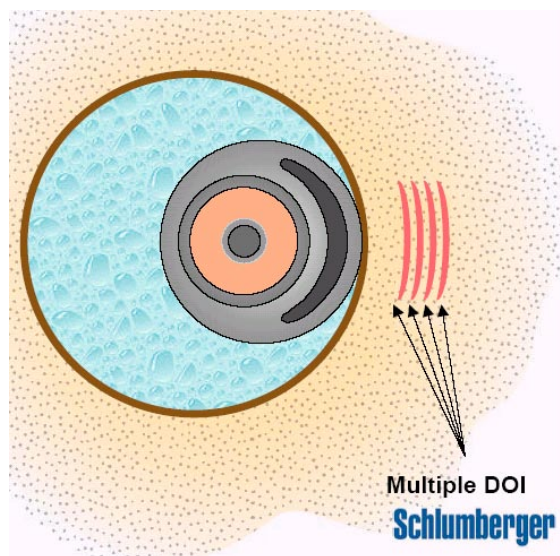


Figure 1.3: Cross-sectional view of sensitive regions for other NMR tools. Sensitive regions for Schlumberger MRX tool are curved slices at different depths of investigation are shown. (Figure developed by Schlumberger and obtained courtesy of Brian Stambaugh, NMR Petrophysics, Inc.)

Chapter 2: Theory and Background

Before proceeding to the objectives of this work, this chapter provides some explanation of mechanisms involved in NMR and motivation for using NMR measurements to derive information about fluid viscosity, composition, density, or diffusivity. This chapter proceeds from providing an account of NMR attenuation through relaxation and diffusion to introducing some models for relaxation for fluids likely to be encountered in this research. The chapter also includes correlations developed for particular classes of molecules. The chapter concludes with the magnetic resonance fluid (MRF) model, which relates T_2 relaxation times to viscosities and diffusivities of crude oil constituents.

2.1 Relaxation Processes

Spin-lattice and spin-spin relaxation, associated respectively with relaxation times T_1 and T_2 , can be expressed in terms of the relaxation mechanisms responsible for restoring the bulk magnetization to equilibrium. For ^1H molecules, T_1 follows the expression (Coates *et al.* 1999)

$$\frac{1}{T_1} = \frac{1}{T_{1,\text{bulk}}} + \frac{1}{T_{1,\text{surface}}} \quad (2.1)$$

for conditions encountered in oilfield samples. In Equation 2.1, the relaxation rates are expressed as inverses of relaxation times. T_1 is the spin-lattice time constant for the fluid in the sample being measured, $T_{1,\text{bulk}}$ is the intrinsic relaxation time of the fluid, and $T_{1,\text{surface}}$ is the relaxation time due to any solid surfaces contacting the fluid. For the purposes presented here, the sample is

always a fluid or mixture of fluids; therefore, the second term in Equation 2.1 does not contribute to the relaxation.

Spin-spin relaxation behaves according to (Coates *et al.* 1999)

$$\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \frac{1}{T_{2,\text{surface}}} + \frac{1}{T_{2,\text{diffusion}}} \quad . \quad (2.2)$$

T_2 , $T_{2,\text{bulk}}$ and $T_{2,\text{surface}}$ are analogs to the respective quantities for spin-lattice relaxation. However, $T_{2,\text{diffusion}}$ is unique to spin-spin relaxation. It represents relaxation due to motion of the spins, which requires the presence of some gradients in the magnetic field. For cases with no solid surfaces, like in this work, the surface relaxation term in Equation 2.2 drops. Once the expression for the relaxation due to diffusion is included, the result is Equation 2.3 (Bendel, 1990),

$$\frac{1}{T_2} = \frac{1}{T_{2,\text{bulk}}} + \frac{D(\gamma G T_E)^2}{12} \quad . \quad (2.3)$$

The new terms in this equation are D , the diffusivity of the fluid being measured; γ , the proton gyromagnetic ratio; G , the magnetic gradient strength, and T_E , the time between RF pulses, called the echo spacing. The expression for $T_{2,\text{diffusion}}$, the second term on the right hand side of Eq. 2.3, applies under typical logging conditions. Specifically, it assumes a constant gradient (not shorter-duration, pulsed gradients) and a CPMG pulse sequence.

2.2 Diffusion and Viscosity

The previous section briefly mentioned the role of diffusion in relaxation measurements. Theoretical considerations also relate diffusion to viscosity. This will be treated first, before proceeding to relating relaxation times and viscosity

through relaxation mechanisms. The diffusivity can be defined as an autocorrelation function of velocity (Einstein 1926):

$$D = \int_0^{\infty} \langle U(0) U(t) \rangle dt . \quad (2.4)$$

This diffusivity can then be related to parameters of the fluid (Abragam 1961):

$$D = \frac{k T}{4 \pi a \eta} . \quad (2.5)$$

This is the famous Stokes-Einstein relationship, relating viscosity, temperature and diffusivity. Note that the characteristic dimension a in this equation is for a sphere of radius a . Thus, diffusivity is related to viscosity as

$$D \propto \frac{T}{\eta}, \quad (2.6)$$

a proportionality that is being used in industrial practice (Freedman *et al.*, 2001b).

One can relate T_1 and T_2 directly to diffusivity if the relation in Equation 2.5 is used with expressions for relaxation mechanisms in terms of viscosity. Expressions to relate relaxation and viscosity are shown in the following section.

2.3 Bulk Fluid Relaxation Mechanisms

2.3.1 Types of Mechanisms

This section considers the situation where NMR relaxation by diffusion is neglected. For fluids under this provision, one term remains in the respective relaxation rate expression for each relaxation process, namely $T_{1,bulk}$ or $T_{2,bulk}$. These remaining terms correspond to bulk fluid relaxation. The bulk relaxation in fluids can occur by several mechanisms. Hence, a rate expression can be

written to describe the contribution to each of these mechanisms to the bulk relaxation. The rate expression is as follows for relaxation mechanisms encountered for the fluids in this thesis (Lo 1999):

$$\frac{1}{T_{n,bulk}} = \frac{1}{T_{n, intra_dp-dp}} + \frac{1}{T_{n, inter_dp-dp}} + \frac{1}{T_{n, para}} + \frac{1}{T_{n, sr}} \quad . \quad (2.7)$$

In Equation 2.7, T_n refers to either relaxation process, T_1 or T_2 . $T_{n, intra_dp-dp}$ is the relaxation due to intramolecular dipole-dipole interactions, $T_{n, inter_dp-dp}$ is the relaxation due to intermolecular dipole interactions, $T_{n, para}$ is the relaxation due to paramagnetic species, and $T_{n, sr}$ is the relaxation due to spin-rotation.

A brief description of each of these mechanisms follows. Both intermolecular and intramolecular dipole-dipole interactions refer to ^1H magnetic dipoles interacting with each other to cause relaxation. In the intramolecular dipole-dipole mechanism, the magnetic dipoles are on the same molecule; and in the intermolecular dipole-dipole mechanism, the dipoles are on different molecules. Intermolecular dipole-dipole interactions depend on translational motion of molecules, whereas intramolecular dipole-dipole interactions are more sensitive to molecular rotations (McConnell 1987). Intramolecular dipole-dipole interactions dominate for larger liquid molecules, where molecules translate relatively slowly for intermolecular interactions to be important. For smaller molecules, intermolecular interactions become more significant, potentially becoming the more substantial mechanism in gases. Paramagnetic relaxation can be due to metal ions (Coates *et al.* 1999) or dissolved oxygen (Chen *et al.* 2004) in the measured fluid. This mechanism occurs due to magnetic properties of electrons, whose gyromagnetic ratio is over two orders of magnitude greater

than that of the proton γ (Farrar and Becker 1971). So even a small amount of paramagnetic species dominates the relaxation. Spin-rotation interactions occur most prominently with small sphere-like molecules (Fukushima and Roeder 1981). Spin rotation refers to relaxation resulting from coupling of nuclear spins with molecular angular momentum fluctuations (Fukushima and Roeder 1981).

The significance of the relaxation mechanisms included in Equation 2.7 is that previously developed theory for relaxation mechanisms suggests relationships between relaxation time and viscosity or diffusivity. Theoretical expressions for each of the relaxation mechanisms will now be shown, as will correlations based on these mechanisms. The development has been shown in prior works (Lo, 1999; Y. Zhang, 2002). Therefore, what follows will be limited to presenting expressions for each of the mechanisms. One fact to remember is that in most of the expressions, one assumes fast motions (called “extreme narrowing”), which means that fluid molecules containing the ^1H spins are moving fast enough that all spins, on average experience the same field to average any local field that may develop (Slichter 1963). The practical effect is that T_1 becomes equal to T_2 when extreme narrowing applies (Farrar and Becker 1971).

When conditions for extreme narrowing no longer hold, T_1 and T_2 can differ. This happens for fluids with high viscosities, as in heavy crude oils, or when the Larmor frequency is large (Y. Zhang 2002). Both result in the time scale of molecular motions being slow compared to the Larmor period (Farrar and Becker 1971). A method to address this situation will be mentioned below.

A good source for relaxation mechanisms and correlations for oilfield fluids is Hirasaki, *et al.* (2003).

2.3.2 Theory of Dipole-dipole Interactions

Intramolecular dipole-dipole interactions between like spins can be described with Equation 2.8 (McConnell, 1987),

$$\frac{1}{T_{1,\text{intra_dp-dp}}} = \frac{8\gamma^4 \hbar^2 I(I+1) \pi \sigma^3 \eta}{3r^6 kT} \quad . \quad (2.8)$$

Equation 2.8 uses rotational Brownian motion theory, assuming spherical top molecules. It is further assumed that rotation and translation can be treated independently and that rotation or vibrations internal to the molecule can be neglected (McConnell, 1987). In Equation 2.8, I is the angular momentum quantum number, $\hbar$ is Planck's constant divided by 2π , γ is the ^1H gyromagnetic ratio, k is the Boltzmann constant, and T is the absolute temperature. The remaining quantities are σ , the characteristic length of the intermolecular potential; η , the fluid viscosity; and r , the distance separating the two spins that interact in a dipolar fashion on the same molecule.

For intermolecular dipole-dipole interactions, the expression relating the relaxation rate to the viscosity is (McConnell, 1987)

$$\frac{1}{T_{1,\text{inter_dp-dp}}} = \frac{32\pi^2 N \gamma^4 \hbar^2 I(I+1) \eta}{15kT} \quad . \quad (2.9)$$

This equation assumes Brownian motion and a uniform density of independent spins (McConnell, 1987). The new quantity in Equation 2.9 is N , the number of independent magnetic spins per unit volume.

For both dipole-dipole interactions above, note that the relaxation rate is proportional to η/T . When dipole-dipole interactions are dominant, this provides a basis for correlating relaxation to viscosity and to diffusion, the latter using the Stokes-Einstein relation. The work by R. J. S. Brown (1961) first provided experimental evidence for a potentially quantitative relationship between relaxation times and viscosity for crude oils. What follows will recount the subsequent work that has expanded on this point.

2.3.3 Empirical Relationships for Dipole-Dipole Interactions

2.3.3.1 Linear Alkanes

One of the primary constituents of crude oils is alkanes (McCain Jr. 1990). In liquid linear alkanes (a.k.a. n-alkanes), dipole-dipole interactions are dominant (Kashaev *et al.* 1964). Some of the previous work using NMR to study linear alkanes will be reviewed.

In the work of Kashaev, *et al.* (1964), spin-lattice relaxation times and viscosity were measured for n-alkanes from pentane to heptadecane. The alkanes were initially deoxygenated to remove the paramagnetic contaminant, oxygen. For the normal alkane series from hexane through hexadecane, it was found that a “relaxation parameter” remained constant within experimental error. The relaxation parameter is defined as (Kashaev *et al.* 1964)

$$\beta = \frac{1}{T_1 \eta}. \quad (2.10)$$

In Equation 2.10, β is the relaxation parameter, T_1 is the spin-lattice relaxation time, and η is the viscosity. Hence, this relation shows that an inverse relationship holds between T_1 and viscosity.

In 1987, Zega confirmed the results obtained by Kashaev, *et al.* The results were within 10% of each other. Some of the difference is attributed to the different temperatures of measurement (Zega 1987). Kashaev *et al.* performed experiments at 22 °C, whereas Zega conducted measurements at 25 °C.

Lo (1999) included this temperature effect in the relationship between n-alkane viscosity and relaxation time with

$$T_1 = T_2 = 0.00956 \frac{T}{\eta} \quad . \quad (2.11)$$

In Equation 2.11, T_1 is the log-mean spin-lattice relaxation time, T_2 is the log-mean spin-spin relaxation time, T is the temperature in Kelvin, and η is the viscosity in centipoises (cp). The relaxation times are in units of seconds.

Note that T_1 and T_2 follow a single correlation for linear alkanes, as established by the equality in Equation 2.11. This equality between T_1 and T_2 was first observed by Zega (1987) and later confirmed by Lo (1999). Fig. 2.1 shows the correlation in Equation 2.11, along with data obtained by Kashaev, Zega, and Lo.

Lo (1999) also developed correlations for diffusivity in linear alkanes. The empirical relationship between diffusivity and relaxation times is (Lo 1999)

$$D = 4.90 * 10^{-6} T_1 = 4.90 * 10^{-6} T_2 \quad . \quad (2.12)$$

In this equation, D is the diffusivity in cm^2/s and relaxation times are in seconds. Once again, the known equality of the two relaxation times is stated explicitly in Equation 2.12. Lo (1999) also determined the relationship between diffusivity and viscosity,

$$D = 5.05 * 10^{-8} \frac{T}{\eta} \quad (2.13)$$

As with Equations 2.11 and 2.12, the numerical constant in Eq. 2.13 comes from an empirical fit and the D is in cm^2/s and η is in cp.

2.3.3.2 Dead Oils

In addition to the above expressions for linear alkanes, correlations relating relaxation time to viscosity have also been developed for dead crude oils. A “dead” crude oil is a crude oil without its reservoir gases. As with linear alkanes, dipole-dipole interactions dominate for dead crude oils (Y. Zhang 2002). The correlations, which also hold for viscosity standards, are (Morris *et al.* 1997, Q. Zhang *et al.* 1998, Vinegar 1995, respectively)

$$T_{2,LM} = \frac{1.2}{\eta^{0.9}}, \quad (2.14)$$

$$T_{2,LM} = \frac{1.2}{\eta^{0.9}} \left(\frac{T}{298} \right)^{0.9} = 0.00712 \left(\frac{T}{\eta} \right)^{0.9} \quad (2.15)$$

$$T_{2,LM} = \frac{1.2 T}{298 \eta} = 0.00403 \frac{T}{\eta} . \quad (2.16)$$

The quantities in these equations are the same as in Equation 2.11, with the same units. Note that Equation 2.15 is a generalization of Equation 2.14 to include temperature. $T_{2,LM}$, rather than $T_{1,LM}$, is used because T_2 is typically measured in NMR well-logs. Unlike Equation 2.11, these relationships are for liquids for which oxygen is not removed.

In addition to Equations 2.14-2.16, other investigations relating NMR relaxation times and viscosity for crude oils have appeared. For all the correlations shown in the previous paragraph, the exponent is near 1 for the viscosity term. In contrast, one report has appeared (Jacob and Davis, 1999) that suggests that the exponent should be near 3 for crude oils at elevated temperatures. However, this has not gained acceptance in the industry. Another investigation explored crude oil and pure component liquid $T_{2,LM}$ as plotted against viscosity divided by temperature or specific gravity (Chen *et al.* 2004). Although regressions are provided with the plots, no claim is made that these regressions should supersede existing correlations. In fact, the result for $T_{2,LM}$ versus viscosity divided by temperature is stated to match Equation 2.16 within experimental error, despite correcting for the effect of oxygen at different temperatures on $T_{2,LM}$. The correction is needed because oxygen is not removed for a majority of the samples measured. The importance of doing this will be mentioned in Section 2.3.4.

Thus far in the discussion of dead oils, only relaxation time correlations with viscosity have been shown. Correlations with diffusivity have also been

applied in previous works. They are (Toumelin *et al.* 2004, Freedman *et al.* 2001a, respectively)

$$D = 5 * 10^{-6} T_{2,LM} \quad (2.17)$$

$$D = 1.26 * 10^{-5} T_{2,LM} \quad . \quad (2.18)$$

Equation 2.17 is based on Equation 2.12 for linear alkanes, except that it is stated to lesser precision. Equation 2.17 is used in conjunction with D - T_2 interpretation for simulations of various saturation states encountered in NMR logging. Equation 2.18, on the other hand, uses Equations 2.13 and 2.16, which relate D and $T_{2,LM}$, respectively, to viscosity. Combining the two equations yields the relationship in Equation 2.18 between D and $T_{2,LM}$. In Equation 2.18, Equation 2.16 (for dead oils) is used for correlating $T_{2,LM}$ to viscosity rather than Equation 2.11 (for n-alkanes) because it was developed with crude oils rather than alkanes (Freedman *et al.* 2001a). In addition to the correlations above, Hürlimann (2004) has suggested that “universal” correlations between D and $T_{2,LM}$ do not apply to crude oils. Instead, it is stated that each crude oil must be correlated separately (Hürlimann 2004).

Y. Zhang (2002) observed the behavior of T_1 and T_2 of dead crude oils with changes in Larmor frequency and viscosity-temperature ratio. Increasing Larmor frequency results from increased magnetic field strength of the magnet. At low to intermediate values of Larmor frequency and viscosity-temperature ratio, the ratio of T_1 to T_2 remains at a value of 1. When the viscosity-temperature ratio or Larmor frequency increase further, the ratio of T_1 to T_2 starts to increase, so that T_1 no longer equals T_2 (Y. Zhang 2002). In the regime of

high Larmor frequency and viscosity for which T_1 and T_2 are not equal, the assumptions for extreme narrowing break down; namely, the motion of the molecules in the oil are no longer fast compared to the resonance frequency.

Under conditions where extreme narrowing no longer applies, the relaxation times behave differently than when extreme narrowing is valid. First, T_1 stops following the expected linear trend with viscosity-temperature ratio, as shown in Fig. 2.2 (Y. Zhang 2002). Second, the behavior at different Larmor frequencies varies. This latter effect was found to disappear when scaled relaxation time and scaled viscosity-temperature ratio are used. The normalization is described by (Y. Zhang 2002)

$$T_{1,2N} = \frac{2}{\omega_0} T_{1,2} \quad (2.19.a)$$

$$\left(\frac{\eta}{T} \right)_N = \frac{\omega_0}{2} \left(\frac{\eta}{T} \right). \quad (2.19.b)$$

$T_{1,N}$ is the normalized T_1 and $(\eta/T)_N$ is the normalized viscosity-temperature ratio. The term ω_0 describes the ^1H frequency used in Megahertz (MHz). The result is seen in Fig. 2.3 (Y. Zhang 2002).

2.3.4 Paramagnetic Relaxation

In addition to dipole-dipole interactions, another relaxation mechanism mentioned above is paramagnetic relaxation. The form of the equation describing relaxation from paramagnetic impurities is as follows (Abragam 1961, Lo 1999):

$$\frac{1}{T_{1,para}} = C\gamma^2\gamma_e^2\frac{\eta}{T} \quad (2.20)$$

In Equation 2.20, C represents a constant of proportionality. The other new quantity, γ_e , is more significant. It represents the gyromagnetic ratio for an electron. Since this quantity is approximately 600 times γ (Farrar and Becker 1971), relaxation rates are drastically affected by the presence of even a small amount of paramagnetic species. Oxygen is one important paramagnetic species that often needs addressing when measuring relaxation times. Oxygen gas is not present in downhole fluids, but it is dissolved in fluids examined at the surface. Note from Equation 2.20 that the dependence on η/T holds even for paramagnetic relaxation because it is also due to dipole-dipole interactions. However, the difference is that dipole interactions are between ^1H atoms and electron magnetic dipole moments (Chen *et al.* 2004).

2.3.5 Theory of Spin-Rotation Interactions

As paramagnetic impurities imply paramagnetic relaxation, the presence of small nearly spherical molecules, like the hydrocarbon gases methane and ethane, bring the spin-rotation relaxation mechanism into play (Fukushima and Roeder 1981). Fig. 2.4 (Y. Zhang 2002) shows relaxation time data for various fluids where spin-rotation is important, compared to the correlation developed for alkanes.

Spin-rotation can be interpreted in the context of either of two models, the kinetic or the diffusion model (Y. Zhang 2002). In the kinetic model, molecular motions are treated as momentum driven with interruptions by binary collisions

(Gordon 1966). In the diffusion model, molecular rotation is regarded as a random walk, interrupted by the confining surrounding molecules (McConnell 1987). Kinetic models holds mostly for dilute gases, whereas the diffusion model finds application in liquids and dense gases (Armstrong and Courtney 1972, Wang 1973). In the following paragraphs, each of the models will be described in more detail. The descriptions below for both models are for resonant nuclei off of the symmetry axis of the molecule, which is the typical position of ^1H nuclei in hydrocarbons.

2.3.5.1 Kinetic Model

The kinetic model for spin-rotation interactions assumes the following (Courtney and Armstrong 1972, Y. Zhang 2002):

1. Energy transitions resulting from rigid rotation and centrifugal distortion are neglected.
2. The reorientation time of molecules is much shorter than the period associated with the Larmor frequency.
3. The correlation functions of molecules that do not collide are independent of time, and collisions cause the “free molecule” correlation time to decay to zero exponentially.
4. The free molecule correlation time has negligible effect resulting from oscillatory contributions.
5. The rotational angular momentum is statistically dependent on the rotation matrix used in calculations for frame transformation.

Equation 2.21 shows the resulting relationship between molecular parameters and spin-rotation relaxation for the kinetic model (Armstrong and Courtney, 1972),

$$\frac{1}{T_{1,\text{sr}}} = \frac{2\pi^2}{\alpha} \left\{ \left(1 - \frac{y^2}{3} \right) C_{\text{av}}^2 \tau_J + \frac{4}{9} y^2 \Delta C C_{\text{av}} \tau_{12}' + \frac{1}{9} (\Delta C)^2 \left[9 \left(\frac{1-y^2}{y^2} \right)^2 \left(-1 - \frac{1}{3} y^2 + s \right) - 1 + \frac{5}{3} y^2 \right] \tau_{12} \right\} \quad (2.21)$$

This equation is for symmetric top molecules, and assumes that collisions cause the reorientation of angular momentum to the molecular axis of symmetry (Armstrong and Courtney 1972). For Equation 2.21, some of the parameters therein are defined in Equations 2.22 (Y. Zhang 2002 for 2.22.d, Armstrong and Courtney 1972 for remaining),

$$y = \left(1 - \frac{I_{\parallel}}{I_{\perp}} \right)^{1/2} \quad (2.22.a)$$

$$s = \begin{cases} \frac{1}{2y} \ln \left(\frac{1+y}{1-y} \right) & \text{for } I_{\perp} > I_{\parallel} \\ \frac{1}{|y|} \tan^{-1} |y| & \text{for } I_{\perp} < I_{\parallel} \end{cases} \quad (2.22.b)$$

$$\alpha = \frac{\hbar^2}{2I_{\perp} kT} \quad (2.22.c)$$

$$\Delta C = (C_{\perp} - C_{\parallel}) \left(1 - \frac{3}{2} \sin^2 \theta \right) \quad (2.22.d)$$

$$C_{\text{av}} = \frac{1}{3} (C_{\parallel} + 2C_{\perp}) \quad (2.22.e)$$

The remaining quantities from Equations 2.21 and 2.22 that require explanation are as follows. $I_{\parallel}$ and $I_{\perp}$ are moments of inertia of the molecule in the parallel and perpendicular directions (referenced to the symmetry axis of the molecule), $C_{\parallel}$ and $C_{\perp}$ are spin rotation constants for coupling between nuclear and molecular angular momenta in the parallel and perpendicular directions, the various τ 's are correlation times associated with various modes of the angular momentum operator, and θ is one-half the angle supplementary to the angle formed by the resonant nucleus (namely ^1H) and the symmetry axis of the molecule to which it is attached. The quantities k , T , and $\hbar$ are familiar from previous equations.

In Equation 2.21, note that each term is multiplied by some correlation-time factor. In the kinetic model, such a correlation time is proportional to $T^{1/2}$ (Gordon 1966). Combining this fact with Equation 2.21 and Equation 2.22.c shows that the kinetic model predicts the following dependence on temperature for spin rotation relaxation time,

$$\frac{1}{T_{1,SR}} \propto T^{\frac{3}{2}}. \quad (2.23)$$

Note that no dependence on viscosity is predicted and that the relationship with temperature is not inversely proportional. Thus, Equation 2.23 for the kinetic model predicts a different behavior compared to dipole-dipole interactions.

2.3.5.2 Diffusion Model

The diffusion model for spin-rotation interactions relies on different assumptions from the kinetic model, and results in a different expression describing relaxation. The diffusion model presented here will follow the treatment of Wang (1973). It is appropriate for the situation where the changes in molecular reorientation happen in times much shorter than the Larmor period. The diffusion model here assumes that anisotropic intermolecular interactions need to be considered. If, in addition, the molecular orientation and its angular momentum do not couple, the resulting expression for spherical top molecules is (Wang 1973)

$$\frac{1}{T_{1,\text{sr}}} = \frac{2kT}{3\hbar^2} \left\{ I_{\parallel} (C_{\parallel} + \Delta C \sin^2 \theta)^2 \tau_{J\parallel} \right\} + I_{\perp} (\Delta C)^2 \sin^2 \theta \cos^2 \theta [\tau_{J\perp} + \tau_{J\parallel} / (1 + D_{\parallel} \tau_{J\parallel})] + I_{\perp} [(C_{\perp} - \Delta C \sin^2 \theta)^2 + C_{\perp}^2] \tau_{J\perp} \} \quad (2.24)$$

A further assumption in the above equation is that $D_{\perp} \tau_{J\perp}$ and $D_{\perp} \tau_{J\parallel}$ are small (Wang 1973). In Equation 2.24, the new quantities are $\tau_{J\parallel}$ and $\tau_{J\perp}$ the angular momentum correlation times along parallel and perpendicular to the symmetry axis respectively, and $D_{\parallel}$, the rotational diffusivity in the parallel direction. Note that $D_{\perp}$ is the rotational diffusivity in the perpendicular direction. Furthermore ΔC is given by Equation 2.25:

$$\Delta C = C_{\perp} - C_{\parallel} \quad (2.25)$$

Like in the kinetic model, the terms in Equation 2.24 for the diffusion model are multiplied by certain correlation times. For the diffusion model, correlation times are proportional to η^{-1} (Alms *et al.* 1973). In conjunction with

Equation 2.24, the following proportionality relates viscosity and temperature to spin rotation relaxation time,

$$\frac{1}{T_{1, sr}} \propto \frac{T}{\eta}. \quad (2.26)$$

This is the inverse relationship expected from dipole-dipole interactions. Therefore the diffusion model, like the kinetic model, predicts a different basis for relating relaxation time to viscosity and temperature than for dipole-dipole interactions when spin-rotation occurs.

2.3.5.3 Gas Mixtures

The above theoretical relationships treat spin-rotation in gases and liquids, but do not explicitly address mixtures. Y. Zhang (2002) developed a model for gas mixtures based on the kinetic model for spin-rotation. Using the definition of a logarithmic mean,

$$T_{1, LM} = \prod_{i=1}^n T_{1, i}^{f_i}, \quad (2.27)$$

relaxation times of mixture components and the logarithmic-mean relaxation time of the mixture are related. In this equation $T_{1, LM}$ signifies the log-mean T_1 relaxation time, $T_{1, i}$ is the component relaxation time for each component i in the mixture, and f_i is the proton fraction of the component in the mixture. These proton fractions sum to 1. The search for a model is thus reduced to characterizing $T_{1, i}$.

The expression developed for mixtures of gases follows. Based on the kinetic model for spin-rotation interaction (Y. Zhang 2002), it is expressed as

$$T_{1,i} = \sum_{j=1}^n \rho_j \frac{\hbar^2 N_A}{4\pi^2 I_{\perp i} C_{\text{eff},i}^2} \sqrt{\frac{2}{\pi k}} \frac{\sigma_{i-j}}{\sqrt{T \mu_{i-j}}} . \quad (2.28)$$

Equation 2.28 makes the fundamental assumption that the T_1 contributions from various collision partners are additive (Gordon 1966), borne out by experimental studies (Jameson *et al.* 1991, Rajan *et al.* 1975). In this equation, ρ_j is the partial molar density of the j -th component of the mixture, N_A is Avagadro's number (6.023×10^{23}), and C_{eff} is a quantity describing coupling between nuclear and molecular angular momentum. The other quantities have been mentioned previously or are defined by one of the following equations (Y. Zhang 2002).

$$\mu_{i-j} = \frac{1}{m_i} + \frac{1}{m_j} \quad (2.29.a)$$

$$\sigma_{i-j} = \frac{300}{T} \sqrt{\sigma_{j-j}(300K) * \sigma_{i-i}(300K)} \quad (2.29.b)$$

In Equations 2.29, m_i and m_j are the atomic masses of the two colliding molecules and σ refers to the collision cross-section for angular momentum transfer. The overall result is that individual contributions to T_1 from each component are proportional to $T^{-1.5}$, which is expected for the kinetic model.

2.3.6 Correlations for Spin-Rotation Interactions

2.3.6.1 Pure Components

METHANE OR ETHANE GAS:

As with situations where the predominant mechanism is dipole-dipole interactions, correlations have also been developed for cases where spin-rotation plays a significant role in relaxation. The first such instance is for methane gas,

which is the major component of natural gas. A pair of empirical correlations between T_1 and density for methane gas is (Prammer *et al.* 1995, Lo 1999, respectively)

$$\frac{T_1}{\rho} = \frac{2.5 * 10^4}{T^{1.17}} \quad (2.30)$$

$$\frac{T_1}{\rho} = \frac{1.57 * 10^5}{T^{1.50}}. \quad (2.31)$$

In these equations, T_1 is the spin-lattice relaxation time in seconds, T is the temperature in K, ρ is the density in g/cm³. Note that these empirical equations, especially the latter, resemble what would be expected for the kinetic model for spin-rotation, in which T_1 is proportional to $T^{-1.5}$.

In addition to methane, ethane gas also relaxes by spin-rotation. Y. Zhang (2002) developed correlations for methane and for ethane based on the kinetic and the diffusion model, respectively. Y. Zhang calculated expressions for T_1 in methane and ethane by applying the theoretical equations shown in Section 2.3.5. The result for methane gas is (Y. Zhang 2002)

$$\frac{1}{T_1} = 7.24 \times 10^8 T \tau_J \quad (2.32)$$

and for ethane gas is (Y. Zhang 2002)

$$\frac{1}{T_1} = T \left[9.26 \times 10^7 \tau_{J\parallel} + 9.02 \times 10^7 (\tau_{J\perp} + 1/D_{\parallel}) + 1.71 \times 10^8 \tau_{J\perp} \right] \quad (2.33)$$

In these equations, T_1 is the spin-lattice relaxation time in seconds, τ_J is the angular momentum correlation time, $\tau_{J\parallel}$ is τ_J in the direction parallel to the axis of symmetry of the molecule, $\tau_{J\perp}$ is τ_J in the perpendicular direction, and $D_{\parallel}$ is

the rotational diffusion constant in the parallel direction. Both equations above assume only spin-rotation contributes to relaxation.

Equation 2.32, for methane, is based on the kinetic model because the diffusion model was not found to adequately describe spin-rotation in methane. Equation 2.33, for ethane, is based on the diffusion model even though either the kinetic or the diffusion model was satisfactory for ethane. The diffusion model is shown instead of the kinetic model because it is more appropriate for spin-rotation in ethane vapor and liquid phases, which will be treated presently.

ETHANE VAPOR-LIQUID EQUILIBRIUM:

In liquid and vapor ethane, both dipole-dipole interactions and spin-rotation interactions contribute to relaxation (Y. Zhang 2002). Y. Zhang (2002) developed separate expressions for contributions from the various mechanisms. The expressions below for dipole-dipole interactions in ethane are based on theoretical parameters, as for Equations 2.32 and 2.33 in the previous paragraph, not on empirical data as in Equations 2.30 and 2.31. For intermolecular dipole-dipole interactions (Harmon and Muller 1969, Y. Zhang 2002),

$$\frac{1}{T_{1,inter}} = 1.274 \times 10^5 \frac{\rho \eta}{T} \left[1 + \left(\frac{5}{12} + 0.0672\Omega \right) + 0.0521\Omega \right] \quad (2.34)$$

describes the calculated contribution to T_1 . In this equation, ρ is the density of the fluid in g/cm^3 , η is the viscosity in cp, and T is the temperature in Kelvin. The term Ω is (Harmon and Muller 1969)

$$\Omega = \frac{4}{3} \pi n \sigma^3, \quad (2.35)$$

where n is the number density and σ is the distance of closest approach between molecules. For intramolecular dipole-dipole interactions (Moniz *et al.* 1963, Harmon 1968, Y. Zhang 2002),

$$\frac{1}{T_{1,\text{intra}}} = \frac{0.125}{T^{1/2}} \quad (2.36)$$

describes the contribution to T_1 , where T is in Kelvin. Finally, the spin-rotation contribution is obtained empirically and is given by (Y. Zhang, 2002)

$$T_{1,\text{sr}} = 4.2 \times 10^5 \left(\frac{\eta}{T} \right)^{0.74}, \quad (2.37)$$

assuming that the diffusion model is adequate. In Equation 2.37, η is in cp and T is in Kelvin. Equation 2.37 is empirical because the numerical constants result from a fit using experimental data.

PROPANE GAS:

So far, correlations involving methane and ethane have been shown. Another important gas is propane. Like methane and ethane, propane is a component of natural gas. Y. Zhang (2002) measured spin-lattice relaxation time, T_1 , and diffusivity for gaseous ethane and propane. However no model-based correlation for propane appears because of lack of knowledge of molecular constant for propane. However, gaseous methane, ethane, and propane all follow the Stokes-Einstein based relation in Equation 2.13 (Y. Zhang 2002).

2.3.6.2 Gas-Oil Mixtures

In addition to gases alone, Lo (1999) developed a correlation for mixtures of n-alkanes and methane. This involves a parameter called the gas-oil ratio or GOR, which is a volumetric ratio of gas to non-gaseous components in the mixtures. The correlation is (Lo 1999)

$$T_1 = \frac{0.00956 \frac{T}{\eta}}{f(GOR)} = \frac{2.04 * 10^5 D}{f(GOR)} \quad , \quad (2.38)$$

where the two expressions relate T_1 (in seconds) to viscosity (cp) and diffusivity (cm^2/s), respectively. The viscosity and diffusivity in these expressions refer to the live oil whose T_1 relaxation time is measured. The quantity $f(GOR)$ is expressed by (Lo 1999)

$$f(GOR) = 10^{10^\alpha} \quad , \quad (2.39)$$

where α is given by (Lo 1999)

$$\alpha = -0.127[\log_{10}(GOR)]^2 + 1.25\log_{10}(GOR) - 2.80 \quad . \quad (2.40)$$

The empirical correlation above correlates relaxation time, viscosity, and diffusivity for methane-n-alkane mixtures. It should be noted that recent measurements suggest that Equations 2.39 and 2.40 may not be appropriate for a liquid phase at elevated pressures, when the liquid phase is not in vapor-liquid equilibrium (Winkler *et al.* 2004).

The CO_2 -n-alkane system is another case of interest because dissolved CO_2 is sometimes present in crude oils. Etesse (1992) has measured T_1 relaxation time and NMR diffusivity for mixtures of hexadecane and CO_2 . Fig. 2.5 (Y. Zhang 2002, Etesse 1992) shows how the relaxation and diffusivity data

obtained by Etesse (1992) compares with measurements made by Lo (1999) and Y. Zhang (2002) for other substances and mixtures. Because CO₂ is invisible to ¹H NMR, CO₂-hexadecane mixtures appear to follow the linear alkane correlation. At sufficiently high diffusivities (which happens at high CO₂ concentrations), CO₂-n-hexadecane mixtures start to deviate from the alkane correlation. This may happen because the viscosity is becoming low enough that mechanisms other than intramolecular dipole-dipole interactions are becoming significant even in n-hexadecane.

Fig. 2.6 (Y. Zhang 2002, Etesse 1992) shows T_1 relaxation time from Etesse (1992) plotted against viscosity divided by temperature. Data for other substances and mixtures are also included, similar to Fig. 2.4. The viscosities for CO₂-n-hexadecane are calculated using SUPERTRAPP (NIST 1999) for the conditions under which NMR measurements were made in Etesse (1999). Fig 2.6 shows that data points for CO₂-n-hexadecane mixtures behave similar to those for methane-n-hexadecane. The relaxation times are generally higher for mixtures with CO₂, which is expected due to absence of relaxation mechanisms present for methane.

2.4 Model for Relaxation in Porous Media

To address more general mixtures, Freedman *et al.* (2001a) developed a model that accounts for spin-spin relaxation measurements from various fluids in a reservoir setting. The model has since been tested in the application setting (Freedman *et al.* 2001b, Freedman *et al.* 2002). Fluids explicitly accounted for in

the model are crude oils, water in pores, gases, and any oil-based drilling fluids. Crude oils and water in pores are described by a set of relaxation times. Crude oils require a set of relaxation times because they consist of many components, each with its own characteristic relaxation time. Water on the other hand is often subject to surface relaxation effects that differ for different pores sizes, resulting in a distribution of relaxation times. Gases and oil-based drilling fluids will tend to have a single effective relaxation time.

Working on this framework, Freedman *et al.* (2001a) proposed the magnetic resonance fluid (MRF) model, which relates the measured total relaxation, observed with time, to relaxation from crude oil components, from water components, and from gases and oil-based drilling fluids. Performing a series of measurements, called a “suite”, determines the relative contribution of these various fluids.

The most fundamental assumption made using the MRF model is the underlying model of relaxation as it relates to diffusion and viscosity. This underlying model is called the constituent viscosity model (CVM). The CVM assumes that crude oils constituent relaxation times can be described by (Freedman *et al.* 2001a)

$$T_{2,k} = \frac{aT}{\eta_k(T)} \quad (2.41)$$

$$D_k = \frac{bT}{\eta_k(T)}. \quad (2.42)$$

In Equation 2.41, $T_{2,k}$ refers to the T_2 value of a crude oil constituent. In Equation 2.42, D_k is the diffusivity of this constituent. For both equations, η_k is the

viscosity of the constituent and T is the temperature. The constants a and b are proportionality factors. The assumption in Equation 2.41 is based on the expected relationship between T_2 and viscosity for dipole-dipole interactions, which has been confirmed in experiments. In Equation 2.42, the basis is the Stokes-Einstein relation and experimental confirmations of that relationship.

From Equation 2.27, $T_{1,LM}$ is the logarithmic mean of the spin-lattice relaxation time. An identical relationship holds for $T_{2,LM}$, the log-mean spin-spin relaxation time,

$$T_{2,LM} = \prod_{k=1}^n T_{2,k}^{f_k}. \quad (2.43)$$

In Equation 2.43, $T_{2,k}$ is the component relaxation time for each component k in the mixture, and f_k is the proton fraction of the component in the mixture. Note that these proton fractions sum to 1. The CVM assumes that viscosity and diffusivity can be described by analogous expressions (Freedman *et al.* 2001a),

$$\eta = \prod_{k=1}^n \eta_k^{f_k} \quad (2.44)$$

$$D_{LM} = \prod_{k=1}^n D_k^{f_k}. \quad (2.45)$$

In Equation 2.44, η is the viscosity of the crude oil and η_k is the viscosity of component k of the crude oil. In Equation 2.45, D_{LM} is the log-mean diffusivity of the crude oil, and D_k is the component diffusivity. The quantity D_k is the same as for Equation 2.42.

Combining Equation 2.41-2.45, yields (Freedman *et al.* 2001a)

$$\eta = \frac{aT}{T_{2,LM}} = \frac{bT}{D_{LM}} . \quad (2.46)$$

Furthermore, combining Equation 2.41 and 2.42 and rearranging the latter part of Equation 2.46 results in (Freedman *et al.* 2001a)

$$\frac{D_k}{T_{2,k}} = \frac{b}{a} = \frac{D_{LM}}{T_{2,LM}} . \quad (2.47)$$

The significant conclusion of Equation 2.47 is that one can regard the diffusivity of a crude oil constituent as being linked with the relaxation time of that constituent (Freedman *et al.* 2001a). Note that the basic MRF model in Equations 2.46 and 2.47 can be modified to account for dissolved gases using Equation 2.38.

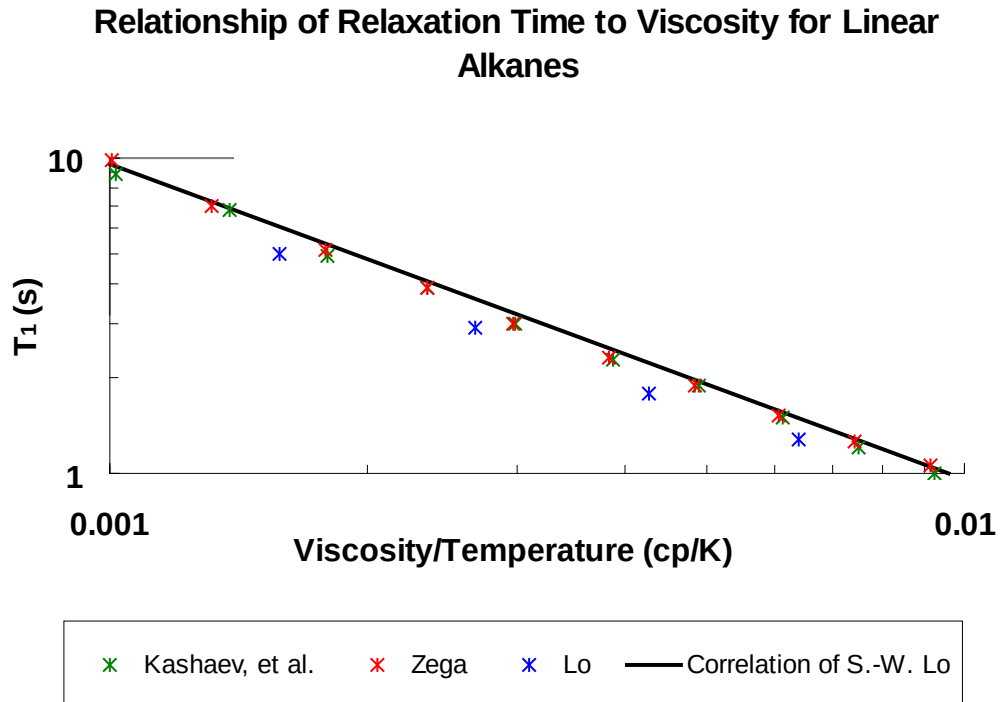


Figure 2.1: Correlations for Linear Alkanes

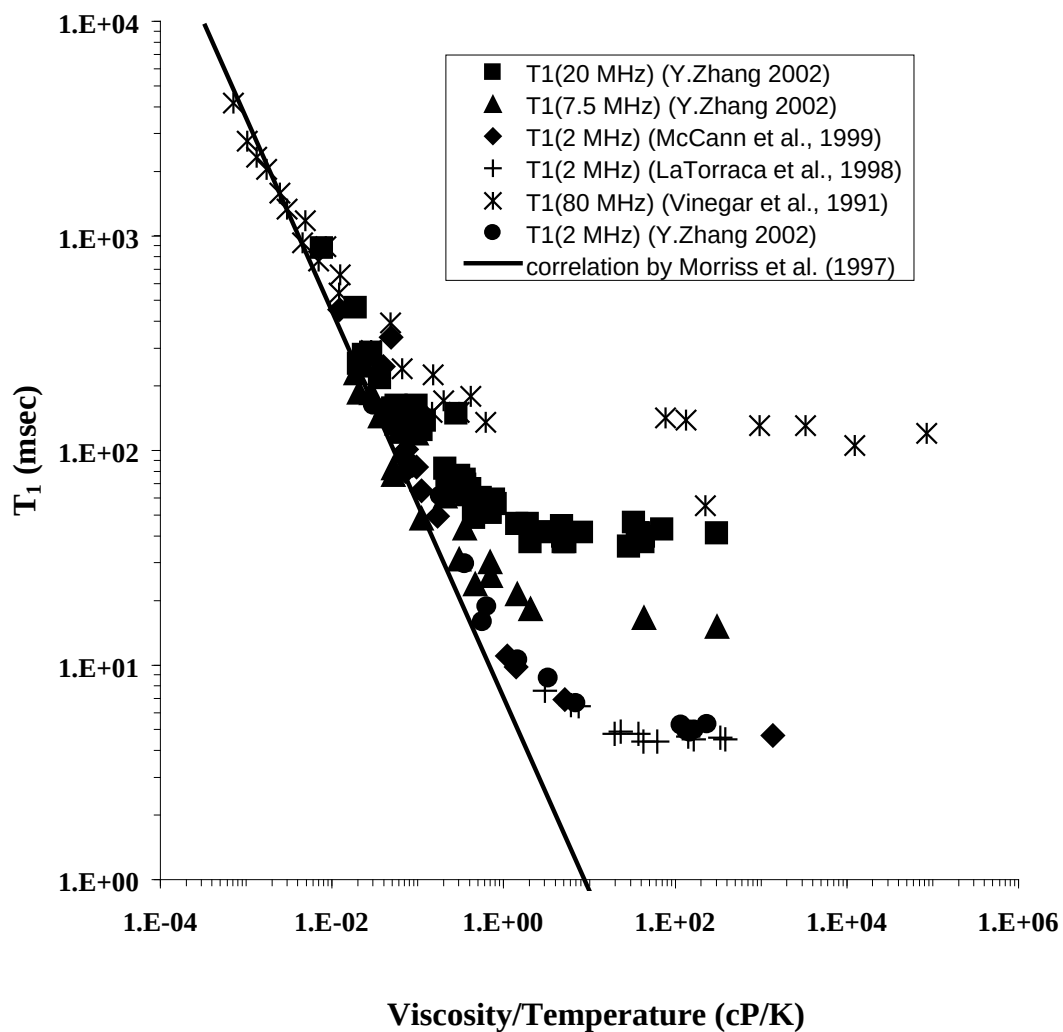


Figure 2.2: Illustration of variation of T_1 with Larmor frequency for crude oils (Reproduced from Y. Zhang, 2002)

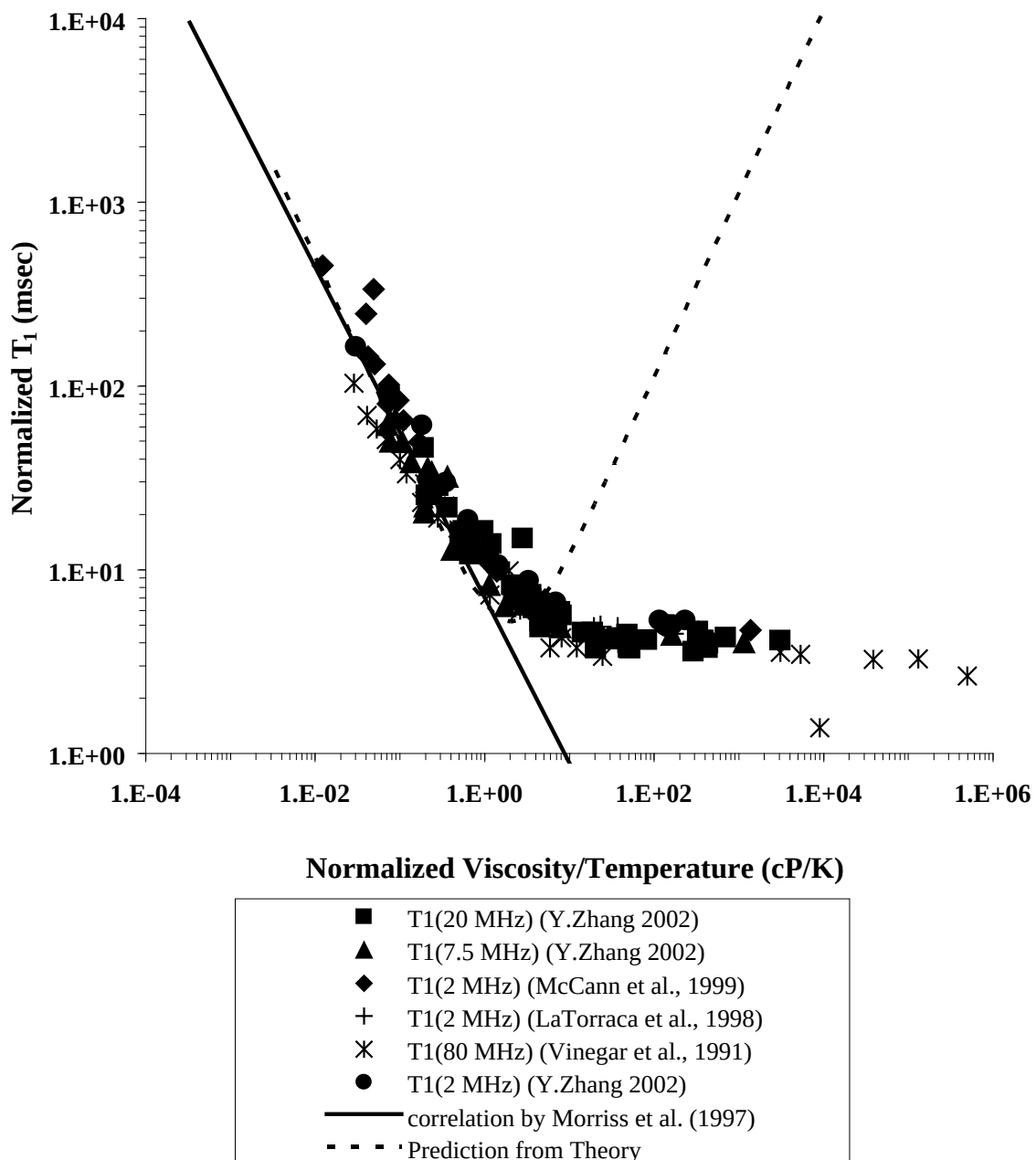


Figure 2.3: Normalization of T_1 and η/T removes Larmor frequency dependence in the correlation plot (Reproduced from Y. Zhang, 2002)

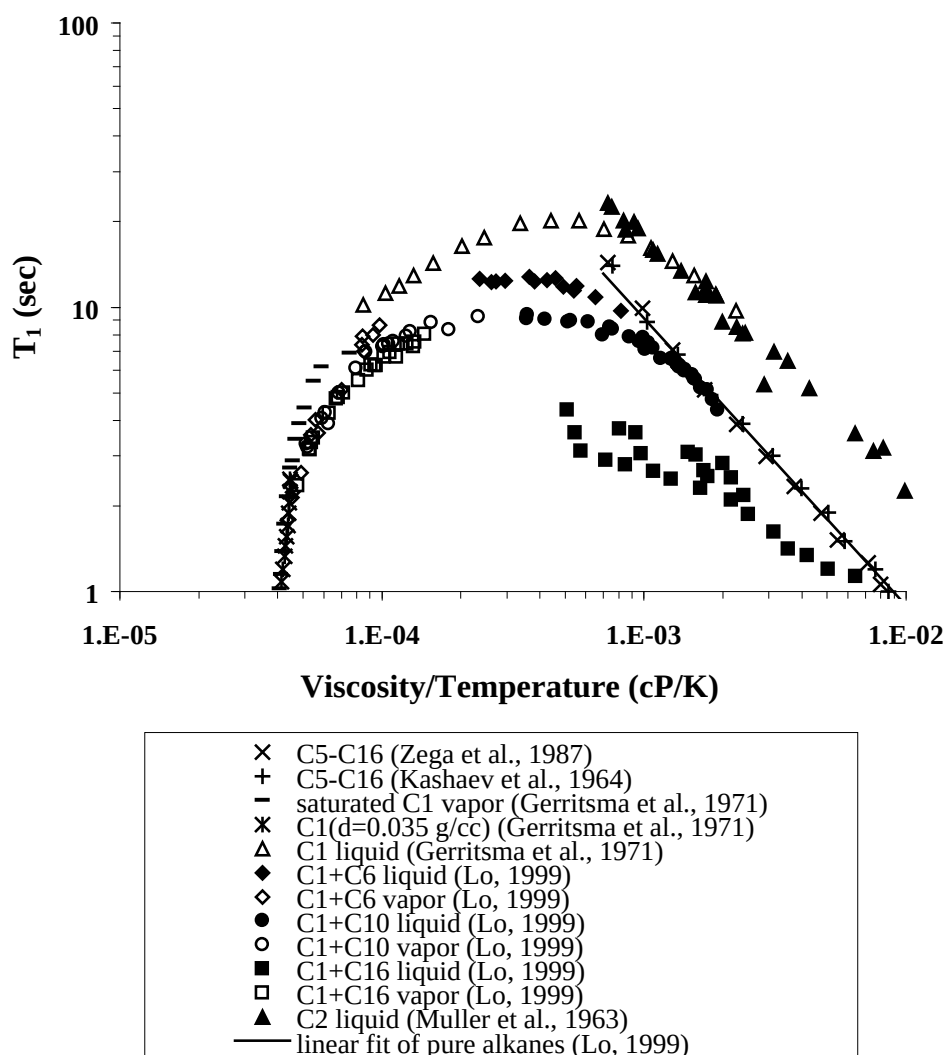


Figure 2.4: Data illustrating the behavior of systems demonstrating spin-rotation relaxation, as compared to the dipole-dipole relaxation correlation (Reproduced from Y. Zhang, 2002)

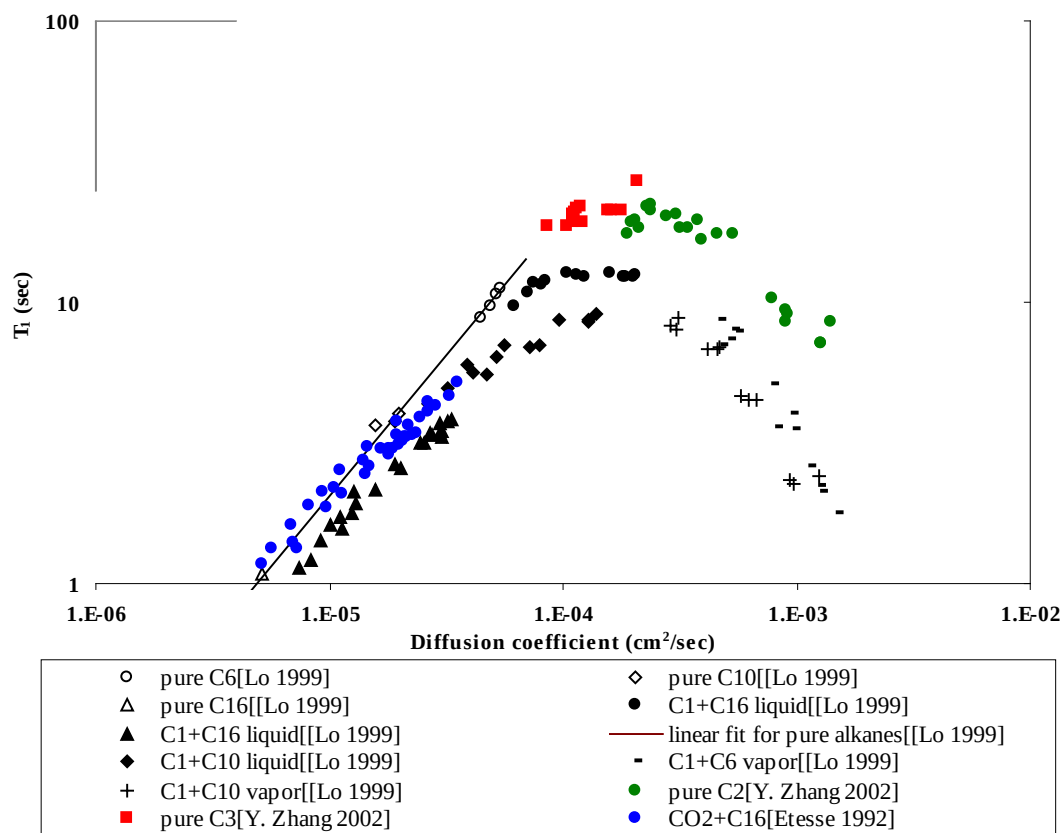


Figure 2.5: Comparison of T_1 and diffusivity data for CO₂-n-hexadecane mixtures with that of other alkanes and alkane mixtures.

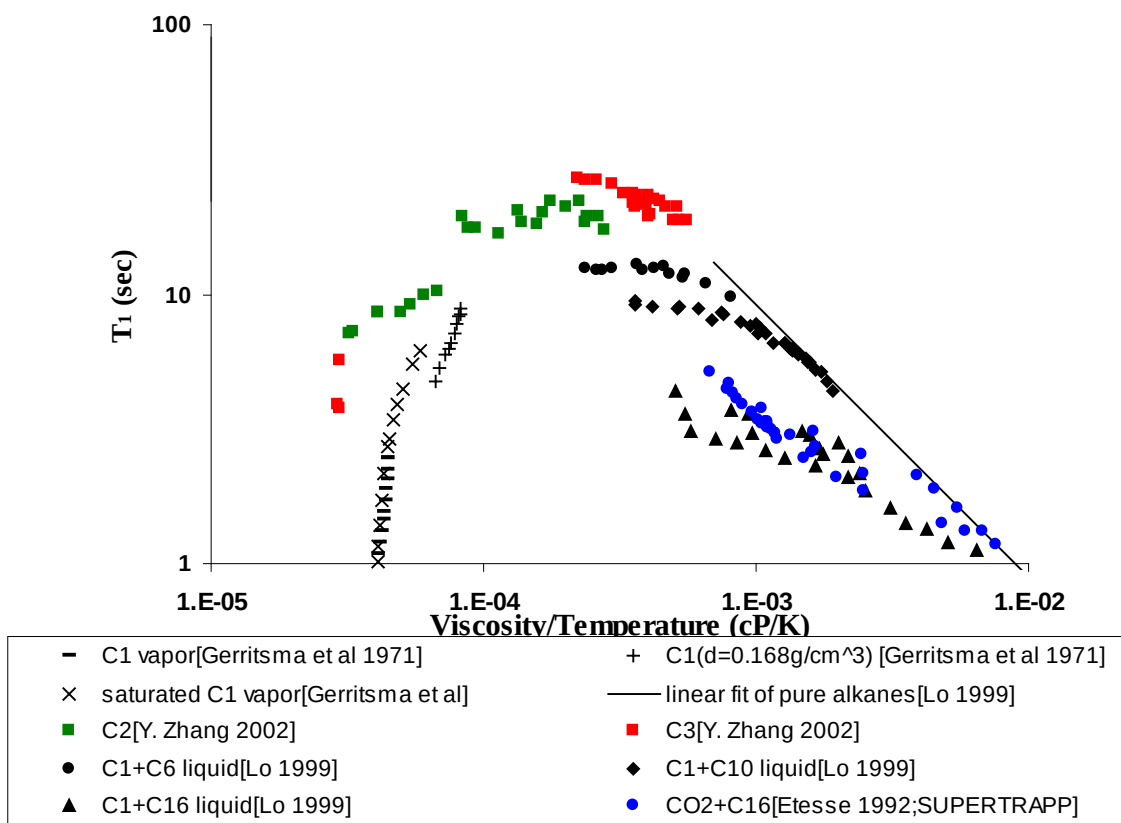


Figure 2.6: Comparison of T_1 and viscosity data for CO₂-n-hexadecane mixtures with that of other alkanes.

Chapter 3: Materials and Methods

The previous chapter has shown how NMR measurements of relaxation times relate to diffusivity and to viscosity, both theoretically and in terms of correlations based on the theory. This chapter will describe the measurements relevant to achieving the goals of this research. Specific experimental details are presented in subsequent chapters, as the procedures here are adapted to the task in question.

3.1 Materials

The work described in this thesis involves measurements made in a laboratory setting. The samples for these measurements are dead crude oils, base oils, pure liquid hydrocarbons, and gases. Each one of these samples is briefly described below.

Dead crude oils are liquid hydrocarbon mixtures present in formations, without their dissolved gases. Although live crude oils do contain dissolved gases, these gases no longer remain in laboratory samples unless special sample-handling measures are taken. Specific attributes of crude oils employed will be mentioned in conjunction with the appropriate application.

Base oils are oils added at the well site by field engineers to remove drill cuttings, among other functions (Lummus and Azar 1986). Base oils are typically used with additives (Lummus and Azar 1986); however, this work only considers the unmodified base oils. Details of specific base oil samples will be mentioned with the applications where they are used.

The next variety of fluid mentioned is liquid hydrocarbons. These pure compounds are purchased from Sigma-Aldrich Corporation. They are chosen to represent components of crude oils. The liquids samples obtained are hexane, benzene, toluene, cyclohexane, α -methyl naphthalene, decalin, and tetralin.

The final class of material to be used is gas. Matheson Gas Products, Air Liquide, and Aeriform are typical providers. Future plans call for methane, ethane, and propane. These gases may be obtained commercially either as single components or as a mixture of two or more of the components listed.

3.2 Deoxygenation

Before addressing sample preparation for each of the material types described above, the deoxygenation process is described. Deoxygenation is the removal of oxygen from a sample. The necessity for removing oxygen stems from the paramagnetism of oxygen. Oxygen causes significant reduction in relaxation time in liquid samples with less than 16 carbon atoms per molecule, which are characterized by relaxation times greater than approximately 1 second at 30 °C (Lo, 1999). For such samples, deoxygenation is likely to influence the measured relaxation times. The deoxygenation process employed is different depending on whether the sample is a liquid or gas.

For gases, an adsorbing process achieves deoxygenation, using a Model 6411 purifier from Matheson Gas Products (Lo 1999). This purifier, also called an oxygen scavenger, is placed inline from the gas cylinder. Thus, a gas is deoxygenated as it moves from cylinder to pressure vessel, reducing the oxygen

content of the each gas from an approximate range of 2 to 300 parts per million (ppm) to less than 0.1 ppm (Y. Zhang 2002).

For liquids, the process used is called the freeze-pump-thaw method of deoxygenation (Nederbragt and Reilly, 1956). The liquid deoxygenation process used in this work is described below. The apparatus used consists of a glass manifold, with connections to a nitrogen gas line, a vacuum pump line, and a line that attaches to the sample container. The freeze- pump-thaw method using such an apparatus is described below:

1. The liquid sample is frozen in a bath of liquid nitrogen (~15 minutes)
2. The vapor contents of the sample compartment are evacuated using a mechanical vacuum pump (~30 minutes)
3. Nitrogen gas is introduced to the previous evacuated vapor space
4. The sample is thawed under ambient condition (~15 min)
5. Steps 1-4 are repeated, typically two additional times to improve the purification.

3.3 Equipment and Other Data Attainment Approaches

The equipment and apparatus employed in this work are mentioned below. Equipment used includes those to measure NMR, to measure viscosity, as well as peripheral equipment such as that to handle gases at elevated pressures. Furthermore when experimental capability does not exist to measure thermodynamic properties (e.g., gas density for gases at elevated pressure), a software package is used.

MARAN instruments are used to measure T_1 and T_2 . MARAN's are bench-top NMR spectrometers, manufactured by Oxford Instruments (formerly Resonance Instruments). Two MARAN's are used, one donated by Shell Oil Company and Schlumberger Oil Services (labeled MARAN-SS) and the other donated by Marathon Oil Company (labeled MARAN-M). These instruments operate at a ^1H resonance frequency of 2 MHz. Unlike with logging tools, the magnetic field of the permanent magnet is spatially uniform in the probe, where the sample is placed. Because the magnetic field is uniform, no gradients exist and diffusivity cannot be measured in the pre-existing magnetic field. In order to measure diffusivity, the MARAN's are equipped with pulsed or continuous gradient coils, which provide magnetic field gradients of limited duration.

The MARAN's have the following temperature and pressure capabilities. MARAN-SS accommodates elevated pressures, owing to a Temco © pressure vessel rated to 5000 psi. Furthermore, the pressure vessel can be connected to a manifold apparatus for NMR measurements of natural gas components or mixtures. A schematic diagram is shown in Fig. 3.1. The pumps in Fig 3.1 allow pressure to be increased beyond the initial cylinder pressure of the gas mixture. The pressure increase can also be achieved with a Ruska positive displacement pump connected inline between gas cylinder and the inlet of the manifold. More details on the high-pressure NMR system appear in Chapter 6. MARAN-M, in contrast, operates only at atmospheric pressures for this work. However, the temperature of both instruments is fixed at 30 °C.

In addition to T_1 and T_2 with MARAN equipment mentioned above, viscosity is often measured. Either of two types of instruments is used to measure viscosity of liquids. They are Cannon-Fenske capillary viscometers or a Brookfield viscometer. Cannon-Fenske viscometers are used for low-viscosity, transparent oils. A temperature-controlled Brookfield viscometer, model LVDV-III+, is used for intermediate viscosity oils (3 - 1000 centipoises). The temperature control is provided by a Haake DC50-K35 bath using silicon oil as the circulating fluid. The Brookfield viscometer can be used with crude oils in addition to refined and pure substances.

For mixtures involving gases at non-ambient pressures, data from published experiments or SUPERTRAPP (NIST 1999) is used to determine density. SUPERTRAPP is a thermodynamic property calculation software package. SUPERTRAPP is used when available experimental data confirms the validity of software calculations for conditions similar to the desired conditions. Furthermore, SUPERTRAPP is used to determine viscosity for data from other workers when NMR comparisons are made with their data, but no viscosity is provided.

3.4 Sample preparation

This section mentions preparations required for particular materials or their mixtures. The preparation needed ranges from nearly no preparation steps for studies with pure hydrocarbon liquids to a more elaborate scheme for bringing gas up to desired pressure and minimal oxygen content. Treated below are

“separate” liquids (e.g., pure component oils or crude oil or base oil), mixture of liquids (e.g. base oil mixed with crude oil), or hydrocarbon gases (pure components or mixtures).

Pure liquid compounds, crude oils, and base oils do not require special sample preparation, except possibly deoxygenation. Deoxygenation is used for less viscous, lower molecular weight liquids for which oxygen would affect the results, as mentioned in Section 3.2. Higher viscosity fluids can be placed directly into a suitable apparatus for measurement.

For liquid mixtures, this work involves only ambient measurements. In contrast to the “separate” fluids above, liquid mixtures may require some preparation. These mixtures are not deoxygenated because the mixtures of concern are too viscous for oxygen to affect NMR properties. In this work, liquid mixing is usually done on a volumetric basis. The components are combined and then mixed. After sufficient mixing, the sample can then be used for NMR or viscosity measurements.

For studies of gas mixtures, which are obtained commercially at the desired composition, no mixing is necessary. However, the gas mixtures need to be delivered from the cylinder to the NMR pressure vessel at elevated pressure. The default procedures to prepare for an NMR measurements follow:

1. Evacuation of system to remove air, especially to reduce oxygen content.
(This step is disregarded in cases where an experiment begins at an elevated pressure obtained in a previous measurement.)

2. Pressurization to small elevated pressure (typically approximately 500 psi) and purging this pressure to slightly above atmospheric pressure (typically approximately 20-50 psig). This step is repeated for a desired number of rounds (typically 3-5 rounds)
3. Pressurization of system to up to gas cylinder pressure, controlling the gas cylinder regulator pressure.
4. Final pressurization using the hand pressure generation pumps or Ruska positive displacement pump.

Note that steps 2 and 3 must be performed carefully to allow any oxygen in the methane sample enough time to contact the oxygen scavenger. This is achieved by raising the pressure in increments of less than 90 psi. A pressure drop, ΔP_{O_2} , across the oxygen scavenger of 90 psi is the specified maximum pressure differential to reduce the oxygen content of a sample gas to 0.1 ppm, the level stated in Section 3.2. Once the steps above are taken, the sample is ready for NMR measurements.

3.5 NMR Relaxation Time Measurements

This work involves measurements of the two basic NMR relaxation times, T_1 and T_2 . The method by which the measurement is made, and how the measurement yields quantifiable values deserves some attention. In subsequent chapters, some of this development will be repeated to emphasize modifications in the procedure for the application treated.

3.5.1 Measuring T_1

Fig. 3.2 shows the inversion recovery sequence for measuring T_1 . The magnetization is characterized by Equation 3.1,

$$M = M_0 \left(1 - 2e^{\frac{-t}{T_1}} \right). \quad (3.1)$$

M is the magnetization and M_0 is the equilibrium magnetization. M attains a value of $-M_0$ at time zero. T_1 is the characteristic relaxation time of the system, and t is the time during which spin-lattice relaxation takes place. Repetition of the inversion recovery pulse sequence for several values of t_w forms the basis of relating magnetization to time in Equation 3.1.

It should be noted in passing that the inversion recovery sequence is not the only choice to measure T_1 . Saturation recovery can also be performed, where the magnetization at time zero is zero. The saturation recovery sequence is often used in field applications because it can be performed in less time than inversion recovery. However, the inversion recovery sequence is preferred here because it provides a larger dynamic range for magnetization (from $-M_0$ to M_0 versus from 0 to M_0).

3.5.2 Measuring T_2

The CPMG sequence is used to measure T_2 . Figure 3.3 shows the events in the CPMG sequence. Equation 3.2 describes the magnetization decay:

$$M = M_0 e^{-\frac{t}{T_2}}. \quad (3.2)$$

In this equation, M is the magnetization at time t and M_0 is the magnetization at time 0. The new quantity from Equation 3.1 is that T_2 is involved instead of T_1 . T_2 is the characteristic spin-spin relaxation time for the process.

3.5.3 Processing T_1 and T_2 Measurements

Equations 3.1 and 3.2 above are appropriate for relaxation measurements of a single component. However, different expressions are required to account for the T_1 and T_2 relaxation behavior of samples with multiple relaxation times. The following equations fit data for T_1 and T_2 , respectively (Y. Zhang 2002):

$$M(t) = \sum_i M_{0_i} \left(1 - 2e^{\frac{-t}{T_{1i}}} \right) \quad (3.3)$$

$$M(t) = \sum_i M_{0_i} e^{\frac{-t}{T_{2i}}}. \quad (3.4)$$

Equations 3.3 and 3.4 describe the multi-exponential model used to fit collected data. They are multi-component versions of Equations 3.1 and 3.2. The terms in the two sets of equations have analogous meanings, with the difference that the multi-exponential equations sum contributions from multiple relaxation times.

Using Equations 3.3 and 3.4, processing occurs by means of an algorithm developed by Chuah (1996) and Huang (1997) at Rice University. An overview of processing will be mentioned; more details appear as warranted within particular tasks in subsequent chapters. Processing takes data measured in the time domain and resolves it in the T_1 relaxation time or the T_2 relaxation time domain, depending on the measurement. The resulting data in the relaxation

domain are called “distributions”, either T_1 distributions or T_2 distributions. The distributions are histograms of magnetic amplitude at various relaxation times. It should be noted that the process of obtaining relaxation distributions is not a straightforward calculation. The problem is ill-posed and therefore requires a “regularization” factor (Dunn *et al.* 1994). This regularization factor controls the smoothness of the relaxation-domain distributions, where higher values of the regularization factor result in smoother distributions.

Thus far this document has discussed the background and operational details of the project outlined in Chapter 1. The next chapter focuses on one particular application, namely the estimation of crude oil contamination by base oils.

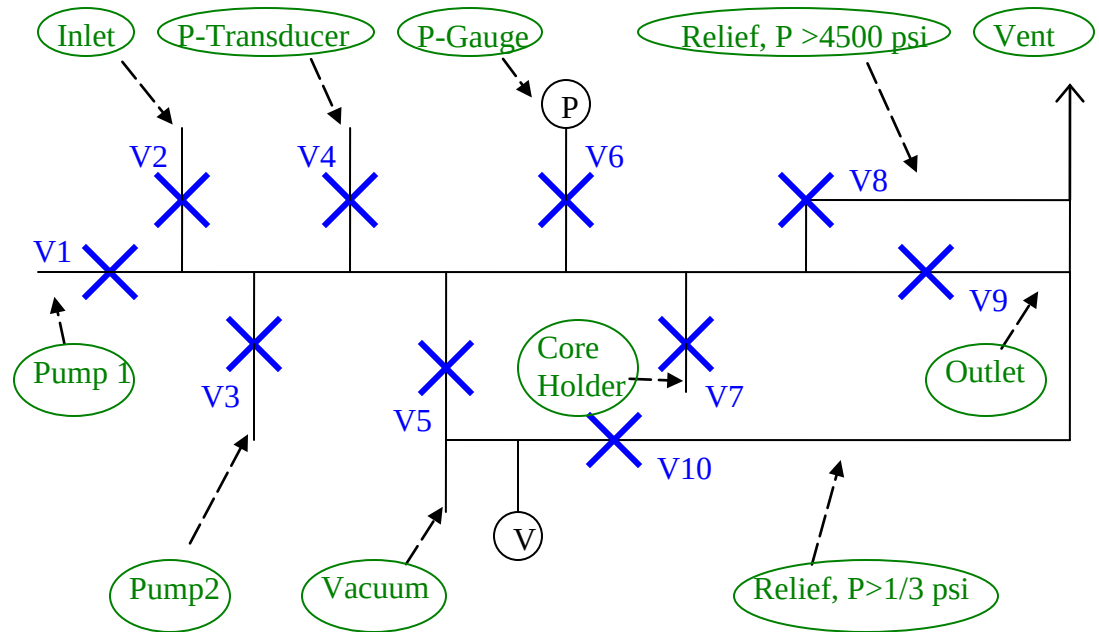


Figure 3.1: Schematic for manifold apparatus for use with gas mixtures having desired composition.

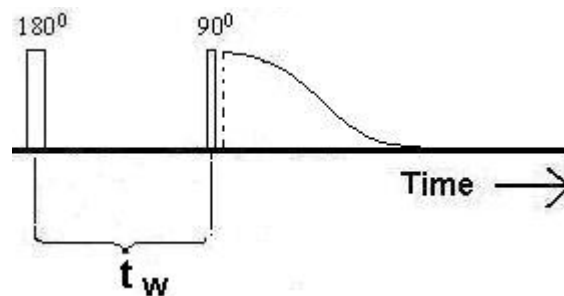


Figure 3.2: The Inversion Recovery pulse sequence.

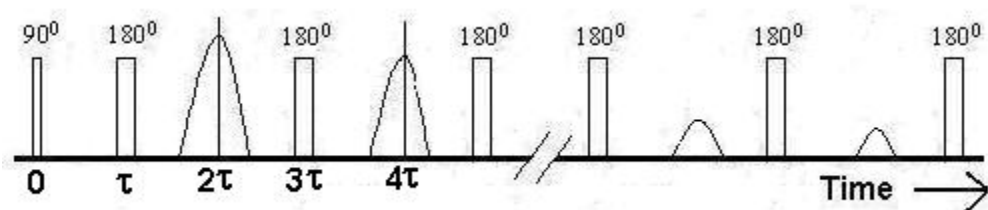


Figure 3.3: The CPMG pulse sequence.

Chapter 4: Drilling-Mud Base-Oil Contaminated Crude Oils T_2 Distributions

This chapter is devoted to some of the work performed to date. In this chapter, the topic is base oil contamination of crude oils. The chapter proceeds as follows. First, some of the reasons to address crude oil contamination are recounted, and the approach taken is introduced. Following this is a description of the measurements performed. The data are then presented and discussed, followed by concluding remarks. The research in this chapter was presented at the 2005 Society of Petrophysicists and Well Log Analysts annual conference (Kurup and Hirasaki 2005).

4.1 Motivation and Approach

Some of the motivation for tackling crude oil contamination by base oils has been mentioned earlier. This section will reiterate the introduction, while providing a fuller perspective of the problem. The problem of contamination exists because oil wells are often drilled with the aid of oil-based fluids. During the drilling process, an oil-based mud (OBM) is formed from the mixture of drilling fluid and drill cuttings. Filtrates from these oil-based muds invade oil-bearing formations and mix with crude oils. OBM filtrates alter the properties of the crude oils with which they mix. In NMR well logging, one concern is whether the measured T_2 relaxation time distribution (or T_2 distribution) changes enough to affect the estimated viscosity, which can be derived from these measurements through existing correlations. Such concerns are particularly valid because OBM filtrates are similar in molecular structure to the crude oils themselves. This

inhibits attempts to separate the OBM filtrate signal from the crude oil signal in NMR logs.

Other works have considered the use of NMR to investigate OBM contamination of crude oils, in the context of the pumpout phase of downhole fluid sampling. Bouton, *et al.* (2001) developed a sharpness parameter to characterize T_1 relaxation times of mixtures of crude oils and base oils. Base oils are the predominant component in OBM filtrates. The sharpness parameter is at a maximum for the base oil alone and decreases monotonically for higher concentrations of crude oil. Continuing this work, Masak, *et al.* (2002) used a downhole fluid sampler to characterize contamination by measuring T_1 relaxation times during the pumpout process. Here, measurements occur as time progresses, and the change in measured signal amplitudes is used to characterize the contamination. More recently, Akkurt, *et al.* (2004) have extended the analysis by developing time and T_2 domain approaches to assess contamination from the pumpout phase in the application of the downhole fluid sampler.

In the present investigation, new approaches to study contamination are developed based on the following fluids. NovaPlus, a commonly used base oil in drilling, is the contaminant. NovaPlus (3 cp) is a mixture of 16- to 18-carbon internal olefins. Nova Plus will be abbreviated as SNP. The crude oils used are from the North Sea (13.7 cp), from offshore China (207 cp), and from the Gulf of Mexico (18.7 cp). Henceforth, the crude oils will be called STNS, PBB, and SMY, respectively. The above information is summarized in Table 4.1.

The objective in this study is to relate the degree of contamination to features in the T_2 distributions. Another goal is estimating the extent of contamination from measured T_2 distributions of samples at unknown degrees of contamination. The traditional approach in studying fluids in NMR logs is using a logarithmic-mean T_2 (log-mean T_2 , $T_{2,LM}$). The new approaches are compared with using $T_{2,LM}$ to estimate contamination.

Table 4.1: Viscosities and Abbreviations for Fluids Investigated at $T = 30\text{ }^{\circ}\text{C}$

Fluid	Type	Abbreviation	Viscosity (cp)
Nova Plus	Base oil	SNP	3.3
North Sea	Crude oil	STNS	13.7
Offshore China	Crude oil	PBB	206.7
Gulf of Mexico	Crude oil	SMY	18.7

Two new approaches will be described and implemented herein. In one approach, contamination is characterized by amplitudes at a limited range of relaxation times in each T_2 distribution. In contrast, the default approach using $T_{2,LM}$ agglomerates data at all T_2 into a weighted average. Thus, using a limited range of relaxation times from the T_2 distribution would increase NMR sensitivity to contamination. This would salvage information from useful regions of the T_2 distribution, without needing to consider the entire distribution as in $T_{2,LM}$. The second approach uses a hypothesized probability distribution to fit the experimental T_2 distribution. Data in the T_2 domain are fit to a skewed Gaussian distribution, whose parameters can be related to contamination. With either of

the two approaches, a polynomial fit extends the characterization over the entire contamination range. The polynomial can then be used to estimate the degree of contamination.

4.2 Experimental

The experimental samples are as follows. Crude oil mixtures with the model contaminant, NovaPlus, were prepared at various volumetric concentrations. The concentrations used for STNS and PBB mixtures are 10, 20, 50 and 75% SNP. The crude oil (0% SNP) and SNP (100% SNP) are also included in the measurements. For mixtures of SMY and SNP, concentrations prepared were 0, 10, 20, 50, 80, 90, and 100% SNP. For 20% and 50% SNP, two samples were prepared to assess reproducibility.

The following measurements were performed. For all but the second samples of SMY mixtures at 20% and 50% SNP, the T_2 relaxation time and the viscosity are measured. For the two samples mentioned, the T_2 relaxation time was measured but the sample volume was too low to do the viscosity measurement.

Deoxygenation, the removal of the paramagnetic contaminant oxygen, was not performed before any of the T_2 measurements for two reasons. First, invading base oil in a drilled formation would contain oxygen (Chen *et al.* 2004). Furthermore, the amount of dissolved oxygen is expected to play only a small role because the relaxation time distributions for the base and crude oils in this

study fall below 1 second, for which the effect of oxygen on T_2 distributions is minimal (Lo 1999) as mentioned in Section 3.2.

The procedures to use the CPMG pulse sequence for performing T_2 experiments were provided in Section 3.5. T_2 measurements in this chapter were made with MARAN-SS or MARAN-M. In these measurements, the decay in signal amplitude, or magnetization, is measured as a function of time. The resultant data is said to be in the time domain. Data inversion leads to a histogram or frequency distribution of magnetic amplitudes at particular values of relaxation time. This representation is called the relaxation time domain, or specifically T_2 domain for this chapter.

In the time domain, the decay process is characterized by the following equation:

$$M(t) = \sum_i M_{0,i} e^{-\frac{t}{T_{2,i}}}, \quad (4.1)$$

which is the same as Eq. 3.4. In this expression, M is the total magnetization at time t , $M_{0,i}$ is the initial magnetization of component i , and $T_{2,i}$ is the T_2 value corresponding to component i . Before any inversion is done, the typically large number of time-domain data points is parsed. This process, called “sampling and averaging”, reduces the computational load in the conversion with minimal sacrifice to data quality (Chuah 1996). Sampling and averaging operates by segmenting the acquisition time of a CPMG measurement into equal logarithmic intervals and determining the average value of magnetization for the data within

the interval. These average values replace the original data for the purpose of inversion.

In the relaxation time domain, the inversion process is performed using a Levenberg-Marquardt algorithm (Chuah 1996). The inversion determines the amplitudes $M_{0,i}$ in Eq. 4.1 for the predetermined relaxation times $T_{2,i}$, which are spaced apart equally in logarithmic scale. Each occurrence of specific values in the T_2 domain, $T_{2,i}$, where the resultant amplitudes are placed will be called T_2 bins or simply bins. Thus, the T_2 distribution is a plot of bin amplitudes, $M_{0,i}$, against bin T_2 , $T_{2,i}$, for the total number of bins.

The number of T_2 distributions determined for each set of mixtures differs depending on the crude oil. For mixtures containing STNS or PBB, one T_2 distribution measurement is done. For the SMY mixtures, four separate T_2 distribution measurements of the same set of samples are made, for the statistical analysis below. The separate measurements will be called Run 1, Run 2, Run 3, and Run 4.

NMR data were obtained using the following conditions. Runs 1, 2, and 3 were performed with MARAN-SS and Run 4 was performed with MARAN-M. In experiments for the mixtures mentioned above, the acquisition conditions used are 128 scans, 9216 (9k) echoes (time-domain data points), 320 μ s echo spacing (time between echoes in each scan), and a 5 s wait time between neighboring scans. The only exception to this is that for Run 3 and Run 4, the number of scans was not 128, but was adjusted such that the signal-to-noise ratio is 100. Data acquisition software automatically determines the actual number of scans.

The viscosities are measured using a Brookfield viscometer, Model LVDV-III+. Measurements are made near the maximum shear rate that does not exceed torque limits or the rotation speed of the instrument. For the STNS and PBB mixtures, the viscosity for each set was measured after the T_2 distribution was obtained. For the SMY samples, only samples having enough volume had their viscosity measured. This measurement was done after Run 1. The temperature of both T_2 relaxation time measurements and viscosity measurements is 30 °C.

4.3 Overview of Approaches

The results will be divided into three approaches. The first approach is traditional, characterizing mixture viscosity and log-mean T_2 . The second approach applies a selective contamination index (SCI) for relating measured T_2 distributions to contamination. The third approach shows how a skewed Gaussian model for the relaxation time distributions performs in estimating contamination.

Before proceeding, a brief explanation as to the difference in the methods used for the $T_{2,LM}$ approach, the SCI approach, and the distribution parameter approach is warranted. Using $T_{2,LM}$ involves a one-stage analysis. All the data contributes to $T_{2,LM}$. The value of $T_{2,LM}$ equally involves all bins, depending only on the signal amplitudes in all the bins. The methods in the SCI approach and distribution parameter approach involve two stages.

The two stages in the SCI approach and the distribution parameter approach are described below. In the first stage of the SCI approach, a subset of the available T_2 bins is used to define intermediate quantities, called binwise contamination indices. The second stage creates a quantity, the selective contamination index or SCI, from a function of these intermediate quantities. For the distribution parameter approach all the data is used, similar to using $T_{2,LM}$. However, the approach is still in two stages. In the first stage, one obtains the parameters of the skewed Gaussian model used to fit the data. The second stage defines a single figure, the distribution parameter index (DPI), which is a function of a subset of these parameters.

4.4 Preliminary Measurements

Fig. 4.1 shows the incremental T_2 distributions (as opposed to cumulative distributions) for mixtures of STNS and SNP. The plots represent data from 50 T_2 bins. The top panel shows the distribution for the contaminant SNP, and subsequent panels contain increasing amounts of STNS. For a light crude oil like STNS, the mode, or T_2 value corresponding to the highest amplitude in the distribution, does not differ greatly from the base oil, SNP. As SNP contamination decreases, the most noticeable change is that the T_2 distribution becomes more skewed toward shorter relaxation times. However, much of the amplitude for all contamination levels is localized at relatively high relaxation times.

The situation is different for PBB mixtures, Fig. 4.2. Fig. 4.2 shows T_2 distributions for mixtures in the same format as for Fig. 4.1. In these mixtures, all

measured contamination levels can be differentiated. Both the mode and the tail of the distribution noticeably shift as the contamination level changes. These features are seen even at a contamination of 10% SNP.

Fig. 4.3 shows the same diagram for six of the samples from Run 1 with SMY mixtures. The mode and tail of the T_2 distributions vary less than PBB mixtures and more than STNS mixtures. This is expected given that the viscosity of SMY lies between the other two crude oils. The trends for SMY are reproducible in the other runs. The reproducibility is demonstrated at a base oil volume fraction of 0.5 in Fig. 4.4.

The T_2 distributions in Figs. 4.1-4.3 can be assessed in terms of the logarithmic mean relaxation times ($T_{2,LM}$), which appear in Table 4.2 and Table 4.3. Table 4.2 shows the log-mean relaxation times for mixtures containing STNS or PBB crude oils with SNP. One trend from Table 4.2 is that $T_{2,LM}$ increases as more base oil is added. A second trend is that this increase in $T_{2,LM}$ is more severe for PBB, the heavier crude oil. $T_{2,LM}$ values for Run 1 through Run 4, on mixtures containing the crude oil SMY, are shown in Table 4.3. As with STNS and PBB mixtures, $T_{2,LM}$ increases with increasing concentrations of base oil.

Viscosities appear in Table 4.4 and Table 4.5. Table 4.4 shows the measured viscosities for the same mixtures in Table 4.2, namely for mixtures containing STNS or PBB crude oils. As with $T_{2,LM}$, the viscosity changes more drastically for heavier crude oils. However, viscosity decreases as more base oil, SNP, is present in the mixture. A similar table for viscosity of SMY mixtures is

shown in Table 4.5. Note that some samples have insufficient volume for the measurement of viscosity.

Table 4.2: Log-mean T_2 Values for Mixtures of STNS and PBB crude oils with SNP base oil

SNP Content (Volume Fraction)	$T_{2,LM}$ (ms)	
	STNS	PBB
0.00	114.7	9.9
0.10	145.3	16.4
0.20	171.7	27.8
0.50	288.3	52.6
0.75	403.2	233.5
1.00	534.6	512.4

Table 4.3: Log-mean T_2 Values for Mixtures of SMY crude oil with SNP base oil

SNP Content (Volume Fraction)	$T_{2,LM}$ (ms)			
	Run 1	Run 2	Run 3	Run 4
0.00	72	70	70	54
0.10	94	93	88	56
0.20 (1 st)	112	110	117	95
0.20 (2 nd)	157	109	139	106
0.50 (1 st)	251	180	214	214
0.50 (2 nd)	343	262	255	248
0.80	448	N/A	N/A	425
0.90	586	586	641	622
1.00	660	587	728	685

Fig. 4.5 shows a cross-plot between $T_{2,LM}$ and viscosity for the three sets of mixtures. For the SMY mixtures, $T_{2,LM}$ comes from Run 1, because the viscosity measurement corresponds to Run 1. The line is the expected behavior

based on an existing correlation between $T_{2,LM}$ and viscosity, η , for dead crude oils. The correlation is given by

$$T_{2,LM} = \frac{1200}{\eta^{0.9}}, \quad (4.2)$$

and is called the Morriss Correlation (Morriss, *et al.* 1997). As Fig. 4.5 shows, the mixtures appear to follow this expected behavior.

Table 4.4: Viscosities for Mixtures of STNS and PBB crudes with SNP base oil

SNP Content (Volume Fraction)	Viscosity (cp)	
	STNS	PBB
0.00	13.7	206.7
0.10	11.1	103.0
0.20	9.2	57.0
0.50	5.8	26.8
0.75	4.3	6.3
1.00	3.3	3.3

Table 4.5: Viscosities for Mixtures of SMY Crude Oil with SNP Base Oil

SNP Content (Volume Fraction)	Viscosity (cp)
0.00	18.7
0.10	14.8
0.20 (1 st)	11.0
0.20 (2 nd)	No measurement
0.50 (1 st)	6.2
0.50 (2 nd)	No measurement
0.80	4.0
0.90	3.4
1.00	3.1

Fig. 4.5 showed how $T_{2,LM}$ and η are related for each of the measured samples. To observe trends in either of these quantities, one can represent the measured data in terms of their variation with contamination level. This is shown in Figs. 4.6 and 4.7.

Fig. 4.6 compares measured and interpolated $T_{2,LM}$ for the mixtures of each crude oil with SNP. The experimental values of $T_{2,LM}$ are compared with a linear interpolation between the measured log-mean T_2 values for the crude oil and for SNP. The interpolations are based on the $T_{2,LM}$ values for SNP and the crude oil in question according to the following equation:

$$T_{2,LM}^{mix} = (T_{2,LM}^{crude})^{1-f} (T_{2,LM}^{SNP})^f. \quad (4.3)$$

In Equation 4.3, $T_{2,LM}^{mix}$ is the interpolated log-mean relaxation time of the mixture, and $T_{2,LM}^{crude}$ and $T_{2,LM}^{SNP}$ are the experimental log-mean relaxation times for the crude oil and for SNP, respectively. The quantity f is the volume fraction of SNP. In Fig. 4.6, experimental data are shown as points and interpolated data are represented as lines. Only one run is shown for mixtures of SMY for illustrative purposes. Other runs show similar behavior. Fig. 4.6 shows that the characterization of $T_{2,LM}$ as a weighted log-mean of the $T_{2,LM}$ values of the two components provides a fair description of the trend seen in the experimental data.

Fig. 4.7 repeats the comparison for viscosities. The equation for the interpolation of mixture viscosities is analogous to that for $T_{2,LM}$:

$$\eta^{mix} = (\eta^{crude})^{1-f} (\eta^{SNP})^f \quad (4.4)$$

In this expression, η^{mix} is the interpolated viscosity of the mixture, η^{crude} is the experimental crude oil viscosity, and η^{SNP} is experimental SNP viscosity. Again,

f is the SNP volume fraction. As with Fig. 4.6, the interpolated equation (lines in Fig. 4.7) describes the trend of the experimental data (points in Fig. 4.7).

4.5 Selective Contamination Index Approach

Although Figs. 4.6 and 4.7 suggest a trend from concentration-weighted logarithmic-mean averages for mixtures of SNP and crude oils, deviations of up to 60% are observed. In order to improve the characterization of contamination from T_2 distributions, an attempt is made to utilize a more appropriate summary of NMR T_2 behavior than the log-mean value, $T_{2,LM}$. Using signal amplitudes at specifically chosen T_2 bins allows a portion of the collected data to serve in mixture analysis, without being lumped in an overall average like the logarithmic mean.

To do this, it is convenient to use cumulative distributions. The amplitude of a cumulative distribution at a specific bin is a running sum of amplitudes from the incremental T_2 distributions shown earlier, belonging to that bin and to all bins at lower values of T_2 . Thus, cumulative distributions continually increase from low to high relaxation times. Cumulative distributions are preferred because they exhibit a more monotonic behavior when the same T_2 bin is compared for different contamination levels. The cumulative distributions here are in the T_2 domain, just like incremental distributions, and are normalized such that the final amplitude (after amplitudes from all relaxation times have been summed) for each sample is equal to 1.

For illustration, Fig. 4.8 shows the cumulative distributions, G_f , for PBB mixtures with the base oil SNP. The subscript f refers to the SNP volume

fraction. The information in Fig. 4.8 is the same as in Fig. 4.2, presented in a different form. Fig. 4.8 demonstrates the monotonic increase in amplitude for a given bin as the base oil content decreases. Note that the cumulative T_2 bins, $G_{f,i}$, are shown explicitly as points in Fig. 4.8, where i is the index for bins.

In Fig. 4.9, cumulative amplitudes $G_{f,i}$ from 11 of the 50 bins used to obtain T_2 distributions are shown for SMY mixtures in Run 1. The data in each bin, plotted as separate entities in Fig. 4.9, includes information from T_2 distributions at all measured contamination levels. Note that bins placed in the upper part of the legend are the bins where $G_{f,i}$ is the largest. The lines shown result from linear regression. Those bins having regression lines of the greatest slope are most responsive to contamination and thus would be more useful in characterizing the relative amounts of SNP and crude oil.

Fig. 4.10 is a direct representation of slopes in plots such as Fig. 4.9, for STNS mixtures. Fig. 4.10 includes all 50 bins (shown as points), whereas Fig. 4.9 showed only 11 bins. Note that the plotted slope is large, as desired, only for a limited range of relaxation times. Also, more bins appear on the left side of the maximum slope, corresponding to the peak in Fig. 4.10, than on the right. In fact, the SCI approach uses only those bins on the left side of the maximum slope whose slopes are between 20% and 80% of the maximum slope in figures such as Fig. 4.10. This choice of bins to use in determining SCI results from considering both sensitivity to contamination, as indicated by the aforementioned slopes, and consistency of the binwise contamination index, defined in the next paragraph, for the selected bins. In particular, the latter criterion applies to bins

with the largest slope (80% to 100% of maximum), namely that they are not consistent with bins between 20% and 80% of the maximum slope in terms of the binwise contamination index.

The binwise contamination indices are determined for the chosen bins as follows:

$$I_{f,i} = \frac{G_{f,i} - G_i^{crude}}{G_i^{SNP} - G_i^{crude}} \quad (4.5)$$

In this equation, $I_{f,i}$ is the binwise contamination index (not yet the SCI) for SNP volume fraction f and bin i . $G_{f,i}$ refers to the cumulative amplitude for sample with SNP volume fraction f for bin i and G_i^{SNP} and G_i^{crude} are the cumulative amplitudes in bin i of SNP ($f = 1$) and of the appropriate crude oil ($f = 0$), respectively. The binwise contamination index can be understood by reviewing Fig. 4.8. For a particular bin, which lies along a vertical line in Fig. 4.8, $I_{f,i}$ is the ratio of two quantities. The numerator is the difference along the vertical line of the cumulative amplitude $G_{f,i}$ of a mixture with particular SNP volume fraction f from the cumulative amplitude of the crude oil G_i^{crude} . The denominator is the maximum difference in cumulative amplitudes for the same bin, namely the difference of G_i^{crude} and G_i^{SNP} . The binwise contamination index $I_{f,i}$ is defined by this ratio such that it runs from 0 (for crude oils) to 1 (for SNP). The goal of such a characterization is to calculate a quantity that correlates with the contamination in terms of the SNP volume fraction f .

The SCI is determined by taking the arithmetic means of binwise contamination indices for the pre-selected bins, namely those bins with slopes

between 20% and 80% of maximum slope illustrated in plots like in Fig. 4.10.

So, SCI can be expressed as

$$SCI = I_f = \frac{1}{n_i} \sum_{i \text{ selected bins}} I_{f,i} \cdot \quad (4.6)$$

The new term, n_i , is the number of selected bins. Table 4.6 shows the SCI values for each concentration of SMY and PBB mixtures. Table 4.7 shows the SCI values for the SMY measurements. In Table 4.7, the SCI shown is a mean SCI for each concentration across the four runs. For 80% SNP, only the SCI values from Run 1 and Run 4 are used because instrumental errors caused erroneous results in the other runs. Note that all error values shown are standard deviations. Standard deviations for SNP and for the crude oil are zero because of the definition of the binwise contamination index and SCI.

Table 4.6: Selective Contamination Indices for Mixtures of STNS and PBB Crude Oils with SNP Base Oil

SNP Content (Volume Fraction)	SCI	
	STNS	PBB
0.00	0.00 ± 0.00	0.00 ± 0.00
0.10	0.20 ± 0.05	0.28 ± 0.03
0.20	0.36 ± 0.02	0.50 ± 0.04
0.50	0.70 ± 0.02	0.68 ± 0.04
0.75	0.88 ± 0.03	0.94 ± 0.02
1.00	1.00 ± 0.00	1.00 ± 0.00

Table 4.7: SCI values for Mixtures of SMY Crude Oil with SNP Base Oil

SNP Content (Volume Fraction)	SCI
0.0	0.00 ± 0.00
0.1	0.16 ± 0.03
0.2 (1 st)	0.33 ± 0.02
0.2 (2 nd)	0.42 ± 0.04
0.5 (1 st)	0.67 ± 0.04
0.5 (2 nd)	0.76 ± 0.03
0.8	0.90 ± 0.02
0.9	0.96 ± 0.01
1.0	1.00 ± 0.00

Figs. 4.11-4.13 show the SCI values in Table 4.6 and Table 4.7. The curves shown on the figures represent cubic

polynomial fits of the data points. Fig. 4.11 is the cubic polynomial fit for mixtures

containing STNS crude oil. Fig. 4.12 shows this data for PBB crude oil mixtures. Fig. 4.13 shows SCI data for SMY mixtures in Runs 1-4. In Fig. 4.13, the data correspond to the mean SCI values shown in Table 4.7 and the bars are the corresponding standard deviations. For each set of mixtures, Figs. 4.11-4.13 provide a relationship between SCI and contamination level.

From this relationship, the degree of contamination is estimated as follows. T_2 distributions of an unknown mixture of a particular system (for example, SMY and SNP) are measured. Then, binwise contamination indices are calculated for bins previously identified as optimal. This requires the distributions of the crude oil and base oil separately, which are available because they go into developing the fit. The average of the values calculated gives an SCI. This value can be used with the polynomial fitting, which is of the following form:

$$I_f = P(f) \quad (4.7)$$

I_f is the SCI for a particular SNP volume fraction, f . This is the quantity that would be calculated from the measurement. P is the functional form of the polynomial in f . The equation can then be placed in the following form:

$$P(f) - I_f = 0 \quad (4.8)$$

The only physical root of this equation, namely when f is between 0 and 1, yields the SNP volume fraction or contamination level, f .

The result of this procedure can be compared statistically with contamination levels estimated from $T_{2,LM}$ for SMY. Such a comparison for SMY is shown in Fig. 4.14. Fig. 4.14 shows both SCI (plot on the left) and $T_{2,LM}$ (on right) as a function of contamination. The points represent the data from

Runs 1-4. The central line in both cases is a cubic polynomial fit. For the SCI, the construction of the cubic polynomial was mentioned above. For $T_{2,LM}$, the cubic polynomial is constructed between the logarithm (base 10) of $T_{2,LM}$ and contamination. The two curves flanking the central line on each plot are 95% confidence intervals for the respective polynomial fit.

The width of these confidence intervals shows the uncertainty in contamination level given a particular parameter, whether $T_{2,LM}$ or SCI. Notice that the width of the interval is smaller for the SCI measurements than for $T_{2,LM}$ over a large concentration range. In particular at contaminations near 20% SNP, the width of the confidence interval is 0.23 for $T_{2,LM}$ and 0.11 for the SCI, both in units of SNP volume fraction. This shows that a particular measured $T_{2,LM}$ for a sample with contamination near a SNP volume fraction of 0.20 would yield twice the uncertainty in contamination level as the corresponding SCI. This suggests that the SCI is better than interpolation of $T_{2,LM}$.

4.6 Distribution Parameter Approach

A more intuitive way of addressing NMR contamination data is by using a statistical distribution. In the distribution parameter approach discussed here, a skewed Gaussian distribution models T_2 -domain data. The basis for choosing a skewed Gaussian distribution is as follows. When T_2 domain amplitudes are charted against a logarithmically scaled T_2 axis, a pure component typically shows a Gaussian distribution. Crude oils typically have T_2 distributions that are skewed toward short relaxation times. The skewed Gaussian model allows for

this difference in two sides of the mode and maintains the Gaussian character for single components.

Equation 4.9 shows the equation for the model itself:

$$A(T_{2,i}^*) = \begin{cases} C_4 \exp \left[-\frac{(T_{2,i}^* - C_1)^2}{2C_2^2} \right]; T_{2,i}^* \leq C_1 \\ C_4 \exp \left[-\frac{(T_{2,i}^* - C_1)^2}{2C_3^2} \right]; T_{2,i}^* \geq C_1 \end{cases} \quad (4.9)$$

In this equation, $A(T_{2,i}^*)$ is the amplitude of the fitted model at a given T_2 bin, $T_{2,i}^*$.

The superscript on $T_{2,i}^*$ indicates that it is the logarithm of $T_{2,i}$ that is fit with a Gaussian distribution, not $T_{2,i}$ itself. C_1 is the logarithmic mode of the skewed Gaussian model and C_4 is the pre-exponential factor. The model is skewed because of C_2 and C_3 , which represent standard deviations on respective sides of the mode of the distribution. C_1 , C_2 , C_3 , and C_4 form the parameters of the model. A non-linear least squares regression was used to achieve the fit between experimental data and the posited model.

The objective function in the fitting procedure is

$$\Phi_{T_2}(C_1, C_2, C_3, C_4) = \sum_i (A(T_{2,i}^*) - A_i)^2. \quad (4.10)$$

Here, Φ_{T_2} is the objective function for the T_2 domain fit. It depends on the model parameters because these can be changed to achieve the best match between the set of fitted amplitudes $A(T_{2,i}^*)$ and the experimental amplitudes, M_i .

The resulting fits for STNS mixtures are given in Fig. 4.15. The data points are the experimental data and the line represents the fit. Note that the fit

captures the shape of the peak associated with the mode of the distribution. The fits for the tails at shorter relaxation times are still good, but some discrepancies are visible.

Fig. 4.16 repeats the treatment for mixtures of PBB and SNP. Again, the peaks associated with modes are more accurately fit than the tailing portion of the T_2 distribution. However, the modes are not fit as well as with STNS mixtures. The fits also extend farther toward short relaxation times than with STNS mixtures because of the greater amplitude for PBB mixtures at these relaxation times.

Fig. 4.17 shows fits for six representative samples from Run 1 with SMY mixtures. The nature of the fits for other runs is similar to that for the corresponding concentrations in Run 1. Fig. 4.17 shows good fits for the peak associated with the mode. As the SNP concentration increases, the mode is fit better but the fit for the tailing portion of the T_2 distribution is poorer. In the fits for all three crude oil mixtures, the skewness of the model is visible in that the two sides of the fitted distribution have noticeably different widths.

As mentioned earlier, the models used to construct the fits have four parameters. The most relevant parameters in terms of their variation with contamination are C_1 and C_2 , the model logarithmic mode relaxation time and the standard deviation at short relaxation times. Specifically, C_1 should increase with contamination, and C_2 should decrease with increasing contamination. The actual variation of the parameters is seen in log-log plots of the two parameters charted against each other, shown in Fig. 4.18 for PBB mixtures. Fig. 4.18

shows the expected trend from crude oil (lowest, right-most point) to SNP (highest, leftmost point) for PBB mixtures. Note that the actual plotted quantities are 10^{C_1} and 10^{C_2} , called the model mode and short-time standard deviation factor, respectively. These modifications of the parameters, rather than the parameters themselves, are plotted because the skewed Gaussian model involves a logarithmic representation of T_2 , as mentioned before.

To develop a quantity that is similar in spirit to the SCI, the distribution parameter index (DPI) is defined. This parameter, defined by Equation 4.11

$$DPI = \sqrt{0.5 \left[\left(\frac{C_{1,sample} - C_{1,crude}}{C_{1,SNP} - C_{1,crude}} \right)^2 + \left(\frac{C_{2,sample} - C_{2,crude}}{C_{2,SNP} - C_{2,crude}} \right)^2 \right]}, \quad (4.11)$$

accounts for both C_1 and C_2 , and is a scaled distance from the crude oil data point in parameter cross-plots like Fig. 4.18.

In this equation, C_1 and C_2 are the model parameters mentioned earlier. The additional subscripts refer to different T_2 distribution measurements. $C_{1,sample}$ and $C_{2,sample}$ refer to the value of C_1 or C_2 for a sample with a particular contamination level, $C_{1,crude}$ or $C_{2,crude}$ refer to the parameter value for the T_2 distribution of crude oil in that sample, and $C_{1,SNP}$ and $C_{2,SNP}$ refer to the parameters for the T_2 distribution of SNP base oil measured with that mixture set.

Figs. 4.19 and 4.20 show the respective DPI for mixtures involving STNS and PBB crude oils as a function of the contamination. The DPI is correlated to the contamination with a cubic polynomial (lines in the figures). Figs. 4.19 and 4.20 show that the DPI is monotonic with contamination over the entire contamination range. Table 4.8 shows DPI values for STNS and PBB mixtures.

The treatment in Figs. 4.19 and 4.20 and in Table 4.8 can be repeated for SMY mixtures. However for statistical analysis, it is worthwhile to first point out the similarity between the DPI and the SCI. Both are defined such that their value is 0 for a crude oil and 1 for SNP. The DPI, like the SCI, is correlated to contamination with a cubic polynomial. Thus, contamination can be estimated from DPI values from fits of an NMR measurement in the same style as for the SCI. Finding the appropriate roots of the polynomial fits developed above for DPI in a manner similar to Equations 4.7 and 4.8 for the SCI would provide a contamination level corresponding to an obtained DPI.

Table 4.8: DPI Obtained from Model Parameters for T_2 Domain Fits of STNS and PBB Mixtures

SNP Content (Volume Fraction)	STNS	PBB
0.00	0.000	0.000
0.10	0.325	0.190
0.20	0.388	0.333
0.50	0.747	0.563
0.75	0.939	0.903
1.00	1.000	1.000

Considering the similarity between the DPI and SCI approaches, one can extend the analysis of DPI values in the same manner as was done with the SCI. Fig. 4.21 shows the DPI for SMY mixtures with 95% confidence intervals included. As such, Fig. 4.21 resembles the left side of Fig. 4.14 for the SCI approach. Table 4.9 shows the mean DPI and the respective standard deviations corresponding to the data in Fig. 4.21.

As with SCI, one can compare the reliability of DPI values with the other approaches by comparing the width of the confidence interval at 20% contamination. This width is 0.19 for the DPI in Fig. 4.21. The units for both quantities are units of SNP volume fraction. This compares to a width of 0.23 for the $T_{2,LM}$ confidence interval and 0.11 for the SCI confidence interval, both at 20% contamination. This implies that the DPI is an improvement over treatment with $T_{2,LM}$, but does not perform as well as the SCI.

Table 4.9: DPI Obtained from Model Parameters for T_2 Domain Fits of SMY Mixtures

SNP Content (Volume Fraction)	Mean
0.0	0.00 ± 0.00
0.1	0.26 ± 0.02
0.2 (Both Samples)	0.50 ± 0.10
0.5 (Both Samples)	0.71 ± 0.06
0.8	0.85 ± 0.00
0.9	1.00 ± 0.03
1.0	1.00 ± 0.00

4.7 Conclusions

Mixtures of three crude oils and SNP have been measured, yielding NMR T_2 relaxation times and viscosity values. Incremental T_2 distributions show that more viscous crude oils show a greater effect from contamination with SNP. For all sets of mixtures, effects were more pronounced in samples with more SNP content. The mixtures behave according to the Morriss correlation, relating viscosity to $T_{2,LM}$. Furthermore, mixture log-mean relaxation times and viscosities can be interpolated to a moderate degree of accuracy with Equations 4.3 and 4.4, respectively.

In order to improve accuracy, the selective contamination index (SCI) was introduced. Starting with cumulative distributions in the T_2 domain, the SCI is calculated from bins that show a strong dependence on concentration. This method yields strong correlations for contamination when appropriate bins are selected. For these bins, the binwise contamination indices at measured SNP

concentrations are consistent, as indicated by the small standard deviations in Table 4.6 and 4.7. Polynomial fits are then used to construct curves that extend over the entire SNP concentration range. These curves can be used to obtain concentrations, or contamination levels, from the SCI.

Another method pursued is distribution parameter approach, leading to the distribution parameter index (DPI). This approach begins with the characterization of contamination by fitting CPMG data to a skewed Gaussian distribution. An index is developed from a subset of the parameters in this distribution. Namely, the model mode and short-time standard deviation factor, are combined into a distribution parameter index (DPI). DPI can be correlated to contamination.

Comparing the two methods above, the DPI is less reliable than the SCI in terms of the uncertainty in degree of contamination corresponding to a particular index value. However, it does outperform the $T_{2,LM}$ method using the same criteria. Thus, using the SCI or DPI approaches would be recommended improvements to characterizing contamination using $T_{2,LM}$.

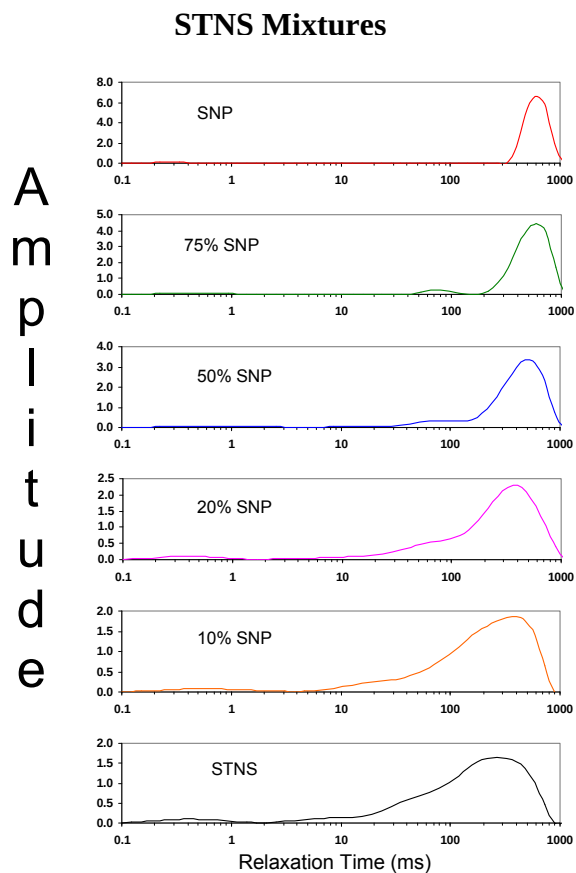


Figure 4.1: Stacked plots showing incremental T_2 relaxation time distributions for mixtures of STNS crude oil and SNP base oil. Note that the amplitude axis is not to scale for all curves in the stack.

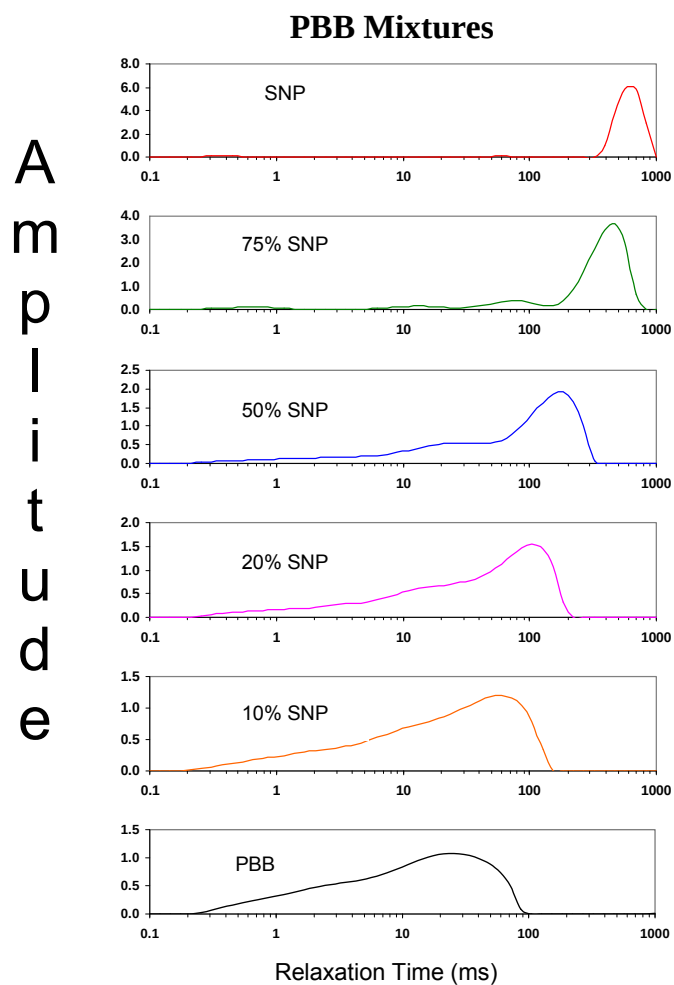


Figure 4.2: Stacked plots showing incremental T_2 relaxation time distributions for mixtures of PBB crude oil and SNP base oil. Note that the amplitude axis is not to scale for all curves in the stack.

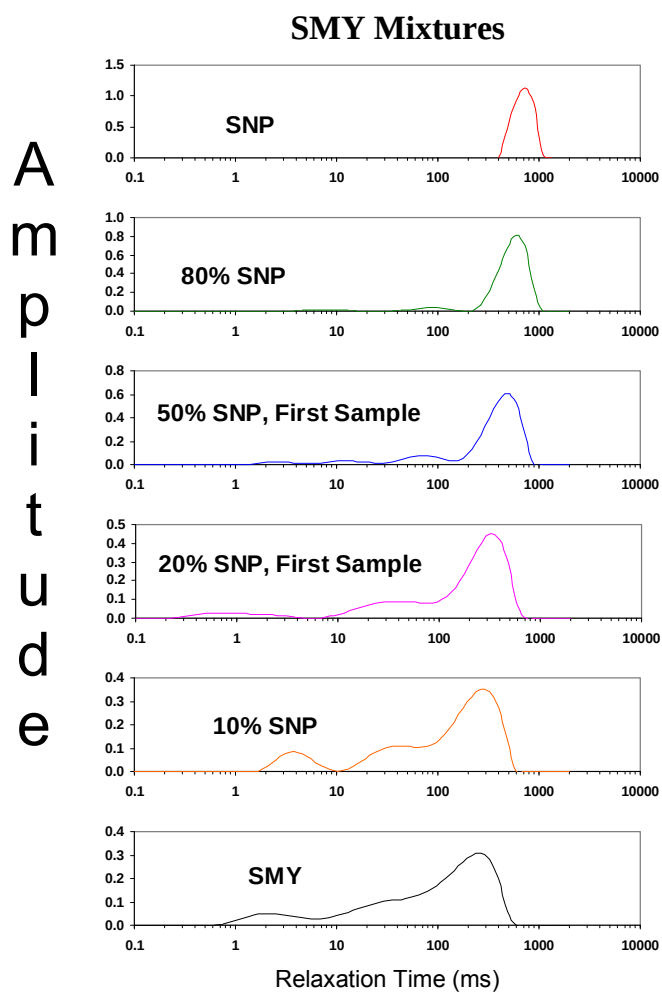


Figure 4.3: Stacked plots showing incremental T_2 relaxation time distributions for mixtures of SMY crude oil (Run 1) and SNP base oil. Note that the amplitude axis is not to scale for all curves in the stack.

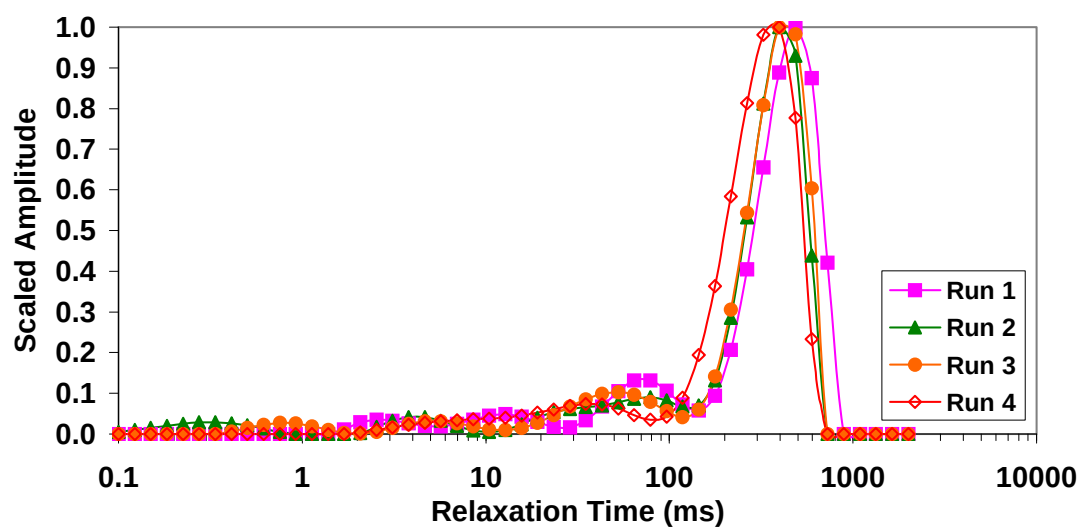


Figure 4.4: Incremental T_2 distributions for repeated measurements of the first sample containing 50% SMY crude oil and 50% SNP base oil.

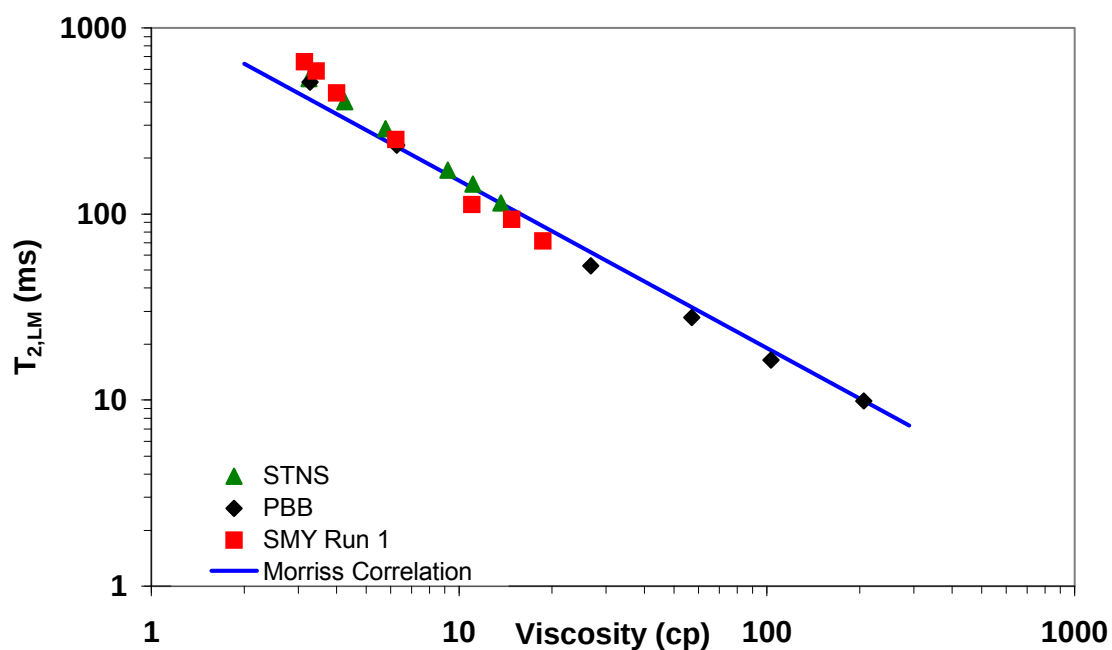


Figure 4.5: Relationship between viscosity and $T_{2,LM}$: Comparison to Morriss Correlation.

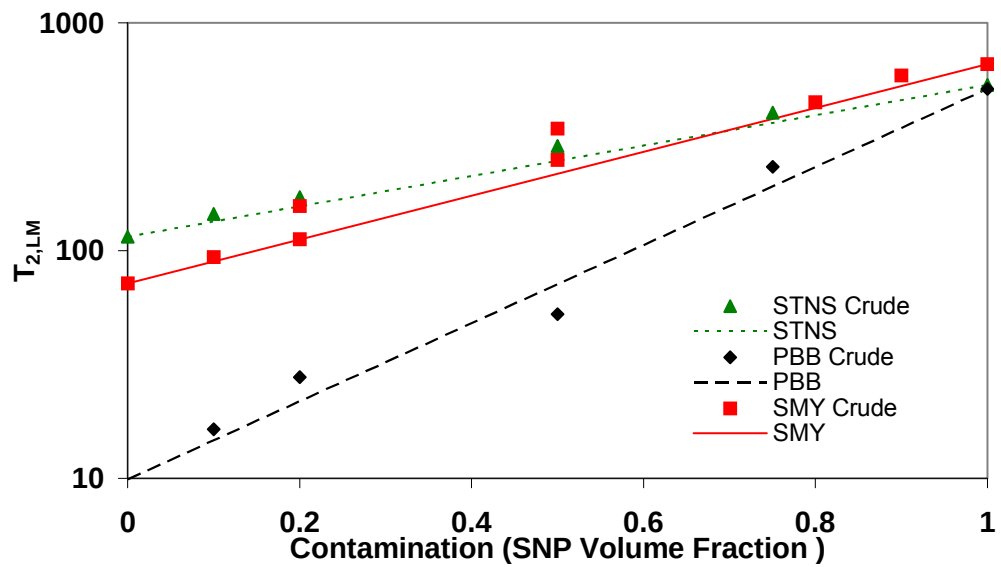


Figure 4.6: Comparison of experimental $T_{2,LM}$ values with interpolations for mixtures of crude oil and SNP based on Equation 3.

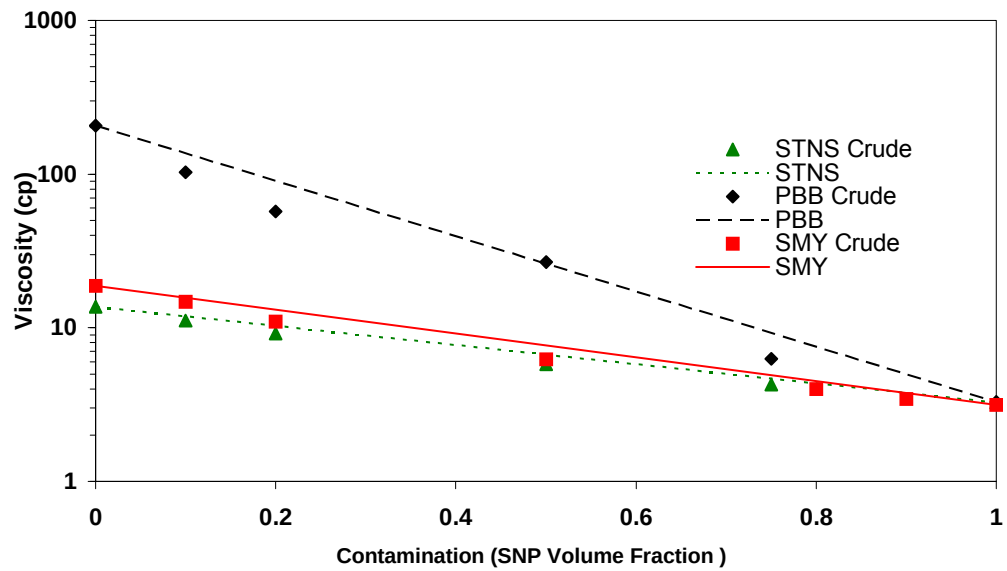


Figure 4.7: Comparison of experimental viscosities with interpolations for mixtures of crude oils and SNP based on Equation 4.

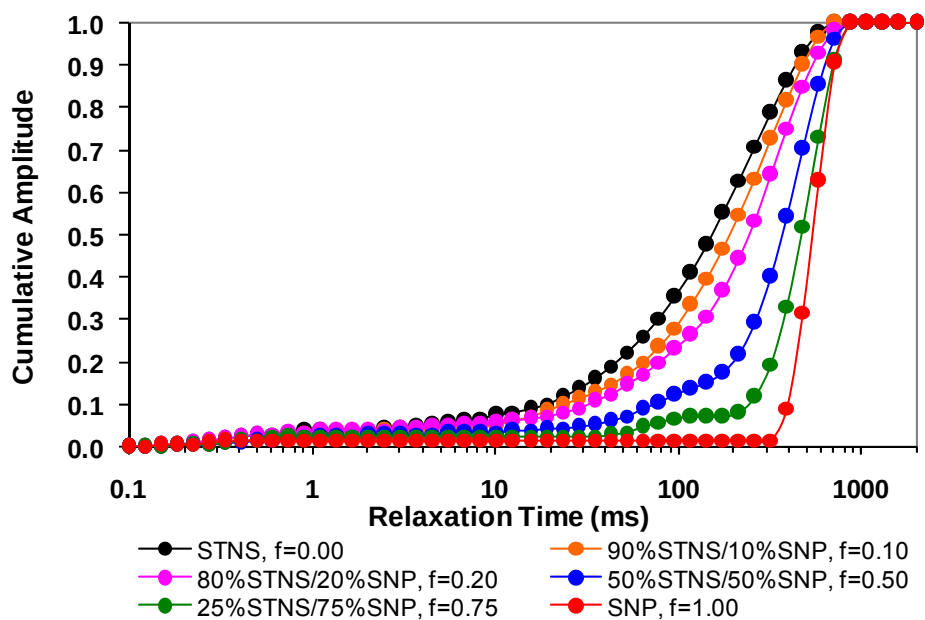


Figure 4.8: Normalized, cumulative T_2 distributions (G_f) for SNP volume fraction (f) for mixtures of STNS crude oil and SNP base oil

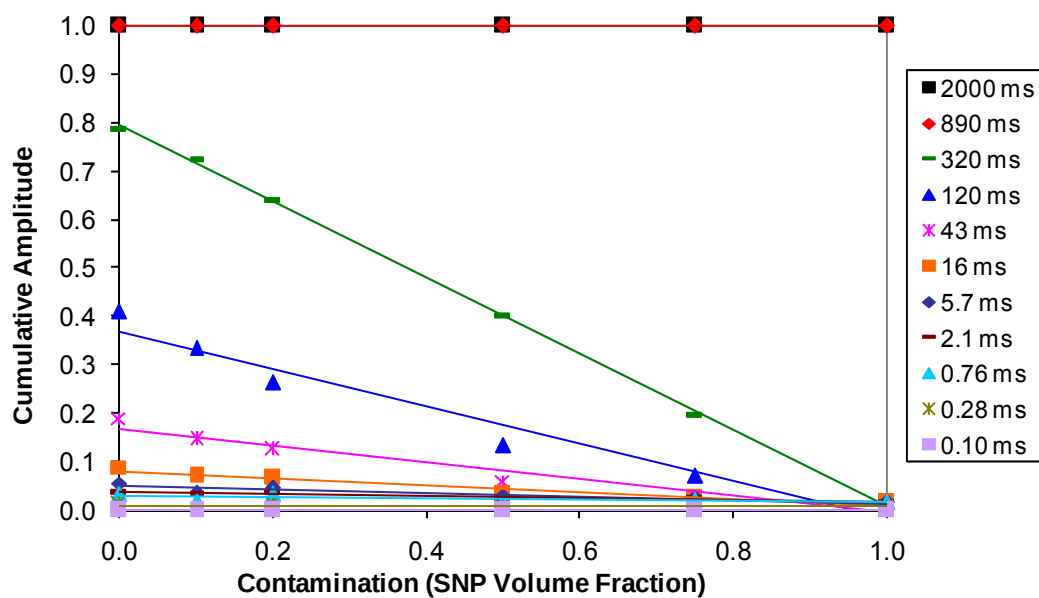


Figure 4.9: Behavior of signal amplitude in selected T_2 bins as a function of SNP concentration in Run 1 of mixtures of STNS crude oil and SNP base oil.

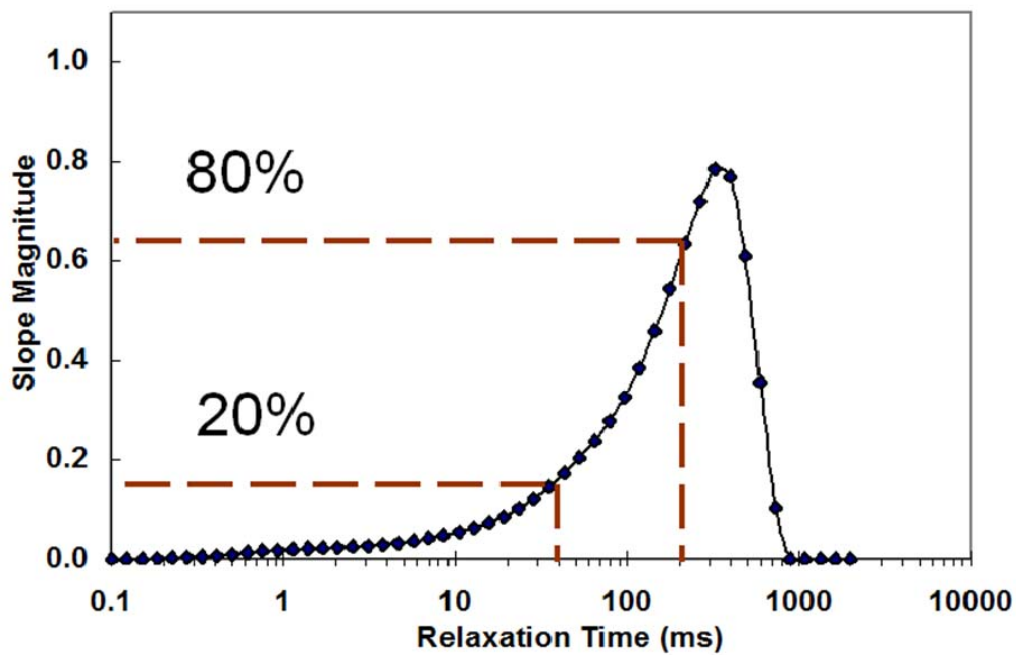


Figure 4.10: Slope of T_2 cumulative amplitude against contamination for all bins in mixtures of STNS crude oil and SNP base oil. The bins selected for further analysis are between 20% and 80% of the maximum slope.

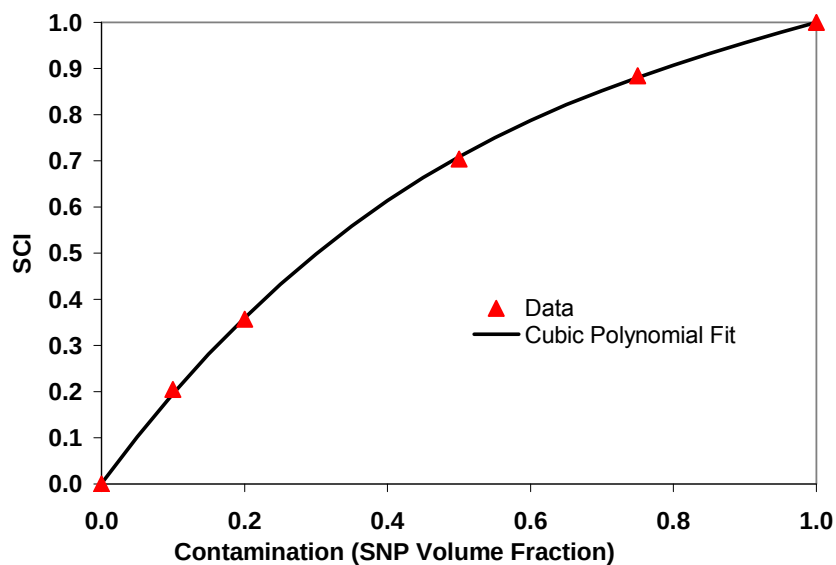


Figure 4.11: Selective contamination index and polynomial interpolation for mixtures of STNS crude oil and SNP base oil.

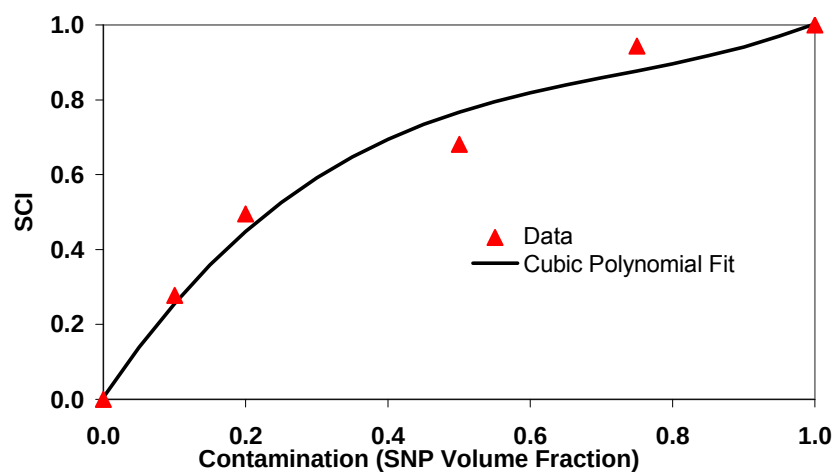


Figure 4.12: Selective contamination index and polynomial interpolation for mixtures of PBB crude oil and SNP base oil.

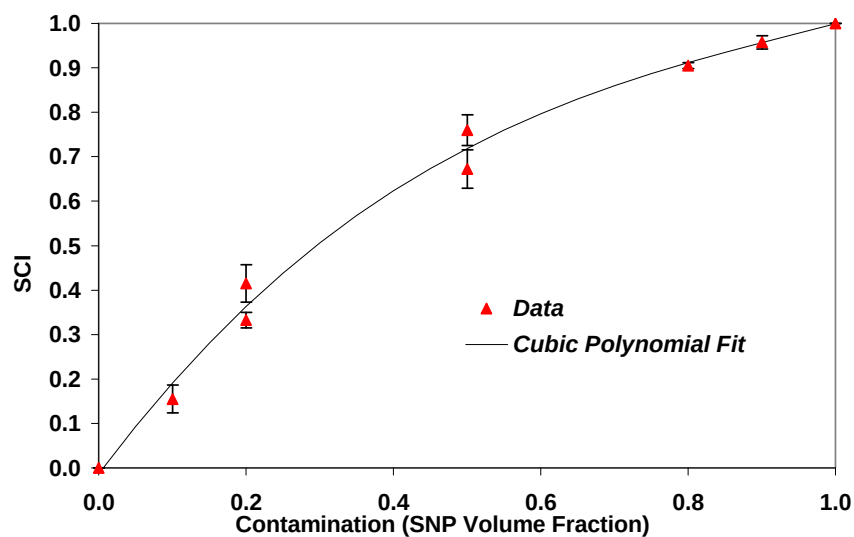


Figure 4.13: Selective contamination index and polynomial interpolation for repeated measurements of mixtures containing SMY crude oil and SNP base oil.

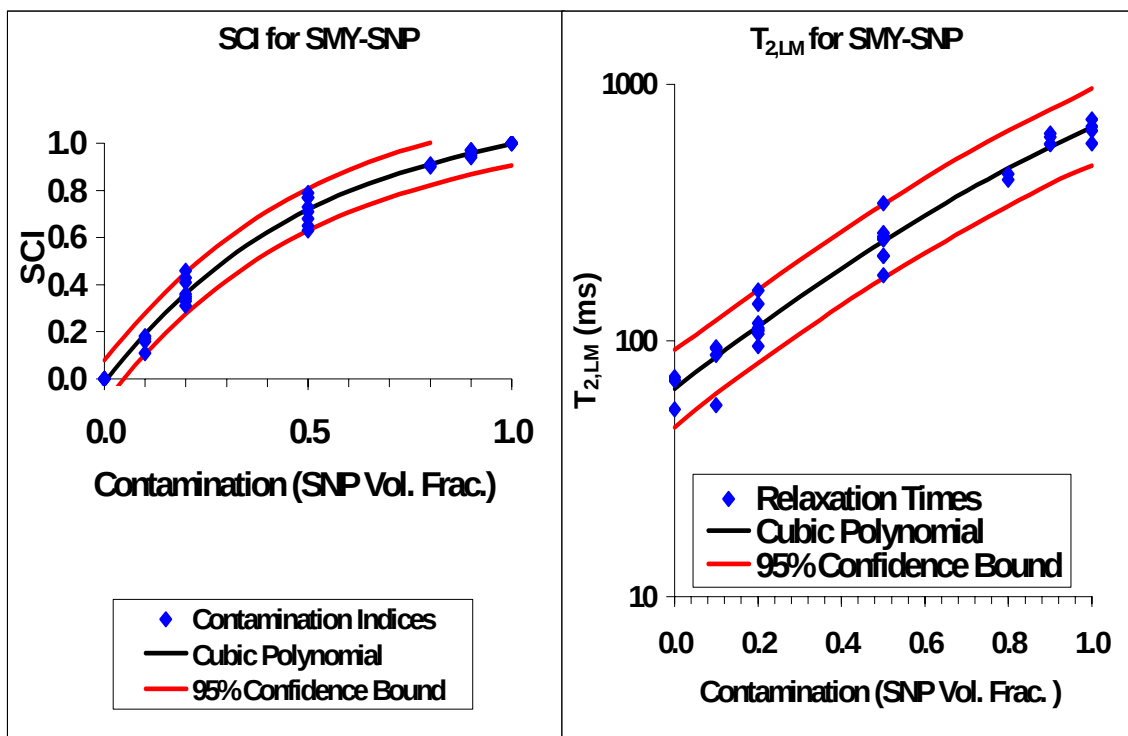


Figure 4.14: Selective contamination index and $T_{2,LM}$, each with polynomial interpolation and confidence intervals for repeated measurements of mixtures containing SMY crude oil and SNP base oil.

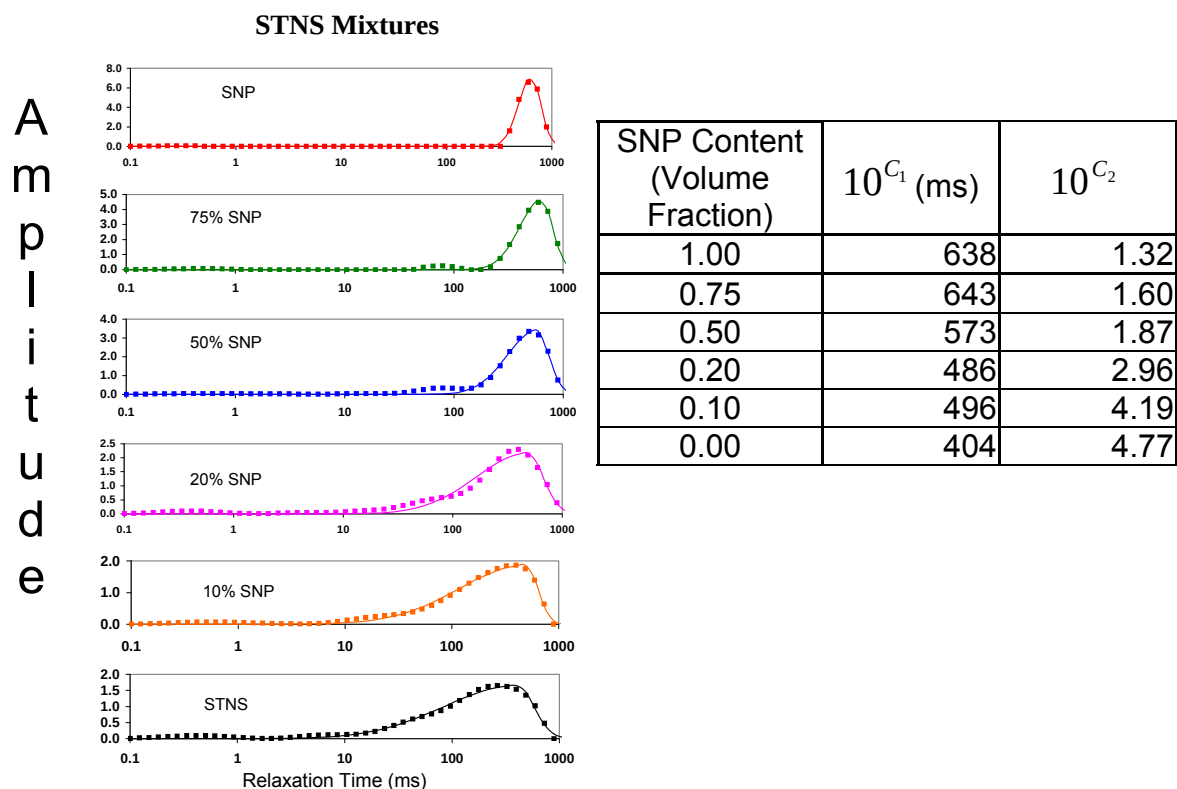


Figure 4.15: Stacked plots showing T_2 relaxation time distributions and the corresponding fit for mixtures of STNS crude oil and SNP base oil. Note that the amplitude axis is not to scale for all curves in the stack. Table shows the two fitting parameters that go into the DPI, C_1 (mode) and C_2 (short-time standard deviation factor).

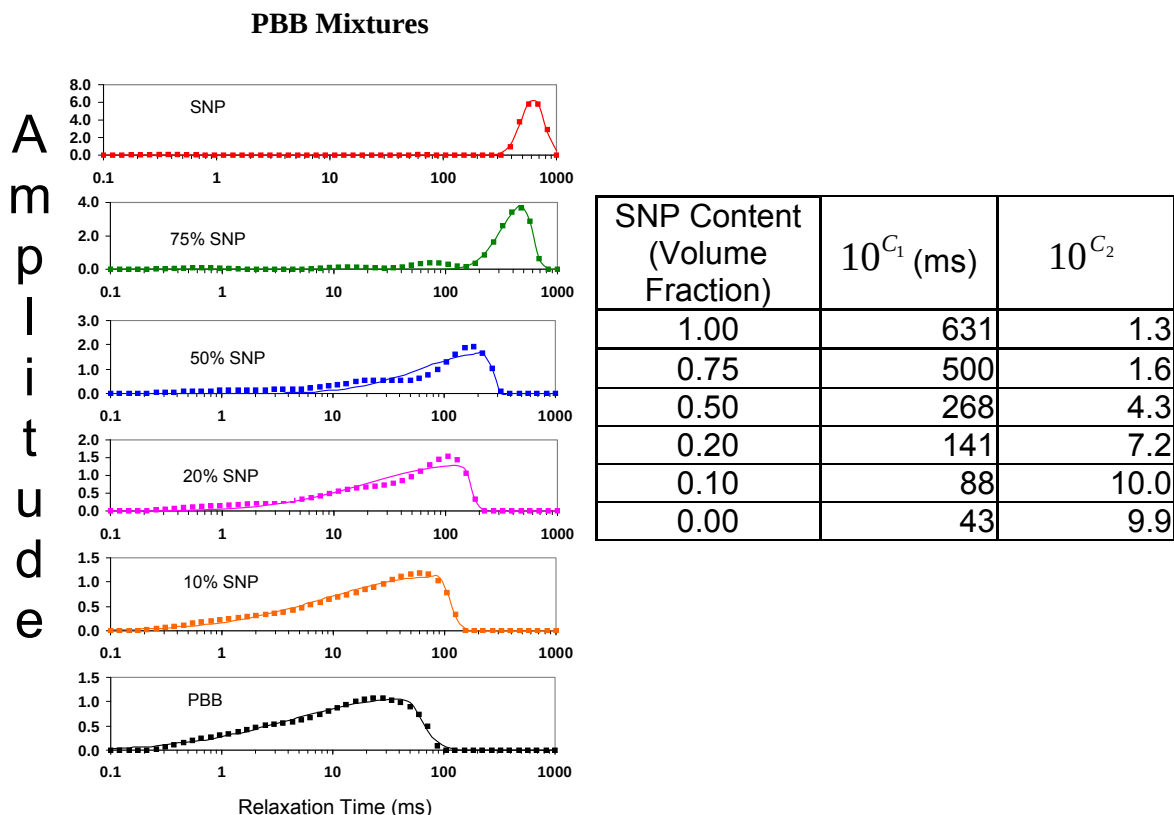


Figure 4.16: Stacked plots showing T_2 relaxation time distributions and the corresponding fit for mixtures of PBB crude oil and SNP base oil. Note that the amplitude axis is not to scale for all curves in the stack. Table shows the two fitting parameters that go into the DPI, C_1 (mode) and C_2 (short-time standard deviation factor).

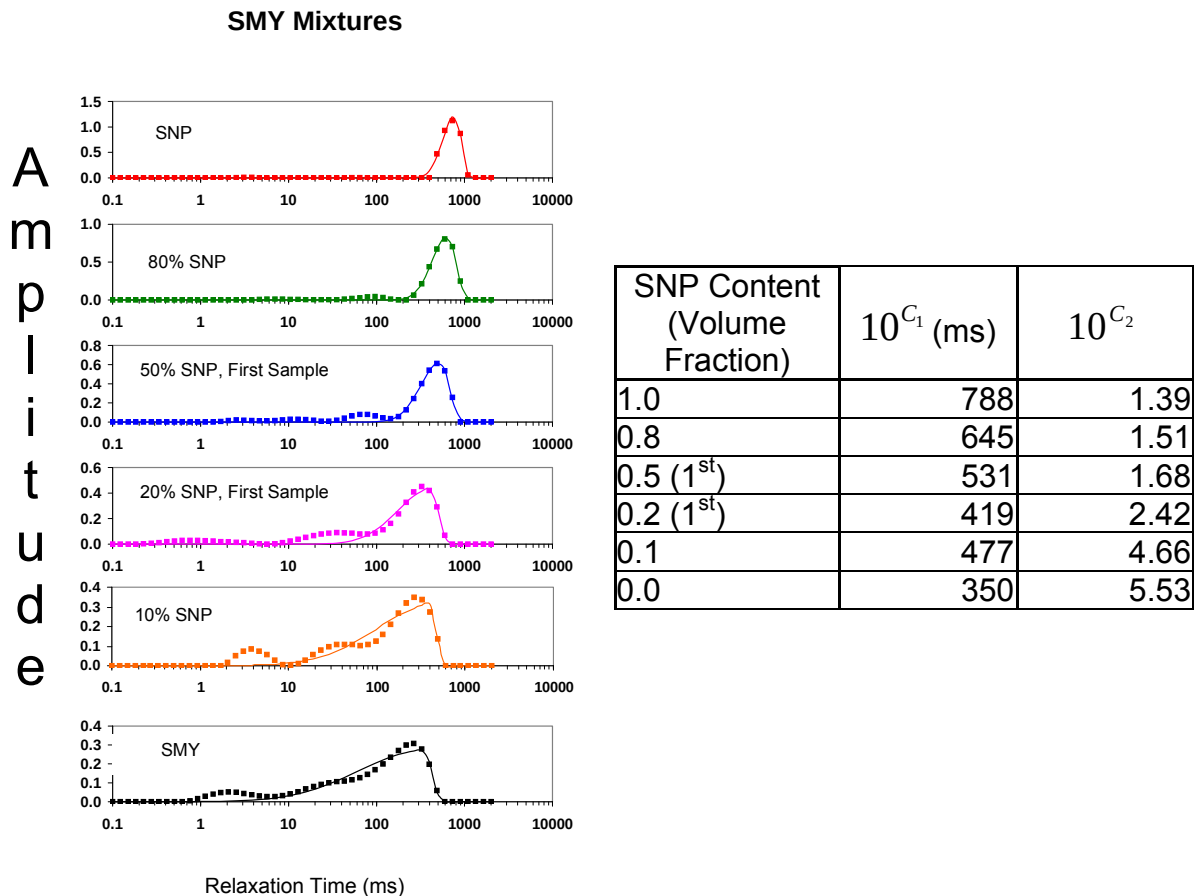


Figure 4.17: Stacked plots showing T_2 relaxation time distributions and corresponding fits for mixtures of SMY crude oil and SNP base oil (Run 1). The amplitude axis is not to scale for all curves in the stack. Table shows the two fitting parameters that go into the DPI, C_1 (mode) and C_2 (short-time standard deviation factor).

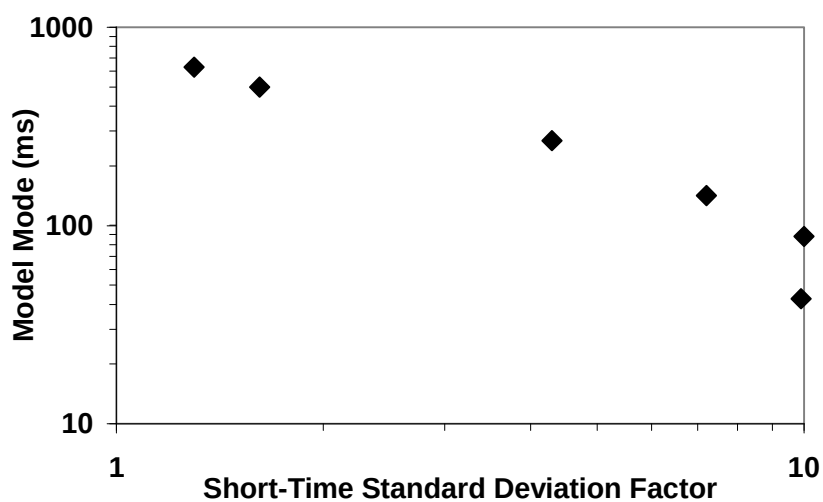


Figure 4.18: Cross-plot of two parameters of skewed Gaussian model for T_2 domain fits of mixtures of PBB crude oil and SNP base oil.

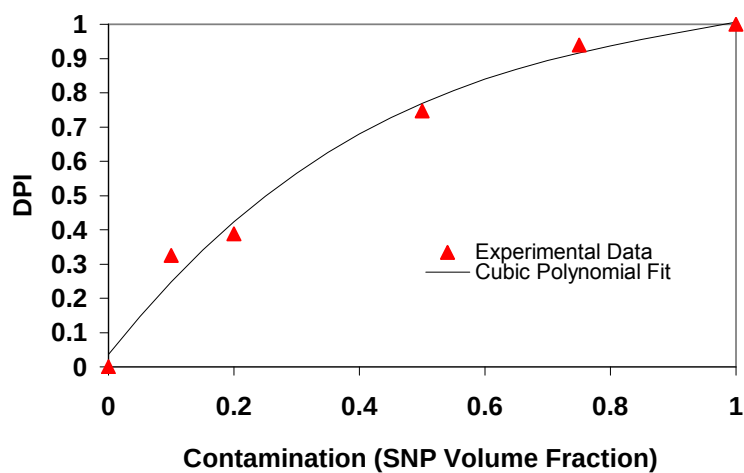


Figure 4.19: DPI obtained from model parameters and cubic polynomial fit for T_2 domain fits of mixtures of STNS crude oil and SNP base oil.

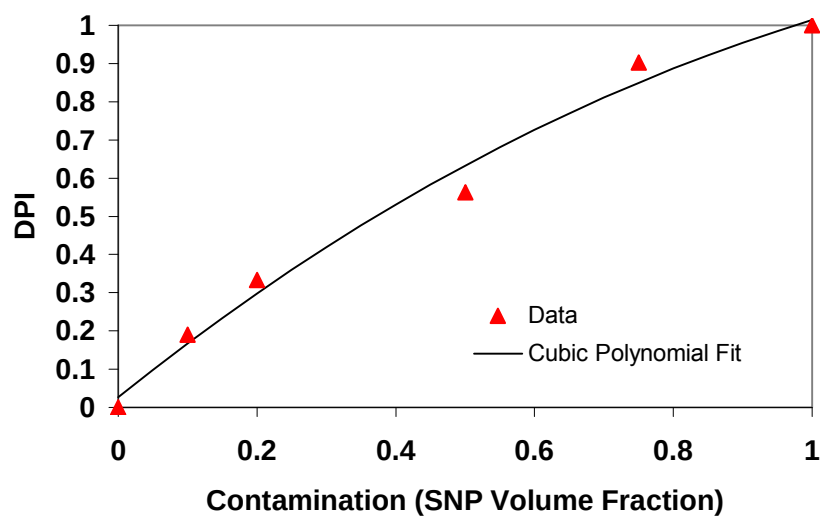


Figure 4.20: DPI obtained from model parameters and cubic polynomial fit for T_2 domain fits of mixtures of PBB crude oil and SNP base oil.

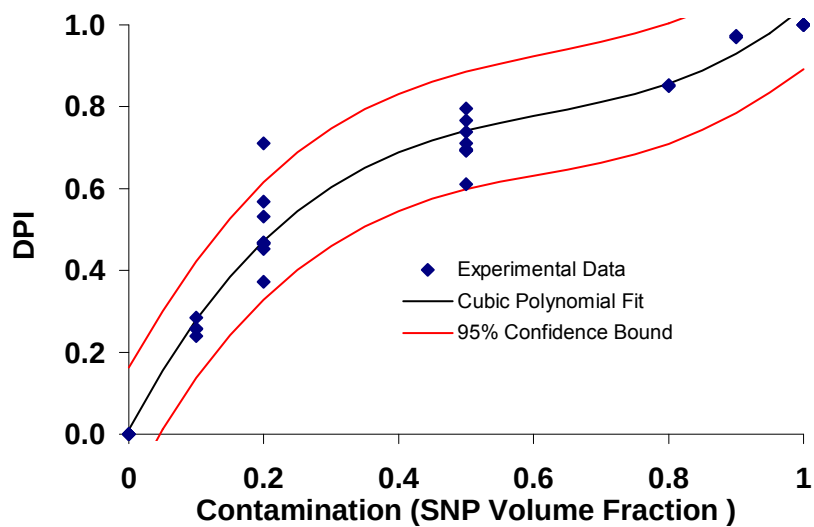


Figure 4.21: DPI data and fit with 95% confidence bounds for all runs of mixtures of SMY crude oil and SNP base oil.

Chapter 5: NMR Correlations for Base Oils and Cyclic Molecules

This chapter presents another area of petrophysical NMR research, namely the study of oil constituents that are not linear alkanes. These molecules deserve attention because crude oils exist as a mixture of many compounds, with functional groups other than linear alkanes represented in the mixture. If these components relax by different relaxation mechanisms than linear alkanes, then one would expect that correlations developed for linear alkanes would not be valid for these other molecules.

5.1 Motivation

This chapter details two cases whose study would help improve the NMR characterization of crude oils. The first case is base oils for drilling fluids (or simply base oils), and the second case is cyclic molecules. By studying components of potential mixtures encountered in the formation, the mixtures themselves may be better understood.

Base oils potentially contribute to the observed oil relaxation time distributions. This is because base oils from drilling fluids often contaminate native oils in the drilling process, as shown in the previous chapter. Whereas the focus of the previous chapter was contamination itself—that is, how the different properties of crude and base oils affect the expected signal from the crude oil when the two fluids mix—the focus here is on whether base oils exhibit a fundamentally different behavior than correlated for linear alkanes in

Equation 2.11. Each base oil contains molecules with particular functional groups, with olefins and ester base oils in common use.

In addition to base oils, examining the behavior of cyclic molecules also aids in clarifying the relaxation behavior of crude oils. These cyclic molecules may be either aliphatic or aromatic. The more constrained structure of these compounds subjects their protons to different interactions than for linear molecules, perhaps affecting the relaxation time. In particular, intermolecular dipole-dipole interactions or spin rotation interactions rather than intramolecular dipole-dipole interactions may be more important than for linear alkanes (Mitchell and Eisner 1960, Powles and Figgins 1966).

One study has appeared that considers the interpretation of the NMR response from base oils and specific non-alkane compounds (Chen, *et al.* 2004). There it was found that alkanes, alkenes, and esters follow one dead oil correlation, Equation 2.16, whereas cyclic and aromatic compounds do not. Some base oils considered in the work apparently obeyed Equation 2.16, whereas others did not. Additives were mentioned as a potential cause for the deviations that do occur (Chen, *et al.* 2004).

5.2 Experimental and Conditions for Literature Data

The base oils included are SF Base and Petrofree/LE Base, both provided by Baroid, a Halliburton company; Escaid 110, provided by Western Atlas; and NovaPlus (a product of Marshall & Ilsley Corporation) provided by Shell. SF Base and NovaPlus are 16- to 18-carbon internal olefin mixtures. Escaid 110

consists of light, hydrotreated petroleum distillates. Petrofree/LE Base is a mixture of 90% LE Base and 10% Petrofree. Petrofree is a fatty acid ester and LE Base consists of olefins.

For base oils, the relaxation times T_1 and T_2 were measured using MARAN-SS, which operates at 30 °C and 2 MHz. Only Escaid 110 was deoxygenated prior to measurement because it has longer relaxation times than the other base oils. Table 5.1 shows the experimental conditions for T_1 measurements, and Table 5.2 shows the conditions for T_2 measurements. Viscosities of the base oils were obtained using a Cannon-Fenske capillary viscometer for SF Base and Escaid 110. For NovaPlus and Petrofree/LE Base, data is obtained from K. Y. Song (private communication). The temperature for all obtained viscosities is 30 °C.

The cyclic molecules measured in this work are α -methylnaphthalene, tetralin, and decalin. The compound α -methylnaphthalene consists of two fused benzene rings and a pendant methyl group. Tetralin is also bicyclic, with one aromatic ring and one aliphatic ring. Decalin is similar to tetralin, with the distinguishing feature that the fused rings are both aliphatic. The relaxation times, T_1 and T_2 , are measured at 30 °C with MARAN-SS.

Experimental conditions for measurement with the bicyclic molecules above and with literature measurements of monocyclic molecules are now presented. The experimental conditions for the T_1 measurements are shown in Table 5.3, and T_2 experimental conditions are in Table 5.4. In addition to the measured compounds, T_1 data are obtained from the literature for four monocyclic

compounds: benzene, toluene, cyclohexane and cyclopentane. Table 5.5 shows the conditions used along with the sources for the data.

Viscosities for both monocyclic and bicyclic molecules are all obtained from the literature. For benzene, cyclopentane, cyclohexane, and decalin, empirical correlations from Viswanath and Natarajan, eds. (1989) were used. For toluene, data is taken from F.D. Rossini, *et al.*, eds. (1953). The exception to these statements is that viscosity data provided in Pendred, *et al.* (1966) is used for benzene and toluene measurements from that source. The other sources of relaxation time data do not provide information on viscosity. Viscosity for tetralin is obtained from Byers and Williams (1987). Finally, SUPERTRAPP (NIST 1999) is used for the viscosity of α -methylnaphthalene. The quality of the SUPERTRAPP results was checked with data from Byers and Williams (1987), which reports viscosity for α -methylnaphthalene at a slightly different temperature. All viscosities mentioned here are obtained at temperatures matching the temperatures of the corresponding relaxation time measurement, namely either 30 °C or the appropriate temperature in Table 5.5.

5.3 Results and Discussion

Table 5.6 shows the results of T_1 and T_2 measurements for the drilling fluid base oils studied. The viscosities obtained are also shown. As the data show, there is no significant difference between T_1 and T_2 , except for Escaid 110. This was the only sample deoxygenated, and it appears that the deoxygenation was more successful for the T_2 measurement than for T_1 . This leads to a T_2

value that is greater than the apparent T_1 . This suggests that the time scale of T_1 measurements is too long for a deoxygenated sample to retain its oxygen-free state. Hence although the correlation plot between relaxation time and η/T , Fig. 5.1, is only shown for T_1 relaxation time, the data for Escaid 110 is T_2 data. For the base oils here, the behavior seen matches that of linear alkanes, represented by the line in Fig. 5.1. This information is useful because it suggests that base oils cannot be differentiated from linear alkanes by a single relaxation time, such as $T_{2,LM}$. So, methods using relaxation time distributions, such as those of the last chapter are important to identify base oils using NMR.

Table 5.7 shows the T_1 and T_2 values, along with the viscosities of bicyclic compounds. Even more than for the drilling-fluid base oil data, the difference between T_1 and T_2 is negligible. The slightly greater value for T_2 as compared to T_1 in two of the measurements is an indication of the level of error in the data, because T_1 should not be less than T_2 .

Table 5.8 shows T_1 data and calculated viscosities for the monocyclic compounds from other workers. Unlike both the drilling fluid base oil data and bicyclic compound data measured in this work, these values are not logarithmic means. However, since the distributions are sharp for all samples measured, the different definitions of T_1 would give only slightly different values. For the data from the literature, several values are reported, the scatter of which is mostly an indication of the different conditions of measurement.

Fig. 5.2 shows all the data for cyclic molecules together. In this plot, α -methylnaphthalene is called 1-methylnaphthalene. The data for monocyclic

compounds show a clear deviation from the correlation line for alkanes. However, the bicyclic compounds fall on the correlation line for the linear alkanes. This may indicate that deviations are present only for lower-molecular weight cyclic molecules.

In order to discern a cause for the exceptional behavior of monocyclic molecules, the interproton distances of geminal hydrogen atoms for n-hexane, cyclohexane, and benzene are compared. The interproton distance is an important feature in intramolecular dipole-dipole interaction as seen in Equation 2.8 in Chapter 2. The interproton distances for n-hexane and cyclohexane appear to be indistinguishable. For n-hexane, using carbon-hydrogen bond lengths from one source (Bonham *et al.* 1959) yields an interproton distance of 1.83 Å. Using carbon-hydrogen bond lengths from the CRC Handbook (Lide, Ed. 2004), weighted appropriately for sp^3 -hybridized methyl and methylene carbon atoms, yields an interproton distance of 1.77 Å for n-hexane. In both cases, the bond angle was assumed as 110° , typical of a tetrahedral structure. For cyclohexane, using reported bond lengths and angles (Chiu *et al.* 1982), the calculated interproton distance is 1.80 Å. For benzene the reported interproton distance is 2.48 Å (Moniz, *et al.* 1963).

The significance of these interproton distances is as follows. According to Equation 2.8, the difference in interproton distance between aliphatic and aromatic molecules would be expected to yield a seven-fold increase in relaxation time for aromatics compared to aliphatics. The observed factor from Fig. 5.2, however, is only approximately three times that of aliphatics. Thus

reasons other than interproton distance alone contribute to relaxation in aromatic molecules. The spin-rotation mechanism has been suspected to contribute for benzene (Powles and Figgins, 1966), and could account for why the discrepancy in relaxation times between aliphatic and aromatic molecules is not as large as expected from interproton distances. Furthermore, bicyclic compounds could relax relatively faster than monocyclic compounds because by being larger molecules, intramolecular dipole-dipole interactions again overwhelm other mechanisms unlike with monocyclic compounds. On the other hand, because aliphatic cyclic molecules and n-alkanes have comparable interproton distances, the discrepancy in their relaxation times must be from other causes. A suitable cause for this is not known.

5.4 Conclusions

It has been found that the base oils studied here follow the linear alkane correlation in general, but monocyclic molecules do not. Bicyclic molecules appear to follow the correlation for linear alkanes. This work gives attention to classes of molecules other than alkanes that could potentially contribute to the observed NMR signal of oils. A database consisting of various molecules of a particular type serves to suggest trends, the incorporation of which may ultimately benefit the interpretation of NMR well logs.

Table 5.1: Acquisition Parameters for T_1 Measurements of Drilling Fluids Base Oils

Drilling Fluid Base Oil	Number of Data Points	Interval Spanned by Data Points (s)	Wait Time (s)	Number of Scans	Signal Acquisition Interval (μ s)
SF Base	20	0.1 – 3.0	4.0	16	8.0
Escaid 110	30	0.5 – 6.0	7.5	16	8.0
NovaPlus	20	0.1 – 3.0	6.0	16	8.0
Petrofree/LE Base	20	0.1 – 4.0	3.6	16	8.0

Table 5.2: Acquisition Parameters for T_2 Measurements of Drilling Fluids Base Oils

Drilling Fluid Base Oil	Echo Spacing (ms)	Number of Echoes	Wait Time (s)	Number of Scans
SF Base	0.50	5120	4.0	16
Escaid 110	0.40	8192	7.5	16
NovaPlus	0.40	6144	3.0	16
Petrofree/LE Base	0.40	7168	3.6	16

Table 5.3: Acquisition Parameters for T_1 Measurements of Bicyclic Molecules in this Work

Compound	Number of Data Points	Interval Spanned by Data Points (s)	Wait Time (s)	Number of Scans	Signal Acquisition Interval (μ s)
α -methylnaphthalene	20	0.1 – 5.0	7.5	16	8.0
Tetralin	20	0.1 – 7.0	7.0	16	8.0
Decalin	20	0.1 – 6.0	6.0	16	8.0

Table 5.4: Acquisition Parameters for T_2 Measurements of Bicyclic Molecules

Compound	Echo Spacing (ms)	Number of Echoes	Wait Time (s)	Number of Scans
α -methylnaphthalene	0.40	7168	7.5	32
Tetralin	0.32	13312	7.0	64
Decalin	0.32	11264	6.0	64

Table 5.5: Some Experimental Details for Monocyclic Compounds

Source	Larmor Frequency (MHz)	Temperature (°C)	Experimental Method	Compounds Measured
Pendred, <i>et al.</i>	30	25	Adiabatic rapid passage (a.r.p.)	benzene toluene cyclohexane cyclopentane
Moniz, <i>et al.</i>	Not stated	25 (toluene) 27 (cyclopentane) 20 (cyclohexane)	Not stated	toluene cyclohexane cyclopentane
Nederbragdt and Reilly	40	25	Saturation recovery; a.r.p.	benzene toluene
Homer, <i>et al.</i>	Not stated	36	a.r.p.	benzene toluene

Table 5.6: Relaxation Times and Viscosities for Drilling Fluid Base Oils

Drilling Fluid Base Oil	T_1 (ms)	T_2 (ms)	Viscosity (cp)
SF Base	670	642	2.75
Escaid 110*	993	1400	1.49
NovaPlus	670	653	2.80
Petrofree/LE Base	784	764	2.04

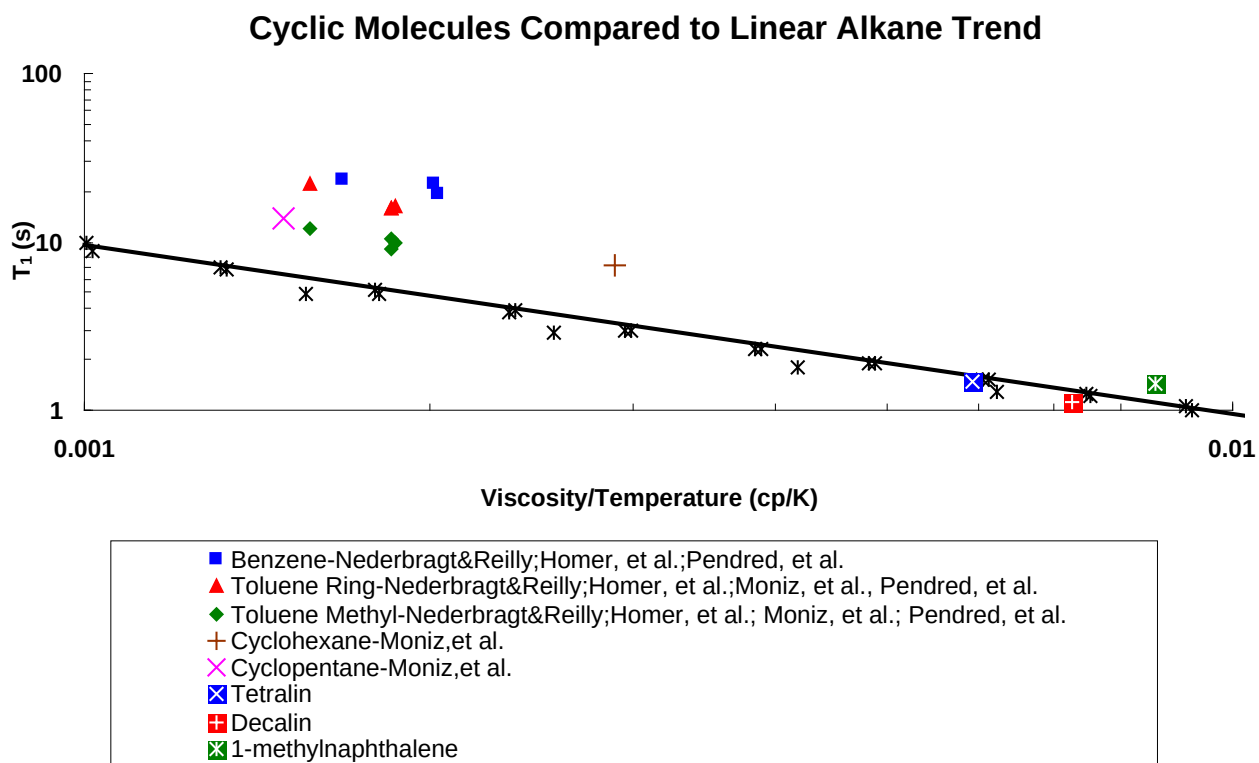
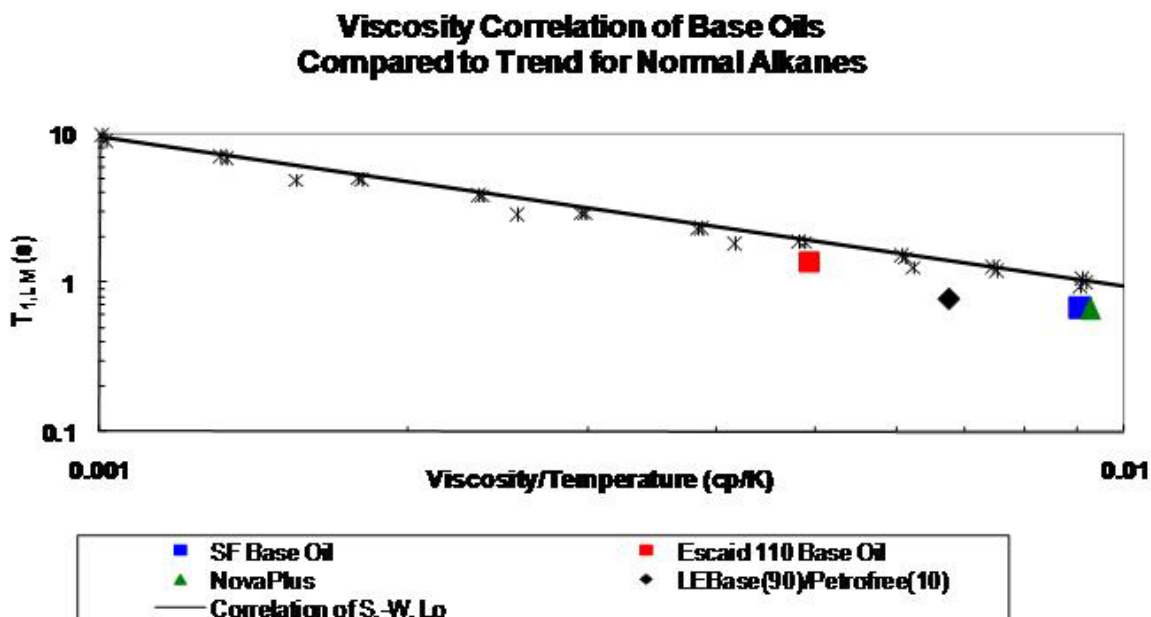
*Deoxygenated

Table 5.7: Relaxation Times and Viscosities for Bicyclic Compounds

Compound	Temperature (°C)	T_1 (s)	T_2 (s)	Viscosity (cp)
α -methylnaphthalene	30	1.43	1.44	2.6
Tetralin	30	1.47	1.41	1.9
Decalin	30	1.13	1.16	2.2

Table 5.8: T_1 Relaxation Times and Viscosities for Monocyclic Compounds

Compound	Temperature (°C)	T_1 (s)	Viscosity (cp)	T_1 Source
Benzene	25	19	0.606	Nederbragt & Reilly
Benzene	36	24	0.519	Homer, <i>et al.</i>
Benzene	25	22	0.600	Pendred, <i>et al.</i>
Toluene—Ring	25	16	0.552	Nederbragt & Reilly
Toluene—Ring	36	22	0.486	Homer, <i>et al.</i>
Toluene—Ring	25	16	0.556	Pendred, <i>et al.</i>
Toluene—Ring	25	16	0.552	Moniz, <i>et al.</i>
Toluene—Methyl	25	9	0.552	Nederbragt & Reilly
Toluene—Methyl	36	12	0.486	Homer, <i>et al.</i>
Toluene—Methyl	25	10	0.556	Pendred, <i>et al.</i>
Toluene—Methyl	25	10	0.552	Moniz, <i>et al.</i>
Cyclohexane	20	7	0.867	Moniz, <i>et al.</i>
Cyclopentane	27	14	0.437	Moniz, <i>et al.</i>



Chapter 6: Natural Gas Mixtures

This chapter shows NMR properties of natural gas components and their mixtures. The samples measured are pure methane, pure ethane, and two mixtures of methane and ethane. A modified procedure required to obtain relaxation times (T_1 and T_2) from natural gases is illustrated with data for methane, with an explanation of the subsequent benefit. Application of the mixture data to verify a mixing rule also appears. The mixing rule is based on the kinetic model of spin rotation mentioned in Chapter 3.

6.1 Introduction

This section provides additional background for the work presented in this chapter. Motivation is provided for the value of measuring NMR relaxation times (T_1 and T_2). To relate the measurements with mixing rule calculations, some theoretical considerations are reintroduced from Chapter 2, with focus on applicability to measurements shown below.

NMR properties of methane have been studied, both in the laboratory setting (Gerritsma *et al.* 1971, Lo 1999, Dawson 1966, Oosting and Trappeniers 1971, Harris 1978), and in natural gas reservoirs (Prammer *et al.* 1995, Akkurt *et al.* 1996). For the purposes of reservoir evaluation, it has been previously assumed that the presence of non-methane components can be accounted for simply by the gas density (Akkurt *et al.* 1996). However as Fig. 6.1 shows, different gases show different NMR behavior (T_1 relaxation time in Fig. 6.1) for

the same normalized density (Zhang 2002). Thus, non-methane components of natural gas require distinct treatment.

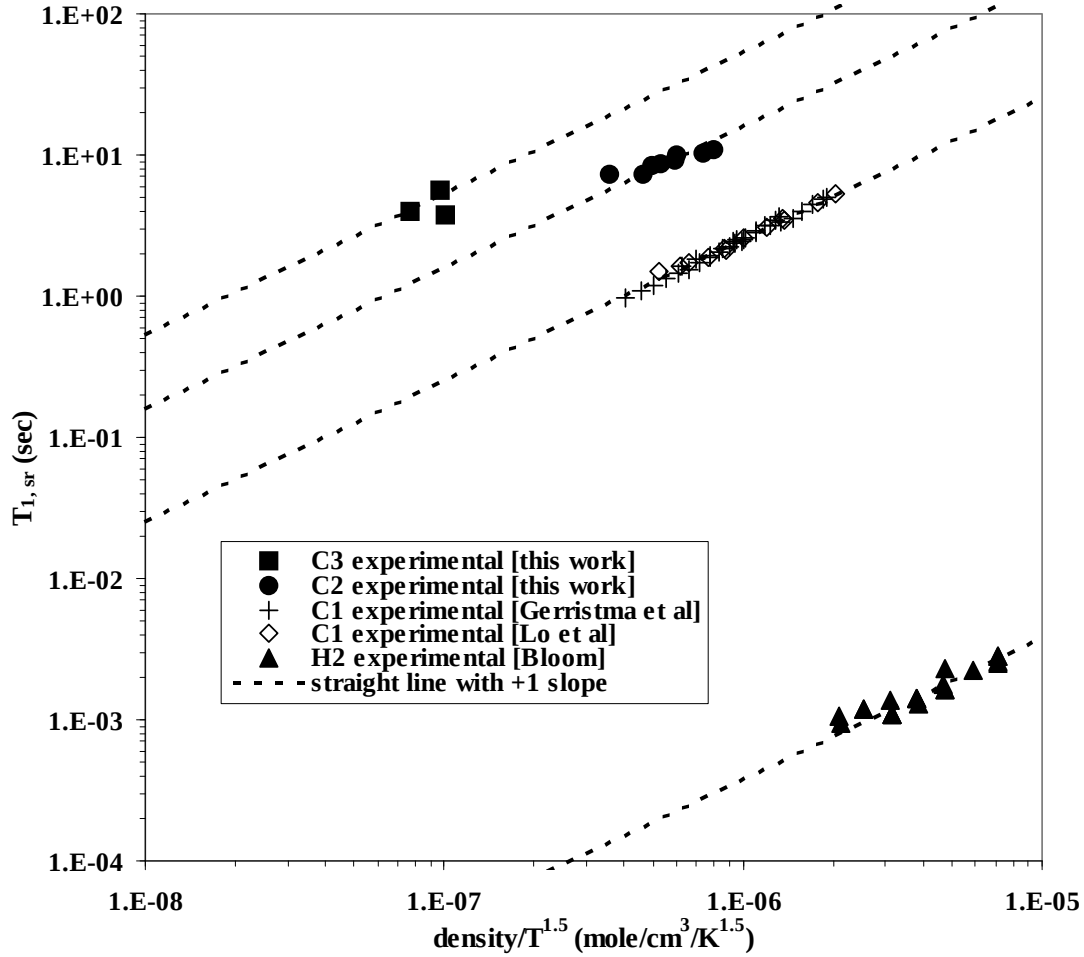


Figure 6.1: Relaxation behavior of various pure gases as a function of density and temperature. Reproduced from Zhang (2002).

Based on the kinetic model of spin rotation, discussed in Section 2.3.5 in Chapter 2, Zhang (2002) presents a model for relaxation of gas mixtures based on the relaxation behavior of each gas in the mixture. The resulting expression is

$$T_{1,i} = \sum_{j=1}^n \rho_j \frac{\hbar^2 N_A}{4\pi^2 I_{\perp i} C_{\text{eff},i}^2} \sqrt{\frac{2}{\pi k}} \frac{\sigma_{i-j}}{\sqrt{T \mu_{i-j}}}, \quad (6.1)$$

which is identically Equation 2.28. $T_{1,i}$ is the T_1 relaxation time of the i^{th} component in the mixture, ρ_j is the partial molar density of the j -th component of the mixture, and T is the temperature; the meaning of the remaining variables in Eq. 6.1 are given in Chapter 2.

The model in Eq. 6.1 was then verified by comparison with data by Rajan, *et al.* (1975) for up to approximately 100 psia of pressure for two methane mixtures, one with carbon dioxide and one with nitrogen (Zhang 2002). The data are shown in Fig. 6.2 for methane-carbon dioxide mixtures and Fig. 6.3 for methane-nitrogen mixtures. Note that the axes in Figs. 6.2 and 6.3 are slightly different from Fig. 6.1 in that T_1 is normalized by density on the ordinate, which is plotted against simply temperature (T) rather than a ratio of density and $T^{1.5}$. Zhang (2002) calculated T_1 for the conditions in Rajan, *et al.* (1975), and Figs. 6.2 and 6.3 show that the model and data match well.

Though the spin-rotation model in Eq. 6.1 is valid for low-pressure methane-carbon dioxide and methane-nitrogen mixtures, a more complete validation requires treatment of mixtures with other natural gas components and at higher pressures. The work shown here includes both these characteristics by providing experimental data for gas mixtures of methane with ethane at pressures up to 2600 psia. One can then validate the mixing rule for this measured data, the process for which will be described presently.

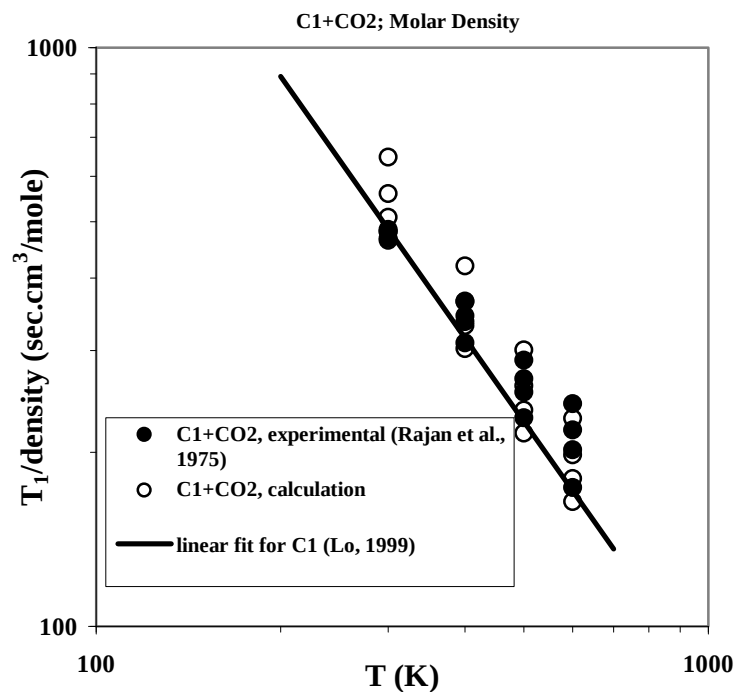


Figure 6.2: For CH₄-CO₂ mixtures, demonstration of agreement between mixing rule calculation and experimental data. Reproduced from Zhang (2002).

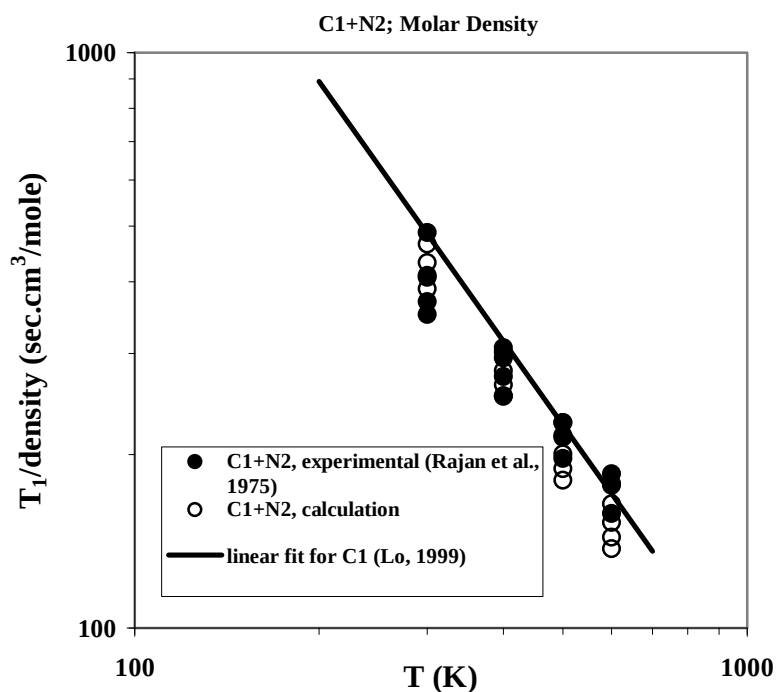


Figure 6.3: For CH₄-N₂ mixtures, demonstration of agreement between mixing rule calculation and experimental data. Reproduced from Zhang (2002).

To compare measurements to the mixing rule, the form of Eq. 6.1 requires a slight modification. In practice, this is achieved by a simplified version of Eq. 6.1 (Zhang 2002),

$$T_{1,i} = \sum_{j=1}^n \rho_j \frac{G_{ij}}{T^{1.5}} \quad (6.2)$$

where G_{ij} is a binary interaction term that collects the constants in Eq. 6.1. Zhang (2002) determined values for G_{ij} for gas mixture components, which are shown in Table 6.1. Another aspect of Eq. 6.2 is that it keeps the temperature dependence explicit, incorporating the temperature dependence of σ_{i-j} , the binary collision parameter, from Eq. 6.1.

Table 6.1: Values of the coefficients G_{ij} ($\text{sec} \cdot \text{K}^{1.5} \cdot \text{cm}^3 \cdot \text{mole}^{-1}$) for proton relaxation in the gas mixture of CH_4 , C_2H_6 , C_3H_8 , CO_2 , and N_2 . Adapted from Zhang (2002)

$j \rightarrow$	CH_4	C_2H_6	C_3H_8	CO_2	N_2
$I \downarrow$					
CH_4	2.41×10^6	3.77×10^6	4.06×10^6	3.55×10^6	1.90×10^6
C_2H_6	1.06×10^7	1.58×10^7	1.66×10^7	1.45×10^7	8.02×10^6
C_3H_8	3.09×10^7	4.47×10^7	4.60×10^7	2.84×10^7	2.28×10^7
CO_2	0	0		0	0
N_2	0			0	0

The values in Table 6.1 and the expression in Eq. 6.2 are used to calculate the relaxation behavior of a few specified natural gas mixtures. Fig. 6.4 shows the expected relaxation response of a few methane-ethane mixtures,

compared to the behavior correlated for the individual gases. Fig. 6.5 shows the calculated response for a methane-ethane-propane mixture, as an indication of the expected behavior in the presence of a third component.

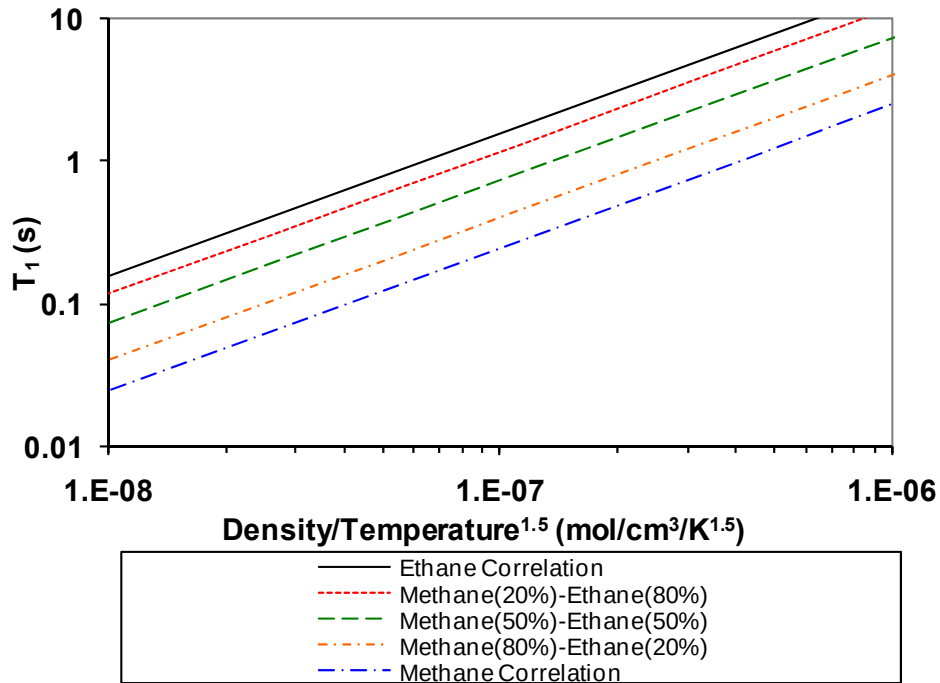


Figure 6.4: Calculated relaxation behavior of methane-ethane mixtures with relation to prior correlations for methane and ethane

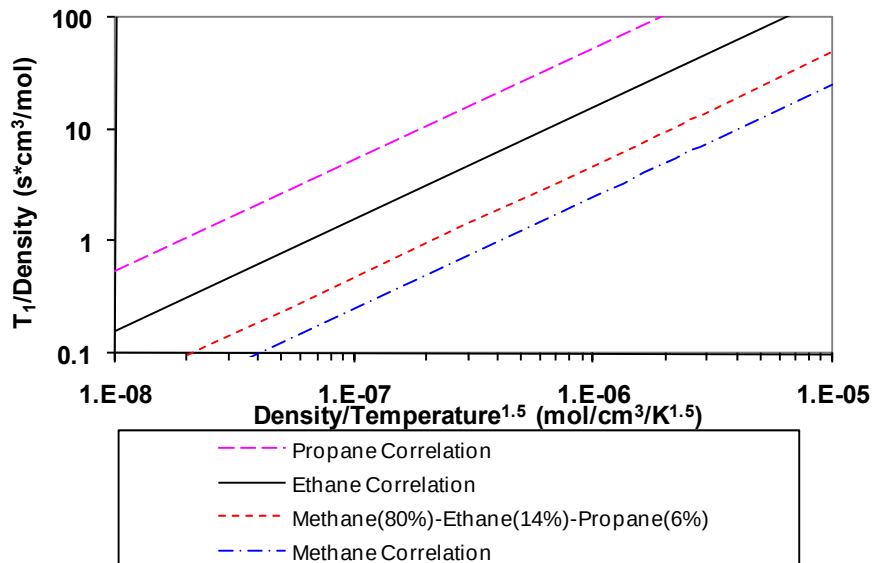


Figure 6.5: Calculated relaxation behavior of a methane-ethane-propane mixture with relation to prior correlations for methane, ethane, and propane

6.2 Equipment and Capabilities

This section discusses the apparatus in the operation of NMR measurements at elevated pressures. The manifold and its peripheral components are described, and the pressure vessel is described in some detail. The section concludes with tests to verify the functionality of the complete system.

The manifold is the central component of the NMR high pressure system. It is built from stainless steel fittings, manufactured by Swagelok. A schematic of the manifold and its ports, which form the NMR high pressure system, is shown in Fig. 6.6. (A similar diagram already appeared in Chapter 3.) The manifold is mounted on a wall near MARAN-SS, and is rated to a pressure of 5000 psi.

Through the manifold, the high pressure system consists of various components which can influence experimental conditions. First, gas cylinders with appropriate gas or gas mixture are connected to the inlet side of the apparatus. The inlet line is equipped with an oxygen scavenger (Matheson model 6411) to remove traces of oxygen from the contents of the gas cylinder. The oxygen scavenger is rated for a maximum pressure differential of 90 psi between inlet and outlet. Second, the manifold is equipped with a vacuum line. This is used to evacuate the system prior to injection of gases at elevated pressure. The line is connected to a mechanical vacuum pump, with a trap, cooled by dry ice (freezing point of -78.5 °C) in isopropanol. Furthermore, to prevent accidental exposure of the vacuum line to high pressure, the vacuum line is double-valved. The third feature is the two lines to two hand pressure

generation pumps (hand pumps), models 87-6-5 and 62-6-10 manufactured by High Pressure Equipment Company. These hand pumps can be used to increase the system pressure beyond tank pressure by compressing the system volume. This can also be done with a Ruska positive displacement pump in between the gas cylinder and the oxygen scavenger. The fourth feature of the high pressure NMR system is the pressure gauges that allow monitoring of pressure during NMR measurements. One gauge is a pressure transducer manufactured by Sensometrics, Inc. coupled to the manifold using an adapter and connected to a digital readout meter. Both the adapter and meter (model DP41-S) are made by Omega.

The system is also equipped with a few safety features. The entire system outlets to a vent to safely remove gases after measurements are complete. Another safety feature is the relief lines in the system. A check valve in the relief line for the vacuum portion protects the vacuum side from overpressurization; the check valve opens to the vent line should any positive pressure occur in the vacuum line. The relief line of the high-pressure portion of the manifold also discharges into the vent. However in this case, relief is provided by a diaphragm-type blowout valve manufactured by Autoclave Engineers, where the diaphragm is designed to yield at pressures greater than 5000 psi.

A photograph of the NMR high pressure system is shown in Fig. 6.7. The system is rated to 5000 psi pressure, except the vacuum line (designed for running at subatmospheric pressure) and the inlet line, where the gas cylinder is

rated to at least the initial cylinder pressure and the oxygen scavenger is rated to 3000 psi. On the right side of Fig. 6.7 is the NMR pressure vessel, encased by its holder on the table. A detailed description of the pressure vessel follows.

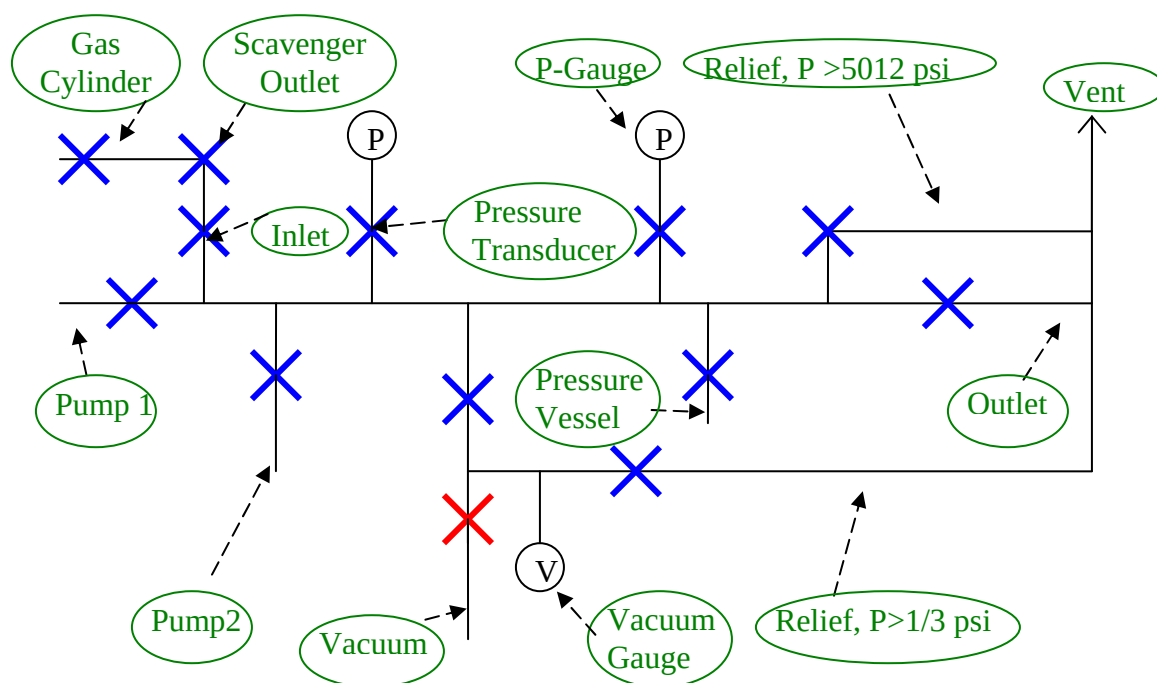


Figure 6.6: Schematic of manifold and attachments for preparing gases for NMR analysis

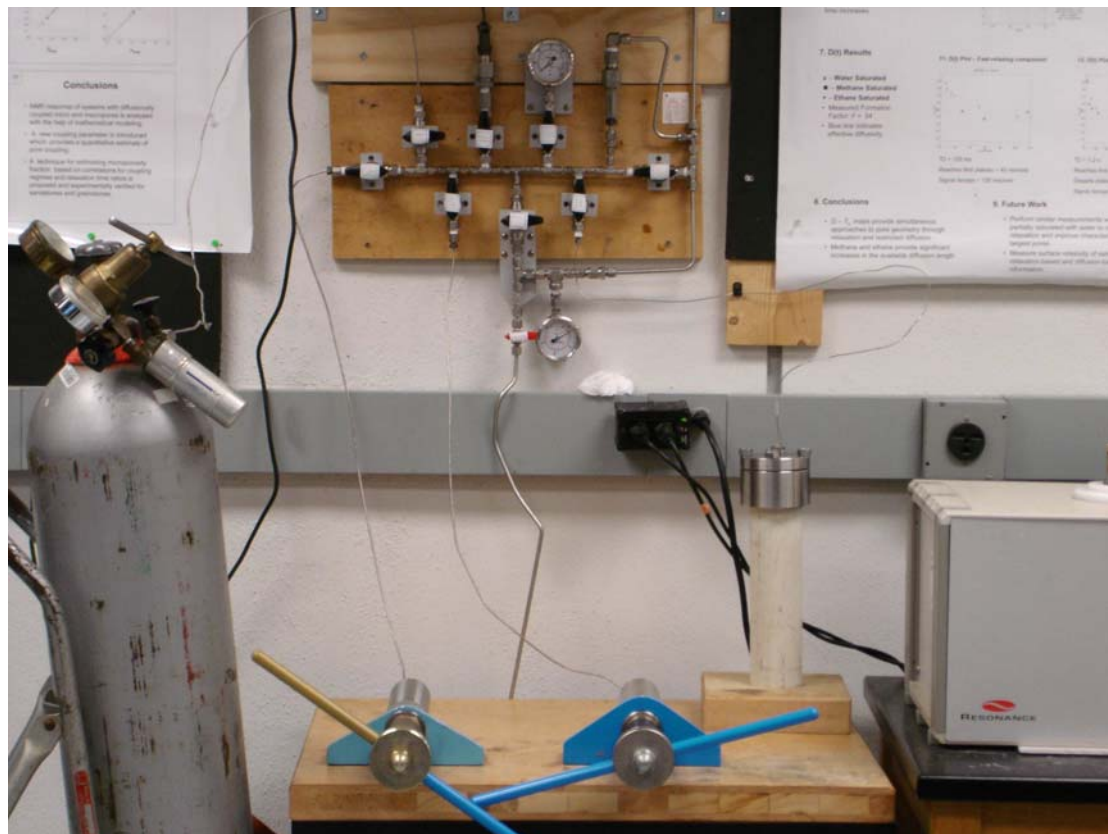


Figure 6.7: Photograph of high pressure NMR system, including gas cylinder, hand pumps, and NMR pressure vessel.

The NMR pressure vessel is the component of the high pressure NMR system that is placed in the MARAN 2 MHz instrument to make NMR measurements. A diagram of the design of the NMR pressure vessel is shown in Fig. 6.8. As shown, the pressure vessel has three layers. The outermost layer is the pressure-bearing surface, made of fiberglass in an epoxy matrix. The middle layer seals the system and connects it to the manifold. The top of this portion of the NMR pressure vessel is a stainless steel flange. The flange has ports at the top which connect to a line from the manifold and o-rings that contact the inside of the PEEK liner. The PEEK liner is the body of the NMR pressure vessel, as

the inner layer is contained inside it. The middle layer is sealed at the bottom with a stainless steel end piece capped with an o-ring. The inner layer consists of two PEEK cylinders, one that allows gas to pass along a small orifice along its axis and the other serving as a sample chamber (which is aligned in the magnetic field of the MARAN 2 MHz instrument) with a hollow region of approximately 12.9 ml where the measured gas resides. The NMR pressure vessel, like the manifold is rated to 5000 psi.

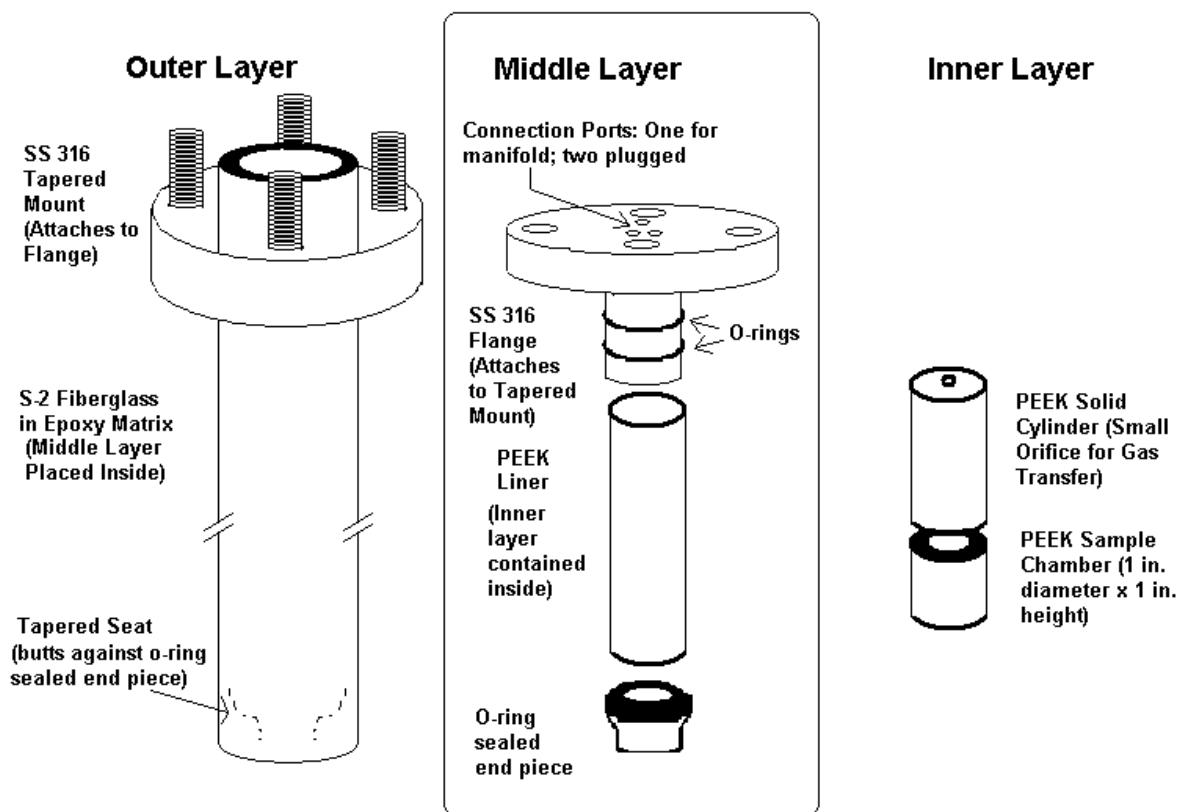


Figure 6.8: Drawing of Temco ® NMR pressure vessel

Prior to use, the manifold and pressure vessel were tested under pressure. First, the NMR high pressure system was tested with water in the

system. Pressures up to 5000 psig were achieved. The high-pressure relief line was found to operate correctly during this test because the diaphragm failed (as designed) at slightly beyond 5000 psig. The manifold, without the NMR pressure vessel, was found to maintain pressure when tested under pressure at 4500 psig. However, when the NMR pressure vessel is incorporated, a slow decrease in pressure of approximately 10 psi/hr was being observed at pressures near 2000 psia. The magnitude of the pressure loss was deemed to be acceptable for measurements to proceed. This assessment can be made by calculating the effect of variations in pressure (for the experimental pressure loss) on NMR measurements. When this calculation was made, the difference in NMR relaxation times is found to be 2% or less.

6.3 Elevated Pressure NMR Measurements with Methane

Using the high pressure NMR apparatus shown in Figs. 6.6-6.8, NMR measurements on methane gas have been performed to determine T_1 and T_2 . Data for methane are available in the literature, and the methane measurements performed here serve as a comparison. Relaxation time measurements obtained in this work fall within approximately 10% of the expected value, but show a bias toward short relaxation times.

The methane relaxation data obtained behaves as shown in Fig. 6.9, which is the time domain response of a typical CPMG measurement in semi-log scale. Two important aspects of the response in Fig. 6.9 are the early-time dip and the deviation from single-exponential response. The early-time dip refers to

a sharp reduction that occurs at short times in the observed T_2 response as seen in Fig. 6.9. The deviation from single-exponential response, which also occurs at early times, means that data does not match the later-time single exponential fit shown as a straight line in Fig. 6.9. This propensity for deviance of early time data is also present in the T_1 response, but is not readily visible in the corresponding time-domain data and so is not shown. To address these features, the following paragraph presents a variation on determining T_1 and T_2 from that shown in Chapter 3.

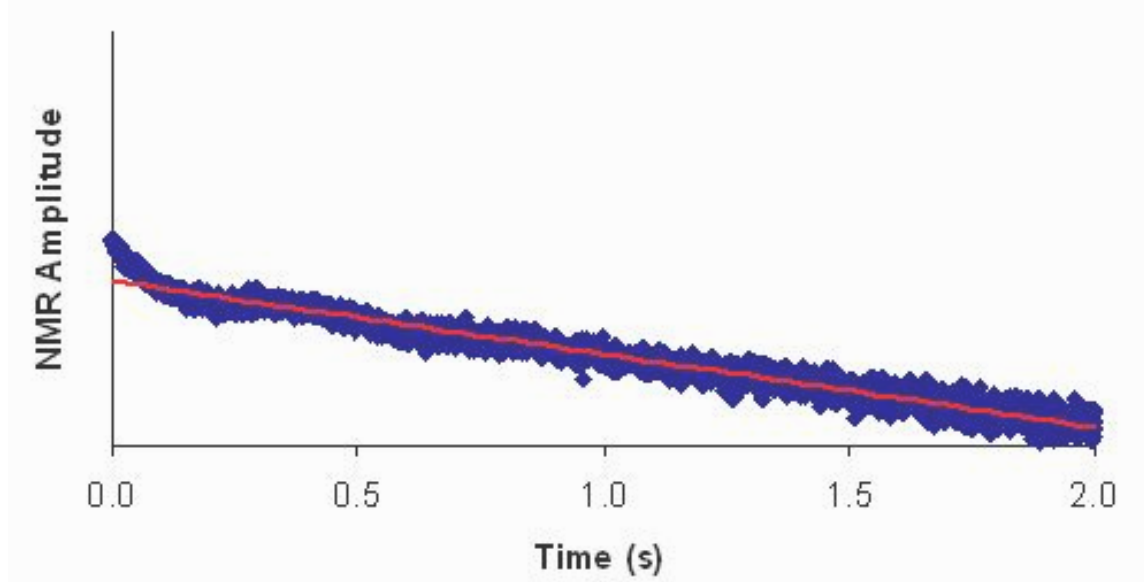


Figure 6.9: Typical T_2 measurement for methane at elevated pressures in semi-log scale, illustrating faster decay at early times

The variation in analyzing the relaxation times for methane essentially means the early time data was edited. The editing was done either in the time domain or relaxation time domain (also called relaxation domain below). For time domain editing, the early-time data corresponding to the observed anomaly

was removed before fitting the data to a straight line in semilog scale. An example is shown in Fig. 6.10, where the truncated data is shown in gray and utilized data is in blue with the red line representing a single-exponential fit. For relaxation domain editing, all the data is first inverted. Then the logarithmic mean of the peak observed for large relaxation times is retained, removing contributions from artifacts at shorter relaxation times. Fig. 6.11 shows an example T_2 distribution, where the utilized data are red points joined by a blue line. The rest of the distribution is not used for determining relaxation time, and is in gray. Note how the calculated logarithmic mean changes when all data is used (gray vertical line) compared to when only the single peak highlighted in Fig. 6.11 is used (red vertical line). The latter relaxation time is significantly longer. Since relaxation times edited in both time and relaxation time domains use only longer-time data, they will be demarcated with a suffix, “long”.

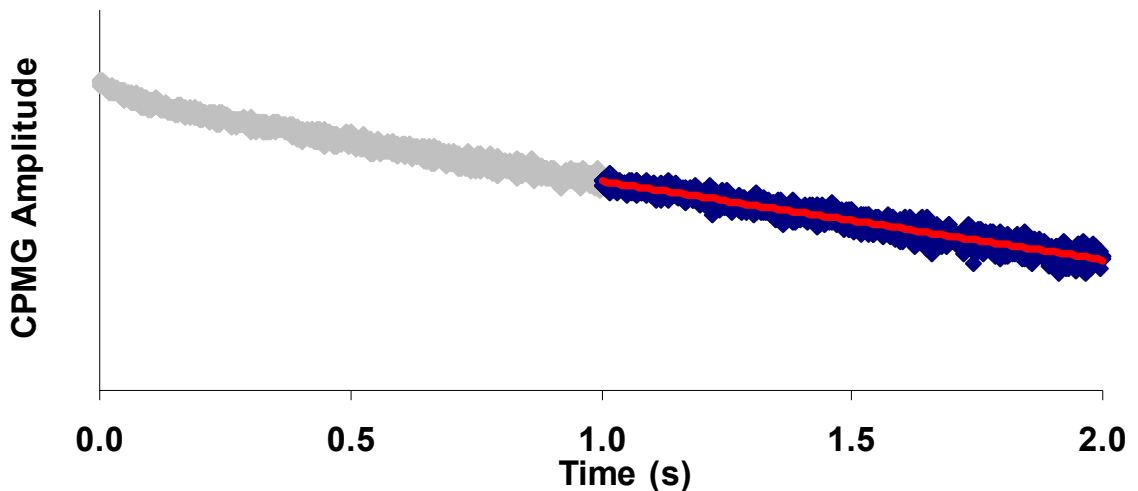


Figure 6.10: *Editing in time domain for a CPMG response demonstrating data truncation and relaxation time determination from later times*

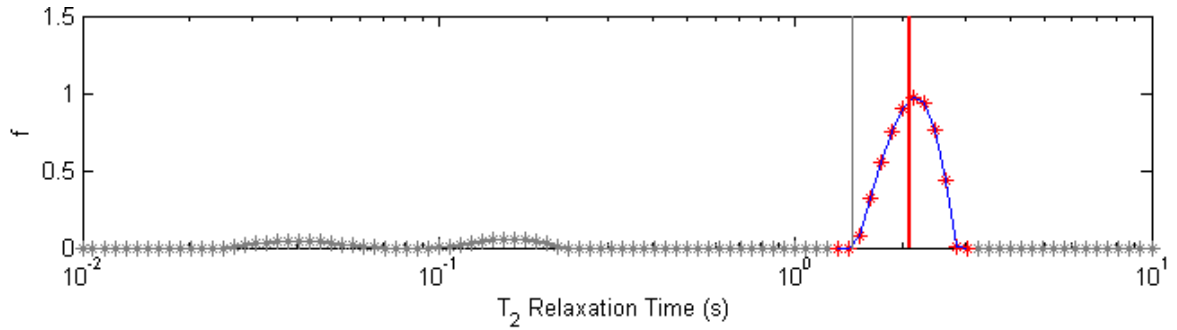


Figure 6.11: *Editing in relaxation domain for an example T_2 distribution showing data truncation and relaxation time determination from longer relaxation times*

Methane T_1 and T_2 results for pressures of approximately 1980 psig are shown in Figs. 6.12-6.13 (for T_1) and Figs. 6.14-6.15 (for T_2). Figs. 6.12 and 6.14 show results for time domain editing, whereas Figs. 6.13 and 6.15 are for relaxation domain editing. Figs. 6.12-6.15 show two correlations for T_1 (Lo 1999, Prammer, et al. 1995, respectively), which should be valid for T_2 as well:

$$T_1 (s) = 1.57 \times 10^5 \frac{\rho}{T^{1.5}} \quad (6.3)$$

$$T_1 (s) = 2.5 \times 10^4 \frac{\rho}{T^{1.17}} \quad (6.4)$$

In these equations, ρ is the density (g/cm^3) and T is the temperature in Kelvin. For T_2 , the quality of the results from time domain editing (Fig. 6.14) and results from relaxation domain editing (Fig. 6.15) is comparable; for T_1 , the results from relaxation domain editing (Fig. 6.13) is more precise than results from time domain editing (Fig. 6.12). Therefore, subsequent figures will focus on relaxation domain data. For Figs. 6.12-6.15 however, the relaxation times shown are near expected values, but are consistently below the correlation lines.

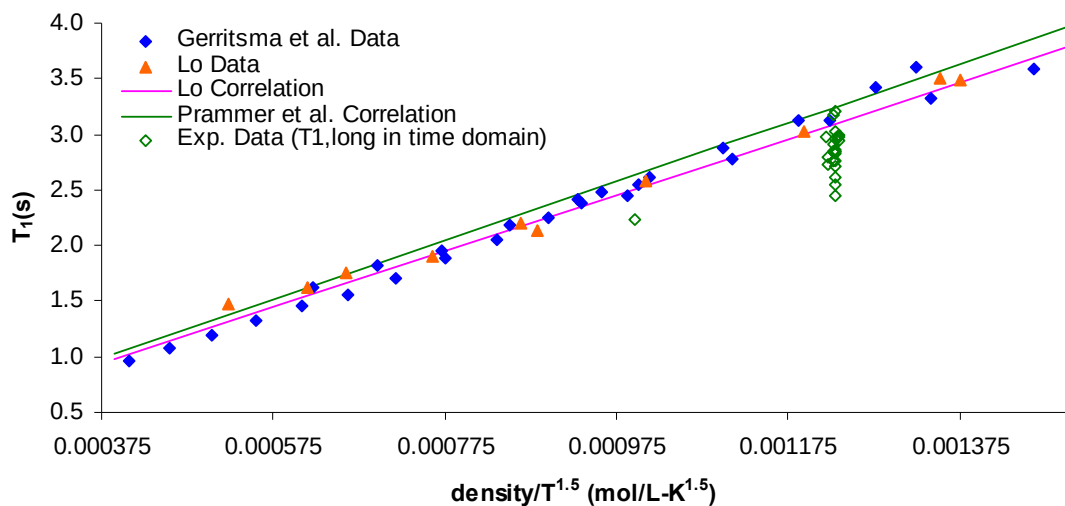


Figure 6.12: NMR T_1 measurements (time domain editing) at $P \sim 1980$ psig compared with literature data and correlations

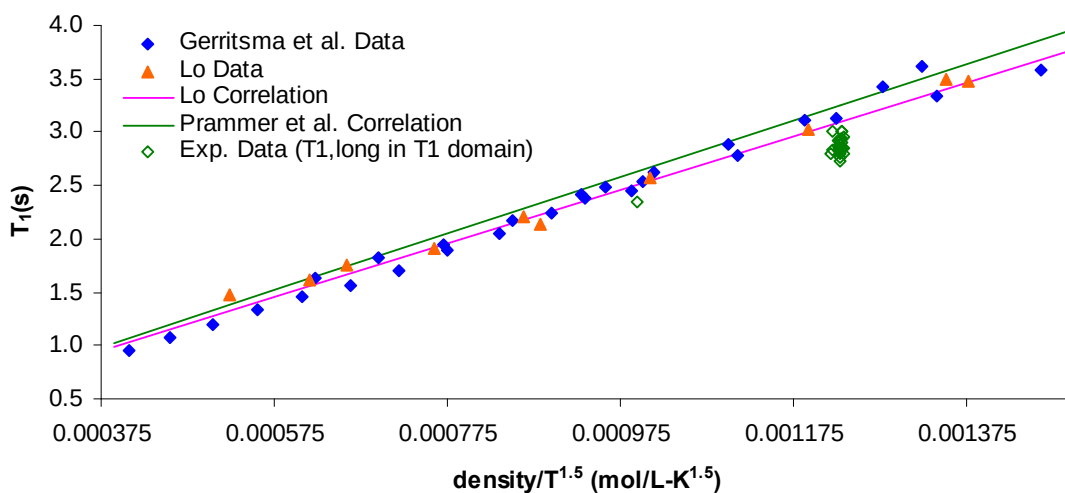


Figure 6.13: NMR T_1 measurements (T_1 domain editing) at $P \sim 1980$ psig compared with literature data and correlations

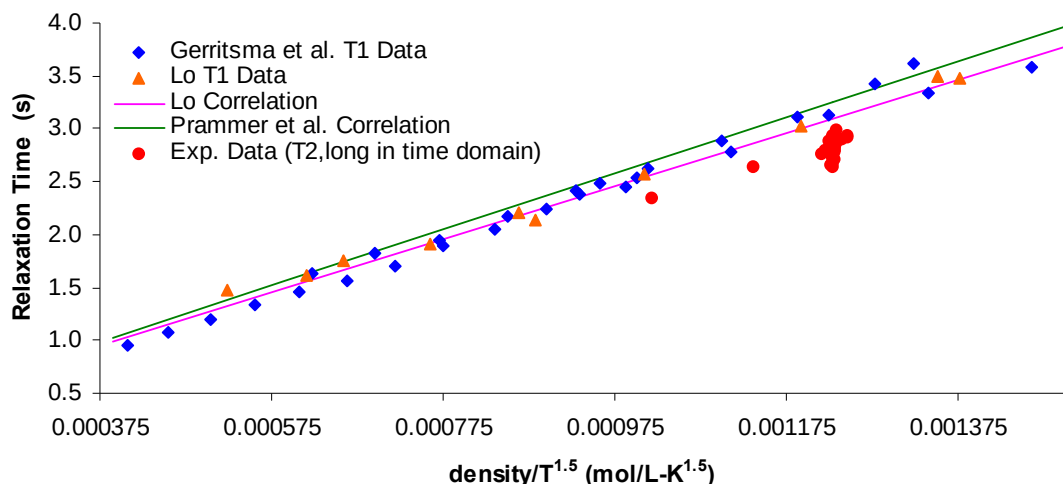


Figure 6.14: NMR T_2 measurements (time domain editing) at $P \sim 1980$ psig compared with literature data and correlations

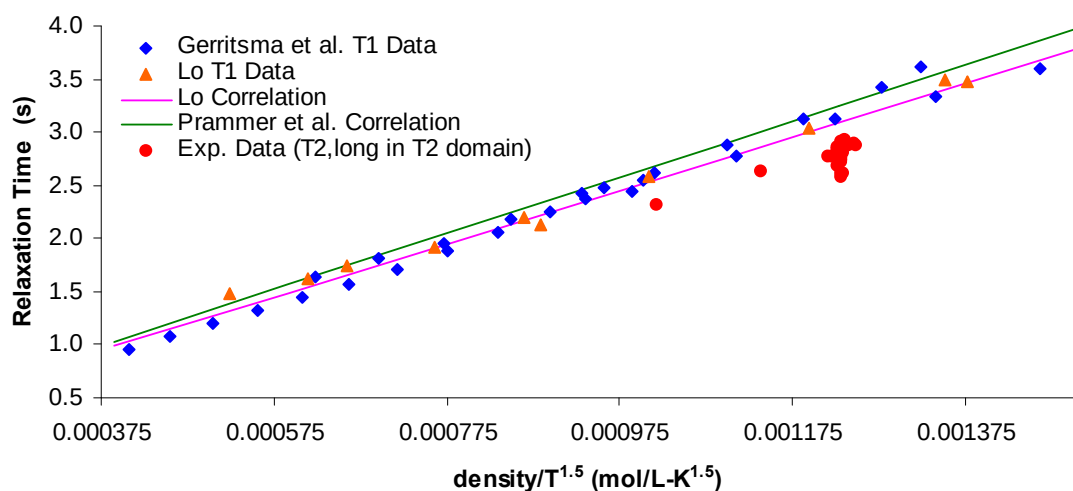


Figure 6.15: NMR T_2 measurements (T_2 domain editing) at $P \sim 1980$ psig compared with literature data and correlations

Despite falling below the correlation lines, the data in Figs. 6.12-6.15 demonstrate an expected result, namely the equality of T_1 and T_2 . This was assessed by taking the ratio (T_1/T_2) for several cases where T_1 and T_2 measurements were done in tandem. Often multiple T_2 measurements are done for one T_1 measurement. In such cases, the ratio (T_1/T_2) is calculated for each of

the values of T_2 . The results are shown in Table 6.1 for 28 such ratios (T_1/T_2). Table 6.1 shows the mean and standard deviation for these cases. Note that a T_1/T_2 of unity falls with the standard deviation from the mean value. Hence, T_1 and T_2 can be said to be equal because their ratio (T_1/T_2) is not statistically distinguishable from 1.0.

Table 6.2: Relaxation time difference for time and relaxation domain editing

Case	Relaxation Time Ratio (T_1 / T_2) (s)
Time Domain Editing	0.97±0.08
Relaxation Time Domain Editing	1.04±0.08

Data for methane at pressures of approximately 1980 psig serves to show that measurements obtained are consistent despite varying experimental parameters intended to increase the measured relaxation time. The premise behind changing experimental procedure was to counteract a perceived limitation in the measurement. For instance, the most troubling possible limitation is the presence of oxygen in the measured sample. However, whether one changes the number of times the high pressure NMR apparatus is flushed with relatively low pressures of the gas to be measured (Figs. 6.16 and 6.17), the pressure differential across the oxygen scavenger during pressurization (Figs. 6.18 and 6.19), or the presence or absence of the oxygen scavenger (Figs. 6.20 and 6.21); the values of T_1 and T_2 remain the same within measurement error. In each pair of the figures just mentioned, the first is for T_1 and the second is for T_2 .

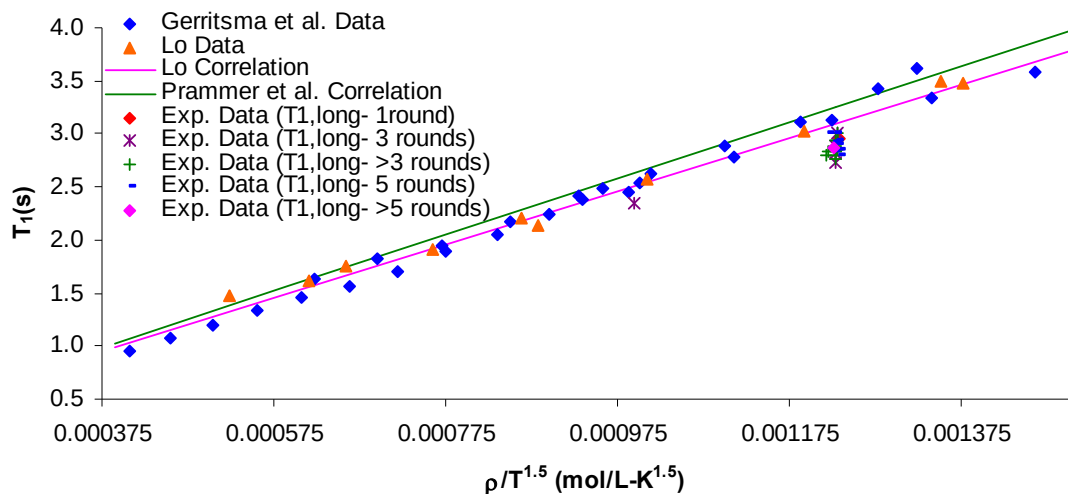


Figure 6.16: NMR T_1 measurements (T_1 domain editing) at $P \sim 1980$ psig showing the number of rounds of preparatory flushes with the measured gas and its lack of effectiveness in increasing T_1

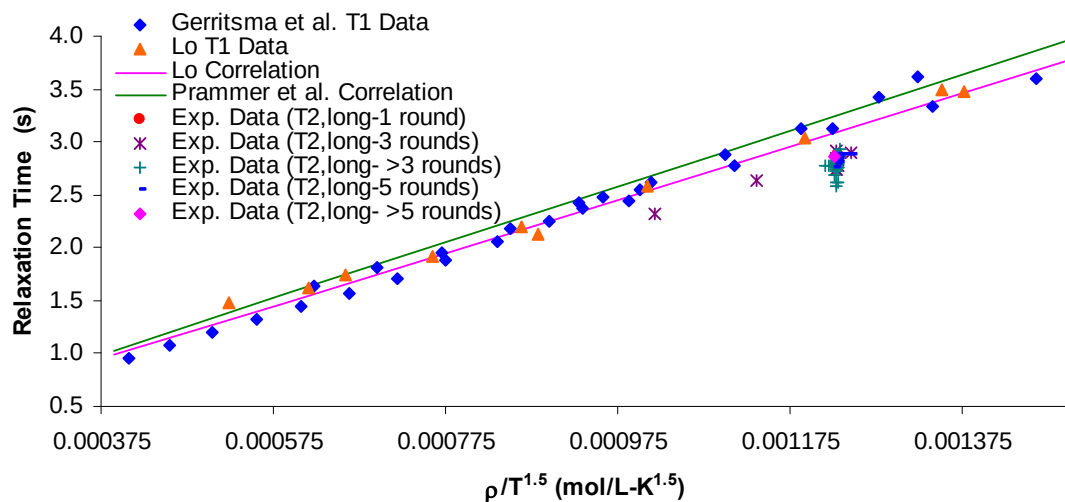


Figure 6.17: NMR T_2 measurements (T_2 domain editing) at $P \sim 1980$ psig showing the number of rounds of preparatory flushes with the measured gas and its lack of effectiveness in increasing T_2

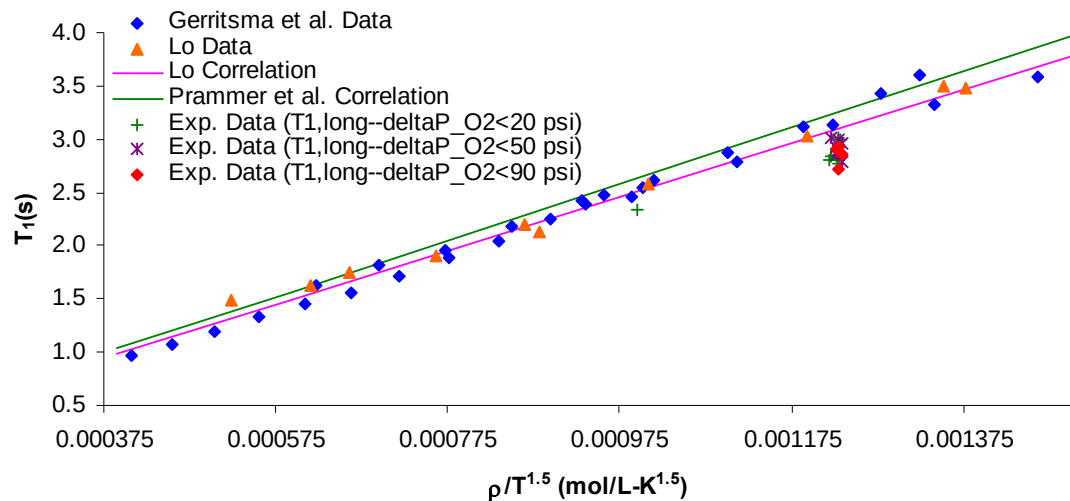


Figure 6.18: NMR T_1 measurements (T_1 domain editing) at $P \sim 1980$ psig showing lack of effectiveness in increasing T_1 by reducing the pressure differential across the oxygen scavenger

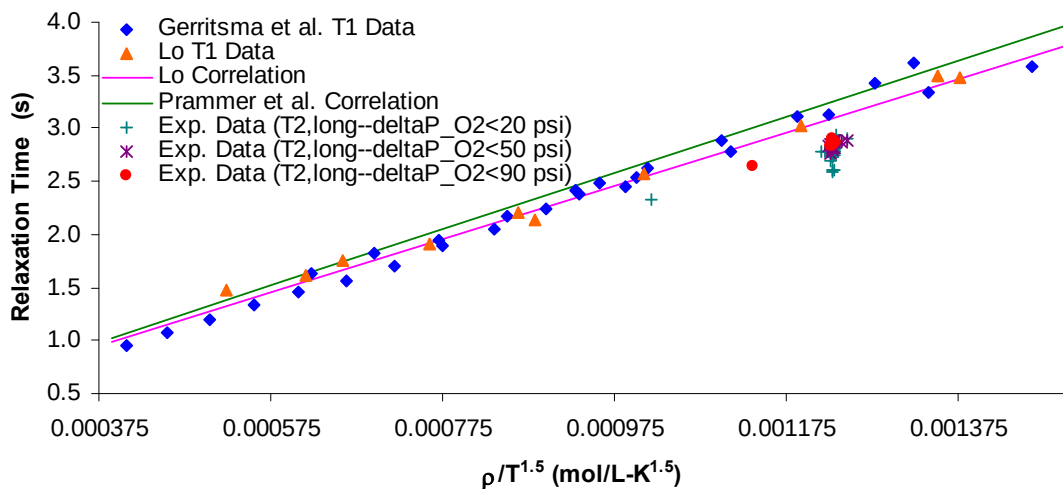


Figure 6.19: NMR T_2 measurements (T_2 domain editing) at $P \sim 1980$ psig showing lack of effectiveness in increasing T_2 by reducing the pressure differential across the oxygen scavenger

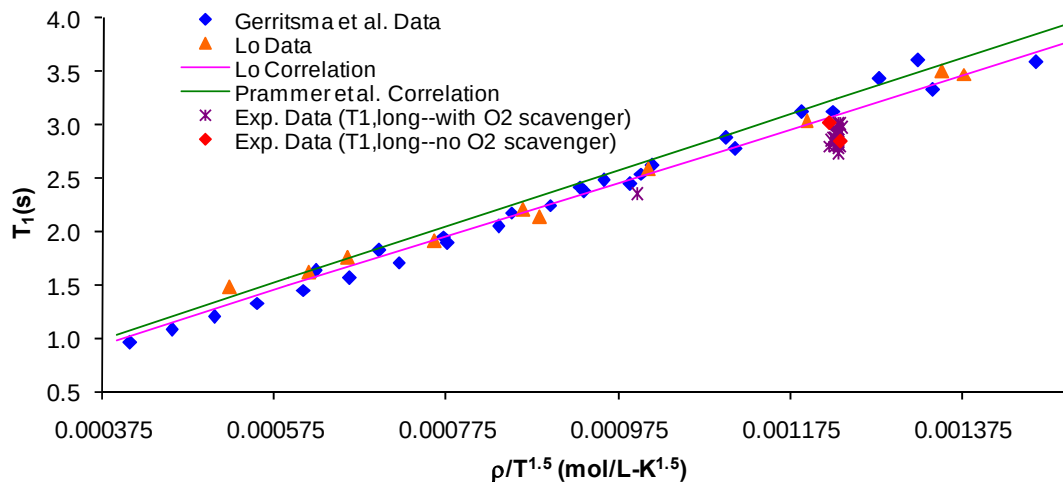


Figure 6.20: NMR T_1 measurements (T_1 domain editing) at $P \sim 1980$ psig showing lack of effectiveness in increasing T_1 by using the oxygen scavenger

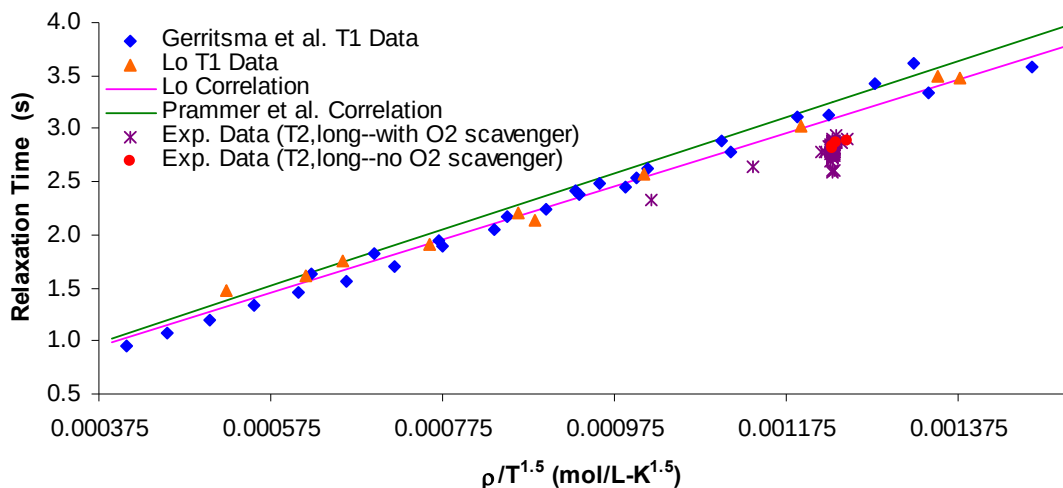


Figure 6.21: NMR T_2 measurements (T_2 domain editing) at $P \sim 1980$ psig showing lack of effectiveness in increasing T_2 by using the oxygen scavenger

T_1 and T_2 data are also obtained for a range of pressures from 1500 psig to 4000 psig. Such data is shown in Fig. 6.22. The data from measurements performed here (shown in red symbols and black symbols) follows a trend

indicated by the red dashed line, albeit different from the trend of previous workers. The equation for the correlation is

$$T_{1,2} \text{ (s)} = 1.38 \times 10^5 \frac{\rho}{T^{1.5}}. \quad (6.5)$$

In Eq. 6.5, ρ is the density (g/cm^3) and T is the temperature in Kelvin. The new correlation line was chosen such that it retains a linear relationship with $\frac{\rho}{T^{1.5}}$ while still adequately representing the data. Note that this equation resembles Eq. 6.3, but with a smaller coefficient. The value of the coefficient accounts for the data obtained here lying below results from previous workers. However, since the data is still described well with a linear relation in Fig. 6.22, spin-rotation describes the relaxation behavior well.

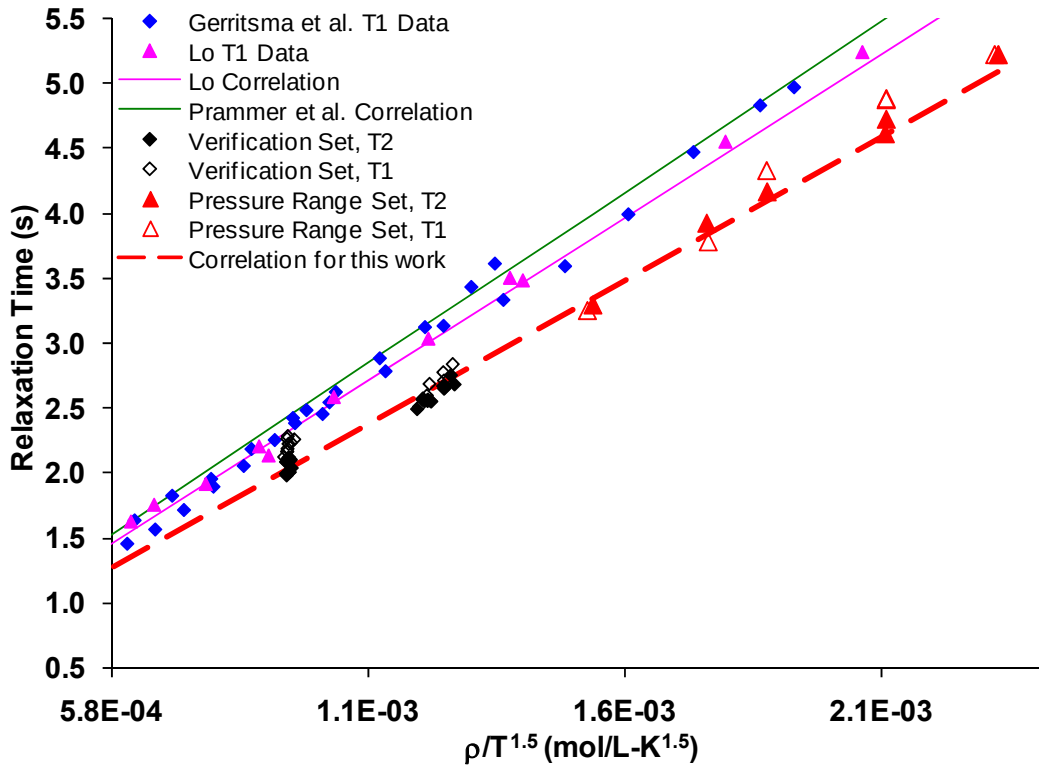


Figure 6.22: NMR T_2 measurements (T_2 domain editing) for methane compared with literature data and correlations

6.4 Elevated Pressure NMR Measurements with Ethane

This section reports NMR T_1 and T_2 measurements for C_2H_6 vapor. The values for T_1 were found to be larger than T_2 , but both were larger than existing data for ethane from Zhang (2002). The pressure range for NMR measurements on ethane is from approximately $P = 480$ psig to $P = 615$ psig. Since ethane condenses at 660 psig at temperature $T = 30$ °C (Funke *et al.* 2002), NMR data for ethane vapor is not obtainable at higher pressures. Also note that these measurements are at $T = 30$ °C, near the critical temperature of C_2H_6 ($T_c = 32$ °C).

Measurements with ethane require additional attention to a pair of parameters in the acquisition of NMR data. This is owed to the longer relaxation time of ethane. These comments also hold in principle and become increasingly important for mixtures of methane and ethane, described below. One parameter that is of concern is the recycle time (the time for repolarization between scans, RD). The value of RD was lengthened as compared to CH_4 because the corresponding relaxation times are longer. The value of $RD = 60$ s is used for pure C_2H_6 . This required correspondingly lengthening the second parameter, namely data acquisition times. For inversion recovery, this means that the wait time (the time after the 180° pulse and before the 90° read pulse, $D1$) reached a value as long as approximately 48 s. Longer values for $D1$ do not function because the total experimental time for a standard inversion recovery measurement on MARAN instruments is little larger than 107 s. For the CPMG, the acquisition time lengthens to 27.8 s. This collection time uses the maximum

number of echoes (34816) with an echo spacing of 0.8 ms. Larger echo spacings are not used because trial measurements with both methane and water suggest that the measured T_2 decreases when the echo spacing is increased beyond this point (data not shown).

Fig. 6.23 shows a summary of measured values of T_1 and T_2 after editing in the relaxation time domain. The density is obtained by interpolation from data in ^aFunke *et al.* (2002). Also shown are data from Zhang (2002). The line is one that captures the appropriate relation from the kinetic model of relaxation by spin rotation that passes through the data by Zhang. These data were obtained by Zhang at 89 MHz Larmor frequency, at temperatures of 19 to 35 °C and pressures of 418 to 684 psig.

The most salient features of Fig. 6.23 are as follows. First, the relaxation times measured for this report are consistently larger than those from previous work by Zhang (2002), shown as black diamonds in Fig. 6.23. This is somewhat surprising since the CH₄ relaxation times measured in this work are consistently less than values by previous workers. This is also encouraging because it suggests that measurements made on the MARAN instrument are not intrinsically of poorer quality (indicated by lower relaxation time) than higher magnetic field instruments used by other workers. The second important feature of Fig. 6.23 is that the value of T_1 appears to be consistently larger than that of T_2 . This behavior seems to be mitigated at the lower end of the pressure range, where T_1 and T_2 are nearly equal for pressures near 480 psig. As furthered below, it appears that the value of T_2 is more dependable since the resultant

relaxation time distributions are more symmetric and are more qualitatively consistent with pressure.

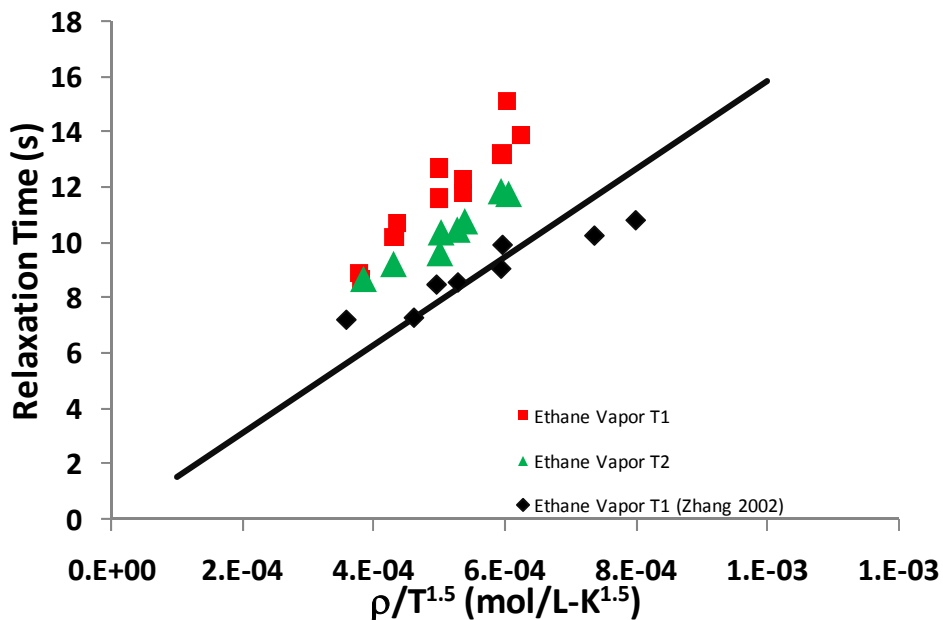


Figure 6.23: NMR Ethane T_1 and T_2 measurements compared with literature data (The experimental data from this work are for pressures ranging from 480 to 610 psig.)

The data in Fig. 6.23 are tabulated in Table 6.3. Results for the inversion recovery measurement at $P = 603$ psig in Table 6.3 are shown in Fig. 6.24. At pressures that are relatively high, notice that the distribution appears skewed slightly. As in Fig. 6.24, this skewing is typically to the right. Another T_1 distribution is shown in Fig. 6.25, where the pressure is slightly less, at $P = 519$ psig, results in a more symmetric distribution. The qualitative changes with pressure notwithstanding, the values of T_1 obtained appear valid because data at higher pressures follow the trend at lower pressures, as seen in Fig. 6.23. T_2 distributions, as exemplified in Fig. 6.26, do not show disparate trends depending on pressure. The rightmost peak in Fig. 6.26 is symmetric even at relatively high

pressure as in Fig. 6.26, $P = 607$ psig. This symmetry holds as the pressure decreases.

Table 6.3: *Relaxation times for ethane, after editing in the relaxation domain*

Pressure (psig)	Measurement Type	Relaxation Time (s)
614	T_1	13.9
606	T_1	15.1
603	T_1	13.2
579	T_1	12.3
578	T_1	11.8
562	T_1	12.7
562	T_1	11.6
521	T_1	10.7
519	T_1	10.2
484	T_1	8.69
607	T_2	11.8
602	T_2	11.9
575	T_2	10.5
580	T_2	10.8
563	T_2	9.64
565	T_2	10.4
519	T_2	9.24
488	T_2	8.70

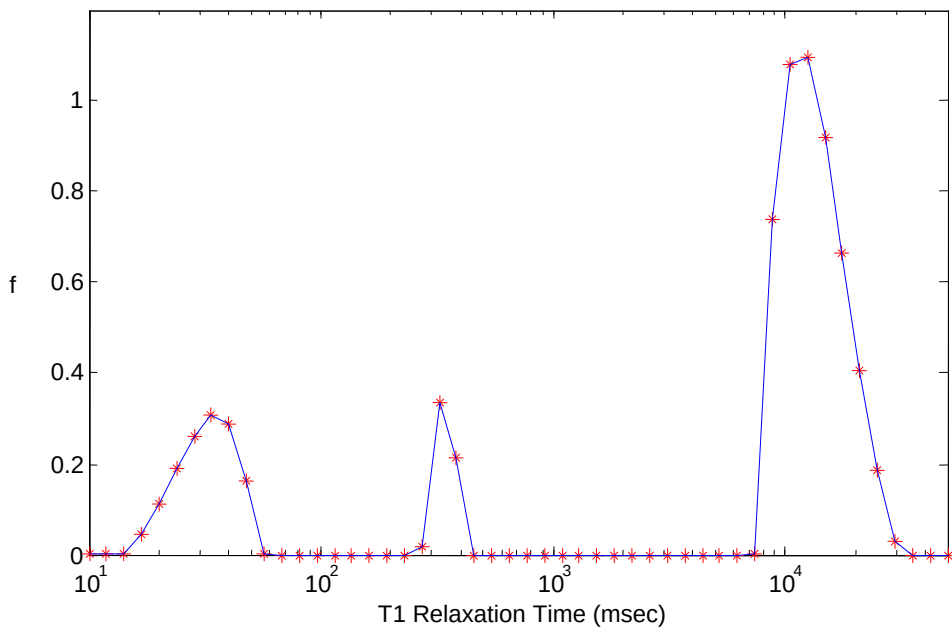


Figure 6.24: *NMR ethane T_1 distribution for $P = 603$ psig, showing that the distribution is skewed at relatively high pressures.*

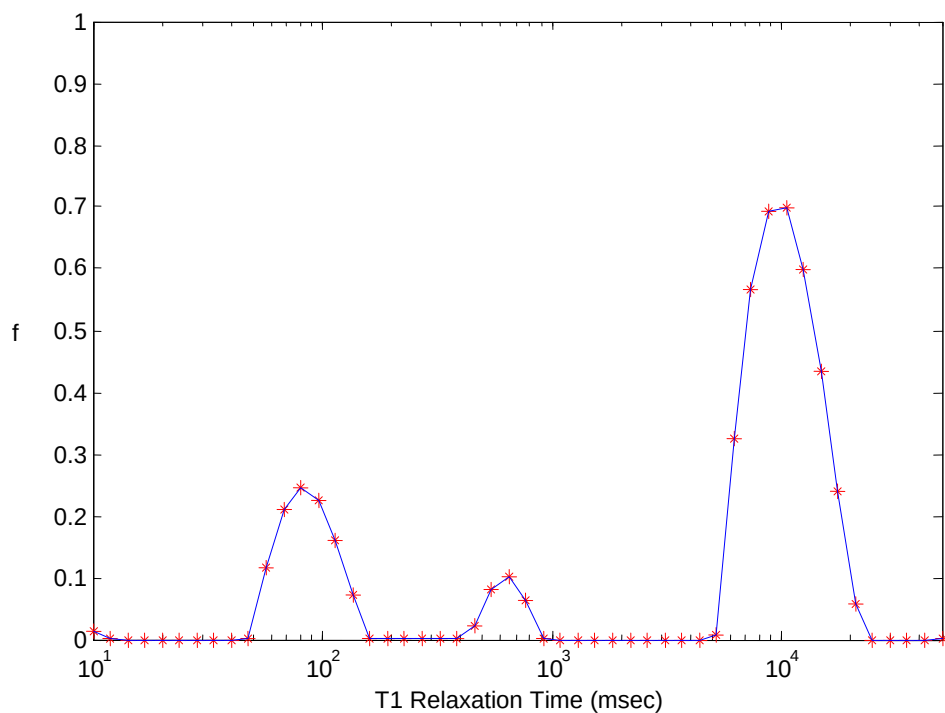


Figure 6.25: NMR ethane T_1 distribution for $P = 519$ psig, showing that the ethane peak at 10^4 ms in the T_1 distribution is more symmetric

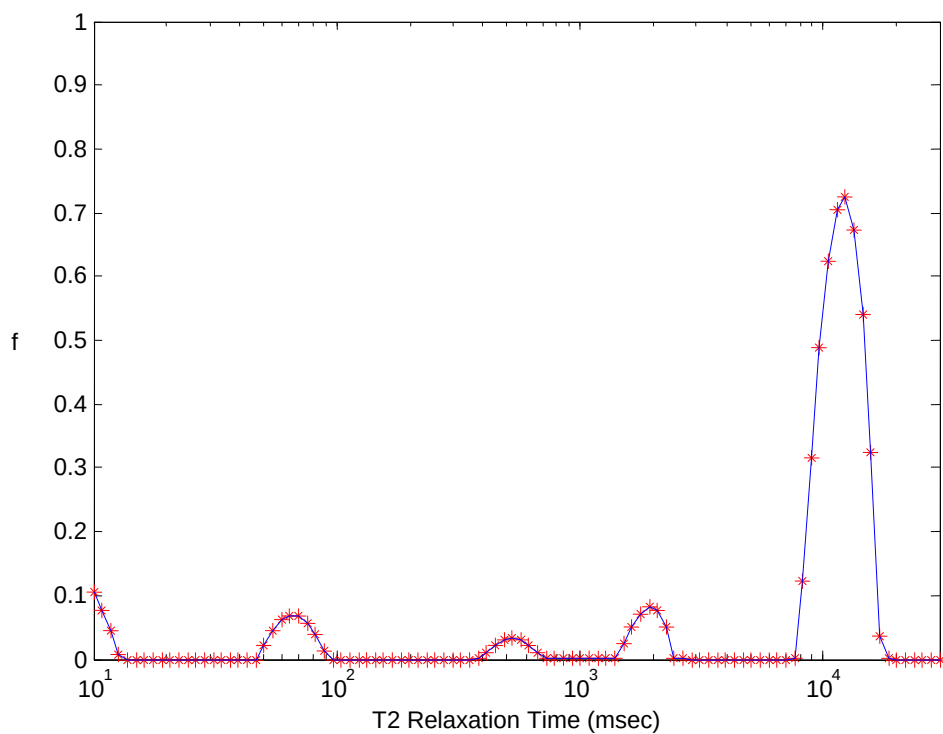


Figure 6.26: NMR ethane T_2 distribution for $P = 607$ psig showing that the ethane peak near 10^4 ms in the T_2 distribution is symmetric.

The data displayed in Fig. 6.23 motivates the correlation shown in Fig. 6.27. The correlation is described by

$$T_{1,2} \text{ (s)} = 6.87 \times 10^5 \frac{\rho}{T^{1.5}}. \quad (6.6)$$

In Eq. 6.6, ρ is the density (g/cm^3) and T is the temperature in Kelvin. This correlation takes into account both T_1 and T_2 data, and is intentionally biased slightly toward T_2 because, given the comments above on the respective relaxation time distributions, T_2 is likely more reliable. Furthermore, the correlation retains the functional relationship described by the kinetic model for spin-rotation relaxation, which was found by Zhang (2002) to adequately describe ethane NMR relaxation.

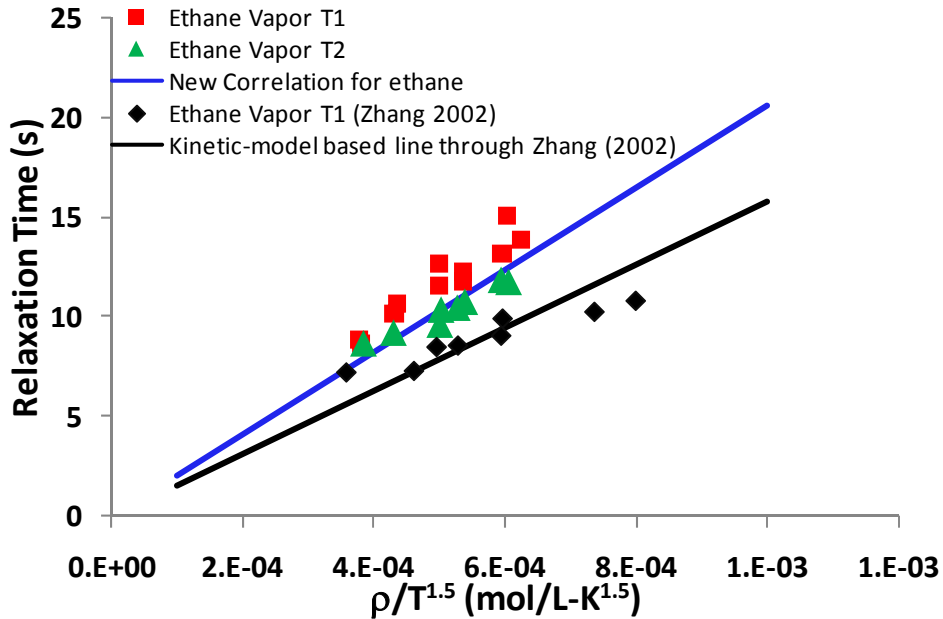


Figure 6.27: NMR Ethane T_1 and T_2 measurements with correlation line included.

6.5 NMR Measurements with 80% Methane/20% Ethane

This section shows NMR T_1 and T_2 measurements for a mixture of 80% methane and 20% ethane (by mole). For convenience, the mixture will be called C1 80-C2 20 below. In these measurements, one can distinguish two separate peaks in T_2 measurements but not in all T_1 measurements. At higher pressures, T_1 peaks are at least partially merged, although individual peaks for methane and for ethane become visible as pressure decreases. The measured relaxation times for the mixture reveal logmean values where T_2 appears larger than T_1 in some cases, but the methane component—when acquirable—appears to follow the previously developed methane correlation.

Data for C1 80-C2 20 are summarized in Fig. 6.28. Correlations developed in this work for ethane (Eq. 6.6) and methane (Eq. 6.5) are shown as lines in Fig. 6.28. Furthermore, the mixture data is presented as logmean values (both T_1 and T_2) and as logmeans for each constituent (i.e. methane or ethane) when the two are distinct or at least show an appreciable valley (i.e. a local minimum) between peaks. In addition, the data in Fig. 6.28 are presented as a log-log plot so that the difference of nearly an order of magnitude in the methane and ethane component relaxation times can be reasonably displayed in one figure.

From Fig. 6.28, the data motivate the following observations. The relaxation times for the methane component in the mixture appear to follow the correlation line for pure methane, and the logmean values slope similarly to the correlation line included for methane. However, the ethane component of the C1

80-C2 20 mixtures is shifted downward from the correlation for pure ethane. This is likely due to ethane being influenced by interaction with methane. On the other hand, the methane component is less affected likely because of its larger proportion in the mixture, yielding relaxation times in Fig. 6.28 that fall nearly on the methane correlation line. Another observation stems from comparing logmean T_1 and T_2 for the mixtures. T_1 and T_2 match for lower pressure, but T_2 is slightly larger than T_1 at higher pressures. Considering that gas mixtures fall within the NMR regime of extreme narrowing, T_1 and T_2 are expected to be equal. This suggests that acquisition parameters, whose importance was mentioned in the discussion above for pure ethane, may unduly influence the measured value of T_1 at higher pressure. Data in Fig. 6.28 for the gas mixture is presented in Table 6.4, which also explicitly includes the corresponding pressure for the measurements.

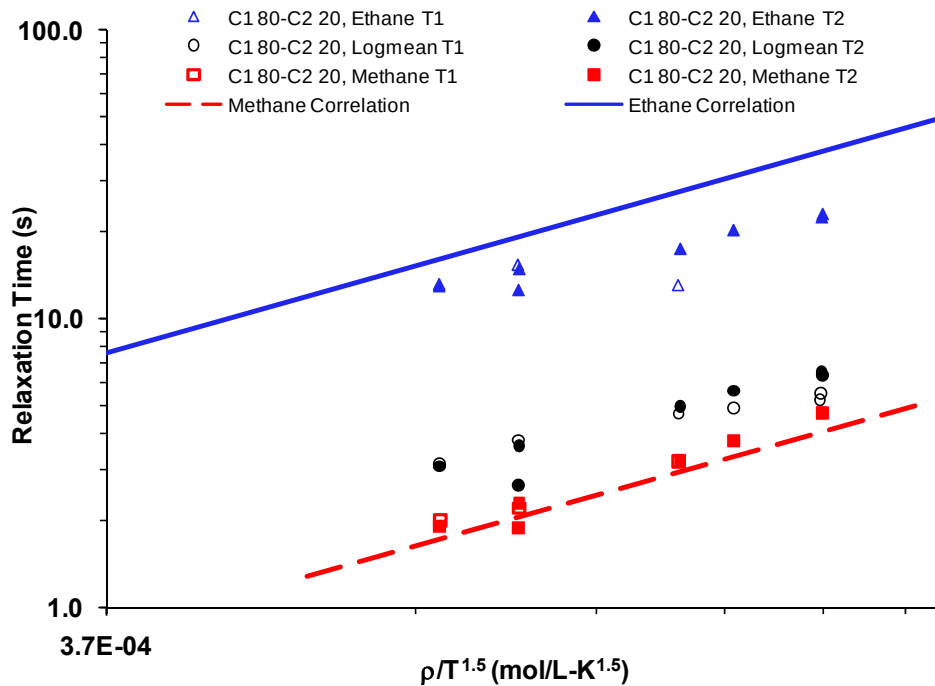


Figure 6.28: NMR C1 80-C2 20 T_1 and T_2 measurements compared with pure component methane (Eq. 6.5) and ethane (Eq. 6.6) correlation lines

Table 6.4: *Relaxation times for C1 80-C2 20, edited in the relaxation domain*

Pressure (psig)	Measurement Type	Methane Relaxation Time (s)	Ethane Relaxation Time (s)	Logmean Relaxation Time (s)
2600	T_1	--	--	5.51
2594	T_1	--	--	5.20
2124	T_1	--	--	4.88
1900	T_1	3.23	13.0	4.68
1397	T_1	2.22	15.3	3.80
1203	T_1	2.01	13.1	3.15
2605	T_2	4.74	23.1	6.38
2599	T_2	4.72	22.5	6.58
2122	T_2	3.79	20.3	5.64
1904	T_2	3.24	17.5	5.00
1399	T_2	2.31	14.9	3.63
1397	T_2	1.89	12.6	2.65
1204	T_2	1.92	12.9	3.08
1202	T_2	1.92	13.0	3.09

A description of trends observed in the NMR measurements of the C1 80-C2 20 mixtures follows. T_1 distributions change their qualitative behavior depending on the pressure. For a relatively high pressure ($P = 2600$ psig) in Fig. 6.29, a peak corresponding to the expected range for methane is visible, but no clear ethane peak is seen. However, Fig. 6.29 does show a tail towards long relaxation times that can be attributable to ethane. Fig. 6.30 shows the effect of lowering the pressure to $P = 2124$ psig. Again the peaks for methane and ethane are not well-resolved, but two separate features can be seen. At a lower pressure still, $P = 1397$ psig in Fig. 6.31, the T_1 distribution demonstrates a clearly divided pair of peaks for methane (mode at ~ 2 s) and ethane (mode at ~ 12 s).

For CPMG experiments, the methane and ethane peaks are distinct even at the highest measured pressures. The peaks remain separated down to the lowest pressures measured for the C1 80-C2 20 mixture. This is shown at high pressure in Fig. 6.32 ($P = 2605$ psig) and at low pressure in Fig. 6.33 ($P = 1202$ psig).

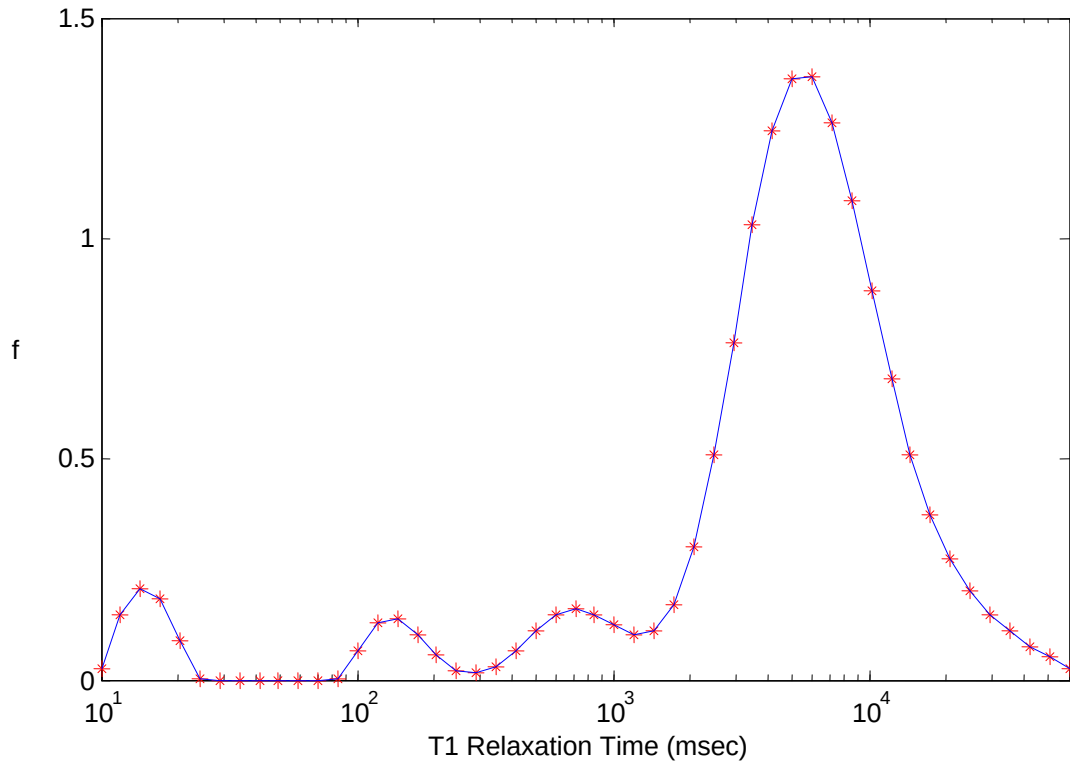


Figure 6.29: NMR C1 80-C2 20 T_1 distribution for $P = 2600$ psig showing a signature for methane with mode near 6s, but without a clearly visible ethane peak

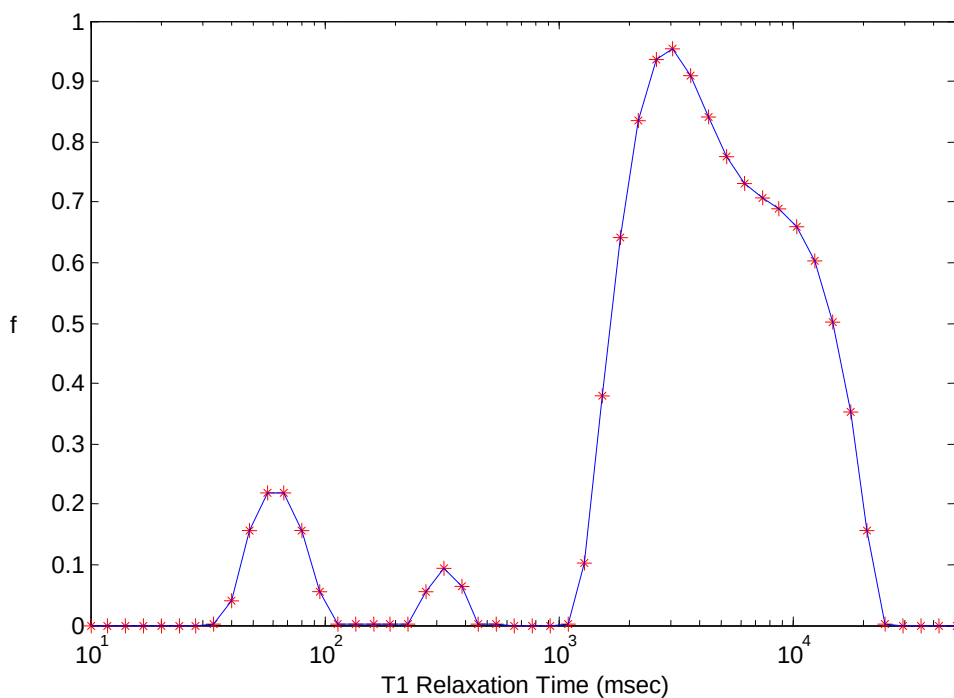


Figure 6.30: NMR C1 80-C2 20 T_1 distribution for $P = 2124$ psig where both methane and ethane peaks are visible, but overlap precludes obtaining separate relaxation time for each

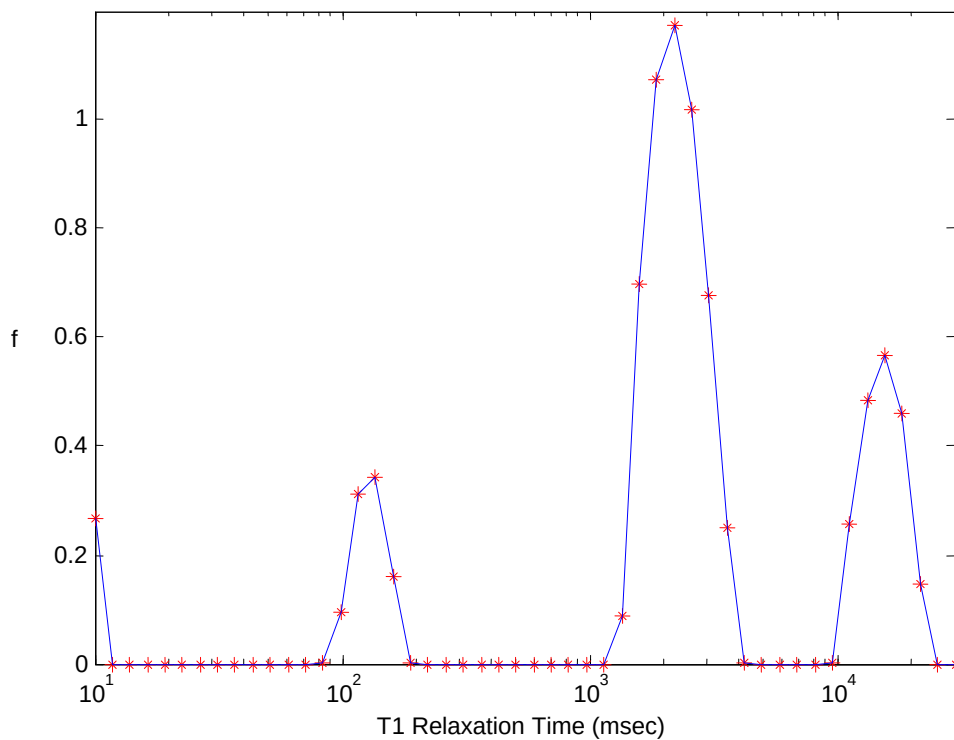


Figure 6.31: NMR C1 80-C2 20 T_1 distribution for $P = 1397$ psig where methane and ethane peaks are both visible and separate

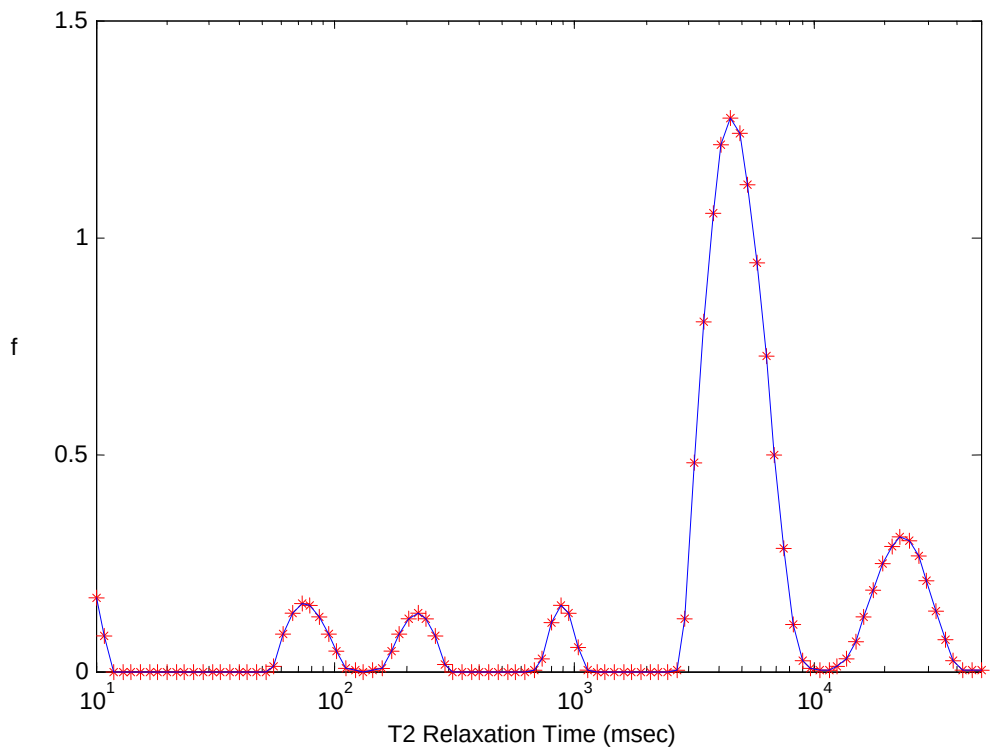


Figure 6.32: NMR C1 80-C2 20 T_2 distribution for $P = 2605$ psig, for which pressure, unlike T_1 , both methane and ethane peaks are separated

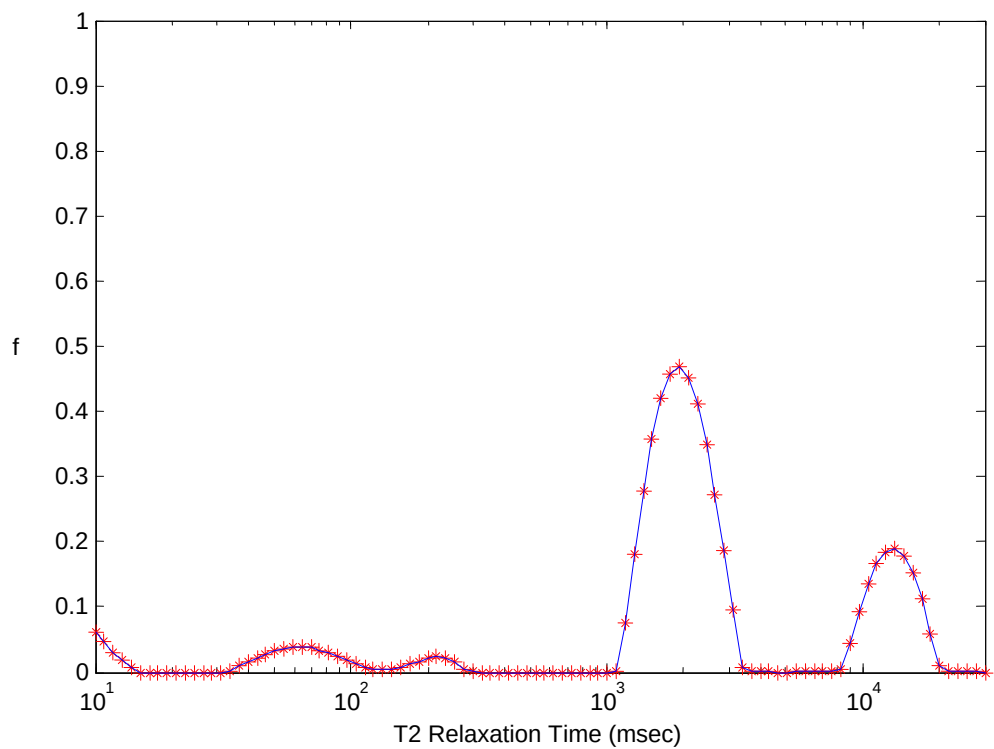


Figure 6.33: NMR C1 80-C2 20 T_2 distribution for $P = 1202$ psig where the separation between methane and ethane peaks remains

The data shown in Fig. 6.28 is replotted in Fig. 6.34 below, but including two calculations using the NMR mixing rule given by Eq. 6.2. The upper dashed line corresponds to the mixing rule for values of G_{ij} determined by Zhang (2002), shown in Table 6.1. The lower solid line uses correlations embodied by Eqs. 6.5 and 6.6 (developed in this thesis) and uses a least squares fit simultaneously to the C1 80-C2 20 mixture data and to the C1 50-C2 50 mixture data, the latter described in the following section, to determine values of G_{ij} not obtained from Eqs. 6.5 and 6.6. Though the mixing rule represented by solid line is more appropriate for the data shown in Fig. 6.34, it is interesting to note that the mixing rule with the independently determined sets of G_{ij} values are within 15% of one another.

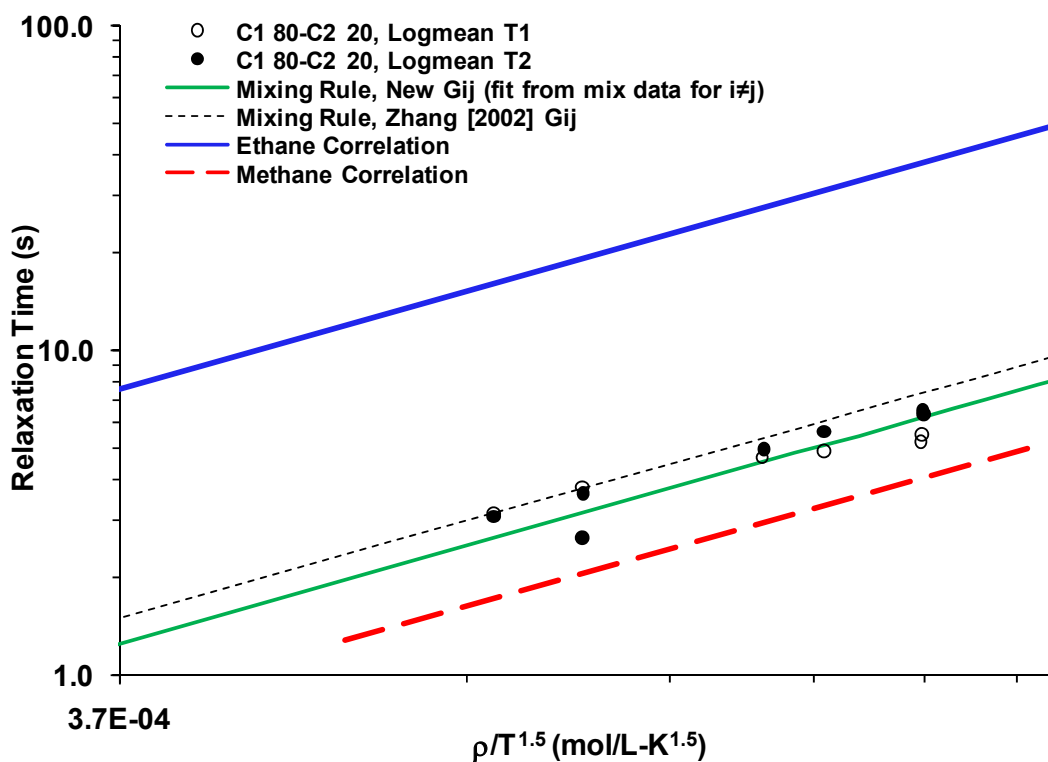


Figure 6.34: NMR C1 80-C2 20 T_1 and T_2 measurements and comparison to mixing rule calculation and pure component correlation lines (Eqs. 6.5 and 6.6)

6.6 NMR Measurements with 50% Methane/50% Ethane

This section shows NMR T_1 and T_2 measurements for a mixture of 50% methane and 50% ethane (by mole). As with the C1 80-C2 20 mixture, the present C1 50-C2 50 mixture presents two well-separated peaks in T_2 measurements but not in all T_1 measurements. At higher pressures, T_1 peaks are at least partially merged, although individual peaks for methane and for ethane become visible as pressure decreases. The measured logmean relaxation times for the mixture show that T_1 and T_2 appear largely equal.

Data for C1 50-C2 50 are summarized in Fig. 6.35. Included are the same correlations from the previous section, resulting from measurements of methane and of ethane individually. Furthermore, the mixture data is presented as logmean values (both T_1 and T_2) and as logmeans for each constituent (i.e. methane or ethane) when the two are distinguishable. From Fig. 6.35, the T_1 and T_2 relaxation times appear equal for both the methane component and the ethane component in the C1 50-C2 50 mixture. Note that either component data appears to slightly deviate from the correlation of the respective pure compound. This demonstrates that each component significantly influences the other in the C1 50-C2 50 mixture. As with ethane or methane components in the mixture, the logmean T_1 value generally agrees with the logmean T_2 value over the pressure range measured. Data in Fig. 6.35 for the gas mixture is presented in Table 6.5, where lower pressures in Table 6.5 correspond to the left side of Fig. 6.35.

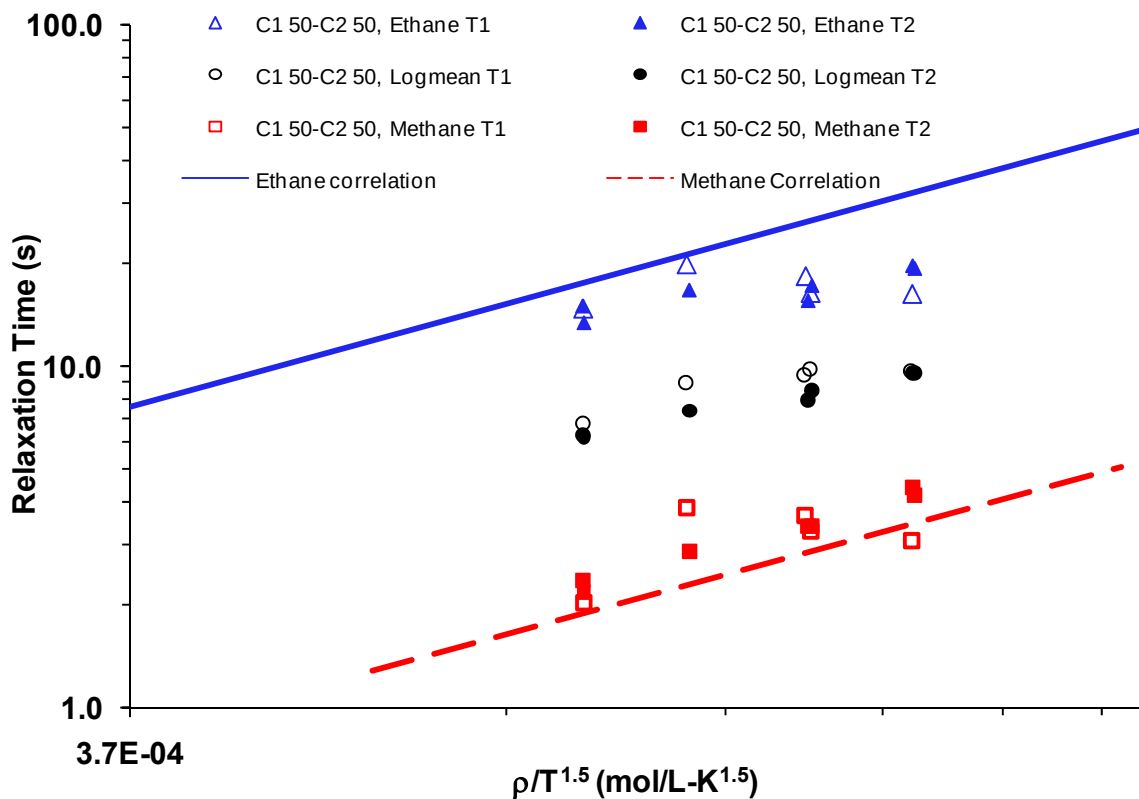


Figure 6.35: NMR C1 50-C2 50 T_1 and T_2 measurements compared with pure methane (Eq. 6.5) and pure ethane (Eq. 6.6)

Table 6.5: Relaxation times for C1 50-C2 50, edited in the relaxation domain

Pressure (psig)	Measurement Type	Methane Relaxation Time (s)	Ethane Relaxation Time (s)	Logmean Relaxation Time (s)
1665	T_1	3.09	16.36	9.70
1446	T_1	3.27	16.46	9.86
1437	T_1	3.63	18.47	9.48
1241	T_1	3.84	20.01	9.03
1092	T_1	2.04	14.79	6.84
1674	T_2	4.18	19.46	9.59
1668	T_2	4.43	19.83	9.60
1443	T_2	3.38	15.65	7.95
1450	T_2	3.40	17.33	8.50
1246	T_2	2.87	16.81	7.42
1094	T_2	2.17	13.46	6.22
1092	T_2	2.35	15.08	6.32

The trends with pressure for the C1 50-C2 50 mixture are similar to the C1 80-C2 20 mixture. At higher pressures, peaks in the T_1 distribution for ethane and methane are more merged. Methane and ethane signals in the T_2 distribution are separated at all measured pressures.

However, a notable difference between the C1 80-C2 20 mixtures and the C1 50-C2 50 mixture will be mentioned here. For a relatively high pressure ($P = 1665$ psig), methane and ethane peaks are partially merged in Fig. 6.36, but a signature can be distinguished for both. In Fig. 6.37, the signals for methane and ethane are still partially overlapping for $P = 1241$ psig. This is different than for C1 80-C2 20 because the two signals had already separated at the greater pressure $P = 1397$ psig (Fig. 6.31). At $P = 1092$ psig, Fig. 6.38, the two peaks have fully separated. This extended pressure range over which methane and ethane peaks are overlapping as compared to C1 80-C2 20 indicates a greater interaction between the two types of molecules. Thus, the behavior observed in the T_1 distributions supports the claim above that ethane influences the NMR response of methane more than in the C1 80-C2 20 mixture. For comparison, a CPMG distribution is included in Fig. 6.39 at $P=1450$ psig, where the methane and ethane signals are well separated.

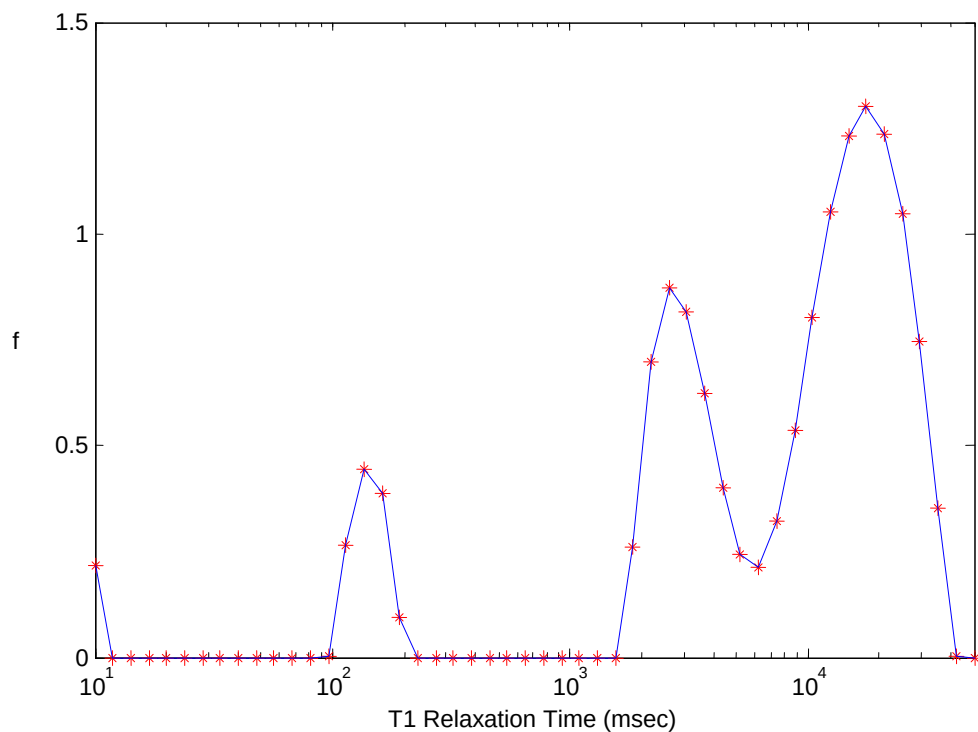


Figure 6.36: NMR C1 50-C2 50 T_1 distribution for $P = 1665$ psig showing two partially-merged peaks for methane and ethane

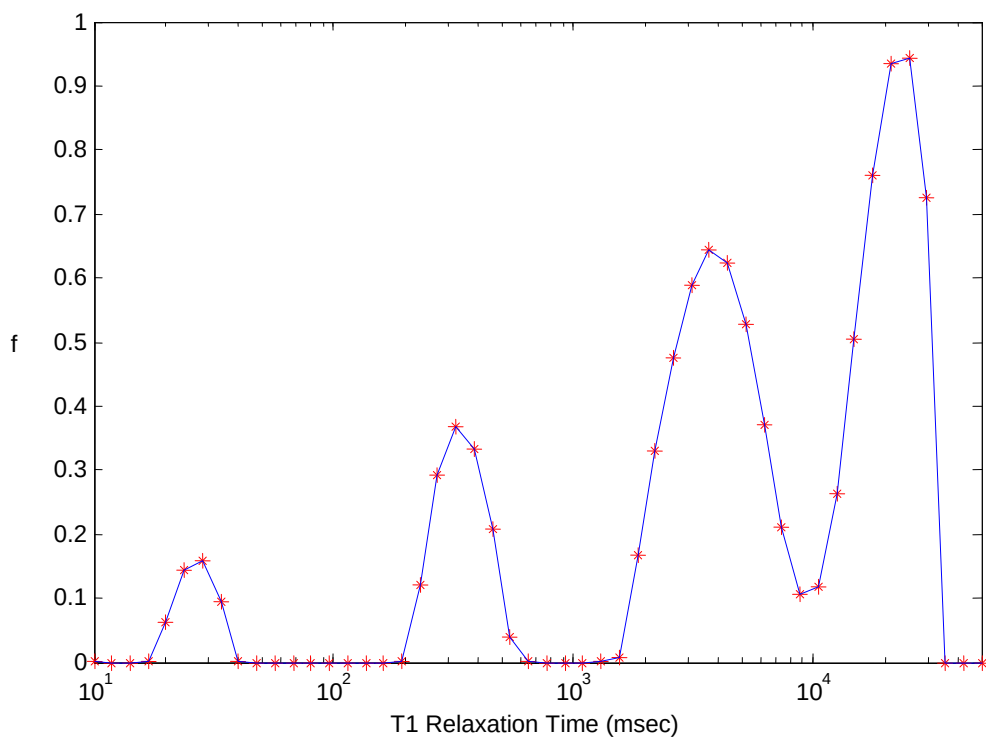


Figure 6.37: NMR C1 50-C2 50 T_1 distribution for $P = 1241$ psig showing two peaks for methane and ethane are still partially merged

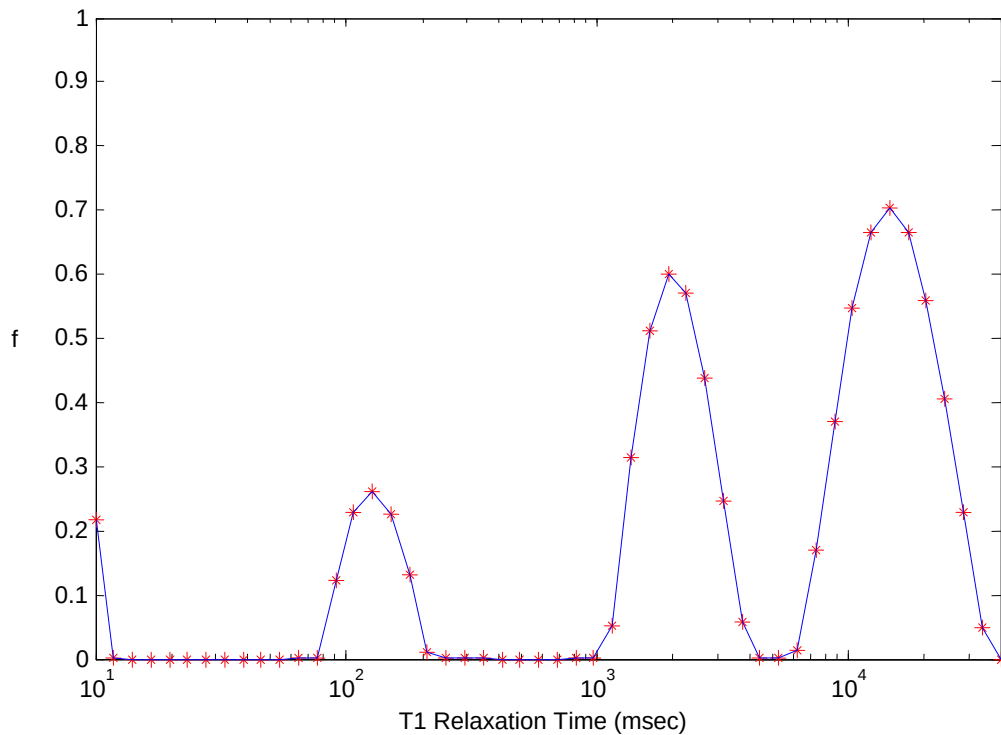


Figure 6.38: *NMR C1 50-C2 50 T_1 distribution for $P = 1092$ psig where methane and ethane peaks are both visible and separate*

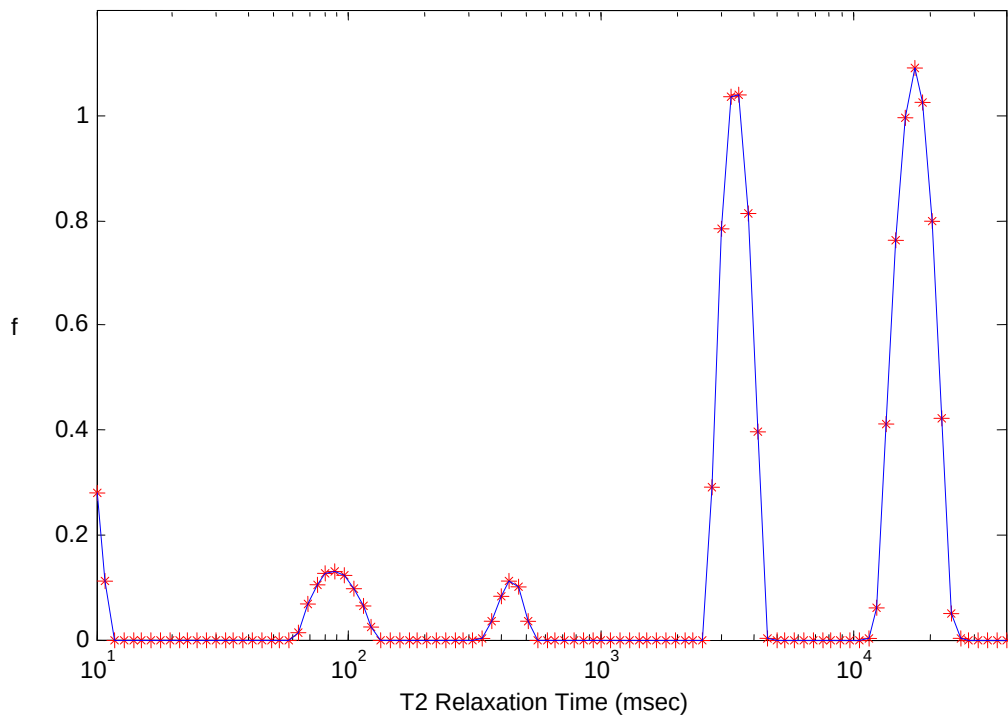


Figure 6.39: *NMR C1 50-C2 50 T_2 distribution for $P = 1450$ psig, for which pressure, unlike T_1 , both methane and ethane peaks are separated*

As with the C1 80-C2 20 mixture, the logmean data measured for the C1 50-C2 50 mixture can be compared with the mixing rule for natural gas mixtures for two independently determined sets of the binary interaction terms G_{ij} . This is demonstrated in Fig. 6.40. The figure includes the two calculations using the NMR mixing rule given by Eq. 6.2, the dashed line corresponding to the mixing rule for values of G_{ij} from Zhang (2002) and the solid line using G_{ij} values determined in this work. Note that both lines pass through the data points, and the difference between the two mixing rule lines themselves is 8%.

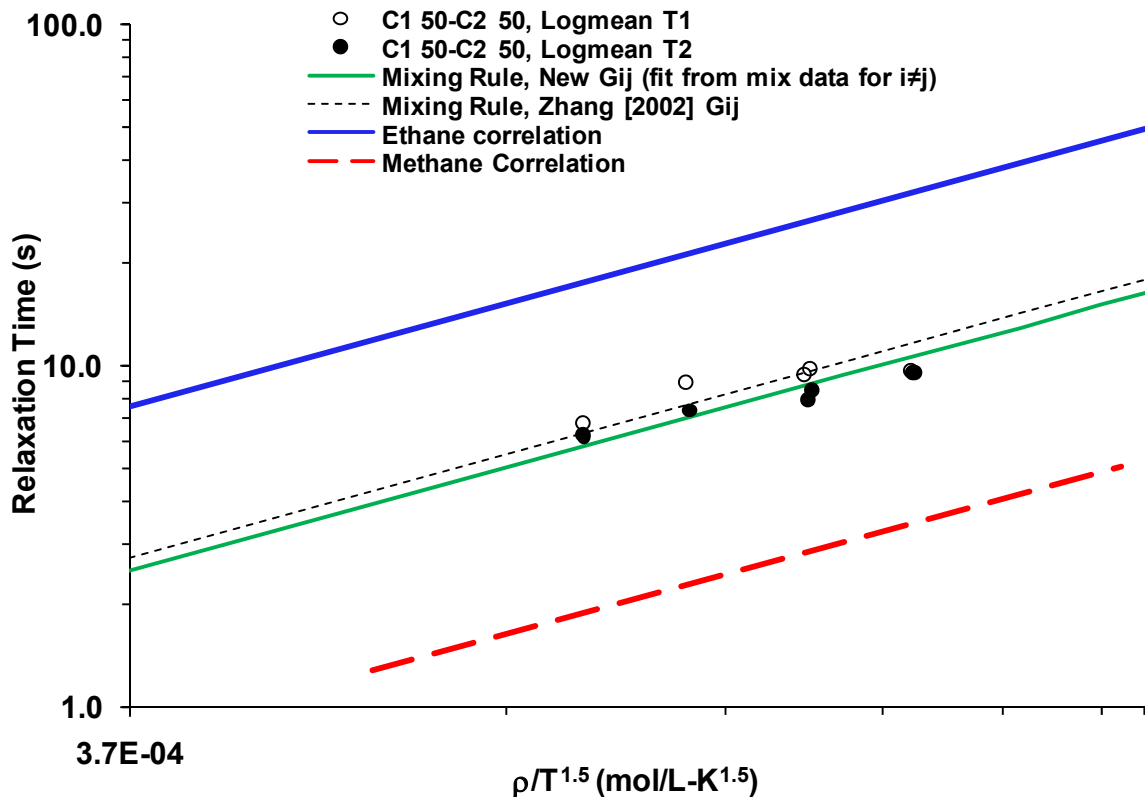


Figure 6.40: NMR C1 50-C2 50 T_1 and T_2 measurements and comparison to mixing rule calculations and pure component correlations (Eqs. 6.5 and 6.6)

6.7 Binary Interaction Terms G_{ij} for Methane-Ethane Mixtures

The previous two sections demonstrate the suitability of the NMR mixing rule to specific mixtures of methane and ethane. This section provides further information regarding the binary interaction terms G_{ij} , which particularize the mixing rule in a quantitative fashion to the components in the mixture. The binary interaction terms from this work are compared with G_{ij} values from Zhang (2002).

Table 6.6 shows G_{ij} for mixtures of methane and ethane. Values are compared with those from Zhang (2002), presented earlier in Table 6.1. In Table 6.6, the first and last entries corresponding to G_{ij} values determined in this thesis are obtained from the data in Sections 6.3 and 6.4 respectively. The values do not match the coefficients in Eqs. 6.5 and 6.6 because the units are different. As stated in Section 6.5, the other two values of G_{ij} were obtained by a least squares fit of the combined C1 80-C2 20 and C1 50-C2 50 mixture data.

Table 6.6: G_{ij} values for mixtures of methane and ethane

Relaxing Molecule (i)	Affecting Molecule (j)	G_{ij} (This work) $s \cdot K^{1.5} cm^3 mol^{-1}$	G_{ij} (Zhang 2002) $s \cdot K^{1.5} cm^3 mol^{-1}$
Methane	Methane	2.21×10^6	2.41×10^6
Methane	Ethane	2.08×10^6	3.77×10^6
Ethane	Methane	8.71×10^6	1.06×10^7
Ethane	Ethane	2.07×10^7	1.58×10^7

Table 6.6 is depicted graphically in Fig. 6.41. Fig. 6.41 permits a ready comparison of G_{ij} values from independent sources. It shows that the values compare well, especially for the methane-methane interaction. Differences in the G_{ij} terms involving both methane and ethane (i.e. cross terms) likely stem from the G_{ij} value of the ethane-ethane interaction in this research being 31% larger than that from Zhang (2002).

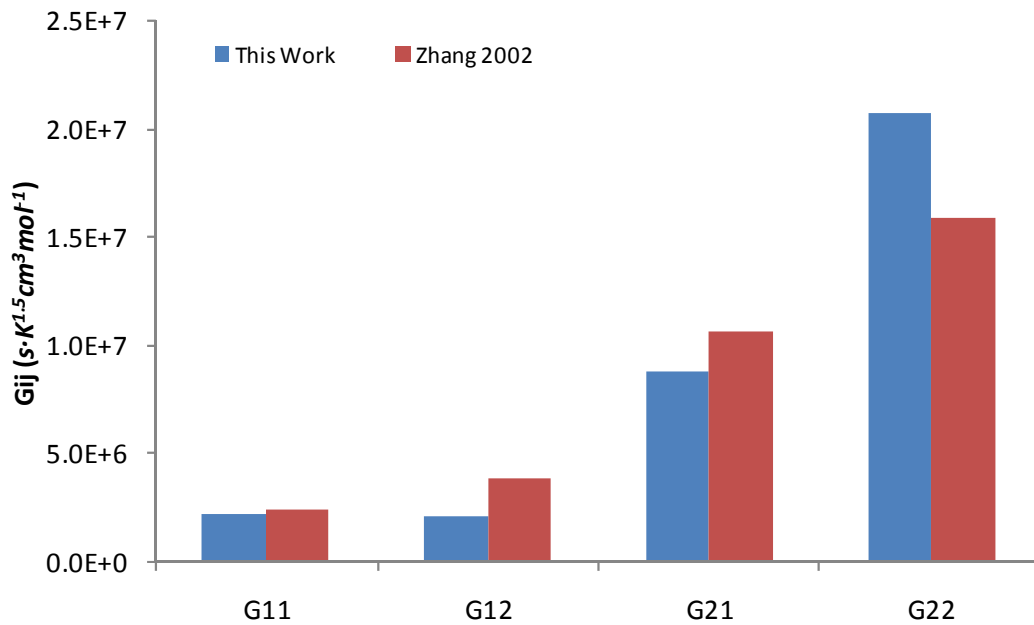


Figure 6.41: Comparison of G_{ij} values in this work with Zhang (2002)

6.8 Conclusions

This chapter has shown NMR measurement results for methane gas, ethane vapor, and two gas mixtures, one with 80% methane and 20% ethane and the other with 50% methane and 50% ethane. The pure component NMR data was correlated with density and temperature. The mixtures were assessed for their agreement with the mixing rule in Eq. 6.1, and mixing rule results were found to appropriately match the data.

Extensive experiments on methane show that methane relaxation times are lower than reported by previous workers, which occurred at higher magnetic field strengths. The measurements with methane also introduce an editing method to determine relaxation times despite the presence of anomalies that occur at early times. After this procedure, T_1 and T_2 for methane are found to be equal in general. A correlation was developed for NMR data for pressures from 1500 to 4000 psig, given by Eq. 6.5. The coefficient for this correlation is 12% less than that reported in Zhang (2002).

Ethane NMR measurements were performed for pressures between 480 and 610 psig. The values of T_1 and T_2 were obtained by editing in the relaxation domain, and were consistently larger than those measured in previous work. For ethane, both relaxation times follow a consistent trend with pressure. This is true even for T_1 at higher pressures, despite the corresponding T_1 distributions containing skewed peaks. Thus, the artifacts in the ethane T_1 distributions do not significantly alter the measured T_1 value. A correlation was developed for pure ethane, Eq. 6.6, based on the data measured for this research. The corresponding coefficient is 31% larger than that determined by Zhang (2002) for Larmor frequency of 89 MHz.

Mixture NMR measurements, both C1 80-C2 20 and C1 50-C2 50 mixtures, generally showed expected trends. The logmean relaxation times generally follow a trend of similar slope to the existing trend for methane and ethane, and lie intermediate between relaxation times trends for methane and ethane individually. Furthermore, when the relaxation time distributions can be

resolved into individual components, the relaxation times for either the methane or ethane peak lie in the vicinity of the correlation line established from pure methane or pure ethane data. For the C1 50-C2 50 mixture, a slightly elevated tendency for the component relaxation times to deviate toward the logmean value is observed, suggesting a greater interaction between the different types of molecules. However, T_1 measurements for the C1 80-C2 20 mixture at the highest pressures in the measured range result in relaxation times being shorter than expected, presumably because of limitations of the MARAN instrument on inversion recovery measurement acquisition parameters.

For both mixtures, the mixing rule for NMR natural gas mixtures was applied, using G_{ij} values determined in this work. The mixing rule was found to be satisfactory for the experimental data, where the data show an average absolute deviation from the mixing rule of 11%. Hence, the mixing rule in Eq. 6.1 is experimentally validated for mixtures with two components that are detectable by proton NMR and a higher pressure range than validation with previous measurements of mixtures of methane and either carbon dioxide or nitrogen. The posited mixing rule using the new G_{ij} values was compared to the situation with G_{ij} values from Zhang (2002) and the two were found to compare well. The difference between mixing rule with the two sets of parameters is 15% for the C1 80-C2 20 mixture and 8% for the C1 50-C2 50 mixture.

The appendix provides specific details of the NMR experiments on natural gas constituents and mixtures of methane and ethane performed in this work. Experimental parameters, preparation details, and plots appear there.

6.9: Potential Avenues of Future Work

This section presents in outline a series of potential opportunities of continued research predicated on the work in this thesis. The directions considered here deal mainly with extending the measurements in this chapter, perhaps also combining with previous works by other authors.

The first and most straightforward extension is the validation of the natural gas NMR mixing rule for ternary mixture of methane, ethane, and propane. This would serve to confirm the mixing rule for three-component systems, as well as provide relaxation time data for an important combination of natural gas constituents.

Another rather straightforward extension is the measurement of diffusivities of natural gas mixtures. This is a useful measurement because gas diffusivity is often the key characteristic that differentiates gases and oils (Akkurt *et al.* 1996) when they are present together.

Considering mixed oil and gases is another extension possible from the current work. The work by Lo (1999) can be expanded upon by measuring the NMR properties of natural gas mixtures with linear alkanes. This would combine the work earlier in this thesis on natural gas mixtures with that by Lo (1999) regarding live oils consisting of a liquid alkane and methane.

The last extension that will be mentioned here is the observation of NMR properties of natural gas mixtures in porous media. The effect on the NMR response of interaction between the mixture of gases and solid surfaces in the rock matrix could reveal important contributions from such interactions in the

overall relaxation behavior of the gas mixture. Such work would serve to extend laboratory investigations by Straley (1997), who investigated the relaxation behavior of methane in porous media.

This chapter has shown how the work on NMR gas mixtures contributes to the knowledge of the behavior of natural gas constituents in NMR measurements. The research here adds to prior contributions that relate NMR relaxation times to properties of the oilfield fluids, shown in previous chapters. Through this work, the benefit expected is to contribute to the ability to interpret a larger range of data obtained from NMR well logging. In addition, an increased confidence is garnered in the NMR mixing rule for natural gases, developed prior to this thesis, but validated in this research.

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Appendix

Gathered here are accumulated data for pure ethane and for mixtures of methane and ethane. Relaxation time distributions (T_1 and T_2) will be shown, but including the time domain fit and values salient to processing the data. Tables will also state the acquisition parameters, and mention will be given to pertinent prevailing conditions during the measurement.

A few features are common to all measurements mentioned here. First, a 30 °C water bath circulates water through the gradient coils of the MARAN instrument to dissipate heat from RF pulses. This is especially important in the CPMG, where a large number of pulses is used. Another common feature is that the gradient amplifier is kept on. This helps improve the magnetic field homogeneity in MARAN-SS, which is used for all elevated pressure gas NMR measurements mentioned in this thesis. Another procedure common to all gas mixture measurements, to all ethane measurements, and to the larger pressure methane measurements (>2000 psig) is that the pressure is released through the outlet valve in switching from one pressure to a lower one. So, subsequent measurements are at lower pressure than previous measurement by releasing small quantities of gas or vapor at a time. When either the pressure is changed (by opening the outlet as mentioned) or the water bath is refilled, a waiting period of at least 12 hours is typically adopted.

A.1 C1 80-C2 20 Mixtures

The preparation conditions for C1 80-C2 20 mixtures are as follows. First, the manifold and pressure vessel were evacuated for approximately 145 minutes. The system is then pressured to low pressures of C1 80-C2 20 (approximately 500 psig) and purged to approximately 30 psig. This is repeated for three rounds. Finally the system is pressurized to approximately 2600 psig. For each subsequent measurement, the pressure is reduced and further NMR measurements are made. These measurements will now be detailed in tables and figures, in the same order as they appeared in Table 6.4

A.1.1 Tables for C1 80-C2 20

The following tables show acquisition parameters for inversion recovery and CPMG measurements of C1 80-C2 20 mixtures. The tables focus on parameters not presented in the plots to follow in Section A.1.2, so they are intentionally somewhat incomplete.

Table A.1: *Acquisition conditions and parameters for C1 80-C2 20 NMR inversion recovery measurements*

Pressure (psig)	ΔP (psi), pressure variability	NS	RD (s)
2600	± 4	16	60
2594	± 5	8	60
2124	± 2	8	60
1900	± 6	32	60
1397	± 4	32	60
1203	± 4	32	60

Table A.2: Acquisition conditions and parameters for C1 80-C2 20 NMR CPMG measurements

Pressure (psig)	ΔP (psi), pressure variability	NECH	NS	RD (s)	SNR
2605	± 2	34816	52	60	100
2599	± 2	34816	60	79	100
2122	± 5	34816	72	79	100
1904	± 2	34816	84	79	100
1399	± 2	34816	44	79	50
1397	± 4	34816	172	79	100
1204	± 1	34816	72	79	50
1202	± 5	34816	288	79	100

A.1.2 Plots for C1 80-C2 20

The following plots show the fit of inversion recovery or CPMG measurement and the resultant distributions, with calculated values appearing in the plot. Note that relaxation times are for the entire distribution, not edited in the relaxation domain as shown in Chapter 6.

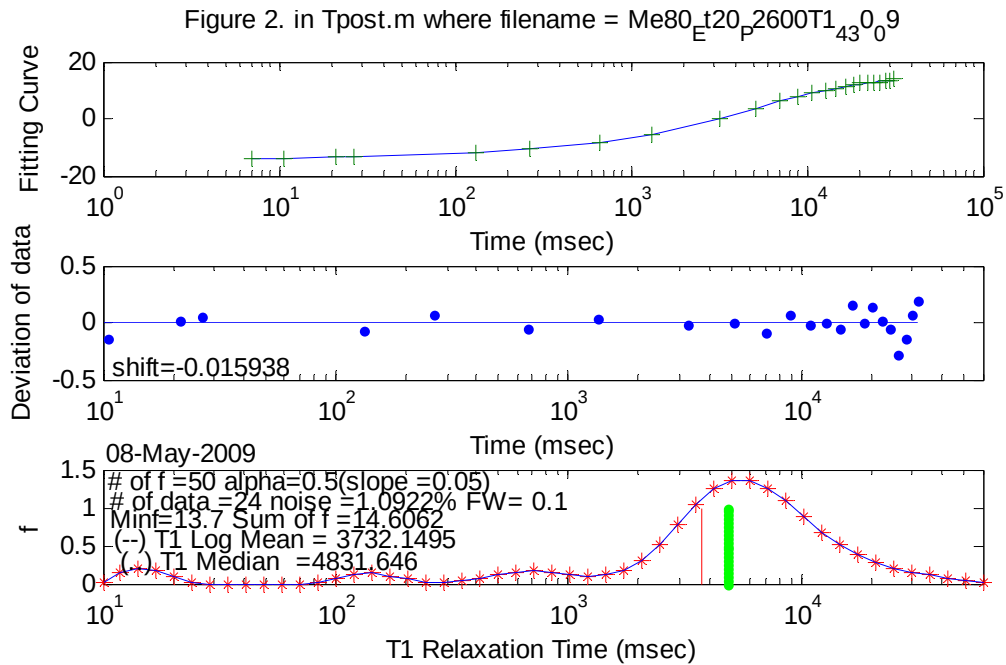


Figure A.1: Inversion recovery response and T_1 distribution for C1 80-C2 20 mixture at $P = 2600$ psig

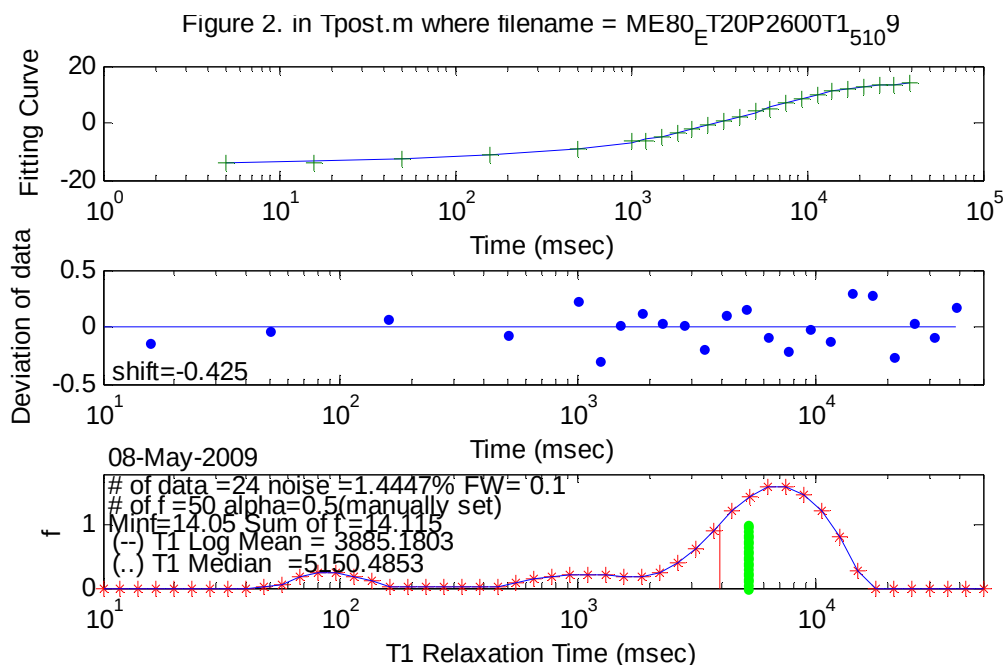


Figure A.2: Inversion recovery response and T_1 distribution for C1 80-C2 20 mixture at $P = 2594$ psig

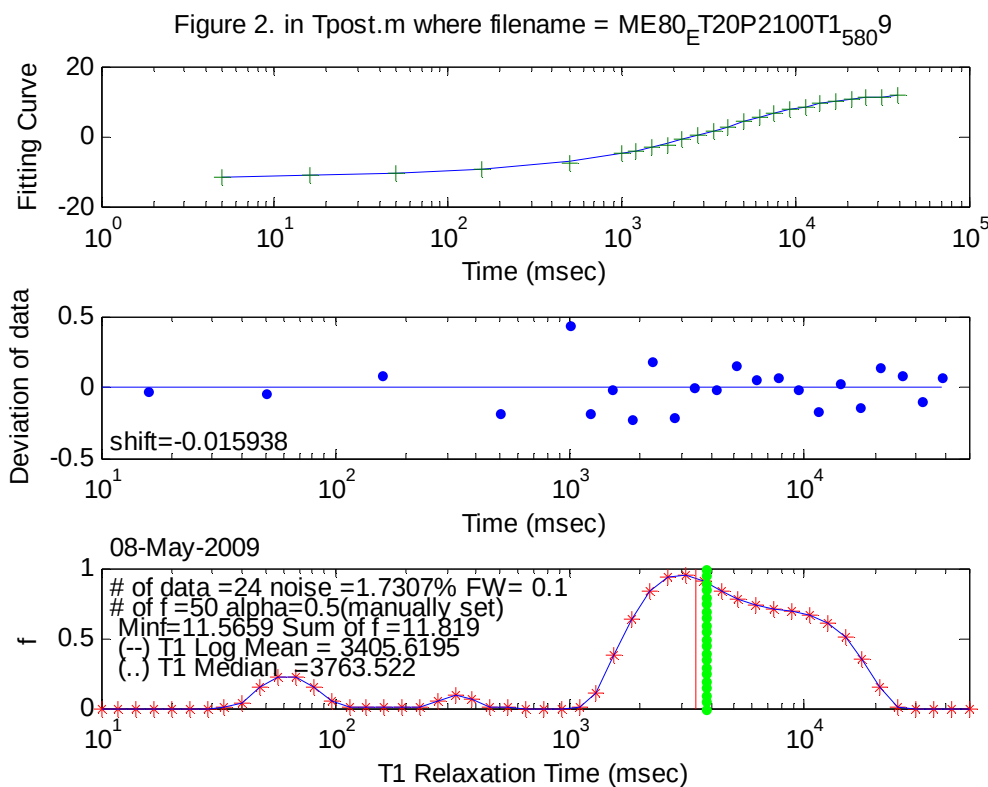


Figure A.3: Inversion recovery response and T_1 distribution for C1 80-C2 20 mixture at $P = 2124$ psig

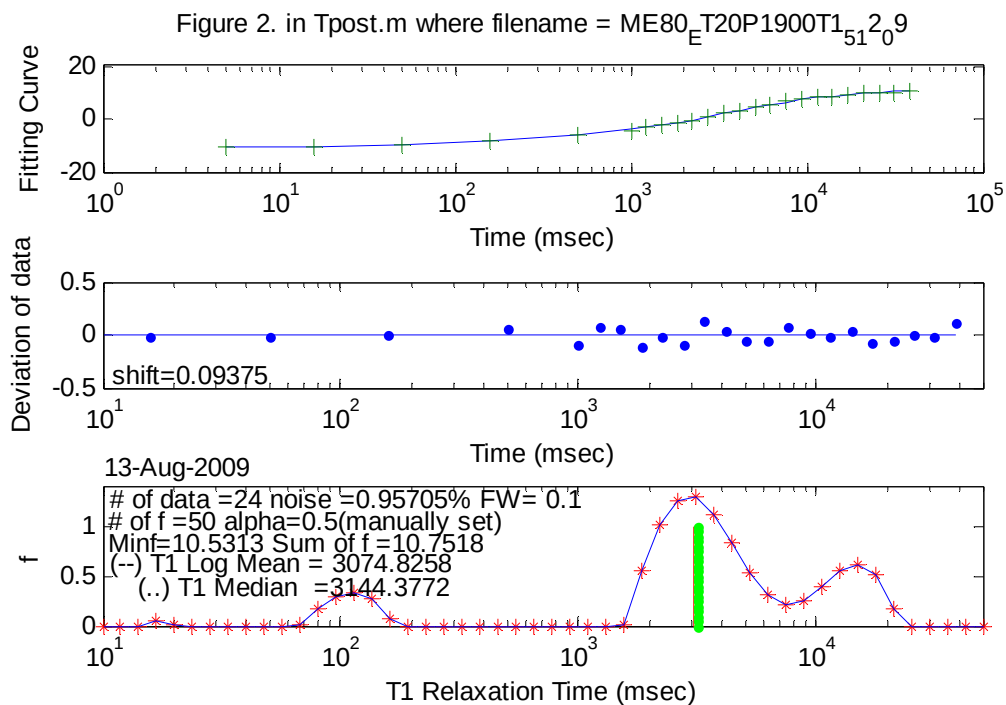


Figure A.4: Inversion recovery response and T_1 distribution for C1 80-C2 20 mixture at $P = 1900$ psig

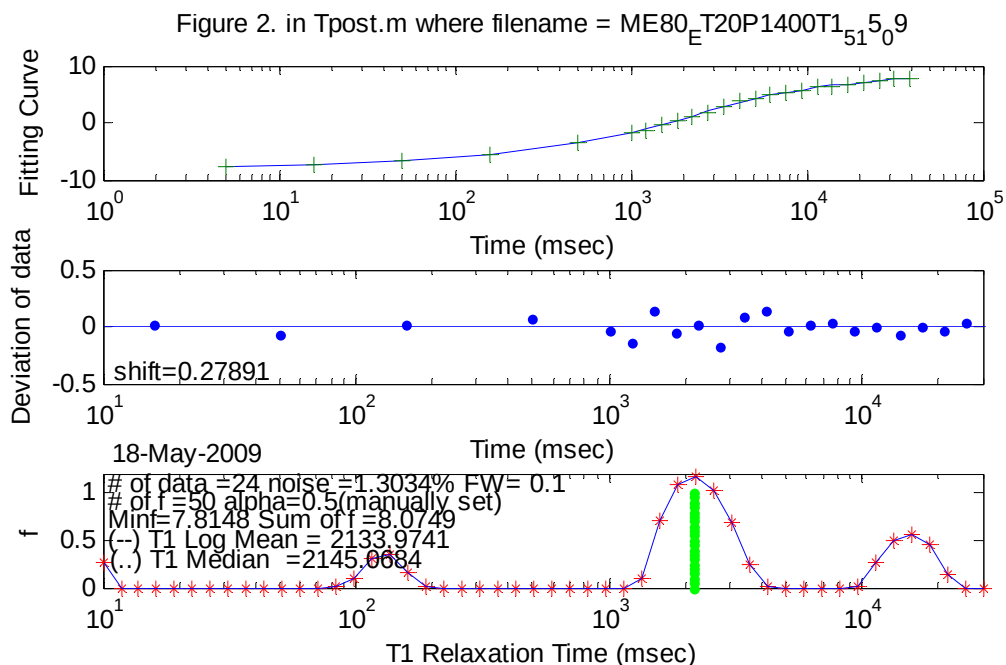


Figure A.5: Inversion recovery response and T_1 distribution for C1 80-C2 20 mixture at $P = 1397$ psig

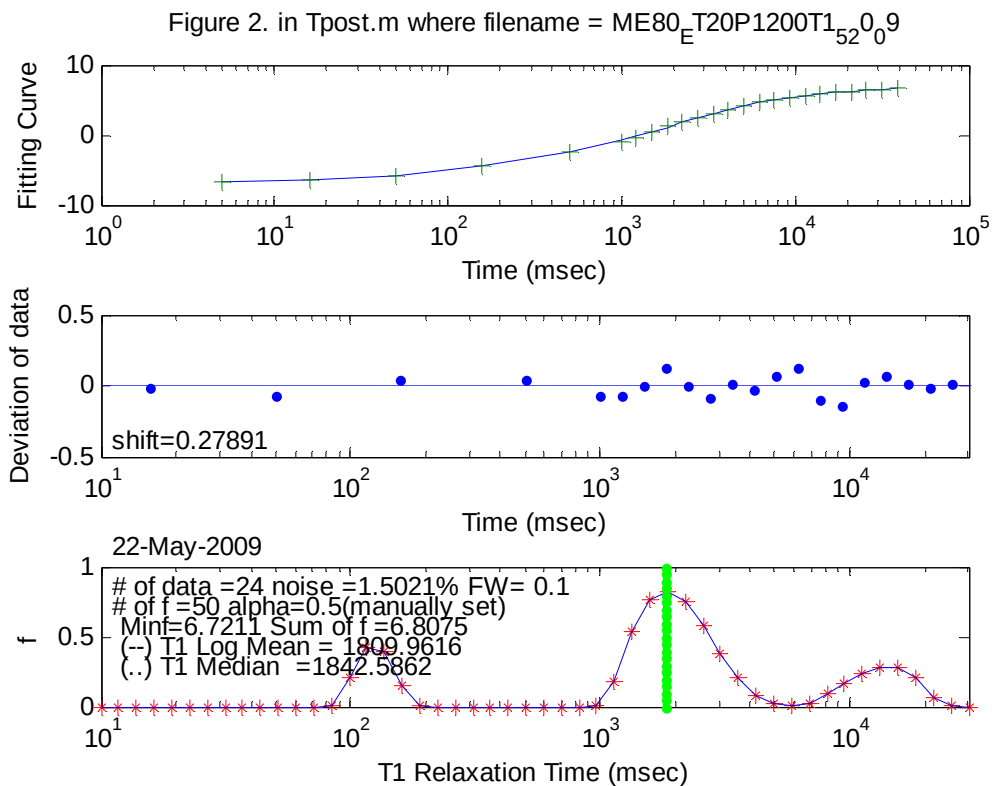


Figure A.6: Inversion recovery response and T_1 distribution for C1 80-C2 20 mixture at $P = 1203$ psig

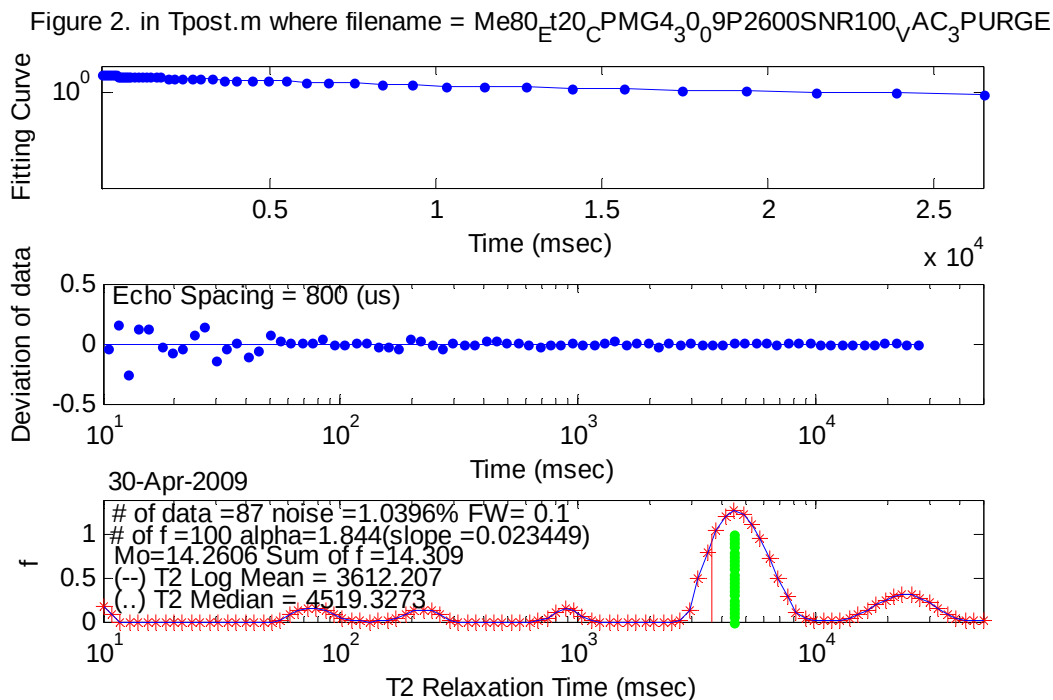


Figure A.7: CPMG response and T_2 distribution for C1 80-C2 20 mixtures at $P = 2605$ psig

Figure 2. in Ipost.m where filename = ME80_E120CPMG4_30_9P2600SNR100_VAC3_PURGE

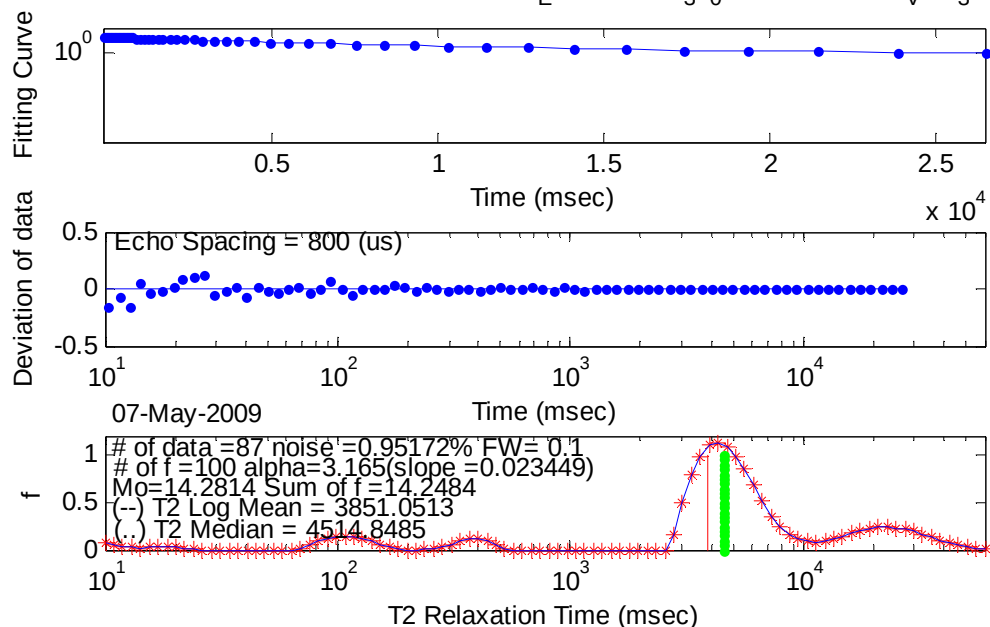


Figure A.8: CPMG response and T_2 distribution for C1 80-C2 20 mixtures at $P = 2599$ psig

Figure 2. in Ipost.m where filename = ME80_E120CPMG5_80_9P2100SNR100_VAC3_PURGE

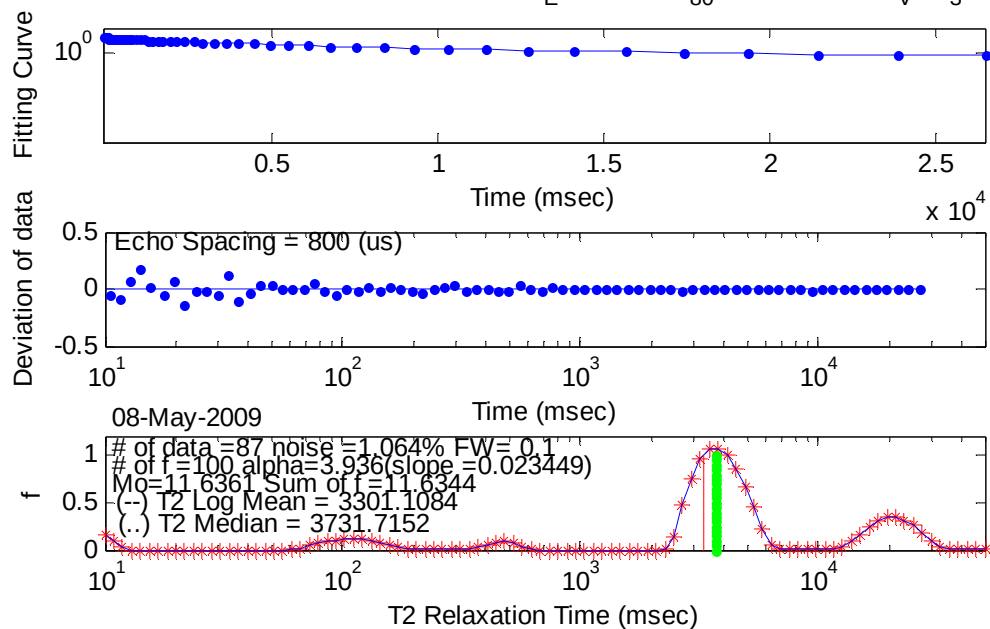


Figure A.9: CPMG response and T_2 distribution for C1 80-C2 20 mixtures at $P = 2122$ psig

Figure 2. in Tpost.m where filename = ME80_E T20CPMG5_1 2_0 9P1900SNR100_V AC_3PURGE

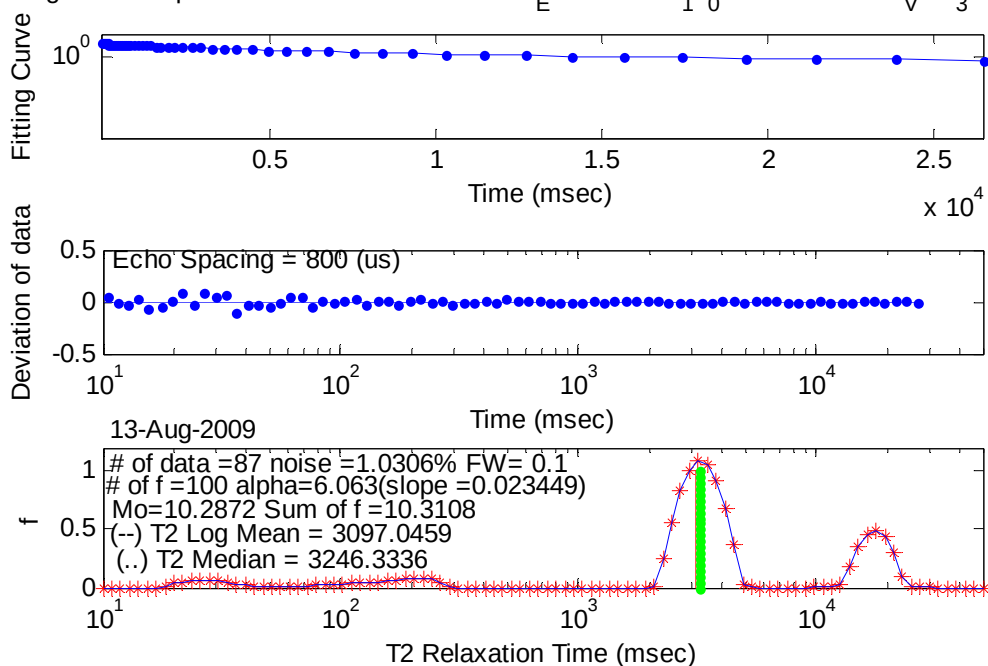


Figure A.10: CPMG response and T_2 distribution for C1 80-C2 20 mixtures at $P = 1904$ psig

Figure 2. in Tpost.m where filename = ME80_E T20CPMG5_1 4_0 9P1400SNR50_V AC_3PURGE

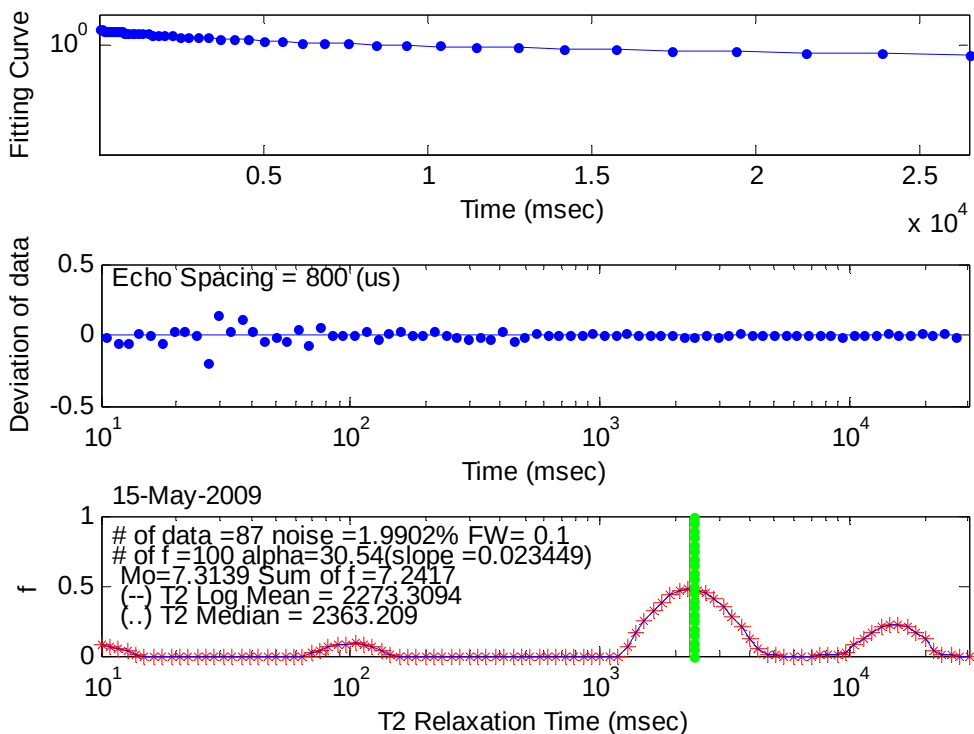


Figure A.11: CPMG response and T_2 distribution for C1 80-C2 20 mixtures at $P = 1399$ psig

Figure 2. in Tpost.m where filename = ME80_ET20CPMG5₁5₀9P1400SNR100_VAC₃PURGE

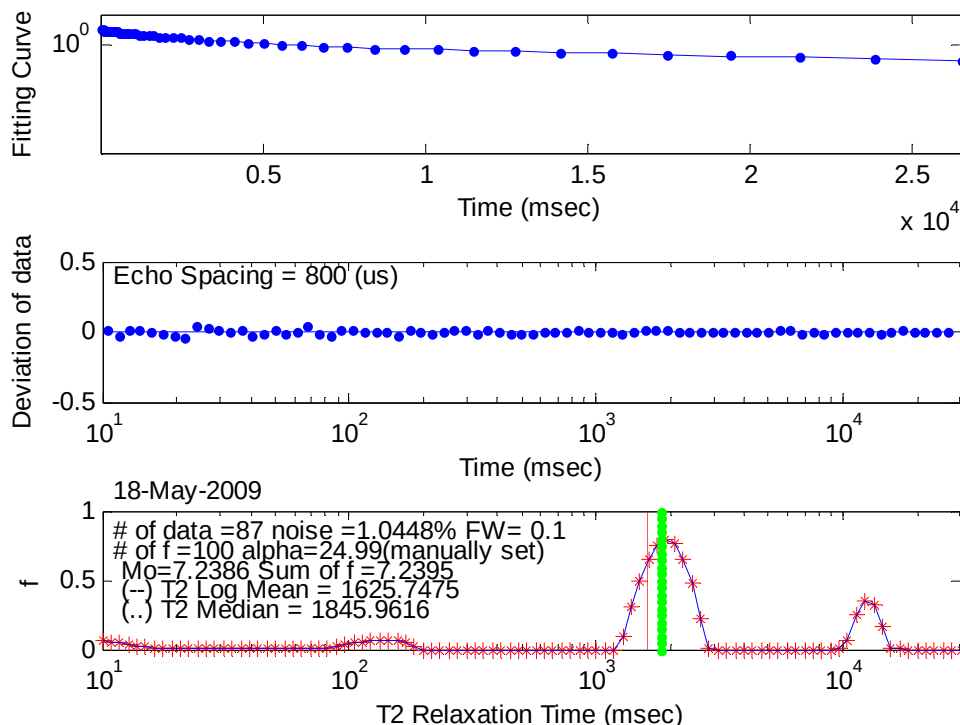


Figure A.12: CPMG response and T_2 distribution for C1 80-C2 20 mixtures at $P = 1397$ psig

Figure 2. in Tpost.m where filename = ME80_ET20CPMG5₂0₀9P1200SNR50_VAC₃PURGE

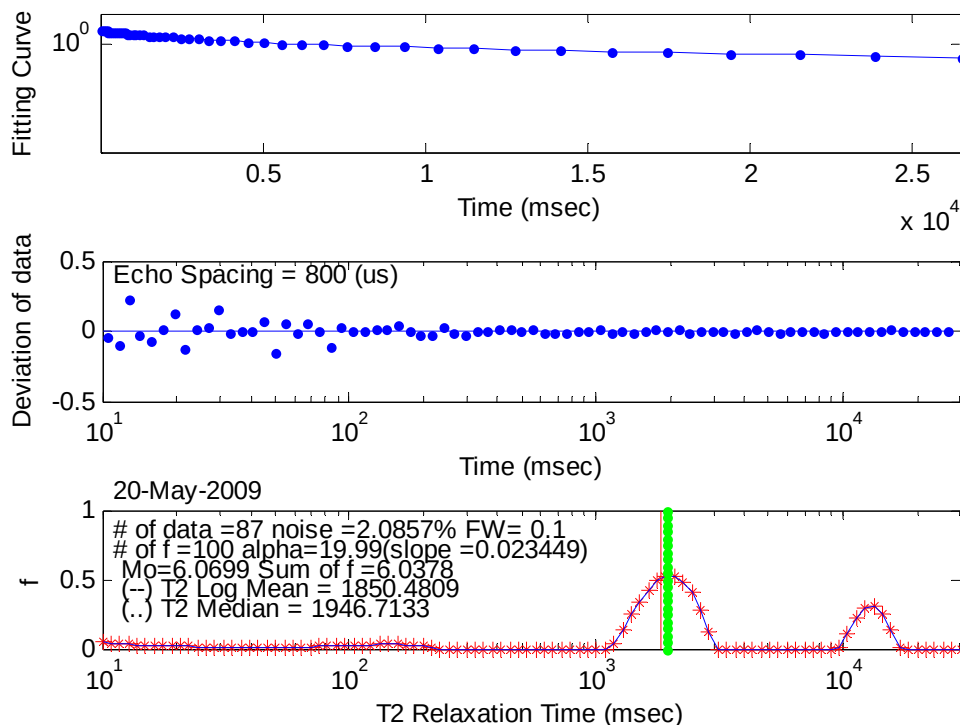


Figure A.13: CPMG response and T_2 distribution for C1 80-C2 20 mixtures at $P = 1204$ psig

Figure 2. in Tpost.m where filename = ME80_ET20CPMG5₂0₉P1200SNR100_VAC₃PURGE

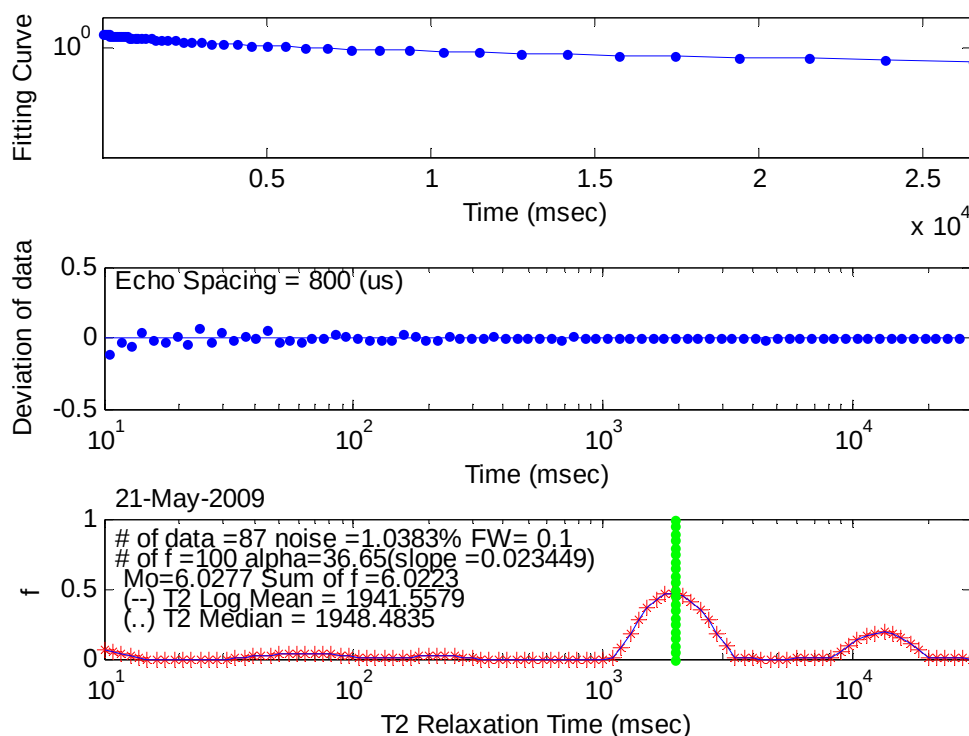


Figure A.14: CPMG response and T_2 distribution for C1 80-C2 20 mixtures at $P = 1202$ psig

A.2 C1 50-C2 50 Mixtures

The preparation conditions for C1 50-C2 50 mixtures are as follows. First, the evacuation time for the manifold and pressure vessel is approximately 140 minutes. The system is then pressured to low pressures of C1 50-C2 50 (approximately 520 psig) and purged to approximately 25 psig. This is repeated for three rounds. Finally the system is pressurized to approximately 1670 psig. For each subsequent measurement, the pressure is reduced and further NMR measurements are made. These measurements will now be detailed in tables and figures, in the same order as they appeared in Table 6.5

A.2.1 Tables for C1 50-C2 50

The following tables show acquisition parameters for inversion recovery and CPMG measurements of C1 50-C2 50 mixtures, analogous to the tables for C1 80-C2 20 mixtures.

Table A.3: Acquisition conditions and parameters for C1 50-C2 50 NMR inversion recovery measurements

Pressure (psig)	ΔP (psi), pressure variability	NS	RD (s)
1665	± 5	8	167
1446	± 4	8	167
1437	± 6	8	114
1241	± 2	8	114
1092	± 1	16	114

Table A.4: Acquisition conditions and parameters for C1 50-C2 50 NMR CPMG measurements

Pressure (psig)	ΔP (psi), pressure variability	NECH	NS	RD (s)	SNR
1674	± 2	34816	56	186	100
1668	± 2	34816	64	186	100
1443	± 5	34816	36	186	N/A
1450	± 2	34816	68	186	100
1246	± 4	34816	104	186	100
1094	± 2	34816	40	150	50
1092	± 1	34816	164	150	100

Notice that in Tables A.3 and A.4, the values of RD are higher than corresponding tables for C1 80-C2 20. This is because these measurements were performed with extended time versions of the inversion recovery and CPMG sequences, called CPMGRDHI and IRECRDHI respectively. These sequences allow an extra 107 s to effectively be added to RD *at the beginning of*

each scan in the sequence, in the form of three time durations called D5, D6, and D7. Each quantity can be up to 50s, and the sum is limited to approximately 107s. In addition to providing more time for signal repolarization, this additional time allows one to shorten the repolarization time at the end of the pulse sequence. This is useful in inversion recovery because it permits longer wait times between inversion and read pulses since the time not occupied by D5, D6, and D7 is also constrained in total to 107s.

A.2.2 Plots for C1 50-C2 50

The following plots show the fit of inversion recovery or CPMG measurement and the resultant distributions, with calculated values appearing in the plot.

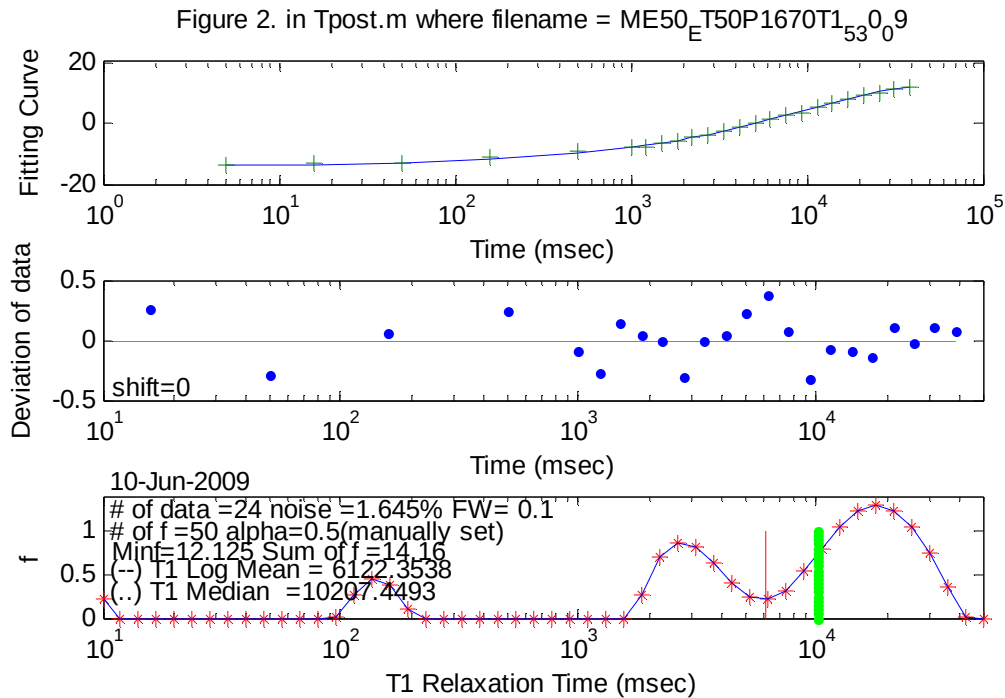


Figure A.15: Inversion recovery response and T_1 distribution for C1 50-C2 50 mixture at $P = 1665$ psig

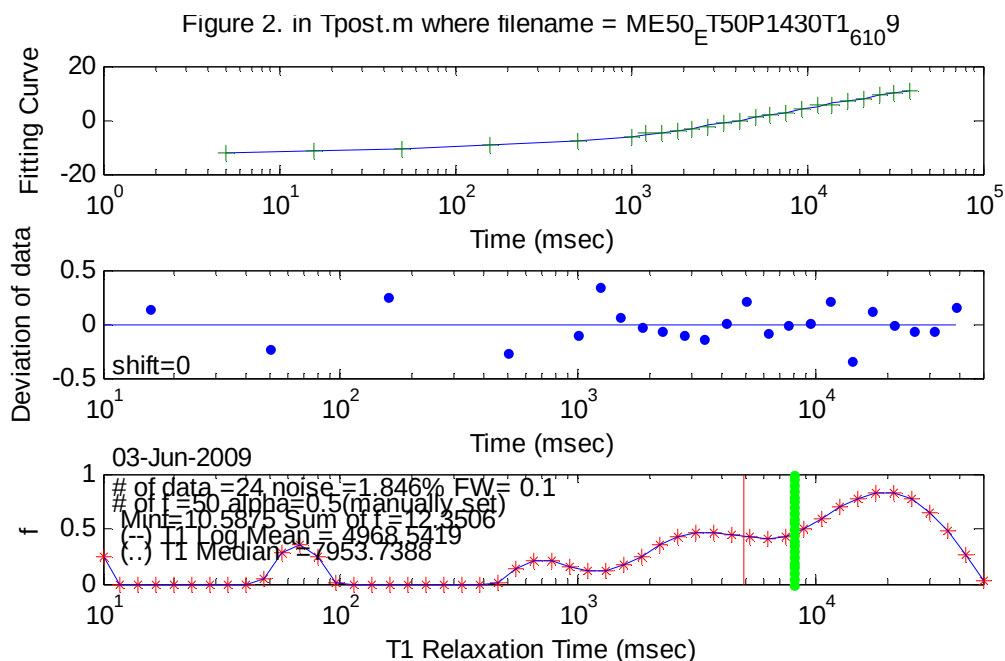


Figure A.16: Inversion recovery response and T_1 distribution for C1 50-C2 50 mixture at $P = 1446$ psig

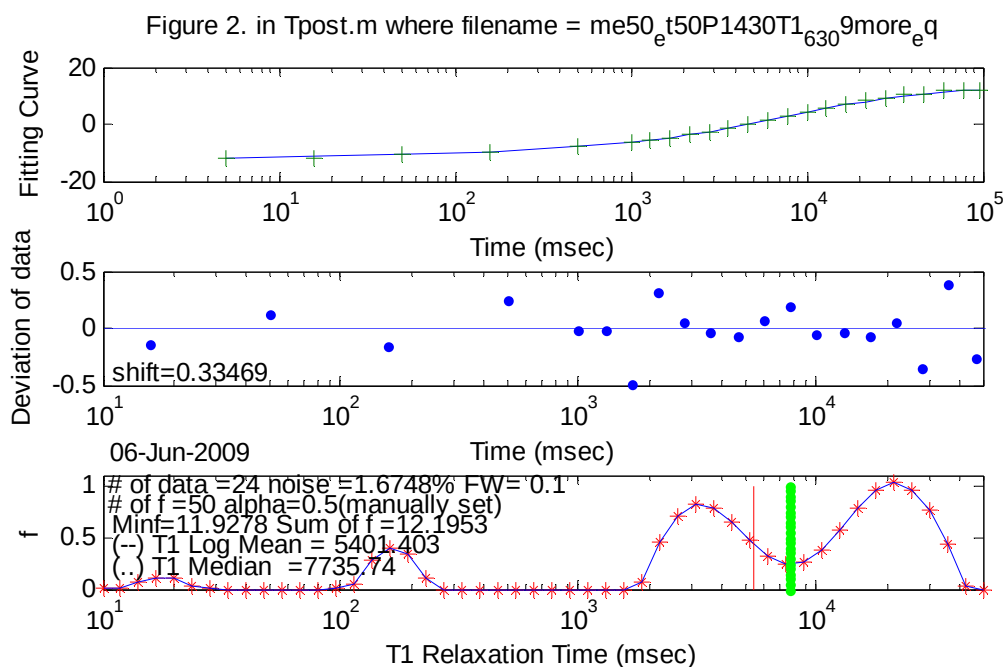


Figure A.17: Inversion recovery response and T_1 distribution for C1 50-C2 50 mixture at $P = 1437$ psig

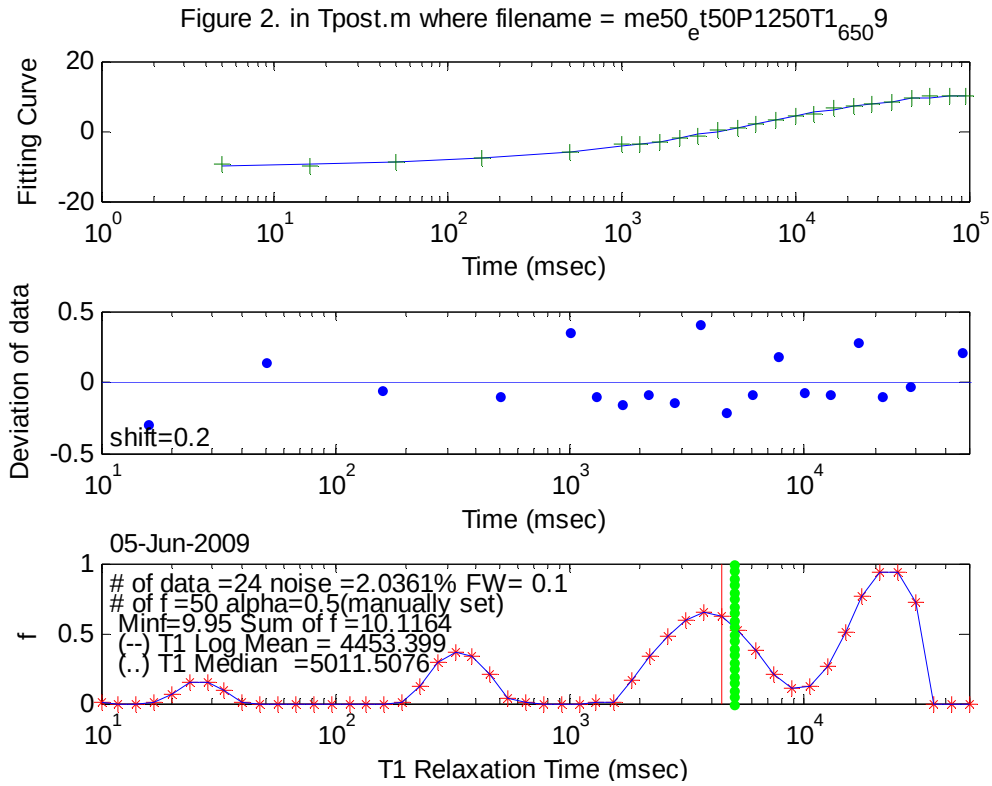


Figure A.18: Inversion recovery response and T_1 distribution for C1 50-C2 50 mixture at $P = 1241$ psig

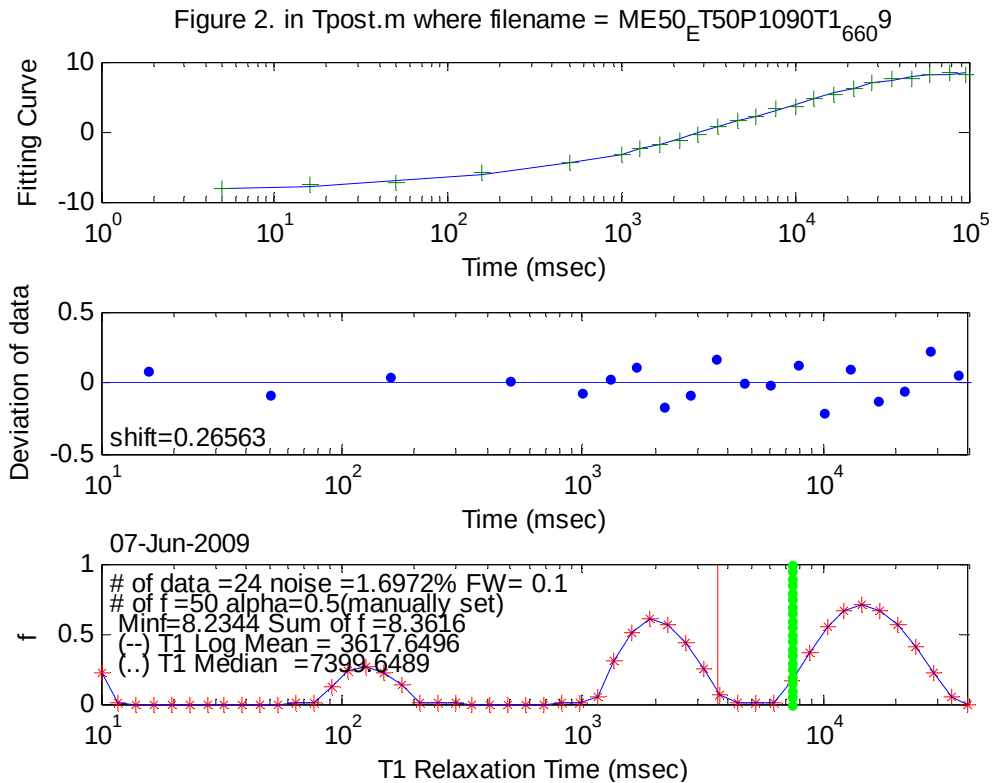


Figure A.19: Inversion recovery response and T_1 distribution for C1 50-C2 50 mixture at $P = 1092$ psig

Figure 2. in Tpost.m where filename = ME50_ET50CPMG5₂0₉P1670SNR100_√AC₃PURGE

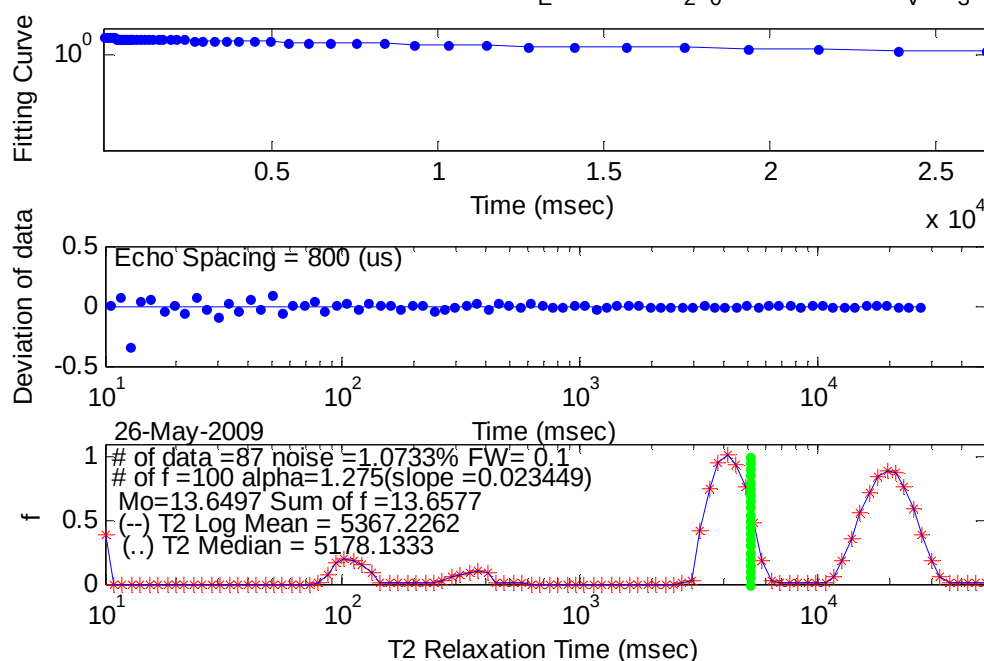


Figure A.20: CPMG response and T_2 distribution for C1 50-C2 50 mixture at $P = 1674$ psig

Figure 2. in Tpost.m where filename = ME50_ET50CPMG5₃0₉P1670SNR100_√AC₃PURGE

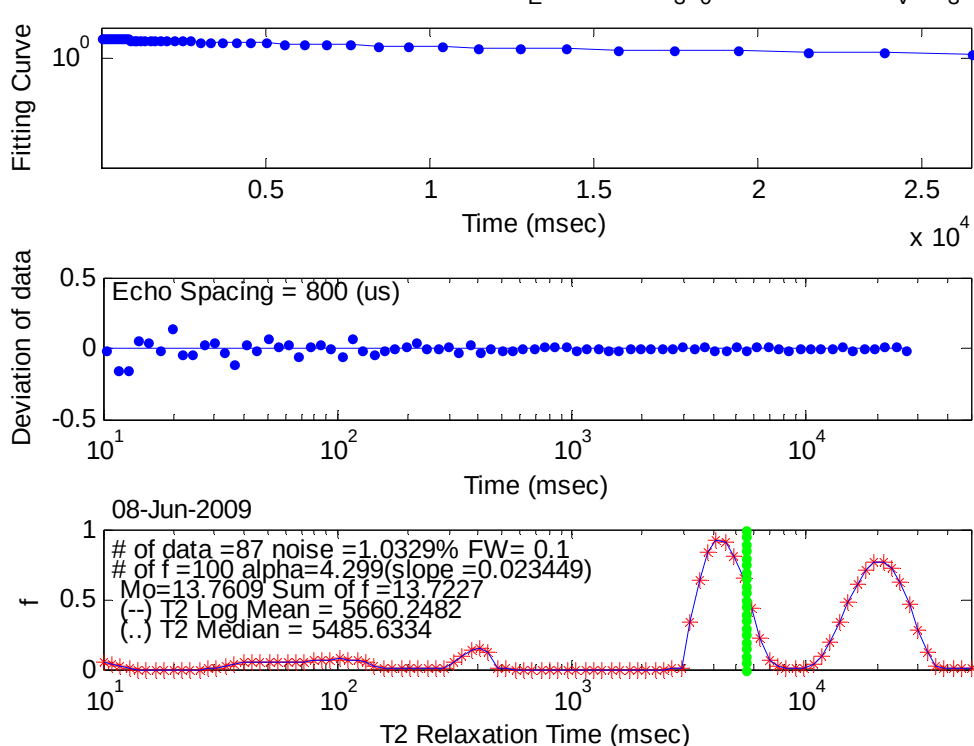


Figure A.21: CPMG response and T_2 distribution for C1 50-C2 50 mixture at $P = 1668$ psig

Figure 2. in Tpost.m where filename = ME50_ET50CPMG6₁₀9P1440NS36_VAC₃PURGE

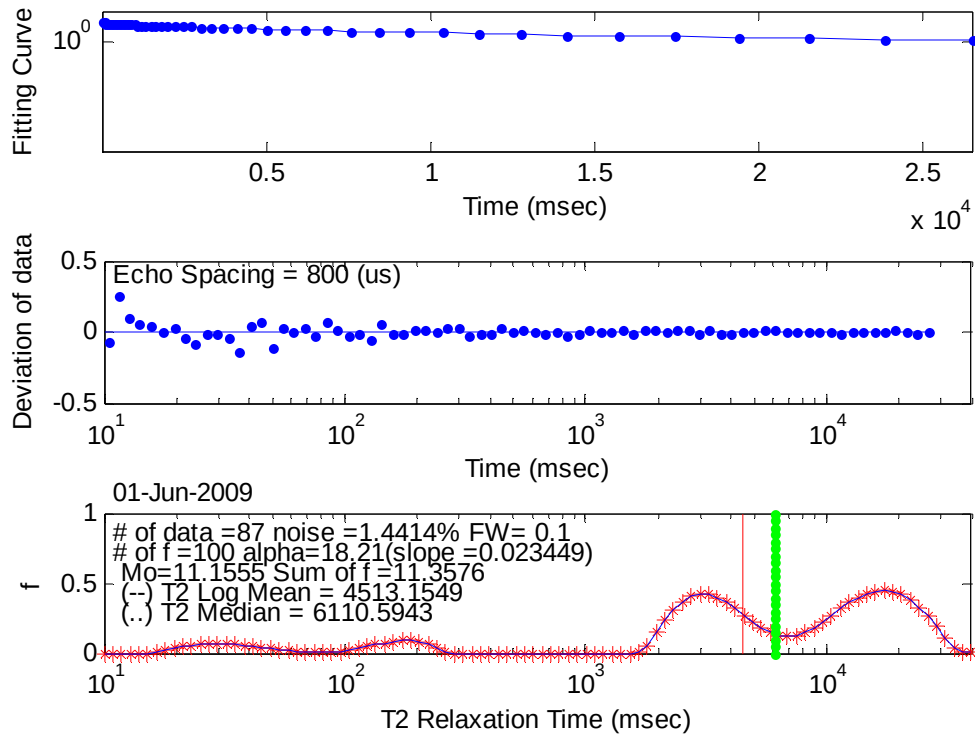


Figure A.22: CPMG response and T_2 distribution for C1 50-C2 50 mixture at $P = 1443$ psig

Figure 2. in Tpost.m where filename = ME50_ET50CPMG6₁₀9P1430SNR100_VAC₃PURGE

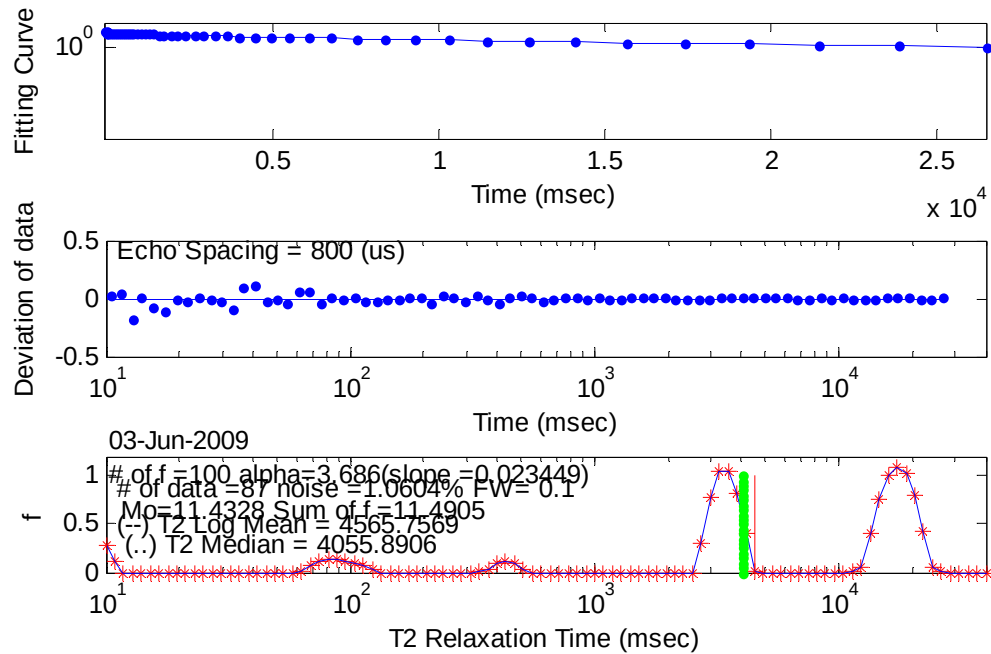


Figure A.23: CPMG response and T_2 distribution for C1 50-C2 50 mixture at $P = 1450$ psig

Figure 2. in Tpost.m where filename = ME50_ET50CPMG6₄₀9P1250SNR100_VAC₃PURGE

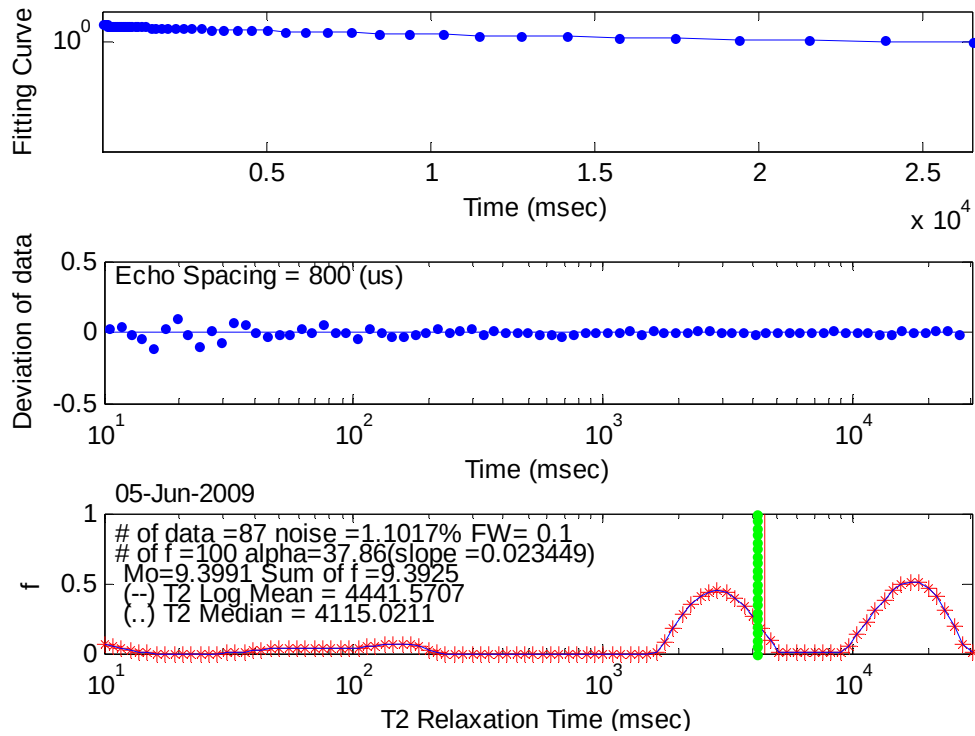


Figure A.24: CPMG response and T_2 distribution for C1 50-C2 50 mixture at $P = 1246$ psig

Figure 2. in Tpost.m where filename = me50_et50CPMG6₆₀9P1090SNR50_Vac₃PURGE

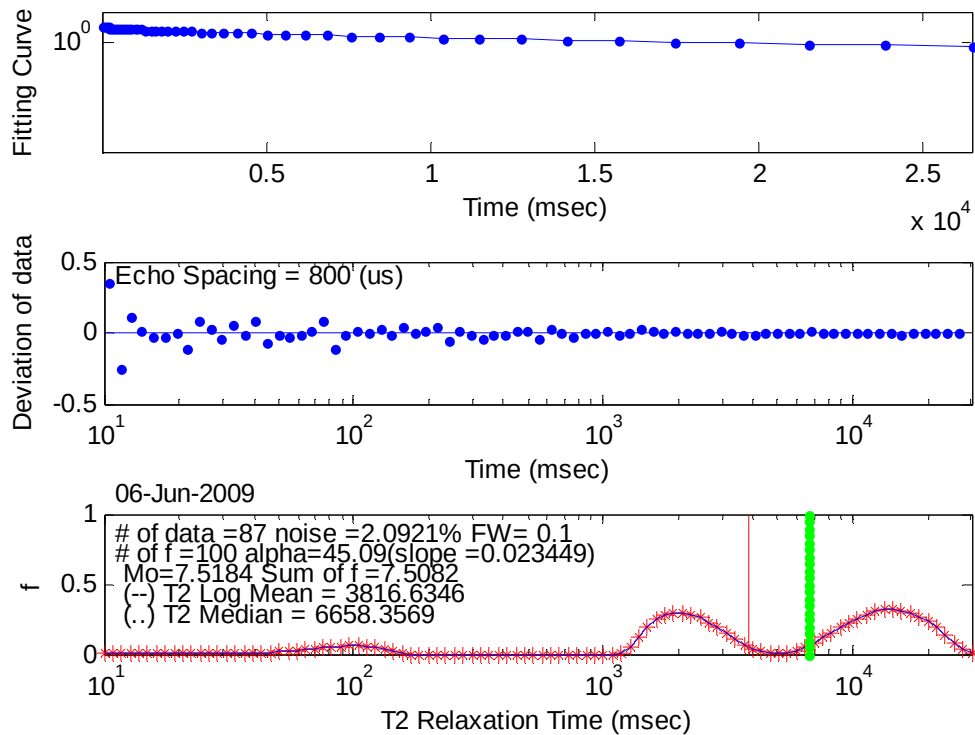


Figure A.25: CPMG response and T_2 distribution for C1 50-C2 50 mixture at $P = 1094$ psig

Figure 2. in Tpost.m where filename = ME50_E T50CPMG6_60_9P1090SNR100_V AC_3PURGE

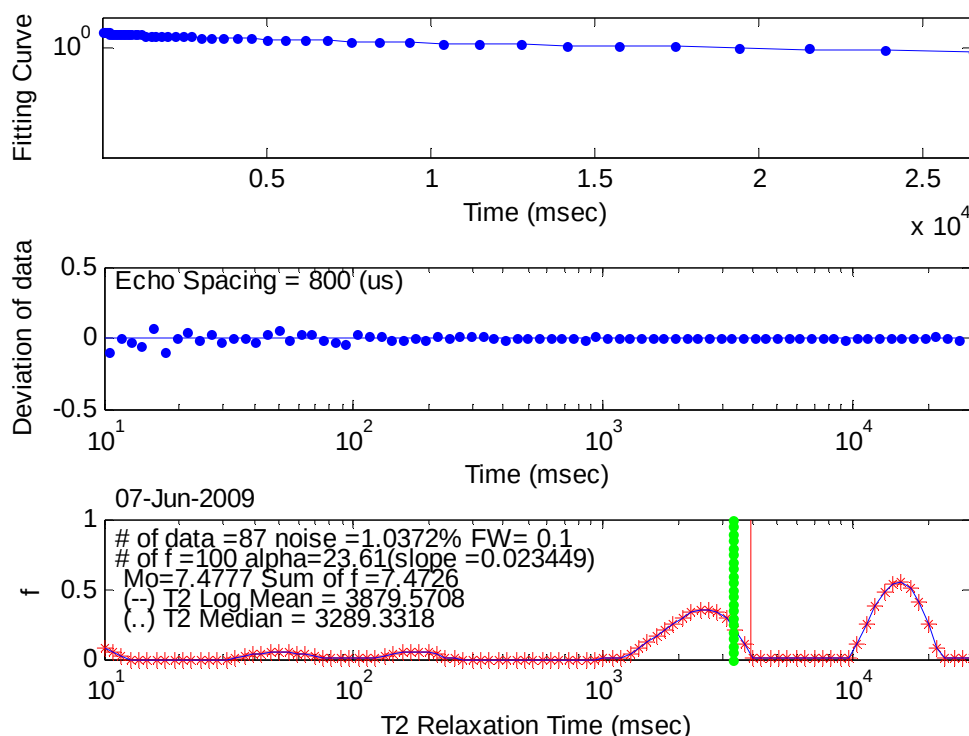


Figure A.26: CPMG response and T_2 distribution for C1 50-C2 50 mixture at $P = 1092$ psig

A.3 Ethane

The preparation conditions for ethane are as follows. First, the manifold and pressure vessel were evacuated for approximately 120 minutes. The system is then pressured to low pressures of ethane (approximately 450 psig) and purged to approximately 30 psig. This is repeated for three rounds. Finally the system is pressurized to approximately 610 psig. For each subsequent measurement, the pressure is reduced and further NMR measurements are made. These measurements will now be detailed in tables and figures, in the same order as they appeared in Table 6.3

A.3.1 Tables for Ethane

The following tables show acquisition parameters for inversion recovery and CPMG measurements of ethane vapor. The two tables resemble the style of those presented for the mixtures shown above. The next section shows the time domain fits and relaxation distributions associated with Tables A.5 and A.6 in the same order as above, first for inversion recovery and then for the CPMG. Additional parameters for the ethane experiments appears in those figures.

Table A.5: Acquisition conditions and parameters for ethane NMR inversion recovery measurements

Pressure (psig)	ΔP (psi), pressure variability	NS	RD (s)
614	± 2	16	60
606	± 4	32	45
603	± 4	16	60
579	± 3	16	60
578	± 3	16	60
562	± 3	16	60
562	± 3	16	60
521	± 2	16	60
519	± 2	16	60
484	± 4	16	60

Table A.6: Acquisition conditions and parameters for ethane NMR CPMG measurements

Pressure (psig)	ΔP (psi), pressure variability	NECH	NS	RD (s)	SNR
607	± 5	34816	400	60	N/A
602	± 4	34816	400	45	84
575	± 1	34816	100	60	N/A
580	± 3	34816	300	60	100
563	± 1	34816	76	60	N/A
565	± 2	34816	352	60	100
519	± 1	34816	400	60	N/A
488	± 2	34816	400	60	N/A

A.3.2 Plots for Ethane

Figure 2. in Tpost.m where filename = C2H6P600T1₄₇₀⁹

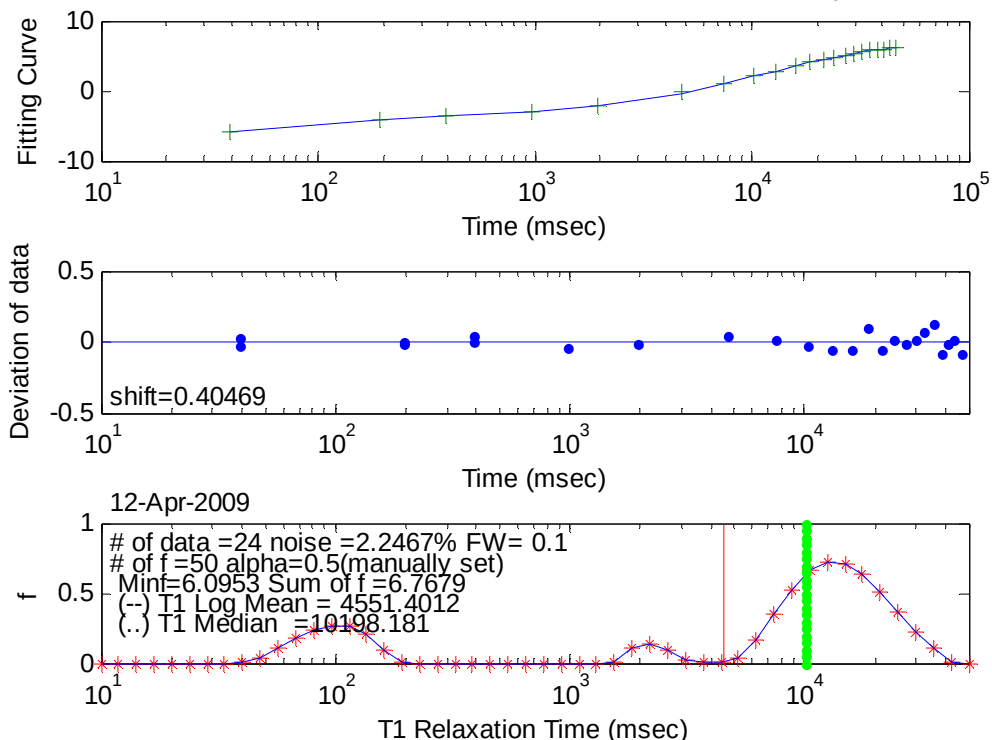


Figure A.27: Inversion recovery and T_1 distribution for ethane at $P = 614$ psig

Figure 2. in Tpost.m where filename = C2H6P600T1₄₂₀⁹

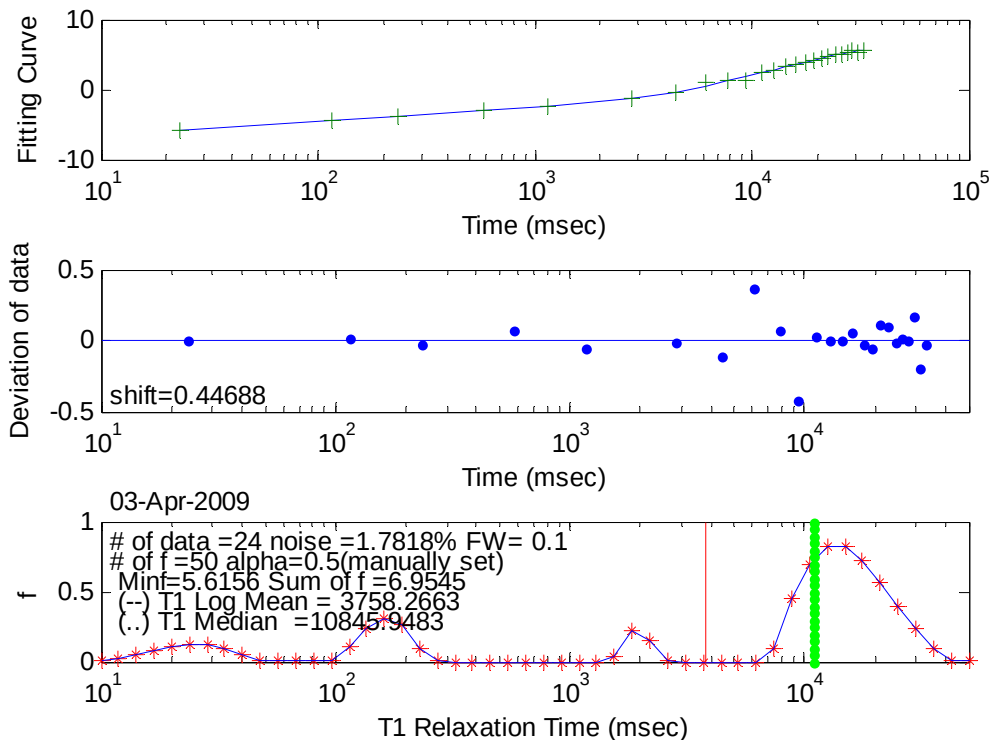


Figure A.28: Inversion recovery and T_1 distribution for ethane at $P = 606$ psig

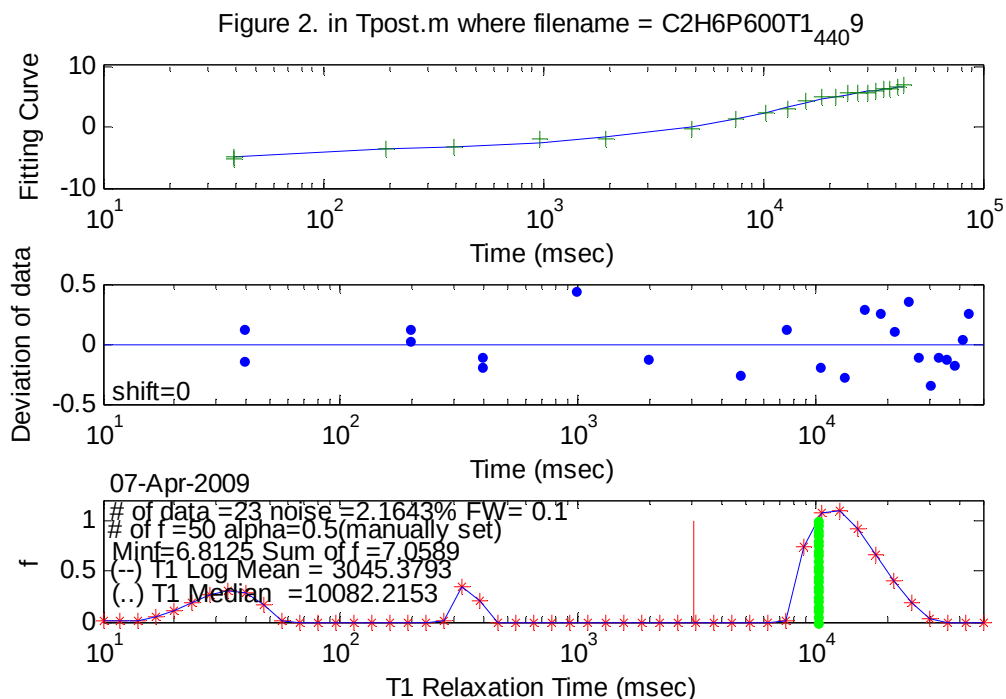


Figure A.29: Inversion recovery and T_1 distribution for ethane at $P = 603$ psig

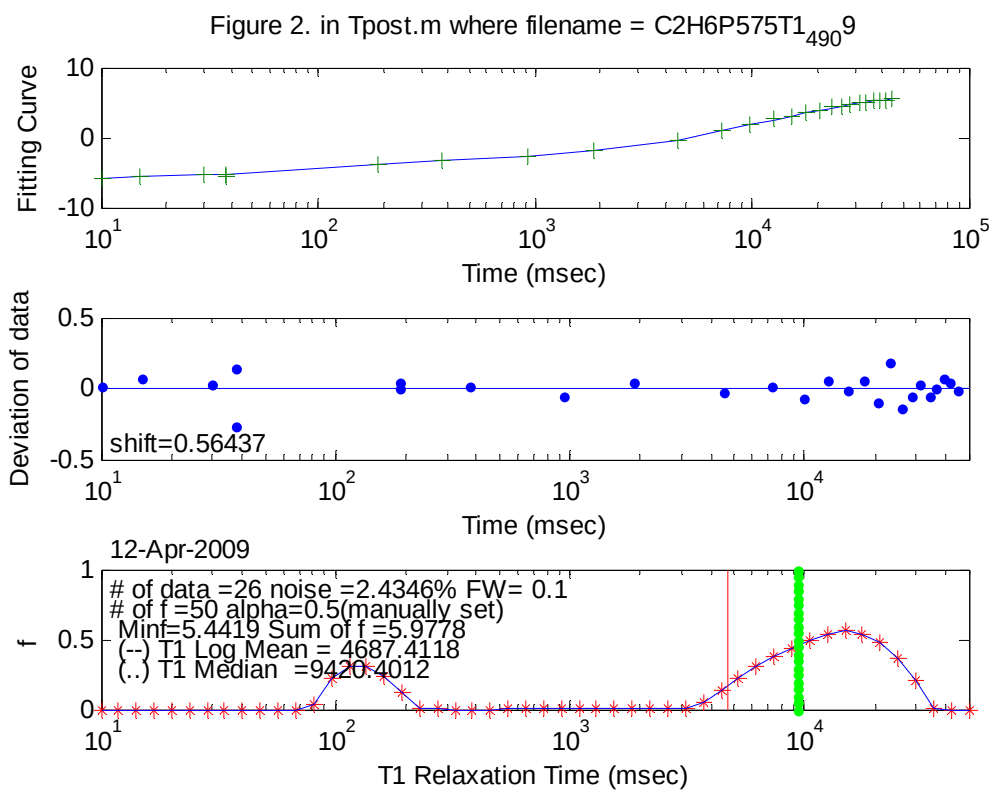


Figure A.30: Inversion recovery and T_1 distribution for ethane at $P = 579$ psig

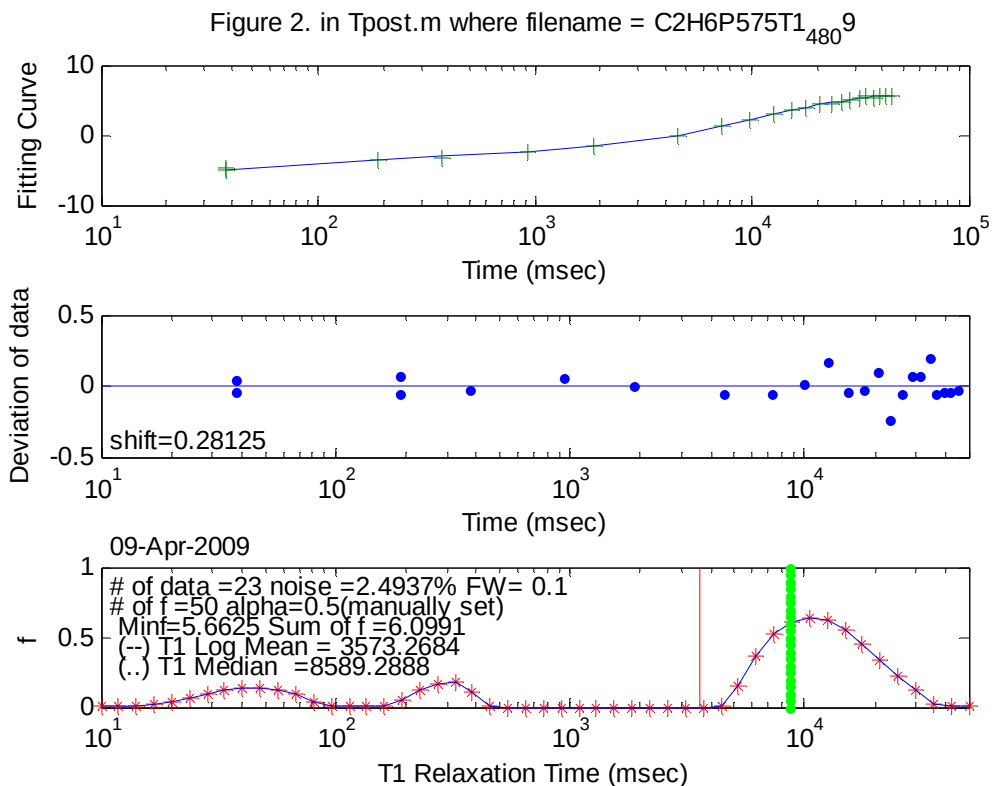


Figure A.31: Inversion recovery and T_1 distribution for ethane at $P = 578$ psig

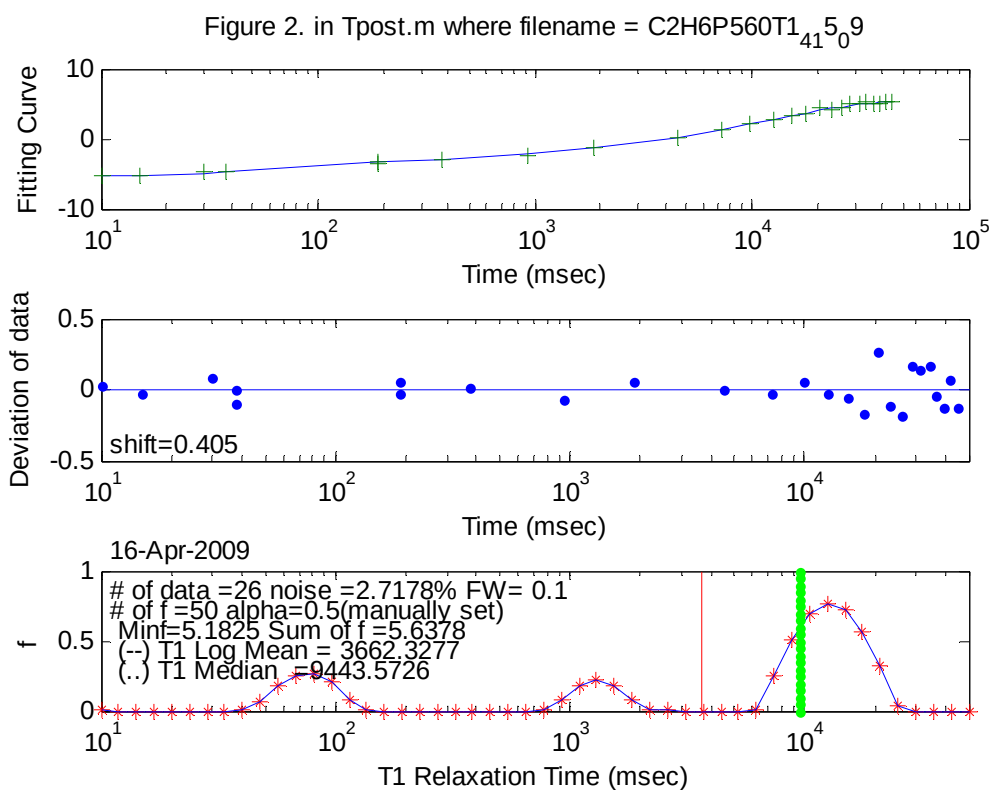


Figure A.32: Inversion recovery and T_1 distribution for ethane at $P = 562$ psig

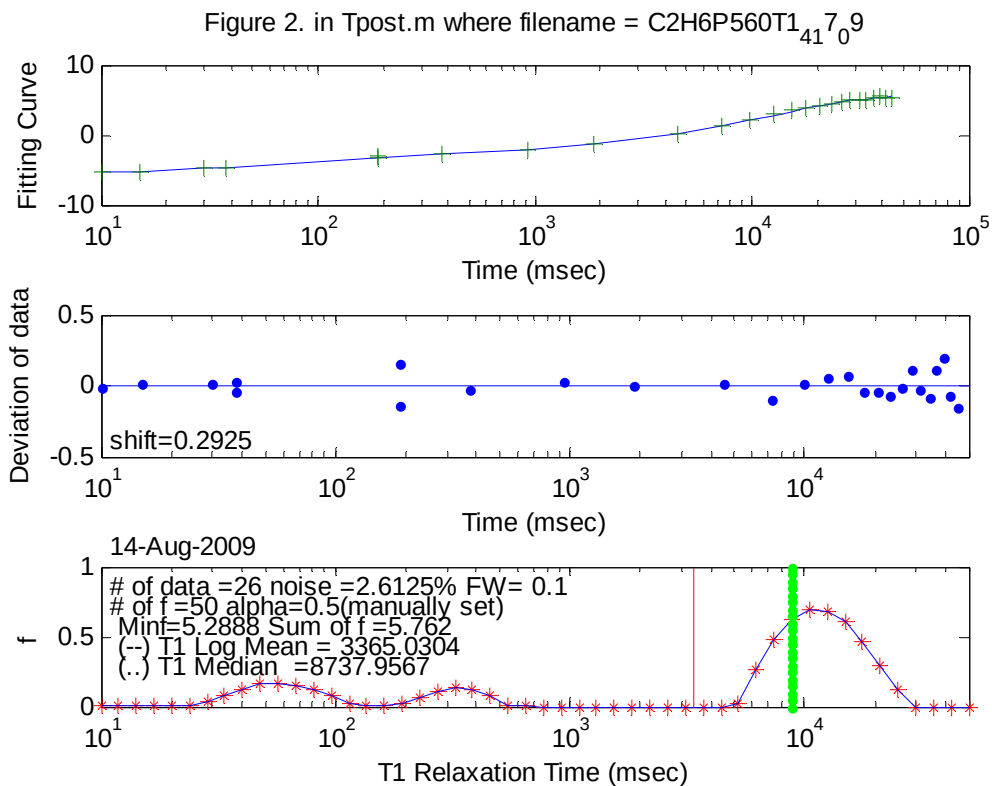


Figure A.33: Inversion recovery and T_1 distribution for ethane at $P = 562$ psig

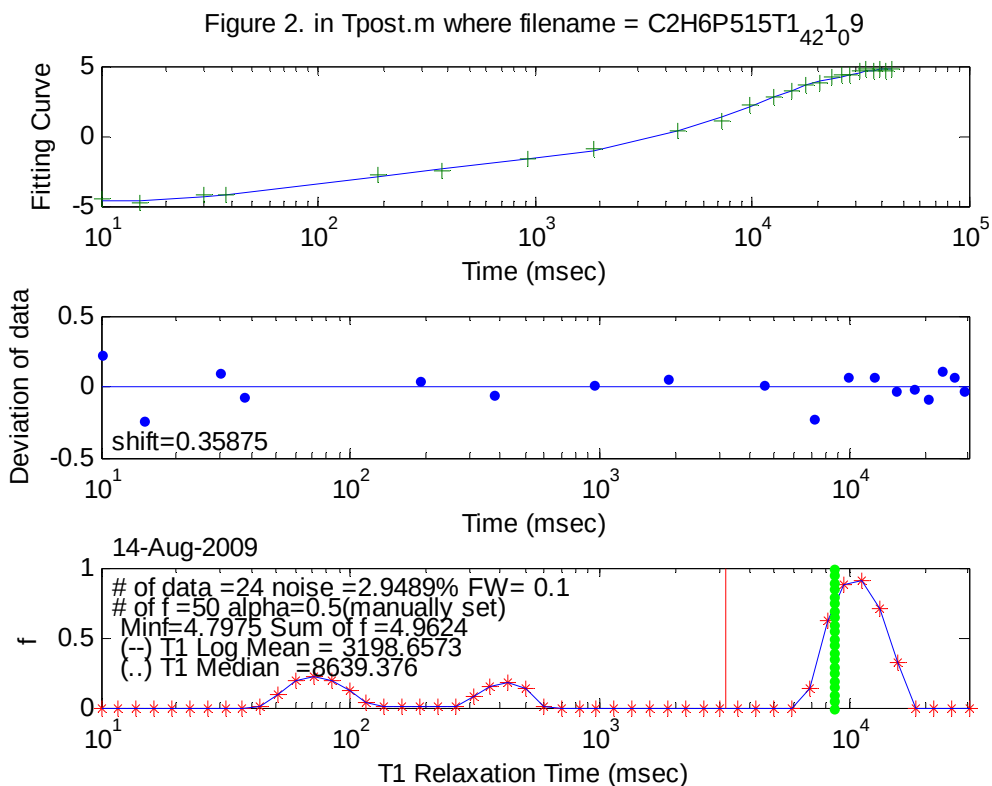


Figure A.34: Inversion recovery and T_1 distribution for ethane at $P = 521$ psig

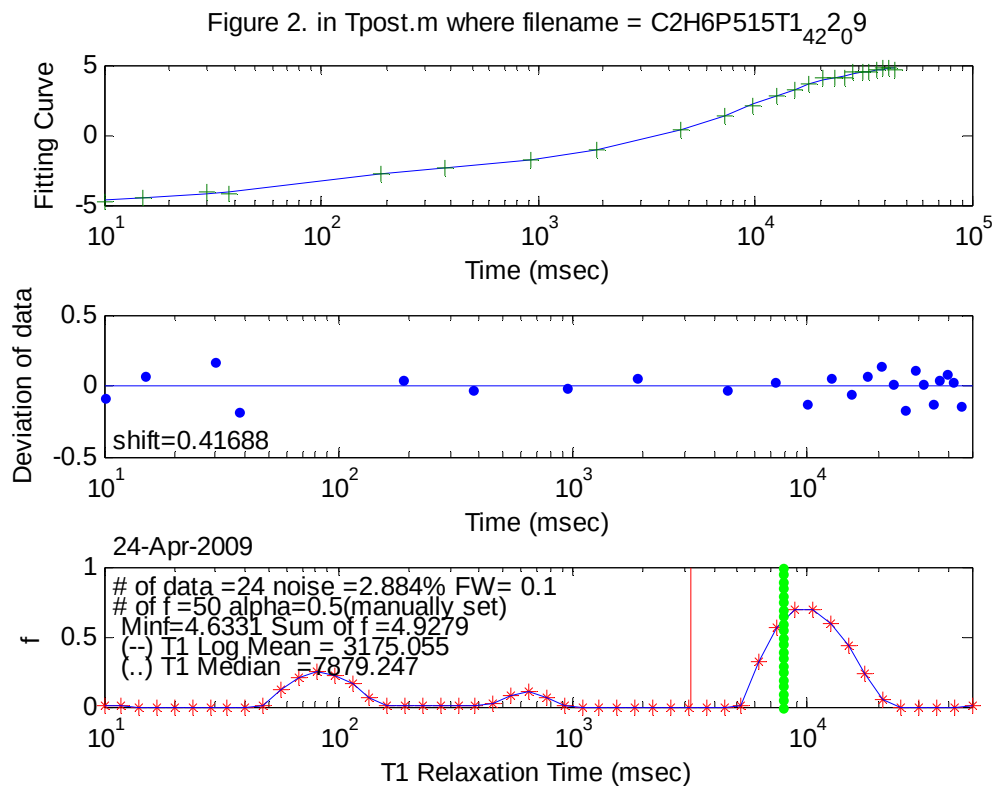


Figure A.35: Inversion recovery and T_1 distribution for ethane at $P = 519$ psig

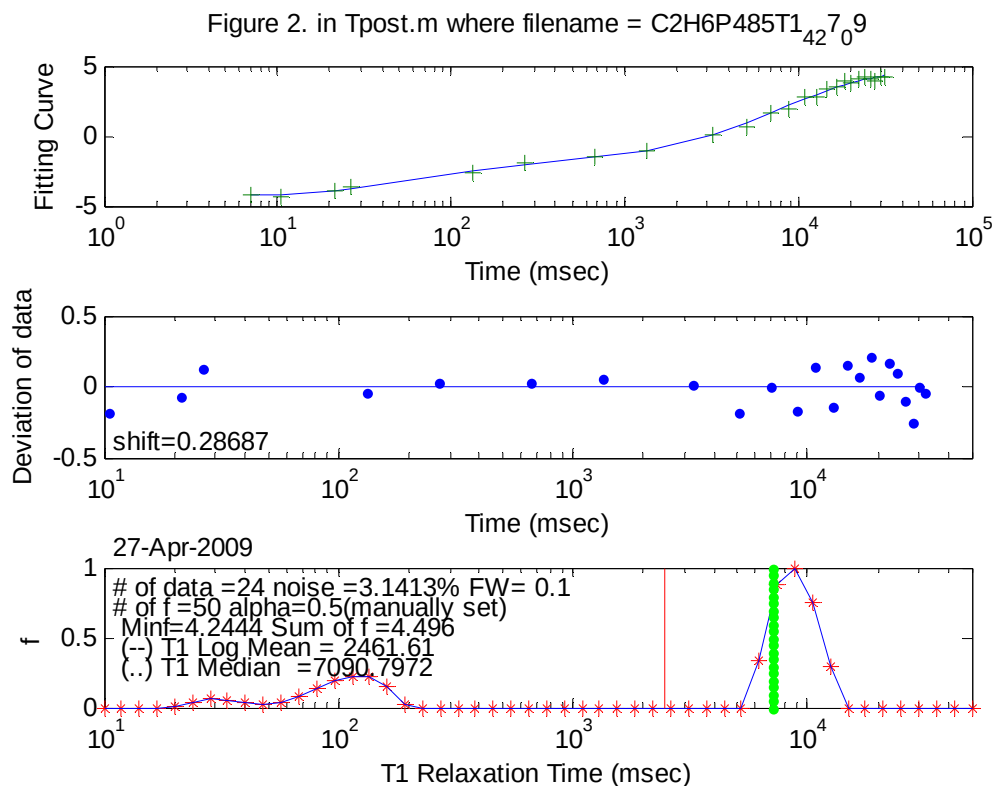


Figure A.36: Inversion recovery and T_1 distribution for ethane at $P = 484$ psig

Figure 2. in Tpost.m where filename = C2H6CPMG4₃₀9P600SNR50√ac₃PURGE

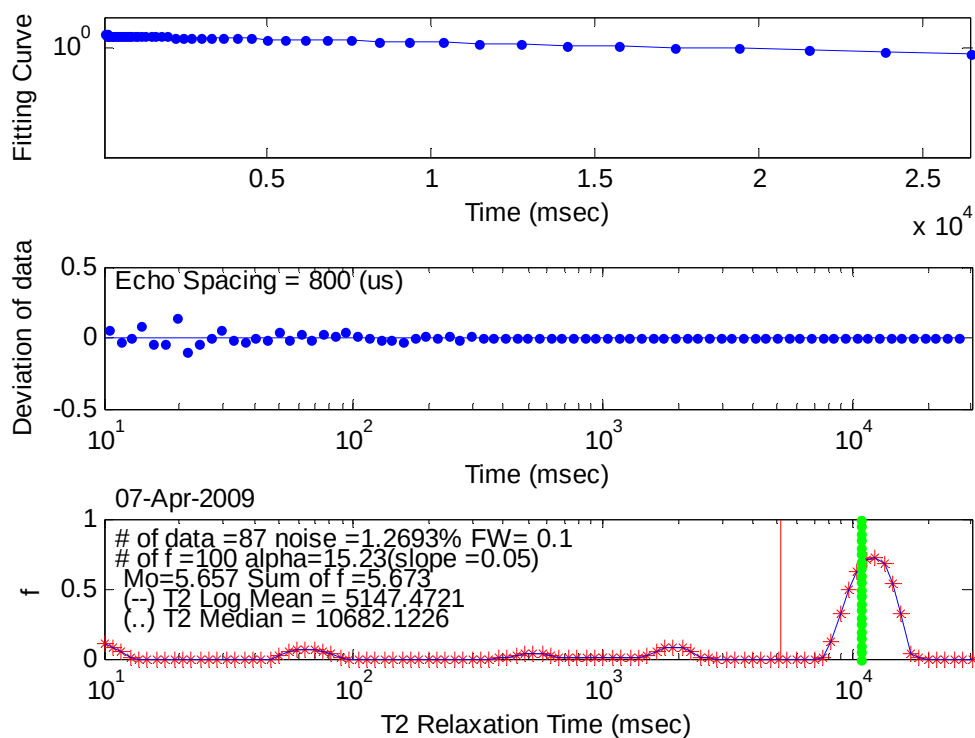


Figure A.37: CPMG response and T_2 distribution for ethane at $P = 607$ psig

Figure 2. in Tpost.m where filename = C2H6CPMG4₁₀9P600SNR84√ac₃PURGE

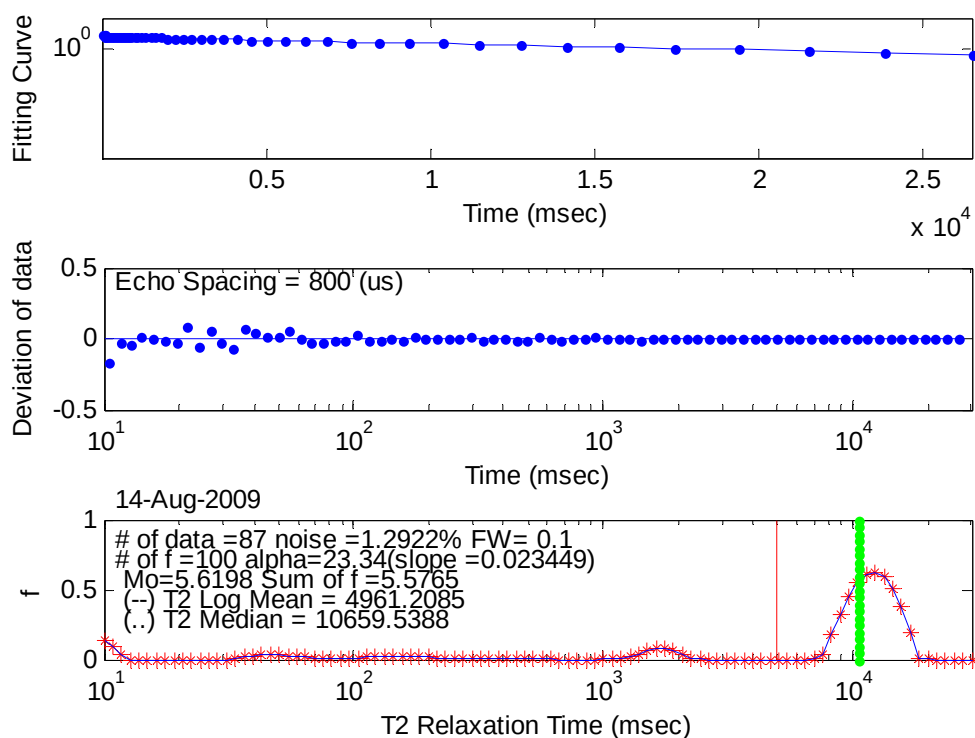


Figure A.38: CPMG response and T_2 distribution for ethane at $P = 602$ psig

Figure 2. in Tpost.m where filename = C2H6CPMG4₈₀9P575NS100VAC₃PURGE_depressure

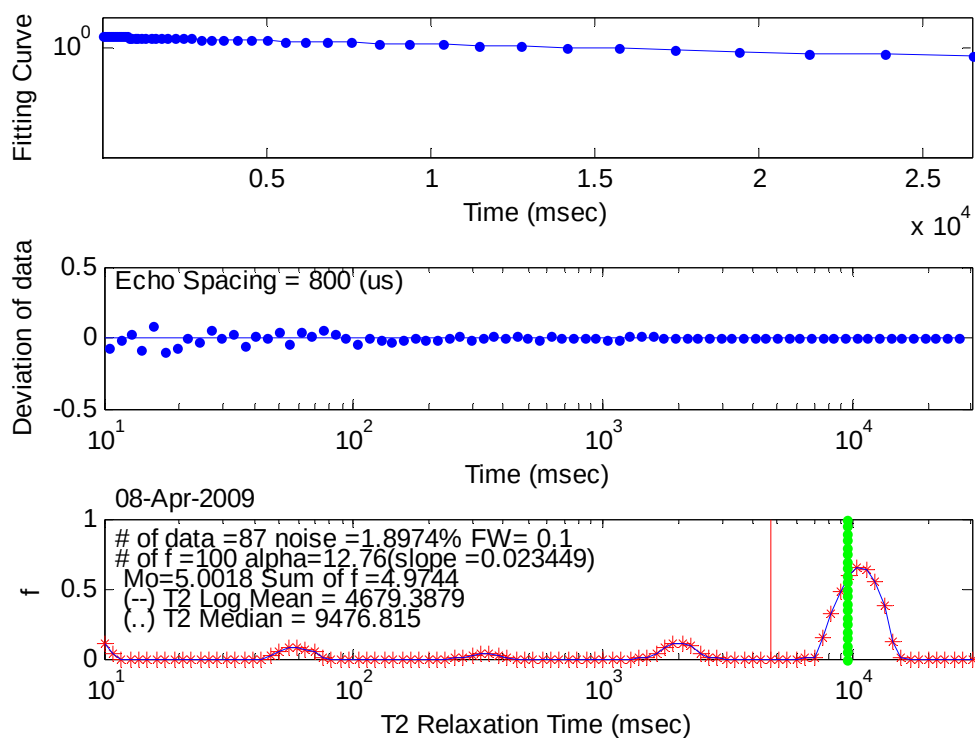


Figure A.39: CPMG response and T_2 distribution for ethane at $P = 575$ psig

Figure 2. in Tpost.m where filename = C2H6CPMG4₈₀9P575NS400VAC₃PURGE

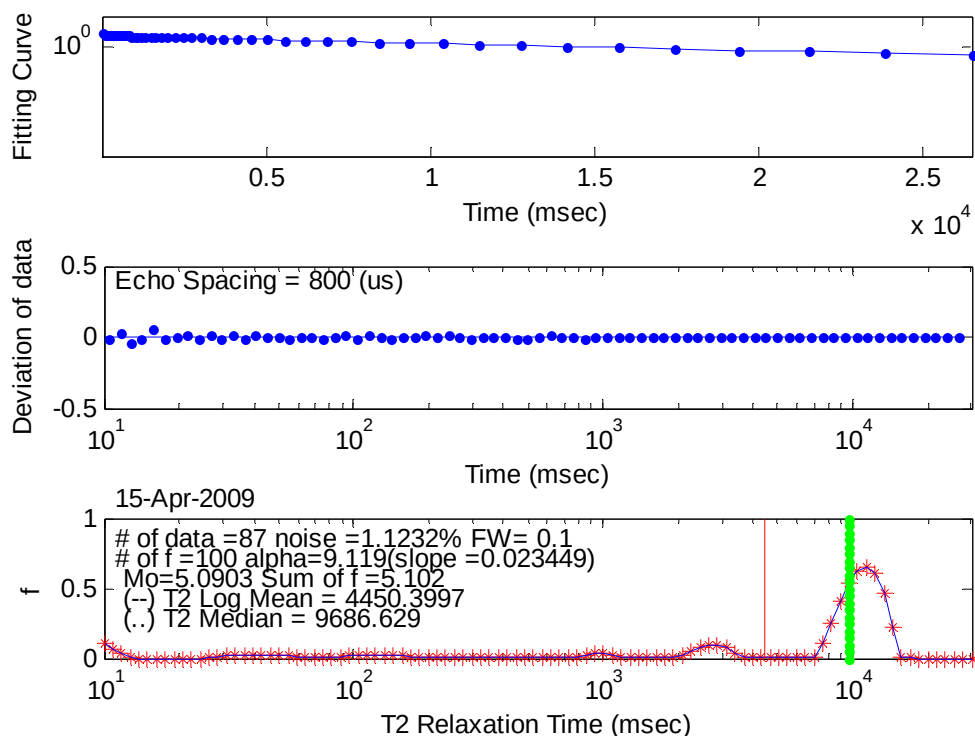


Figure A.40: CPMG response and T_2 distribution for ethane at $P = 580$ psig

Figure 2. in Tpost.m where filename = C2H6CPMG4₁5₀9P560NS100_VAC₃PURGE_depressure

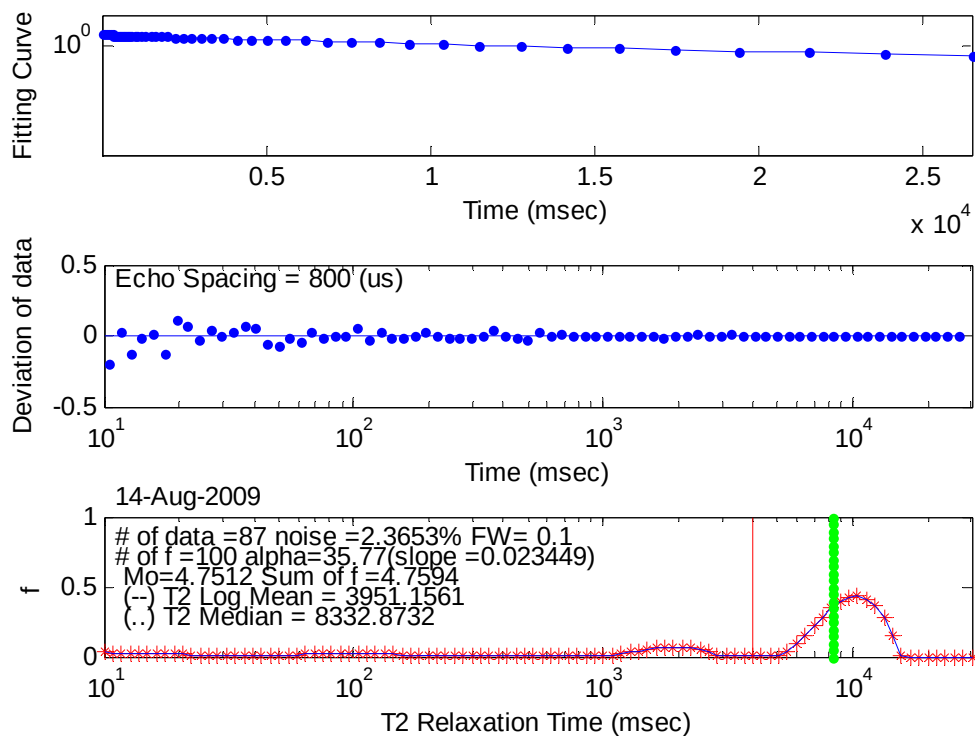


Figure A.41: CPMG response and T_2 distribution for ethane at $P = 563$ psig

Figure 2. in Tpost.m where filename = C2H6CPMG4₁5₀9P560NS400_VAC₃PURGE

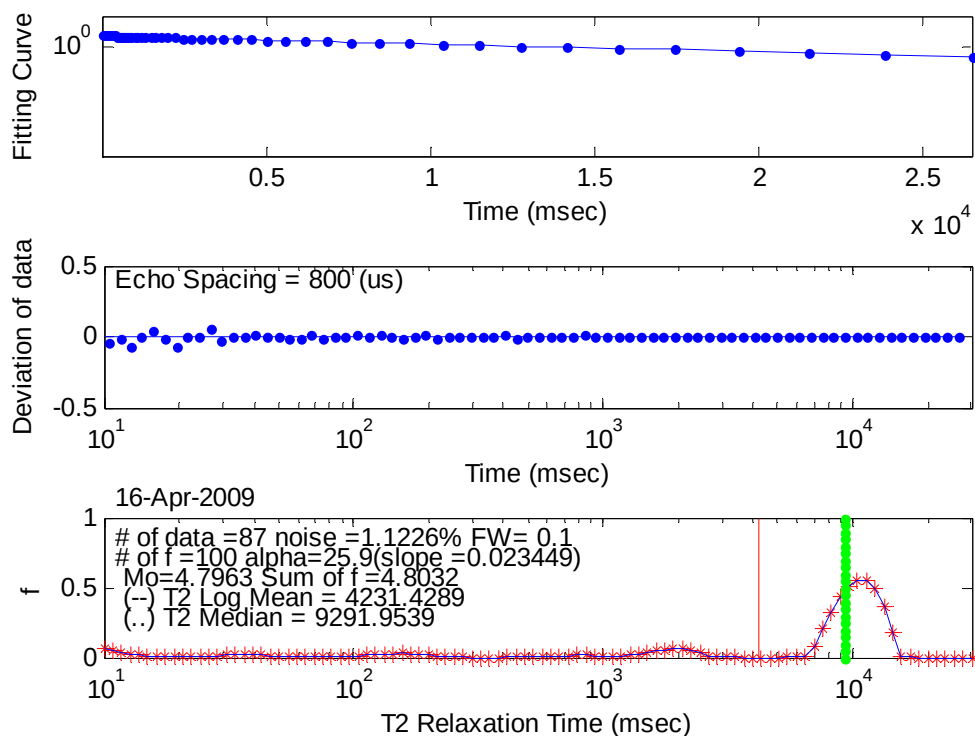


Figure A.42: CPMG response and T_2 distribution for ethane at $P = 565$ psig

Figure 2. in Tpost.m where filename = C2H6CPMG4₂0₉P515SNR50_√AC₃PURGE

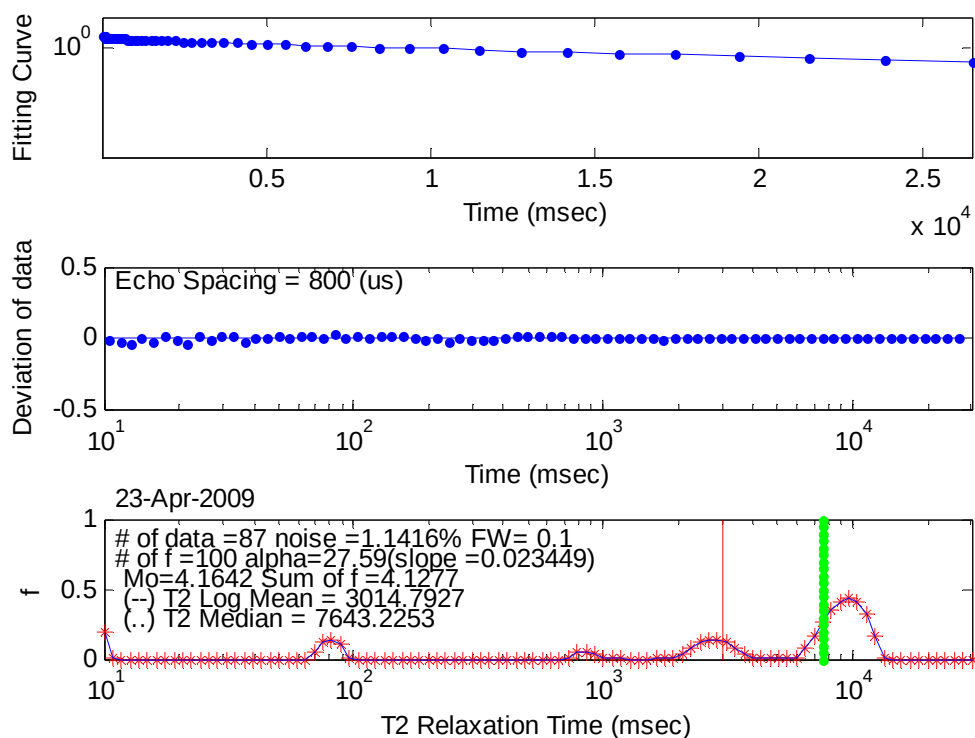


Figure A.43: CPMG response and T_2 distribution for ethane at $P = 519$ psig

Figure 2. in Tpost.m where filename = C2H6CPMG4₂4₀9P485NS400_√AC₃PURGE

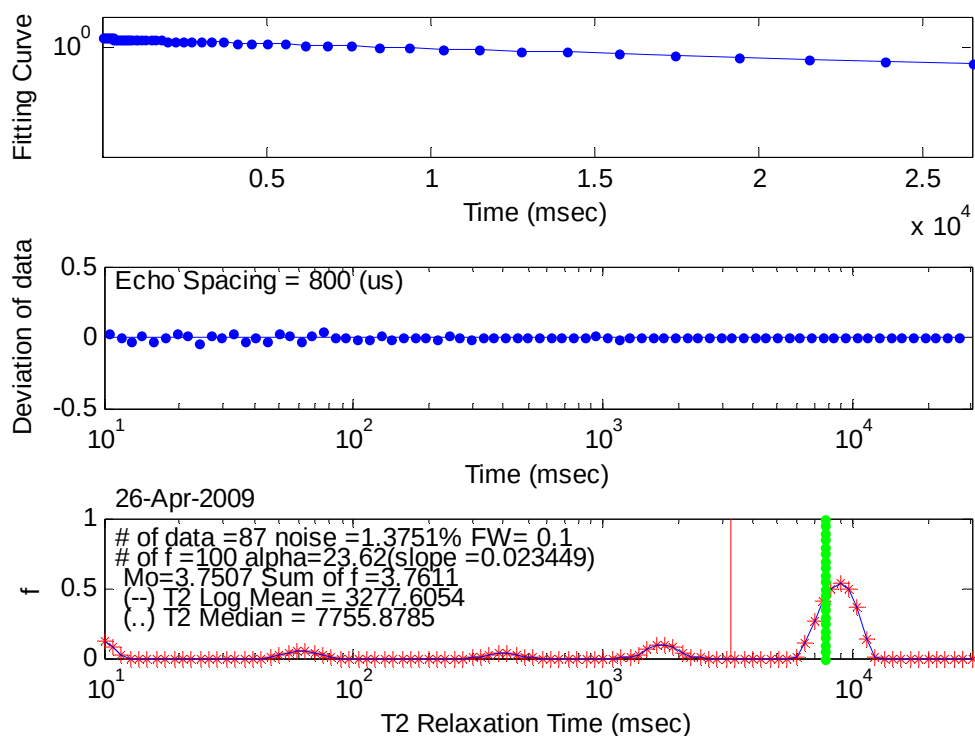


Figure A.44: CPMG response and T_2 distribution for ethane at $P = 488$ psig

A.4 Methane

For pure methane, only a small subset of the total measurements will be shown. This subset is the group of measurements at the highest values of pressure in this work. Prior to this set of measurements, the manifold and pressure vessel were already prepared with elevated pressures of methane (in a fashion similar to measurements in other sections above). The RUSKA pump is used to attain a pressure of approximately 4000 psig. For subsequent measurements, the pressure is reduced successively and further NMR measurements are made. The examples are presented below.

A.4.1 Tables for Methane

The following tables show acquisition parameters for inversion recovery and CPMG measurements of methane gas. Many of the remaining relevant parameters appear in the graphs in the following section.

Table A.7: *Acquisition conditions and parameters methane NMR inversion recovery measurements*

Pressure (psig)	ΔP (psi), pressure variability	NS	RD (s)
3978	± 8	32	30
3480	± 3	16	30
3479	± 4	16	30
2407	± 2	16	30

Table A.8: Acquisition conditions and parameters for methane NMR CPMG measurements

Pressure (psig)	ΔP (psi), pressure variability	NECH	NS	RD (s)	SNR
3996	± 2	34816	64	30	100
3479	± 4	32768	72	30	100
3011	± 4	32768	104	30	100
2408	± 3	27648	152	30	100

A.4.2 Plots for Methane

NMR data for the methane measurements in Section A.4.1 are presented in Figs. A.45 to A.52. As with ethane in Section A.3, the relevant data is contained in the peak on the right side of the relaxation time distributions. However, relaxation times provided in the figures are for the entire distribution.

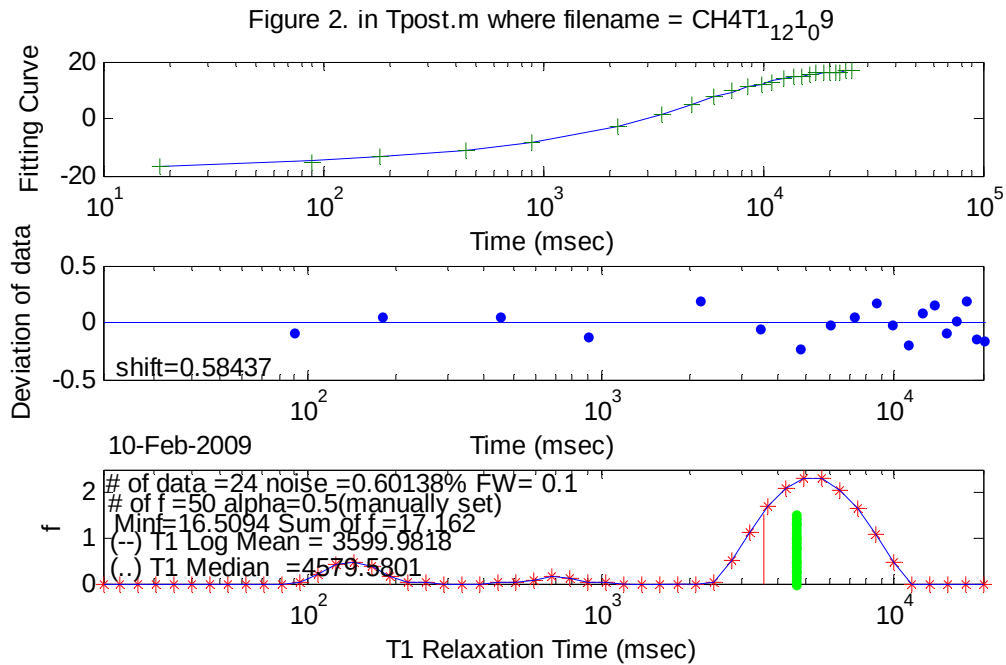


Figure A.45: Inversion recovery and T_1 distribution for methane at $P = 3978$ psig

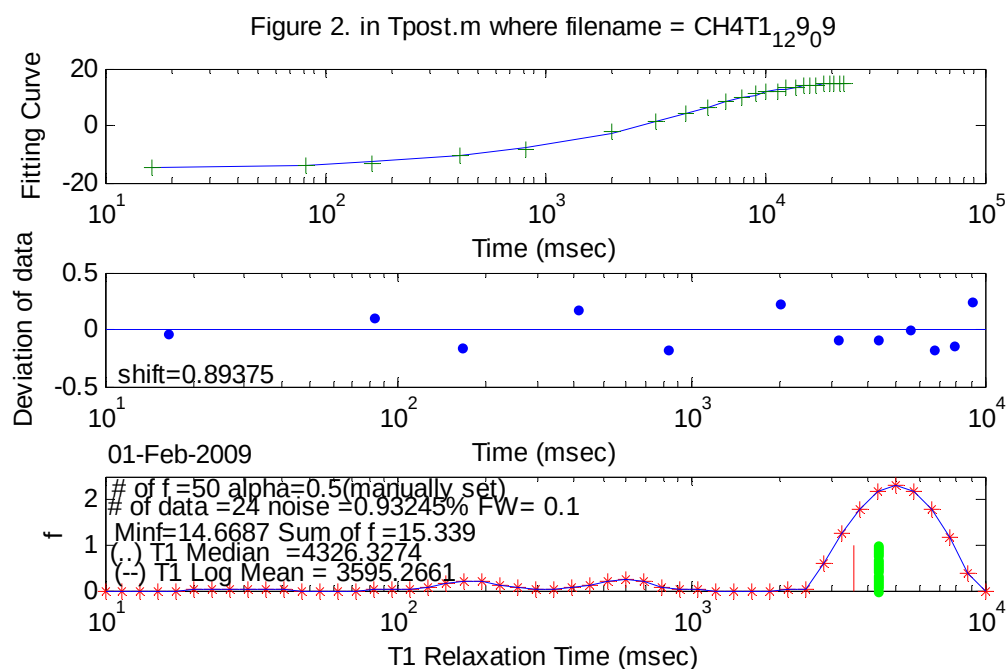


Figure A.46: Inversion recovery and T_1 distribution for methane at $P = 3480$ psig

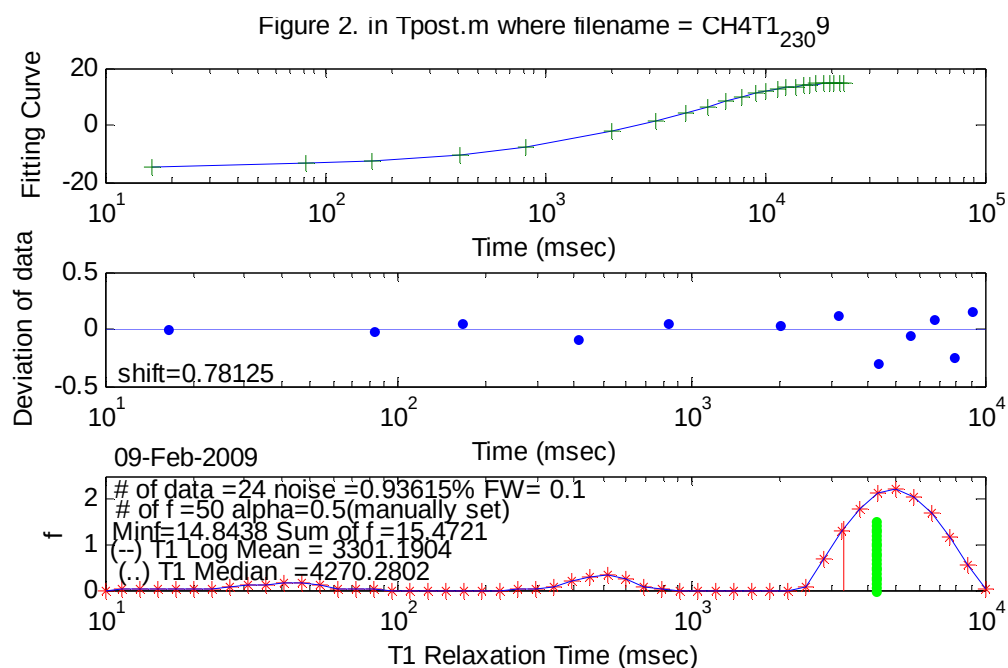


Figure A.47: Inversion recovery and T_1 distribution for methane at $P = 3479$ psig

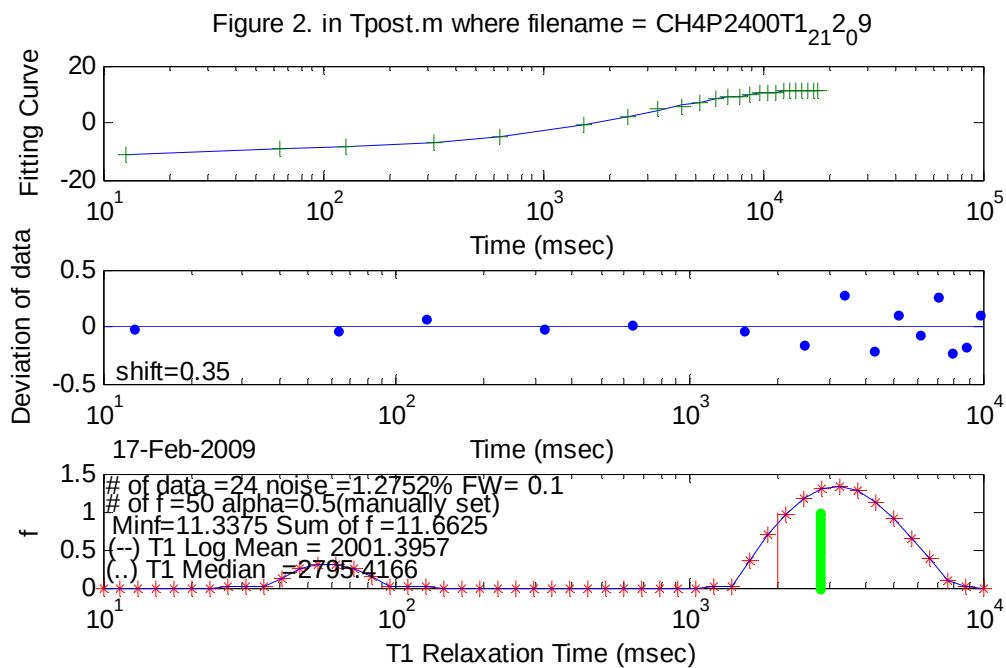


Figure A.48: Inversion recovery and T_1 distribution for methane at $P = 2407$ psig

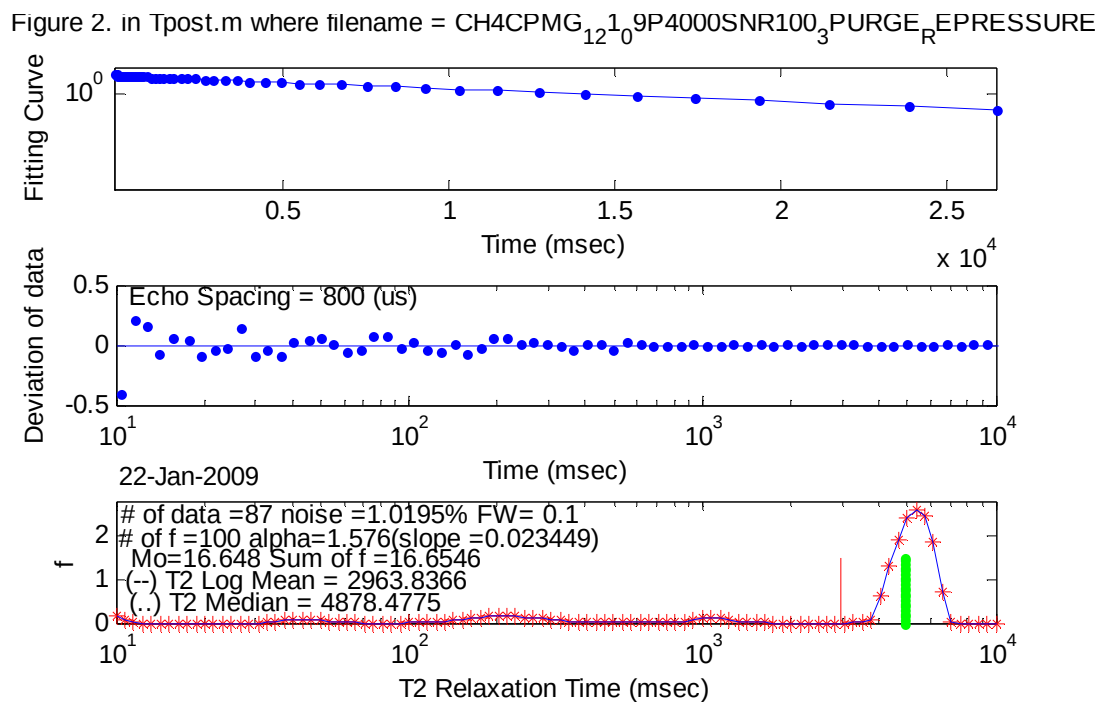


Figure A.49: CPMG response and T_2 distribution for methane at $P = 3996$ psig

Figure 2. in Ipost.m where filename = CH4CPMG2₃₀9P34/USNR100₃PURGE_REPRESSURE

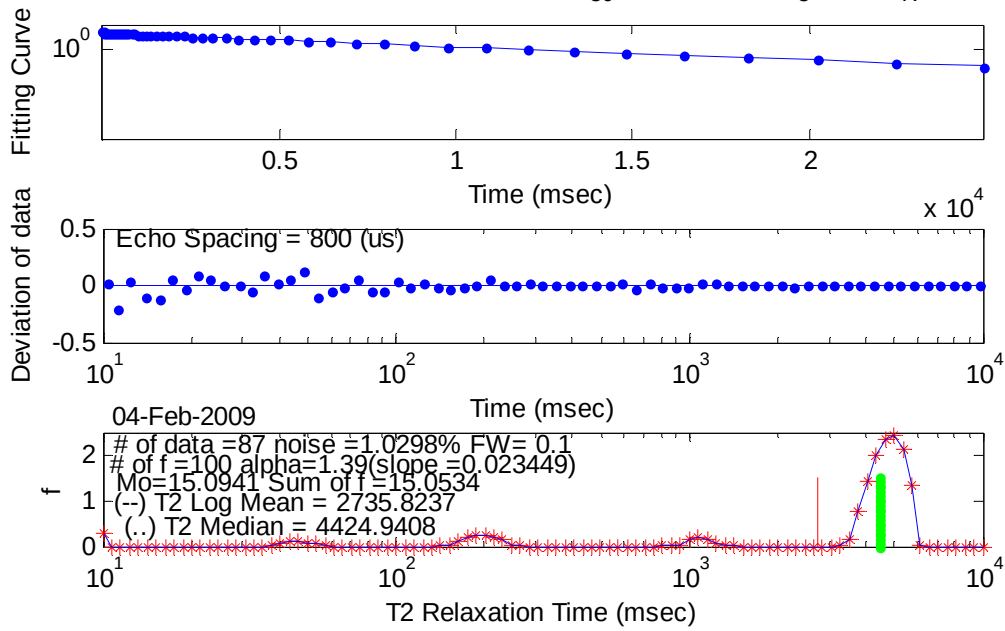


Figure A.50: CPMG response and T_2 distribution for methane at $P = 3479$ psig

Figure 2. in Ipost.m where filename = CH4CPMG2₉₀9P3000USNR100₃PURGE_REPRESSURE

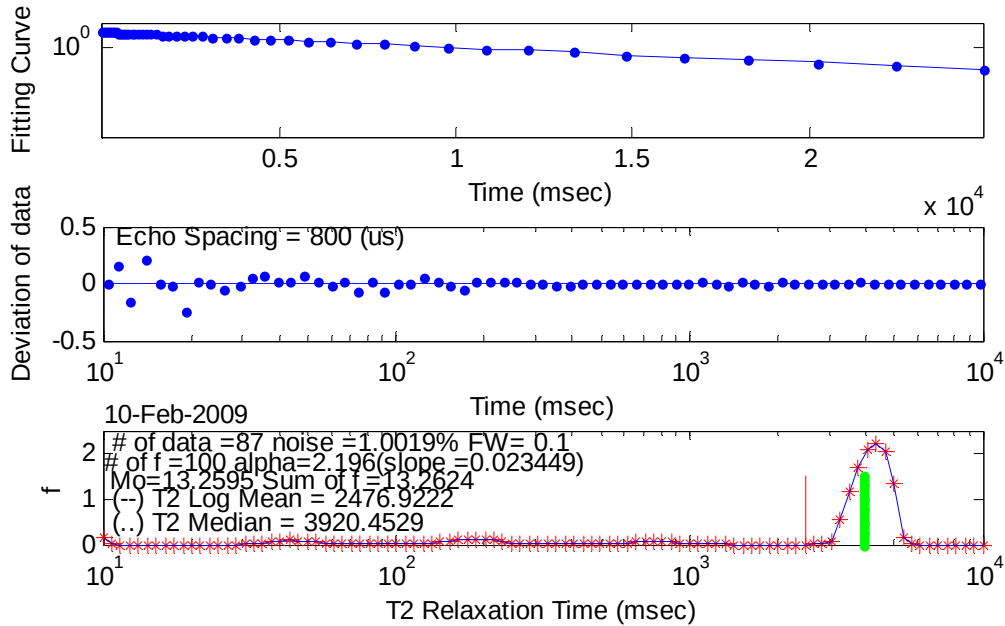


Figure A.51: CPMG response and T_2 distribution for methane at $P = 3011$ psig

Figure 2. in Ipost.m where filename = CH4CPMG2₁2₀9P2400SNR100₃PURGE_REPRESSURE

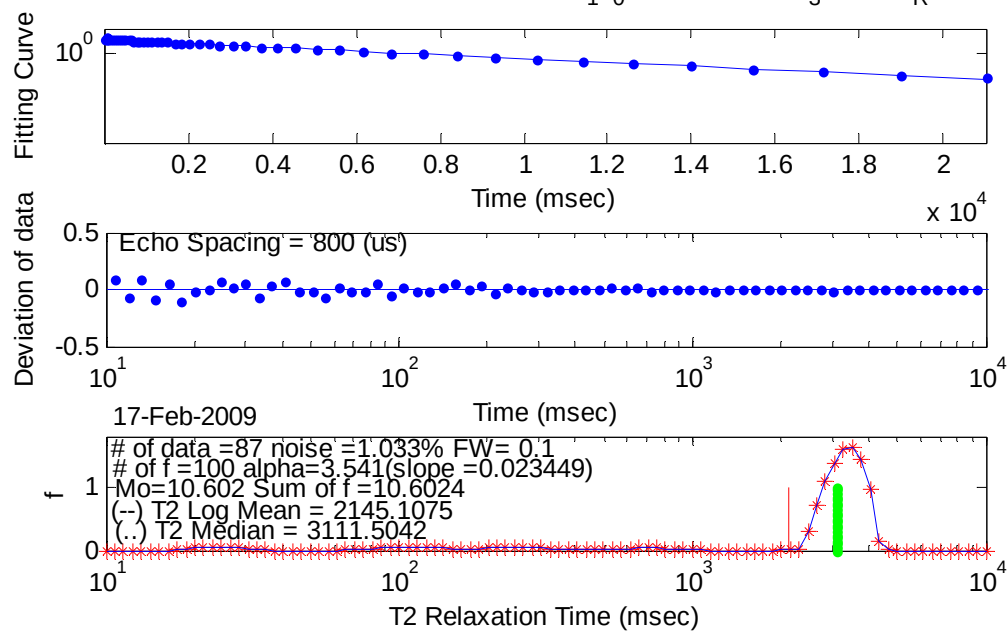


Figure A.52: CPMG response and T_2 distribution for methane at $P = 2408$ psig