

NMR relaxometry analysis of lubricant oils degradation

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Received 3 September 2004, in final form 6 July 2005

Published 16 September 2005

Online at stacks.iop.org/JPhysD/38/3746

Abstract

The present work was undertaken in order to investigate lubricant oil degradation at the molecular level. Ageing effects, as reflected on the proton spin-lattice relaxation rate (T_1^{-1}) dispersion, were studied in two different lubricant engine oils. The proton field cycling technique was used to scan relaxation of new and aged samples of monograde and multigrade oils. Relaxation dispersions were interpreted in terms of self-diffusion and molecular rotations. Our study shows that proton T_1^{-1} could be very sensitive to degradation processes, especially at low Larmor frequencies. The analysis reveals a noticeable sensitivity of the involved correlation times. The pros and cons of the technique are also discussed.

1. Introduction

Lubricant oils are compounds constituted by a base oil (70–90%) and additives (30–10%). Their main function is to reduce the friction between surfaces in relative motion.

The physical and chemical properties of lubricant oils strongly depend on the base oil formulation, type and proportion of oil additives and operating conditions [1]. As a mineral engine oil is used, it undergoes degradation processes mainly due to oxidation, nitration, sulfating, heat and contamination by internal (soot, wear metals) and external (fuel, water) agents [2–5]. Relationships between bulk macroscopic properties and molecular dynamics or structure are still not clearly understood.

Degradation processes in lubricant oils have been widely studied in the past [6–16]. Considerable efforts have been devoted to the seeking of an on-line sensor capable of determining the degree of oil degradation. However, the large variety of oil formulations has complicated significantly the task of implementing such a device [8, 10, 14].

The analysis of degradation processes is usually based on the detection of oxidation, nitration, sulfating products and/or contaminants. The most important and commonly used methods to sense the quality of a lubricant are Fourier transform infrared spectroscopy (FTIR) [17], high-pressure differential scanning calorimetry (PDSC) [13] and bulk oil oxidation stability test (ASTM D943) [18]. Nuclear magnetic resonance (NMR) spectroscopy has been

occasionally employed for this purpose [6, 9, 15, 16]. In most of these works, a combination of ^{13}C NMR with ^1H NMR spectroscopy is utilized in order to determine CH_3 , CH_2 , CH and quaternary carbon contents [9, 15, 16].

Understanding various physical processes related to the molecular dynamics in complex fluids attracted a great deal of both experimental and theoretical attention in the past decades. Spin-lattice NMR relaxation is a powerful technique that has been used extensively and successfully for the study of molecular dynamics in liquids, polymer melts, liquid crystals, surfactants and related materials. In particular, it is well known that the proton spin-lattice relaxation rate T_1^{-1} in liquids is governed mainly by two kinds of molecular motions: self-diffusion of individual molecules and rotations of the whole molecule or internal groups [19].

NMR relaxometry, that is, the study of the Larmor frequency (ν) dispersion of the relaxation parameter, is particularly suitable for scanning the correlation times that characterize the underlying molecular dynamics [20]. In turn, the relaxation rate dispersion may be extremely sensitive to the presence of solid particles or confining structures [21, 22]. Besides, changes in the molecular structure or molecular segmentation in the case of lengthy polymeric chains could modify the T_1^{-1} dispersion significantly [20]. One of the key features of our study is the finding of possible links between the different processes that evolve during degradation and the corresponding induced effects on the molecular dynamics.

The purpose of using field cycling relaxometry was mainly to investigate and characterize the effects produced by ageing processes in lubricant oils, as observed in the proton T_1^{-1} dispersion. Since the main effects were observed at low Larmor frequencies (sub-megahertz regime), the field cycling technique became convenient [23]. Care must be exercised in its use when dealing with specimens showing relevant local field contributions. However, this appeal does not affect the current case.

For the present work, the proton T_1^{-1} relaxation rate was measured in two different kinds (monograde and multigrade) of commercial lubricant oils. The results were interpreted in terms of self-diffusion and molecular rotations.

2. Experimental

The experiment was planned with the idea of having a direct comparison between new and degraded specimens at a fixed temperature. YPF (monograde) and Shell (Helix-multigrade) oils were used for this purpose.

The experiment, as done, had the basic weakness that no complete information was available on the history of the samples. While the Helix sample was obtained from a fuel car engine after 5000 km (strongly used on dusty roads), the YPF sample was obtained from a truck diesel engine after similar use. Nevertheless, within the context of the present work, this weakness plays a secondary role; our current purpose is directed more to the examination of the NMR relaxometry capabilities for this kind of study. In other words, the focus is pointed to the experimental technique more than the study of a particular sample.

Relaxation experiments were performed by using a Stelar FC2000 fast field cycling NMR relaxometer. T_1^{-1} values were measured using the standard pre-polarized (PP) and non-polarized (NP) sequences [23]. A 0.25 T polarization field and a 0.23 T detection field (10 MHz and 9.3 MHz in Larmor proton frequency units, respectively) were used in the T_1^{-1} measurements. For the YPF oil, the dispersion curve was determined by 50 points in a Larmor frequency (ν) window that ranges from 1 kHz to 10 MHz. Magnetic field compensation was used to get the extended Larmor frequency range up to 1 kHz [24]. Measurements in Shell oil resulted in curves defined by 19 points in a Larmor frequency range of 10 kHz–10 MHz.

Sixteen points (four scans each) were used to determine the T_1^{-1} values. In all cases, the relative errors in the T_1^{-1} measurements were between 1.5% and 4%.

Temperatures of (294 ± 1) K for Shell oil and (292 ± 1) K for YPF oil were fixed in all the experiments for both, new and degraded cases. No relevant shifts of the relaxation rates were observed within an interval of 2 K. A further possible spurious effect, thermal gradients along the sample, was not likely since the sample volume was limited to less than 1 ml.

No relevant differences in the NMR free induction signals were observed in degraded samples.

3. Theory

To physically understand the results, we refer to the standard relaxation theory. It is well known from different theoretical

approaches [19, 25–28] that the spin-lattice relaxation rate T_1^{-1} due to dipolar coupling in a system of two like spins obeys the following equation:

$$(T_1)^{-1} = K[J_1(\omega) + J_2(2\omega)], \quad (1)$$

where K is a constant that depends on the spin gyromagnetic ratio γ , the Planck constant h and the spin number I ; $\omega = 2\pi\nu$, where ν is the Larmor frequency and $J_q(\omega)$ are the spectral densities corresponding to a determined molecular motion. They are given by

$$J_q(\omega) = \int_{-\infty}^{\infty} \overline{F^q(t)F^{-q}(t)} e^{iq\omega t} dt, \quad (2)$$

where $F^q(t)$ are the lattice operators associated with the dipolar interaction Hamiltonian. The bar indicates ensemble average.

In liquids, two relaxation mechanisms basically govern the spin-lattice relaxation rate dispersion: translational diffusion and rotational motions.

3.1. Translational diffusion

When the molecules diffuse from one site to another, the dipole–dipole interaction is affected causing intermolecular spin-lattice relaxation.

Torrey [29] extended the pioneering work of Bloembergen *et al* [25] in order to describe the spin-lattice relaxation rate due to translational diffusion $(T_1^{\text{Tr}})^{-1}$. Using a model of random flights and under the approximation of low correlation times τ_D ($\omega\tau_D \ll 1$) it is possible to arrive at the following expression for $(T_1^{\text{Tr}})^{-1}$ [19, 30, 31]:

$$(T_1^{\text{Tr}})^{-1} = \frac{A_D\tau_D}{x^4} [j(x) + j(\sqrt{2}x)], \quad (3)$$

where

$$j(\alpha, x) = \frac{x}{2} - \frac{1}{x} + \frac{x}{2} e^{-x} \left[\left(1 - \frac{2}{x^2}\right) \sin(x) + \left(1 + \frac{4}{x} + \frac{2}{x^2}\right) \cos(x) \right]. \quad (4)$$

In the last equations, $x \equiv (\omega\tau_D/2)^{1/2}$, τ_D is the correlation time of the translational molecular jump, and constant A_D depends on the spin density n , the diffusion constant D , the mean squared jump distance $\langle r^2 \rangle$ and the closest distance between two nuclei b .

3.2. Rotations

Rotations of the whole molecule (due to collisions with other molecules, for example) as well as rotations of different parts of the molecule may cause changes in the inter-spin vector, thus producing spin-lattice relaxation [19].

Assuming that the probability of finding the inter-spin vector in a particular solid angle satisfies the diffusion equation, it is possible to arrive at the following expression for the spin-lattice relaxation rate $(T_1^{\text{Rot}})^{-1}$ due to rotational motions [19]:

$$(T_1^{\text{Rot}})^{-1} = A_R \left[\frac{\tau_R}{1 + (\omega\tau_R)^2} + \frac{4\tau_R}{1 + (2\omega\tau_R)^2} \right], \quad (5)$$

where τ_R is the correlation time and A_R is a constant.

If the two processes described above are assumed to be statistically independent and dominant in different timescales, the total spin-lattice relaxation rate T_1^{-1} will be given by [31]:

$$(T_1)^{-1} = (T_1^{\text{Tr}})^{-1} + (T_1^{\text{Rot}})^{-1}. \quad (6)$$

In all cases, equation (6) was used to explain the relaxation rate dispersions obtained.

4. Results

Figures 1(a) and (b) show the T_1^{-1} dispersion plots corresponding to YPF and Shell lubricant oils, respectively. In both cases, filled and hollow points correspond to the new and degraded samples.

From a direct visual inspection of the data we can state that: (i) for degraded samples, the relaxation becomes more efficient leading to a faster regime (higher T_1^{-1}), (ii) the differences between new and degraded samples become more noticeable at lower frequencies and (iii) these changes are more remarkable in the Shell oil.

In order to study the processes that determine the obtained relaxation rate dispersions, equation (6) was used to fit the data shown in figures 1(a) and (b). It is possible to quantify, to a certain extent, the involved parameters. In all cases, the simplified model (equations (3) and (4)) for $(T_1^{\text{Tr}})^{-1}$ was employed. This assumption is supported by the fact that $\omega\tau_D \ll 1$ in the whole observed frequency range (τ_D is the diffusion correlation time obtained from the corresponding fittings). A_D , A_R , τ_D and τ_R were considered as fitting parameters in the whole analysis.

The obtained fitting curves consistent with the model provided are also shown in figures 1(a) and (b). The corresponding fitting parameters are listed in table 1.

The infrared spectra for both cases were recorded for comparison. The spectra can be seen in figure 2. The different degradation processes are identified in figure 2(a).

5. Discussion

Due to the large number of fitting parameters involved and the complexity of the theoretical model, only a purely comparative and qualitative analysis can be done. Nevertheless, from the obtained fitting parameters, it is possible to establish some common behaviour:

- A remarkable increment in the diffusion correlation time τ_D is obtained in both aged oils, indicating a radically modified diffusional process. Then, according to the model provided, diffusion becomes slower with ageing. The presence of oxidation and nitration compounds may be responsible for this behaviour. They produce an increment in the viscosity, thus slowing down the diffusional mobility.
- Rotational correlation time τ_R increases in both aged oils, but the increment is higher (almost an order of magnitude) in the monograde oil. This would appear to imply that oxidation and nitration processes could make the rotation of the molecules (or part of them) more difficult, in correspondence with an increment in τ_R .

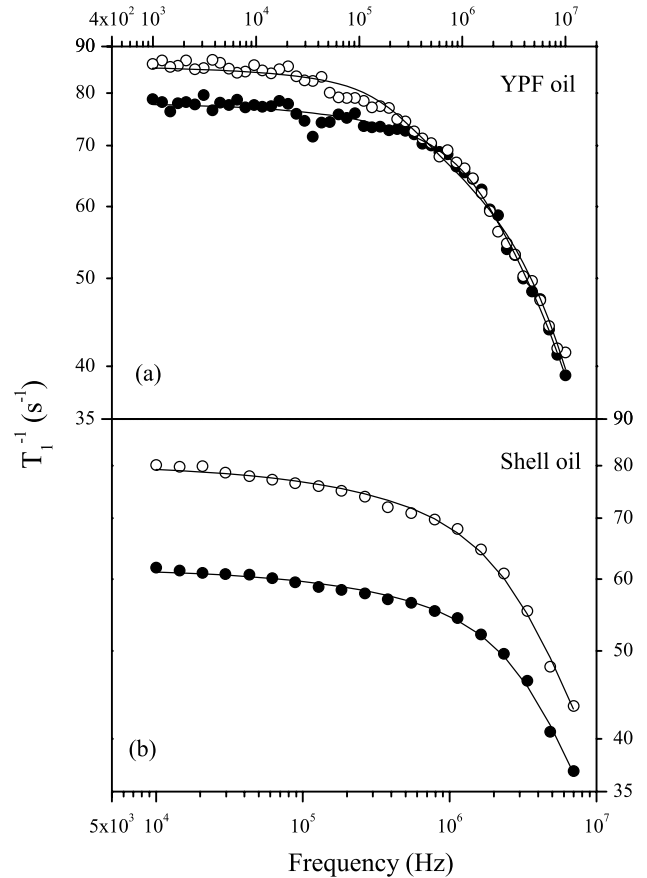


Figure 1. T_1^{-1} dispersion curves and their corresponding fittings using equation (6). In both cases, YPF (a) and Shell (b) oils, filled and hollow points were used to represent new and aged oils, respectively.

- Translational diffusion and rotational amplitudes (A_D and A_R) decrease in both degraded oils. However, the relative change in A_R is larger and consistent with a minor rotational relaxation weight in degraded oils, as indicated by the theoretical model. The most likely cause of this is the formation of long molecular compounds during the oxidation process that might turn the rotational process more difficult than the diffusional one.

Clear differences are present between the relative changes in the observed parameters for both samples. This is most likely due to a different lubricant formulation, quality, age and/or use conditions. From a simple comparison between the relaxation rate dispersions and the conventional infrared spectra, we may conclude that relaxometry is more sensitive to the degradation state of a given specimen. However, a systematic study of different samples under different ageing conditions is still needed to understand how different degradation processes are reflected in the relaxation rate dispersion.

6. Conclusions

In summary, we report for the first time a change in the T_1^{-1} dispersion of two commercial aged lubricant oils. Important changes were detected in the fitting parameters (as stated by

Table 1. Fitting parameters.

Parameters	YPF lubricant oil		Shell lubricant oil	
	New	Aged	New	Aged
A_D (10^9 s $^{-2}$)	4.27 ± 0.29	3.78 ± 0.16	3.65 ± 0.51	3.40 ± 0.39
τ_D (10^{-8} s)	4.82 ± 0.46	6.08 ± 0.34	4.00 ± 0.58	5.90 ± 0.84
A_R (10^7 s $^{-2}$)	4.15 ± 0.97	0.60 ± 0.16	15.2 ± 3.1	12.0 ± 2.7
τ_R (10^{-8} s)	4.60 ± 0.45	30.7 ± 6.1	1.74 ± 0.27	2.25 ± 0.42

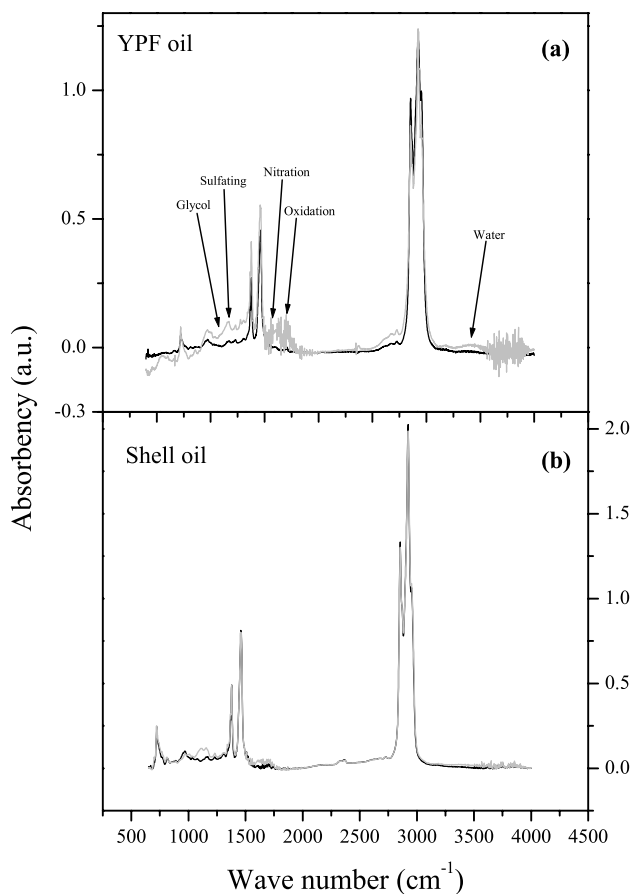


Figure 2. Infrared spectra for new (black line) and degraded (grey line) for YPF (a) and Shell (b) lubricant oils. The influence of various degradation processes on the spectrum are pointed out in (a).

the model provided), suggesting that degradation is strongly connected to alterations in the molecular dynamics. In turn, this behaviour can be attributed to the different involved ageing mechanisms (oxidation, nitration, thermal degradation, presence of solid particles, etc). However, in the present implementation, it turns out that the experiment is indecisive in the sense that it cannot distinguish different degradation mechanisms. This problem can probably be circumvented by studying samples where a controlled degradation is induced in the laboratory through selected known mechanisms (e.g. after oxidation). In any case, an understanding of the involved molecular dynamics seems to be essential to the interpretation of how a given degrading process is reflected in the measured relaxation rate dispersion.

The observed differences in the relaxation rate dispersions showed them to be strongly dependent on the oil formulation. This is also an interesting feature: NMR relaxometry allows us

to get a ‘fingerprint’ of a given fresh formulation, which will mainly reflect the nature of the dominant molecular weight composition.

As was previously stated, remarkable changes in the dispersion curves tend to manifest at low frequencies (see figure 1). Certainly, this feature makes the field cycling technique highly convenient to observe them. This fact suggests that NMR relaxometry is a convenient tool for the study of the physicochemical processes linking the performance decay of a lubricant oil and the changes appearing at the molecular level.

Acknowledgments

The authors acknowledge the economic support of Secretaría de Extensión Universitaria (UNC), Fundación Antorchas and of CONICET. EA is a fellow of CONICET. The collaborations of CEAM–METAS SRL, Stelar srl (Italy) and Fiat Auto Argentina are also acknowledged.

References

- [1] Cipris D, Walsh A and Palanisamy T 1990 *The Electrochemical Society Proc. Series* ed D R Turner (Pennington) p 401
- [2] Wang S S, Lee H S and Smolenski D J 1994 *Sensors Actuators B* **17** 179
- [3] Igarashi J 1990 *Japan. J. Tribol.* **35** 1095
- [4] Fox M F, Picken D J, Symons M C R and Thomson A L 1997 *Tribol. Int.* **30** 417
- [5] Mortier R M and Orszulik S T 1997 *Chemistry and Technology of Lubricants* (Suffolk, UK: Edmundsbury) pp 98–144
- [6] Hosonuma K, Yoshida K and Matsunaga A 1985 *Wear* **103** 297
- [7] Offune G C, Maduako A U and Ojinnaka C M 1989 *Tribol. Int.* **22** 401
- [8] Lee H S, Wang S S, Smolenski D J, Viola M B and Klusendorf E 1994 *Sensors Actuators B* **20** 49
- [9] Basu B, Singh M P, Kapur J S, Nazakat Ali, Sastry M I S, Jain S K, Srivastava S P and Bhatnagar A K 1998 *Tribol. Int.* **31** 159
- [10] Dickert F L, Lieberzeit P and Tortschanoff M 2000 *Sensors Actuators B* **65** 186
- [11] Smiechowski M F and Lvovich V F 2002 *J. Electroanal. Chem.* **534** 171
- [12] Toujou F, Tsukamoto K and Matsuoka K 2003 *Appl. Surf. Sci.* **203** 590
- [13] Sharma B K and Stipanovic A J 2003 *Thermochim. Acta* **402** 1
- [14] Smiechowski M F and Lvovich V F 2003 *Sensors Actuators B* **96** 261
- [15] Owrang F, Mattsson H, Olsson J and Pedersen J 2004 *Thermochim. Acta* **413** 241
- [16] Santos J C O, Santos I M G d, Souza A G, Sobrinho E V, Fernandes U J and Silva A J N 2004 *Fuel* **83** 2393
- [17] Henderson H E, Fefer M and Legzdins A 1999 *Am. Chem. Soc., Div. Pet. Chem.* **44** 284

- [18] Colclough T 1987 *Ind. Eng. Chem. Res.* **26** 1888
- [19] Abragam A 1961 *Principles of Nuclear Magnetism* (Oxford: Clarendon) p 289
- [20] Kimmich R and Anoardo E 2004 *Prog. Nucl. Magn. Reson. Spectrosc.* **44** 257
- [21] Grinberg F, Vilfan M and Anoardo E 2003 *NMR of Ordered Liquids* ed E E Burnell and C A de Lange (Amsterdam: Kluwer) p 375
- [22] Anoardo E, Grinberg F, Vilfan M and Kimmich R 2004 *Chem. Phys.* **297** 99
- [23] Anoardo E, Galli G and Ferrante G 2001 *Appl. Magn. Reson.* **20** 365
- [24] Anoardo E and Ferrante G 2003 *Appl. Magn. Reson.* **4** 85
- [25] Bloembergen N, Purcell E M and Pound R V 1948 *Phys. Rev.* **73** 679
- [26] Goldman M 1988 *Quantum Description of High Resolution NMR in Liquids* (Oxford: Clarendon) p 245
- [27] Wolf D 1979 *Spin Temperature and Nuclear Spin Lattice Relaxation in Matter* (Oxford: Clarendon) p 105
- [28] Wangness R K and Bloch F 1953 *Phys. Rev.* **89** 728
- [29] Torrey H C 1953 *Phys. Rev.* **92** 962
- [30] Pfeifer H 1961 *Ann. Phys. (Germany)* **7** 1
- [31] Noack F 1986 *Prog. Nucl. Magn. Reson. Spectrosc.* **18** 171