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**MOLECULAR MOBILITY OF CRUDE OILS VIA ELECTRON
PARAMAGNETIC RESONANCE OF ORGANIC FREE
RADICALS**

Londrina
2019

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Tese apresentada ao Programa de Pós-Graduação em Física da Universidade Estadual de Londrina para obtenção do grau de Doutor em Física.

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Orientador: Prof. Dr. Eduardo Di Mauro

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ALAMZEB KHAN

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PARAMAGNETIC RESONANCE OF ORGANIC FREE RADICALS**

Thesis Presented for Doctorate, Graduate Program in
Physics, Londrina State University, Parana, Brazil.

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Londrina, June 5, 2019

Dedication

To my loving parents, who have helped me throughout my life.

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ABSTRACT

Electron Paramagnetic Resonance (EPR) spectroscopy technique was applied to investigate the molecular mobility properties in different Pakistani origin crude oil samples. All the samples used in the present study, were of paraffinic and aromatic in nature. EPR experiments at X-band with variation in temperature (298-553K) were performed to predict the molecular mobility in both crude oil samples, by analysing the line-width of the organic free radical signal. The viscosity of the samples was measured by using MCR Serie 301 Rheometer, in order to study the mobility of the oil samples. A change in the values of the viscosities has been observed, due to the different nature and composition of the oils. The line-width studies in the EPR spectrum of the organic free radical exhibited significant changes with the variations in temperature condition, which is an important parameter to detect changes in molecular mobility of the samples, leading us to determine the different regimes of the mobility of the oils at the different temperatures. The linewidths of the crude oil samples were also affected by temperature, although g-value was constant, revealing the changing in the chemical structure and the surrounding environment of free radicals during the studies. The concentrations of the free radical follow the trends in the whole temperature range, first increasing and then decreasing. This may be attributed to the competing mechanism of the generations and decomposition of the free radicals. The present study proposes a new method to predict molecular mobility of oils by EPR of free radicals.

Keywords: Petroleum. ESR. NMR. Viscosity. Temperature variation. Asphaltene.

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CHAPTER 1:

INTRODUCTION

Petroleum (or crude oil) is a complex, naturally occurring liquid mixture containing mostly hydrocarbons, and some compounds of oxygen, nitrogen and sulphur. It is also called black gold as they are valuable. Crude oils are classified, normally, by considering their different proportions of the precipitations of Aromatics, Saturates, Asphalt and Resins (Ahmad et al. 2018). A number of different techniques, such as, Gas chromatography, Infrared Spectroscopy, Nuclear Magnetic Resonance, Electron Paramagnetic Resonance, Mass spectrometry and thermogravimetry etc (Abdulkadir, S. Uba, A. Salihu A 2016, Ahmad et al. 2018 and Cho et al. 2012) have been used for the characterization of the crude oil samples. The thermal maturity, biodegradation and photodegradation of the crude petroleum oil samples, along with the factors involving such kind of changes, were also being studied (Guedes et al. 2006 e Sugiura et al. 1997). The Viscosity is considered a major problem in the petroleum industry, causing a slow flow rate of the crude oil in the tubes and pipelines of the refinery plants (Espinosa Pena, Manjarréz e Campero, 1996). Low field NMR technique is widely used to study the flow-rate of the petroleum crude oils (Bryan et al. 2007). Bellehumeur et al. developed a mathematical model, by relating the time relaxation of the NMR data with the molecular mobility, to study the viscosity of the samples (Bellehumeur et. al 2007). Thus, NMR technique can be used to study the molecular behaviour and the structural changes temperature dependence of the crude oil samples (Gonçalves et al. 2011). Electron Paramagnetic Resonance (EPR) Technique was also being applied to study the molecular structure and paramagnetic centres in the Asphaltene of the petroleum crude oil samples (Guedes et al. 2006).

Since, the paramagnetic properties of the crude oil, due to the presence and distribution of the central metal ion i.e Vanadium, Nickel, Cobalt and Copper etc in the porphyrin, structures, changes with the temperature. It is being reported that, the structural changes of the porphyrin could possibly be occurred by considering the degradation behaviour of the samples at higher temperature ((Crude Oil Emuls. Compos. Stab. Charact., 2012). Guedes et al reported the EPR parametric information's of iron (Fe^{3+}) in the marine crude oil samples. Where the authors, studied the mobility of the free radicals in non-prophyrine structure throught the EPR technique (Barbosa Guedes et al. 2003b). Furthermore, the hyperfine line of the free radical paramagnetic species of the EPR signal was used to characterize the molecular structure of the crude oils, where insufficient/less content of the vanadylporphyrin complex, belonging to different regions. Where, the hyperlines for the Vanadylcomplex in the porphyrin and a single EPR line for the free organic radical in the non-prophyrin samples had been used, as a parameter to study the quality of different petroleum crude oils, such as Venezuela, Colombia, Brazil and Arabian oil (Hernández et al. 2019 e Di Mauro et al. 2005). Di Mauro et al. reported that, most of the free radicals present in the asphaltenes of such crude oils were imprisoned inside their aromatic systems, and the multiplicity of the molecular structures reduces the access to investigate/understand their molecular mobility nature. The authors determined the molecular mobility behaviour of the non-porphyrin free radicals, which are found next to the vanadyl perpendicular spectral lines, in the petroleum crude oil samples (Biktagirov *et al.*, 2014).

Generally, the characteristic hyperfine lines of Vanadyl specie cannot be seen in the spectra, due to the insufficient/less content of Vanadyl porphyrin complex, in those crude oil samples. Therefore, in such cases, spectroscopic factor (g-value) of the free radical, on

different frequency band EPR technique, such as X-band, Q-band and W-band is proposed to study the samples of crude oil, (Mauro, Di, Guedes and Nascimento, 2005)

In this work, the growth in the number of free radicals and the changes caused by the increase in temperature in the crude oils samples were investigated. Analytical techniques, such as Electronic Paramagnetic Resonance Spectroscopy (EPR) and Nuclear Magnetic Resonance (NMR) were used to study the alteration in the Molecular mobility behaviour and its effects on the viscosity of the Petroleum crude oil samples of the interests.

OBJECTIVE

The objective of this study is to directly probe the Phases of regime where alteration occurs in molecular mobility in crude oils according to their nature via Electron Paramagnetic Resonance. Whereas to monitor the changes occur in low field NMR and to predict the viscosity from NMR data of crude oils. the focus of this work is to develop a new method to discuss the molecular mobility occurs in crude oils.

Chapter 2: FUNDAMENTALS THEORY

2.1 Electron Paramagnetic Resonance (EPR)

The first observations of the technique of Paramagnetic Resonance Electronics were carried out by Zavoisky (1945) (ORTON, 1968) and are based on the absorption of microwave energy by an unpaired electron in the presence of a magnetic field. The RPE technique, also known as EPR (Electron Paramagnetic Resonance) and ESR (Electron Spin Resonance), is used for the study of several systems, due in large part to their versatility and its non-destructive character. It has now been applied to a wide range of problems of condensed matter physics and chemistry.

Systems that have unpaired electrons, and can be atoms with an odd number of electrons, partially electron-ions fillers, free radicals, colour centres, crystal structures, molecular complexed compounds of paramagnetic centres, among others. That is, compounds in which its electrons are free to bind to other electrons (ROHN, KROH, 2005; BIKTAGIROV et al., 2014). Specifically on transition metals and crystal structures, the unpaired electrons are relatively stable and consequently easier to detect. However, many radicals Because of their high reactivity and low concentration, they cannot be detected directly by RPE, needing the help of spins traps to be observed.

The phenomenon of electronic paramagnetic resonance is consequence of the existence of the intrinsic property of the electron to possess moment angular S, known as spin (DONOSO; BARBERIS, 1997), whose momentum magnitude is directly proportional to this angular momentum (Ikeya, 1993),

$$\mu_e = -g\beta S \quad (1)$$

The negative sign is the result of the magnetic moment being antiparallel to the angular momentum of spin. For the free electron, the Landé factor is known as g and has an approximate value of 2.0023 and is known as Bohr's magneton(Ikeya, 1993).

Although it is quantum in nature, the basic understanding of phenomenon does not require extensive knowledge, but some important information, such as: possible projections

for the spin of an electron, concept of half-life, among others (OLIVEIRA, 1980). When applying a field magnetic direction H oriented in the Z direction, on an electron, the interaction of this field with the magnetic moment of the electron is described by a spin Hamiltonian (RIEGER, 2007).

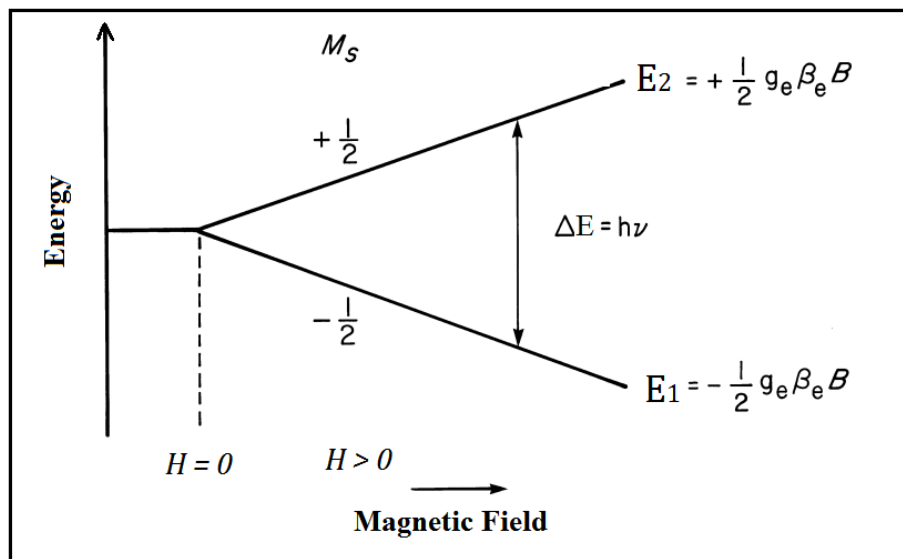
$$H = -\mu_e \cdot H = g\beta H S_z \quad (2)$$

Since S_z has only two permissible orientations, $M_s = \pm 1/2$, for the electron interaction, we have only the interaction energy between the magnetic moment μ_e and the external magnetic field H , so that the energy levels for the possible values are given by:

$$E = g\beta H M_s \quad (3)$$

In this case, there are two degenerate states of energy in the absence of external magnetic field. With the introduction of an external field, the separation between the two energy states occurs and this effect is known as the "Zeeman effect". Figure 1 shows the energy levels of an electron $S = \pm 1/2$ in the absence and in the presence of an external magnetic field.

Figure 1 Energy-level scheme for the simplest system (e.g., free electron) as a function of applied magnetic field H , showing EPR absorption. E_1 and E_2 represent the energies of the $M_s = +1/2$ and $M_s = -1/2$ states.



Source : (Weil e Bolton, 2006)

In order for the transition between the two spin states to occur, it is necessary to apply an amount of energy $h\nu$, which is exactly equal to the energy difference ΔE between the two energy levels. That is, the resonance condition is satisfied when a photon of energy $h\nu$, where ν is the frequency of an oscillating magnetic field, reaches this energy difference,

$$\Delta E = h\nu = g\beta H \quad (4)$$

In addition, transitions between power levels are only possible following the selection rule.

$$\Delta M_s = \pm 1 \quad (5)$$

In equation 4, the factor g in isotropic systems does not depend on the direction of the magnetic field, whereas for anisotropic systems the resonance properties are described as a function of the orientation of this field (RIEGER, 2007).

According to Abragam and Pryce and Bleaney and Stevens (Charles P. Poole e Horacio A. Franch, 1987), the spin Hamiltonian that describes the interaction energy of a paramagnetic atom with a constant magnetic field can be described as:

$$\mathcal{H} = \mathcal{H}_{el} + \mathcal{H}_{cc} + \mathcal{H}_{ls} + \mathcal{H}_{ss} + \mathcal{H}_{zee} + \mathcal{H}_{hf} + \mathcal{H}_Q + \mathcal{H}_N \quad (6)$$

Where the terms have the following typical forms:

\mathcal{H}_{el} = electronic energy

\mathcal{H}_{cc} = crystalline field energy

\mathcal{H}_{ls} = spin-orbit interaction

\mathcal{H}_{ss} = spin-spin interaction

\mathcal{H}_{zee} = Zeeman energy

\mathcal{H}_{hf} = Hyperfine Structure

\mathcal{H}_Q = Quadruple Energy

\mathcal{H}_N = nuclear spin energy

It is worth remembering that both the electronic magnetic moment S , magnetic moment I , interacts with the magnetic field, so that each component contributes to the construction of the Hamiltonian.

Another determining factor for the resonance to occur is related to the way lower and higher energy levels are occupied by unpaired spins. This population ratio of spins is given according to distribution of Boltzmann,

$$\frac{N_s}{N_i} = e^{\frac{-\Delta E}{KT}} \quad (7)$$

Where, N_i = the population of spins in the upper state

N_i = Population of spins in the lower state

K = Boltzmann's constant ($1.38 \times 10^{-23} \text{ KJ}^{-1}$)

T = absolute temperature (K)

If there is no population difference between energy levels, result, no absorption will occur as the number of spins excited would be the same number of spins induced to the state the RPE signal will disappear. In this way, an intense radiation that tends to equalize populations, leads to a decrease in absorbing liquid that is not instantly restored since the radiation is removed. This important trend is called saturation and the return of the system of spin to thermal equilibrium shows the importance of the net spin relaxation mechanism (Weil e Bolton, 2006).

Among the most important relaxation mechanisms are the process and the Raman process. The direct process is a mechanism predominant at low temperatures. On the other hand, the Raman process becomes more relevant as the temperature of the system increases (Ikeya, 1993).

The difference between energy levels, the fundamental level E_1 immediately excited state E_2 , helps to determine the relaxation time T_1 of the spin in the network, with the typical formulas for $S = 1/2$:

$$T_1 = \frac{10^4(E_2 - E_1)^4}{\lambda H^4 T} S \quad (\text{Direct process}) \quad (8)$$

$$T_1 = \frac{10^4(E_2 - E_1)^6}{\lambda^2 H^2 T^7} S \quad (\text{Raman process}) \quad (9)$$

Where E_1 , E_2 and λ are expressed in cm^{-1} , H in Gauss and T is the absolute temperature and s is the time in seconds (POOLE, 1967)

In liquids, the rate at which molecules move is characterized by the correlation time τ_c , which is a function of the viscosity through the ratio from Debye

$$\tau_c = \frac{(4\pi\eta a^3)}{(3KT)} \quad (10)$$

Where a is the molecular ray. In liquids, relaxation times T_1 are found in terms of the angular frequency of magnetic resonance ω_o ,

$$\frac{1}{T_1} = C \left[\frac{\tau_c}{1+(\omega_o\tau_c)^2} \right] + \left[\frac{2\tau_c}{1+(2\omega_o\tau_c)^2} \right] \quad (11)$$

Where C is constant.

2.1.2 Line shape

The shapes of EPR lines are usually described by either Lorentzian or Gaussian line shapes. The expected line shape of the resonance line is Lorentzian, if there is no hyperfine broadening. A Gaussian shape arises from the statistical distribution of the spin magnetic moments, resulting in a dipolar (inhomogeneous) broadening. If the concentration of paramagnetic centres is low and if there is dynamic averaging, say in liquid solution, lines often approach the Gaussian shape if the line is a superposition of many components. One usually refers to such composites as inhomogeneous broadened.

2.1.3 Line broadening

There are various mechanisms that result in homogeneous and inhomogeneous broadening of EPR spectra. Several, relevant for this work, are discussed here. The natural line shape for dipole transitions is a Lorentzian profile, with the width being determined by

the inverse lifetime of the observed transition – also called natural linewidth. Processes that shorten this lifetime are homogeneous, while all other interactions lead to inhomogeneous broadening, which is often of Gaussian shape. Most of these mechanisms are due to differences in the local environment. Usually several broadening mechanisms apply at the same time, resulting in a Voigt profile – the convolution of Gauss and Lorentz functions.

2.1.3.1 Homogeneous Broadening

Saturation of the EPR transition at sufficiently high microwave powers has the effect that not only regular microwave photon absorption, but also stimulated emission occurs. This leads to a reduction of the effective radiative lifetime and consequently, a homogeneous broadening of the EPR spectrum. Additionally, the population of upper and lower spin states are equalized and the observed EPR intensity saturates.

2.1.3.2 Inhomogeneous Broadening

Dipole–dipole interactions with nearby spin carrying particles of the same or different kind are possible. The second particle has its own local magnetic field, which superimposes with the external magnetic field and thus shifts the resonance field for the first particle. If distances are statistically distributed, a Gaussian broadening can be expected. This mechanism is directly related to the description of systems with vanishingly small dipole interaction.

Unresolved hyperfine interactions are also a type of dipole–dipole interaction. In this case with the spins of surrounding nuclei. If the number of interacting nuclei is very large, no individual hyperfine structure with a discrete splitting in the EPR spectrum is observed. Instead, the spectrum is averaged over many possible hyperfine interactions. Hence one detects the envelope of all lines. This effect is also observed for the linewidth of polarons in organic semiconductors, where it is referred to as motional narrowing.

The electronic mobility and hence the diffusive motion of polarons is here strongly temperature dependent. Therefore the amounts of protons that interact with a polarons in a given time are a function of mobility and temperature. At cryogenic temperatures, a broadening of the detected linewidth due to unresolved hyperfine interactions with these surrounding protons is observed. At higher temperatures the same mechanism yields a

narrowing of the linewidth (Brustolon e Giamello, 2008; Marumoto *et al.*, 2005; Marumoto, K. *et al.*, 2006; Marumoto, Kazuhiro *et al.*, 2006).

An inhomogeneous external magnetic field might be applied to the sample, setting a lower limit to the observable linewidth. A typical Bruker X-band EPR magnet has a local homogeneity of $\sim 10^{-6}$ over the sample width of 3 mm. However this needs serious consideration for superconducting magnets, which are usually a lot less homogeneous.

Modulation broadening is present if the modulation amplitude, expressed in magnetic field units, cannot be considered small in comparison to the observed linewidth. In general it is safe to apply a field modulation that is less than half of the observed linewidth, to avoid spectral distortions. All the broadening mechanisms presented above are isotropic. Hence, the whole EPR spectrum is convoluted with the additional broadening profile. However, for many spin-systems the linewidth also needs to be considered anisotropic. This is typically expressed by the **g-strain** tensor, which compliments the *g*-factor tensor. The strain can be understood as a measure of the heterogeneous environment, when one or another *g*-tensor component is not exactly determined any more, mainly owing to the interaction with the environment. In a first order approximation, the bigger the initial shift of the *g*-tensor component from the free electron *g*-factor g_e , the stronger the *g*-strain effect (Vassilikou-Dova, A.B., Lehmann, 1987).

2.2 NMR and Viscosity

In a nucleus a proton possesses magnetic moment and when exposed to an externally applied magnetic field, their net magnetization will eventually reach towards some equilibrium state of magnetization which is also determined by relaxation curves. These relaxation curves either be longitudinal or transverse magnetization, in the establish nomenclature, T_1 is the time constant for longitudinal relaxation and T_2 is the symbol for transverse relaxation (Kenyon, 1992).

NMR phenomena are observed when the nucleus, which contains magnetic moment of nuclear spin, is subjected to an external magnetic field B_0 , promoting an interaction and the consequent alignment of nuclear spins, parallel or antiparallel to this external field (Barbosa

et al., 2015). There are two relaxation moments named as: longitudinal relaxation (T_1) and (T_2) that characterize the time of the recovery process of energy balance. Longitudinal relaxation also called relaxation spin-network corresponds to the exchange of energy between the excited nuclear spin and the energy reduction. Transversal relaxation, also called spin-spin relaxation, is the interaction between nuclear magnetic moments (spins), refers to the total energy of the nuclear system which remains (Zhang, Saleh e Shen, 2013).

Nuclear Magnetic Resonance is an effective tool in evaluating rapidly and non-destructively rocks and fluid properties. Bloembergen, Purcell and Pound (1948) demonstrated an intimate relationship between viscosity and the relaxation times found by the resonance technique Nuclear Magnetic Resonance (NMR). NMR was initially used for the measurement of viscosity of crude oils, as it is an important parameter for determine the flow characteristics of the fluids through the pores of the rocks, is also a significant variable in oil exploration and in its transport(Deng *et al.*, 2014).

Several authors have proposed equations that establish the relationship between viscosity and the respective relaxation times (LATORRACA, G. A.; STONARD, S. W.; WEBBER, 1999; ZEGA, J.A.; HOUSE, W.V.; KOBAYASHI, 1989; Zhang, Lo e Huang, 1998).

(Nicot, Fleury e Leblond, 2006) point out that numerous correlations can be found to connect relaxation times found by NMR at the viscosity. However, they point out three main issues to use these relationships. The detection of small relaxation times. In this case, for viscous oils, the small relaxation times are underestimated or not detected, resulting in a loss of signal. The variation of the signal between the ratio T_2 and the dependence of the characteristics of the NMR instrument. Finally these authors propose an equation that encompasses all these alternatives. The constants presented, refer to empirical values presented by the authors,

$$\eta = K T_{2ml}^{-n_1} \frac{1 + C T_{2ml}^{-n_2}}{1 + C} \quad (12)$$

Where $K = 5300$,

$C = 1$

$n_1 = 1,1$.

$n_2 = 2$,

$T_{2ml} =$ Values found in NMR

Viscosity is a property of great interest in the processing and handling of oils and fats. It is treated as the measure of the internal friction of a fluid, that is, it is the measure of the that it will flow when subjected to shear force (Skovgaard, 2001). Some factors alter the viscosity of a solution, among temperature, concentration, molecular weight of the solute, pressure and quantity of suspended matter. The increase in temperature directly changes the viscosity of the oil (Bourne, 2002; Skovgaard, 2001)

Dynamic viscosity is often called viscosity or absolute viscosity and corresponds to an internal friction of a liquid or its tendency to not flow (Bourne, 2002), usually denoted by η . According to (Bourne, 2002), kinematic viscosity ν is defined as viscosity divided by the density of the fluid.

CHAPTER 3:

3.1 Petroleum

Petroleum is a mixture of naturally occurring hydrocarbons that may exist in the solid, liquid or gaseous states, depending upon the conditions of pressure and temperature to which it is subjected. Virtually all petroleum is produced from the reservoir in either liquid or gaseous form, and commonly, these materials are referred to as either crude oil or natural gas, depending upon the state of the hydrocarbon mixture. Petroleum consist of approximately 11-13 wt % hydrogen and 84-87 wt % of carbon. Traces of oxygen, sulphur, nitrogen and helium may be found as impurities in crude oil, which is shown in table 1, where described each element by weight. Crude oils obtained from different oil reservoirs have widely different characteristics. Some are black, heavy, and thick like tar, and others are brown or nearly clear with low viscosity and low specific gravity. However, nearly all crude oils have elemental analyses within the limits given in table 2.1(Manar el-syed., 2012)

Table 1. Elemental Analysis of Typical Crude oils by % weight

Elements	% by Weight
Carbon	84-87
Hydrogen	11-14
Sulpher	0.06-2.0
Nitrogen	0.1-2.0
Oxygen	0.1-2.0

When the crude oil is passed by fractional distillation plant, the fractions are separated by their boiling points.

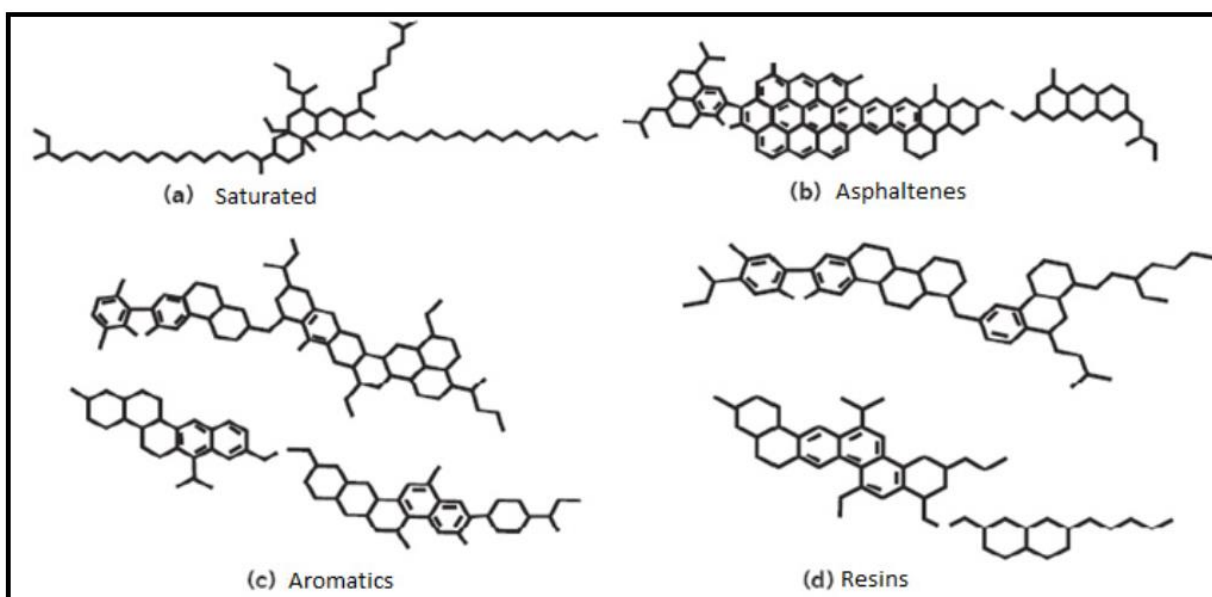
3.2 Classification of Crude oil

The classification of oils, according to their constituents, it has an interest from geochemists to the refiners. The crude oil is classified by its composition and physical properties.

Paraffinic oils are excellent for the production of aviation kerosene (jet fuel), diesel, lubricants and paraffins; naphthenic oils produce significant fractions of gasoline, naphtha, aviation fuel and lubricants; while the aromatic oils are best suited for the production of gasoline, solvents and asphalt (Thomas *et al.*, 2001).

The hydrocarbons present in oil can be classified into four main classes: saturated (alkanes and cycloparaffins), aromatics (hydrocarbons, mono, di and polyaromatic), resins (fractions consist of polar molecules containing heteroatoms such as N, O or S) and asphaltenes (they are molecules similar to the resins, but with a higher molecular weight and polyaromatic core). The molecular structures of each classification is shown in figure 2, where it can be seen the saturates or Paraffinic have chain and branched hydrocarbons. This classification is obtain by Gas chromatography technique, and also known as SARA (Wang, J.; Fan, T.; Buckley, 2002).

Figure: 2 Structures representing saturated, asphaltenes, aromatics and resins



(Bernucci *et al.*, 2008).

The relative amounts of individual compounds within each group of hydrocarbons are characteristic of each type of oil.

Metals can be found at levels ranging from 1 to 1200 ppm, the main being iron, zinc, copper, lead, molybdenum, cobalt, arsenic, manganese, chromium, sodium, nickel and vanadium, the latter two with the highest incidence.

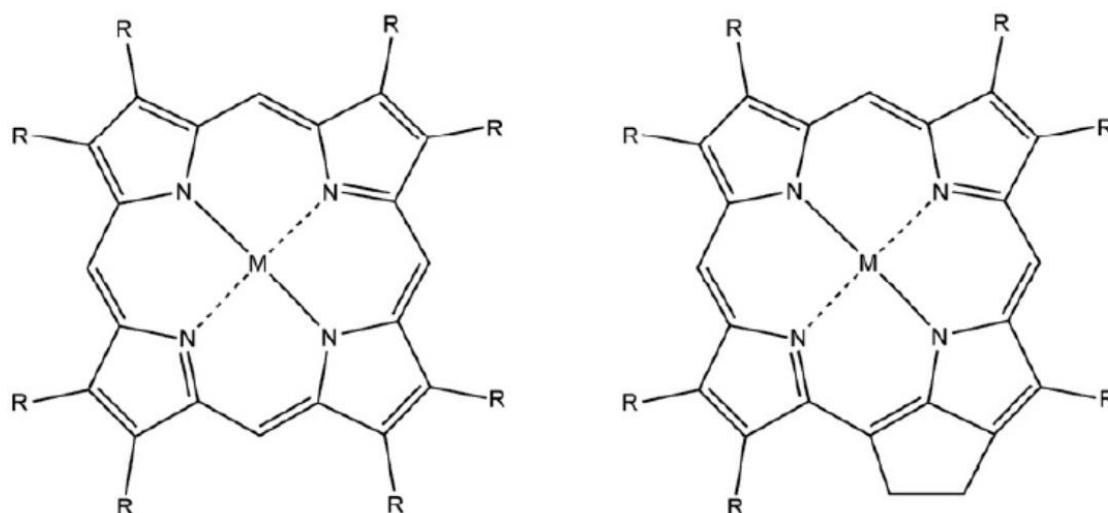
Lighter oils produce greater volume of gasoline, LPG and naphtha, and so exhibit a higher commercial value, while heavy fuel oils produce higher volumes of oil yield and asphalt. The average derivatives, such as diesel and kerosene, are also particularly important for our country where the highway is intense and the demand for diesel is great.

The asphaltenes are a mixture of high molecular weight aromatic components oil shale. Coal and oil can vary from 1% by weight in light oils, up to 17% in heavy oils. According to (León, Contreras e Rogel, 2001), the asphaltenes are considered the fraction of oil that has the highest number of aromatic rings and higher molecular weight.

The asphaltenes are arguably the most complex fraction of oil. In variations of pressure variation, temperature or composition of oil, asphaltenes tend to associate and precipitate causing several costly operational problems from transport to refining (Trejo e Ancheyta, 2007).

The asphaltenes consist of a heterogeneous complex mixture of molecules highly polydisperse in size and with a chemical composition poly condensed aromatic rings, Aliphatic chains, naphthenic rings, and containing heteroatoms such as nitrogen, oxygen, sulfur, presenting itself in the form of carboxylic acids, amides, amines and alcohols, and metals such as iron, nickel and vanadium. Different types of metals (Ni, V, Fe, Al, Na, Ca, Mg) are present in crude oils and tend to accumulate in the asphaltenic fraction in trace amounts. Vanadium and nickel are the most commonly found and in most cases present as porphyrin complexes, being responsible for the poisoning of catalysts in the improvement of oil. The figure 3 shows the schematic structure of Porphyrin, where the metallic paramagnetic specie is centre of the porphyrin, and this metallic paramagnetic specie is surrounded by Aromatics rings and cyclic saturated hydrocarbons (Al-Sabawi, Seth e Bruijn, De, 2011; Nordgård, Sørland e Sjöblom, 2010).

Figure 3 Structures of metal porphyrins. oil



Source: (Al-Sabawi, Seth e Bruijn, De, 2011)

Variations in temperature, pressure and chemical composition can cause precipitation of asphaltenes from crude oil. Rainfall and subsequent deposition of asphaltenes can cause problems in all stages of production, for example, transportation and processing, causing the loss of efficiency equipment in steps of production of crude oil. In the reservoir rock, seal can cause partial or complete its pores, resulting in the loss of oil recovery.

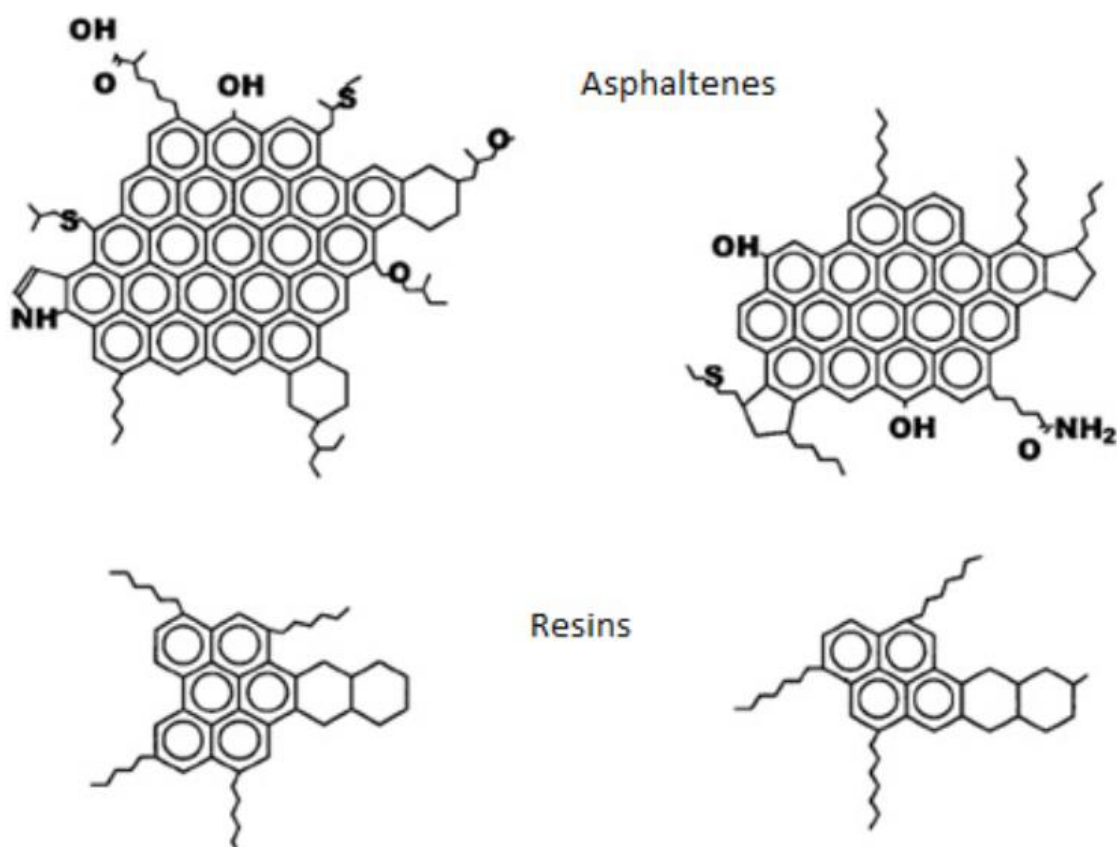
The formation of the asphaltenes deposit is one of the most studied phenomena in the production and processing of crude oil. Researches are looking increasingly for the improvement about the chemical structure of molecules present in the asphaltene fraction and, consequently understand its behaviour in oil.

The dispersion of asphaltenes is mainly attributed to the resins (polar aromatic). The resin molecules play a role of surfactants in stabilizing colloidal particles of asphaltenes in oil. There are concepts about precipitation of asphaltenes and the most widely accepted says that the dissolution of resins is followed by precipitation of asphaltenes. On this basis, the stability of oil can be represented by three phase systems: asphaltenes, aromatics (including resins) and saturated, which are delicately balanced(SPEIGHT *et al.*, 2000).

The presence of resins in oil prevents the precipitation of asphaltenes by keeping the same particles in colloidal suspension. When a solvent is added to oil, resins are dissolved in the liquid, leaving active areas of asphaltene particles, which allow the aggregation of the same and, consequently, precipitation. The stability of asphaltenes in oil depends on the ratio resin/asphaltene in the oil. In contrast to the asphaltenes, resins are soluble in n-alkanes as n-heptane and n-pentane (which are paraffinic in nature).

Resins compared to asphaltenes have a lower content of aromatics, but are rich in heteroatoms, mainly oxygenates (Gerson e Huber, 2004), which is shown in figure 4. It should be noted that during the process of purification and precipitation of asphaltenes due to the existence of clusters, always exists the possibility of a certain amount of resin precipitate with the asphaltenes.

Figure: 4 Structures of hypothetical resins



Source: (León, Contreras e Rogel, 2001)

The classification of crude oil done by many parameters. The proportion of saturates, aromatic components, also can be determine by the Watson characterization constant, or can know by correlation index (Ahmad *et al.*, 2018).

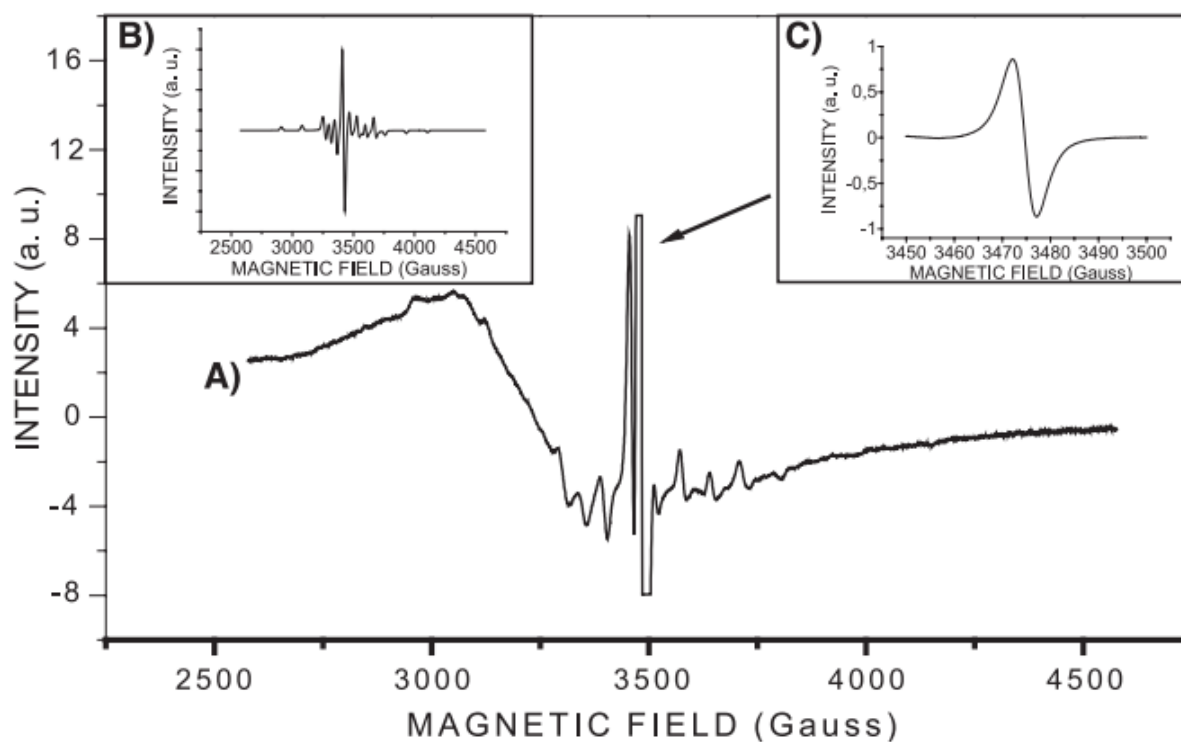
2.3 EPR of Crude oils

A lot of research has been done on crude oil for betterment in quality of crude oils. The characterization of crude oil has been done chemically by means of different techniques. EPR is also used as technique describes the quality and the change in behaviour in crude oils.

Electron paramagnetic resonance (EPR) or Electron spin resonance (ESR) is a high resolution spectroscopy that consists in energy absorption of microwave, for electron spin, in the presence of a magnetic field (Ikeya, 1993). As the name itself suggests, ESR is applied in samples containing some paramagnetic species or used as an investigative method, to verify the presence of some paramagnetic species. Paramagnetism is characteristic of species with a total magnetic moment different from zero.

The EPR spectra of crude oils show signals of two different paramagnetic centers, namely, the vanadyl group VO^{2+} and free radical (Guedes *et al.*, 2001, 2003). These are overlapped in the same magnetic field range (Fig. 5), being the very intense central line associated with organic free radical (Montanari *et al.*, 1998; Scott & Montanari, 1998; Yen *et al.*, 1962)

Figure:5 EPR Spectrum of Brazilian crude oil at room temperature (a) whole spectra of crude oil (b) simulated spectra of Vanadyl specie which indicates 16 spectral lines (c) Spectra of Organic free radicle.

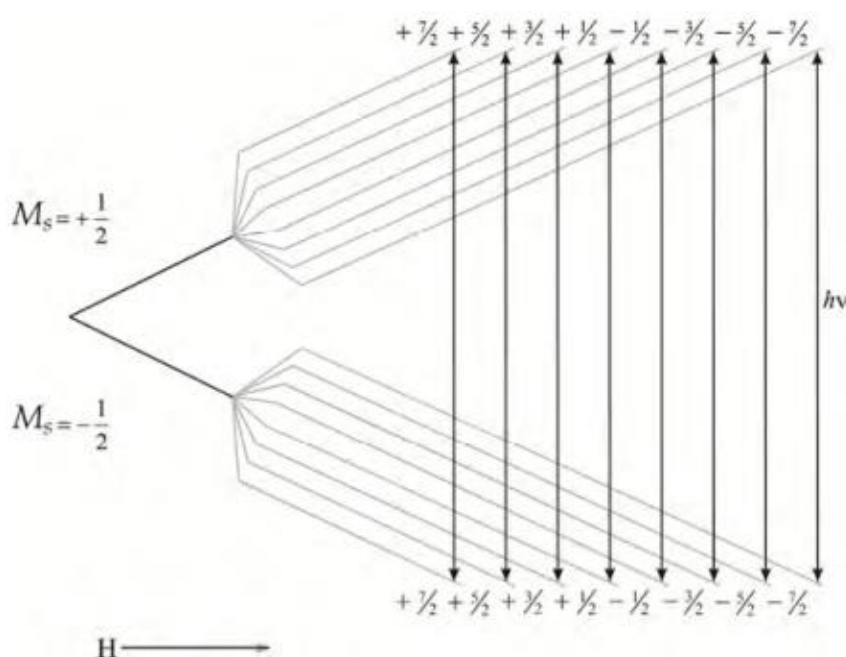


Source : (Barbosa Guedes *et al.*, 2003b)

In above Spectra it is seen the impurity of Iron oxide. The 16 spectral lines of vanadyle species in which 8 lines are parallel and 8 lines are perpendicular. The very intense line is Organic free radicle.

For vanadyl compound (VO^{+2}) produce EPR signals with anisotropic g-factor and hf splitting, for example vanadium in the presence of an external magnetic field, the interaction of electron spin ($S = 1/2$) with the nucleus $V^{51}(I = 7/2)$ has 16 possible states distributed between the two values S ($M_s = +1/2$ and $M_s = -1/2$) as shown in figure below

Figure:6 Schematic diagram of the hf splitting for unpaired electron interaction with a nucleus ($V^{51}(I = 7/2)$)



Source :(Piccinato, Guedes e Mauro, 2017)

These 16 spectral lines are splitted by 8 parallel lines and 8 perpendicular lines. The perpendicular lines are intense as compared to parallel lines and also form a derivative line. While parallel line shapes as Gaussian shape line. The perpendicular lines are more intense as compared to parallel lines because the interaction of electron spin with nuclear spin cause two directional transitions. There are 2 perpendicular transition as compared to one parallel line. Which cause perpendicular line of vanadyl spectral line more intense.

The radical present in petroleum asphaltene is associated with a nonlocalized π system of electrons stabilized by resonance. Garif 'ianov and Kozyrev (Garif 'ianov & Kozyrev, 1956) were the first to briefly mention the presence of unpaired electrons in crude oils.

Petroleum and related materials such as heavy oils, asphalt, pitch, coal tar, tar sands, kerogen, and oil shale have been studied by ESR (Ikeya, 1993). ESR is a useful method for the investigation of free radicals.

The free radical gives rise to a single line corresponding to the transition between the spin $+1/2$ and $-1/2$. The two possible configurations for an unpaired electron in the presence of an external magnetic field (spin up and spin down) have different energies, which are

represented by energy level diagrams (Fig. 1). In the absence of an applied magnetic field, the two spin states are of equal energy (Weil e Bolton, 2006).

The parameters are used to identify an EPR signal of free radical. Among them we can point out the g -factor and the line width (ΔH).

The g parameter is sensitive to the chemical neighbourhood of the unpaired electron, although the asphaltenes (the heavy fraction of oil) have the nature of a mixture of free radicals. In a non-localized system an unpaired electron travels over the different atoms, and therefore the g value tends to increase when heteroatoms are present in the system (Montanari et al., 1998).

The g values for the free radicals of asphaltenes in some investigated oils range from 2.0028 to 2.0034, being higher than those of the aromatic hydrocarbon radical ions and increasing with the decrease of the aromatic fraction and the related carbon content (Montanari et al., 1998). The relation between g value and aromatic fraction can be seen with the Arabian and Colombian oils: the fact that Arabian oil ($g = 2.0033 \pm 0.0001$) presents a heteroatom weight percentage of 2.79%, smaller than Colombian oil (19.77%wt), and the fact that nitrogen and sulphur are located mainly in the aromatic systems in petroleum, indicate that this oil is less aromatic than the Colombian oil ($g = 2.0030 \pm 0.0001$) (Guedes et al, 2006).

The g parameter values for the radicals in petroleum asphaltenes were found to be closest to certain types of neutral carbon and nitrogen radicals. To Arabian petroleum (2.0033 ± 0.0001) and Colombian petroleum (2.0030 ± 0.0001) (Guedes *et al.*, 2006), one possible interpretation for the g values observed likewise corresponds to neutral radicals of carbon or nitrogen. To Brazilian petroleum (Campos Basin in the state of Rio de Janeiro), the $g = 2.0045$, suggest the presence of phenoxy radicals, i.e. radicals partially localized in aromatic systems due to the oxygen (Barbosa Guedes *et al.*, 2003a)

In all crude oils, the signal of free radicals in the ESR spectra consist of an unresolved linewidth with a width of about 5 G (Barbosa Guedes *et al.*, 2003a; Luísa e Guedes, 2001; Mauro, Guedes e Nascimento, 2005), in many works the Linewidth peak to peak of free radical signal are different, which dependents upon the chemical composition of Asphaltenes with Paraffines (Guedes *et al.*, 2006). No hyperfine structure is observed. In petroleum

asphaltenes, the hyperfine interaction is generally between the electron spin delocalized in an aromatic π orbital.

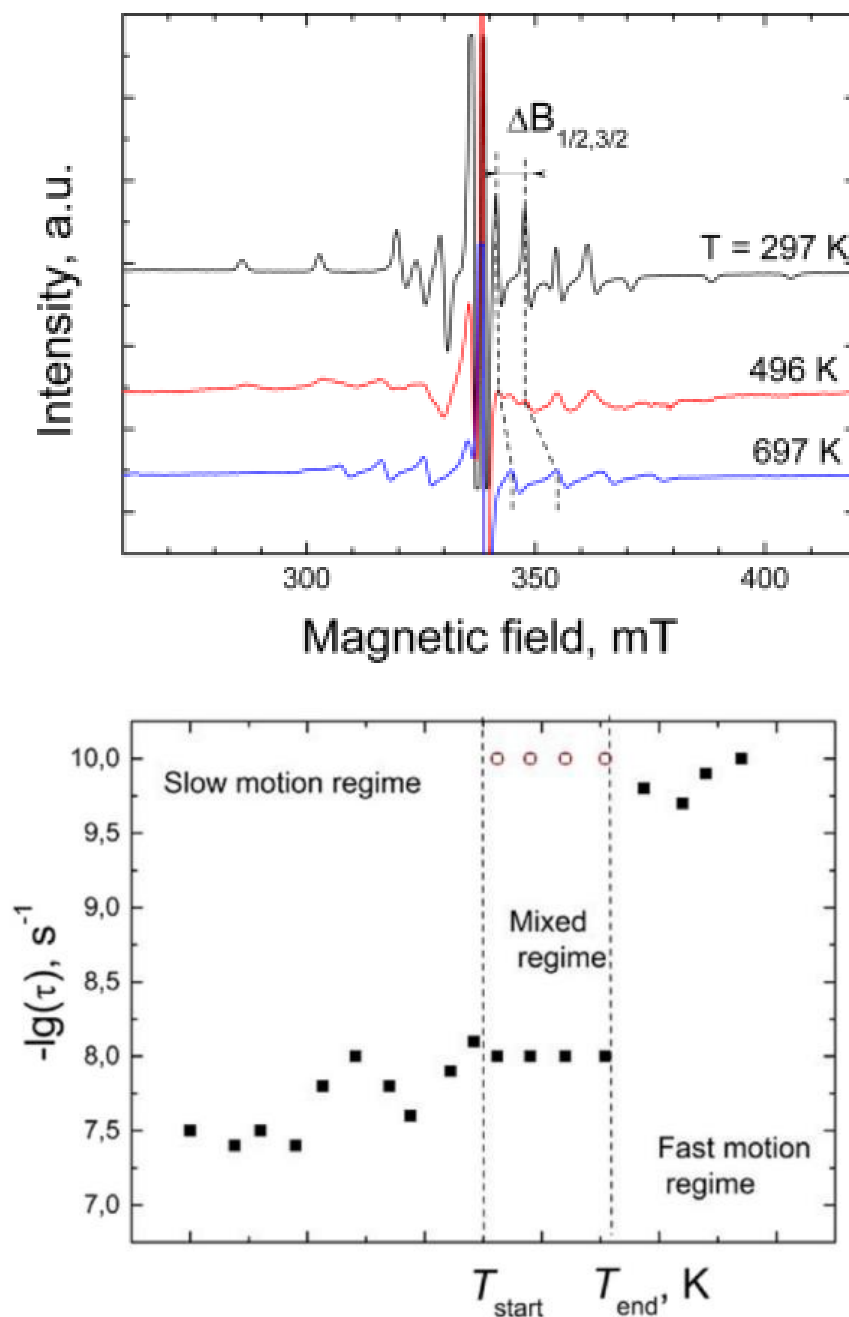
These free radicals present in the asphaltenes of this crude oil are imprisoned inside aromatic systems, which it can be determined by EPR. Solar irradiation reduces the aromaticity of petroleum degrading porphyrin complexes and destroying, at least in part, the asphaltene fraction of oil. The Fe^{3+} signal observed is not part of the molecular structure of crude oil; it is present in Fe_2O_3 . The EPR technique proved to be useful in the characterization of the molecular structure of asphaltenes in this Brazilian oil and also revealed changes of the photochemical nature in the oil under the effect of sunlight (Barbosa Guedes *et al.*, 2003b).

The precipitation of asphaltene raises the spectral lines of porphyrin, where these spectral lines characterize the crude oil. Such as at high temperature the crude oil having vanadium in porphyrin of the crude oil shows a different behaviour of crude oil comparatively to room temperature. The two of any spectral line hyperfine distance measured with the temperature variation, showed the different transition phases (Biktagirov *et al.*, 2014).

The time relaxation to the vanadyl paramagnetic species increase with the temperature variation. Which also describe the mobility factor at room temperature and high temperature (Biktagirov *et al.*, 2014).

The rotational correlation time can be determined by putting the Asphaltene molecular diffusion measurements. It can be seen that the rotational correlation changes with temperature. These phase transition are determined by any hyperfine distance of vanadyl specie. Where the molecular diffusion exhibits slow motion, intermediate and fast motion regimes (Biktagirov *et al.*, 2014). The EPR spectra and the time rotational correlation in Figure 7

Figure: 7 (a) Simulation of EPR spectra of VO_{+2} in X-band for different values of rotational time expressed in the decimal logarithms (b) Extracted value of τ_c as a function of temperature



Source : (Biktagirov *et al.*, 2014).

When the crude oil have less precipitation of Asphalt, and the porphyrin of Asphalt having very less proportion of Vanadyl species, where EPR spectra's indicates almost

negligible. That the Free radical which is only the simple paramagnetic specie in the crude oil can be detect the similar behaviour of molecular motion changes.

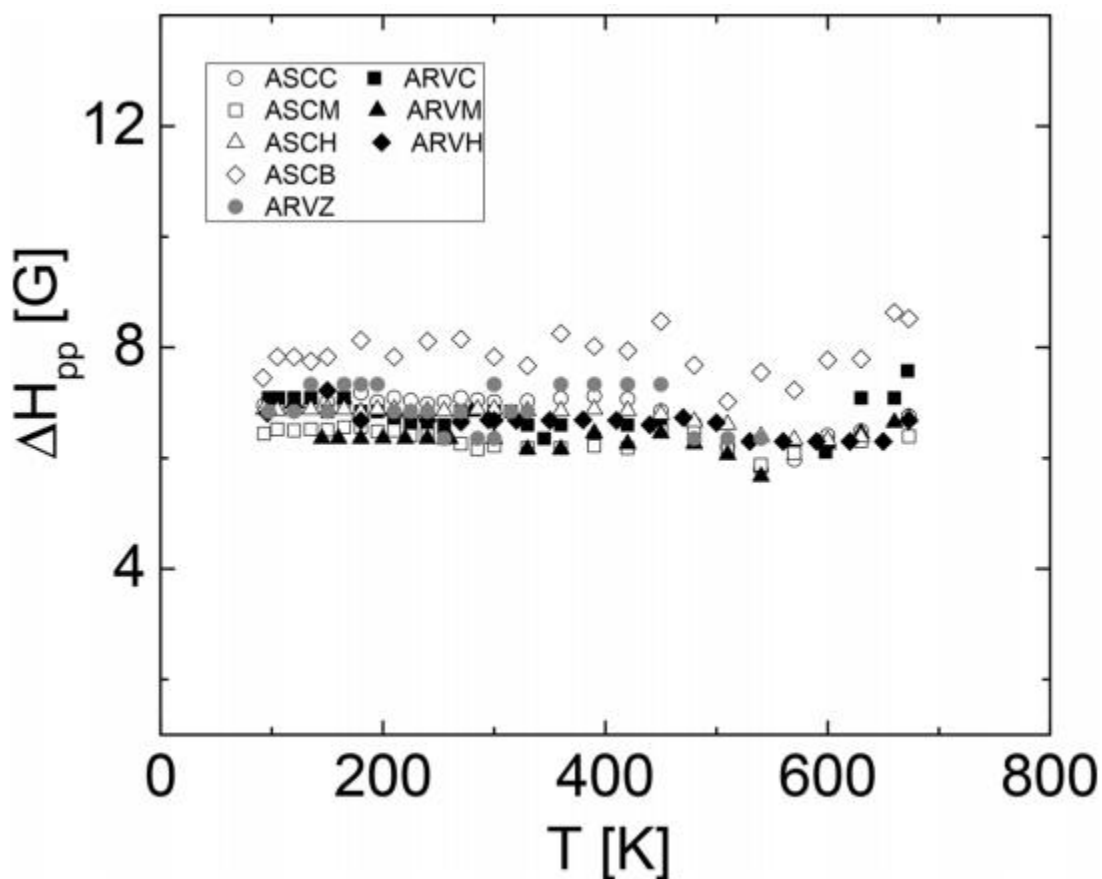
The effect can be studied in all form of oils, if it is heavy or light. But in the case of free radicle the parameter can only be use is line width of the free radicle signal. This can give the information of time rotational correlation and the phase change.

With increasing high temperature the spectral lines of vanadyl specie start altering. The parallel lines coming closer to perpendicular lines and these parallel lines intensities getting lower. At a certain point of temperature the hyperfine line distance of any two perpendicular lines start increasing. The time of relaxation shorter with high temperature. A time where all parallel spectral lines superposing on parallel lines. These alterations in hyperfine line distances make an indication of behaviour molecular mobility, that with high temperature the molecular mobility changes. This molecular behaviour is predicated by EPR spectra's, and also high temperature the prediction of change in molecular mobility from vibration to rotational motions of molecules is measured by hyperfine line distance of perpendicular spectral lines. This effect is show in figure above

The line width is parameters necessary for this transition phase occurrence. These parameters can also determine the limits of phase of intermediate regime for each type of oil by its chemical composition. In case any paramagnetic specie can be responsible to determine the phase change in molecular mobility.

Recently in 2019 a work has been published about line width of free radical with temperature variation of heavy and extra heavy crude oils. Although there is a small tendency at temperature where crude oil changes its behaviour to molecular mobility. But due to its extra heavy molecular weight there is difficult to visualise the variation in initial. The descending of line width of organic free radical is due to more Asphaltenic precipitations, secondly the crude oil having its parallel and perpendicular lines are dissolved in each other. the figure (8) is given below.

Figure 8: Temperature dependence of Line width peak to peak P of the FRs for all of the samples studied.



Heavy crude oils having less tendencies in their line width of EPR signal of organic free radical, while lighter crude oil having high tendencies in their line width of EPR signal of organic free radical. Which means that free electron are interlock in heavier asphaltenes have less movements as compared to lighter crude oils. This indicates that free radicals are a good probe for detecting structural changes in the samples; these changes line width of organic free radicals leads us to study the alteration in molecular mobility of crude oil.

Chapter 4: Material Methods

This chapter discusses the technical details of the Crude oil samples extractions, sample handling, as well as the experimental setup used for temperature dependent conduction electron paramagnetic resonance spectroscopy (EPR), and other techniques of the interest.

4.1 Samples Extractions

The experimental work was involved the analysis of Pakistani based crude oils. Which were collected from the Hydrocarbon development institute of Pakistan, Peshawar/KPK. The origin of these crude oil samples were from the Kohat-Potwar Basin (Upper Indus Basin) belonging to the Kohat City of Khyber-Pakhtunkhwa Province, Pakistan.

The Kohat region crude oils used in the study were of Paraffinic and Aromatic origin. Figure 9 shows the geographical explorations centres of the explorations points of the Pakistani crude oil at Kohat-potwar basin.

Figure 9: Petroleum Systems and Related Geologic Studies in Region 8, South Asia, where show the Kohat potwar and indus basin. [C.J. Wandrey, 2004]

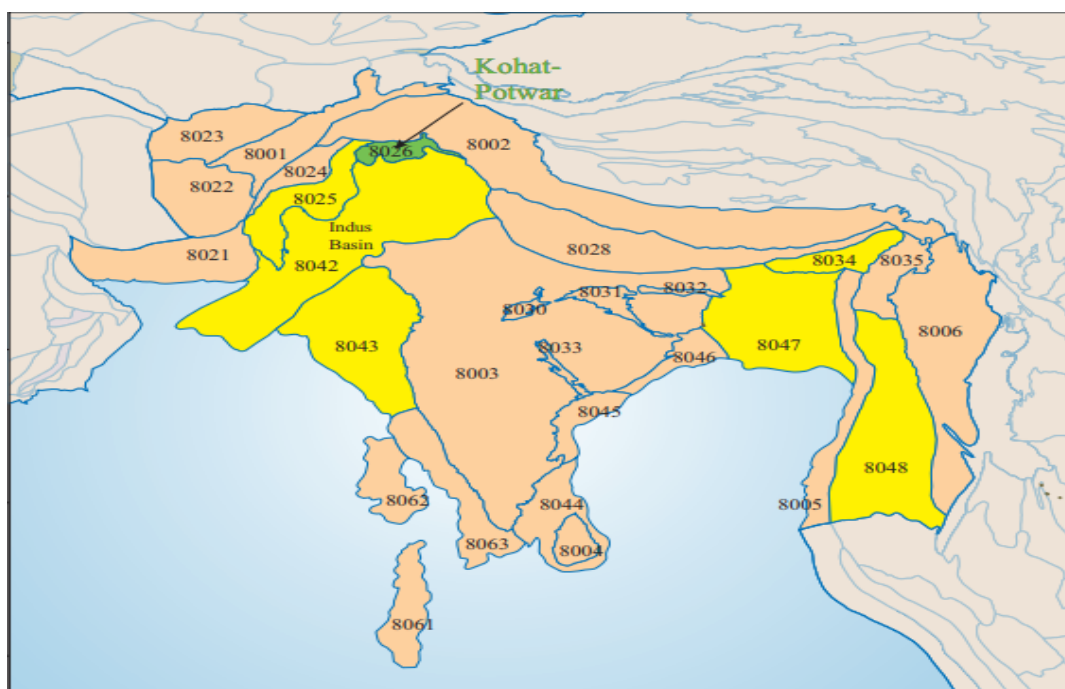


Table 2 : Chemical composition of Pakistani crude oil of each origin

Samples	Density at 289K (g/cm³)	API gravity @ 298K	Aromatics	Saturates	Asphaltene % weight
Paraffinic *(s1)	0.877	54	33	45	10
Aromatic *(s2)	0.94	22	49	28	12

* **Paraffinic, aromatic**(Ahmad *et al.*, 2018)

The characterization of samples has been done in Hydrocarbon development institute of Pakistan, Peshawar/KPK. Samples were investigated by means of the saturate, aromatic, resin, and asphaltene (SARA) fractioning technique.(Ahmad *et al.*, 2018).

4.2 EPR Spectrometer Setup

Data Acquisition System

The analysis of the samples with the temperature variation were performed with the temperature variable controller (JES-VT-3A), coupled to the spectrometer, which allows the variation of the temperature in between 103K to 573K.

The experiments were performed in sealed quartz tubes of 3 mm diameter in the temperature range from 300 to 553 K. Pure Samples of 0.92g of Paraffinic and 0.97g of Aromatic crude oils were introduced in the quartz tubes, inserted in the resonant cavity of the EPR spectrometer.

A variable temperature EPR experiments were performed with the crude oil samples at X-band (ca. 9 GHz) with a modulation amplitude of 1 G and a magnetic field modulation of 100 kHz on a JEOL (JES-PE-3X) spectrometer with a variable temperature controller (JES-VT-3A) unit. MgO: Mn²⁺ was used in the experiments a g marker which was maintained in the cavity of the spectrometer, whose signals were obtained simultaneously with the signals of the samples.

The experiment was carried out at room temperature as well at different temperature in the laboratory of fluorescence and electron paramagnetic resonance (LAFLURPE) in the *Centro de Ciências Exatas* at the state university of Londrina.

4.3 NMR Spectroscopic Setup

All experiments of NMR were performed at equipment Bruker Minispec MQ20, with the static magnetic field of 0.5 T of Larmor frequency of ~ 20 MHz and the temperature controlled by a Bruker BVT, with a ± 3 K error. The sequence used was a CPMG, with 50k pulses and 15s recycling time (it is the time for the sample to thermalize after the application of the radiofrequency. of 400 microseconds. The Temperature was adjusted using controller with Bruker BVT 3000.

The experiment was carried out at room temperature as well at different temperature in *Laboratório de Ressonância Magnética Nuclear* at Federal University of São Carlos.

4.4 Viscosity Measurement:

The Cannon brand of serial number U 558 viscometer was used, at temperature 40 °C and 100 °C with a correction factor of 0.0082216 mm/S² and 9.99 mm/S². The experiments of viscosity were performed with the help of a thermostatic bath of the mark Lactea Flash model. The experiments were performed at Laboratory of Combustion and Fuel at State University of Londrina.

4.6 RHEOMETER

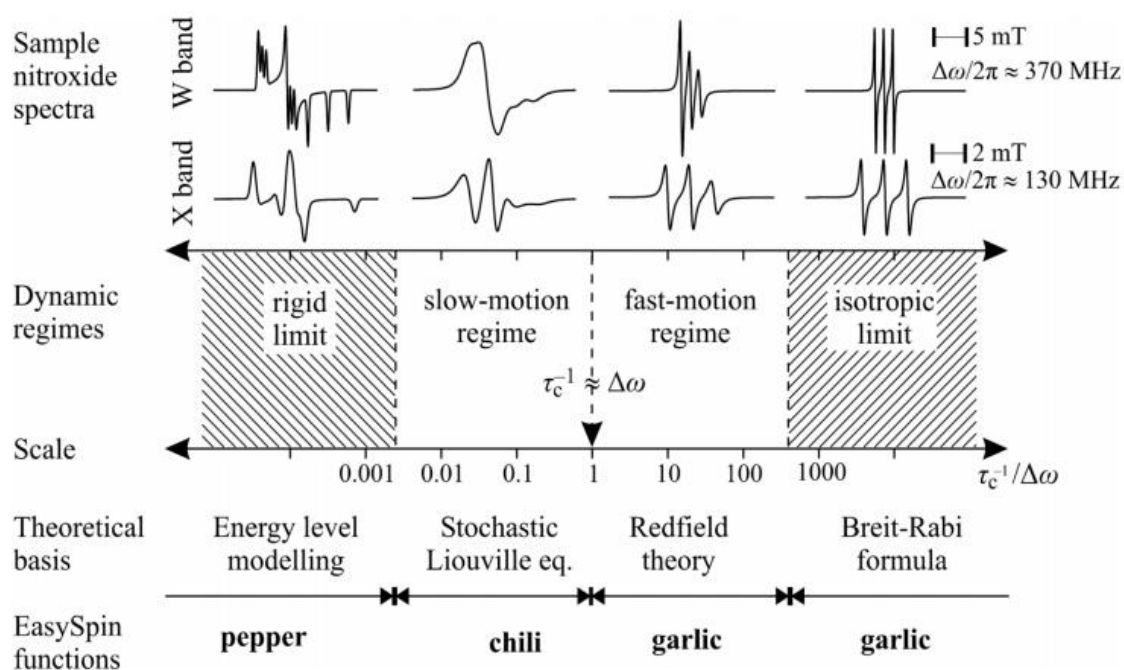
The equipment used was the Physica MCR Serie 301 rheometer - brand Anton Paar Germany GmbH, Rheoplus software, coupled to a Peltier P-PTD200 with temperature control from -30 to +200 ° C. The amount of sample use is 18ml each by means of Paraffinic and Aromatic samples only. The shear rate is constant at 100 s⁻¹ and the measurement system used was

The experiments were carried out at *Lab. Nanotecnologia* of *Embrapa Instrumentação* Research Centre São carlos.

Chapter 5 Result and Discussion

According to (Stoll e Schweiger, 2006), the most dynamic important and most visible observed by RPE in membranes or solutions, which is the in the case of oils, is the change in molecular motility. The rotational component of the motion modulates the resonant frequencies and gives rise to fluctuations in magnetic fields that induce transitions. The correlation time τ_c , which denotes the characteristic time, in which the molecules that were initially identical orientations lose their alignment, they can then be related to the D_{rot} rotational diffusion coefficient of each molecule and the viscosity η of the medium using the Stokes-Einstein relation (Nicot, Fleury e Leblond, 2006). Still according to these same authors, when comparing the speed of the diffusion of rotation τ_c , it is possible to distinguish four dynamic regimes with different types of spectra of RPE: (1) Rigid regime (2) Slow motion (3) Fast motion (4) isotropic boundary. They are shown in Figure 11, together with the spectra of the sample of a radical nitroxide in the X-band and W-band.

Figure 10: Forms of lines according to velocity of diffusion



Regarding changes in line shapes, the temperature changes in a more touching way the reaction medium, because, when changing it, the coefficient of viscosity of the oil. It is observed that for liquids of low viscosity, molecules may have an opportunity to go through a few cycles of rotation, which before they collided with each other (Weil e Bolton, 2006).

The intensities of the resonance signals, in turn, are influenced by the direct action of temperature (Wilson, 1966). Demonstrated that this effect extends all lines equally, amount of extra energy to the system, the between population levels.

By analysing the EPR spectra of all the oils, there is behaviour in relation to the influence of temperature on the line width of organic free radical signal. According to Canciam (2010), the concentration of and rheological parameters are related. This energy indicates viscosity sensitivity due to temperature change. The crude oils with higher concentrations of Asphaltene will require higher temperatures to achieve a lower viscosity.

5.1 EPR at room Temperature

The Paraffinic and Aromatic crude oils were analysed through Electron Paramagnetic resonance (EPR) Technique. The Organic free radical signal was being observed during the analysis for both samples, while applying a magnetic field of 3270.

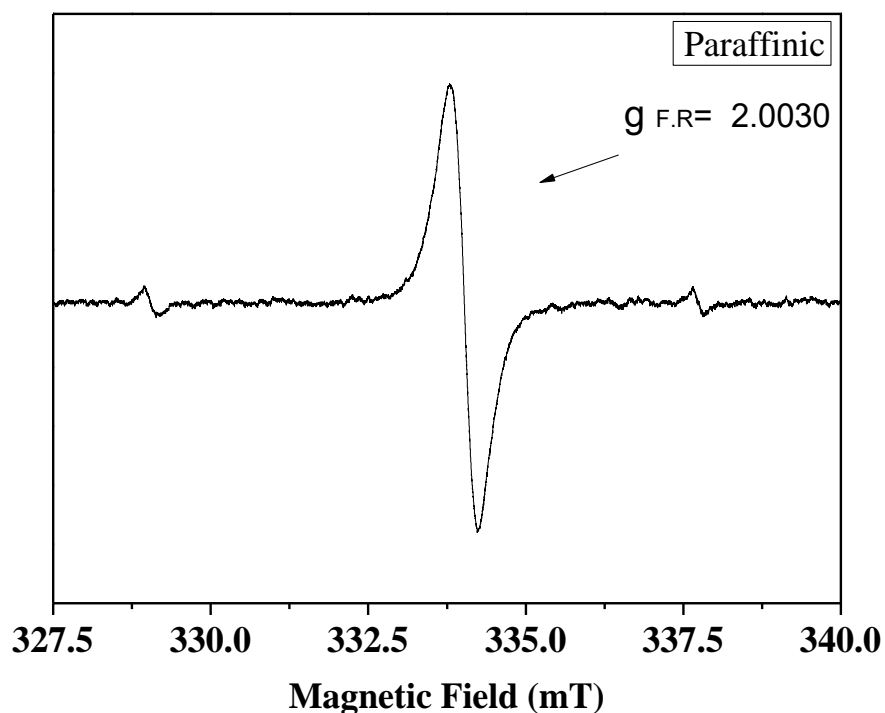
The vanadyl VO^{+2} signals of EPR was not observed, due to the absence of the paramagnetic ions of vanadyl VO^{+2} , as a very low proportion of the porphyrin in the crude oil samples is suggested.

The spectroscopic factor (g value) was also calculated for the Paraffinic and Aromatic crude oils, the samples which show a presence of the stable free radical at room temperature.

Paraffinic Crude oil

The Paraffinic crude oil was submitted to EPR measurement in room temperature. After obtaining the spectra of EPR, there was only free radical signal of EPR observed. due to less precipitation of Asphaltene, it is hardly to see any VO^{+2} (Vanadyl) signals. The figure 11 displays the derivative of EPR absorption spectra where one can see the presence of free radical.

Figure 11: EPR of Paraffinic crude oil at room temperature (298K).



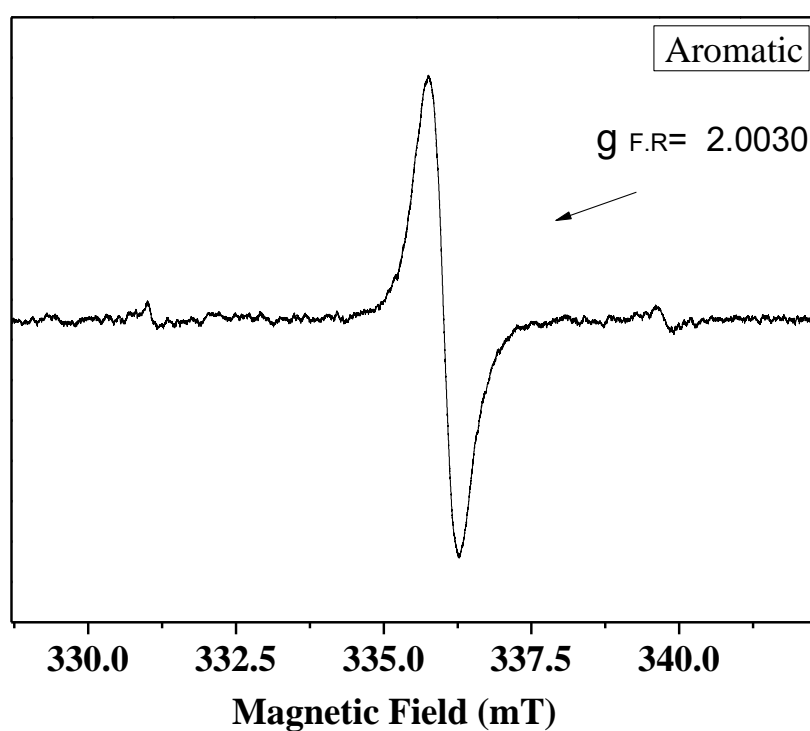
The spectra of Paraffinic at room temperature show an intense resonance line, centered at $g = 2.003$, with linewidth peak-to-peak $\Delta H_{PP} = 0.42$ mT and $\Delta H_{1/2} = 0.96$ mT. This resonance line is characteristic of organic free radical and the parameters obtained are in accordance with those in literature (Barbosa Guedes *et al.*, 2003b; Mauro, Di, Guedes e Nascimento, 2005). The pair of lines at sides of the spectra are due to the MgO:Mn²⁺ field marker.

The crude oil can also be classified by g -value. Whereas Arabian crude oil ranges of g -values is 2.0030-2.0045. The crude oil from Brazil and Venezuela values are above 2.0045. (Barbosa Guedes *et al.*, 2003b).

Aromatic crude oil

Aromatic crude oil measurement done by EPR technique; the line shape exhibits same as Paraffinic crude oil. The intensity of signal is intense and Sharpe. The spectrum of aromatic crude oil is given below in figure 12. The resonance line, centered at $g = 2.003$, with linewidth peak-to-peak $\Delta H_{PP} = 0.49$ mT and half line height width $\Delta H_{1/2} = 1.1$ mT.

Figure 12: EPR Free radical signal of Aromatic Crude oil (s2) at room temperature (298K).



The line width of aromatic is 5.04 mT at room temperature. As earlier in table 2, we discussed about density, at room temperature the aromatic crude oil is denser and viscous compare to Paraffinic crude oil, in the table we discussed that aromatic crude oil have more asphaltenes and aromatic rings compared to paraffinic. it may happen that the relaxation time to form a signal is shorter as compared to paraffinic crude oil. The free radical in aromatic crude oil mobility is comparatively rigid and the motional averaging is not significant.

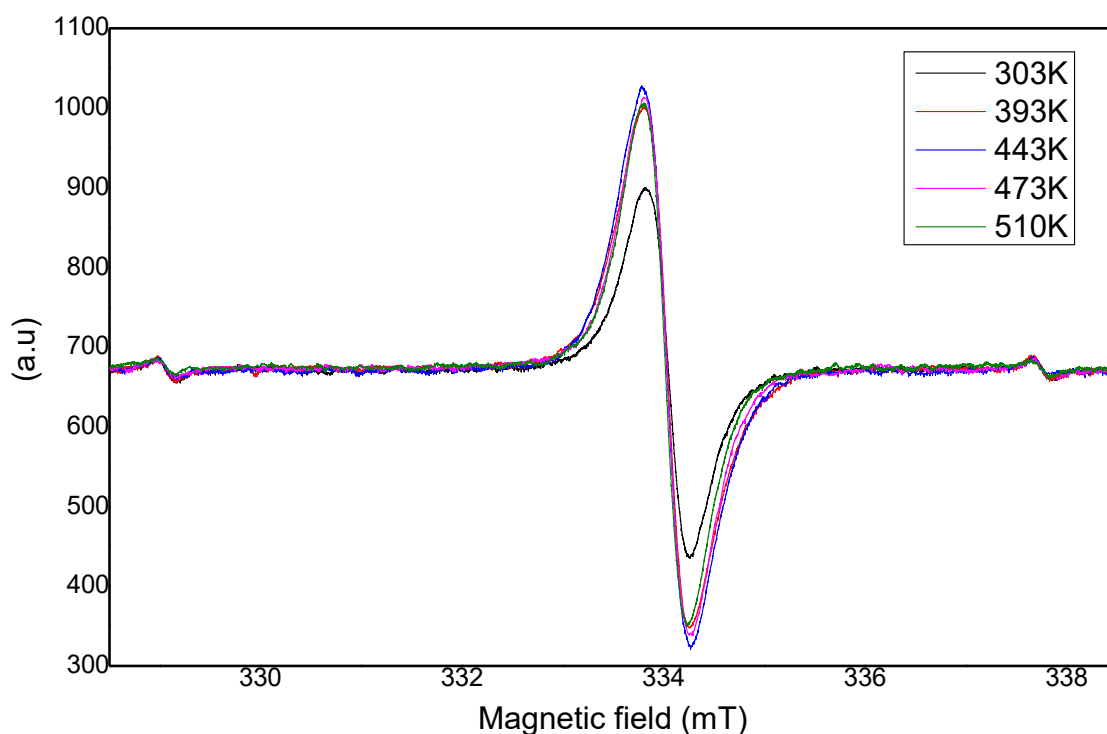
5.2 EPR with Temperature Variation

The samples were analysed by EPR in the presence of high temperature, having similar spectra's. Which have only one paramagnetic specie; free radicle. The EPR signal intermediate corresponds to free radical.

Paraffinic Crude oil

The temperature variation of EPR signals of free radicle in figure: 13 it was observed in the increase in line width and half line width of organic free radical signal with temperature variation. Below in the graph there are some selective spectra's of EPR free radicals.

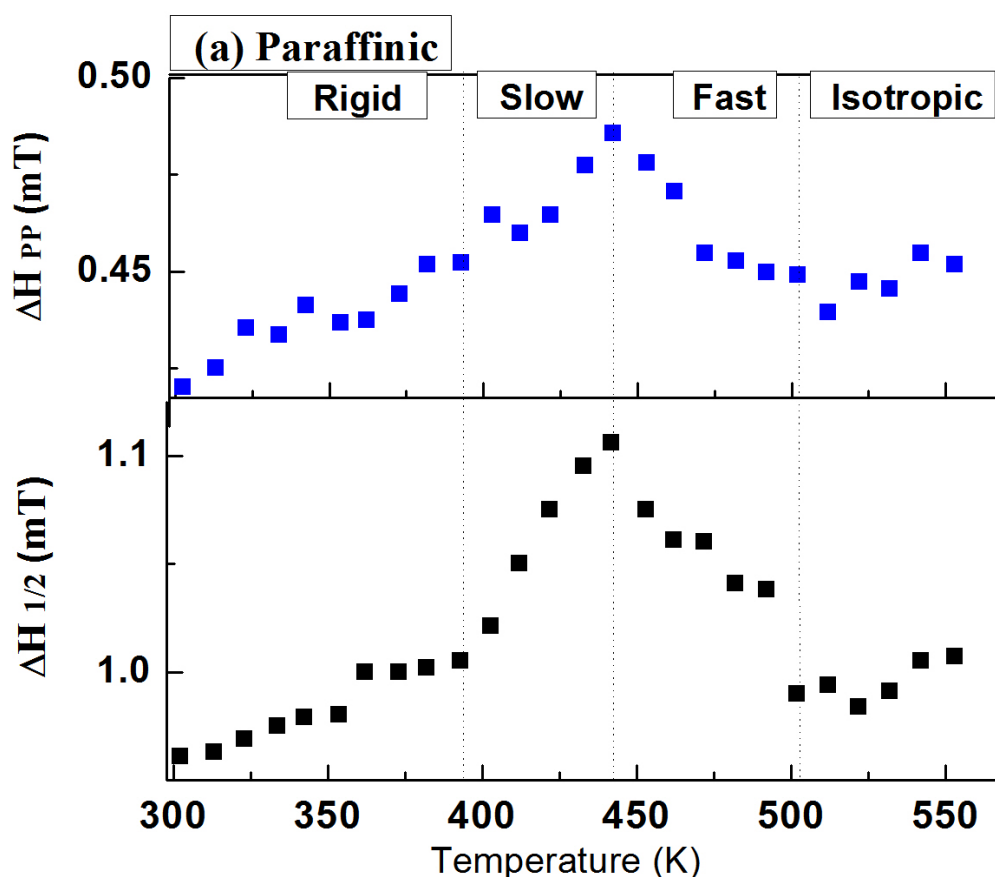
Fig.13: EPR free radical signal of Paraffinic crude oil with temp variation



The analysis of EPR spectra allowed us to find a spectroscopic parameter sensitive to the motional regime of Free Radicle. We have chosen a distance (peak to peak of the magnetic field values) of the spectral line related to the of free radicle.

In Figure: 14 the temperature variation of EPR signals of free radicle shows similar properties (increase in linewidth and half line width of signal of free radical by EPR). Paraffinic oil line tendency starts at 393K and then peak at 443 K, After that declining the line width till 523K. This increase and decrease of line width corresponds to four regions of mobility of molecule (Stoll e Schweiger, 2006). And also gives similar behaviour to the heavy crude oil having VO^{+2} (Biktagirov *et al.*,2014) .

Figure.14: Temperature dependency of peak to peak linewidth of free radical and half line width of free radical, of Paraffinic crude oil. Where the vertical lines drawn means the temperature where transition occur.



To understand the linewidth variation of EPR lines is necessary to remember that crude oils usually presents high values of viscosity at room temperature, which means that the behaviour of these crude oils could be considered such as a rigid system, with regard of its molecular mobility (Biktagirov *et al.*, 2014). In this kind of systems is common to observe an EPR spectrum similar to a powder spectrum (O'Reilly, 1958; Turini, Barbosa Guedes e Di, 2012), in which is possible to observe both parallel and perpendicular values of g (Barbosa Guedes *et al.*, 2003b; Biktagirov *et al.*, 2014; Turini, Barbosa Guedes e Di, 2012). Indeed, this behavior it was observed in crude oil samples, where the hyperfine parameters of vanadium, common in some crude oils, showed both parallel and perpendicular values of g (Biktagirov *et al.*, 2014; Gafurov *et al.*, 2018). In the case of the free radical spectrum of crude oil, it is possible to expect the parallel and perpendicular components, but these components are not settled, because of an overlay of the resonance lines.

With increasing temperature, and consequently decreasing in viscosity, two effects can be expected on crude oils samples: a decreasing in relaxation time; and an approximation of the parallel and perpendicular values of g . These two effects would cause variations in EPR linewidth of the free radical spectrum. The gradual changing in mobility regime will cause decreasing in relaxation time, contributing to a broadening of the resonance lines (Gerson e Huber, 2004). On the other hand, with the increasingly change of the regime of rigid to a liquid regime, the EPR spectrum migrates from a powder spectrum to an isotropic spectrum. This effect will cause an approximation of the parallel and perpendicular resonance lines, until the isotropic regime, where a total overlay of the lines will occur. This way, considering that the free radical EPR lines of paraffinic crude are composed of both parallel and perpendicular component, with the decreasing of viscosity we might expect a decreasing of linewidth.

Two competing effects regard to EPR linewidth, the line width and Half line width variations with increasing temperature, it can be divided in regions.

Rigid Region: As in Figure: 15 it is seen that with the increase in temperature, there are four regions of molecular mobility. The interval of this region is from room temperature to 393K. As Paraffinic crude oils have branched saturated hydrocarbon. Which make difficult to do orientations, the majority of asphaltenes which are joined with paraffenes are predominant

rigid. The molecule behaves like solid or a powdered spectrum, and it's difficult to see the variation in line width of free radical signal in this region.

Slow motion Region : In this slow-motion regime (393K- 443K) in figure: 15, the broadening in EPR linewidth, caused by the decreasing in relaxation time, overcomes the narrowing caused by the approximation of the parallel and perpendicular components.

Fast Motion region : in the fast-motion regime (443K-503K)in figure:15, *i.e.* the overcoming of the isotropic phase in relation to the rigid, the effect of narrowing overcomes the effect of broadening, so is observed a decreasing in linewidth. The faster rotational diffusion leads to the effective averaging of g-factor anisotropy. In this region the parallel line and perpendicular lines are dissolved completely, which gives in the result the decreasing in linewidth of free radical.

Isotropic region: in the last region (above 503K) in figure: 15, the system is considered predominantly isotropic, after 503K the line width either no appreciable variation of linewidth or again another tendency in increase of line width can occur. This variation after 503K in isotropic actually happens due to more precipitation of asphaltenes. In case of Paraffinic crude the variation is negligible.

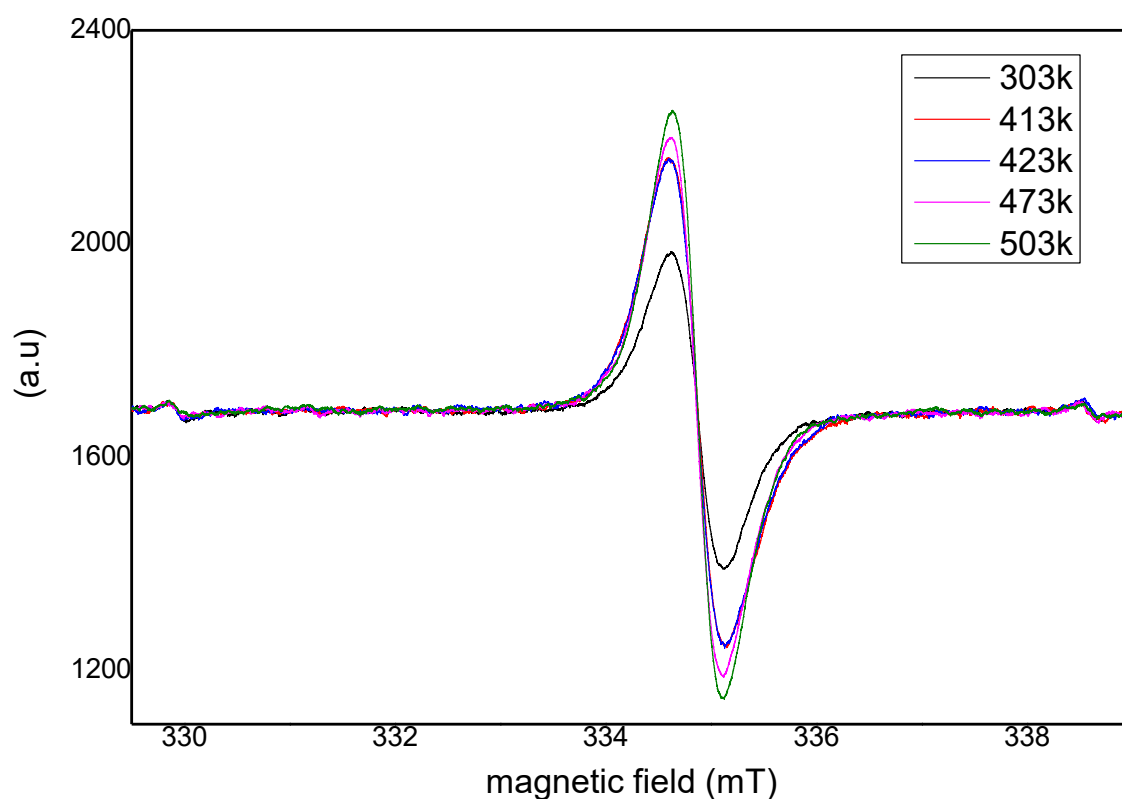
One more reason is why there is no variation in line width doesn't occur in isotropic region of less denser oils. Equation (7) tells us that at certain high temperature the energy giving to system is either equal or less to heat energy. Where the transition of electron happens in very least energy levels, therefore it cannot observe the appreciable variation of line width.

Aromatic Crude oil:

Aromatic crude oil measured by EPR technique with temperature variation. Temperature rang was 298K to 553K in all temperature the free radical spectra was sharped and parameters were set with the increase in temperature the line width of radical increase till certain temperature where line width doesn't increase more and start declining .

The EPR signal of free radical with temperature increasing of selective spectra's is given in figure :16

Figure. 15: EPR free radical signal of Aromatic crude oil with temp variation.



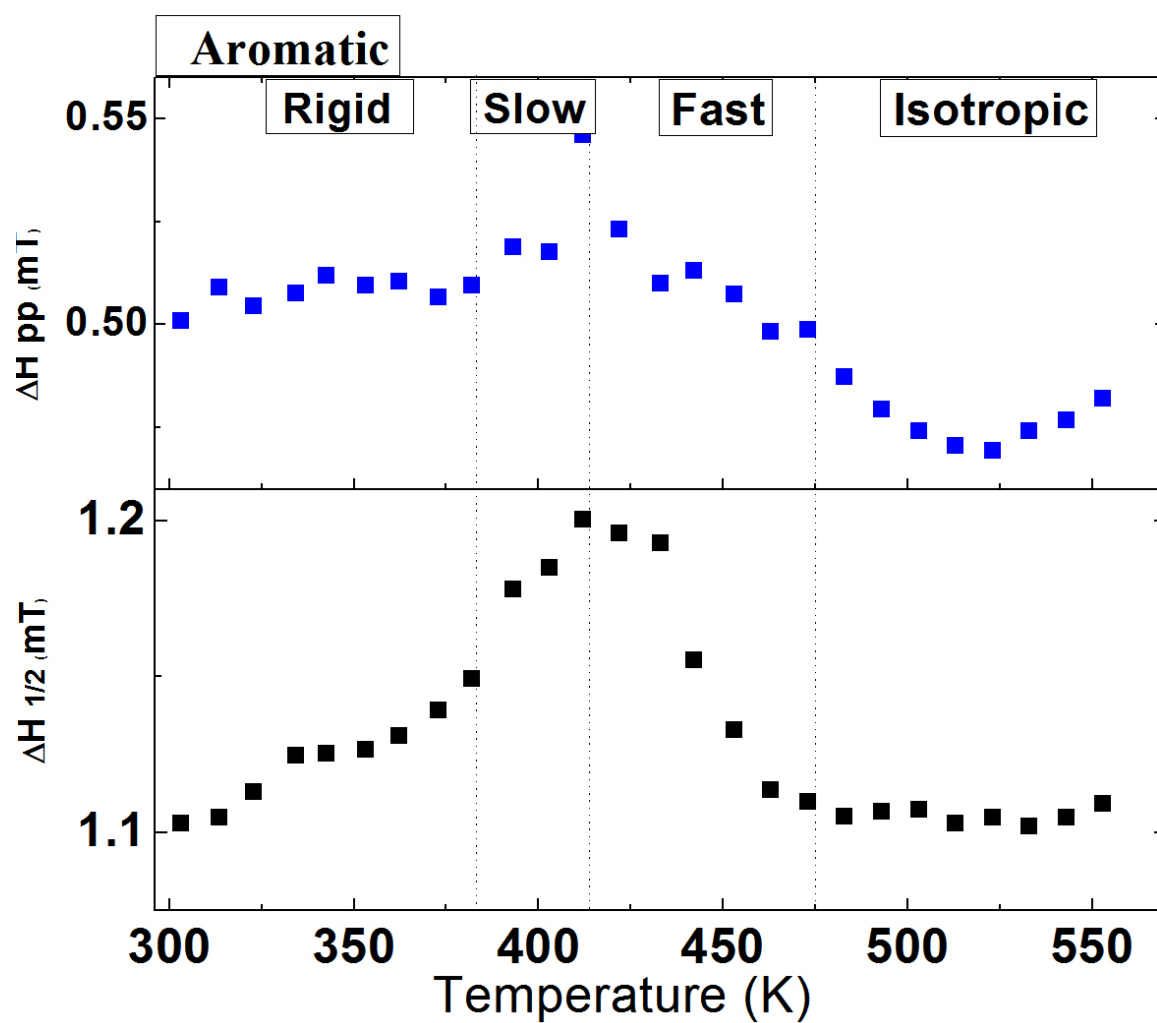
After finding the line width of all spectra's from 298K to 553C. It can be seen that there are three regions. The graph of line width and temperature variation is given below..

In Figure:15 the temperature variation of EPR signals of free radicle shows similar properties (increase in linewidth and half line width of signal of free radical by EPR).

Aromatic crude oil has less variation in line width as compared to paraffinic with increasing temperature, and it obvious because the aromatic sample have more asphaltenes and aromatic rings, which are heavier part of crude oils. These heavier precipitations make it difficult to show major difference in line width variation.

secondly the sample have more asphaltene which is shown in Table 2 and as free radicles are found in the π system of asphaltenes, which can say us the parallel line and perpendicular lines are resolved or overlapped in each other. Below the figure :17 shows the four regions of molecular mobility measured by line width of organic free radical.

Figure.16: Temperature dependency of peak to peak linewidth and half line width of free radical signal, of aromatic crude oil.



Molecular mobility regions in Aromatic crude oil.

Rigid Region: As in Figure (16) in interval of (room temperature to 383K) there is likely constant line width and half line width. In this region the oil have the behaviour of powder spectra. With this higher molecular weight it could be expected a lower decrease of relaxation time with temperature increase, resulting in a less sensible variation of linewidth observed. Asphaltene cause difficult in molecular motion in early on stages to temperature dependency. But Aromatic rings open earlier as compared to saturated hydrocarbons. This is a reason that the denser crude oil having more asphaltene doesn't cause the early on stage of Rigid to slow motion region. This result also seen in literature (Hernández, Coll e Silva, 2019) for heavy crude oil.

Slow motion Region : In this slow-motion regime (383K- 423K) in figure 17, the broadening in EPR linewidth, caused by the decreasing in relaxation time, overcomes the narrowing caused by the approximation of the parallel and perpendicular components. But this approximation of parallel and perpendicular components happens quickly.

Unlike paraffinic crude oil, the aromatic oil does not have long chains, its chains are closed, and this facilitates the mobility of these asphaltene molecules in the oil. Even in the interval preceding the solid / liquid transition, it is possible that these molecules already begin to acquire sufficient mobility to exhibit some properties similar to the properties of molecules in liquids. In this way, we observe that before the solid / liquid transition itself, the EPR line width in this case has grown, reaching the apex just when the above transition occurs. The line width growth is not as intense as that presented by the Paraffinic petroleum sample, since the viscosity of this oil is higher at the same temperature, making it harder for the mobility that the aromatic molecules tend to acquire.

Fast motion Region: in this region (423K-473K) in figure (17) the parallel and perpendicular components are overlapped so that the line width starts decreasing. The majority of components are predominant liquid, therefore the interval in small for aromatic as compared to paraffinic.

Isotropic Region: (above 473K) the system of crude oil is completely isotropic. And here the half line width plays a role to determine the region of isotropic. Because the line width have more variation. And it is should be, because the aromatic sample is heavier and its behaviour

is similar to heavy and extra heavy oil. Which were discussed in literature (Hernández, Coll e Silva, 2019).

5.4 Low Field NMR

In highly viscous liquids, nuclear magnetic resonance (NMR) exhibits certain unique singularities at high viscosity and high temperature; these singularities become clearly manifest in the temperature variation of the longitudinal relaxation time T_1 . Upon cooling, which is accompanied in the case of such liquids by a strong increase in the viscosity, T_1 varies likewise viscosity.

It is assumed that the motion of the molecules in the liquid constitutes Brownian rotation and displacement of individual molecules, oil consists of many components, and relaxation time in these NMR correlations is usually the geometric mean relaxation time, T_2 .

For higher viscosity samples like heavy oil, the relationship between T_2 and viscosity is no longer linear. In fact, for very high viscosity samples, relaxation is so fast that the fluid is relaxing at the limits of what low field NMR can measure, and T_2 changes only marginally with changes in viscosity (Bryan, Kantzas e Bellehumeur, 2002).

For these fast-relaxing, a portion of the signal also relaxes too quickly to be measured with conventional low field NMR tools Therefore, high viscosity fluids also have relatively lower amplitudes than lower viscosity fluids

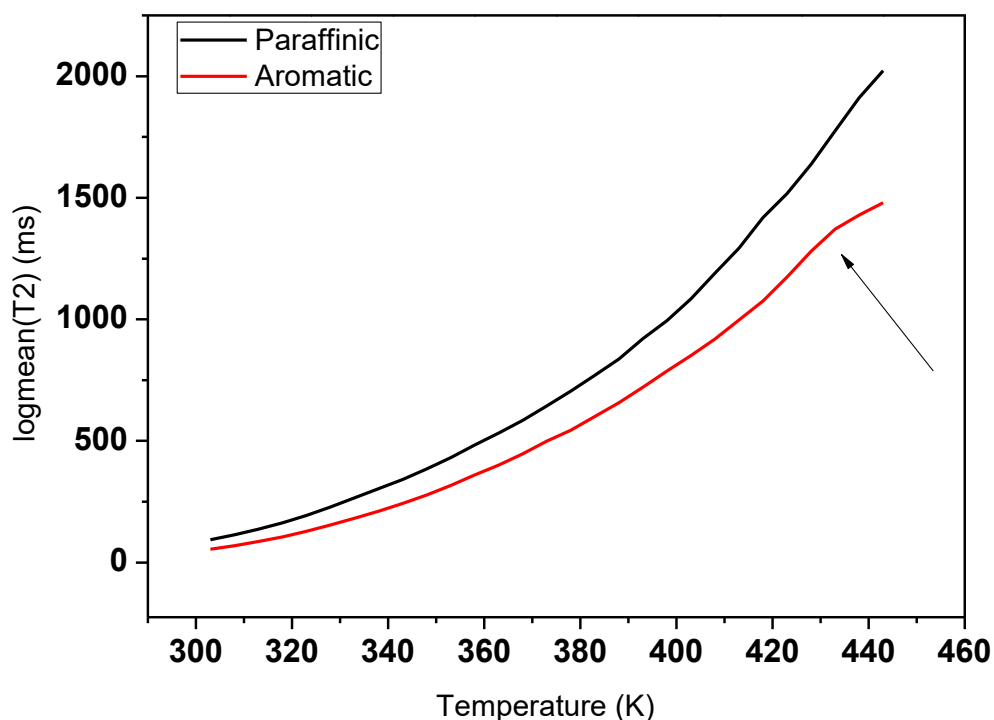


Fig : 17 Low Field NMR relaxation of crude oils with temperature variation, where the arrows describe at which temperature the relaxation changes.

As shown in above Figure 17 with the increase in temperature, in all samples the time of relaxation increases, till certain temperature the value of log means value of time relaxation changes but tendencies occurs at several temperatures for Aromatic crude oil at 433K, while for Paraffinic Crude oil have no change have seen.

For oils when if the logarithmic means of relaxation is above 2000, the behaviour is already considered to be in liquid form. Which in case of paraffinic have similar behaviour.

The fact that each type of crude oil has its own temperature in which it changes its logarithmic means of relaxation (T_2), together with the line width or in case of VO+2 the hyperfine line splitting effect detected by EPR also occur at different temperatures, lead us to consider the hypothesis that the temperature is not predominant factor altering the line shape, but rather it acts to alter viscosity index of crude oils, being this the determinant factor for changes occurring in the reaction in the reaction medium, in order to observe the line width in free radical or in case of VO+2 the hyperfine line splitting in between 2 perpendicular lines.

5.4 Viscosity

The idea presented that there is minimum viscosity in which all different kind of crude oils begins to have to a new molecular dynamics. This verification can be sustained with the visualization of the variation in the line width of free radical that occurs in the EPR spectra, since these changes in the reaction medium make the interaction with the intense hydrogen enough to be observed by EPR, then it can be stated that when visualizing the variation in linewidth of free radicals EPR spectra, the minimum viscosity was reached.

From this concentration of precipitation of Asphalt in crude oil, it can be assumed that even crude oils that have their viscosity modified or disturbed by other factors, when reaching this variation can be detected by EPR. The above hypothesis can be republished with the table 3 below, the viscosities found for each crude oil analysed.

Table 3 : EPR crude oils 1st mobility phase temperatures comparison with NMR time relaxation along with viscosity values. Where shown that phase of transition is at same temperature with.

Samples	Temperature (K) +/-5 K error	Temperature(K) +/-5 K error	Viscosity (CP)
	EPR (in term of line width of free radical)	NMR(in term of time relaxation T₂)	
Paraffinic	393	undefined	2.60
Aromatic	423	430	2.66

The temperatures at which EPR line width varying and minimum viscosities calculated by log means values provided by NMR of crude oils have almost same viscosity values.

The oxygen cause change in viscosity calculation by low field NMR, to get absolute viscosity values from NMR time relaxation, the samples are deoxidized first. And majority the disturbance in viscosity cause by oxygen seen in those crude oils of having less

viscosities. In medium crude oil and heavy crude oils the disturbance is negligible or week (Nicot, Fleury e Leblond, 2006).

The Kinematic viscosities were measured in laboratory to see comparison with the calculated viscosities by NMR time relaxation data, which is shown in the table below 4 . the kinematic viscosities of both samples were only measured at 313K and 373K.

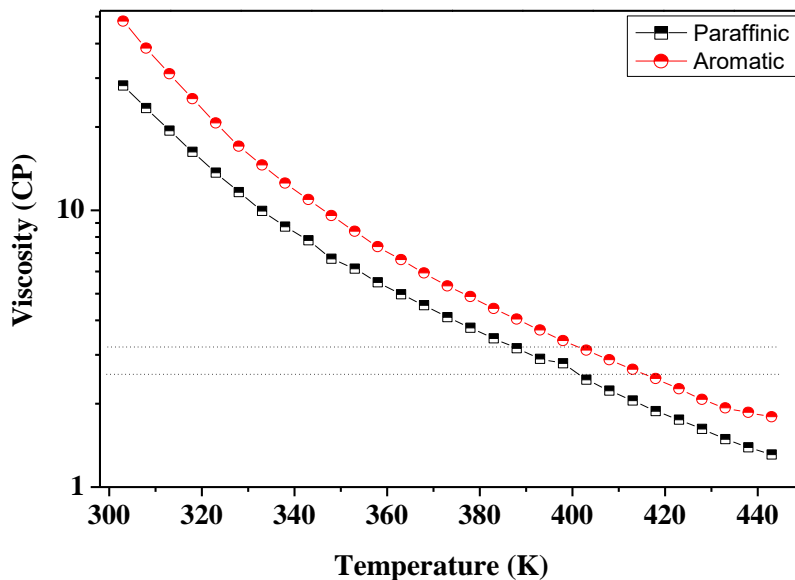
Table 4 : The experimental viscosities of Paraffinic and aromatic crude oil measured

Samples	Temperatures (K)	Viscosity (CS) (Experimental)	Viscosity (CS) (NMR)
Paraffinic	313	20	19.35
Paraffinic	373	4.11	4.11
Aromatic	313	35	32.5
Aromatic	373	5.31	5.30

In the table 4 the experimental viscosity which coincide to the theoretical viscosity value. It can be assume that the theoretical viscosity have less error in case of high temperature as compared to low temperature. earlier told that oxygenation can cause the difference in viscosity in less viscous oils, the difference is low as negligible(Bryan, Kantzas e Bellehumeur, 2002).

The Figures bellows shows the descending curves of viscosities in figure below

Figure.18: calculated viscosity by low field NMR with temperature variation of each sample, where shows the minor deflection at certain temperature.



Viscosity decreases exponentially with increasing temperature. As temperature increases, the fluid molecules gain more energy, and the spacing between molecules increases, so it becomes easier for them to overcome the attractive forces of their neighbours. This is observed as increased shear rate for any given shear stress. Most viscous Newtonian fluids, including crude oils, exhibit this exponential relationship between viscosity and temperature, so long as the fluid temperature is not near the phase transition temperature (Bryan, Kantzas e Bellehumeur, 2007).

Viscosity behaviour as a function of temperature. The curves of figure represent the fall in the coefficient of dynamic viscosity of crude oil. It is clear that the increase in temperature is responsible for the reduction in its value. As crude oil is mixture of different hydrocarbons and structure that their change in behaviour of molecular dynamics alteration happen at different temperature for each sample and different viscosity value at transition phase, but in case of Paraffinic crude oil the viscosity value is similar or close at phase of transition (Rigid to intermediate or Slow region) shown in above table 5.4. This transition phase is confirmed by the variation in linewidth of free radicle detected by EPR and log means time relaxation by low field NMR.

Free radicals in petroleum have little mobility due to high viscosity of the oil. So the EPR line corresponding to these radicals shows an asymmetry resulting from all possible orientations of the paramagnetic species in the system and also from the contribution of different chemical species that interact with unpaired electrons (Mauro, Di, Guedes e Nascimento, 2005).

Where the viscosity seen descending quicker by the figure 19 and a tiny change have been seen in all crude oil. As in case of the any oil or any liquid have viscosity lower than 10 CS at room temperature. When apply variation temperature and there can be seen the clear deflection in viscosity. Such temperatures at which the deflections or change in exponential line of viscosity is called critical temperatures.

Low field NMR technique was used to indicate the critical temperatures which were indicated by EPR technique. Second to measure the viscosity by means of transvers relaxation of each sample. As Low Field NMR equipment cannot concede or cross 443K, because of its limitations . So it is difficult to have to see the change in behaviour in the mobility of heavy crude oils or the crude oil which start it relaxation with resonance later.

Having more precipitation of Asphaltenes in crude oil, it is much difficult to estimate or visualize the tendencies in calculated viscosities at high temperatures, at which we can define the regions where molecular mobility alterations occur.

The crude oil having only signal of free radical gives more accurate critical temperature along with regions of molecular mobility. The first order of critical temperature region is called rigid motion regime. Because the radical in molecule behaves the spectra of crystals and more intense. After passing the first order critical temperatures the radical behaves like intermediate or inter solid-liquid.

The second order critical temperature gives the indication of radical molecular mobility as liquid or fast motion regime (Biktagirov *et al.*, 2014).

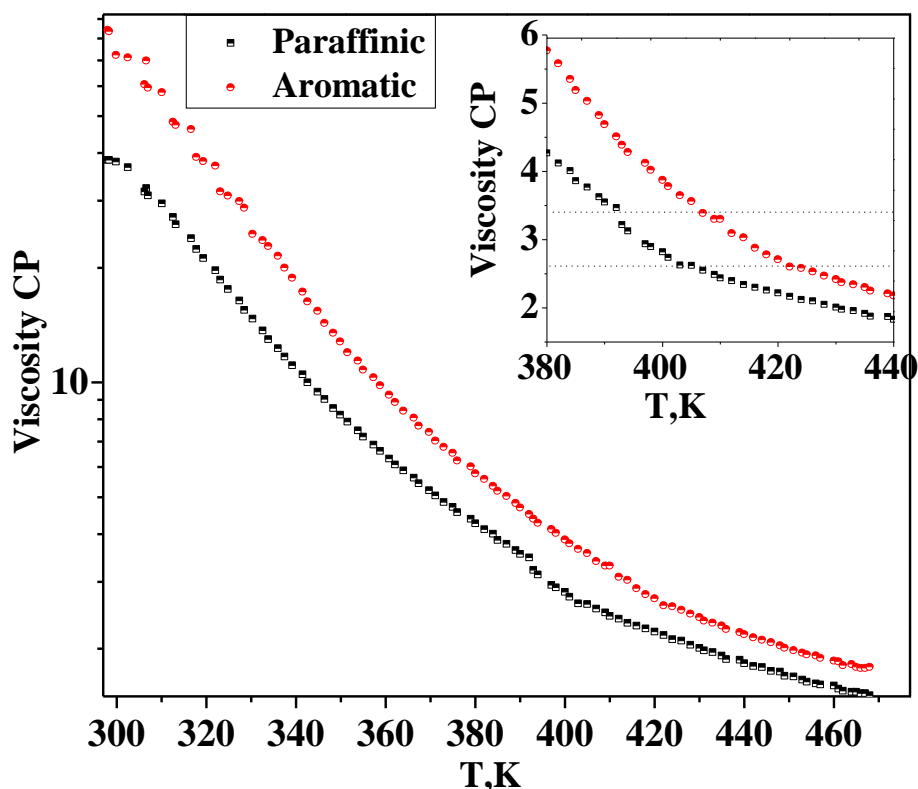
Increase in line width of free radical at second order or the maximum depletion in VO+2 hyperfine lines are same. At high temperature in all crude oil the solvent start evaporation and also some of boiling, said to be mass losing in oil.

5.5 Rheometer

Rheometer is use to deliver a solution that has both the simplicity and flexibility to meet the requirement for rheological characterization of dispersion and other complex fluids and soft solids. It helps to define and understand material characteristics from viscosity to viscoelasticity and to solve material problems. In order visualize that kinematic viscosity alone with theoretical viscosity (obtained from Log mean time relaxation value of NMR) have same property of phase change to dynamic viscosity.

The Dynamic viscosity is measured by Rheometer from room temperature 298K to 473K of both samples Paraffinic and Aromatic.

Figure 19 : Dynamic Viscosity dependency on Temperature variation of Paraffinic crude oil and Aromatic crude oil.



In above figure 19, shows same behaviour in change of molecular mobility. The dropping the viscosity with dependency on temperature variation, at determinant temperature the tendency in viscosity occur. As when oils having high viscosity, there are more turbulences occurs.

with temperature increasing the dynamic viscosity descending but at certain temperature happens a tendency in spectra if viscosity. This turbulence occurs in both samples. In paraffinic is quite visible but in aromatic this turbulence is viscosity is less as compared to paraffinic. The only reason may suggest is the abundances of poly aromatic rings.

It is quite interesting that both samples of having different compositions have started change in there molecular mobility at certain viscosity value, which is about 3,48 CP. While after 2,66 CP the viscosity becomes stabilize. It may suggest a theory that the oils having different viscosities may fall at same viscosity value at region where molecular mobility alteration occurs. And after that turbulence or disturbance in dynamic viscosity the stability is viscosity have same value.

Hence we can say that either its dynamic viscosity or Kinematic Viscosity, if it is time relaxation by EPR or Log mean time relaxation by low field NMR, every technique approach to same point of molecular mobility.

Conclusion:

Aromatic and Paraffinic samples showed EPR signal characteristics of organic free radical.

EPR half height linewidth of the free radical signals with temperature variation showed a similar tendency for both samples. With the analysis of this variation it was proposed different regions for the molecular mobility regimes of crude oils. The linewidth variation with temperature was related to changes in the relaxation time and with the parallel and perpendicular values of g . The half-height linewidth showed to behave as follows: approximately constant in rigid regime; increasing in slow motion regime; decreasing in fast motion regime; and approximately constant for isotropic regime.

From the behaviour of dynamic and kinematic viscosity as function of temperature, obtained by Rheometry and NMR, respectively, it was verified a change in the decrease trend just for the paraffinic sample. This change was related with a transition in the regime from rigid to slow motion.

EPR technique showed more detailed information about the regime transition for the studied oil samples.

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