Т. 89, № 1 **ЖУРНАЛ ПРИКЛАДНОЙ СПЕКТРОСКОПИИ** ЯНВАРЬ — ФЕВРАЛЬ 2022
V. 89, N 1 **JOURNAL OF APPLIED SPECTROSCOPY** JANUARY — FEBRUARY 2022

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

A. Khan [1], D. F. Valezi [1], M. T. Picinato [1,2], B. L. S. Vicentin [1*],
A. M. Netto [3], A. C. G. Mantovani [1], E. Di Mauro [1]

[1] Laboratório de Ressonância Paramagnética Eletrônica (LARPE), Departamento de Física,
Universidade Estadual de Londrina (UEL), Londrina, PR, Brasil; e-mail: bruno.vicentin@uel.br
[2] Departamento Acadêmico de Física, Universidade Tecnológica Federal do Paraná (UTFPR),
Londrina, PR, Brasil
[3] Braskem S.A. São Paulo, SP, Brasil

This study aimed to investigate the molecular mobility of crude oils using the linewidth of the free radical electron paramagnetic resonance signal (EPR) as a molecular mobility probe. For this, aromatic and paraffinic crude oil samples were analyzed by X-band EPR spectroscopy, NMR experiments in time domain (TD-NMR), and rheometry. The variations on the half height linewidth with temperature presented a similar behavior for both samples, being related to different molecular mobility regimes. EPR results were compared to the variation of viscosity with temperature obtained by rheometry and TD-NMR. The results showed changes in the decrease trend of viscosity for the paraffinic sample at a temperature close to the range in which it is observed the transition from rigid to liquid regime in the EPR analysis. EPR technique showed more detailed information about the regime transition for the oil samples studied, which is in agreement with the results obtained by rheometry and TD-NMR.

Keywords: *petroleum, electron paramagnetic resonance, NMR experiments in time domain, viscosity, temperature variation, asphaltene.*

ОПРЕДЕЛЕНИЕ МОЛЕКУЛЯРНОЙ ПОДВИЖНОСТИ СЫРОЙ НЕФТИ С ПОМОЩЬЮ ЭЛЕКТРОННОГО ПАРАМАГНИТНОГО РЕЗОНАНСА СВОБОДНЫХ РАДИКАЛОВ

A. Khan [1], D. F. Valezi [1], M. T. Picinato [1,2], B. L. S. Vicentin [1*],
A. M. Netto [3], A. C. G. Mantovani [1], E. Di Mauro [1]

УДК 543.429.22;543.422.25

[1] Университет Лондрины (UEL), Лондрина, Бразилия; e-mail: bruno.vicentin@uel.br
[2] Федеральный технологический университет Параны (UTFPR), Лондрина, Бразилия
[3] Braskem S.A. Сан-Паулу, СП, Бразилия

(Поступила 27 октября 2020)

С использованием ширины линии сигнала электронного парамагнитного резонанса (ЭПР) свободных радикалов в качестве зонда молекулярной подвижности изучена молекулярная подвижность сырой нефти. С помощью спектроскопии ЭПР, ЯМР и реометрии проанализированы образцы ароматической и парафиновой сырой нефти. Изменения ширины линии на полувысоте в зависимости от температуры демонстрируют сходное поведение для обоих образцов, что связано с различными режимами молекулярной подвижности. Результаты ЭПР по изменению вязкости в зависимости от температуры сравнивались с полученными с помощью реометрии и ЯМР. Отмечена тенденция к снижению вязкости парафинового образца при температуре, близкой к диапазону, в котором наблюдается переход из твердого состояния в жидкое при анализе ЭПР. Методика ЭПР позволяет

[**] Full text is published in JAS V. 89, No. 1 (http://springer.com/journal/10812) and in electronic version of ZhPS V. 89, No. 1 (http://www.elibrary.ru/title_about.asp?id=7318; sales@elibrary.ru).

получить более подробные данные об изменении состояния исследуемых образцов нефти, которые согласуются с полученными с помощью реометрии и ЯМР.

Ключевые слова: *нефть, электронный парамагнитный резонанс, ядерный магнитный резонанс, вязкость, изменение температуры, асфальтены.*

Introduction. Petroleum is formed mostly by mixtures of hydrocarbons and in less proportion by oxygen, nitrogenous, sulfated, and heavy metal compounds. Its aspect and composition are dependent on geologic formation and the nature of its precursor organic material. The brown to black color presented by many crude oils and oil derivatives is due to the presence of materials with high molecular weight [1], associated mainly with asphaltenes [2]. Asphaltenes are important compounds of crude oils that even in small concentrations negatively affect several petroleum operations, such as exploration, production, transportation, and refinement [3–5]. Many of these problems are related to its capacity to form aggregates, affecting its rheological properties [6].

Obstruction of pipelines is directly related to the high viscosity of some crude oils. Heavy crude oils are not easily pumped through pipelines because of the high concentration of asphaltenes and several metals in its composition, particularly, vanadium, and nickel [7]. The long chain of the paraffin hydrocarbons in crude oil forms an interlocking gel-like structure, which can potentially block the pipeline under severe situations [8], causing damages, and bursting [9]. Pipelines are generally regarded in the petroleum industry as one of the most economical methods for transportation of crude oils [8]. Therefore, the study of crude oil viscosity became a very important area, and new methods to probe molecular mobility are needed. Among them, electron paramagnetic resonance (EPR) is gaining popularity as crude oils present a strong free radical signal in EPR studies.

Regarding different fractions of crude oils, the highest unpaired electron concentration is observed from asphaltene samples, mainly as stable free radicals [10]. In lower proportions, there are some paramagnetic species due to metal ions presence in the oil's macromolecular components like vanadium, which generates the paramagnetic ion vanadyl (VO^{2+}). These two paramagnetic species related to the asphaltene fraction of crude oils (free radical and VO^{2+}) can be assessed by EPR spectroscopy [11, 12]. Traces of manganese and iron were also found, as revealed by EPR investigations of crude oils [13].

EPR probe of vanadyl has been used to investigate the asphaltene macrostructures under different temperatures using dilute solutions of isolated asphaltene [14]. Recently, the VO^{2+} signal was used to study the dynamics of asphaltenes in a native hydrocarbon environment, relating changes in the EPR spectra with rotational mobility in the crude oil when submitted to temperature variation [15–17].

Whereas not all crude oils have a concentration of vanadium that is detectable via EPR spectroscopy (and even if it is detectable, the free radical signal is always much more intense, masking the vanadium signal), the present study investigated the use of the linewidth of the free radical signal to probe molecular mobility in two different crude oils. It was possible to divide the variation of half height linewidth into four different regions that can be linked to molecular mobility as a temperature function. Rheology and NMR experiments in time domain (TD-NMR) showed complementary information that corroborates with the EPR analysis.

Materials and methods. The two crude oil samples were obtained from Kohat-Potwar Basin (Upper Indus Basin) in the Kohat City, Khyber-Pakhtunkhwa Province, Pakistan. The samples were labeled as aromatic (P-RCA-III) and paraffinic (P-RCP-I), according to a previous study describing sample characterization [18]. EPR experiments were conducted at the Electron Paramagnetic Resonance Laboratory (LARPE) (State University of Londrina, Londrina, Brazil) with a X-band JEOL JES-PE-3X EPR spectrometer coupled to a temperature variation controller JES-VT-3A. The samples were inserted into sealed quartz tubes, and the temperature ranged from 298 to 555 K. In all measures a modulation magnetic field of 0.1 mT was used, and the microwave power was set to 1 mW (saturation was not observed in the saturation test). The magnetic field marker $MgO:Mn^{2+}$ was used as an internal standard for the experiments. The field marker was positioned offset from the cavity's center, so that the spectra were obtained simultaneously (the marker is protected from the air flow used for temperature variation). The viscosity measurements were performed with a Physica MCR Serie 301 rheometer (Anton Paar Germany GmbH, Germany) using Rheoplus software, coupled to a Peltier P-PTD200. Measures were conducted in a temperature range from 300 to 473 K. The shear rate was constant at 100 s^{-1}.

TD-NMR were performed with a Bruker Minispec MQ20, with a static magnetic field of 0.5 T, Larmor frequency of 20 MHz, and a Bruker BVT 3000 temperature controller, with an error of ±3 K. The CPMG [19, 20] sequence was used, with 50 k pulses and 15 s recycling time. The experiment was conducted in a temperature ranging from 303 to 443 K. Transverse relaxation times (T_2) were extracted by bi-exponential curve fitting and correlating with viscosity through [21]

$$\mu(T_2) = a/T_2^b, \tag{1}$$

where μ is the fluid's viscosity, and *a* and *b* are the empiric parameters related to the fluid.

Results and discussion. EPR spectra at room temperature from the aromatic and paraffinic samples showed similar characteristics, as presented in Fig. 1. It is possible to observe an intense resonance line centered at $g = 2.003$ with a peak-to-peak linewidth (ΔH_{PP}) of 0.49 mT and a half height linewidth ($\Delta H_{1/2}$) of 1.10 mT for the aromatic crude oil. For the paraffinic sample the resonance line is centered at $g = 2.003$, with $\Delta H_{PP} = 0.42$ mT and $\Delta H_{1/2} = 0.96$ mT (parameters calculated according to well-known methods [22]). These resonance lines are characteristic of organic free radicals, and the parameters obtained from the spectrum are in accordance with literature [11, 23]. The two small lines at both sides of the spectra are due to the MgO:Mn^{2+} field marker.

From the increasing temperature experiments we observed the variation of the linewidth with the EPR signal. Figure 2 shows the $\Delta H_{1/2}$ variation as a function of temperature from both samples, revealing similar behavior between them. It is possible to observe an increase and a posterior decrease in $\Delta H_{1/2}$. In addition to the temperature variation experiments, EPR spectra were recorded after heating and subsequent cooling to room temperature. In this case, no significant changes in parameters were observed when the samples were measured after cooling. Thus, effects caused by possible evaporation of oils with increasing temperature were disregarded.

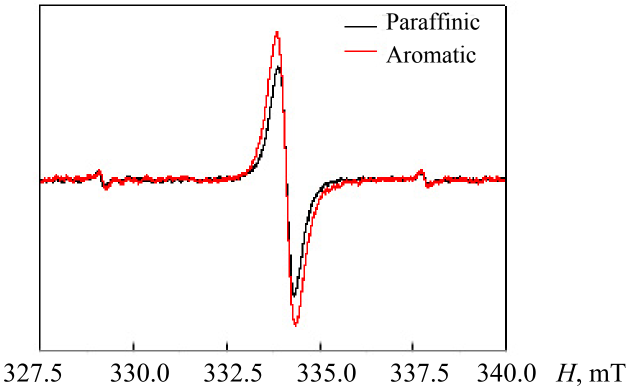

Fig. 1. Free radical EPR spectrum at room temperature for the paraffinic and aromatic samples.

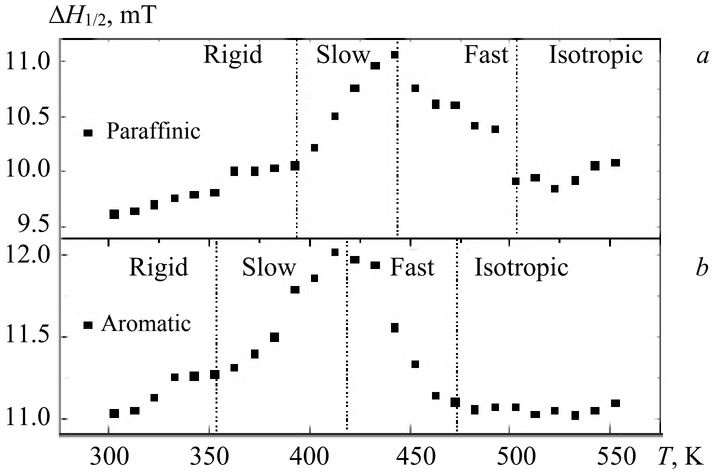

Fig. 2. Half height linewidth of free radical EPR signal for paraffinic (a) and aromatic (b) samples.

Crude oils usually present high viscosity at room temperature, which means that these oils could be considered as rigid systems regarding their molecular mobility [11, 15, 24]. In rigid systems, it is common to observe EPR signal similar to those obtained from powders [24, 25], presenting both parallel and perpendicular components of the spectroscopic factor (*g* factor) [11, 15, 24]. Indeed, this behavior was obtained from crude oil samples at room temperature, where the hyperfine parameters and the *g* factor of vanadium presented parallel and perpendicular components [15, 17]. In this research, the samples under analysis presented only the free radical signal; thus, one can also expect to observe both perpendicular and parallel components of the *g* factor. However, these components are not resolved in X-band EPR spectroscopy because of the overlapping of resonance lines.

With temperature increase (and consequent decrease in viscosity), there are two effects expected: a decrease in the relaxation time and an approximation of the parallel and perpendicular values of *g* (due to the gradual change of the system from a rigid to an isotropic regime). These two effects cause variations of the linewidth of free radicals. The gradual changes in the mobility regime ~~leads~~ to a decrease in the relaxation time, contributing to broadening the resonance lines [26]. Spin exchange interactions between paramagnetic centers within the asphaltene can also contribute to this effect. On the other hand, with the macromolecular mobility changing from the rigid to the liquid regime, the EPR signal changes from powder to isotropic signal. This effect leads to approximation of the parallel and perpendicular resonance lines, where a complete overlap can be observed. Thereby, considering that the free radical lines can be composed of parallel and perpendicular components, with decreasing viscosity the linewidth is expected to decrease.

Thus, a possible explanation to the observed result lies in the fact that there are two competing effects regarding the linewidth of free radical. Let us divide the variation of half height linewidth with temperature increase into four different regions.

When the regime is predominantly rigid, an appreciable variation of the linewidth (Fig. 2, rigid region) is not observed. The crude oil shows a mixture of regimes, but the rigid behavior still predominates (Fig. 2, slow motion region). In this slow-motion regime, the broadening in EPR linewidth (caused by the decreasing in the relaxation time) overcomes the narrowing caused by the approximation of the parallel and perpendicular components. With the fast-motion regime, i.e., with the overcoming of the isotropic phase in relation to the rigid, the effect of narrowing overlaps the broadening effect, resulting in the observed linewidth decrease (Fig. 2, fast motion; region). The system is considered to be predominantly isotropic, and no marked linewidth variation is observed (Fig. 2, isotropic region).

From Fig. 2 it is observed that the temperature for maximum linewidth (which represents the transition from slow to fast motion regime) is higher for the paraffinic sample (443 K for paraffinic and 418 K for aromatic samples). This can be associated with the molecular structure of the sample. It must be emphasized that EPR spectroscopy detects free radicals, which are mainly present in the asphaltene fraction. In paraffinic samples, the asphaltene fraction is composed of longer chains than that in aromatic samples [27], leading to a lower molecular mobility, which explains the described behavior.

The viscosity variation as a function of temperature can be related with the linewidth variation of the free radical signal. Figures 3 and 4 show the variation of viscosity measured by rheometry and TD-NMR. From Figs. 3 and 4 it is observed that the aromatic sample presented higher values for both dynamic and kinematic viscosities in the whole temperature range. From Fig. 2, it can be observed that the aromatic sample showed transition from the rigid to the isotropic regime at lower temperature, which agrees with the higher molecular mobility of the aromatic sample [27].

From Figures 3 and 4 we observed a subtle change in the decrease trend of the viscosity with temperature from the paraffinic sample, which does not occur for a specific temperature but in a range of temperatures. These changes in the viscosity are observed in a temperature range close to that temperature range where the linewidth shows mixed behavior (solid and liquid).

A possible explanation for the slight discontinuity observed at ~380 to ~400 K in Figs. 3 and 4 could be the changes in the viscosity due to the transition from the rigid to the isotropic regime. As this study is limited by the lack of information regarding the behavior of the molecular mobility and properties of the samples under analysis, more studies are necessary to support this hypothesis. This first analysis can be complemented with future works applying this method to crude oil samples that show EPR signals of free radicals and vanadium.

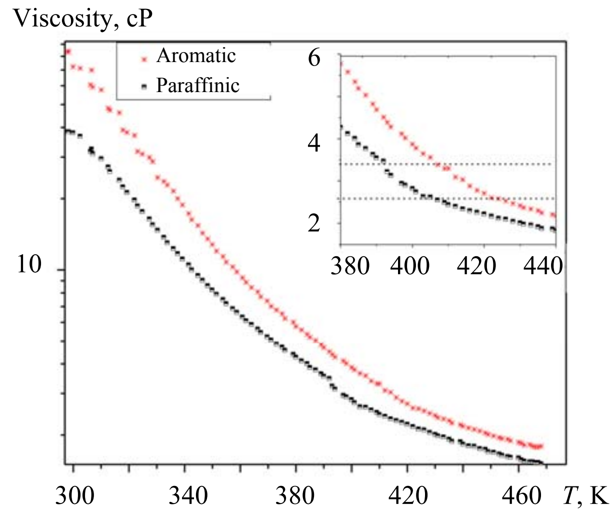

Fig. 3. Dynamic viscosity obtained by rheometry experiments of paraffinic and aromatic crude oils.

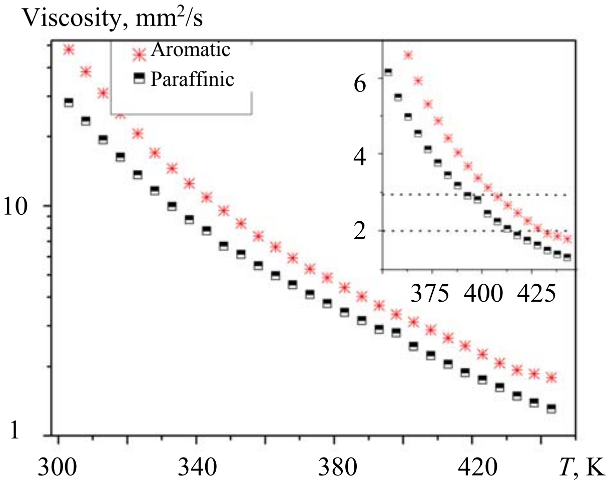

Fig. 4. Kinematic viscosity calculated by TD-NMR data of paraffinic and aromatic crude oil.

Conclusions. Aromatic and paraffinic samples presented EPR signals with characteristics of organic free radicals. The linewidth variation with temperature was related to the changes in the relaxation time and the parallel and perpendicular values of spectroscopic factor *g*. The half heights linewidth was approximately constant in the rigid regime, presented an increasing trend in the slow-motion regime, decreased in the fast motion regime, and was approximately constant for the isotropic regime. EPR spectroscopy showed more detailed information about the mobility regime transition for the crude oil samples under study, which can be related to results obtained by rheometry and TD-NMR techniques.

Acknowledgements. We would like to thank Mr. Sohail Mohammad for providing the samples; “Coordenação de Aperfeiçoamento de Pessoal de Nível Superior” (CAPES-Brazil) and “Conselho Nacional de Desenvolvimento Científico e Tecnológico” (CNPq-Brazil) for financial support; the Magnetic Resonance, Spectroscopy and Magnetism Group from University of São Paulo, São Carlos Institute of Physics, for the viscosity TD-NMR measurements, and LNNA/Embrapa for rheometry measurements.

REFERENCES

1. T. F. Yen, J. G. Erdman, A. J. Saraceno, *Anal. Chem.*, **34**, 694–700 (1962).
2. L. Montanari, M. Clericuzio, G. Del Piero, R. Scotti, *Appl. Magn. Res.*, **14**, 81–100 (1998).
3. L. Artok, Y. Su, Y. Hirose, M. Hosokawa, S. Murata, M. Nomura, *Energy Fuels*, **13**, 287–296 (1999).
4. J. G. Speight, B. Ozum, *Petroleum Refining Processes*, Marcel Dekker, New York (2002).
5. J. S. Buckley, *Energy Fuels*, **13**, 328–332 (1999).
6. I. N. Evdokimov, N. Y. Eliseev, B. R. Akhmetov, *Fuel*, **82**, 817–823 (2003).
7. A. Ahmadpour, K. Sadeghy, S. R. Maddah-Sadatieh, *J. Non-Newton Fluid Mech.*, **205**, 16–27 (2014).
8. J. A. Carrillo, L. M. Corredor, *Fuel Proc. Technol.*, **109**, 156–162 (2013).
9. G. T. Chala, S. A. Sulaiman, A. Japper-Jaafar, *J. Non-Newton Fluid Mech.*, **251**, 69–87 (2018).
10. J. Uebersfeld, A. Étienne, J. Combrisson, *Nature*, **174**, 614 (1954).
11. C. L. Barbosa Guedes, E. Di Mauro, V. Antunes, A. S. Mangrich, *Mar. Chem.*, **84**, 105–112 (2003).
12. M. T. Piccinato, C. L. B. Guedes, E. Di Mauro, In: *Analytical Characterization Methods for Crude Oiland Related Products*, Ed. K. Shukla, John Wiley & Sons Ltd., ISBN 9781119286318, New Jersey, 77–99 (2018).
13. N. M. Khasanova, D. T. Gabdrakhmanov, G. P. Kayukova, A. N. Mikhaylova, V. P. Morozov, *Magn. Res. Solids*, **19**, No. 17102, 1–11 (2017).
14. G. K. Wong, T. F. Yen, *J. Pet. Sci. Eng.*, **28**, 55–64 (2000).
15. T. B. Biktagirov, M. R. Gafurov, M. A. Volodin, G. V. Mamin, A. A. Rodionov, V. V. Izotov, A. V. Vakhin, D. R. Isakov, S. B. Orlinskii, *Energy Fuels*, **28**, 6683–6687 (2014).
16. M. S. Hernández, D. S. Coll, P. J. Silva, *Energy Fuels*, **33**, 990–997 (2019).
17. M. R. Gafurov, M. A. Volodin, A. A. Rodionov, A. T. Sorokina, M. Y. Dolomatov, A. V. Petrov, A. V. Vakhin, G. V. Mamin, S. B. Orlinskii, *J. Pet. Sci. Eng.*, **166**, 363–369 (2018).
18. I. Ahmad, S. M. Sohail, H. Khan, W. Ahmad, K. Gul, R. Khan, A. Yasin, *Energy Fuels*, **32**, 181–190 (2018).
19. H. Y. Carr, E. M. Purcell, *Phys. Rev.*, **94**, 630–638 (1954).
20. S. Meiboom, D. Gill, *Rev. Sci. Instrum.*, **29**, 688–691 (1958).
21. Z. Yang, Z. Ma, Y. Luo, Y. Zhang, H. Guo, W. Lin, *Geofluids*, Article ID 9542152 (2018).
22. M. Ikeya, *New Applications of Electron Spin Resonance: Dating, Dosimetry and Microscopy*, WSPC, ISBN 978-981-02-1200-1, Osaka University, Japan (1993).
23. E. Di Mauro, C. L. B. Guedes, O. R. Nascimento, *Appl. Magn. Res.*, **29**, 569–575 (2005).
24. M. Turini, C. L. Barbosa Guedes, E. Di Mauro, In: *Crude Oil Emulsions – Composition, Stability, Characterization*, Ed. M. El-Sayed Abdel Raouf, 147–168, InTech, ISBN 978-953-51-0220-5, Rijeka, Croatia (2012).
25. D. E. O'Reilly, *J. Chem. Phys.*, **29**, 1188–1189 (1958).
26. F. Gerson, W. Huber, *Electron Spin Resonance Spectroscopy of Organic Radicals*, Wiley-VCH, ISBN 978-3-527-30275-8, Weinheim, Germany (2003).
27. J. R. Fanchi, R. L. Christiansen, *Introduction to Petroleum Engineering*, Wiley, New Jersey (2017).