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DETECTION AND CHARACTERISATION OF FREE RADICALS IN GUNESHLI OILS USING ELECTRON PARAMAGNETIC RESONANCE METHOD

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Abstract: Herein, has been presented the results of electron paramagnetic resonance investigations in irradiated and non-irradiated petroleum oils from platform 8, Guneshli oilfields. Free radicals in non-irradiated and irradiated crude oils were identified and determined EPR spectral parameters. This study demonstrates that the EPR technique is suitably applied to the detection of free radicals in petroleum oil and increasing irradiation dose significantly couldn't influence the radical concentration. The electron paramagnetic resonance method is presented as an eco-friendly approach for monitoring d-elements in petroleum.

Key words: crude oil, irradiated petroleum, free radical, irradiation, electron paramagnetic resonance

1. Introduction

The world reserves of light petroleum are being replaced by an increasing amount of heavier feedstocks. Most crude petroleum oils contain vanadium. It's known that the majority of the vanadium is contained within the highly aromatic petroleum and highly polar asphaltene fraction of crude oils. The concentration of this element in bitumen and vacuum residue is generally much higher. It poses a problem for the economical upgrading of such petroleum [1-3].

The aggregation of petroleum asphaltenes has been measured by a variety of methods. The work [4] studied the diffusion of asphaltenes from heavy petroleum oils using in situ UV-vis spectroscopy. As vanadium-containing petroleum were used Athabasca, Safaniya, and Venezuela crude oils. It was revealed that the presented method is widely applicable only to C_7 asphaltenes and is not universal.

It was investigated that the asphaltene fraction of petroleum could be aggregate significantly in most solvents and presented possible mechanisms of the molecular association of asphaltenes in solution, which help to understand the molecular interactions and the nature of the metalloporphyrins [5]

The adsorption of asphaltenes on mineral surfaces is important in petroleum production. It was studied the adsorption of Athabasca asphaltenes onto kaolinite and shown the adsorption was not selective for specific species in the asphaltene mixture. The presence of Al and Si proved that the asphaltene adsorption layer is not continuous on the kaolinite surface. The asphaltene adsorption occurred preferentially on the asphaltenes already adsorbed on the kaolinite surface [6-11].

Asphaltenes are the heaviest constituents of crude oil. This compound class is recovered by its solubility characteristics. Asphaltenes are soluble in light aromatics and insoluble in light kinds of paraffins. The main features of their behavior include the tendency to aggregate, instability, surface activity, and low reactivity. By these features, refining is impacted by asphaltene affecting the miscibility of different crude oils, giving rise to incompatibility within certain blending ranges [12]. Asphaltenes obtained by the standard methods and may contain different constituents. In particular, asphaltenes are often referred to as the "cholesterol of petroleum". Asphaltene constituents isolated from different sources are remarkably constant in terms of ultimate elemental composition. The experimental methods most suitable for studying the molecular structure and the aggregation behavior of asphaltenes in the performed experiments are those of "optical interrogation", in particular of high-precision refractometry (HPR). The HPR technique appears to be especially suited for studies of dilute asphaltene solutions with evolving structural heterogeneity induced by molecular aggregation [13]. Many kinds of radicals are stable enough to isolate, handle, and store without special precautions. These correspond to a class of free radicals that have been identified as chemical species with unpaired electrons with sufficiently long lifetimes that can be observed by conventional spectroscopy methods. Petroleum is formed by the thermal degradation of kerogen and may also contain large amounts of asphaltene. Asphaltenes are macromolecular compounds, comprising polyaromatic nuclei linked by aliphatic chains or rings of various lengths and sometimes by functional groups. Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) is high-resolution spectroscopy that consists in energy absorption of microwave, for electron spin, in the presence of a magnetic field. In crude oil and oil by-products, the presence of free radicals allows the ESR technique to assist researchers in their attempts to elucidate the complex chemical composition of the systems [14].

Homologous series of n-alkenes and dimethyl alkanes with the odd or even number of carbon atoms in the molecule have been identified in chloroform extracts from the organic matter of Upper Paleozoic deposits of the Vilyui syncline penetrated by the superdeep well SV-27 at depths below 5 km. It is presumed that these unusual hydrocarbons resulted from the destruction of asphaltene occlusions under severe *P-T* conditions at great depths and that the hydrocarbon generation began in the zone of postdiagenetic transformations of sediments. This hypothesis was tested in the sections of deposits whose organic matter underwent catagenesis of different grades. Based on these results, zones of emergence, transition, and destruction of occlusions have been recognized [15]. In work [16] was described a microfluidic approach for measuring the solubility of asphaltenes in a sample of crude oil. The microfluidic data were used to determine asphaltene solubility parameters that ranged from 20 to 23 $MPa^{1/2}$ for the crude oils used in this study, in agreement with previous investigated works. The more efficient use of labor and the reduction in measurement time enabled by the microfluidic method will allow for more frequent asphaltene characterization for evaluating stability and tuning models [16].

Temperature dependencies of electron paramagnetic resonance spectra of intrinsic paramagnetic vanadyl complexes and dynamical viscosity for two heavy crude oils and asphalt samples are measured in work [17]. The rotational correlation times (in the model of the isotropic diffusion) are extracted. It is shown that the characteristic temperatures for the motional regime transitions are mainly defined by the asphaltenes' content. From analysis, it follows that the thermal treatment leads to the destruction of the asphaltene complexes onto the 4–5 small pieces. The results indicate that paramagnetic vanadyl complexes are the sensitive intrinsic probes to study qualitatively and quantitatively structural transformations of aspahltenes of heavy crude oils in-situ [17]. Prediction of crude oil stability and solubility of asphaltenes under specified conditions requires the fundamental knowledge of the character of intermolecular interactions between asphaltenes and other heavy oil components present in the local environment. This knowledge can be gained only using in situ studies of local rheological properties of crude oils and molecular dynamics of asphaltenes under various conditions (Martyanov et al., 2017, Trukhan et al., 2017). Electron paramagnetic resonance (EPR) techniques do not require the diluted samples and can sense the intrinsic paramagnetic centers

(PC) also in the unfractionated species, i.e., in the native environment (see Yen and Chilingarian, 2000; Khasanova et al., 2017; Gafurov et al., 2018 for reviews on this topic). Following the changes of the EPR spectroscopic parameters of PC (for example with temperature), one can gain additional information about ODS [18].

Taking into account the up-mentioned date, to study the hydrocarbon generation of petroleum crude oils, the EPR investigation of free radicals in Guneshli petroleum in the presence of bentonite clay is focused on. The aim of this paper is detection and characterization of free radicals in irradiated and virgin crude oils by EPR method.

2. Experimental part

Transforming the hydrocarbons of crude oil using the radiolysis process was achieved using the influence of gamma rays at room temperature in the presence of raw bentonite clay from the Alpoid deposit of Azerbaijan. The crude oil samples were irradiated with gamma radiation from the ^{60}Co isotope under static conditions, within vacuum-sealed quartz tubes at room temperature.

Reaction conditions: Given the amount of catalyst- bentonite sample (in the range 0.01-0.03 g) was added to crude oil (2.0 g) in glass ampules and sealed, then subjected to various doses of radiation energy (from 5.12 kGy to 259,2 kGy). Radiation carried out for 1-300 hours at room temperature: with and without bentonite clay.

Electron Paramagnetic Resonance (EPR) method is used to study paramagnet centers (ions metals and radicals) involved in chemical processes. Experimental measurements were obtained from EPR techniques (“Bruker” EMX plus) at room temperature. Parameters for signal measurement: microwave frequency 9.87 GHz, modulation frequency 100 kHz, modulation amplitude 5 G, sweep width 100G, microwave power 2.2Mw.

The crude oil was obtained from a well of platform 8 of Gunashli field in Balakhani X Horizon in Azerbaijan and irradiated. Irradiation was carried out for 1-300 hours at a dose rate of 10.5 Rad/ sec. Crude oil isomerization was conducted with and without bentonite at a dose of 0.72- 259.2 kGy at room temperature.

3. Results and discussion

Firstly, we present the EPR results. Fig. 1 shows the EPR spectra of irradiated samples (5.12 kGy) with and without catalyst and Fig.2 shows the EPR spectra for samples irradiated at dose values (5.12 up 259.2 kGy) from platform 8. The existence of paramagnetic centers in ODS is generally caused by the presence of d metals (mainly V, Ni, Fe) and stable carbon-centered “free” radicals (FR). It is established that the majority of the organic FR are concentrated in the structure of a condensed polyaromatic core of asphaltene molecule while the metals located in the polar fractions (both resin and asphaltene), with a further majority concentrated in the asphaltenes (Yen and Chilingarian, 2000) [18].

Pure asphaltene radicals are resonance stabilized over a polyaromatic structure and are stable in air and unreactive. These radicals are similar to semiquinone-type, environmentally persistent free radicals. Pure asphaltene radicals are resonance stabilized over a polyaromatic structure and are stable in air and unreactive. We can identify for the first time the various paramagnetic species present in the native state of these samples and understand their molecular structures and bonding. Although the lower-field EPR signals from the organic free radicals in fossil fuel samples have been investigated over the last 5 decades, the observed signal was featureless.

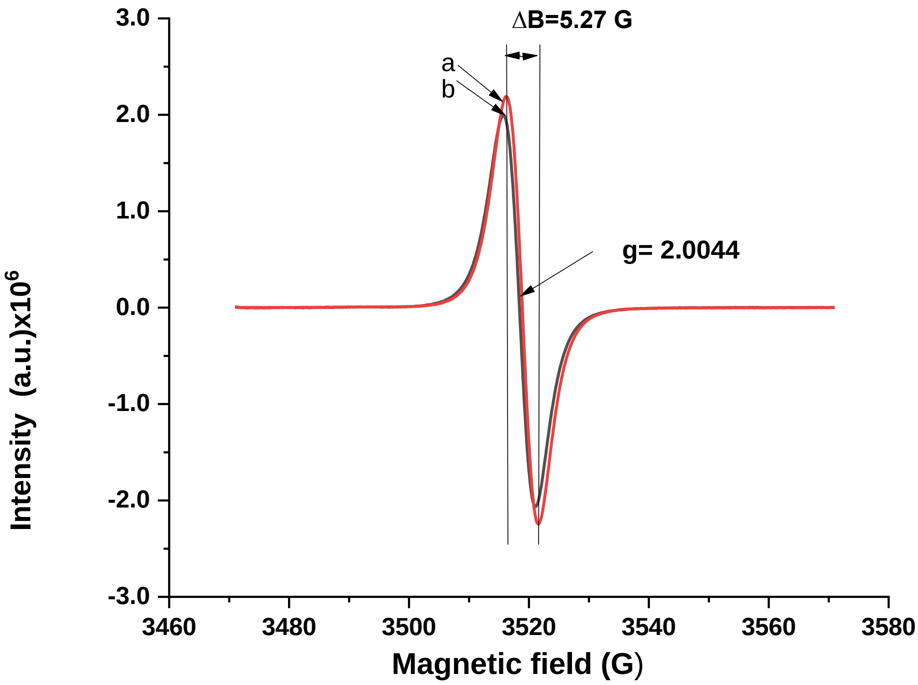

Fig.1. EPR spectra of 5.12 kGy irradiated oil: a) without catalyst; b) with catalyst

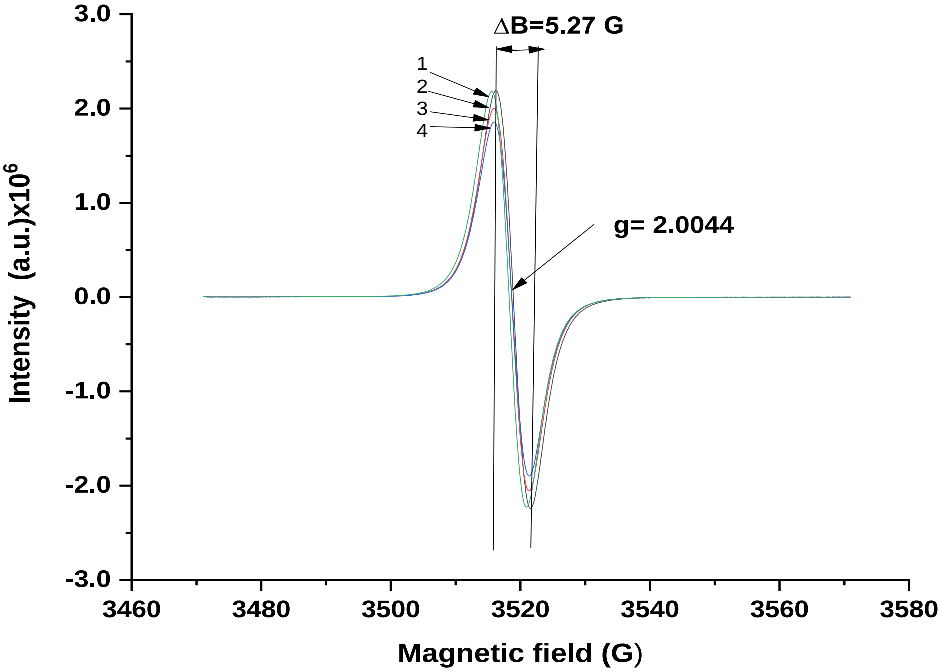

Fig.2. EPR spectra of irradiated at difference dose values oil: 1) crude oil; 2) 5.12kGy; 3) 129.6 kGy 4) 259.2 kGy

From the spectrum in fig.1, it can be obtained that, g factor for free radical is 2.0044± 0.0002; and line width ΔB=5.27G±0.05. This value of g factor is constant for each irradiated crude oil sample and is not dependent on the irradiation dose investigated at 5.12 ÷259.2 kGy. Also, it was discovered that after irradiation, the petroleum samples with and without bentonite catalysts, do not change line width, g factor, and the form of EPR spectra of the free radical. Therefore, irradiation does not influence the chemical substance of the paramagnet centers assigned to free radicals.

The absence of any lines in specters EPR at low magnetic field shows, that there are not any mixtures and heavy d metals in the samples of investigated oils.

No variations in g-factor were observed in non-irradiated and irradiated samples with and without a catalyst for any of the paramagnetic species (fig.1 and fig.2) in Guneshli oil from platform 8.

Monitoring the paramagnetic species in crude oil by EPR is possible to follow the changes in the molecular structure of the oils, once it reflects changes in the unpaired electron neighborhood. We envisage that the measured g-value components will serve as a sensitive basis for electronic structure calculations.

4. Conclusion

Taking into account that EPR is a non-destructive method and there is no need for sample preparation, it demonstrates that EPR can be used for online monitoring or even for the EPR logging to follow the influence of thermal or radio-catalytic treatment of heavy crude oil. This method is eco-friendly, for monitoring the molecular structure of crude and irradiated petroleum samples.

References

1. Greg P.Decline and Flora T. T. Ng**.** A New Coated Catalyst for the Production of Diacetone Alcohol via Catalytic Distillation._Industrial & Engineering Chemistry Research 2008, 47, 23, 9304-9313**.** DOI: 10.1021/ie800009u
2. Marzie Derakhshesh, Murray R. Gray and Greg P.Decline. Dispersion of asphaltene nanoaggregates and the role of rayleigh scattering in the absorption of visible electromagnetic radiation by these nanoaggregates. Energy & Fuels 2013, 27, 2, 680693 DOI: 10.1021/ef3015958
3. Greg P.Decline Yadollah Maham, Xiaoli Tan and Murray R. Gray. Regular solution theories are not appropriate for model Compounds for Petroleum Asphaltenes. Energy & Fuels 2011, 25, 2, 737-746 .DOI: 10.1021/ef101405t
4. Greg P.Decline and Murray R. Gray. Membrane diffusion measurements do not detect exchange between asphaltene aggregates and solution phase. Energy Fuels 2011, 25, 2, 509–523, https://doi.org/10.1021/ef101050a
5. Greg P.Decline and Murray R. Gray. Chemistry and association of vanadium compounds in heavy oil and bitumen, and implications for their selective removal. Energy & Fuels 2010, 24, 5, 2795-2808 (Review) DOI: 10.1021/ef100173j
6. Farshid Mostowfi, Vincent Sieben. Determination of Asphaltenes Using Microfluidics.2015, 199-236. https://doi.org/10.1201/b18109-17
7. Zhentao Chen, Linzhou Zhang, Suoqi Zhao, Quan Shi, Chunming Xu. Molecular Structure and Association Behavior of Petroleum Asphaltene. 2015, 1-38. https://doi.org/10.1007/430_2015_181

8. Evgenia B. Golushkova, Artem O. Abramov, Elena Yu. Kovalenko. The Effect of Iron-Containing Powders on Chemical Compositions of Oils. Procedia Chemistry 2015, 15, 127-133. https://doi.org/10.1016/j.proche.2015.10.020
9. Hui Ting Zhang, Rui Li, Zixin Yang, Cindy-Xing Yin, Murray R. Gray, Cornelia Bohne. Evaluating steady-state and time-resolved fluorescence as a tool to study the behavior of asphaltene in toluene. Photochemical & Photobiological Sciences 2014, 13 (6), 917.
10. Lloyd R. Snowdon, John K. Volkman, Zhirong Zhang, Guoliang Tao, Peng Liu. The organic geochemistry of asphaltenes and occluded biomarkers. Organic Geochemistry 2016, 91, 3-15. https://doi.org/10.1016/j.orggeochem.2015.11.00
11. Shanshan Wang, Qi Liu, Xiaoli Tan, Chunming Xu, Murray R. Gray. Adsorption of asphaltenes on kaolinite as an irreversible process. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2016, 504, 280-286. https://doi.org/10.1016/j.colsurfa.2016.05.086
12. Maria Magdalena Ramirez-Corredores. Asphaltenes. 2017, 41-222. https://doi.org/10.1016/B978-0-12-801225-3.00002-4
13. Igor N. Evdokimov. Optical Interrogation of Petroleum Asphaltenes: Myths and Reality. 2017,13-75. https://doi.org/10.1002/9781119286325.ch
14. Marilene Turini Piccinato, Carmen Luisa Barbosa Guedes, Eduardo Di Mauro ESR Characterization of Organic Free Radicals in Crude Oil and By-Products Book Editor(s): Ashutosh K Shukla..2017. https://doi.org/10.1002/9781119286325.ch3
15. V.A. Kashirtsev. Hydrocarbons occluded by asphaltenes. Russian Geology and Geophysics 2018, 59 (8), 975-982. https://doi.org/10.1016/j.rgg.2018.07.017
16. Vincent J. Sieben, Asok Kumar Tharanivasan, Simon I. Andersen, and Farshid Mostowfi. Microfluidic Approach for Evaluating the Solubility of Crude Oil Asphaltenes. Energy & Fuels 2016, 30 (3), 1933-1946. https://doi.org/10.1021/acs.energyfuels.5b02216
17. Sherif Fakher, Mohamed Ahdaya, Mukhtar Elturki, Abdulmohsin Imqam. Critical review of asphaltene properties and factors impacting its stability in crude oil. Journal of Petroleum Exploration and ProductionTechnology 2020, 10 (3), 1183-1200. https://doi.org/10.1007/s13202-019-00811
18. M.R. Gafurov, M.A. Volodin, A.A. Rodionov, A.T. Sorokina, M.Yu. Dolomatov, A.V. Petrov, A.V. Vakhin, G.V. Mamin, S.B. Orlinskii. EPR study of spectra transformations of the intrinsic vanadyl-porphyrin complexes in heavy crude oils with temperature to probe the asphaltenes' aggregation. Journal of Petroleum Science and Engineering, 2018. 166. 363-368. www.elsevier.com/locate/petrol.

ОПРЕДЕЛЕНИЕ И ИДЕНТИФИЦИРОВАНИЕ СВОБОДНЫХ РАДИКАЛОВ ГЮНАШЛИНСКОЙ НЕФТИ С ИСПОЛЬЗОВАНИЕМ МЕТОДА ЭЛЕКТРОННОГО ПАРАМАГНИТНОГО РЕЗОНАНСА

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Резюме: В статье представлены результаты исследования облученных при различных дозах и не облученных нефтяных образцов платформы 8 Гюнашлинской месторождений с использованием метода электронного парамагнитного резонанса. Были идентифицированы свободные радикалы в сырой и облученной нефти и определены параметры спектров ЭПР. Это исследование демонстрирует, что метод ЭПР целесообразно применять для обнаружения свободных радикалов в нефти. Показано, что увеличение дозы облучения не может существенно влиять на концентрацию радикалов.

Ключевые слова: сырая нефть, облученная нефть, свободные радикалы, электронный парамагнитный резонанс

ELEKTRON PARAMAQNİT REZONANS METODU İLƏ GÜNƏŞLİ NEFTİNDƏ SƏRBƏST RADİKALLARIN TƏYİNİ VƏ İDENTİFİKASİYASI

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Xülasə: Məqalədə elektron paramaqnit rezonans metodu ilə Günəşli neft yatağında 8 saylı platformanın xam və şüalandırılmış neft nümunələrinin tədqiqinin nəticələri göstərilmişdir. Xam və şüalanmış neftdə sərbəst radikallar identifikasiya olunmuş və EPR spektrinin parametrləri müəyyən olunmuşdur. Bu tədqiqatlar onu göstərir ki, EPR metodu neftdə sərbəst radikalların təyin olunması üçün istifadəsi məqsədəuyğundur. Müəyyən edilmişdir ki, şüalanma dozasının artması radikalların konsentrasiyasına əhəmiyyətli təsir edə bilməz.

Açar sözlər: xam neft, şüalanmış neft, sərbəst radikallar, elektron paramaqnit rezonansı