

PHYSICOCHEMICAL PROPERTIES OF OIL (PETROLEUM) SAMPLES CONTAINING NANOPARTICLES

R. Khalilov^{1,2}, I. Guliyev³, F. Kadirov⁴, A. Nasibova¹, K. Seyidova¹

¹Institute of Radiation Problems of ANAS,

²Baku State University,

³Institute of Oil and Gas of ANAS,

⁴Institute of Geology and Geophysics of ANAS,

hrovshan@hotmail.com

Abstract: It is of particular interest to discover magnetic nanoparticles within the structure of oil elements. The presence of magnetic nanoparticles in oil provides the possibility of managing the important technological properties of oil (viscosity, deemulsification, paraffin collapse, etc.) with the help of external magnetic field. We explained the impact mechanism to its physical and chemical properties (viscosity, magnetic resonance characteristics, etc.) of structure and composition of fractal colloidal aggregates in oil.

Key words: nanoparticles, stress factor, viscosity, biogeneration, oil samples.

In recent years studies show that iron oxide magnetic nanoparticles are widespread in living and nonliving nature. Our studies in natural systems (plant, oil, etc.) by Electron Paramagnetic Resonance (EPR) spectroscopy method indicate that biogeneration of magnetic nanoparticles occurs in them [1, 2, 3].

During the initial investigations, the effects of radioactive contamination on plants were carried out a comprehensive analysis in order to clarify the mechanisms of biogenic generation of magnetic nanoparticles in natural systems and a large EPR signal ($g = 2.3$; $\Delta H = 400$ Gs) characterizing magnetic nanoparticles in plants was observed (Fig. 1). In figure 1, the free radical signal ($g = 2.00$) appears along with the signal of magnetic nanoparticles. Stress factors have been shown a stimulating effect on the generation of these nanoparticles [1].

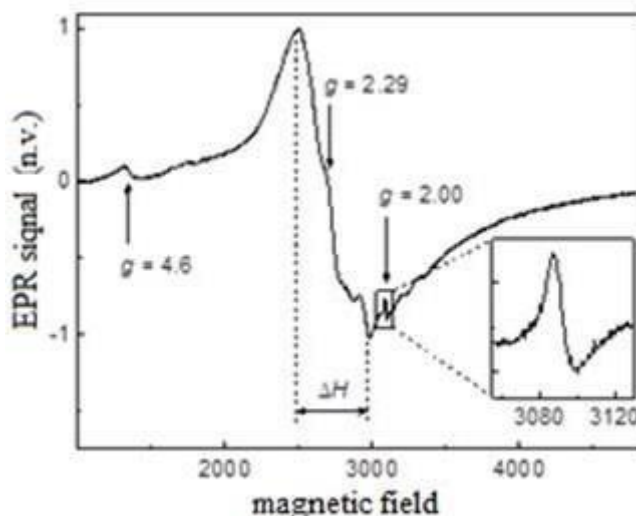


Fig.1. EPR signal characterizing the iron oxide magnetic nanoparticles in plants.

It is also very interesting that in experiments with oil samples, it was possible to observe a large EPR signal characterizing magnetic nanoparticles. Before and after melting the characteristic EPR spectra of oil paraffin samples consisted of intensive resonance line ($g = 2.25$ and $\Delta H = 320$ Gs). Such EPR signal is typical for superparamagnetic iron oxide nanoparticles.

The effective g -factor is considerably greater than the characteristic paramagnetic 2.00 price for the three-dimensional iron, and shows the ferromagnetic character of magnetism and the magnetization of nanoparticles in the sample. After the sample is melted, the width of the EPR signal grows more than three times, and the effective g -factor also increases. The growth of the signal width may be due to the increase in the size of their aggregates because of the agglomeration of magnetic nanoparticles in the molten paraffin. Thus their noticeable change of the paraffin samples after they are melted and parameters of EPR signal, show the presence of magnetic nanoparticles in the paraffin.

It is of particular interest to discover magnetic nanoparticles within the structure of oil elements. The presence of magnetic nanoparticles in oil provides the possibility of managing the important technological properties of oil (viscosity, deemulsification, paraffin collapse, etc.) with the help of external magnetic field. It should be noted that oil belongs to the so-called non-Newtonian fluids such as a series of other fluid colloids, including biological mediums (blood, lymph, plant juice, etc.). These fluids are characterized primarily by strong dependence on the deformation of the viscosity. It is known that the high viscosity of oil is conditioned by the formation of aggregates of colloidal particles having fractal structure [3]. Magnetic nanoparticles can include fractal aggregates of the colloidal components of the oil. Namely, this case lets to influence the structure of the oil aggregates with the help of the external magnetic field and change the oil characteristics.

We explained the impact mechanism to its physical and chemical properties (viscosity, magnetic resonance characteristics, etc.) of structure and composition of fractal colloidal aggregates in oil.

Figure 2 (A, B, C) shows the images taken on the electron microscope of the typical aggregates for this sample at various magnification rates. As can be seen from the figure, the aggregate consists of iron oxide nanoparticles (dark short sticks with a length of 50-100 nm and diameter of 10 nm) and oil particles (circular translucent particles in the diameter of 30-50 nm).



Fig. 2. Pictures of paraffin samples taken from Transistor Electron Microscope.

The aggregate of iron and oil colloidal particles (Fig.2A) have linear measures of up to 2.5-3 μm and consist of characteristic chain branching and intersecting structures for fractal aggregates. The dimensions, magnetic properties, shape and crystallographic parameters of superparamagnetic nanoparticles were determined. Characteristic dimensions of colloidal oil particles were discovered [4-7]. At the same time, the processes of dependence on natural and

artificial magnetic nanoparticles in oil of mechanisms of magnetic field impact on oil viscosity were clarified. EPR spectra of copper, aluminum nanoparticles and bentonite were recorded via EPR radio spectrometry (Fig. 3).

It should be noted that the amplitude of the EPR spectra of the first and third samples was higher than the Al nanoparticles samples. This indicates high electrical conductivity of Al nanoparticles. The EPR signal of Cu nanoparticles can belong to the Cu^{2+} ion, i.e. the oxidized state according to its own state ($g = 2.06$) and width (≈ 400 E).

Depending on the temperature in the EPR spectra of Cu and Al nanoparticles, the formation of superparamagnetism has been studied. Bentonite EPR spectrum consists of paramagnetic ($g = 4.5$) and superparamagnetic ($g = 2.15$) iron, as well as paramagnetic manganese ions.

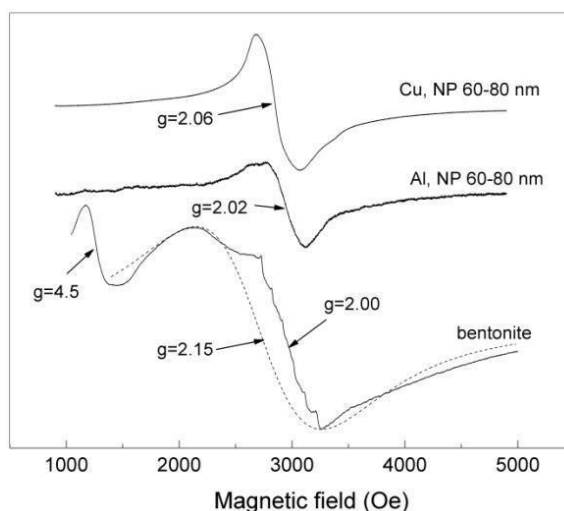


Fig.3. EPR signals of various nanoparticles.

The behavior of EPR spectra of copper and aluminum nanoparticles depending on the temperature was given figure 4 (A, B). As is seen, the narrowing of the resonance line and the amplitude growth with the increase in temperature for both nanoparticles is characteristic.

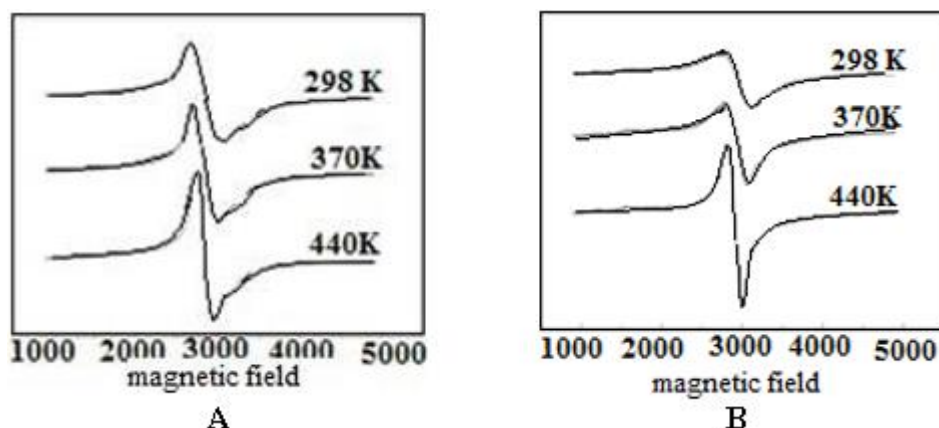


Fig.4. EPR spectra of Cu (A) and Al (B) nanoparticles at different temperatures.

In the following experiments, the characteristics with EPR method of 11 oil samples taken from oil wells in various parts of Absheron (Umbaki, Ateshgah, Gala,

Bibiheybat, etc.) were also learned by us (Fig.5). The analysis of EPR spectra in experiments with oil samples shows that the presence of iron oxide nanoparticles is characteristic for some oil samples (Fig.5). Since these nanoparticles have ferromagnetic properties, it is possible to change the viscosity of oil samples through the external magnetic field. Investigation of the structure and physicochemical properties of some oil samples, paraffinic sediments have shown that magnetic nanoparticles can be an ingredient of the aggregates of the colloidal oil particles [5,8,9].

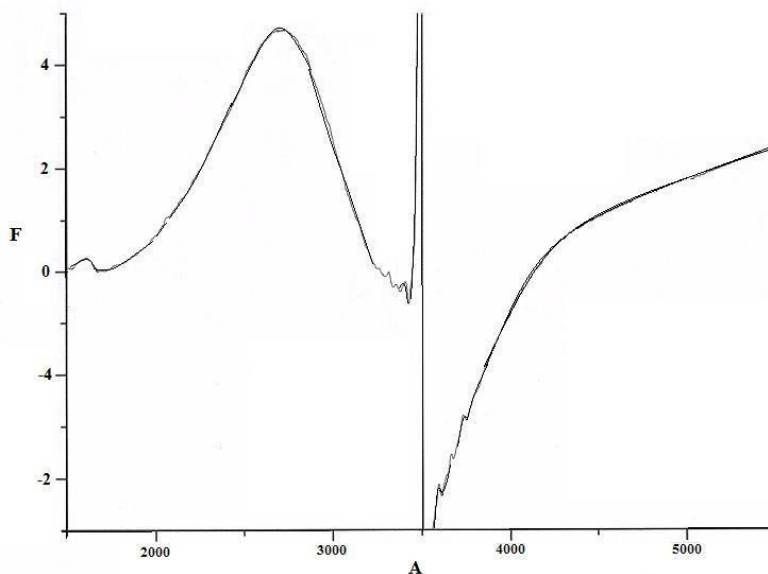


Fig.5. EPR spectrum of oil sample taken from Absheron oil fields.

The analysis of the obtained results allows us to suggest that the influence of magnetic field on the important technological physical and chemical properties of oil occurs with the presence of magnetic nanoparticles produced because of the biomineralization phenomenon. The presence of iron oxide magnetic nanoparticles in oil samples produced on some oil fields of the Absheron peninsula shows the possibility of influencing oil extraction and transportation via external magnetic fields.

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References

1. R.I.Khalilov, A.N.Nasibova., V.A.Serezhenkov, M.A.Ramazanov, M.K.Kerimov, A.A.Garibov, and A.F.Vanin.//Accumulation of Magnetic Nanoparticles in Plants Grown on Soils of Apsheron Peninsula. J. Biophysics, Moscow.2011, vol.56, N2, P.316- 322.
2. Rovshan I. Khalilov, Aygun N. Nasibova, Naglaa Youssef. The use of EPR signals of plants as bioindicative parameters in the study of environmental pollution.// International Journal of Pharmacy and Pharmaceutical Sciences. Issue 9, Vol 7. S.1. P.172-175. 2015.
3. В.И.Лесин, Ю.А.Кокшаров, Г.Б.Хомутов. Магнитные наночастицы в составе агрегатов коллоидных частиц нефти. Транспорт и подготовка нефти. 2009. С.95-97.
4. Petukhov D.I., Poyarkov A.A., Chernova E.A., Lukashin A.V., Eliseev A.A., Pyatkov E.S., Surtaev V.N.// Removal of acidic components of associated petroleum gas by pertraction on microporous membranes. J. NeftyanoeKhozyaistvo - Oil Industry, Sofiiskaya nab (Russian Federation), № 11, с. 55-58.

5. R.I.Khalilov, F.A.Kadirov, I.S.Guliyev, A.N.Nasibova. / Study of effects of physical factors on physical-chemical properties characteristics of petroleum. “Koordinasion Birləşmələrin Kimyası: Analitik Kimyanın Aktual Problemləri”. – International scientific conference. (BSU). Baku-2017. P.210.
6. R. Tao, and X. Xu. Reducing the Viscosity of Crude Oil by Pulsed Electric or Magnetic Field. J. EnergyFuels, 2006, 20 (5), pp 2046–2051.
7. V. I. Lesin, Yu. A. Koksharov, G. B. Khomutov. // Magnetic Nanoparticles in Petroleum. J. Petroleum Chemistry, 2010, Vol. 50, No. 2, pp. 102–105.
8. V.N.Nikiforov, Y.A.Koksharov, V.Y.Irkhin. Magnetic properties of “doped” DNA. Journal of Magnetism and Magnetic Materials. 459, 340-344.
9. Y.A.Koksharov, S.P.Gubin, I.D.Kosobudsky, M. Beltran, Y. Khodorkovsky, A.M.Tishin. // Low temperature electron paramagnetic resonance anomalies in Fe-based nanoparticles. Journal of Applied Physics 88 (3), 1587-1592.

NANOHISSƏCİKLƏR OLAN NEFT NÜMUNƏLƏRİNİN FİZİKİ-KİMYƏVİ XASSƏLƏRİ

R. Xəlilov, İ. Quliyev, F. Qədimov, A. Nəsibova, K. Seyidova

Xülasə: Elektron Paramaqnit Rezonans (EPR) spektroskopiyası üsulu ilə təbii sistemlərdə (bitki, neft və s.) apardığımız tədqiqatlar onlarda maqnit nanohissəciklərinin biogenerasiyasının baş verdiyini göstərir. Neftdə maqnit nanohissəciklərinin olması xarici maqnit sahəsinin köməyi ilə neftin texnoloji mühüm xüsusiyyətlərini (özlülük, deemulsasiya, parafinlərin çökməsi və s.) idarəetmənin mümkünliyünü şərtləndirir. Tərəfimizdən neftdə fraktal kolloidal aqreqatların quruluş və tərkiblərinin onun fiziki-kimyəvi xüsusiyyətlərinə (özlülük, maqnit-rezonans xüsusiyyətləri və s.) təsir mexanizmləri aydınlaşdırılmışdır.

Açar sözlər: nanohissəciklər, stress faktoru, özlülük, biogenerasiya, neft nümunələri.

ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА ОБРАЗЦОВ НЕФТИ, СОДЕРЖАЩИХ НАНОЧАСТИЦЫ

Р. Халилов, И. Гулиев, Ф. Гадимов, А. Насибова, К. Сеидова

Резюме: Исследования, проведенные в природных системах (растение, нефть и т.д.) с помощью электронного парамагнитного резонанса (ЭПР) показывают, что в них происходит биогенерация магнитных наночастиц. Наличие магнитных наночастиц в составе нефти обеспечивает возможность управления важными технологическими свойствами нефти (обезвоживание, деэмульсификация и т.д.) с помощью внешнего магнитного поля. Нами исследован механизм действия структуры и состава фрактальных коллоидных агрегатов в нефти на ее физико-химические свойства (вязкость, магнитно-резонансные характеристики и т.д.).

Ключевые слова: наночастицы, фактор стресса, вязкость, биогенерация, образцы нефти.