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ESTABLISHMENT OF OIL DISPERSED SYSTEMS BY THE PARAMAGNETIC PROBE AND FREE RADICALS

Abstract. We managed to establish experimentally existence of disperse particles of resinous asphaltene substance (RAS) in crude oil.The EPR spectra of nitroxyl in the oils of the Caspian region were studied, and as it can be seen, the component m_z=-1 splits into two lines.Heating up to 100 °C leads to disappearance extreme components which after cooling of a sample to room temperature appears only after long upholding (not less than 2 h).This phenomenon is connected with heterogeneity of oil, that is with existence in it of considerable number the asfaltenosmolistykh of particles.This phenomenon is associated with the heterogeneity of oil, that is, with the presence in it of a significant number of resin-asphaltenic particles. At low concentrations of RAS in oil, they are molecular dispersed and the molecules of the dissolved RAS freely move in the oil independently of each other.With a significant content of RAS in the oil micelles are formed. Particles of nitroxyl radicals are adsorbed on RAS micelles. Non-adsorbed particles of nitroxyl radicals chaotically move in the dispersive environment of oil. Two such different conditions of the nitroxyl radical in oil are in thermodynamic balance.

In low viscosity oils (Tengiz) where RAS is molecularly dispersed, particles of dissolved nitroxyl radicals move freely, and in the EPR spectrum we can observe three lines of them with the same intensities.

Keywords: paramagnetic probe, oil heterogeneity, free radical, disperse systems, adsorption.

As it is known from the literature data [1,2], resinous-asphaltene substances (RAS) of oil are dispersed particles. They are an element of the structure of mainly spherical shape, capable of independent existence in these conditions. The inner region (core) and the solvate shell surrounding the core are distinguished in the composition of the dispersed particle. The inner region of RAS is represented by a supramolecular structure consisting of molecules most prone to the association process. It can be asphaltenes. In turn, asphaltenes are the main source of the so-called "coal" (free) radical, which is fixed in the EPR spectrum of the viscous oil field Zhubantam (pic.1б) between the lines of nitroxyl m_z=0 и m_z=-1.

Nasirov R. N. applied the method of paramagnetic probe [3] to assess the viscosity of the Caspian region oils [4].

There is a connection between the rotational mobility of stable nitroxyl radicals and viscosity, which is determined by the Stokes-Einstein equation:

$$\tau_c = (4\pi/3kT)\alpha^3\eta \qquad (1)$$

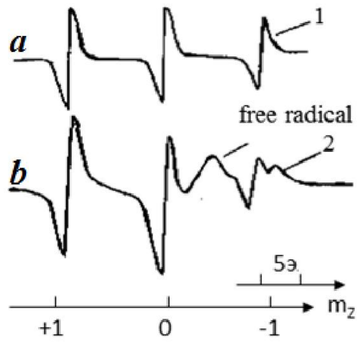
where τ_c - the correlation time of rotational mobility; η - dynamic viscosity of the medium; α - effective hydrodynamic radius of the radical; k - Boltzmann constant; T – temperature.

Value τ_c determined from the ratio

$$\tau_c = 6{,}65\Delta H_{+1}(\sqrt{I_{+1}/I_{-1}}-1)10^{-10} \qquad (2)$$

where I_{+1} – is the intensity of the components of the hyperfine structure (HFS), the corresponding value of the projection of the mechanical moment of the nucleus in the direction of the external magnetic field

m_z=+1; I_{-1}- the intensity of the STS component corresponding to the value of m_z=-1; ΔH- line width corresponding to m_z=+1. Picture 1 shows the EPR spectra of nitroxyl (2,2,6,6-tetrametil-4- oxopiperidine-1-oxyl) in oil fields Kotyrtas and Zhubantam. Nitroxyl was injected into the oil in dry form and dissolved with prolonged stirring (nitroxyl concentration - 10^{-3} mole/l).

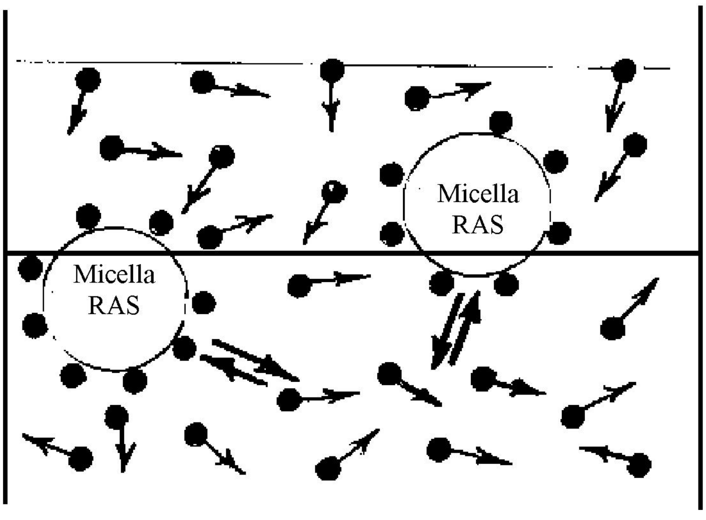


Picture 1- The EPR spectra of nitroxide at a temperature of 25^{0}C in oils:
a – from Kotyrtas, *b* – from Zhubantam

As can be seen from the EPR spectra (pic. 1), relation I_{+1}/I_{-1} varies dramatically depending on the field, due to the different viscosity of these oils.

In this paper, the colloidal structure of oil disperse systems is established using a paramagnetic probe and free radicals.

As can be seen from pic.1b, component m_z=-1 is split into two lines. Heating up to 100°C leads to the disappearance of the extreme component, which appears only after a long settling (at least 2H), through the cooling of the sample to room temperature. This phenomenon is due to the heterogeneity of oil, that is the presence of a significant number of RAS particles in it. At low RAS concentrations in oil, they are dispersed and the dissolved RAS molecules move freely in the oil independently. With a significant content of RAS comes formation of micelles (pic. 2). On the surface of RAS micelles goes the adsorption of nitroxyl radicals particles. Unadsorbed particles of nitroxyl radicals randomly move in the dispersion medium of oil. Two such different states of nitroxyl radical in oil are in thermodynamic equilibrium. In low-viscosity oils (Tengiz, well 38 and Chingiz, well 12), where RAS are molecularly dispersed, the particles of dissolved nitroxyl radicals move freely, and we observe three lines with the same intensities (isotropic spectrum) in the EPR spectrum. Adsorption of nitroxyl on these dispersed RAS particles leads to the change of g-factor and α_N nitroxyl. When heated, the adsorption layer is destroyed, and then slowly restored.



Picture 2- Colloidal structure of oil, which is established by the method of paramagnetic probe: ●- nitroxyl particles adsorbed on the surface of RAS oil micelles; ●➔ - dissolved nitroxyl particles in oil dispersion medium

Thus, the EPR method was able to experimentally establish the presence of RAS dispersed particles in crude oils of Kazakhstan with the help of a paramagnetic probe and FR, and the dynamics of the structure of their models was also confirmed.

Table 1 shows the content of asphaltenes, resins, FR and the value of the radical rotation correlation time of τ_c obtained by formula (2) in crude oils of Western Kazakhstan. The region of the slow rotation of nitroxyl $1{,}0 \cdot 10^{-8}$-$1{,}4 \cdot 10^{-8}$ is observed in oils with a high content of RAS and FR, constituting the dispersed phase, and the region of fast rotations of nitroxyl $\tau_c < 2 \cdot 10^{-11}$ (Chingiz oil) corresponds to the low content of resins and asphaltenes (<0,2%). In low-viscosity oils (Tengiz), where RAS are molecularly dispersed, the particles of dissolved nitroxyl radicals move freely, and we observe three lines with the same intensities (isotropic spectrum) in the EPR spectrum. In the latter case, crude oils approach to become true solutions.

Table 1 - The content of the RAS, FR and the value of τ_c in some crude oils of Western Kazakhstan

Field, well number	Content, %		$\tau_c \cdot 10^{10}$, c	CP $\cdot 10^{-17}$, spin/g
	silica resin	asphaltenes		
Karazhanbas, 850	17,4	6,40	14,5	31
Zhubantam, 14	15,2	3,40	13,0	13,3
Uzen, 5118	20,1	0,70	5,5	15,9
Zaburun, 11	8,8	0,30	4,9	6,3
South-East Kamishitov,4	8,7	0,20	2,3	4,9
South-West Kamishitov,118	2,5	следы	1,0	0,2
Kotyrtas,28	7,2	0,28	1,8	3,3
Tengiz,38	2,3	0,18	0,3	1,5
Chingiz, 12	следы	0,2	0,2	0,4

EXPERIMENTAL PART

EPR spectra of oil samples were taken on the E-12 spectrometer of “Varian” at room temperature [5]. Oil samples before the analysis were purified from associated water and mechanical impurities by centrifugation (centrifuge T-22) at a speed of 4000 rpm. The oil samples prepared in this way were sealed in order to avoid evaporation of gasoline fractions into glass ampoules 0.2 cm in diameter and 10-15 cm in length. We have found EPR signals from both vanadium and FR ions in the oils of the studied fields. To determine the concentration, the most intense hyperfine structure (HFS) line from the complexes of tetravalent vanadium and a single line from FR were used. Urichtausk oil (from well 8) with known vanadium (27,6 г/т) and FR ($7{,}8 \cdot 10^{17}$ spin/sm^3) content was taken as the concentration standard. Nitroxyl was injected into the oil in dry form and dissolved with prolonged stirring.

CONCLUSIONS

Thus, the method of paramagnetic probe and free radicals was able to experimentally determine the presence of dispersed particles of RAS in crude oils. Free radical in oils does not affect the accuracy of determination τ_c, since it is fixed in the EPR spectrum of nitroxyl between the lines m_z=0 and m_z=-1

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ПАРАМАГНИТТІ ЗОНДЫ ӘДІСІМЕН ЖӘНЕ БОС РАДИКАЛ КӨМЕГІМЕН МҰНАЙДЫҢ ДИСПЕРСТІ ҚҰРЫЛЫМЫН АНЫҚТАУ

Аннотация. Біз шикі мұнайдағы ШАЗ дисперсті бөлшектерінің болуын эксперименталды түрде анықтадық. Каспий маңы аймағындағы мұнайлардағы нитроксил радикалының m_z = -1 сызығы екі сызыққа

ыдырайды. Бұл сызықтар 100°С дейін қыздырғанда, бір сызыққа бірігеді, ал одан кейін бөлме температурасында екі сағат шамасында екі сызыққа бөлінеді. Бұның себебі мұнайдың құрамындағы шайыр асфальтен затына ғана байланысты. Шайыр асфальтен заттарының едәуір дәрежесінде ШАЗ мицеллі түзіледі. ШАЗ мицеллінде нитроксил радикалдары адсорбцияланады. Адсорбцияланбаған бөлігі мұнайдың дисперсті ортасында хаосты қозғалады. Осындай нитроксил радикалың екі күйі бір-бірімен термодинамикалық тепетендікте болады.

Тұтқыр емес мұнайларда (Теңіз) ШАЗ молекеулалары дисперсті болады. Сондықтан да нитроксил радикалдары еркін қозғалыста болады. Соның нәтижесінде біз ЭПР спектрінде үш бірдей сызықтан тұратынын көреміз.

Түйін сөздер: парамагнитті зонд, мұнайдың гетерогендігі, бос радикал, дисперсті жүйелер, адсорбция.

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УСТАНОВЛЕНИЕ НЕФТЯНЫХ ДИСПЕРСНЫХ СИСТЕМ С ПОМОЩЬЮ ПАРАМАГНИТНОГО ЗОНДА И СВОБОДНЫХ РАДИКАЛОВ

Аннотация. Нам удалось экспериментально установить наличие дисперсных частиц смолисто-асфальтеновых веществ (САВ) в сырых нефтях. Изучены ЭПР спектры нитроксила в нефтях Прикаспийского региона, и как видно компанента m_z=-1расщеплена на две линии. Подогрев до 100°С приводит к исчезновению крайней компоненты, которая после охлаждения образца до комнатной температуры появляется лишь после длительного отстаивания (не менее 2ч). Это явление связано с гетерогенностью нефти, то есть с наличием в ней значительного числа смолисто-асфальтеновых частиц. При малых концентрациях САВ в нефти они молекулярно дисперсны и молекулы растворенного САВ свободно перемещаются в нефти независимо друг от друга. При значительном содержании САВ в нефтях образуются мицеллы. На мицеллах САВ адсорбируются частицы нитроксильных радикалов. Неадсорбированные частицы нитроксильных радикалов хаотично движутся в дисперсионной среде нефти. Два таких разных состояния нитроксильного радикала в нефти находятся в термодинамическом равновесии.

В маловязких нефтях (Тенгиз) где САВ молекулярно дисперсны, частицы растворенных нитроксильных радикалов свободно перемещаются, и в спектре ЭПР мы наблюдаем от них три линии с одинаковыми интенсивностями.

Ключевые слова: парамагнитный зонд,гетерогенность нефти, свободный радикал,дисперсные системы, адсорбция.

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