

Environmental Pollution of the Caspian Region of Azerbaijan

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Abstract - EPR and low-temperature photolysis methods have been used to study the processes of phototransformation in oil systems under the influence of solar radiation and photosensitizers: polycyclic aromatic hydrocarbons, asphaltenes, resins. It is shown that in organic compounds (alcohols and paraffins) with the addition of a photosensitizer Sh_1 ($C=10^{-7}$ mol/l) to their solution, alcohol, alkyl radicals and atomic hydrogen R^* are formed under the influence of full light from a mercury lamp DRSh-500, which reacts with hydrocarbons to form molecular hydrogen (H_2), easily reacting with oxygen O_2 , form peroxide radicals $R'O_2$, then the process proceeds by the mechanism of a chain reaction. It has been established that in the presence of izo- compounds in oil, radicals of substituted aromatic hydrocarbons are formed in them under the influence of solar radiation. It is shown that methylperinaphthene radicals with photochromic properties are registered in the products of secondary oil refining (cracking, pyrolysis). The kinetic patterns of the generation of methylperinaphthene R'_{mpn} radicals, their reduction under the action of irradiation and the restoration of $[R'_{mpn}]$ after the cessation of exciting light have been established. Polycyclic aromatic hydrocarbons with the participation of naphthene-paraffin hydrocarbons and olefins in the process of solar irradiation are also subjected to phototransformation with the formation of ion radicals, endoperoxides, quinones and phenols. All of the above radicals are very toxic and pose a great danger to the vital activity of the flora and fauna of the oil republic.

Keywords: EPR, asphaltenes, resin, methylperinaphthene, atomic hydrogen, phenols, quinines

Introduction

Significant areas of oil production in Absheron and the Caspian "oil sector" of Azerbaijan are contaminated with oil and its refined products. It is known that environmental pollution in the oil production complex begins with exploratory drilling and construction of oil and gas producing wells. In the oil production complex, environmental pollution, as a rule, begins with exploratory drilling and construction of oil and gas producing wells. The main sources of pollution during the construction of wells are diesel exhaust from drilling rigs, degassing of drilling mud, for the preparation of which about twenty dozen chemical reagents are used. As a result, adjacent lands are polluted with drilling mud and oil, which are washed away by meltwater onto adjacent lands and reservoirs. When burning liquid fuel air pollution is significant since the vanadium-porphyrin complex released in the form of soot, belonging to the class of poisons, is dispersed throughout the territory and pollutes the region. Oil has a particularly strong effect on the water surface due to its ability to spread with the formation of a thin film, which even in small quantities disrupts the nervous system of living organisms, reduces the growth and death of algae, and the number of commercial fish and seals decreases due to. Under the influence of solar radiation, temperature, and weathering in polluted soils and reservoirs of the environment, various complex photophysical and photochemical processes occur in oil components, often proceeding by a free radical mechanism, which contribute to the release of gaseous and liquid toxic products into the atmosphere. This is especially true for atomic hydrogen, resinous asphaltene substances (RAS), asphaltenes, methylperinaphthene radicals and many radicals of substituted aromatic hydrocarbons formed in heavy oil. Photochemical processes occurring in oil and heavy oil residues in our environment remain an insufficiently studied area and an urgent area of research in the field of petrochemistry and physical chemistry.

Experimental part

To study the paramagnetic nature of oil, the methods of electron paramagnetic resonance (EPR) and low-temperature photolysis were used as the main physical research method. EPR spectra were recorded at liquid nitrogen temperature (-

196°C) on a RE-1306 radio spectrometer. The standard of the magnetic field scale was Mn^{+2} ($S=5/2$) in MgO. A single crystal of $CuCl_2 \cdot 2H_2O$ with a known number of ions ($1.2 \cdot 10^{17}$ spin/g) was used as a reference. The samples were irradiated with full light of a DRSh-500 mercury lamp at a temperature of liquid nitrogen in sealed ampoules. Some experiments were carried out on a BRUKER BIOSPIN radio spectrometer (Germany) in the X-band (operating frequency 9.85 Hz. The amplitude of the RF modulation (100 kHz) was varied in the range of 150-650 ml. The setting according to the internal field standard was determined by the UDS (ultrafine diamond standard) with $g = 2.0036$. The EPR spectra were recorded at 25°C under conditions of minimal saturation (microwave power level – 0.5 mw).

Results and their discussion

The use of mainly light types of unstructured oil in technological processes did not necessitate the analysis and regulation of the internal structure of oil systems. The available data on the use of EPR in petrochemistry mainly related to the study of complexes of transition metal ions, molecules of surfactants and asphaltenes. In light oils, a high concentration of asphaltene radicals $[R_{asf}^{\bullet}] \cdot 10^{18}$ spin/g (a single EPR signal with $(\Delta H_{width}=0.88$ mtl, $g=2,0023$), as a rule, shield all other paramagnetic particles. Fractionation of oil (fr.120-230°C) made it possible to register iron oxide in them $\Delta H_{width}=168.1$ mtl, $g=2.24$), copper microcrystals ($\Delta H_{width}=108.9$ mtl, $g=2.27$), nickel oxides ($\Delta H_{width}=117.4$ mtl, $g=2.21$), cobalt ion $\Delta H_{width}= 5.12$ mtl, $g = 4.76$) [1]. Unlike light oils, EPR spectra of asphaltenes and metal complexes c (D) are recorded in heavy commercial oil ($\Delta H_{width}=25.0$ mtl, $g=2.4$) and an intense EPR signal of the radical ($\Delta H_{width}=7.5$ mtl, $g=2.4$), observed in all heavy oils[2-5].

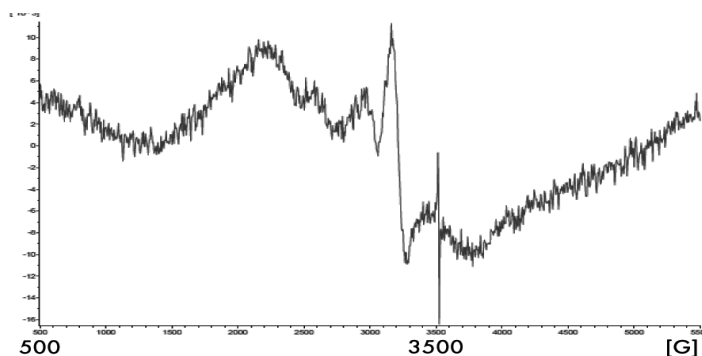
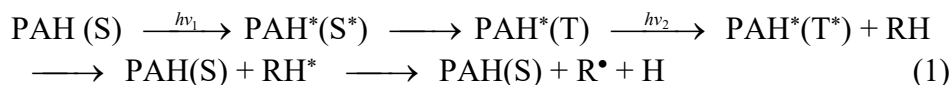


Fig.1: EPR spectrum of West Absheron oil -fr.(120-230°C) and R_{asf}^{\bullet} .

In Fig.1 except for the hydrocarbon radical ($\Delta H_{width}= 7.5$ mtl, $g = 2.4$), a single spectrum of the asphaltene radical is clearly observed ($\Delta H_{width}= 0,88$ mtl, $g=2.0023$). The formation of an aromatic hydrocarbon radical can occur of petroleum compounds (izo-paraffin, naphthenaromatic, condensed hydrocarbons, acetals, esters, aldehydes), containing atomic hydrogen donors, the primary initiation of which could be carried out due to the continuous action of the natural background of ionizing radiation, UV -solar radiation, heat, leading to the separation of atomic hydrogen from CH_2 , CH_3 groups and the formation of a substituted aromatic hydrocarbon radical (SAH). The presence of SAH in the fractions of heavy oils causes the shift of the bands of the electronic absorption spectra to the region of maximum solar radiation [6,7], which contributes to the effective utilization of solar energy by them, leading to photochemical and photooxidation processes. Under the influence of ionizing radiation by the interaction of excited molecules of polycyclic aromatic hydrocarbons (PAHs) -naphthalene, phenanthrene, chrysene, benzphenanthrene, pyrene, perylene groups (the total content of which is about 40% by weight), known initiators of photochemical processes (present in luminescent concentrate-Sh₁ isolated from heavy catalytic cracking gas) with molecules of organic compounds – alcohols, paraffins ,as a result of two-photon absorption by PAH molecules acting as photosensitizers, with their transfer to the highly excited triplet state of $PAH^*(T^*)$ [8] . Being at the triplet level, and having a long lifetime (2.5 and 3 s), the aromatic molecule has the ability to absorb another quantum of $h\nu_2$ energy with a transition to a more highly excited triplet level

T*. A doubly photoactivated PAH molecule can transfer energy to the molecules of alcohols and paraffins in the neighborhood and cause a rupture of the valence bond with the formation of alcohol, alkyl radicals (R[•]) and atomic hydrogen by the reaction :



where S, S* and T, T* are, respectively, the basic and excited singlet and triplet states of PAH molecules. H atoms react with RH hydrocarbons by the reaction $\text{RH} + \text{H}^\bullet = \text{H}_2$ to form radicals and molecular hydrogen. R[•] radicals react readily with O₂ to form peroxide radicals.

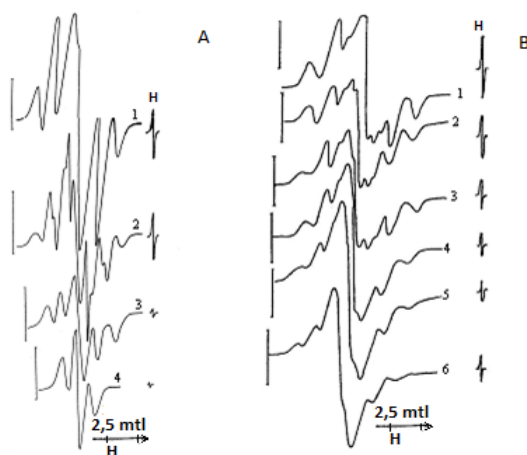


Fig.2: A- EPR spectra of photoradiated solutions of Sh1 (C=10⁻⁷ mol/l) in alcohols: 1 – butanol, 2 – propanol, 3 – ethanol, 4 – methanol; b, b' are, respectively, components of the line of the H atom. Exposure time 2 h, T= -196 ° C.

B -EPR spectra of photoradiated solutions: 1 phenanthrene in hexane, W1 (C=10⁻⁷ mol/l) in saturated hydrocarbons: 2 – hexane, 3 – heptane, 4 – octane, 5 – nonane, 6 – undecane . Exposure time is 2 hours, T= -196 ° C.

The analysis of the EPR spectra of irradiated samples shown in Fig.1 made it possible to identify some of the radicals formed. The observed shape of the spectra of these radicals corresponds to the superposition of at least the spectra of several radicals, one of which belongs to the alkyl radical R[•]₁ (-CH₂-C[•]H-CH₂-) a six-component EPR line with $\Delta H_{\text{width}} = 12.5$ mT, $\Delta H_{\text{rast}} = 2.0$ mT, $g = 2.0$. The second EPR spectrum was interpreted by us as a quintet from a radical with R[•]₂(C[•]H(CH₃)CH₂) with $\Delta H_{\text{width}} = 10.0$ mT, $\Delta H_{\text{rast}} = 1.8-2$ mT. One of the components of atomic hydrogen is shown to the right of the main spectrum $\Delta H_{\text{width}} = 50$ mT, $g = 2.0$ [8]. The resulting radicals easily react under normal conditions with molecular oxygen O₂ to form R[•]O₂. Next, the process follows a chain reaction mechanism. The presence of PAHs in the luminescent concentrate, which are a singlet oxygen generator, leads to oxidative processes. One of the inhibition mechanisms is associated with the formation of compounds such as phenols, and the other is associated with the generation of mono- and biradicals capable of recombining with naphthenic-paraffin radicals during photovoltaics [9].

Certain patterns in changes in paramagnetism (an increase in the concentration of asphaltene radicals) in oil residues were also observed during heat treatment, in particular, in products of catalytic cracking, pyrolysis, etc., due to the formation of hydrocarbon methylperinaphthene radicals. This radical was detected by us under slight heating (30-100°C) in a luminescent concentrate isolated from a polymer gas oil of catalytic cracking >500 ° C [10]. The small values of the constants (4.6 mT) of the EPR spectrum indicated the aromatic character of the radical (methyl-substituted perinaphthene).

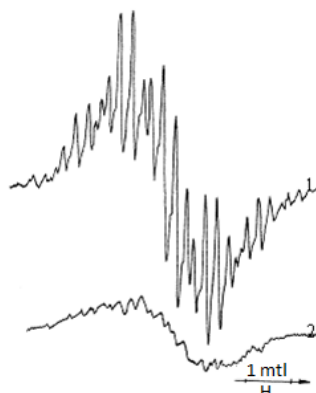


Fig.3: EPR spectra of the methylperinaphthene radical before(1) and after irradiation for 6 min (2).

Photochromic transformations of the methyl perinaphthene radical in petroleum residues have shown that under the action of short-term (6min) photovoltaics, the thin-structured part of the spectrum practically disappears (Fig.3), a single EPR line remains, characteristic of RAS. However, after the cessation of exciting light for 60 minutes, the EPR spectrum is largely restored [11].

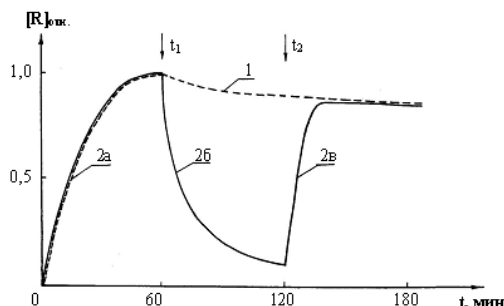
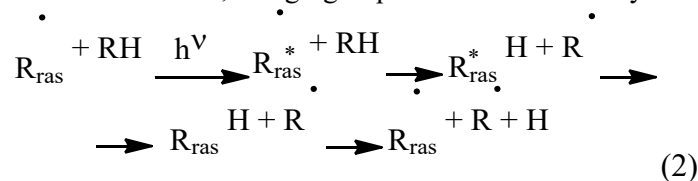


Fig.4: Kinetic curves of radical generation depending on the heating time (1), photo-emission (2).

Considering that RAS and asphaltenes are photosensitizers (paraffins, paraffin naphthenes, alcohols) [6-8], their electronically excited states can play a certain role in photochemical and photooxidation processes of light oil systems. RAS radicals in oil have electronic absorption spectra shifted to the long-wavelength region, contributing to the expansion of their sensitivity range to 550 nm [7], which leads to their efficient use of solar energy. It should be noted that, in contrast to PAHs, in the presence of which the decomposition of compounds occurs by a two-quantum reaction mechanism (1), the C-H bonds of organic compounds are destroyed with the formation of alcohol, alkyl radicals and atomic hydrogen by a single - quantum mechanism, using light quanta with a relatively low energy of about 2 eV :



During photo-irradiation asphaltenes isolated from heavy oil residues of secondary oil refining [9], was found that in solutions of asphaltenes, unlike resins, when exposed to light, only a part of the concentration of free radicals of asphaltenes decreases during their transition to diamagnetic peroxides, dimers. When exposed to light photoexcitation of asphaltenes, about 40% of paramagnetic particles die within 2 hours, which indicates the existence of at least 2

paramagnetic particles with different localization of the spin of an unpaired electron in an asphaltene molecule with different photostability. It is usually assumed that the unpaired electrons of free carbon bonds are located inside the condensed structure of asphaltenes with high delocalization. It is allowed to find a free bond on some periphery of molecules with less delocalization of the spin field. When such molecules are photo-irradiated (with sufficient proximity), activation and recombination occur due to peripheral unpaired electrons, which leads to the formation of an asphaltene framework. At the same time, due to the large shielding by the shells of molecules, the 'central' unpaired electrons are mainly preserved and cause residual paramagnetism.

Conclusion

Thus, based on the analysis of our own experimental data on the study of thermo-, photo-transformations in high-molecular oil compounds (resins, asphaltenes), heavy catalytic cracking gas oils, heavy pyrolysis resin, tar, deasphaltation asphalts, residual oil extracts, it was found that free radicals of asphaltenes do not completely die (40%) under the influence of solar radiation; PAHs photosensitize the decomposition of organic compounds, alcohols, and paraffins to form alkyl radicals and active atomic hydrogen PAHs with the participation of NPS (naphthene-paraffine substrate) and olefins undergo transformations during irradiation with the formation of ion radicals, endoperoxides, quinones, phenols; the methylperinaphthene radical under photo-irradiation (6min) turns into asphaltenes, after 1-2 hours it completely returns to its original state; in residual petroleum products, a decrease in the concentration of R_{asf}^{\bullet} after 2h irradiation - in fuel oil (12%), tar (33%), in de-asphalting asphalt(16%), in bitumen(28%). All of the above radicals are very toxic and pose a great danger to the vital activity of the flora and fauna of the oil republic. We consider it necessary to timely recultivate the lands around the spills of existing wells, as well as deep burial of oil cracking and pyrolysis residues in places far from water resources and underground currents.

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