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THE PHOTOCHEMICAL PROCESSES UNDER THE INFLUENCE OF UV RADIATION IN MODEL SYSTEM OF CRUDE OIL – WATER

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Abstract: The photochemical processes under the influence of UV radiation of crude oil – distilled water was studied as a model system. 0.1÷0.5 ml crude oil from the Dubandi terminal was added to 40 ml of distilled water. The absorption intensity increases as the amount of crude oil on the surface. The observed patterns of photolysis of the crude oil – distilled water model systems are associated with the absorption of UV radiation by molecules with absorption bands in the region > 220 nm. These molecules are monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, m- / p-xylene, o-xylene, and polycyclic aromatic hydrocarbons - acetonaphthalene, fluorene, phenanthrene were identified as components of crude oil.

Keywords: UV radiation, crude oil, photochemical processes, polycyclic and mono-aromatic hydrocarbons, solar radiation

1. Introduction

The main industrial facilities that pollute sea water are oil platforms, oil terminals and refineries, the petrochemical industry, electricity and industrial wastewater. A reliable and accurate analysis of the concentration of oil and its components in seawater is urgent, since oil production on the shelf and the operation of oil terminals pose a significant environmental hazard to the environment[17]**.** Currently, the IR spectrometers, UV refractometers, UB fluorimeters, gas and liquid chromatographs are using to analyze oil and oil products. Optical methods make it possible to quickly, without sample preparation, measure the integral concentration of hydrocarbons[3]**.** However, a significant drawback is the lack of the ability to measure the partial concentrations of individual hydrocarbons contained in oil, which does not allow identifying, for example, various grades of oil and oil products [2, 17]

Photochemical degradation of crude oil in an aqueous medium is one of the physicochemical processes, taking place under the influence of UV part of solar radiation and constitutes about 10% of oil conversion in case of oil film on the surface of seawater. Degradation of crude oil occurs under the influence of various physical factors - including the effects of temperature, wind speed, chemical composition and the biological state of seawater. Simultaneous influence of the abovementioned factors makes it very difficult to clarify the mechanism of the degradation process of crude oil. Taking into account the abovementioned features of photochemical degradation, it is expedient to study a model system consisting of crude oil and distilled water.

This work is devoted to the study of photochemical processes under the influence of UV radiation in the model system of crude oil – water.

2. Experimental

Irradiation was conducted under the influence of the entire spectrum of a mercury lamp PRK-4, which has a resonance line in the region 253 -546 nm and a continuous spectrum in the region of >546nm [12]. The intensity of the UV part of radiation was calculated on acetone actinometry and was $5x10^{15}$ quanta/sec. 0.1÷0.5 ml crude oil from the Dubandi terminal was added to 40 ml of distilled water. Two-phase systems were prepared by placing them in quartz ampoules in a Vol. of 80 ml. Under the experimental conditions, crude oil creates a 0.1-0.5 mm thick film on the water surface. Systems were prepared by placing them in quartz ampoules in a volume of 4 ml by Cary-50 UV-spectrophotometer.

3. Results

UV spectra of UV irradiated samples of crude oil -distilled water model systems are given in fig.1.

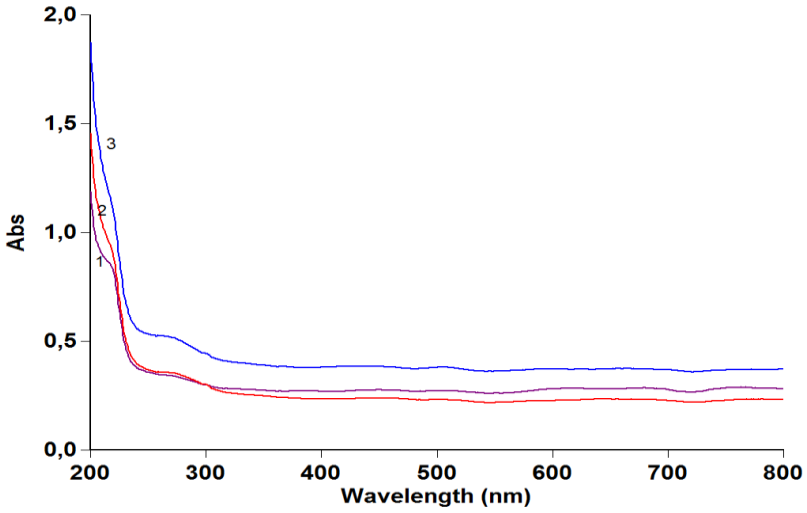

Fig. 1 UB spectra of UV irradiated crude oil -distilled water model systems (τ=15 min, 1-0,1 ml, 2-0,2 ml, 3-0,5 ml)

As can be seen from fig.1. the absorption intensity increases as the amount of crude oil on the surface. The extracted crude oil belongs to the medium density oil (0.840-0.879 g / cm3). This group includes oil with relatively high volatile fractions. This type of oil has a relatively high evaporation capacity and is characterized by evaporation of 40% by Vol. within 10-20 hours.

Comparison of UV-spectra crude oil-distilled water model systems photolysis for 15 minutes are given in fig.2.

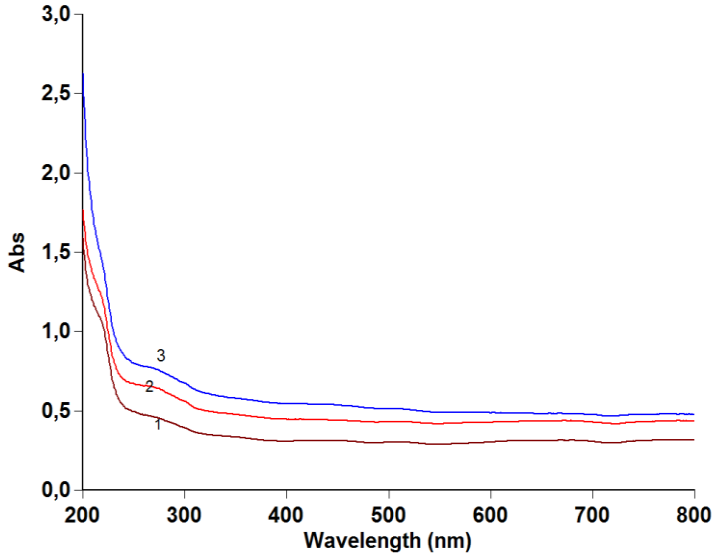

Fig.2. UV spectra crude oil -distilled water model systems
(τ=15 min, 1-0,1 ml, 2-0,2 ml, 3-0,5 ml)

As can be seen from fig.2, an increase in the amount of crude oil spilled on the surface is also observed during the photolysis of the system.

However, in this case, the absorption in the range of 200-220 nm is higher than in non-irradiated samples. Probably this increasing is due to the increase of concentration of oxidized molecules, as carbon acides and aldehydes.

The observed patterns of photolysis of the crude oil – distilled water model systems are associated with the absorption of UV radiation by molecules with absorption bands in the region $\lambda \geq 253$ nm. These molecules are monoaromatic hydrocarbons such as benzene, toluene, ethylbenzene, m-/ p-xylene, o-xylene, and polycyclic aromatic hydrocarbons - acetonaphthalene, fluorene, phenanthrene wide identified by us as components of crude oil.

In [4,9,10], the role of PAH and aromatic compounds in the sensitization of saturated hydrocarbon components was shown through the transfer of energetically excited triplet states of PAH molecules and two quantum processes of transfer of excitation energies (During full irradiation of the mercury lamp).

$$PAH(s) \xrightarrow{h\upsilon} PAH(s^*) \rightarrow PAH(T^*) \xrightarrow{h\upsilon_2} PAH(T^*) \xrightarrow{RH} PAH(s) + RH^* \rightarrow PAH\ (s) + R^* + H$$

$$R + O_2 \rightarrow RO_2$$
$$H + O_2 \rightarrow RO_2$$

Another way for dissolved oil degradation is oxidation with O_3, the product of O_2 photolyzes:

$$O_{2dissolv} \xleftrightarrow{h\upsilon} O + O$$
$$O + O_2 \rightarrow O_3$$
$$O_3 + Ar.compounds \rightarrow Products$$

Because oxygen is readily available in natural waters, this energy can be transferred to oxygen molecules generating singlet oxygen $^1O_2$. This formation has been demonstrated in the photo-oxidation study of dimethylnaphtalenes in which the authors have explained the formation of the photoproducts by singlet oxygen mechanism[16].

Molecules in the triplet state also may take part in photochemically promoted electron-transfer reactions. For instance, the superoxide radical anion, $O_2^{-\cdot}$, is formed through an electron transfer from a photoexcited molecule to molecular oxygen. In water, O_2^- is partly protonated to its conjugate acid, HOO· which can undergo disproportionation to oxygen and hydrogen peroxide (H_2O_2).It has been reported that H_2O_2 forms in various natural-waters exposed to sunlight[11].

Photo-oxidation by free radicals has been suggested in model studies such as the sensitized oxidation of alkyl benzenes [15], hexadecane [5], pentadecane [7].nonlinear hydrocarbons [12, 13] and cycloalkanes [6].

A combination of singlet oxygen and free radical induced photo-oxidation mechanisms have also been proposed to explain the products in some studies such as in the photolysis of thiophene oxides in which the photolysis has regenerated the thiophene and eliminated atomic oxygen [17] which has then abstracted hydrogen and formed free radicals.

As a result, the decomposition of hydrocarbon molecules occurs with the formation of addition and abstraction products, as well as oxidation in the presence of oxygen.

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ФОТОХИМИЧЕСКИЕ ПРОЦЕССЫ ПОД ВОЗДЕЙСТВИЕМ УФ- ИЗЛУЧЕНИЯ В МОДЕЛЬНОЙ СИСТЕМЕ НЕФТЬ – ВОДА

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Резюме: В качестве модельной системы исследованы фотохимические процессы под действием УФ-излучения нефть - дистиллированная вода. 0,1 ÷ 0,5 мл сырой нефти с терминала Дубанди добавляли к 40 мл дистиллированной воды. Интенсивность поглощения увеличивается по мере увеличения количества сырой нефти на поверхности. Наблюдаемые закономерности фотолиза модельных систем сырая нефть - дистиллированная вода связаны с поглощением УФ-излучения молекулами с полосами поглощения в области $\lambda > 220$ нм. Эти молекулы представляют собой моноароматические углеводороды, такие как бензол, толуол, этилбензол, м- / п-ксилол, о-ксилол, а полициклические ароматические углеводороды - аценафталин, флуорен, фенантрен были идентифицированы как компоненты сырой нефти.

Ключевые слова: УФ-излучение, сырая нефть, фотохимические процессы, полициклические и моно-ароматические углеводороды, солнечное излучение, Фурье ИК-спектроскопия

UB- ŞÜALARININ TƏSİRİ ALTINDA XAM NEFT – SU MODEL SİSTEMİNDƏ BAŞ VERƏN FOTOKİMYƏSİ PROSESLERİN TƏDQİQİ

T.S. İdrisov, M.A. Qurbanov, Ü.Ə. Quliyeva

Xülasə: UB şüalarının təsiri altında xam neft – distillə suyu model sistemində baş verən fotokimyəvi proseslər tədqiq edilmişdir. Dübəndi terminalından 0,1÷0,5 ml xam neft götürülərək 40 ml distillə suyunda həll edilərək model sistemlər hazırlanmışdır. Müəyyən edilmişdir ki, səthdə xam neftin miqdarı

artdıqca udulmanın intensivliyi artır. Xam neft – distillə suyu model sistemlərinin fotolizi prosesində müşahidə edilən qanunauyğunluqlar $\lambda > 220$ nm oblastda yerləşən molekullar tərəfindən udulması ilə əlaqələndirilir. Bu molekulların benzol, toluol, etilbenzol, m-/p-ksilen, o-ksilen kimi monoaromatik karbohidrogenlər və asetonaftalin, flüoren, fenantren kimi politsiklik aromatik karbohidrogenlər olduğu müəyyən edilmişdir.

Açar sözlər: UB şüalanma, xam neft, fotokimyəvi proseslər, polisiklik və mono-aromatik karbohidrogenlər, günəş radiasiyası.