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FORMS OF OIL PRODUCTS IN THE AQUATIC ENVIRONMENT

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Abstract *In the aquatic environment oil products (OP) are in different migration forms: in the homogeneous phase in the form of droplets of various sizes and films with thickness from 1 to 200 microns; in the emulsified form; in the form of molecular solutions. The distribution of OP in water between these forms depends on the way of their entry into water, time of their stay in the aqueous medium, its temperature, dispersion mode and physicochemical composition of the aqueous medium. It is shown that the distribution of droplets of the dispersed phase of the OP is described by the Kolmogorov function. When determining the concentration of OP, it is necessary to pay attention to the presence of benzene groups in them. With increasing duration of contact of gasoline with water the difference of OP solubility in distillate and ordinary water increases. It is connected with sensitivity of benzenes to salt content of water due to formation of solvate complexes and with competition for free water molecules. The decrease in the concentration of dissolved benzene-containing OP increases according to the law* $S^{1/3}$*, where S is the salt content in water. When designing water treatment systems from OP, it is necessary to use a step system corresponding to the content of different forms of OP.*

Key words: *petroleum products, phase state, distribution of droplets, solutions in water.*

1. Introduction

OP is among the most common environmental pollutants. They are found in surface runoffs, rivers and lakes. The last decades are characterized by an increasing spread of oil products in groundwater of the upper horizon. The processes of mixing of mine water with surface runoffs contaminated with oil products and their penetration into formation water in Donbas mines due to the cessation of water pumping due to military operations pose a special danger.

The most significant sources of such pollution are:

- motor vehicles and their infrastructure, various agricultural and military equipment;
- oil refineries, oil depots, fuel terminals and filling stations;
- enterprises of metallurgical and metalworking industries;
- pipeline transportation of crude oil and oil products, railroad and sea transportation;

- energy enterprises.

In the aquatic environment OP are in different migration forms:

- in homogeneous phase in the form of drops of various sizes and films with thickness from 1 to 200 microns;
- in emulsified form;
- in the form of molecular solutions.

The distribution of OP in water between these forms depends on the way they enter the water, the time of their stay in the aqueous medium, its temperature, the dispersion mode and the physicochemical composition of the aqueous medium.

Due to the formation of films on the surface of water bodies, oil products disturb their oxygen regime, slow down the reaeration processes and inhibit the biochemical oxidation of other organic compounds, including life processes. It should be noted that 1 kg of OP can form a film on the water surface with the area from 10^4 to $10^6 m^2$. In summer time the film of OP decomposes by 50-80% within 7-10 days, and at temperature below $+4^oC$ decomposition is suspended. Wastewaters of oil refineries containing more than 15 mg/dm^3 of OP are not suitable for fish and their fry [1-3]. At the OP content of more than 1.2 mg/dm^3 the normal development of eggs and some representatives of benthos is disturbed. At the concentration of OP more than 0.1 mg/dm^3 water taste quality deteriorates and fish meat acquires "oil taste". Concentration of OP is determined by the competition between the flow of their input into the water body and the rate of oxidation due to aeration and solar radiation. In spring and summer, due to the increase in water temperature and surface aeration with a constant flow of OP input, their total concentration in water decreases, while in fall and winter it increases. If the total flux of OP input and their corresponding oxygen uptake is greater than the aeration flux of a given water body, its total oxygen balance is disturbed, which leads to the death of flora and fauna [3, 4].

Sanitary norms and rules [2] establish maximum permissible concentrations (MPC) of petroleum products in the water of water bodies of I category (fishery use) and II category (sanitary and domestic use):

$$MPC_I < 0,05 \text{ mg/dm}^3;$$

$$MPC_{II} < 0{,}1\ldots0{,}3\ mg/dm^3,$$

(0.1 mg/dm^3 for sulfuric oils, 0.3mg/dm^3 for mineral oils) [2].

Water purification from OP is difficult because a significant part of them (sometimes up to 1-3g/dm^3) is in emulsified and dissolved states. Particular difficulties arise in the presence of surfactants and emulsion stabilizers.

The following methods are used for wastewater treatment: physical, physical-chemical and biochemical methods [3-6].

Physical methods are used to separate film and coarse-dropped forms of OP. They include: sedimentation, centrifugation, flotation, filtration, exposure to acoustic, electric and magnetic fields.

Physicochemical methods include coagulation, sorption, ozonation and chlorination.

Biochemical methods include oxidation of OP by microflora of activated sludge in aeration tanks, ponds and various types of biofilters. Recently, special non-pathogenic bacterial strains have been used for this purpose.

2. Distribution of oil products by phase-dispersed composition and determination of their content in water

Analysis of water treatment methods shows that they are determined by the phase-disperse state of impurities [4, 5]. Petroleum products are not an exception in this respect, which in water can be in three states:

1) homogeneous, in the form of a film on the water surface or large droplets;
2) heterogeneous, in the form of finely dispersed suspensions or stabilized emulsions;
3) molecular, in a dissolved state.

The main feature of a heterogeneous state is the presence of an interface between the dispersion medium and the dispersed phase, i.e., petroleum products. For OP droplets with a size of $r < 10^{-5}$ m, the value of the surface energy depends on their size (r) and increases with its decrease according to the law $\sim r^{-1}$. Aqueous emulsions of OPs with $r > 10^{-6}$ m are unstable with respect to gravitational forces or other types of physical separation. If the particle size of the emulsion $r < 10^{-6}$m, kinetically stable colloidal systems are formed. When the dispersion particles reach a size of $r < 10^{-9}$ m, molecular solutions of petroleum products are formed [3-6].

The distribution of OP between phase-disperse states depends on the type of OP and the method of dispersion formation, its temperature and salt content.

The result of determining the size of the droplets of the OP dispersion formed in this way is shown in Fig. 1, where the logarithmic Kolmogorov distribution function corresponding to the random fractionation of particles is depicted as a solid line, and the experimental data are represented by dots.

$$P(r) = c_0 \cdot \exp\left[-c_1 \cdot \left(\ln\left(\frac{r}{r_0}\right)\right)^2\right], \qquad (2)$$

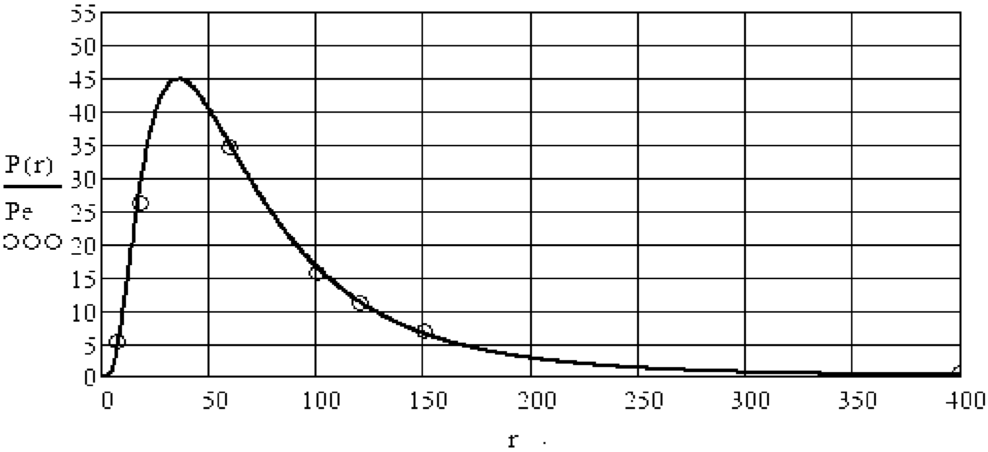

Fig.1. Distribution functions of droplet dispersion of PP by size. The vertical axis is the percentage of PP particles of a given size in µm. Pe - experimental points; P(r) - Kolmogorov distribution function (2) corresponding to random particle splitting. c_0 = 44.89; c_1 = 0.95; r_0 = 36 µm.

Comparing the Kolmogorov distribution and field data, we see that the most likely particle size of the OP is 36 microns. This allows us to conclude that in this case, the droplet phase of petroleum products can be effectively removed by a coalescing filter with a hydrophilic loading.

The situation is quite different when, as a result of long-term storage, water is released from the OP, forming the so-called "sub-commodity water". In such water, the content of emulsified and dissolved OP can be equal to the amount of droplets and reach 2-3 g/dm^3. In addition, "sub-commodity water" can be enriched with fractions of OP containing benzene groups, and therefore the concentration of dissolved OP determined by conventional methods can significantly differ from the total concentration of petroleum organic matter contained in the water, since the solubility of benzene-like compounds in water is much higher than that of classical OP [5, 6].

3. Solubility of oil products in water

It should be noted that the concentration of OPs with benzene groups in ordinary water, curve C95tb, is 10-15% lower than in distillate, curve C95b.

The concentration of A-95 gasoline with methylene groups is significantly, 4.7 times, lower than that with aromatic groups, see curves C95m and C95tm in Fig. 2, and the solubility of such OPs practically does not depend on the salt content of water. At the same time, the difference in solubility of PPs with benzene groups increases with the duration of contact with the solvent (water) in distillate and ordinary water. In our opinion, the reason for this is related to the high solubility of benzene in water and their sensitivity to the salt content in water.

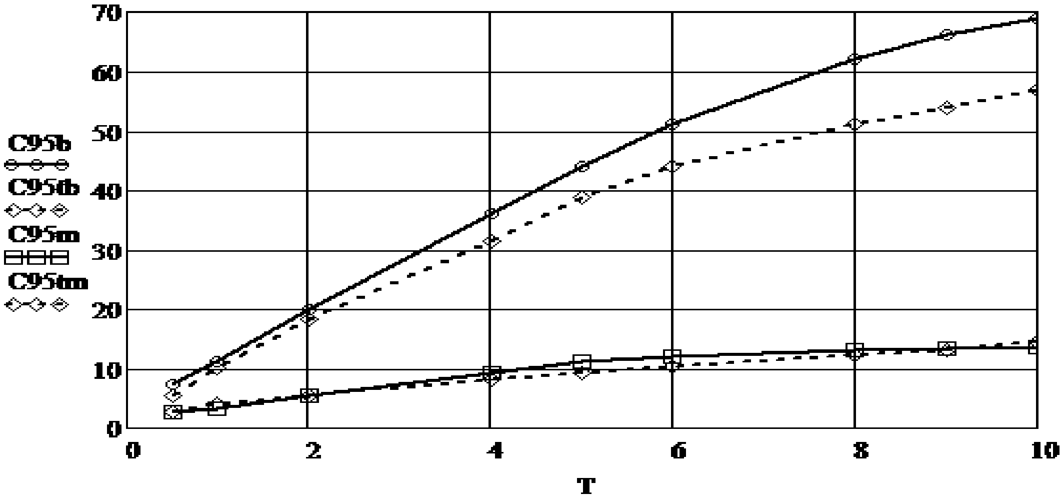

Fig. 2. Dissolution curves of PP A-95, mg/dm^3, with benzene groups C95b and methylene groups C95m in distillate and tap water C95tb and C95tm. In Fig. 2 on the OX axis is time in hours. The conductivity of the distillate is 5-7 µS/cm and that of tap water is 690-720 µS/cm. Dissolution was performed at a temperature of 18-19^{o}C without stirring.

The solubility of benzene is associated with the formation of solvate complexes and with an increase in the salt content of water, competition for free water molecules between benzene and salts occurs. The change in the time difference reflects the dynamics of salt hydration. The decrease in the concentration of dissolved benzene-containing NP should increase as $S^{1/3}$, where S is the salt content of water

Conclusions

1. It has been shown that droplets of an emulsion of OPs in water are distributed according to the Kolmogorov random fractionation law.

2. The solubility of gasoline with benzene groups depends on the salt content of water. As the time of contact of gasoline with water increases, the difference in solubility of OP in distillate and ordinary water increases.

3. The solubility of benzene is associated with the formation of solvate complexes and with an increase in the salt content, competition for free water molecules occurs. Therefore, the decrease in the concentration of dissolved benzene-containing OPs increases according to the law $S^{1/3}$, where S is the salt content in water.

4. Since the MPC for OPs is < 0.05 mg/dm^3, and their concentration in wastewater sometimes exceeds tens of mg/dm^3, it is necessary to apply a multi-stage process based on various physical and chemical principles for their treatment.

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