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CORRELATION BETWEEN BIOLOGICAL ACTIVITY AND PHYSICOCHEMICAL PROPERTIES OF SODIUM DODECYLBENZENESULFONATE IN AQUEOUS SOLUTIONS

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The purpose of this study was to establish a correlation between the effect of the pollutant content on the dimensional and physicochemical characteristics of the investigated solutions and its effect on aquatic organisms. To this end, the surface tension, electrical conductivity, pH, and redox potential of aqueous solutions of sodium dodecylbenzenesulfonate were measured in a wide concentration range ($10^{-7} \div 10^{-2}$ M). The change in the size and number of optical inhomogeneities was investigated using the small-angle reflection method in the micron range. In addition, the behavior of aquatic biological objects (Daphnia Magna) was studied in the investigated solutions. It was shown that the investigated concentration dependences (including the behavior of biological objects) are non-linear: they have either a stepped character or clearly expressed extremes and are well correlated with each other. A comfortable concentration range of sodium dodecylbenzenesulfonate for daphnia (all daphnia are active within 58 hours of the experiment) was established ($\approx 0.018 - 0.037$ mM). The correlation and nature of the concentration dependences indicate that at critical concentrations, structural rearrangements occur in sodium dodecylbenzenesulfonate solutions, not only the formation of micelles and pre-micelles, but also structural rearrangements of the solvent (water) itself. Thus, it has been experimentally shown that the change in the structure of water during interaction with pollutants can significantly affect both the physicochemical properties of aqueous solutions and the behavior of aquatic biological objects.

Keywords: sodium dodecylbenzenesulfonate, daphnia Magna, biological activity, physical and chemical parameters, structural rearrangement.

Introduction

When solving problems related to the analysis of natural waters, scientists mainly pay attention to the composition of the studied waters, namely, the content of matrix components of both inorganic and organic nature. At the same time, insufficient attention is paid to the interaction of the solvent with pollutants, especially if such a solvent is water, which, due to hydrogen bonds, is characterized by significant forces of intermolecular interaction, which in turn, as a result of the self-organization of water molecules, lead to the formation of a special structure that changes under the influence of external factors, including the dissolution of various compounds in water. In addition, a change in the structure of water as a result of interaction with pollutants can significantly affect the bond energy between the molecules in the solution, and thus, as a result, influence the behavior of pollutants in aquatic ecosystems, and not only at concentrations close to stoichiometry, but also at very low, precisely in which ecotoxicants are most often present in natural water bodies. It should be noted that the structure of water (more precisely, an aqueous solution) should be understood as the static orderliness of a complex system «solvent−solute−products of their interaction» in an elementary volume under given conditions, characterized by a certain near and far environment

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of components, the type of internal and intermolecular interactions, and the degree of connectivity of the components. At the same time, an important and experimentally accessible characteristic of the formed structural organization is its size. Therefore, in this work, a study was conducted to establish the correlation of the pollutant's content in a wide concentration range with its dimensional characteristics and physicochemical properties, as well as its impact on aquatic organisms. Aqueous solutions of the anionic surface-active substance (ASAS), sodium dodecylbenzenesulfonate (DDBSNa), were chosen for the study, and daphnia crustaceans Daphnia magna Straus (D. magna) were used as control biological objects.

The choice of surface-active substances (SAS) as objects was primarily due to the need to confirm that structural rearrangements are observed in a wide concentration range and are not exclusively related to the peculiarity of the structure of pollutant molecules, namely, the diphilic nature of surfactant molecules; and secondly, by their wide assortment, as well as mass dumping into the environment. In addition, the analysis of the literature [1−7] showed that the spectrum of negative effects of surfactants is wide and covers almost all the main blocks and trophic levels in aquatic ecosystems. It includes both violations of the behavior of organisms, and violations of processes that contribute to self-purification of water. For example, Venhuis and Mehrvar [6] reported that linear alkylbenzene sulfonates damage the gills of fish, change the swimming patterns of blue mussel larvae, and cause excessive secretion of mucus, as well as decreased respiration. Ostroumov [7] established the ability of synthetic surfactants to reduce the filtration activity of molluscs, while water filtration in the ecosystem is of crucial importance for the self-cleaning and the regulation of the processes occurring in it. In addition, numerous studies and reviews of the literature report the toxicity of various classes of surfactants [1,8] mainly in relation to aquatic organisms. At the same time, ASAS are the most common among all classes of surfactants, and alkylbenzene sulfonates are considered more toxic among ASAS.

Daphnia crustaceans, especially the species Daphnia, Daphnia magna Straus, due to their biological features, are recognized as the most universal test object for sensitivity and adequacy of response to various pollutants. This is due, on the one hand, to convenient and relatively simple cultivation conditions: they are easily kept in laboratory aquariums and multiply quickly. On the other hand, there is a fairly high level of organization

(the presence of circulatory and nervous systems), which allows extrapolating the toxicological results to other multicellular representatives of ecosystems and even humans. In addition, they have large sizes, due to which it is possible to conduct visual observations of many reactions without using specialized measuring tools.

The traditional characteristics used in the study of surfactant solutions, namely surface tension and electrical conductivity, as well as pH and redox potential, were selected as the studied physicochemical parameters. The choice of the two latter is due to the fact that their change with an increase in the concentration of DDBSNa (which does not hydrolyze and is not characterized by redox properties) can be caused precisely by structural rearrangements in the solution.

Therefore, the aim of the work was to establish a correlation in a wide concentration range between the dimensional characteristics of aqueous solutions of sodium dodecylbenzenesulfonate, their physicochemical properties and the effect on aquatic organisms, namely, survival, as well as spatial migration of the model test object D. magna.

Materials and methods

The product of DDBSNa of the «chemically pure» qualification without additional purification was used in this study. Working solutions of DDBSNa were prepared in distilled water.

The size and number of optical inhomogeneities in the micron range were measured by the small-angle reflection method at the «Cluster-1» laboratory facility (Dumanskii Institute of Colloid and Water Chemistry, Ukraine). Each measurement was repeated at least 5 times, and the obtained results were averaged for further analysis. The relative error did not exceed 10%. Electrical conductivity, pH and redox potential were measured with the mV ORP device of the «HANNA» company.

D. magna is a standard sensitive species of crustaceans used in bioassay of water. Laboratory culture of D. magna was established from gravid females originally acquired from Laboratory of biotesting and bioindication (Dumanskii Institute of Colloid and Water Chemistry, Ukraine). The culture was maintained in synthetic laboratory water. D. magna were kept under constant light/dark (16:8 hours) and temperature (20−22⁰C) conditions and were fed a slurry of yeast, with water renewal every two days. All bioassay procedures were performed according to standard methods [9].

Effect of DDBSNa on survival of D. magna

The criterion for assessing the effect of DDBSNa on D. magna was the survival index of

juvenile form of daphnia in water solutions with different concentrations of DDBSNa (from $1.84 \cdot 10^{-6}$ M to $3.31 \cdot 10^{-3}$ M). Control was provided by deionized water without the addition of DDBSNa. The duration of the experiment was 73 hours. The water temperature during the entire experiment was 22^0C with the help of climatic chambers (MIR-3, Russia) with thermo regulators, the light regime corresponded to the change of day and night. All environmental conditions were maintained the same throughout the experiment.

All experiments were in accordance with ethical standards and principles adopted by EU Directives 2010/63/EU for animal testing.

Results and discussion

Study of physico-chemical and dimensional properties of aqueous solutions of DDBSNa

Studies of physico-chemical properties, namely, surface tension, pH, ORP, electrical conductivity, as well as the size and number of optical inhomogeneities in aqueous solutions of DDBSNa, were carried out in a wide range of concentrations of DDBSNa (Figs. 1−4). The choice of pH indicators and redox potential was determined by the fact that their values in aqueous solutions in the absence of additional added components are mainly determined by the presence of CO_2, O_2 and H_2, the content of which depends on their solubility. Atmospheric gases dissolve in water by the clathration type in the «structured» fraction of water, filling the cavities of the frames with the displacement of water molecules. In this regard, we believe that any violations of the structure of the original solution should be reflected in their solubility and, accordingly, in the indicators that are directly related to it (pH and redox potential).

As can be seen, several critical concentrations can be identified on the concentration dependences in the studied interval. Of course, among them, it is possible to single out the generally accepted critical micelle concentration (CMC). According to the literature data [10], the CMC of DDBSNa under experimental conditions is 1.2 mM. The experimentally found value of CMC according to the surface tension isotherm (Fig. 1) correlates well with the literature data.

Another recognized way of determining the CMC is the change in the angle of inclination of the specific electrical conductivity (χ). The point of intersection of the tangents to the concentration dependence c is considered to be the value of CMC. Due to the fact that there are several changes in the inclination angles, the curve χ vs. concentration is presented in different concentration ranges (Fig. 2). As can be seen from Fig. 2,b, according to the indicated measurement method, the CMC is equal to

~0.66 mM, which correlates with the data (0.63 mM) given in ref. [11], and it is ~0.55 CMC according to the measurements of surface tension. This concentration is probably related to the appearance of surfactant premicelles in the solution, which, as noted in ref. [10], are recorded at 40− 67% CMC, and have a zeta potential of -30 mV for DDBSNa. If we assume that the convexity on the surface tension isotherm is not an error (Fig. 1), then ~0.6 mM, respectively, can also be considered the concentration of the formation of premicelles of DDBSNa (CMC*).
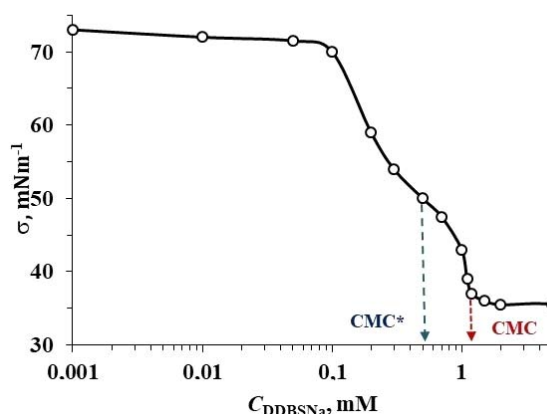

Fig. 1. Isotherm of surface tension of DDBSNa in aqueous solution

Shah et al. [12] considered the value of 0.37 mM to be the CMC of the DDBSNa, which was determined by the specific electrical conductivity. As can be seen from Fig. 2,b, a change in the slope of the concentration curve is also observed in the concentration range of ~0.260 mM. Therefore, in order to determine the value of CMC* with the help of specific electrical conductivity, it is necessary to build a concentration dependence in a wide range of concentrations and with a smaller step. Concentration curves of equivalent electrical conductivity (λ) more reliably reflect critical points. According to this method, the concentration is clearly fixed, which corresponds to the literary value of CMC ~1.2 mM (Fig. 2,b). Therefore, the following concentration intervals can be distinguished from the concentration dependence of the electrical conductivity of DDBSNa solutions: (0.66−0.44) mM, (0.264−0.176) mM, (0.087−0.043) mM, and (0.013−0.08) mM.

As can be seen from Fig. 2, in the studied concentration interval, the most pronounced concentration is ~0.1 mM. The criticality of this range of concentrations for electrolytes of different nature is noted by Lo et al. [13] and considered within the framework of the traditional theory of dilute solutions as the critical concentration of a phase transition of
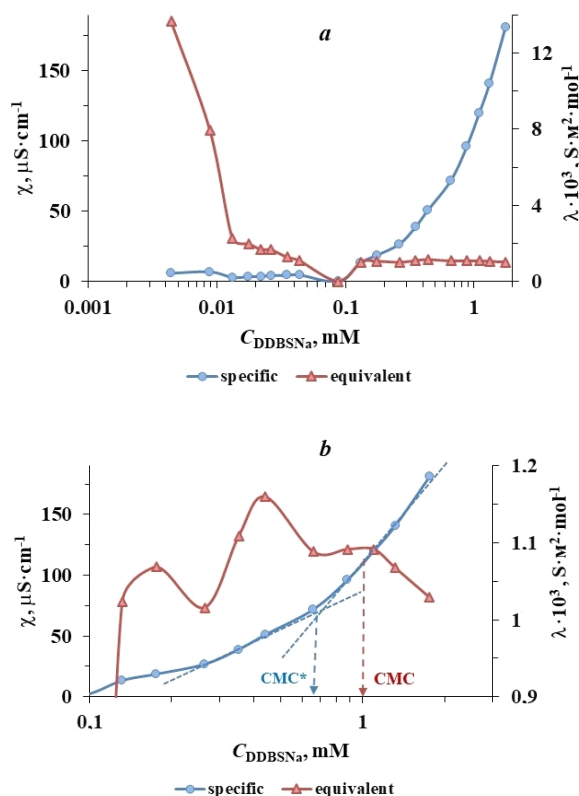
Fig. 2. Concentration dependences of the specific (χ) and equivalent ($\cdot\lambda$) electrical conductivity of aqueous solutions of DDBSNa in different concentration ranges

the second kind. According to these ideas, at concentrations <0.1 mM, dipole-dipole interactions dominate, causing the formation of metastable water clusters. At high concentrations, ionic interactions dominate. Lo et al. [13] believe that 0.150 mM is the beginning of the phase transition, while 0.270 mM is the end. Therefore, in our experiment, the concentration of 0.174 mM can be considered as the beginning, and 0.264 mM as the end of the phase transition.

The critical concentration intervals observed at concentrations of DDBSNa below 0.1 mM are probably related to the rearrangement of metastable water clusters under the influence of surfactants. It should be noted that these concentrations also depend little on the nature of the ions. We indicated the criticality of these concentrations in our early works using the example of KCl [14], and this fact is also indicated in the work [15].

The concentration dependences of pH and redox potential (Fig. 3), similar to specific electrical conductivity, also do not respond very strongly to the formation of micelles. In the region of CMC (~1.2 mM) and CMC* (~0.66 mM), a slight change

in the slope of the concentration curves is observed. However, clearly expressed max and min for concentration curves, respectively, pH and redox potential, which are observed at (0.013−0.018) mM, 0.35 mM and less pronounced changes at 0.13 mM and 0.26 mM.

For the concentration curves of optical inhomogeneities of average size and quantity, which were measured in the microwave range (Fig. 4), on the contrary, more pronounced changes are characteristic for concentration ranges that are close to micellar concentrations. As can be seen from Fig. 4, for the average size of optical inhomogeneities at the concentration of DDBSNa ~1.2 mM, 0.66 mM and 0.35 M, clearly expressed maximum is observed. These concentrations are well correlated with the CMC determined by the surface tension and with the results on the specific electrical conductivity, which were also obtained elsewhere [11,12]. However, although less pronounced, the critical concentrations are fixed at 0.013 mM, 0.044 mM, 0.175 mM and 0.26 mM.
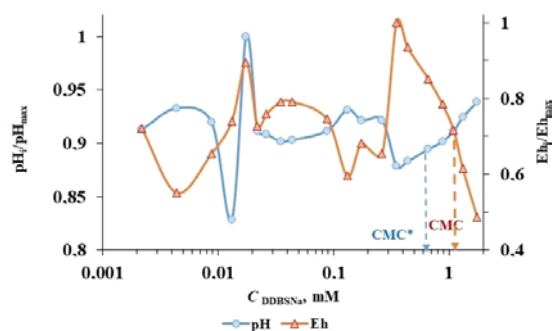

Fig. 3. Max-normalized dependences of pH and redox potential (Eh) in DDBSNa solutions in the range of concentration of 0.002−1.76 mM
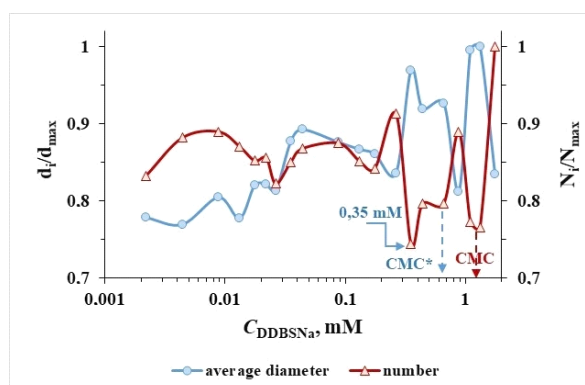

Fig. 4. Max-normalized concentration dependences of the number (N/cm³) and average diameter (d, μm) of optical inhomogeneities in solutions of DDBSNa in the range of 0.002−1.76 mM

Study of the behavior of daphnia in aqueous solutions of DDBSNa

During the first hour of contact with aqueous solutions of DDBSNa, daphnia remain active in a wide concentration interval, but their behavior is different (Table). Thus, at a concentration of DDBSNa of 0.0018 mM, all daphnia float to the surface of the solution and spin in place. At a concentration of ASAS of 0.009 mM, daphnia actively move in the upper part of the glass, whereas daphnia move in the lower part at 0.018 mM. In the concentration range of ~0.037−0.37 mM, daphnia are active in the entire water column. At DDBSNa concentrations of 0.92−3.312 mM, daphnia are active at the bottom of the glass, or in its lower part (1.84 mM).

During the second hour, the behavior of daphnia changes a little (Table). Starting from 0.37 mM, the activity of daphnia decreases, they begin to die intensively. Daphnia are the first to die in a sample with a concentration of 3.312 mM DDBSNa (higher than the CMC of DDBSNa). Mortality is 80% (Fig. 1). In some samples, their location also changes. For example, daphnia at a DDBSNa concentration of 0.009 mM become active in the entire water column, and they crawl along the walls of the glass at concentrations of 0.018 mM and 0.092 mM.

During the third and fifth hours, the location of daphnia does not change. At the sixth hour, daphnia in a water sample with a concentration of 0.009 mM rise to the surface. A further increase in contact time does little to change the location of daphnia. There is a decrease in their activity, an increase in mortality at concentrations before and after (0.018−0.037) mM. Starting from the fifty-first hour, active reproduction of daphnia is observed. At the same time, more active reproduction is observed for more diluted solutions (Table).

It was established that depending on the concentration of DDBSNa in the studied solutions, both vertical and horizontal migration of daphnia is observed. Thus, in sufficiently diluted solutions (0.0018−0.009 mM), daphnia are mostly on the surface of the water. In addition, at 0.0018 mM DDBSNa, they have less activity. At DDBSNa concentrations higher than 0.386 mM, daphnia are at the bottom of the glass, and in the range of 0.018− 0.18 mM, daphnia are active in the entire water column or on the walls of the glass during almost the entire period of research.

Concentration dependences of the degree of mortality of daphnia for different contact times are shown in Fig. 5. As can be seen, the concentration dependences have a jump-like character. Up to two hours of contact, a jump in the degree of mortality is observed after 1.2 mM, i.e. after reaching the CMC of the DDBSNa under the temperature conditions of the experiment (1.2 mM [10]). From the third to the fifth hour, daphnia begin to die at a concentration of DDBSNa ~0.18 mM, which, as mentioned above, corresponds to the beginning of a phase transition from a state dominated by dipole-dipole interactions, which lead to the formation of metastable water clusters, to a state dominated by ionic interactions.

In the time interval of 6−27 hours, the concentration of the beginning of death shifts to ~0.037 mM and then to ~0.020 mM. It was also established that starting from the sixth hour, the indicated dependences have an extreme character with the minimum mortality of daphnia at the concentration of DDBSNa in the concentration range of 0.018−0.037 mM. At the same time, at a concentration of DDBSNa of 0.018 mM, all daphnia are active during the 58 hours of the experiment. As it was already mentioned, the comfortable zone for daphnia in the specified concentration interval is the entire water column. It should be noted that the concentration of DDBSNa ~0.018 mM is clearly fixed as critical on the concentration dependences of physicochemical and dimensional characteristics (Figs. 2−4). In addition, other authors point to its criticality [15].

Conclusions

The research conducted in a wide concentration range of physico-chemical and dimensional characteristics of aqueous solutions of DDBSNa and the behavior of daphnia allowed us to reveal the following.

1. The investigated concentration dependences are non-linear, have either a stepped character, or clearly defined extremes.
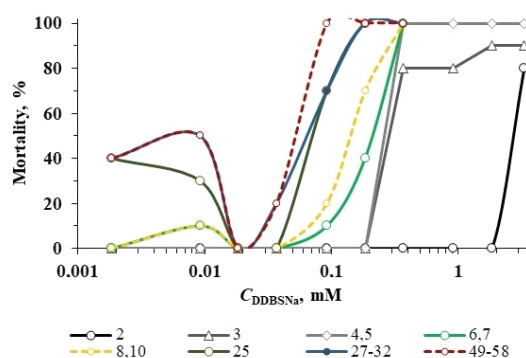

Fig. 5. Dependence of daphnia mortality on the concentration of DDBSNa in the solution at different time intervals. Hours are what's indicated in the legend

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Daphnia behavior at different times of observation

Hours	Sample number									
	1	2	3	4	5	6	7	8	9	10
1	Water surface (spinning in place)	Top part	Bottom part	In the water column				Bottom	Lower part	Bottom
2								Bottom (low mobility)		
3	Water surface (low activity)	In the water column			Along the walls	In the water column				
4–5										
6–10	On the surface of the water, 70% are inactive	On the surface of the water	Along the walls	In the water column	All died			All died		
25–32		On the water surface, inactive								
49–50		30% on the surface, 20% fell to the bottom								
51	On the surface of the water, they are inactive, they multiply actively up to 270% of the initial amount									
52	On the surface of the water, 30% of adults are inactive, 30% of adults have fallen to the bottom	On the surface 30%, 20% fell to the bottom, actively multiply up to 100% of the initial amount	Along the walls, they actively multiply up to 200% of the initial amount	In the water column, the appearance of 10% of young						
53–58	On the surface, 30% of adults are inactive, 30% of adults have fallen to the bottom, juveniles on the surface have lost activity.	On the surface, 30%, 20% fell to the bottom		All died						
73	On the surface, 20% of adults are inactive, the death of 60% of adults and all juveniles	On the surface, 30%, 20% fell to the bottom, the young lost activity	Death of 70% of adults and all young							

2. Critical concentrations that correlate well with each other have been established for the investigated dependences. The established correlation and the nature of the concentration dependencies indicate that at the specified concentrations, structural rearrangements occur in the DDBSNa solutions, and not only the formation of micelles and pre-micelles, but also structural rearrangements of the solvent itself (water) in the presence of SAS.

3. It was established that the critical concentrations responsible for the structural rearrangements of the solvent (water) correlate well with the results of other studies on the influence of various ions, which indicates that the structural rearrangements of water practically do not depend on the nature of the ions.

4. The comfortable range of concentrations for daphnia is ~0.02 mM DDBSNa.

5. It was experimentally shown that the change in the structure of water during interaction with pollutants can significantly affect both the physicochemical properties of aqueous solutions and the behavior of aquatic biological objects.

6. The reaction-responses of biota to the presence of toxic components provide valuable information not only about their toxicity, but also about the structural and dynamic properties of solvated systems in general.

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КОРЕЛЯЦІЯ МІЖ БІОЛОГІЧНОЮ АКТИВНІСТЮ І ФІЗИКО-ХІМІЧНИМИ ВЛАСТИВОСТЯМИ НАТРІЙ ДОДЕЦИЛБЕНЗОЛСУЛЬФОНАТУ У ВОДНИХ РОЗЧИНАХ

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Метою даного дослідження було встановлення кореляції між впливом вмісту забруднювача на розмірні і фізико-хімічні характеристики досліджених розчинів та його впливом на водні організми. Для цього в широкому концентраційному інтервалі ($10^{-7} \div 10^{-2}$ M) було досліджено поверхневий натяг, електропровідність, pH і окисно-відновний потенціал водних розчинів натрій додецилбензолсульфонату. Методом малокутового відбиття в мікронному діапазоні досліджено зміну розміру та кількості оптичних неоднорідностей. Крім того, у досліджених розчинах було вивчено поведінку водних біологічних об'єктів (дафній Magna). Показано, що досліджені концентраційні залежності (в тому числі і поведінка біологічних об'єктів) нелінійні:

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мають або ступінчатий характер, або чітко виражені екстремуми і добре корелюють між собою. Встановлено комфортний (всі дафнії активні протягом 58 годин експерименту) діапазон концентрацій натрій додецилбензолсульфонату для дафній (≈0,018−0,037 мМ). Кореляція і характер концентраційних залежностей вказує на те, що при критичних концентраціях відбуваються структурні перебудови у розчинах натрій додецилбензолсульфонату, причому не тільки утворення міцел та предміцел, а також структурні перебудови самого розчинника (води). Отже, експериментально показано, що зміна структури води при взаємодії з забрудниками може суттєво впливати як на фізико-хімічні властивості водних розчинів, так і на поведінку водних біологічних об'єктів.

Ключові слова: натрій додецилбензолсульфонат, дафнія Magna, біологічна активність, фізико-хімічні параметри, структурні перебудови.

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The purpose of this study was to establish a correlation between the effect of the pollutant content on the dimensional and physicochemical characteristics of the investigated solutions and its effect on aquatic organisms. To this end, the surface tension, electrical conductivity, pH, and redox potential of aqueous solutions of sodium dodecylbenzenesulfonate were measured in a wide concentration range ($10^{-7} \div 10^{-2}$ M). The change in the size and number of optical inhomogeneities was investigated using the small-angle reflection method in the micron range. In addition, the behavior of aquatic biological objects (Daphnia Magna) was studied in the investigated solutions. It was shown that the investigated concentration dependences (including the behavior of biological objects) are non-linear: they have either a stepped character or clearly expressed extremes and are well correlated with each other. A comfortable concentration range of sodium dodecylbenzenesulfonate for daphnia (all daphnia are active within 58 hours of the experiment) was established (≈0.018−0.037 mM). The correlation and nature of the concentration dependences indicate that at critical concentrations, structural rearrangements occur in sodium dodecylbenzenesulfonate solutions, not only the formation of micelles and pre-micelles, but also structural rearrangements of the solvent (water) itself. Thus, it has been experimentally shown that the change in the structure of water during interaction with pollutants can significantly affect both the physicochemical properties of aqueous solutions and the behavior of aquatic biological objects.

Keywords: sodium dodecylbenzenesulfonate; daphnia Magna; biological activity; physical and chemical parameters; structural rearrangement.

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