# CHAPTER «CHEMICAL SCIENCES»

## ADSORPTION OF IONIC AND NON-IONIC SURFACTANTS MIXTURES FROM AQUEOUS SOLUTIONS AT THE SURFACE OF CARBON SORBENTS

**Kochkodan Olga**[1]
**Maksin Viktor**[2]

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**Abstract**. The influence of intermolecular interaction on the surface properties of aqueous solutions of binary mixtures of nonionic surfactants (Tritons X-45, X-100, X-305), anionic surfactants – sodium alkyl sulfates (SAS-TX) and cationic surfactants – alkylpyridinium bromides (APB-TX) has been investigated. The effect of synergism of mixture components on surface activity is apparent for these mixtures. The regularities of change in surface activity of surfactant mixtures at the liquid – solid sorbent interface correlate with those for the liquid-air system with the increase in the total concentration of surfactants in solution, but are more pronounced. Surface adsorption layers are enriched with nonionic surfactants TX; and the parameters of intermolecular interaction $\beta^{\sigma}$ have a negative value indicating an increased interaction of surfactant molecules in the adsorption phase. According to the results of calculating the interaction parameters and the thermodynamic adsorption characteristics, it has been established that the effects of negative nonideality are more pronounced in SAS-TX systems compared with APB-TX systems. Composition of the mixed adsorption layers on non-porous carbon sorbent and the interaction parameters in the adsorption layers $\beta^{\sigma}$ have been calculated and compared with similar characteristics in the solution volume and

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[1] Candidate of Chemical Sciences, Associated Professor
at Department of General, Organic and Physical Chemistry,
National University of Life and Environmental Sciences of Ukraine, Ukraine

[2] Doctor of Sciences, Professor at Department of Analytical
and Bioinorganic Chemistry and Water Quality,
National University of Life and Environmental Sciences of Ukraine, Ukraine

on the air boundary within the phase separation model using the Rubin and Rosen approach. It has been established that the ionic component of the mixture have a specific impact on parameters of intermolecular interaction, thermodynamic characteristics of surface layer formation and adsorption amount

## 1. Introduction

Surfactants are the most common organic compounds among those needed to be removed from natural and waste water. In practice, we deal with mixtures rather than an individual surfactant. Adsorption of surfactants at the solid-fluid interface plays an important role in many processes, such as ore flotation, oil extraction and application of surfactants in households and for personal hygiene, in textile industry, biotechnology and for water purification.

In this regard, it is important to study the effect of surfactant mixtures on interfacial energy at the interface between different phases, in particular, liquid-solid. Today there is practically no data on the mutual effect of surfactants on adsorption from aqueous solutions on hydrophobic sorbents, including carbon ones. Understanding of adsorption processes occurring in such systems is necessary for creation of effective technological processes of separation and concentration of organic substances on solid surfaces.

Adsorption of surfactants on solid surfaces can change their hydrophobicity, surface charge and other key properties that adjust interfacial processes such as flocculation / dispersion, flotation, moisturization and adsorption, washing processes, increasing oil production, and corrosion inhibition. In general, adsorption is regulated by a number of forces, such as covalent bond, electrostatic attraction, hydrogen bond or nonpolar interactions between adsorbed particles, lateral associative interactions, solvation and desolvation. Total adsorption is usually a cumulative result of some or all of the above interactions. It is important to consider surfactant adsorption mechanisms with regard to various forces involved and factors that control them.

The necessity and importance of the study of adsorption of compound surfactants is associated with its relevance for practical systems using compounds of several surfactants.

### 1.1. Adsorption of surfactants by carbon sorbents from individual solutions

No clear and quite overall picture of adsorption process in a wide range of surfactant concentrations has been proposed until now for a surfactant – carbon sorbent system, unlike polar sorbents. One of the reasons is that the surface of carbon sorbents varies considerably depending on the nature and method of pre-treatment, such as washing and graphitization. Therefore, experimental data of different researchers for close systems are often ambiguous [1, p. 130]. Besides, application of a number of known physicochemical research methods for such systems is hampered by electronic conductivity and optical opacity of carbon materials.

The most common cause of physical adsorption, which mainly determines the adsorption on carbon surfaces, is the dispersion interaction that arises as a result of coordinated motion of electrons in adjacent molecules [2, p. 74]. As shown by research [3, p. 115], hydrophobic interactions play an important role in the adsorption system containing diphilic molecules of micelle-forming surfactants and hydrophobic sorbent. The radius of their action exceeds the radius of action of molecular forces by at least 1-2 orders, which causes association of diphilic molecules and their attraction to the hydrophobic surface at greater distances than to the hydrophilic surfaces.

A specific peculiarity of behaviour of nonionic surfactant molecules during their adsorption on carbon sorbents is the ability of oxyethylene units of hydroxyl chains, in contrast to polar groups of ionic surfactants, to be adsorbed from aqueous solutions due to dispersion interaction between carbon atoms of methylene groups of oxyethylene units and carbon atoms of the sorbent. Therefore, competition between alkyl and polyoxyethylene chains affects the character of orientation on the phase separation surface in adsorption of diphilic molecules of nonionic surfactants. As the density of packing of molecules increases in the adsorption layer, the polyoxyethylene chains are gradually displaced in liquid phase volume. The magnitude of angle of hydrophilic part deviation to the solution depth is determined by relationship of decrease in free energy of adsorption of alkyl and polyoxyethylene chains [2, p. 192].

It was previously believed that association in the adsorption layer on a carbon sorbent at the degree of filling of adsorption layer $\theta<1$ occurred in a two-dimensional space, i.e. thickness of associates did not exceed thickness of monomolecular layer. Formation of three-dimensional (volume) associates was expected only in the area of critical micelle concentration (CMC). Experimental data available at that time did not contradict this hypothesis and could be described with sufficient degree of probability [1, p. 139]. Modern physicochemical research methods showed the predominant role of associative interactions during surfactant adsorption on hydrophilic sorbents in the area of equilibrium concentrations below CMC. There is an obvious need for further study of the issue of hydrophobic, in particular, carbon sorbents.

Adsorption of cationic surfactants on non-porous carbon surfaces was studied in the papers [4; 5]. The authors of [6] carried out both adsorption and calorimetric measurements for hexyl-, octyl-, dodecyl- and tetradecyltrimethylammonium bromides and dodecylpyridinium chloride during adsorption on a graphite surface. The results has showed that adsorption process involves hydrophobic interactions between a surfactant and a nonpolar surface, hydrophobic aggregation of hydrocarbon chains on the surface and in the volume of solution and electrostatic interactions between polar groups of surfactant molecules.

In the research papers [7-9] on adsorption of ionic and nonionic surfactants on porous carbon sorbents, the course of adsorption isotherm is interpreted in terms of ordering of adsorbed molecules in the surface layer. It is noted that adsorption isotherms of ionic surfactants on activated carbon at different temperatures are well described by the Freundlich equation and adsorption isotherms of nonionic surfactants by the Langmuir equation. Comparison of adsorption measurements with a change in differential molar enthalpy of adsorption during filling of adsorption layer indicates that approximately 50% of molecules are adsorbed chemically and others are adsorbed by specific adsorption mechanism.

Paper [10, p. 237] indicates a chemisorptive nature of interaction of sodium dodecylbenzenesulfonate on activated carbon. This conclusion is based on the calculated values of enthalpy, growth of adsorption with increasing temperature and irreversibility of adsorption.

It is obvious that the porous structure of adsorbents substantially affects conditions for adsorption phase formation. Depending on how much the formation of three-dimensional associates is limited by the adsorbent size and pore structure, adsorption isotherms of surfactants can take different forms ranging from a stepped one to a curve having one or more peaks [11, p. 160].

The type of adsorption isotherms of oxyethylated esters of n-decyl alcohol from aqueous solutions on mesoporous actived carbon SCN-100 [11] suggests that conditions of adsorption equilibrium in this case are similar to those existing at adsorption of surfactants on outer surface of non-porous particles of acetylene carbon black. Adsorption isotherms on a microporous sorbent (active carbon AG-3) have a peal in the area of equilibrium concentrations equal to 0.2 – 0.3 CMC. At the same time, in the area of concentrations exceeding the CMC, the volume of supermicropores for the studied surfactants is completely excluded from the adsorption space of activated carbon. According to authors of the paper this indicates that surfactants are adsorbed from micellar solutions not only in the form of individual molecules, but also in the form of micelles.

Thus, based on the structure of adsorption layer on a separation surface and the structural characteristics of ions and micelles, availability of a peak can be explained by inaccessibility of carbon pores to surfactant micelles. Surfactants adsorption isotherms with shorter hydrocarbon radical do not have a peak and do not differ fundamentally in form from adsorption isotherms on non-porous carbon adsorbent, an acetylene black.

According to the Giles's classification, the following types are typical for adsorption isotherms of ionic and nonionic surfactants on solid sorbents: S2; S3: S4; S5; L2; L4; L3; L5; H2; H4 [1, p. 141]. The form of adsorption isotherm gives a preliminary idea of the type of interaction between the dissolved surfactant and the sorbent surface.

N.A. Klimenko [12, p. 156] proposed taking a change in the adsorption isotherm form as a major distinguishing feature at reaching the critical concentration of micelle formation in solution volume. Thus, adsorption isotherms at adsorption of anionic surfactants on hydrophobic carbon sorbents have the following forms:

a) with a sharp increase in the area of CMC (S3; S4; H3; H4);

b) without a bend in the area of CMC (L2);

c) with a peak in the area of CMC (S5; L5).

Each form of adsorption isotherm corresponds to a certain structure of adsorption layer. The paper [12] substantiates the hypothesis that proposes a single concept of appearance of different structures of adsorption layers of surfactants on sorbents of different chemical nature, and hence different forms of adsorption isotherms. According to the hypothesis, the main role in the appearance of various adsorption structures of surfactant on the surface of a solid adsorbent belongs to associative interactions. Depending on a number of factors, association can be either preferably on sorbent surface, or in solution volume, resulting in a complete suppression of surfactant adsorption. Factors that influence the establishment of equilibrium surfactant distribution between the two phases (adsorbent surface and micelles) are the reduction of molar free energy of adsorption and molar energy of micelle formation and the ratio of surfaces of both phases in a limited system volume.

### 1.2. Adsorption of mixtures of ionic and non-ionic surfactants

Adsorption of surfactants at the solution-solid interface is the subject of many theoretical and experimental studies [1-12]. However, most of papers in this area are devoted to the study of adsorption from single-component solutions. At the same time, the study of behaviour of mixed systems is of great interest both from a scientific and applied point of view.

The use of binary mixtures of surfactants makes it possible to more effectively regulate properties of disperse systems in comparison with individual components of the mixed solution. This is connected with synergism of adsorption of mixture components at different interfaces [13, p. 200]. In particular, wetting and modifying action of binary mixture solutions in relation to solids of different nature differs greatly from the action of surfactant solutions contained in the mixtures. It is shown that behaviour of mixtures can be predicted on the basis of isotherms of surface tension of the corresponding solutions while wetting low-energy surfaces. At the same time, non-additive contribution of mixture components to the contact angle values are determined. It is due to synergism of adsorption of surfactants, the components of mixtures at the solution-air and solution-solid interfaces [14, p. 33].

The value of effect non-additivity depends on mixture concentration and composition, as well as surface energy of hydrophobic lining. Analysis of wetting and modifying action of solutions of binary surfactant mixtures on high-energy and, usually, charged surfaces is more complex [15; 16]. However, in this case, non-additive effects depending on concentration and composition of the mixed solution are detected. For example, synergistic effect of wetting and modification for a glass and quartz surface is controlled by the nature of a cation of cationic surfactant, which is associated with peculiarities of formation and structure of mixed adsorption layers on a solid surface [17, p. 402]. These results were obtained for aqueous solutions of binary mixtures of classical low-molecular micelle-forming surfactants (nonionic and ionic). The study of surface and bulk properties of solutions of micelle-forming and high-molecular surfactant binary mixtures is of evident interest.

Adsorption process depends on numerous factors including molecular structure of surfactant, pH, ionic strength, and composition of aqueous phase [3; 18; 19]. A number of works concerning the adsorption of various types of surfactants on the surface of carbon sorbents for improving the aggregation stability of aqueous dispersions or finding out surfactant adsorption mechanisms are known today [20-23]. At the same time there are a very limited number of studies related to the adsorption of surfactant mixtures on the surface of carbon sorbents [24-26]. The authors of [24] studied the change of surface charge of activated carbon particles in aqueous dispersions of mixtures of different-type surfactants. It is shown that adsorption value depends on the type of surfactant and functional groups on a sorbent surface. Adsorption of surfactant on a sorbent surface leads to electrostatic or sterile repulsion of suspension particles.

Aggregation stability of GCB dispersions in mixed solutions of sodium dodecyl sulfate and oxyethylated nonylphenols has been evaluated in the paper [25]. The authors have shown that the amount of adsorbed ionic surfactant decreases significantly in the presence of a nonionic surfactant. Adsorption of a series of sodium polystyrene sulfonates and ethoxylated nonionic surfactants (NP-12, NP-40, NP-100) on GCB surface has been studied in the paper [26]. Adsorption isotherms of the Langmuir type and negative values of free adsorption energy have been obtained for all surfactants studied. The authors have hypothesized that the ethylene oxide chains of adsorbed nonionic surfactants assume a helical conformation on GCB surface.

Analysis of literary data shows that, despite a great interest in mixed systems and an intensive study of their properties, there are many unsolved problems in this area of colloidal chemistry. There is no universal theory allowing us to describe interactions in micelles and adsorption layers. Causes of deviations from ideal behaviour have not been clarified for many surfactant systems; many combinations of surfactants have been studied fragmentarily; there is practically no data for a systematic study of binary mixtures. In addition, contradictory data are often found when comparing results of various studies. Patterns of adsorption of binary mixtures on a solid surface have not been established; there are very few works in this important, from the practical point of view, area of study. One of the possible reasons is limitation of adsorption research methods. For example, the classical method for calculating the change in concentration of a surfactant in a solution after adsorption by the surface tension isotherm turns out to be unsuitable in connection with a possible change in mixture composition after adsorption. Another reason is that it is necessary to study behaviour of a mixed system in volume and at the solution-sorbent interface for competent interpretation of the observed results. This is quite a complex task, as according to the previous studies there are often significant deviations from ideality in the mixed systems.

It should be noted that nonionic and cationic surfactant mixtures are the least studied and complex as regards explanation of the effects observed, therefore determination of their characteristics and quantitative analysis of interactions in such systems is of great interest in terms of development of general ideas about colloid-chemical patterns of behaviour of mixed systems.

The task of the paper is a comprehensive research of binary mixtures of cationic and nonionic surfactants. It studies the adsorption of individual surfactants and their mixtures on the surface of hydrophobic carbon sorbents and analyzes the influence of pH, the adsorbent nature, the type of interactions between individual surfactants and the surface, as well as interactions of surfactants in solution volume and in the surface layer in terms of patterns of adsorption of surfactants from individual and mixed solutions.

### 1.3. Structure of adsorption layers on the surface of carbon sorbents

At present, many features of adsorption of organic substances, in particular, surfactants, by solid sorbents are insufficiently studied, especially the structure of adsorption layers and the influence of various factors thereon. This information is extremely important, as it is background information for calculating and optimizing many technological processes.

Unlike sorbents of hydrophilic nature, for which a number of adsorption aspects are addressed through application of physicochemical methods of analysis [27], for surfactant-carbon sorbent systems the use of these methods is complicated due to electrical conductivity and optical opacity of carbon materials. In addition, the surface of carbon sorbents varies considerably depending on the nature and method of pre-treatment. Therefore, experimental data for close systems are often ambiguous, which complicates synthesis of research results and determination of general adsorption process patterns within a wide range of surfactant concentrations.

Moreover, application of patterns determined for simple organic substances to adsorption of micelle-forming surfactants is limited by the specific behaviour of surfactants in aqueous solutions. The principal feature of systems containing surfactants is the capacity for reverse phase transitions in aqueous solutions from molecular-disperse to micellar state. Processes of adsorption from micellar solutions differ significantly from processes of adsorption from molecular-disperse systems. This is connected with the important task of studying relationship between adsorption and associative interactions in systems containing hydrophobic sorbent and diphilic molecules of micelle-forming surfactants under different conditions of contact of aqueous solution of surfactant with surface of a solid sorbent.

As it follows from the analysis of data available in literature, special attention should be paid to the study of factors influencing the association of surfactant in the adsorption layer at equilibrium concentrations below the critical micelle concentration (CMC). One of these factors is the effect of temperature on the adsorption of surfactants, since hydrophobic interactions that cause association of diphilic surfactant molecules are endothermic and should increase with increasing temperature [28-30].

Data on the structure of adsorption layers of surfactants on solid surfaces are background information for calculating and optimizing many technological processes. Despite the large number of studies [31-35], this is one of the most debatable issues of the adsorption theory.

Thus, description of aggregation of ionic surfactants on polar surfaces has involved different structures: hemimicelles in Fuerstenau and Somasunduran, admicelles in Harwell [31, p. 518]. The authors of [32, p. 1482] described the adsorption of nonionic and ionic surfactants on the basis of a segmental distribution on a surface, and proposed small surface spherical aggregates containing counterions. However, none of these models provides full description of adsorption of ionic surfactants on polar surfaces, because they do not take sufficient account of influence of various factors.

The paper [31] presents a detailed consideration of structure of adsorption layers of ionic surfactants on a hydrophilic surface. A large number of experimental results are interpreted by the model of small individual surface aggregates. The adsorption model takes into account the influence of various factors: electrostatic and hydrophobic interactions, concentration, structure of surfactant, type of coions, pH, adsorbent structure, surface charge density and surface polarity.

It is envisaged that adsorption has a two-stage mechanism and adsorption of ionic surfactants from aqueous solutions on opposite-charged surfaces is based on two types of interactions: electrostatic and hydrophobic. They are the basis of the first and second stage of adsorption mechanism, respectively. Contribution of electrostatic interactions depends mainly on surfactant ion charge, surface charge density, electrolyte concentration and pH. Hydrophobic interactions depend mainly on structure of surfactants and counterions, electrolyte concentration and CMC.

At low equilibrium concentrations surfactant ions are bound by electrostatic forces to adsorption spots on the surface. Nonpolar groups are oriented to the aqueous phase within the hemisphere, whose radius is equal to the effective length of a hydrocarbon chain. In the region of average concentrations, hydrophobic interactions occur between nonpolar parts of surfactant ions, and part of counterions are adsorbed. At equilibrium concentrations higher than CMC adsorption saturation is observed. If the average distance between two adjacent adsorption spots on a solid surface is greater than the size of an aggregate, then they are isolated on the surface. Aggregation number of these surfactants is in the range of 3-20, which is noticeably less than in micelles. Counterions are located near or between the main groups, reducing their mutual repulsion and simultaneously shielding a hydrophobic surface of a nucleus.

Various adsorption physicochemical methods have been recently used to study adsorption on hydrophilic sorbents [27]; however, they have limitations for carbon sorbents due to electrical conductivity and optical opacity of the latter.

Application of physicochemical research methods has allowed proving the associative structure of adsorption layers of nonionic and anionic surfactants when adsorbed from aqueous solutions on hydrophilic sorbents [27, p. 226]. Methods of fluorescence extinction have shown that association of surfactants on a surface of oxide sorbents begins long before reaching CMC in solution volume [33, p. 40]. When the adsorption layer filling degree is $\theta<0.5$, the adsorption layer is formed by separate unrelated associates, the shape of which is close to the shape of bulk micelles. Adsorption phase in the region $\theta>0.8$ is a continuous medium with an internally connected network of micellar aggregates. When $\theta$ = 0-0.17, the size of aggregates increases at constant surface density. In the area of $\theta$ = 0.17-0.5 the size of aggregates does not change and their density increases. In the interval $\theta$ = 0.5-0.8, dimensions of associates begin to increase again at constant distribution density.

Unlike hydrophilic sorbents, conclusions on the structure of adsorption layers on carbon surfaces are based in most cases on adsorption and calorimetric measurements [6; 34].

In the paper [35], the method of scattering slow neutrons was first used to study the adsorption layer of a nonionic surfactant on the surface of a non-porous carbon sorbent. Analysis of the data showed that adsorption layer contains surfactant molecules, fixed on the surface of adsorbent by hydrophobic part, free water and mobile hydrophilic parts of molecules with bound water, when a surfactant is adsorbed from aqueous solutions at a concentration below CMC. When a surfactant is adsorbed from solutions at a concentration above CMC, the adsorbent surface may contain surfactant associates, the state of which depends on the method of separation of equilibrium solution from a sorbent. This fact is explained by hydrodynamic factor sensitivity of associative formations caused by hydrophobic interactions.

The analysis of data available in literature shows that the results of studies of adsorption on nonpolar sorbents from micellar solutions are explained by formation of both associates and layers [27; 35]. It is known that at orientation of molecules in associate, minimum Gibbs energy is attained at the smallest difference in polarity of associate-water outer boundary. Therefore, an outer shell of a micelle is formed by hydrophilic groups of surfactant molecules and completion of the shell is limited by the number of molecules included in one associate. At adsorption of surfactant on a hydrophobic carbon sorbent, a shape of semi-ellipsoid surface associates adjoining the surface by equatorial sections is possible due to interaction between carbon radicals and sorbent surface.

In addition to orientation of adsorbed molecules, all changes in the layer occurring with increase in density of its filling and manifestations of associative interactions between surfactant molecules both in the solution volume and on the phase separation surface should be taken into account when considering the adsorption layer structure. The energy of interaction of alkyl radicals on the phase separation surface depends on the following factors: length and structure of a hydrophobic radical, influence of a substitute, presence of other substances containing alkyl groups in solution, concentration of electrolyte in solution and adsorbent surface filling degree.

Thickness of adsorption layer is an important characteristic for interpretation of data on the state of surfactant water solution – solid sorbent system. Traditionally, thickness of adsorption layers of surfactants is estimated by indirect data, for example, by adsorption amount, rheological measurements, and adsorption and electrophoresis data. However, there is a need to apply modern methods for assessing the thickness of adsorption layers of surfactants that would have sufficient separation power.

Establishing the structure of adsorption layers and the patterns of their formation on surfaces of different adsorbents will allow regulating adsorption processes, as well as using both surfactants and sorbents in different technological processes more efficiently.

## 2. Materials and methods

Ionic and nonionic types of surfactants have been used for research. Nonionic surfactants: oxyethylated octylphenols with degree of oxyethylation n = 5, 9-10 and 30 Tritons X-45, X-100 and X-305 of the general formula $C_8H_{17}C_6H_4(OCH_2CH_2)_n$. The surfactants were used without additional purification.

Ionic surfactants:

– hexadecylpyridinium bromide ($C_{16}H_{33}NC_5H_5Br$). To obtain high-purity products, industrial samples of surfactants were purified by recrystallization from methyl ethyl ketone. The degree of purification was controlled in terms of absence of minima in the area of CMC on isotherms of surface tension;

– anionic surfactant: sodium hexadecyl sulfate ($n\text{-}C_{16}H_{25}SO_4Na$). The surfactant was used without additional purification.

Critical micelle concentration (CMC) in solutions of surfactants was determined using tensiometric and conductometric methods. The basis of these methods is the construction of concentration dependence of surface tension and electrical conductivity. CMC of a surfactant is defined as concentration corresponding to the salient point in the dependence $\sigma = f(lnC)$ or $k = f(C)$.

Solution pH was measured by L-Micro pH-meter. A glass electrode with an internal silver chlorine electrode was used in the research. Electrode was calibrated using a series of standards for pH-metry (pH 1.68 – 12.45). Method and measurement accuracy is ± 0.2.

Studies on adsorption kinetics were carried out in order to fix the time required for adsorption equilibration in the system of aqueous solution of organic substance – sorbent.

In order to obtain adsorption solutions containing different initial concentrations of organic substances were shaken with constant weighing of sorbents on a special device executing 6000 variations per hour. The solution volume was 0.025 $dm^3$. After reaching adsorption equilibrium, the solutions were separated from the adsorbent. The values of equilibrium concentrations were determined by spectrophotometric method and values of ionic surfactants by two-phase titration method. Measurement error did not exceed 1%.

Specific adsorption amount was calculated by the relation:

$$a = \frac{C_o - C_e}{m} V, \tag{1}$$

where $a$ is the adsorption amount, mol/kg; $V$ is the volume of solution from which the adsorption amount was determined, $dm^3$; $m$ is the weight of sorbent, kg; $C_o$ and $C_e$ are the initial and equilibrium concentrations of organic substance solution, mol/$dm^3$.

## 3. Ionic and non-ionic surfactants adsorption from individual and mixed solutions on the surface of graphitized carbon black

### 3.1. The ionic surfactants adsorption from individual aqueous solutions

As discussed in the literature review, there is still no unified concept of the adsorption process in the system with an aqueous surfactant solution – a carbon adsorbent, which explains the influence of the system components on the structure of the adsorption layers. Controversy of thoughts about the structure of the adsorption layers of surfactants attracts attention. Information on the structure of the adsorption layers of surfactants on hydrophilic sorbents [27; 31-33], as well as the new data on the surfactants adsorption on carbon sorbents, give grounds to develop a hypothesis about the surfactants bulk association on the surface of carbon sorbents during adsorption, from aqueous solutions whose equilibrium concentration does not exceed CMC, in the light of both the experimental data obtained and published in the literature.

Previously, the basis for hypothesis adopting of the monomolecular thickness of the adsorption layer of surfactants on the carbon adsorbent surface to the CMC in the first approximation was numerous data on the adsorption of organic substances of various structures from aqueous solutions on carbon adsorbents, which showed that already at a distance of two or three molecular layers from the surface adsorbent, the dispersion interaction intensity weakens to such an extent that thermal motion eliminates differences in the ratio of components near the surface and far from it in the liquid volume. However, when the substance molecules, which absorbed are associated in a solution, a more complex structure of the adsorption layer can be expected.

Assumptions about the structure of the adsorption layer surfactants based only adsorption measurements can be made based on the calculation of the area per molecule in the area of the adsorption plateau or at the inflection point of the adsorption isotherm. The calculation was carried out according to the formula:

$$\omega_{\text{exp}} = \frac{S_a}{a_{CMC} N_A} \tag{2}$$

where $S_a$ is sorbent surface area; $a_{\text{CMC}}$ is the amount of adsorption in the field of CMC; $N_A$ is Avogadro constant.

As the Table 1 shows, the data on the area that screens alkyl sulfates and alkyl sulfonates molecules on the surface of non-porous carbon sorbents ($\omega_{exp}$) in the area of CMC is given.

As the Table 1 shows, they fluctuate from magnitude, which roughly corresponds to the parallel orientation of the molecule main axis which is

Table 1

**Adsorption characteristics of anionic surfactants on graphitized carbon black**

| Surfactants | $\omega_{exp}$, nm$^2$ | $\omega_{cal}$, nm$^2$ | $-\Delta G^0_a$, kJ/mol | $t$, nm |
|---|---|---|---|---|
| Sodium octyl sulfate | 1,04 | 0,91 | 17,7 | 0,33 |
| Sodium decyl sulfate | 1,19 | 1,06 | 21,6 | 0,33 |
| Sodium dodecyl sulfate | 0,66 | 1,21 | 25,6 | 0,67 |
| Sodium decyl sulfonate | 0,83 | 1,03 | 18,8 | 0,44 |
| Sodium tetradecyl sulfonate | 0,90 | 1,33 | 29,5 | 0,50 |

relative to the surface ($\omega_{cal}$) to the vertical (0.25 nm$^2$), that is, less than would be expected with a monomolecular coating of horizontally oriented molecules. These facts are explained in different ways, while numerous tests on the adsorption of long-chain organic molecules of non-targeted organic substances from aqueous solutions on carbon sorbents showed that a monomolecular structure of the adsorption layer with a horizontal orientation of the molecular axis to the phase contacting area corresponding to the stored energy minimum.

The most likely cause of "landing site" change is semi-colloid surfactants and even the same substance (for example, sodium dodecyl sulfate) on the same chemical nature sorbents, obviously, their association in the adsorption layer depends on many factors: the CMC size of the surfactants, the degree of the sorbent hydrophobicity, the electrolytes presence in solution, etc. These factors influence the adsorbed substance – adsorbent interaction energy and the higher this value, the greater will be the degree of surfactants concentration in the adsorption phase and the smaller the area per molecule in the dense layer. The surfactants concentration in the surface layer of the adsorbent is due to the manifestation of the hydrophobic and adsorption interactions between the diphilic molecules of the micelle-forming surfactants. Molecules approach each other to a certain critical distance, at which their aggregation occurs (hydrophobic coagulation) and adagulation on the surface earlier than in the solution volume.

Let us consider the case of anionic surfactants adsorption on the same sorbent (graphitized carbon black), how the change in the standard free molar adsorption energy affects, which leads to different degrees of surfactants concentration in the surface layer, replacing the "landing site" surfactant molecules in the adsorption layer formed in CMC area.

The magnitude of the molar free energy standard decrease of the $\Delta G^0_a$ surfactant adsorption of non-porous carbon sorbents was calculated by the formula:

$$\Delta G^0{}_a = -RT \ln K_a, \qquad (3)$$

where $K_a$ is adsorption equilibrium constant, $T$ is absolute temperature °K; $R$ is absolute gas constant.

Table 1 shows the $\Delta G^0_a$ estimated values. The results show that the higher the energy of the adsorbate – adsorbent interaction, the less the area ratio screened by the surfactant molecule in the adsorption layer, to the Van der Waals molecule area (1.14, 1.12, 0.55, 0.81 and 0.68 for octyl-, decyl-, dodecylsulfate, sodium decyl– and tetradecylsulfonate, respectively), the higher degree of surfactants association, due to the molecules concentration in the surface layer.

Additional information about the surfactants association in the adsorption phase can be obtained based on average thickness information of the surfactants adsorption layer. The average thickness of the surfactants adsorption layer can be determined in the same way as the adsorption layer thickness is estimated by de Boer in the t-method [36, p. 7142]. Under the provisions developed by de Boer, the amount of adsorbed substance volume on a homogeneous non-porous sorbent is equal to the molecular volume of this substance molecule ($V_{m,i}$) on the amount of specific adsorption ($\alpha_i$) per unit sorbent mass, and the average adsorption layer thickness ($t_i$) is calculated by dividing the adsorbed volume size on the specific sorbent surface ($S_a$). In the construction of *t*-curves showing the dependence of the average thickness of the molecules layer, benzene derivatives, adsorbed from the aqueous solution on non-porous carbon black $t_i = \alpha_i\ V_{m,i}\ /S_a$ from the solution relative concentration $C_i/C_s$ (where $C_i$ is the mole concentration of the equilibrium solution, $C_s$ is the solubility at the same temperature) it turned out that at $C_i/C_s \rightarrow 1$ $t_i$ approaches the limiting value $t_{i\,\infty} \approx 0.37$ nm, that is, to the thickness of the molecule benzene ring.

At the adsorption of n-methyl aniline and n–chloroaniline, the $t_i$ values were equal to 0.382 and 0.360 nm respectively. In the adsorption of n-nitrophenol $t_{i\,\infty} \approx 0.390 - 0.397$ nm, in the case of nitrobenzene adsorption at $C_i/C_s \approx 0.2$ $t_{i\,\infty} = 0.297 - 0.309$ nm [36], for aliphatic alcohols $t_{i\,\infty} \approx 0.45 - 0.57$ nm.

Figure 1 shows as an example graphic dependences $t$ from $C_e/C_{CMC}$ (where $C_e$ is equilibrium concentration of surfactants solution, $C_{CMC}$ is critical concentration of micelle formation) for alkyl sulfates and alkyl sulfonates.

If the surfactants adsorption is limited only by a monolayer, then, with the relative equilibrium concentration $C_e/C_{CMC} = 1$, its average thickness should be equal to the average thickness of the surfactants molecule, which is oriented parallel to the phase separation surface, taking into account the possible polar group deviation into the solution. As Table 1 shows, the obtained average thickness values of the adsorption layers of anionic surfactants confirm the assumption about the monomolecular structure of the adsorption layer for octyl-, decyl sulfate and sodium decyl sulfonate and associative for sodium dodecyl sulfate and tetradecyl sulfonate. This is also confirmed by the data from the comparison of the areas screened by the molecule in the CMC $\omega_{exp}$ and the calculated $\omega_{cal}$ area, which falls on the molecule, provided the monomolecular surface filling and horizontal orientation of the main axis of the molecule relative to the phase separation surface.

In view of this, during the adsorption study of the same sorbent (graphite carbon black) it appears that when the free adsorption energy is increased in a number of different sorbates, the structure of the adsorption layer from monomolecular (octyl sulfate, decyl sulfate, decyl sulfonate) to the associative (dodecyl sulfate, tetradecyl sulfonate) is observed.

We analyze the results of adsorption of sodium dodecyl sulfate by such carbon sorbents: spheron 6, rinsed spheron 6 and a graphon [36]. As it is known, graphitizing removes from the surface light ionized and oxygenated adsorption centers and leads to a homogeneous and hydrophobic surface. Therefore, the adsorption properties of a graphite carbon black are different from those of the original carbon black. The surface of Spheron is not completely homogeneous and contains anionic groups, as evidenced by the experiments on the adsorption of cetyltrimethylammonium bromide and aerosol-OT on graphite carbon black and its initial form. The anionic

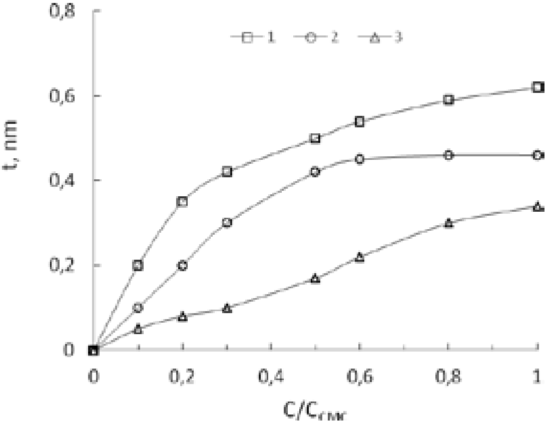

**Figure 1. – *t* -adsorption curves of anionic surfactants on graphite carbon black: sodium dodecyl sulfate (1), tetradecyl sulphonate (2) and decyl sulfonate (3)**

surfactants exhibit a less affinity for the graphite surfaces because of repulsion of the same ionic groups, while the cationic surfactants behave in the opposite way. When rinsing, part of the charged adsorption centers is removed from the surface of the spheron 6, which leads to an increase in the energy of adsorption and smoothing of the maximum at the adsorption isotherm.

With full graphing, the charged centers are removed almost completely and the electrostatic repulsion of the same charged groups is excluded. The homogeneous surface of the graphon contributes to the growth of the anionic surfactants concentration in the surface layer due to the increase in the adsorption forces and hydrophobic interactions. This contributes to a higher degree of molecules association on the graphon surface in comparison with the surfaces of non-graphite and rinsed Spheron. The area that is screened by a single sodium dodecyl sulfate molecule on the graphon surface in the area of CMC is 0.42 nm$^2$, heat-treated at 2770°C of spheron 6 – 0.40 nm$^2$, of the raw spheron 6 – 0.69 nm$^2$ and rinsed spheron 6 – 0.70 nm$^2$. These values are much smaller than the horizontally located molecule area of sodium dodecyl sulfate (1.45 nm$^2$) and more of the area occupied by a vertically positioned molecule (0.25 nm$^2$). As follows from the isotherm of adsorption, the free adsorption energy falls in a number of graphon – a thermally untreated spheron – a rinsed spheron – a raw spheron, which confirms the above assumption of a higher association degree on the graphon surface in comparison with other sorbents.

### 3.2. Adsorption of non-ionic surfactants from individual aqueous solutions

Even more difficult is to identify the adsorption layers structure of the non-ionic surfactants in comparison with the ionic ones due to the complex behavior of the long oxyethyl chain during adsorption. Some data show that the areas that are screened by non-ionic surfactant molecules on the graphite surface ($\omega_{exp}$), are significantly larger than the areas occupied by the solution-air surface and less than the molecule horizontally oriented area by both its parts (alkyl and oxyethyl) relative to the surface ($\omega_{cal}$). In such a case, the $\omega_{exp}$ value is exponentially increasing with the number of oxyethyl group increase.

One of the reasons for this phenomenon may be that different energy characteristics of the alkyl and oxyethyl chains adsorption lead to the oxyethyl chains displacement from the sorbent surface by alkyl radicals due to the mobility of the etheric bond between them [2; 6]. If neglected other interactions in the adsorption layer, then it is possible to determine the conditional deviation angle of the oxyethyl chain from the phase separation surface with the monomolecular surface coating. In this case, the $t_2$ average thickness of the adsorption layer in the CMC$_1$ area should correspond to the $t_1$ molecule average thickness, calculated from molecules of Stuart-Briegleb models, taking into account the deviation angle of the oxyethyl chain respectively [2].

From specific adsorption values of $\alpha_\infty$ when $C_p$ = CMC$_1$ were calculated the areas screened by one surfactant molecule in the adsorption layer. The $\omega_{exp}$ value discrepancy and the area, which involved with alkyl radical ($\omega_{al}$) in the adsorption sphere at the CMC area, is the area occupied by the polyoxyethylene chain on the phase separation surface ($\omega_{oe}$). This area is equal to the projection area of the Van der Waals sizes of the polyoxyethylene group of the adsorbed molecule that is deviant from the phase separation surface at $\alpha$ angle. These data indicate that:

$$\cos\alpha = \frac{\omega_{\exp} - \omega_{al}}{\omega_{oe}} \qquad (4)$$

However, the cause for the discrepancy between the “landing” site of the nonionic surfactant molecule of the determined from the experimental data and the estimated magnitude corresponding to the horizontally oriented molecule, may also be associated in the surface layer, depends on the concentration degree in the surface layer, that is, from $\Delta G^0_a$.

In this manner, the average statistical thickness of the adsorption layer comparison, determined from experimental data and from Stuart-Briegleb molecules models, can provide information about the non-ionic surfactants molecules interaction in the adsorption layer, determines its structure.

To carry out such an analysis, the adsorption of oxyethylated octylphenolide: tritons X-45, X-100 and X-305 on the graphitized carbon black was studied. Adsorption isotherms are shown at Figure 2–4. Table 2 shows the data for standard calculating of the free energy decrease of triton adsorption on graphitized carbon black.

The fractional accuracy in determining the adsorption equilibrium constant was 9%, with the determination of $-\Delta G^0_a$ by the equation (18) (when $lgK_a = 4$) – 5%.

When determining the average molecule thickness by the molecules models, the calculation was carried out taking into account the proportional

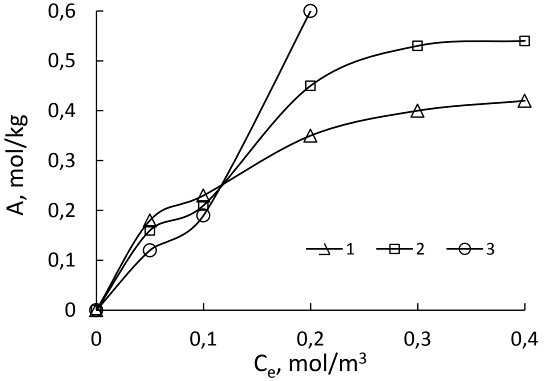

**Figure 2. Adsorption isotherms of TX-45 at CB at different temperatures, °C: 20 (1); 30 (2) and 45 (3)**

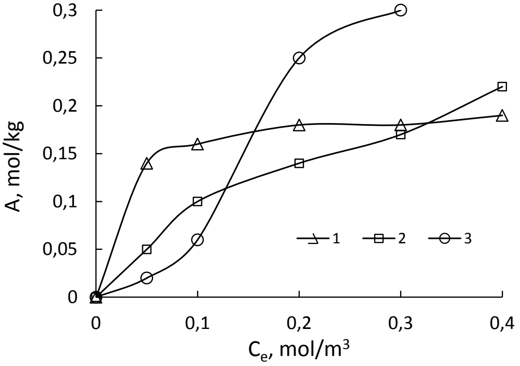

**Figure 3. Adsorption isotherms of TX-100 at CB at different temperatures, °C: 20 (1); 30 (2) and 45 (3)**

contribution to the molecule thickness of its various parts (alkyl radical, deviated oxyethyl chain, benzene ring). The average thickness of the oxyethyl chain was determined by the ratio:

$$t' = \frac{1}{2}(l \sin \alpha + d), \tag{5}$$

where $l$ is the length of the oxyethyl chain deviated in depth; $d$ is Van der Waals thickness of the oxyethyl chain.

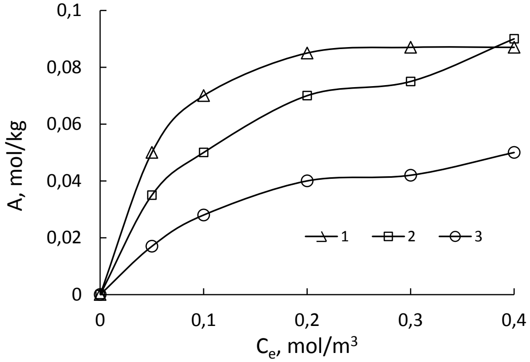

**Figure 4. Adsorption isotherms of TX-305 at CB at different temperatures, °C: 20 (1); 30 (2) and 45 (3)**

Table 2

**Data for calculating the standard free energy thinning of the tritons adsorption on graphitized carbon black**

| $C \cdot 10^2$, mol/m³ | $a \cdot 10^2$, mol/kg | $y \cdot 10^2$ | $x \cdot 10^7$ | $(y/x)\ 10^{-5}$ | $lg(y/x)$ | $a/a_{CMC}$ |
|---|---|---|---|---|---|---|
| TX-45 | | | | | | |
| 0.5 | 4.5 | 3.78 | 0.90 | 4.20 | 5.62 | 0.160 |
| 0.8 | 6.5 | 7.14 | 1.44 | 4.96 | 5.70 | 0.224 |
| 1.0 | 7.1 | 9.63 | 1.80 | 5.34 | 5.73 | 0.259 |
| 1.5 | 9.5 | 19.20 | 2.70 | 7.09 | 5.85 | 0.345 |
| TX-100 | | | | | | |
| 0.5 | 1.5 | 0.99 | 0.90 | 1.09 | 5.04 | 0.053 |
| 1.0 | 3.0 | 2.43 | 1.80 | 1.35 | 5.13 | 0.105 |
| 1.5 | 4.5 | 4.78 | 2.70 | 1.77 | 5.25 | 0.158 |
| 2.0 | 6.5 | 11.76 | 3.60 | 3.26 | 5.51 | 0.228 |
| TX-305 | | | | | | |
| 0.5 | 0.5 | 0.32 | 0.90 | 0.35 | 4.55 | 0.063 |
| 1.0 | 1.0 | 0.74 | 1.80 | 0.41 | 4.62 | 0.125 |
| 1.5 | 1.5 | 1.36 | 2.70 | 0.50 | 4.70 | 0.188 |
| 2.0 | 2.0 | 2.30 | 3.60 | 0.64 | 4.81 | 0.289 |

Table 3

**Characteristics of tritons adsorption on graphitized carbon black**

| Surfactants | $\omega_{exp}$, nm$^2$ | $\omega_{cal}$, nm$^2$ | -$\Delta G^0_a$, kJ/mol | -$\Delta G^0_{acc}$, kJ / mol | $\alpha$ | $t_1$, nm | $t_2$, nm |
|---|---|---|---|---|---|---|---|
| TX – 45 | 0.60 | 1.63 | 30.6 | 31.7 | 88 | 0.52 | 1.64 |
| TX – 100 | 0.61 | 2.14 | 27.6 | 30.7 | 88 | 0.51 | 1.63 |
| TX – 305 | 2.18 | 4.78 | 25.5 | 29.9 | 66 | 4.56 | 0.83 |

As indicated by data obtained (Table 3), change of the standard Gibbs free energy of adsorption -$\Delta G^0_a$ the highest is for TX-45, which is resulting in the adsorption and experimental "landing" sites of surfactant molecules in the CMC area (Table 3). The $\omega_{exp}$ value much less than area occupied by horizontally oriented surfactant molecules and more than area of vertically located molecules (0.32 nm$^2$). The discrepancy of the $\omega_{exp}$ and $\omega_{cal}$ values can be explained by the deviation of the oxyethyl chain either into the solution depth, or by the manifestation of associative interactions in the adsorption layer. If the first hypothesis supposition takes place, then the average thickness of the adsorption layer, calculated from the model, taking into account the oxyethyl chain deviation, should be equal to the average thickness of the adsorption layer determined from the experimental data, depending on $t$ from $\theta$.

As shown by represented in Table 3 data, for the TX-45 triton, the average statistical thickness of the adsorption layer $t_2$ in both systems is much greater than the adsorption layer $t_1$ average thickness. These surfactant molecules, as one would expect, are most closely associated. Probably, associative interactions are also manifested in the case of the X-100 triton adsorption on a carbon black, because $t_2 \gg t_1$. The deviation of the oxyethyl chain obviously effects on the adsorption layer thickness, since $t_2 \approx t_1$. They change in antibatically: $t_1$ increases with increasing degree of oxygenation in surfactants, and $t_2$ decreases. The $t_2$ value decrease within the range of surfactants indicates a decrease in the associative interactions in the adsorption layer with an increase in the degree of surfactant oxyethylation. In this case, associations are likely prevent the presence of hydrated oxyethyl groups, the increase of which in the X-305 triton molecule provide the structure of the adsorption layer approaching a monomolecular one.

In connection with these hypothesis suppositions, it seems advisable to give the oxyethylated alcohols adsorption results to the general formula

$Cn_{2n+1}O(C_2H_4O)_m$ on acetylene carbon black [2]. As the Table 4 shows for $C_5H_{11}O(C_2H_4O)_{30}H$, when one cannot expect the deviation of the oxyethyl chain from the interface phase, because $(-\Delta G^0_a)_{al} \approx (-\Delta G^0_a)_{oe}$ [2], the average adsorption layer thickness is approximately equal to the average surfactant molecule thickness, oriented parallel to the phase separation surface (0.43 nm). This indicates the absence of a three-dimensional association in the adsorption layer and the monomolecular structure of the adsorption layer. Obviously, associative interactions do not manifest, because $t_2 \approx 0.46$ nm, and for $C_8H_{17}O(C_2H_4O)_{23}H$, which contains a small alkyl and long oxyethyl group. In the case of other surfactants, an increase in the alkyl radicals on two carbon atoms leads to an increase in the average thickness of the adsorption layer, and at an unchanged length of the alkyl radical, the increase in the oxyethyl groups content does not change it practically (Table 4). Consequently, the association of surfactant molecules mainly determines the change in the "landing" site of a molecule in a saturated adsorption layer with an increase in the length of the oxyethyl chain, but the deviations of the hydroxy chains can make a certain contribution to this.

In view of this, as indicated by obtain results, when surfactant adsorption from aqueous solutions to a non-porous carbon adsorbent at equilibrium concentrations not exceeding CMC, the adsorption layer may be monomolecular or formed from associates of a greater thickness than the monolayer, depending on the adsorbate-adsorbent interaction energy, hydrophobicity degrees of the surfactant molecule and the adsorbent chemical nature.

Table 4

**Characteristics of the oxyethylated alcohols adsorption on acetylene carbon black**

| Surfactants | $\omega_{exp}$, nm² | $\omega_{cal}$, nm² | $-\Delta G^0_a$, kJ/mol | $\alpha$ | $t_1$, nm (Considering.$\alpha$) | $t_2$, nm |
|---|---|---|---|---|---|---|
| $C_5H_{11}O(C_2H_4O)_{30}H$ | 4.37 | 4.57 | 24.85 | 8 | 0.64 | 0.43 |
| $C_{10}H_{21}O(C_2H_4O)_{13,5}H$ | 1.20 | 2.80 | 26.27 | 71 | 0.89 | 0.90 |
| $C_{10}H_{21}O(C_2H_4O)_{17}H$ | 1.84 | 3.26 | 28.98 | 58 | 1.20 | 0.68 |
| $C_{12}H_{25}O(C_2H_4O)_6H$ | 1.00 | 1.84 | 29.73 | 79 | 0.63 | 0.76 |
| $C_{12}H_{25}O(C_2H_4O)_{15}H$ | 1.54 | 3.16 | 32.32 | 66 | 0.97 | 0.78 |
| $C_{12}H_{25}O(C_2H_4O)_{17}H$ | 1.66 | 3.42 | 33.44 | 66 | 1.10 | 0.79 |
| $C_{12}H_{25}O(C_2H_4O)_{23}H$ | 2.08 | 4.21 | 35.45 | 64 | 1.53 | 0.79 |
| $C_8H_{17}O(C_2H_4O)_{23}H$ | 3.02 | 3.49 | 27.98 | 24 | 0.93 | 0.46 |

### 3.3. Binary mixtures adsorption of cationic and non-ionic surfactants

In many cases, the use of surfactant mixtures is more profitable than the use of individual surfactants [15; 16]. While adsorption from individual surfactant solutions at the boundary between solids and liquids is intensively studied, there is only a limited amount of work related to surfactant mixtures adsorption, and these works were performed mainly on hydrophilic surfaces [17; 27].

In this paper, the adsorption of hexadecylpyridinium bromide (HDPB) and octylphenol ethoxylates of the TX series (TX-45, TX-100 and TX-305) from their mixed solutions on the graphitized CB was studied for determining the mixed adsorption main features of cationic and non-ionic surfactants on the nonpolar solid surface.

The CB is an intense black powder, which is obtained with incomplete combustion or thermal decomposition of carbon-containing organic materials. It is widely used as a pigment, a polymer filler material, as an electrode material in batteries and fuel-consuming cells, and as a sorbent in sewage purification. The CB consists of nanometer size primary particles, which form aggregates of various shapes and structures. The CB particles, generally, are strongly hydrophobic and are prone to aggregation when dispersed in water. One of the main approaches to improving the aggregation stability of the CB particles in aqueous solutions is surfactants adsorption on the CB surface [5].

In this paper, HDPB and non-ionic oxyethylated octylphenols, which are commonly used in paints, emulsions and wetting agents were used to study the adsorption behavior of mixtures of these surfactants on the CB surface. This study aims to promote a better understanding of the surfactants interaction on the surface of a hydrophobic sorbent to optimize such interactions.

By isotherms adsorption and taking into account the total area of the CB surface, the area ($\omega$), force per adsorbed surfactant molecule was calculated with maximum adsorption

$$\omega = \frac{S}{A_{\max} N_A} \qquad (6)$$

where $S$ is CB surface area, $N_A$ is Avogadro constant and $A_{max}$ – maximum adsorption value.

The non-ionic surfactants concentration in the samples was determined by spectrophotometric measurements at 274 nm with the spectrophotometer SPh-46, while the content of the HDPB in the solutions was evaluated using the two-phase titration method [37]. It is shown that the presence of each component in mixed solutions of HDPB – TX does not affect the determination of another surfactant.

The mole fraction of TX on the CB surface and in solutions was determined by the following formulas:

$$\alpha_{TX}^{CB} = \frac{A_{TX}}{A_{TX} + A_{HDPB}} \tag{7}$$

$$\alpha_{TX}^{solution} = \frac{C_{TX}}{C_{TX} + C_{HDPB}} \tag{8}$$

where $\alpha_{TX}^{CB}$ and $\alpha_{TX}^{solution}$ are TX mole fractions on the CB surface and in equilibrium solution, respectively; $A_{TX}$ and $A_{HDPB}$ are the adsorption values of TX and HDPB on the CB surface; $C_{TX}$ and $C_{HDPB}$ are the TX and HDPB concentrations in the equilibrium solution, respectively.

The charge of the CB surface particles was determined using the Zeta-Meter System 3.0+, measuring the particles electrophoretic mobility in the diluted suspension, and turning it into a zeta potential value by the Smolukhovsky equation:

$$\varsigma = \frac{\mu\eta}{\varepsilon} \tag{9}$$

where $\varsigma$ is zeta potential (мB), $\eta$ is dynamic viscosity, and $\varepsilon$ is dielectric constant. The measurements were carried out at pH values of 6.0-6.5 aqueous solution.

Isotherm of HDPB adsorption on the CB surface corresponds to the Langmuir type, as shown at Fig. 5 (curve 1). Isotherm of Langmuir's adsorption is described by the formula:

$$A = \frac{A_{\max} KC}{(1 + KC)} \tag{10}$$

where $A$ is the adsorption value per area unit, $K$ is equilibrium ration and $A_{max}$ – maximum adsorption value.

The amount of adsorbed HDPB grows rapidly with increasing surfactant concentrations and reaches the plateau area at equilibrium HDPB concentration of about 0.4 mmol/l. The HDPB significant adsorption is due to hydrophobic interactions between the alkyl chains of surfactant molecules and CB surface. It can also be assumed that the positively charged HDPB ions and π-electrons of a graphite grate on the CB surface interact with each other.

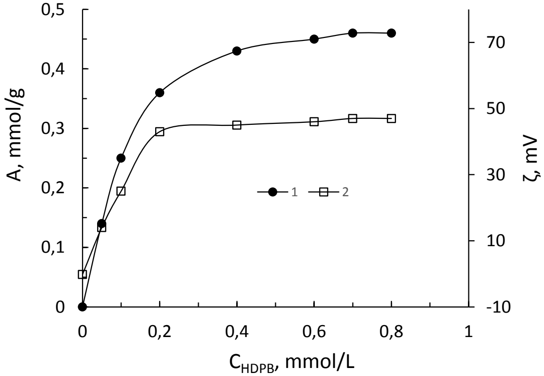

**Figure 5. Isotherms of HDPB adsorption (1) and zeta potential f CB particles in the HDPB solution (2), pH 6.5**

As Fig. 5 shows, the maximum adsorption value for the HDPB is approximately 0.46 mmol/g, which corresponds to a limit area of 0.60 nm$^2$ for one HDPB molecule adsorbed on the CB surface.

It has been shown that the zeta potential of CB particles in aqueous solution without cationic surfactant is very low (-0.2 mV) (Figure 5, curve 2). The HDPB molecules adsorption significantly changes the zeta potential of CB particles even at low surfactant concentrations. The zeta potential is steadily increasing with the HDPB concentration in solutions, reaching the value of the plateau about +48 mV at a surfactant concentration of about 0.4 mmol (Figure 5, curve 2). The change in the zeta potential value in the presence of cationic surfactant clearly indicates a significant surfactant adsorption on the CB surface. There is also a good correlation between adsorbed cationic surfactant amount and the values of the CB particles zeta potential (Figure 5, curves 1, 2). It follows that hydrophobic groups oriented toward the CB particles surface, while the cationic surfactants are turned to the aqueous phase adsorb the HDPB molecules.

Figure 6 shows adsorption isotherms TX-45, TX-100 and TX-305 on the CB surface. All three adsorption isotherms correspond to the Langmuir type with a clearly defined horizontal plateau near the CMC corresponding values. High adsorption quantities of ethoxylated octylphenols are due to hydrophobic interactions between surfactant molecules and CB surface. Hydrophobic interactions between the alkyl macromolecular chain and the graphite surface are well stated experimentally and are considered as the main force responsible for surfactants adsorption on the CB surface [27]. It can also be assumed that the π-electrons of the surfactant molecules phenyl rings and the π-electrons of the CB grating interact with each other.

Whereas TX-45 is a non-ionic surfactant, its adsorption on the CB surface practically does not affect the zeta potential of the CB particles (Fig. 6). Similar values of the zeta potentials were also obtained for the CB particles after TX-100 and TX -305 adsorption.

As the Table 5 shows the maximum adsorption values and the limiting area pertaining to the adsorbed molecule for oxyethylated octylphenols. As table shows, the amount of adsorbed non-ionic surfactant significantly decreases with an increase in the number of EO units in the surfactant molecule. With the EO units number increasing, the tritons molecules become more hydrophilic, and therefore adsorption on the surface of the CB decreases. This also increases the area that falls on the non-ionic surfactant molecule on the CB surface. As a result, the amount of adsorbed non-ionic surfactant decreases. It was previously reported that the exclusion area formed by the polyoxyethylene chain directed to the solution, which is the main parameter that restricts surfactants adsorption. The conformation of the oxyethylated chain of adsorbed surfactant depends on its length and may be spiral, especially for long EO chains.

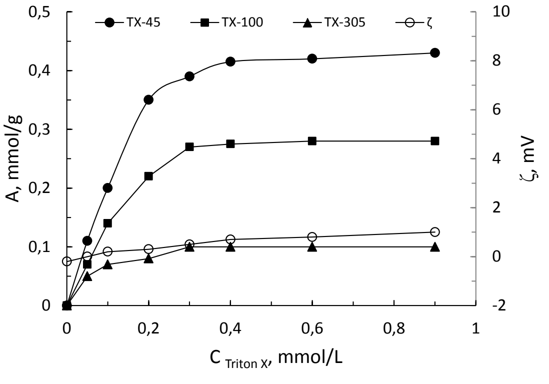

**Figure 6. Adsorption isotherms of Triton X and zeta potentials of CB particles in TX-45 solution. pH 6.5**

Table 5

**The non-ionic surfactants adsorption on the CB**

| Surfactants | $A_{max}$, mol/kg | $\omega$, nm$^2$ | CMC, mol/m$^3$ |
|---|---|---|---|
| TX-45 | 0.42 | 0.60 | 0.16 |
| TX-100 | 0.28 | 0.9 | 0.24 |
| TX-305 | 0.11 | 2.29 | 0.30 |

Figure 7 shows the TX-45 adsorption values on the CB surface, depending on the TX-45 concentration in mixed solutions at HDPB constant concentration.

As is obvious, at concentrations that are lower than corresponding to adsorption saturation, the TX-45 adsorption increases with the HDPB increase in the mixture content. In this concentration range, a synergistic adsorption effect occurs when the adsorption value of the non-ionic surfactant from the mixtures is higher than the amount of adsorption from the TX-45 mono-solution. Thus, cationic surfactant, when present in the mixture, enhances the non-ionic surfactant adsorption, apparently, due to the formation of mixed surfactant aggregates. The main reason for the mixed aggregates formation is obviously dispersion interactions between surfactants alkyl radicals that are adsorbed on a nonpolar CB surface. The ion-dipole interactions between the hydrophilic molecules parts of cationic and non-ionic surfactant molecules can also contribute to the mixed

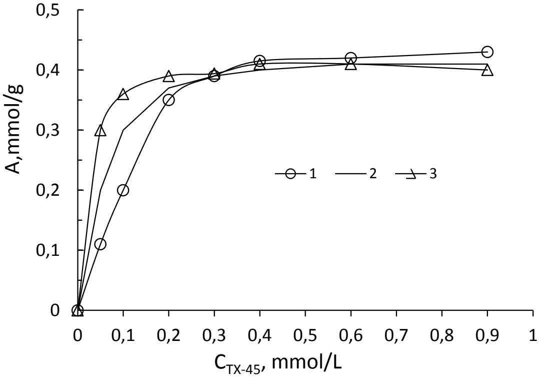

**Figure 7. Adsorption isotherms of TX-45 at CB from the single solution (1) and from mixed solutions of TX-45 with HDPB (2,3) HDPB concentrations are: 0.2 (2) and 0.5 mmol/L (3)**

aggregates formation. In this case, the TX-45 molecules, as well as the mixed TX-45-HDPB aggregates adsorb on the CB surface. As a result, the total number of TX-45 molecules adsorbed from mixed surfactant solutions is higher compared to adsorption from the TX-45 mono-solution.

Similar characteristics were also established at HDPB adsorption from surfactants mixtures. As Fig. 8. shows, the presence of TX-45 molecules promotes HDPB adsorption, especially at surfactant concentrations in a solution, which does not yet achieve adsorption saturation of the sorbent surface. In these cases, the cationic surfactant adsorption from binary mixtures is higher in comparison to adsorption of HDPB from mono-solution surfactant. As mentioned above, this is obviously due to the aggregates formation of mixed surfactants, in this case both individual surfactants molecules and mixed TX-45 aggregates – HDPB are adsorbed on the CB surface. In addition, an increase in HDPB adsorption may be due to decrease in electrostatic repulsion between cationic surfactant ions in the adsorption layer due to the molecules inclusion of the non-ionic surfactant between them. Thus, the synergistic adsorption effect was found in mixtures of TX-45– HDPB when the TX-45 or HDPB adsorption rates from their mixed solutions are higher than the corresponding adsorption quantities from solutions of individual surfactants, especially in the initial rapidly increasing part of the isotherm adsorption.

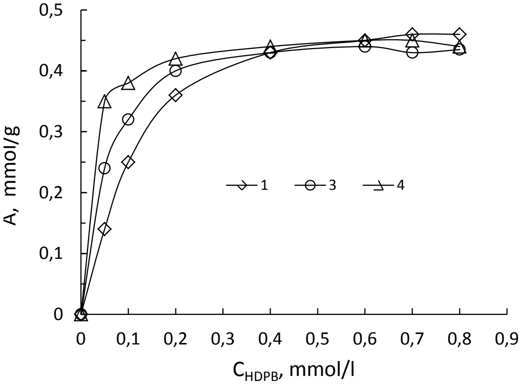

**Figure 8. Adsorption isotherms of HDPB at CB from the single solution (1) and from mixed solutions of HDPB with TX-45 (2,3) TX-45 concentrations are: 0.2 (2) and 0.5 mmol/L (3)**

According to the Rosen model [38], the interaction between two different surfactant molecules can be estimated using the intermolecular interaction parameter $\beta^\sigma$, which can be calculated as follows:

$$\beta^\sigma = \frac{E_{11} + E_{22} - 2E_{12}}{RT} \tag{11}$$

where $E_{11}$, $E_{22}$, $E_{12}$ are interaction energy between individual surfactant$_1$ molecules, separate surfactant$_2$ molecules, surfactant1 and surfactant$_2$ molecules, respectively. Negative $\beta^\sigma$ values indicate the adhesion between surfactant molecules, while positive $\beta^\sigma$ values testify to repulsive interactions between surfactant$_1$ and surfactant$_2$ molecules.

When a mixed saturated adsorption layer is formed on the boundary of a hydrophobic surface-solution, the $\beta^\sigma$ interaction parameter can be calculated using the following formulas [38]:

$$(x_1)^2 \ln(\frac{\alpha_i C_{12}}{C_1^0 x_1}) = (1 - x_1)^2 \ln(\frac{(1 - \alpha_1)C_{1,2}}{C_2^0(1 - x_1)}) \tag{12}$$

$$\beta^\sigma = \frac{\ln \alpha_1 C_{1,2} \ / \ C_1^0 x_1}{(1 - x_1)^2}) \tag{13}$$

where $X^\sigma{}_1$ is TX molar fraction in a mixed layer on the solid-liquid – fluid boundary, $C_1^0$, $C_2^0$ and $C_{1,2}$ are concentrations corresponding to the formation of a saturated adsorption layer for TX, HDPB, and surfactants mixture, respectively.

$X^\sigma{}_1$ meaning is calculated by the equation (12), and then substitutes into formula (13) to calculate the $\beta^\sigma$ intermolecular interaction parameter between the molecules TX and HDPB in the mixed adsorption layer. The data in Table 6 show that the mixed adsorption layer on CB the surface is enriched with molecules of the non-ionic surfactant. The maximum absolute value of the deviation from the ideal mixture was found for a surfactants mixture with a mole fraction where TX is equal to 0.6. The predominance of the non-ionic surfactant content in the mixed adsorption layer may be due to the higher surface activity of TX-45 compared to the HDPB.

As Fig. 9 shows, the content of various non-ionic surfactants in the mixed adsorption layer on the CB surface depends on their molar ratio in mixed surfactant solutions. If the surfactant content on the CB surface was the same as in the solution, the experimental data would fall on the dotted line in this figure, but apparently, the non-ionic surfactants are present in excess on the CB surface, with the molar fraction of oxyethylated octylphenols in the

Table 6

**Parameters of $\beta^{\sigma}$ intermolecular interaction and TX-45 $X^{\sigma}$ mole fraction in the mixed adsorption layer**

| $\alpha_{TX-45}$ | $\beta^{\sigma}$ | $X^{\sigma}$ |
|---|---|---|
| 0 | - | 0 |
| 0.2 | -6.5 | 0.6 |
| 0.4 | -6.8 | 0.7 |
| 0.6 | -8.3 | 0.7 |
| 0.8 | -5.4 | 0.75 |
| 1 | - | 1 |

adsorption layer decreasing TX45 > TX100 > TX305 series. This dependence indicates that more hydrophobic non-ionic surfactant is predominantly adsorbed on the CB surface from mixed solutions with cationic surfactant. Such data are well correlated with the zeta potential values of the CB particles in mixed solutions of oxyethylened octylphenols – HDPB.

As Figure 10 shows, positive zeta potential of CB particles in a HDPB solution (+46 mV) is reduced in the presence of non-ionic surfactants. This can be explained by the substitution of positively charged cationic HDPB molecules that are adsorbed on the CB surface into virtually neutral molecules of non-ionic oxyethylened octylphenols, which reduces the zeta potential of CB particles. When comparing the effect of various oxyethylenic octylphenols

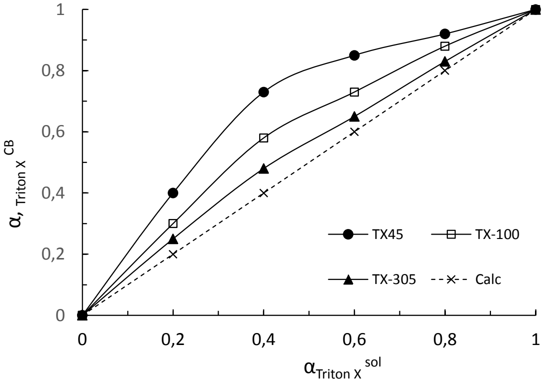

**Figure 9. Mole fraction dependence of the oxyethylated octylphenols on the CB surface from their mole fraction in a mixed solution with HDPB**

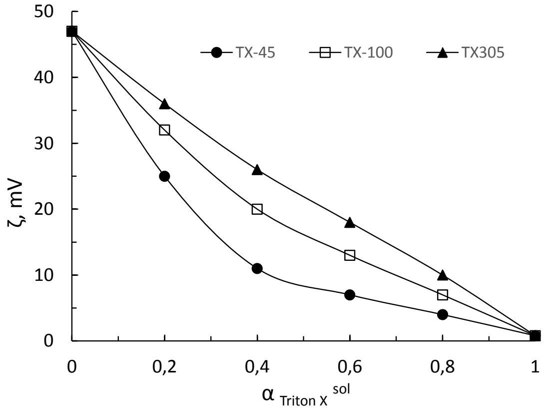

**Figure 10. Zeta potentials of the CB particles in the mixed solutions of Triton X with HDPB at different Triton X mole fraction (α) in the mixed solutions**

on the zeta potential magnitude at the same molar fate of non-ionic surfactant in a mixed solution, the greatest decrease in the CB zeta potential was detected in the TX-45 presence. This can be explained by the higher TX-45 adsorption on the CB surface compared to TX-100 and TX-305.

Thus, the results of studies show that the surfactant composition on the CB surface is significantly different from their composition in the solution and that the adsorption layer composition is significantly different from their volume ratio in the solution. A synergistic effect was found for surfactant mixtures when the adsorption of both non-ionic and cationic surfactants on the CB surface with their binary mixtures was higher than surfactants adsorption from individual solutions. It is shown that the parameters of $\beta^{\sigma}$ intermolecular interaction, which are calculated using the Rubin-Rosen approach, have negative values indicating the presence of significant intermolecular interactions of the components in the mixed adsorption layer. It is shown that non-ionic surfactant molecules are dominant in the mixed adsorption layer. It is established that the molar fraction of non-ionic surfactants on the CB surface decreases in TX-45 > TX-100 > TX-305 series. These data indicate that more hydrophobic non-ionic surfactant is adsorbed predominantly on the CB surface from mixed solutions with cationic HDPB.

### 3.4. Binary mixtures adsorption of sodium hexadecyl sulfate and TX-100

The study of the mutual surfactants interaction with their adsorption from binary solutions at the interface between different phases, including solids, is of interest for the description and explanation of various colloid-chemical processes associated with the surfactants presence, and when modeling the structure and properties of systems containing surfactants mixtures. In recent years, surfactant mixtures adsorption on the solution – air boundary intensively studied, but the surfactant adsorption from solutions of their mixtures on solid surfaces has not been systematically studied. The analysis of the data available in the literature shows that there is no clear idea and unanimous opinion among researchers about the mixtures composition influence of non-ionogenic (non-ionic surfactants) and anionic surfactants on adsorption parameters.

We carried out a study of adsorption of non-ionogenic TX-100 surfactant and SHDS anionic surfactant at different ratios in a binary solution on the CB surface.

The isotherms adsorption of TX-100 and SHDS on the CB surface have a Langmuir shape (Fig. 11). As the figure shows, a synergistic effect manifests itself in increasing the values of the total adsorption of the studied surfactants from binary solutions in comparison with the adsorption values of each component from individual solutions on graphitized carbon black at the same equilibrium concentrations throughout the studied interval of surfactants molar ratios. The surfactant adsorption is due to the nonspecific dispersion interaction between the nonpolar part of the surfactant molecules (hydrocarbon radicals) and the nonpolar graphitized carbon black surface.

With a small TX-100 ($\alpha = 0.2$) content, adsorption from binary solutions on the CB surface is small; at equimolecular surfactant ratios ($\alpha = 0.5$) in the solution adsorption increases due to the formation of mixed aggregates TX-100 – SHDS. The increase in the total adsorption at high content of TX-100 ($\alpha = 0.8$) occurs mainly due to its adsorption; the adsorption of SHDS increases with all studied components ratios.

Table 7 shows the total adsorption values of surfactants, calculated from the additive property assumption from the adsorption data TX-100 and SHDS from individual solutions on CB according to the formula:

$$A_{calc} = \alpha A_{TX-100} + (1-\alpha) \cdot A_{SHDS} \tag{14}$$

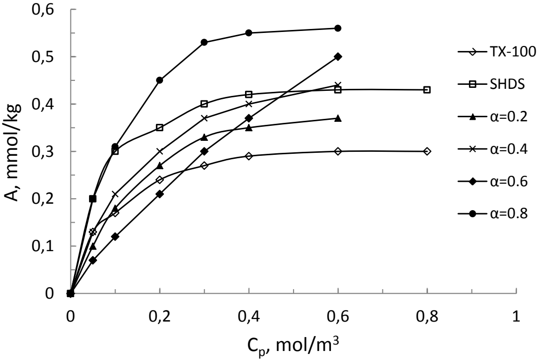

**Figure 11. Adsorption isotherms of TX-100 and SHDS on CB from solutions of separate surfactants and from mixed solutions of TX-100 – SHDS at different molar TX-100 (α) fractions in mixed solution**

Table 7

**Total surfactants adsorption on the CB surface from binary solutions TX-100 – SHDS**

| $\alpha_{TX\text{-}100}$ | $A \cdot 10^6$ (exp), mol/g | $A \cdot 10^6$ (calc), mol/g, |
|---|---|---|
| 0 | 1.8 | - |
| 0.2 | 3.3 | 2.4 |
| 0.4 | 3.9 | 3.1 |
| 0.6 | 5.1 | 4.0 |
| 0.8 | 4.5 | 3.6 |
| 1.0 | 1.7 | - |

For all molar components ratios in a binary solution, the values of total adsorption in systems TX-100 – SHDS, obtained experimentally, are greater than the calculated values ($A_{exp} > A_{calc}$). The maximum deviation from the ideal is found in a surfactant binary solution with equimolecular component content. In this case, surfactants are adsorbed on the CB both in the form of molecules and ions, and in the form of mixed aggregates. The concentration necessary to achieve the maximum surfactant adsorption on the CB surface obtained experimentally can be compared with the corresponding concentration obtained for the ideal system state by the following ratio [38]:

$$1/C_{12} = \alpha_1/C_1 + (1-\alpha_1)/C_2 \qquad (15)$$

where $C_1$, $C_2$ and $C_{12}$ are the concentrations required to achieve maximum adsorption on the CB surface, determined by the adsorption isotherms of surfactants from individual and binary solutions, respectively; $\alpha_1$ – TX-100 molar fraction in solution volume.

Figure 12 shows that concentration dependence ($C_{12}$), required to achieve maximum adsorption on the CB surface ($C_{12}$) from $\alpha$, determined by the adsorption isotherms of surfactant from binary solutions, has a negative deviation from the ideal system state, the maximum of which is observed for TX-100 at $\alpha_{TX\text{-}100} = 0.8$. Reducing the total concentration values required to achieve maximum adsorption on a solid surface in comparison with estimated data indicates a synergistic effect of the studied surfactants upon their adsorption from binary solutions on the CB surface.

With the help of the Rubin-Rosen Model [38], the composition and characteristics in mixed systems of surfactant were quantified. According to this model, the mixed adsorption layer is considered as a regular solution of one surfactant in the other, and the interaction of surfactants molecules is characterized by $\beta^{\sigma}$ dimensionless parameter. Our use of Rosen representations is determined by the choice of CB as adsorbent, which has a low-energy homogeneous nonpolar surface. The calculation was carried out using the formulas (12) and (13). Table 8 shows the results.

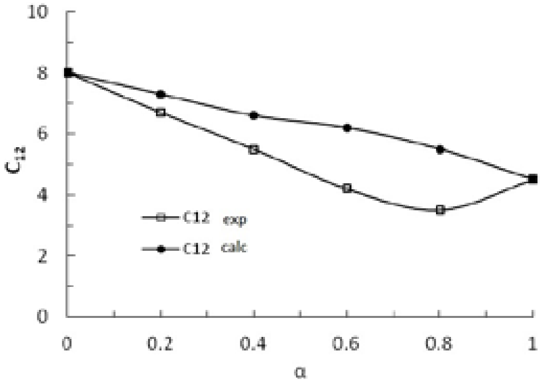

**Figure 12. The concentration dependence required to achieve maximum adsorption on the CB surface in individual and binary solutions versus the TX-100 molar fraction: 1 is estimated data; 2 is experimental data**

The composition calculation of the adsorption layer $\chi^{\sigma}$ and $\beta^{\sigma}$ interaction parameters shows that the mixed adsorption layer on the solution – CB boundary is enriched with non-ionic surfactants molecules already with a small content in the binary solution ($\alpha_{TX\text{-}100} = 0.2$) (Table 8). With the mole fraction, TX-100 increase in the binary solution from 0.2 to 0.8 its share in the adsorption layer increases by approximately 1.6 times.

Negative values of the ($\beta^{\sigma}$) interaction parameters indicate the existence of excess attraction between the TX-100 and SHDS molecules in the mixed adsorption layer.

Additional information on surfactant adsorption from binary solutions on a solid sorbent can be obtained by comparison with adsorption at the interface of the surfactant – air binary solution phases. Using the surface tension isotherms of individual TX-100 and SHDS and their mixtures, obtained by us earlier, were determined the values of maximum adsorption $H_{\infty}$ and the area value that falls on the surfactant molecule in the adsorption layer.

The values of the surfactant boundary adsorption ($A_{\infty}$), found in the plateau area on adsorption isotherms, and the value of the area per molecule in the mixed adsorption layer on the CB surface, were calculated by the formula:

$$S_{spec} = S_{\min} \cdot A_{\infty} \cdot N_A, \tag{16}$$

where $S_{spec}$ is CB specific surface area; $S_{min}$ is the minimum area that falls on the molecule in the adsorption layer; $A_{\infty}$ is the adsorption value of concentration close to saturation.

Table 8

**The mixed adsorption layers composition and the interaction parameters between the surfactant molecules on the CB surface are calculated according to the Rosen model ($A = 2.7 \cdot 10^{-6}$ mol/g)**

| $\alpha_{TX\text{-}100}$ | $\chi^{\sigma}$ | $-\beta^{\sigma}$ |
|---|---|---|
| 0 | - | - |
| 0.2 | 0.59 | 3.2 |
| 0.4 | 0.67 | 5.5 |
| 0.6 | 0.72 | 12.0 |
| 0.8 | 0.78 | 13.3 |
| 1.0 | - | - |

Table 9

**Comparison of the basic adsorption parameters of TX-100 and SHDS from binary solutions at the boundary between solution – air and solution – solid separation phase**

| $\alpha_{TX-100}$ | $H_{\infty} \cdot 10^6$, mol/m$^2$ | $S_{min} \cdot 10^2$, nm$^2$ | $A_{\infty} \cdot 10^6$, mol/m$^2$ | $S_{min} \cdot 10^2$, nm$^2$ |
|---|---|---|---|---|
| 0 | 1.7 | 21.4 | 8.0 | 17.2 |
| 0.2 | 2.5 | 79.3 | 12.0 | 10.5 |
| 0.4 | 2.9 | 75.5 | 15.0 | 7.3 |
| 0.6 | 3.7 | 71.4 | 17.5 | 6.4 |
| 0.8 | 4.5 | 56.5 | 20.0 | 6.0 |
| 1.0 | 4.9 | 39.0 | 10.5 | 16.3 |

As the Table 9 shows the data, where is shown the TX-100 and SHDS adsorption from binary solutions at the boundary between the phases of the binary surfactant solution – CB significantly exceeds adsorption at the interface between the phases of the surfactant solution. This is due to the aggregates formation from TX-100 and SHDS molecules to form a mixed adsorption layer on the CB surface, as well as with the dispersion interaction of surfactant molecules with the nonpolar CB surface.

When adsorption of surfactants on the CB surface, the value of the area occupied by the molecules TX-100 and SHDS, is less from their binary solutions than in adsorption from individual solutions, and less than the corresponding areas of the solution-air (Table 9) interphase boundary. This indicates the adsorption layer consolidation on the solid surface and confirms the fact of surfactants adsorption on the CB surface in the form of aggregates.

## 4. Conclusions

It was established that formation of the surfactants adsorption layer on non-porous carbon sorbent is influenced by the ratio of free molar energy adsorption to free energy of micelle formation, as well as by the ratio of the total surface of the micellar phase to the available effective adsorbent surface.

The adsorption of ionic and non-ionic surfactants from individual and mixed solutions at the interface between aqueous solution of the surfactant and non-porous carbon sorbent was investigated. In the framework of the phase separation model (the Rubin-Rosen approach), the composition of mixed adsorption layers and intermolecular interaction parameters in adsorption layers $\beta^{\sigma}$ as well as the changes in free adsorption energy of the surfactant mixtures were calculated. It was shown that $\beta^{\sigma}$ have negative values, indicating the presence of significant intermolecular interactions of the components in the mixed adsorption layer. The ionic component of the mixture has a specific effect on the parameters of intermolecular interaction and the formation of the adsorption layer. The effects of negative deviation from the ideal system are more notable in the binary systems with anionic surfactants.

A synergistic effect was found for surfactant mixtures when the adsorption of both non-ionic and ionic surfactants at CB surface from their binary mixtures was higher than adsorption of surfactants from individual solutions. Synergetic effects are more pronounced at high molar fraction (α = 0.6-0.8) of the non-ionic surfactant in the mixture. It was shown that changes in the standard free energy of adsorption and intermolecular interaction parameters in adsorption layers are higher in the surfactants mixtures, which contain the anionic surfactant. The adsorption activity of the surfactants at the solution-CB interface is higher than at the air-solution interface due to dispersion interactions of surfactant molecules or ions with hydrophobic surface of the sorbent.

It was found that the composition of the mixed surfactant adsorption layer is significantly different from the surfactant ratio in the bulk solution. Molecules of the non-ionic surfactants are dominated in the mixed adsorption layer and their molar fraction decreases in the row: TX-45 > TX-100 > TX-305. These data indicate that the more hydrophobic non-ionic surfactant is predominantly adsorbed at CB surface from mixed solutions with cationic or anionic surfactants. The conclusions are confirmed by the obtained data on zeta potential values of the sorbent particles with adsorbed surfactants.

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