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ANALYSIS OF INTERMOLECULAR INTERACTIONS IN MIXED ADSORPTION LAYERS OF SURFACTANTS

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The adsorption of the surfactants mixtures of different chemical nature such as Triton X-100 and sodium hexadecyl sulfate at the surface of graphitized carbon black was studied. Using the model of phase separation (the Rubi–Rosen approach), the composition of the mixed adsorption layers and parameters of interaction between the surfactant molecules in the adsorption layers were calculated. It was found that mixed adsorption layers are enriched with molecules of the non-ionic surfactant Triton X-100.

Key words: surfactant, adsorption, adsorption layer, graphitized carbon black.

INTRODUCTION. Adsorption of surfactants (SAS) at the phase boundary solution – solid is the subject of many studies, but most of the work in this area is devoted to the study of adsorption from single-component solutions [1–4]. The study of the behavior of mixed systems of surfactant is relevant from both scientific and applicative points of view. In many cases, the use of mixtures is more advantageous than the use of separate surfactants [5,6]. The use of mixtures of surfactants allows regulating of the disperse systems properties more effectively compared with the individual components that are part of the mixture. This is due to the change in the properties of the components in the mixture, for example, by increasing or decreasing adsorption at the interface of the phases. Thus, the wetting and modifying effect of solutions of binary mixtures on solids of different nature is significantly different from the effect of solutions of individual surfactants [7]. At the same time, there is a very limited number of studies related to the adsorption of surfactant mixtures, and these works were performed mainly on hydrophilic surfaces [8–10]. The analysis of literature data shows that there is

virtually no data on the adsorption of surfactant adsorption on carbonaceous sorbents, which are often used in practice, in particular in water treatment.

The purpose of the work was to study the adsorption of binary mixtures of surfactants of various chemical nature on the surface of non-porous hydrophobic carbon sorbent at different SAS ratio in mixtures.

EXPERIMENT AND DISCUSSION. Surfactants of anionic and nonionic type were used for studies. Non-ionic surfactant – oxyethylated octylphenol with the degree of oxyethylation $n=9-10$ Triton X-100 (TX-100) of the general formula $C_8H_{17}C_6H_4(OCH_2CH_2)_n$, qualification "p.a.". Anionic surfactant – sodium hexadecyl sulfate ($n-C_{16}H_{25}SO_4Na$), qualification "p.a.". Substances were used without additional purification.

As a non-porous carbon sorbent, graphitized carbon black was used, the specific surface area of which, calculated by adsorption of argon by the BET method, was 105 m²/g.

Determination of the critical concentration of micelle formation (CCM) in the solutions of surfactant was carried out using a

tenenziometric method based on the dependence of the surface tension (σ) on the equilibrium concentration of surfactant (C). The CCM of the surfactant is defined as the concentration corresponding to the point of the break in the dependence $\sigma(\ln C)$.

Measurement of the surface tension was carried out by Wilhelm's method by balancing the platinum plate. The cleanliness of the plate was controlled by the surface tension of the bidistilled water ($\sigma=72.5 \text{ mJ/m}^2$). The accuracy of measurements at the results of 3–5 points was $\pm 0.5 \text{ mJ/m}^2$.

To obtain adsorption isotherms of solutions containing different initial concentrations of surfactants, they were shaken with constant sorbent sample weights on a special apparatus, which carries 6000 oscillations per hour. The volume of the solution was 0.025 dm^3 . After reaching the adsorption equilibrium, the solution and sorbents were separated by centrifugation. The equilibrium concentrations of TX-100 were determined by spectrophotometric method, sodium hexadecyl sulfate - by the two-phase titration method [11]. Measurement error did not exceed 1% and 4% respectively. Investigations of the adsorption kinetics have shown that the adsorption equilibrium in the aqueous solution of surfactant - sorbent is reached in 8 hours.

The value of specific adsorption was calculated by the ratio

$$a = \frac{C_o - C_e}{m} V, \quad (1)$$

where a is the adsorption value, mol/g ; V – volume of solution, dm^3 ; m – weight of sorbent, g ; C_o and C_e – initial and equilibrium concentrations of the surfactant solution, mol/dm^3 .

Fig. 1 shows adsorption isotherms for solutions of individual surfactants and their mixtures with different molar ratios of components in the initial solution. The molar fraction of non-ionic surfactant TX-100 in the mixture (α_{mx-100}) was 0.2, 0.4, 0.6 and 0.8.

Fig. 1. Adsorption isotherms of TX100 and SHDS on the GC from solutions of individual SAS and mixed solutions with different molar fraction of TX-100 (α)

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The adsorption isotherms of TX-100 and SHDS on the surface of the GC have a Langmuir form. As can be seen from Fig. 1, with a small content of TX-100 in the mixture ($\alpha_{TX-100} = 0.2$), the adsorption from binary solutions on the surface of the GC is small (0.35 mol/kg). With the growth of α_{TX-100} , the adsorption increases, probably due to the formation of mixed aggregates TX-100-SHDS. The greatest increase in adsorption of surfactant is observed at $\alpha_{TX-100} = 0.8$, when its value reaches 0.56 mol/kg . Previous studies have shown that the adsorption of surfactant on a hydrophobic surface occurs due to the nonspecific dispersion interaction between hydrocarbon radicals of surfactant molecules and the nonpolar surface of graphitized carbon [6].

For comparison with the experimental data, the values of the total surfactants adsorption on the GC were calculated with the assumption of additivity:

$$A_{\text{calc}} = \alpha_{TX-100} \cdot A_{TX-100} + (1 - \alpha_{TX-100}) \cdot A_{SHDS}, \quad (2)$$

where α_{TX-100} is the molar fraction of TX-100 in the mixture, A_{TX-100} and A_{SHDS} - adsorption values TX-100 and SHDS from individual solutions on GC.

Table 1 shows the experimental values of the total adsorption of surfactants on the GC and calculated by the formula (2). The results show that for all molar ratios of components in the mixture, except for $\alpha_{TX-100} = 0.2$, the values of total adsorption in systems TX-100-SHDS, obtained experimentally, are greater than the calculated values ($A_{exp} > A_{calc}$).

Thus, in mixed systems of surfactant with a high content of TX-100 ($\alpha_{TX-100} = 0.4, 0.6$ and 0.8) there is a synergistic effect, which manifests itself in increasing of the surfactant adsorption from the mixture in comparison with surfactant adsorption from individual solutions. The maximum deviation from the ideal was found in the binary solution of surfactants with the highest content of TX-100, when $\alpha_{TX-100} = 0.8$. Probably, in this case, surfactants are adsorbed on the GC both in the form of molecules and ions, and in the form of mixed aggregates.

Table 1.

Total adsorption of TX-100 and SHDS on the surface of GC from binary mixtures of different composition

α_{TX-100}	$A_{exp} \cdot 10^4, \text{M/g}$	$A_{calc} \cdot 10^4, \text{M/g}$
0	4.3	4.3
0.2	3.5	4.1
0.4	4.5	3.9
0.6	5.2	3.6
0.8	5.6	3.4
1.0	3.2	3.2

Experimentally from the data of adsorption isotherms, the concentrations that are necessary to achieve maximum adsorption of surfactants on the surface of the GC were found. The theoretical value of these values for the

ideal state of the system was calculated by the formula [5,12]:

$$1/C_{12} = \alpha_{TX-100}/C_{TX-100} + (1-\alpha_{TX-100})/C_{SHDS}, \quad (3)$$

where C_{TX-100} , C_{SHDS} i C_{12} – concentrations necessary to obtain maximum adsorption on the surface of the GC, determined by the adsorption isotherms of surfactants from individual and binary solutions, respectively; α_{TX-100} – molar fraction of TX-100 in volume of solution.

Fig. 2 Dependencies of concentration required to obtain maximum adsorption on the GC surface in the individual and mixed SAS solutions, on the molar fraction of TX-100 (α); calculated and experimental data.

From Fig. 2 it is evident that experimentally determined concentrations required to achieve maximum adsorption of surfactants from mixtures on the surface of the GC (C_{12}) are lower than those calculated for the ideal state of the system. The most negative deviation of these values is observed with $\alpha_{TX-100} = 0.8$. These data confirm the synergistic effect of TX-100 and SHDS mixtures during adsorption on GC. In order to calculate the composition of mixed adsorption layers of surfactant and parameters of intermolecular interaction, a phase separation model (Rubin-Rosen approach) was used [5, 12]. According to this model, the coefficient of intermolecular interaction in the adsorption layer β^s was estimated by the formula:

$$\beta^s = \frac{\ln \alpha_1 C_{12} / C_1^0 \chi_1}{(1 - \chi_1)^2} \quad (4)$$

where α_1 – molar part of SAS₁ in solution, χ_1 –

molar part of SAS₁ in adsorption layer, C_1^0 and C_{12} – molar concentration of SAS₁ solution and binary mixture with equal adsorption amount.

The composition of adsorption layer was calculated according to [5, 12]:

$$(\chi_1)^2 \ln\left(\frac{\alpha_i C_{12}}{C_1^0 \chi_1}\right) = (1 - \chi_1)^2 \ln\left(\frac{(1 - \alpha_i) C_{12}}{C_2^0 (1 - \chi_1)}\right) \chi (5)$$

Thus, having determined experimentally the concentrations of the mixture and individual surfactants, at which a given adsorption value is reached, the composition of the mixed adsorption layer was calculated for a given adsorption value.

Table 2

Composition of mixed adsorption layers and interaction parameters between SAS molecules on the surface of GC ($A = 1.5 \cdot 10^{-4}$ mol/g)

α_{TX-100}	χ	$-\beta^s$
0	-	-
0.2	0.55	3.1
0.4	0.67	5.3
0.6	0.75	8.4
0.8	0.80	9.5
1.0	-	-

The results of calculations show (Table 2) that the composition of the adsorption layer on the surface of the GC is significantly different from the ratio of surfactants in the solution. The value of the parameter χ indicates that the mixed adsorption layer on the surface of the GC is enriched with non-ionic surfactant molecules, even with a small its content in the solution ($\alpha_{TX-100} = 0.2$). With an increase in the TX-100 molar fraction in the binary solution from 0.2 to 0.8 its share in the adsorption layer increases in approximately 1.5 times. Negative values of the interaction parameters β^s indicate excessive attraction of the molecules and ions of the mixture components in the mixed adsorption layers. An increase in the absolute value of the parameter β^s with an increase in α_{TX-100} in the solution characterizes the enhancement of the

interactions between the components in the adsorption layer.

CONCLUSIONS. Thus, in the course of experiments carried out for mixed systems of SHDS-TX-100, the existence of a synergistic effect in relation to an increase in the adsorption of surfactants on the GC surface was established. It is found that mixed adsorption layers are enriched with molecules of the non-ionic surface active substance of the triton X-100.

АНАЛІЗ МІЖМОЛЕКУЛЯРНИХ ВЗАЄМОДІЙ В ЗМІШАНИХ АДСОРБЦІЙНИХ ШАРАХ ПОВЕРХНЕВО - АКТИВНИХ РЕЧОВИН

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Досліджено адсорбцію бінарних сумішей ПАР різної хімічної природи на поверхні непористого гідрофобного вуглецевого сорбенту при різному співвідношенні ПАР в сумішах. Використано ПАР аніонного та нейонного типу. Нейонна ПАР – оксиетильований октилфенол зі ступенем оксиетильовання $n=9-10$ тритон X-100, аніонна ПАР – натрій гексадецилсульфат. Як непористий вуглецевий сорбент використана графітована сажа.

Виміряно ізотерми адсорбції для розчинів індивідуальних ПАР та їх сумішей при різних мольних співвідношеннях компонентів у вихідному розчині. Мольна доля нейногенної ПАР тритону X-100 в сумішах (α_{TX-100}) складала 0.2, 0.4, 0.6 і 0.8. Ізотерми адсорбції тритону X-100 і гексадецилсульфату натрію на поверхні графітованої сажі мають Ленгмюрівську форму. В змішаних системах ПАР при підвищеному вмісті тритону X-100 ($\alpha_{TX-100}=0.4, 0.6$ і 0.8) виявлено синергетичний ефект, який проявляється в збільшенні величини адсорбції ПАР із суміші порівняно з адсорбцією ПАР із індивідуальних розчинів. Максимальне відхилення від ідеальності встановлено в бінарному розчині ПАР з найбільшим вмістом тритону X-100 ($\alpha_{TX-100} = 0.8$). Визначені експериментально концентрації, не-

обхідні для досягнення максимальної адсорбції ПАР із сумішей, мають менші значення, ніж розрахункові величини для ідеального стану системи.

Для розрахунку складу змішаних адсорбційних шарів ПАР і параметрів взаємодії в них використали модель фазового поділу (підхід Рубіна–Розена). Результати показують, що змішаний адсорбційний шар на поверхні графітованої сажі збагачений молекулами нейонної ПАР навіть при невеликому їх вмісті в розчині ($\alpha_{\text{TX-100}} = 0.2$). При збільшенні мольної частки тритону X-100 в бінарному розчині від 0,2 до 0,8 його частка в адсорбційному шарі зростає приблизно в 1,5 рази. Негативні значення параметрів взаємодії β^s вказують на надмірне притягування молекул та йонів компонентів сумішей у змішаних адсорбційних шарах. Збільшення абсолютної величини параметра β^s зі зростанням $\alpha_{\text{TX-100}}$ в розчині характеризує посилення взаємодій між компонентами в адсорбційному шарі.

К л ю ч о в і с л о в а: поверхнево-активна речовина, адсорбція, адсорбційний шар, графітована сажа.

АНАЛИЗ МЕЖМОЛЕКУЛЯРНЫХ ВЗАИМОДЕЙСТВИЙ В СМЕШАННЫХ АДсорбЦИОННЫХ СЛОЯХ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ

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Исследована адсорбция смесей поверхностно-активных веществ различной химической природы – тритона X-100 и гексадецилсульфата натрия – на поверхности графитированной сажи. С использованием модели фазового разделения (подход Рубина–Розена) рассчитаны состав смешанных адсорбционных слоев и параметры взаимодействия в них между молекулами поверхностно-активных веществ. Установлено, что смешанные адсорбционные слои обогащены

молекулами неионного поверхностно-активного вещества тритона X-100.

К л ю ч е в ы е с л о в а: поверхностно-активное вещество, адсорбция, адсорбционный слой, графитированная сажа.

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