Adsorption of Sodium Hexadecyl Sulfate and Triton X from Binary Aqueous Solutions at Thermally Graphitized Carbon Black

Olga Kochkodan1*, Victor Maksin2, Tetyana Semenenko1

1 Department of General, Organic and Physical Chemistry, National University of Life and Environmental Sciences of Ukraine, Geroiv Oborony Str. 15, 03041 Kyiv, Ukraine
2 Department of Analytical and Bioinorganic Chemistry and Water Quality, National University of Life and Environmental Sciences of Ukraine, Geroiv Oborony Str. 15, 03041 Kyiv, Ukraine
* Corresponding author, e-mail: okochkodan@hotmail.com

Received: 09 October 2019, Accepted: 28 January 2020, Published online: 08 July 2020

Abstract
Adsorption of anionic sodium hexadecyl sulfate (SHS) and nonionic Triton X surfactants with different ethoxylation degree: TX-45, TX-100 and TX-300 from their individual and mixed aqueous solutions at the surface of thermally graphitized carbon black (CB) was studied. It was found that at low solution concentrations addition of the nonionic surfactant increases the amount of SHS adsorbed from SHS/Triton X mixtures compared to SHS amount adsorbed from its individual solution. These findings might be explained by decreasing in electrostatic repulsion between SHS ions due to inclusion of the molecules of the nonionic surfactant in the mixed adsorption layer. At higher solution concentrations, adsorption of SHS decrease as a result of displacement of SHS ions from the mixed adsorption layer by Triton X molecules. It was established that the composition of the mixed adsorption layer at CB surface notably differ from the composition of the surfactant mixture in the bulk solution. The mixed adsorption layer is enriched with the molecules of the nonionic surfactants and this conclusion is confirmed by the results of measuring zeta potential of CB particles with the adsorbed surfactants.

Keywords
mixed adsorption layer, graphitized carbon black, sodium hexadecyl sulfate, Triton X

1 Introduction
Surfactants adsorption at a solution/solid interface is very important phenomenon in many colloid-chemical processes, including flotation of ores, oil recovery, foam forming, detergency, stabilization of the colloids, emulsification, chemical synthesis and water treatment. In many cases the surfactants mixtures are more beneficial than the single surfactants [1–4]. The use of surfactant mixtures allows to more effectively affect the properties of dispersed systems than the individual components. These features are due to the essential variation in the component properties in the mixture, including enhancement or attenuation of surfactants adsorption at an interface. Thus, wetting and adsorption from binary surfactant mixtures at solid surfaces of diverse nature are significantly different compared to the solutions of the individual surfactants [2, 3, 5]. However, there are very limited number of studies related to adsorption of the surfactant mixtures and these studies have been performed mainly on hydrophilic surfaces [6–8]. As a result, it is still challenging to predict the magnitude and mechanism of adsorption of surfactant mixtures at solid surfaces, especially given that adsorption of surfactant mixtures is a complex process affected by many factors such as chemical nature of the surfactant and adsorbent, temperature, feed pH, concentration, etc. [1, 9].

To date, there have been several studies related to the adsorption of different types of the surfactants at hydrophobic solids such as carbon black (CB) in order to improve the aggregation stability of solid powders or to clarify the surfactants adsorption mechanisms [10–12]; however, only few studies related to the adsorption of mixed surfactant systems at CB and activated carbon surfaces have been reported [13, 14–17]. Ridaoui et al. [13] investigated the change of charge of CB particles in mixed aqueous dispersions of polystyrene-polyethylene oxide
copolymers with cetyltrimethyl ammonium chloride. It was shown that the surfactant adsorption depended on type of the surfactant as well as on functional groups at the sorbent surface. The adsorption of the surfactant or polystyrene copolymer at CB surface lead to the electrostatic or steric repulsion of CB particles. Ma and Xia [14] evaluated the effect of the surfactant adsorption on aggregation stability of CB dispersions in binary mixtures of anionic sodium dodecyl sulfate and nonionic etoxylated nonylphenol surfactants. It was shown that the adsorption of sodium dodecyl sulfate essentially dropped when the nonionic surfactant is present in the solution. Bossoleli et al. [15] reported adsorption of sodium polystyrene sulfonates and nonionicethoxylated surfactants (NP-12, NP-40, NP-100) at CB surface. The Langmuir type adsorption isotherms and negative values for adsorption free energies were obtained for all surfactants used.

Liu et al. [16] studied the adsorption of aromatic hydrocarbons in Triton X100 solution at activated carbon. It was shown that the obtained data well fitted to the Langmuir adsorption isotherms and pseudo-second-order kinetics model.

Xiao et al. [17] reported adsorption from binary systems of octyltriethylammonium bromide with sodium dodecylbenzenesulfonate as well as dodecylpyridinium chloride with sodium octanesulfonate at activated carbon. The authors stated that hydrophobic interactions between the surfactants and the sorbent are mainly responsible for the adsorption of these compounds at activated carbon. It was shown synergetic adsorption of the surfactants due to coulombical interactions between the oppositely charged ions of anionic and cationic surfactants [17].

In this work, the adsorption of sodium hexadecyl sulfate (SHS) and p-(1,1,3,3-tetramethylbutyl)-phenoxypolyoxyethylene glycols of Triton X type such as Triton X-45 (TX-45), Triton X-100 (TX-100) and Triton X-305 (TX-305) at CB from the binary surfactants solutions was investigated to reveal main features of the adsorption of the nonionic/anionic surfactant mixtures at the hydrophobic solid surface.

2 Materials and methods

The thermally graphitized CB used in the adsorption studies was purchased from Sigma-Aldrich (USA). The total surface area of CB as was evaluated by BET method with nitrogen adsorption was 105 m² × g⁻¹. Prior to use in experiments CB was washed with deionized water and dried in the oven at 110 °C.

The anionic SHS surfactant of the molecular formula C₆H₁₃SO₄Na and nonionic p-(1,1,3,3-tetramethylbutyl)-phenoxypolyoxyethylene glycols surfactants of the Triton X series of the molecular formula C₆H₁₃C₆H₄O(CH₂CH₂O)ₙH with an average number (n) of ethylene oxide units of 4.5 for TX-45, 9.5 for TX-100, and 30 for TX-305 were obtained from Sigma-Aldrich (USA) and employed as received. The chemical structures of the used surfactants are shown in Fig. 1. The solutions of the surfactants were prepared with distilled water.

For adsorption experiments, 100 mg of CB was added to 50 mL of the surfactant solutions. The dispersions were subject to sonication using a Q500 sonicator probe (Thomas Scientific, USA) for 20 min to disaaglomerate and disperse CB and were left shaken for 24 h at 20 °C and then centrifuged with Eppendorf centrifuge 5810 R at 4000 rpm for 10 min. pH values of surfactant solutions were 6.0–6.5.

The adsorbed amount of the surfactant at CB surface (A, mol × g⁻¹) was calculated from the material balance of the surfactant in the system prior and after adsorption.

Based on the obtained adsorption data and BET surface area of CB particles, the area per adsorbed molecule of the surfactant (ω, m²) at maximum adsorption was calculated using Eq. (1) [18]:

$$\omega = \frac{S}{A_{\text{max}} \times N_A}$$  (1)

where S is the CB surface area (m² × g⁻¹), N_A is the Avogadro number (mol⁻¹), and A_max is the adsorption saturation value (mol × g⁻¹).

The concentrations of the nonionic surfactants in the probes were analyzed by spectrophotometric method by evaluating the optical density of the solution at 274 nm using a Shimadzu UV310 spectrophotometer, while the contents of SHS in the solutions were evaluated by two-phase extraction method with malachite green [19]. In preparing the samples 3 ml of the SHS solution was used and malachite green was added at a 1:1 molar ratio. The pH of the mixture was adjusted to be 5.0 by acetic acid. Ten ml chloroform was added and to the mixture and stirred under shaking for 10 min. Then another 10 ml of chloroform was added and the mixture was

Fig. 1 a) Molecular structures of Triton X and b) SHS surfactants
equilibrated for 20 min. The absorbance of the chloroform phase, in which SHS/malachite green complex was extracted, was measured at $\lambda = 616$ nm [19]. In our preliminary experiments it was found that each surfactant in SHS/Triton X mixtures did not affect the quantification of other component. The measurements errors of the spectrophotometric and two-phase titration methods of evaluation of the surfactants concentrations do not exceed 1 % and 3 %, respectively.

The surfactants solutions were studied within the concentrations of $1.0 \times 10^{-5} – 2.0 \times 10^{-3}$ M. The surfactant mixtures of different composition were prepared by appropriate mixing of the individual surfactant solutions. Triton X mole fractions in the mixtures ($\alpha_{TX}$) were 0.2, 0.4, 0.6 and 0.8.

Mole fractions of Triton X surfactants both in the aqueous solution and at CB surface were evaluated using Eqs. (2) and (3):

$$\alpha_{TX} = \frac{C_{TX}}{C_{SHS} + C_{TX}}$$

$$\chi_{TX} = \frac{A_{TX}}{A_{SHS} + A_{TX}}$$

where $\alpha_{TX}$ and $\chi_{TX}$ are Triton X mole fractions in the mixed solutions and at CB surface, respectively, $C_{TX}$ and $C_{SHS}$ are the concentrations of Triton X and SHS surfactants in the mixed solutions, $A_{TX}$ and $A_{SHS}$ are the adsorption values for Triton X and SHS surfactants at CB surface.

The values of critical micelle concentration (CMC) in the surfactant solutions were evaluated by plotting the solution surface tension ($\sigma$) versus the surfactant concentration ($C$). The CMC value is found from the break point on the $\sigma$(lnC) plot. Measurement of the surface tension ($\sigma$) was carried out by Wilhelmy method with a platinum plate using the tensiometer BT-500 (Analytpryad, Ukraine). The experimental error of the surface tension measurement was ±0.5 mJ × m$^{-2}$.

The surface charge of CB particles before and after surfactants adsorption was evaluated with a Zeta-Meter System 3.0+ (Zeta Meter Inc., USA) by measuring the electrophoretic mobility of dispersed particles and converting it in zeta potential values using the Smoluchowski equation (Eq. (4)) [20]:

$$\zeta = \frac{\mu \times \eta}{\varepsilon}$$

where $\zeta$ is zeta potential (mV), $\mu$ is electrophoretic mobility (m$^2$×s$^{-1}$×V$^{-1}$), $\varepsilon$ is dielectric constant and $\eta$ is viscosity (Pa×s).

Deionized water was used for preparation of CB suspensions. 25 ml of CB suspension at concentration of 100 mg × L$^{-1}$ were used for the experiments at room temperature of 20 °C. The measurement error was 3 %.

Scanning electron microscopy (SEM) QuantaFEG 650 (Thermofisher, USA) operated at 5 KV and high resolution transmission electron microscopy (TEM) Talos (FEI, USA) operated at 200 KV were used for imaging of CB particles.

3 Results and discussion

3.1 SEM and TEM characterization of CB particles

Fig. 2 displays SEM and TEM images of CB particles. The images show that the average diameter of primary CB particles is less than 50 nm and the sizes are not uniform.

3.2 Adsorption of SHS from its single aqueous solutions

The adsorption isotherm of SHS at CB surface is shown in Fig. 3. The SHS amount adsorbed at CB surface sharply increases in the range of equilibrium surfactant concentrations up to $3 \times 10^{-4}$ mol × L$^{-1}$ and attaining a quasi-plateau region at the equilibrium concentration of approximately $6 \times 10^{-4}$ mol × L$^{-1}$ (Fig. 3, curve 1).
The main driving force of SHS adsorption on CB is the hydrophobic driving force \cite{1, 21}. Fig. 3 shows that the maximum adsorbed amount of the anionic surfactant is approximately 0.35 mmol $\times$ g$^{-1}$, which corresponds, as per Eq. (1), to the limiting area of 0.50 nm$^2$ per SHS molecule adsorbed at CB surface.

It was shown that the zeta potential value of CB particles is very low by absolute value (−0.2 mV) in the aqueous solution without the anionic surfactant (Fig. 3). Similarly, Julien et al. \cite{22} reported that the magnitude of zeta potential of the activated carbon treated at 700 °C was close to zero in neutral aqueous solutions. Also it was shown that zeta potential readings for activated carbon particles dispersed in water at pH values of 2–8 were in the range between +0.18 mV to −0.27 mV \cite{17}. Such low values of zeta potential readings indicate a practical lack of chargeable active sites at the sorbent surface \cite{23}.

Adsorption of SHS molecules essentially changes zeta potential of CB particles even at low surfactant concentrations. The absolute values of zeta potential readings were observed to increase steadily with the SHS concentration in the solutions, reaching a plateau value of about −40 mV (Fig. 3). The change in the values of zeta potential of CB particles in the presence of SHS molecules clearly indicates that significant adsorption of the surfactant at CB surface take place. It might be assumed that SHS molecules adsorb with their hydrophobic residues oriented towards the CB surfaces while the anionic groups of the surfactant protrude into the aqueous phase.

The experimental SHS adsorption data were fitted with the Langmuir (Eq. (5)) and Freundlich (Eq. (6)) adsorption isotherm models, which linearized forms can be expressed as follows \cite{24, 25}:

$$\frac{C_e}{A_e} = \frac{1}{A_{\text{max}}} b + \frac{C_e}{A_{\text{max}}}$$  \hspace{1cm} (5)

$$\ln A_e = \ln K_F + \frac{1}{n} \ln C_e$$ \hspace{1cm} (6)

where $A_e$ and $C_e$ are the amount of the surfactant adsorbed per gram of CB and concentration of the surfactant in the solution at adsorption equilibrium, respectively. $A_{\text{max}}$ is the theoretical maximum surfactant adsorption at monolayer coverage, $b$ is the Langmuir adsorption constant related to the affinity between the adsorbent and adsorbate. $K_F$ is the Freundlich constant representing the adsorption capacity and $1/n$ is a constant related to surface heterogeneity and ranges between 0 and 1; the more heterogeneous the surfacae, the closer $1/n$ value is to 0.

The Langmuir model is an ideal adsorption model which assumes that the adsorption takes place at identical homogeneous sites on the adsorbent surface and adsorption is restricted to monolayer formation \cite{24}. The Freundlich isotherm, on the other hand, captures a non-ideal adsorption process on a heterogeneous surface and not restricted to monolayer adsorption \cite{25}.

The regression analysis of $C_e/A_e$ versus $C_e$ data for Langmuir model and $\ln A_e$ versus $\ln C_e$ data for Freundlich model provides parameters of these models (Fig. 4).

To find the best fit model, the statistical parameters such as coefficient of correlation ($R^2$) and sum of square errors (SSE) were used \cite{26} (Eq. (7)):

$$SSE = \sum_{i=1}^{n} \left( A_{\text{exp}} - A_{\text{cal}} \right)^2$$ \hspace{1cm} (7)

where, $A_{\text{exp}}$ and $A_{\text{cal}}$ are the adsorption values obtained from the experiment and the model, respectively.

The calculated and statistical parameters for the adsorption models are listed in Table 1. As can be seen in Table 1 the highest coefficient of correlation ($R^2 = 0.9996$) as well as the smaller value of SSE (0.0004) are derived by fitting

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{adsorption.png}
\caption{Adsorption of SHS at CB: a) Langmuir isotherm model and b) Freundlich isotherms model plots, pH = 6.5.}
\end{figure}

\begin{table}[h]
\centering
\caption{Langmuir and Freundlich isotherm parameters for SHS adsorption at CB}
\begin{tabular}{|c|c|c|}
\hline
\textbf{Langmuir model} & \textbf{Freundlich model} & \\
\hline
$A_{\text{max}}, \text{mmol} \times \text{g}^{-1}$ & 0.369 & 0.392 \\
$K_F, \text{mmol} \times \text{g}^{-1}$ & 0.392 & 0.392 \\
$b, \text{L} \times \text{mmol}^{-1}$ & 25.983 & 1/n \\
$R^2$ & 0.9996 & 0.8691 \\
SSE & 0.0004 & 0.00234 \\
\hline
\end{tabular}
\label{table1}
\end{table}
the equilibrium data with a Langmuir isotherm model. The Freundlich isotherm model showed the lower correlation coefficient ($R^2 = 0.8691$) and the higher values of SSE (0.00234) compared to Langmuir isotherm (Table 1). These findings prove that the adsorption data for SHS on CB are better described by using the Langmuir model. The calculated value of SHS monolayer capacity is near the experimental adsorption capacity (0.35 mmol × g$^{-1}$), indicating an agreement with the Langmuir model.

### 3.3 Adsorption of Triton X surfactants from their single aqueous solutions

Fig. 5 depicts the isotherms of adsorption of TX-45, TX-100 and TX-305 surfactants at CB surface. All three adsorption isotherms have a well-defined horizontal plateau indicating the maximal adsorption value in the region of equilibrium concentrations studied.

Driving forces of adsorption of the octylphenol ethoxylates surfactants at hydrophobic surface of CB are the same as for anionic surfactants [1, 27].

The maximal adsorption values and the area per adsorbed molecule of Triton X surfactants at CB surface are presented in Table 2.

As seen in Fig. 5 and Table 2, adsorption of nonionic surfactants essentially decreases with increasing in a number of ethylene oxide units in the surfactant molecules. Also, the limiting area per the adsorbed nonionic surfactant molecule increases with increasing in ethoxylation degree (Table 2). It was previously reported that the polyethylene oxide residue of Triton X protruded into the bulk solution is the main parameter, which restricts the adsorption of Triton X surfactant [14]. It might be assumed that the adsorption values for TX-100 and TX-305 surfactants are reduced due to the bulky polyoxyethylene chains, which screens the largest areas at the sorbent surface. The conformation of polyoxyethylene chain of the adsorbed nonionic surfactants depend on its length and the long chains could possibly assume a coil conformation in the solution [27, 28].

The experimental adsorption data for Triton X surfactants on CB were fitted with the Langmuir and Freundlich isotherm models and the calculated parameters are displayed in Table 3.

It is evident from Table 3 that the Langmuir model fitted the experimental data better due to higher correlation coefficient ($R^2$) and lower SSE values compared to the Freundlich model.

### 3.4 Mixed adsorption of SHS and Triton X surfactants at CB surface

Fig. 6 show the adsorption isotherms of SHS and Triton X surfactants from their single and mixed solutions. As seen in this Fig. 6, at low surfactant concentrations the presence of Triton X surfactant promotes adsorption of SHS and the amounts of SHS adsorbed at CB from the SHS/Triton X mixtures are higher compared to SDS adsorption from its single solution. These findings might be explained by increasing of SHS adsorption in the presence of Triton X surfactants due to decreasing in electrostatic repulsion between the adsorbed SHS ions after incorporation of the nonionic surfactant molecules into the mixed SHS/Triton X adsorption layer.

Zhou and Rosen [29] and Rosen and Wu [30] previously reported that in a single component solution there is coloumbical self-repulsion between the molecules of the ionic surfactant and steric self-repulsion between the molecules of the nonionic surfactant. Such interactions are reduced by the dilution effect upon mixing the ionic and nonionic surfactants.

The obtained results correlate with previously published data [31] where increased adsorption of anionic \(C_{12}H_{25}OPhSO_3Na\) surfactant from its mixture with the nonionic \(C_{12}H_{25}\text{-N-pyrrolidone}\) than from pure \(C_{12}H_{25}OPhSO_3Na\) solution was reported at hydrophobic polyethylene surface.

It might be also assumed that intensification of intermolecular interactions in SHS/Triton X mixtures could be due to chelation Na$^+$ ions of the anionic surfactant with oxygen atoms in polyoxyethylene chains of Triton surfactants, which possess the lone electron pair [32, 33].

As seen in Fig 6 with further increase in surfactant concentration the amounts of SHS adsorbed at CB from SHS/Triton X mixtures are smaller compared to SHS adsorption from its pure solution. On the other hand, the adsorption

---

**Table 2** Adsorption parameters of Triton X surfactants at CB surface

| Surfactant | $A_{max}$, mmol × g$^{-1}$ | $\omega$, nm$^2$ | CMC, mmol × L$^{-1}$ |
|------------|----------------------------|-----------------|---------------------|
| TX-45      | 0.43±0.03                  | 0.41±0.02       | 0.16±0.02           |
| TX-100     | 0.28±0.02                  | 0.62±0.02       | 0.24±0.02           |
| TX-305     | 0.11±0.01                  | 1.59±0.04       | 0.30±0.02           |
values of the nonionic surfactants from SHS/Triton X mixtures practically do not change at low solution concentrations, but adsorption of Triton X surfactants increase at higher solution concentrations. Obviously in the region of higher surfactant concentrations, the nonionic surfactant displaces the anionic surfactant in the mixed adsorption layer on CB surface.

As seen in Fig. 6, higher adsorption values of SHS and Triton X surfactants were observed in SHS/TX-45 mixture compared to SHS mixtures with TX-100 and TX-305 surfactants. Since Triton X surfactants differ only in length of the oxyethylene chain, it is obvious that its size and macromolecular configuration affect the adsorption value. It might be assumed that the lowest adsorption values in SHS/TX-305 mixture are associated with the bulky polyoxyethylene chain of TX-305 macromolecule, which screens the largest area at the sorbent surface among other Triton X surfactants (Table 2). As was mentioned above long polyoxyethylene chains of Triton X macromolecules can take the coil conformation [34] and therefore limit the packing density of the molecules in the adsorption layer and reduce the adsorption value.

Molar fractions of SHS and Triton X surfactants in the mixed adsorption layer were calculated taking into account the adsorption values of the individual surfactants from their mixtures. Fig. 7 shows that the composition of the mixed adsorption layer at CB surface is notably different from the surfactants composition in the mixed solution. If the molar fractions of the surfactants at CB surface were the same as in the solution, the experimental data would fall in the dashed line in this Fig. 7. The obtained data indicate that the mixed adsorption layer at CB surface is enhanced with the molecules of the nonionic surfactant and the surface molar fraction of Triton X surfactant in the mixed adsorption layer (χ_{TX}) is reduced in the following order: TX-45 > TX-100 > TX-305. These results prove the mole fraction of Triton X in the adsorption layer decreases with increasing in oxyethylation degree of Triton X molecules.

Fig. 8 displays that composition of the mixed adsorption layers correlates with the changes in zeta potential values of CB particles in SHS/Triton X mixed solutions.

| Table 3 Langmuir and Freundlich isotherm parameters for Triton X adsorption at CB |
|---------------------------------|----------------|-----------------|----------------|----------------|
|                                  | TX-45         | TX-100         | TX-305         |                 |
| Langmuir model                  |               |                |                |                |
| A_{max}, mmol x g^{-1}          | 0.506         | 0.330          | 0.107          |                 |
| b, L x mmol^{-1}                | 7.942         | 8.327          | 21.233         |                 |
| R^2                            | 0.9838        | 0.9797         | 0.9966         |                 |
| SSE                            | 0.013         | 0.014          | 0.0007         |                |
| Freundlich model                |               |                |                |                |
| K_f, mmol x g^{-1}              | 0.578         | 0.384          | 0.117          |                 |
| 1/n                            | 0.4735        | 0.4764         | 0.2448         |                 |
| R^2                            | 0.8543        | 0.8414         | 0.8637         |                 |
| SSE                            | 0.0285        | 0.0380         | 0.001          |                 |
The absolute zeta potential value of CB in the mixed surfactant solutions decreases in the presence of non-ionic surfactants compared to the single SHS solution. This effect can be explained by the formation of a mixed SHS/Triton X adsorption layer at the sorbent surface that reduces the absolute value of zeta potential of CB particles.

As seen in Fig. 8, adsorption of TX-45 resulted in the largest change in zeta potential values of CB particles in the surfactant mixtures. This finding might be due to a higher amount of TX-45 adsorbed at CB surface compared to TX-100 and TX-305 surfactants.

4 Conclusions

Adsorption of anionic SHS and nonionic surfactants of Triton X series with different ethoxylation degree: TX-45, TX-100 and TX-300 from their single and mixed aqueous solutions at thermally graphitized CB surface has been studied. It is shown that at low solution concentrations addition of the nonionic surfactant increases SHS adsorption from SHS/Triton X mixtures compared to SHS adsorption from its single solution. These findings are obviously due to decreasing in electrostatic repulsion between SHS ions in the mixed SHS/Triton X adsorption layer as a result of inclusion of the molecules of the non-ionic surfactant. With the increase of solution concentration the amounts of SHS adsorbed at CB from SHS/Triton X mixtures are smaller compared to SDS adsorption from its pure solution.

The adsorption values of the nonionic surfactants from SHS/Triton X mixtures practically do not change at low solution concentrations, while adsorption of Triton X surfactants increase at higher solution concentrations. Obviously at higher concentration of the surfactant mixtures the anionic surfactant in the mixed adsorption layer on CB surface is displaced by the nonionic surfactant.

It was found that the composition of the mixed SHS/Triton X adsorption layer at CB surface is notably different from the surfactants composition in the bulk solution. The mixed adsorption layer is enriched with Triton X molecules and the molar fraction of the nonionic surfactant decreases with increasing in oxyethylation degree of Triton X molecules in a row: TX-45 > TX-100 > TX-305.

Acknowledgement

The work is supported by the Grant from Ministry of Education and Science of Ukraine (Grant No. 110/103-F).

References

[1] Rosen, M. J., Kunjappu, J. T. "Surfactants and Interfacial Phenomena", Jon Willey & Sons, Inc., Hoboken, NJ, USA, 2012. https://doi.org/10.1002/9781118228920

[2] Zhang, R., Somasundaran, P. "Advances in adsorption of surfactants and their mixtures at solid/solution interfaces", Advances in Colloid and Interface Science, 123–126, pp. 213–229, 2006. https://doi.org/10.1016/j.cis.2006.07.004

[3] Elekes, A., Nagy, R., Bartha, L., Vágó, Á. "Comparative Study on Surfactants Mixtures in Aqueous Solution at Atmospheric Pressure and 10bar Reservoir Atmosphere", Periodica Polytechnica Chemical Engineering, 63(3), pp. 508–512, 2019. https://doi.org/10.3311/PPh.12342

[4] Aidarova, S., Bekturganova, N., Kerimkulova, M., Musabekov, K., Sharipova, A. "The influence of surfactants to the stability of coal water suspension", Periodica Polytechnica Chemical Engineering, 58(Supplement), pp. 21–26, 2014. https://doi.org/10.3311/PPh.7300

[5] Chen, L., Xiao, J. X., Ruan, K., Ma, J. "Homogeneous Solutions of Equimolar Mixed Cationic–Anionic Surfactants", Langmuir, 18(20), pp. 7250–7252, 2002. https://doi.org/10.1021/la025878d

[6] Woods, D. A., Petkov, J., Bain, C. D. "Surfactant Adsorption Kinetics by Total Internal Reflection Raman Spectroscopy. 2. CTAB and Triton X-100 Mixtures on Silica", Journal of Physical Chemistry B, 115(22), pp. 7353–7363, 2011. https://doi.org/10.1021/jp201340j

[7] Maňko, D., Zdziennicka, A., Jańczuk, B. "Surface tension of polytetrafluoroethylene and its wetting by aqueous solution of some surfactants and their mixtures", Applied Surface Science, 392, pp. 117–125, 2017. https://doi.org/10.1016/j.apsusc.2016.09.020

[8] Chang, Z., Chen, X., Peng, Y. "The adsorption behavior of surfactants on mineral surfaces in the presence of electrolytes – A critical review", Minerals Engineering, 121, pp. 66–76, 2018. https://doi.org/10.1016/j.mineng.2018.03.002

[9] Musselmann, S. W., Chander, S. "Wetting and adsorption of acetylenic and diol based nonionic surfactants on heterogeneous surfaces", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 206(1–3), pp. 497–513, 2002. https://doi.org/10.1016/S0927-7757(02)00055-9
[10] Gupta, S. D., Bhagwat, S. S. "Adsorption of Surfactants on Carbon Black-Water Interface", Journal of Disperse Science and Technology, 26(1), pp. 111–120, 2005. https://doi.org/10.1081/DIS-200042721

[11] Eisemann, C., Damm, C., Winzer, B., Peukert, W. "Stabilization of carbon black particles with Cetyltrimethylammoniumbromide in aqueous media", Powder Technology, 253, pp. 338–346, 2014. https://doi.org/10.1016/j.powtec.2013.11.051

[12] Kochkodan, O. D., Klimenko, N. A., Karmazina, T. V. "Thermodynamic characteristics of adsorption of non-ionic surfactants onto acetylene carbon black and AG-3 activated carbon", Colloid Journal, 58, pp. 330–334, 1996.

[13] Ridaoui, H., Jada, A., Vidal, L., Donnet, J. B. "Effect of cationic surfactant and block copolymer on carbon black particle surface charge and size", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 278(1–3), pp. 149–159, 2006.

[14] Ma, C., Xia, Y. "Mixed adsorption of sodium dodecyl sulfate and ethoxylated nonylphenols on carbon black and the stability of carbon black dispersions in mixed solutions of sodium dodecyl sulfate and ethoxylated nonylphenols", Colloid and Surfaces, 66(3), pp. 215–221, 1992.

[15] Bossolelti, L., Riccieri, R., Giabrielli, G. "The Adsorption of Polystyrene Sulfonate and Ethoxylated Non-Ionic Surfactants at Carbon Black-water Interface", Journal of Disperse Science and Technology, 16(3–4), pp. 205–220, 1995. https://doi.org/10.1080/01932699508943674

[16] Liu, J., Chen, J., Jiang, L., Yin, X. "Adsorption of mixed polycyclic aromatic hydrocarbons in surfactant solutions by activated carbon", Journal of Industrial and Engineering Chemistry, 20(2), pp. 616–623, 2014. https://doi.org/10.1016/j.jiec.2013.05.024

[17] Xiao, J. X., Zhang, Y., Wang, C., Zhang, J., Wang, C. M., Bao, Y. X., Zhao, Z. G. "Adsorption of cationic–anionic surfactant mixtures on activated carbon", Carbon, 43(5), pp. 1032–1038, 2005. https://doi.org/10.1016/j.carbon.2004.11.039

[18] Zhang, R., Somasundaran, P. "Aggregate Formation of Binary Nonionic Surfactant Mixtures on Hydrophobic Surfaces", Langmuir, 21(11), pp. 4868–4873, 2005. https://doi.org/10.1021/la050058x

[19] Sun, J., Du, K., Fu, L., Gao, J., Zhang, H., Feng, W., Ji, P. "Sodium Hexadecyl Sulfate as an Interfacial Substance Adjusting the Adsorption of a Protein on Carbon Nanotubes", ACS Applied Materials & Interfaces, 6(17), pp. 15132–15139, 2014. https://doi.org/10.1021/am5032715

[20] Marsalek, R., Pospisil, J., Taraba, B. "The influence of temperature on the adsorption of CTAB on coals", Colloids and Surfaces A: Physicochemical and Engineering Aspects, 383(1–3), pp. 80–85, 2011. https://doi.org/10.1016/j.colsurfa.2011.01.012

[21] Parfitt, G. D., Rochester, C. H. "Adsorption from Solution at the Solid/Liquid Interface", Academic Press, London, UK, 1983.

[22] Julien, F., Baudu, M., Mazet, M. "Relationship between chemical and physical surface properties of activated carbon", Water Research, 32(11), pp. 3414–3424, 1998. https://doi.org/10.1016/S0043-1354(98)00109-2

[23] Kitahara, A., Watanabe, A. "Electrical Phenomena at Interfaces: Fundamentals, Measurements, and Applications", Marcel Dekker Inc., New York, NY, USA, 1984

[24] Langmuir, I. "The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids", Journal of the American Chemical Society, 38(11), pp. 2221–2295, 1916. https://doi.org/10.1021/ja02268a002

[25] Freundlich, H. M. F. "Over the Adsorption in Solution", Journal of Physical Chemistry, 57, pp. 385–470, 1906.

[26] Foo, K. Y., Hameed, B. H. "Insights into the modeling of adsorption isotherm systems", Chemical Engineering Journal, 156(1), pp. 2–10, 2010. https://doi.org/10.1016/j.cej.2009.09.013

[27] Kiraly, Z., Findenegg, G. H. "Calorimetric Evidence of the Formation of Half-Cylindrical Aggregates of a Cationic Surfactant at the Graphite/Water Interface", Journal of Physical Chemistry B, 102(7), pp. 1203–1211, 1998. https://doi.org/10.1021/jp972218m

[28] Gellán, A., Rochester, C. H. "Thermodynamics of adsorption of O-n-dodecylpentaneylethylene glycol and O-n-dodecyloctatelethylene glycol from aqueous solutions on to graphitised carbon", Journal of Chemical Society, Faraday Transactions I: Physical Chemistry in Condensed Phases, 81(6), pp. 1503–1512, 1985. http://doi.org/10.1039/F19858101503

[29] Zhou, Q., Rosen, M. J. "Molecular Interactions of Surfactants in Mixed Monolayers at the Air/Aqueous Solution Interface and in Mixed Micelles in Aqueous Media: The Regular Solution Approach", Langmuir, 19(11), pp. 4555–4562, 2003. https://doi.org/10.1021/la020789m

[30] Rosen, M. J., Wu, Y. "Superspreading of Trisiloxane Surfactant Mixtures on Hydrophobic Surfaces. 1. Interfacial Adsorption of Aqueous Trisiloxane Surfactant-N-Alkyl Pyrrolidinone Mixtures on Polyethylene", Langmuir, 17(23), pp. 7296–7305, 2001. https://doi.org/10.1021/la010466a

[31] Zhou, Q., Wu, Y., Rozen, M. J. "Surfactant–Surfactant Molecular Interactions in Mixed Monolayers at a Highly Hydrophobic Solid/Aqueous Solution Interface and Their Relationship to Enhanced Spreading on the Solid Substrate", Langmuir, 19(19), pp. 7955–7962, 2003. https://doi.org/10.1021/la030157f

[32] Goloub, T. P., Pugh, R. J., Zhmud, B. V. "Micellar Interactions in Nonionic/Ionic Mixed Surfactant Systems", Journal of Colloid and Interface Science, 229(1), pp. 72–81, 2000. https://doi.org/10.1006/jcis.2000.6954

[33] Matusbara, H., Ohta, A., Kameda, M., Villeneuve, M., Ikeda, N., Aratono, M. "Interaction between Ionic and Nonionic Surfactants in the Adsorbed Film and Micelle: Hydrochloric Acid, Sodium Chloride, and Tetraethylene Glycol Monooctyl Ether", Langmuir, 15(17), pp. 5496–5499, 1999. https://doi.org/10.1021/la981769g

[34] Levitz, P. E. "Non-ionic surfactants adsorption: structure and thermodynamics", Comptes Rendus Geoscience, 334(9), pp. 665–673, 2002. https://doi.org/10.1016/S1631-0713(02)01806-0