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Mixed adsorption of hexadecylpyridinium bromide and Triton X surfactants at graphitized carbon black

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Abstract: Adsorption of cationic 1-hexadecylpyridinium bromide (HDPB) and non-ionic p-(1,1,3,3-tetramethylbutyl)-phenoxypolyoxyethylene glycols surfactants of the Triton X series (Triton X-45, Triton X-100 and Triton X-305) from their single and mixed aqueous solutions at thermally graphitized carbon black (CB) was studied. It was shown that adsorption of the non-ionic surfactant from its individual solution decreased when a number of ethylene oxide units in the surfactant molecule increased. Addition of the non-ionic surfactants increased the amount of HDPB adsorbed from HDPB/Triton X mixtures. At low solution concentrations it was found that in HDPB/Triton X mixtures, the experimental values of total surfactants adsorption are higher than the adsorption values calculated for the ideal surfactant mixtures. The composition of the mixed HDPB/Triton X adsorption layer and the parameters of the intermolecular interaction ($\beta$) between the components in this layer were calculated by using the Rubingh-Rosen approach. It was shown that $\beta$ parameters have negative values, which indicate notable interactions between Triton X molecules and HDPB ions in the mixed adsorption layer. It was found that the composition of the mixed adsorption layer at CB surface is notably different from the surfactants composition in the bulk solution. The mixed HDPB/Triton X adsorption layer is enriched with Triton X surfactant and the mole fraction of Triton X increases with decreasing of ethoxylation degree of its molecules.

Keywords: adsorption layer, intermolecular interactions, surfactants, Triton X, graphitized carbon black

INTRODUCTION

Adsorption of surfactants at a solid/liquid interface play an important role in numerous industrial and domestic applications, including mineral flotation, oil recovery, wetting, detergency, stabilization of the colloids and nanoparticles, cosmetic and food formulations, in chemical synthesis and water treatment.\textsuperscript{1,2} Usually, the mixtures of the surfactants are employed in these processes.\textsuperscript{2,3} To that end different surfactants are mixed deliberately to prepare the mixture with optimal performance by using synergetic or antagonistic interactions between the components of the mixture.\textsuperscript{1,4} Therefore, understanding the main features of the

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mixed adsorption and the surfactants interactions at solid/liquid interfaces is of vital importance for prediction of the surfactants properties and their application.

While the adsorption from single solutions of the surfactant at a solid/liquid interface has been extensively studied, there are only a limited number of reports related to adsorption from mixed surfactants systems and these studies have been performed mainly at hydrophilic surfaces.

CB is an intense black powder made by incomplete combustion or thermal cracking of carbon-based organic materials. It is widely used as a colour pigment, a reinforced filler in polymers, as an electrode material in batteries and fuel cells, and as a sorbent in wastewater treatment. CB is composed of nanometer-sized primary particles, which form aggregates of various shapes and structures. Typically, the CB particles are strongly hydrophobic and tend to aggregate in water. One of the main approaches to improve the aggregation stability of CB particles in aqueous solutions is by adsorption of surfactants on CB surfaces. The adsorption process depends on numerous parameters, including the molecular structure of surfactants, pH, ionic strength and composition of the aqueous phase. To date, there have been several studies relating to the adsorption of different types of the surfactants at CB in order to enhance the aggregation stability of the CB powders or to clarify the surfactants adsorption mechanisms; however, only a few studies related to the adsorption of mixed-surfactant systems at CB and activated carbon surfaces have been reported.

Ridaoui et al. investigated the change of charge of CB particles in mixed aqueous dispersions of polystyrene-polyethylene oxide copolymers and cetyltrimethyl ammonium chloride. It was shown that the surfactant adsorption depended on the surfactant type. The adsorption of the surfactant or polystyrene copolymer on CB surfaces lead to the electrostatic or steric repulsion of CB particles. Ma and Xia evaluated the stability of CB dispersions in mixed solutions of sodium dodecyl sulfate and ethoxylated nonylphenols. The authors showed that the adsorption of the ionic surfactant essentially dropped in the presence of the non-ionic surfactant. Bossolelti et al. studied the adsorption of sodium polystyrene sulfonates and ethoxylated non-ionic 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. It was assumed that the ethylene oxide chains of the adsorbed non-ionic compounds exhibit coil conformation at CB surface.

Liu et al. studied the adsorption of three polycyclic aromatic hydrocarbons in Triton X100 solution by activated carbon. It was shown that the adsorption data fitted well with the Langmuir isotherm model, Dubinin–Radushkevich isotherm models and pseudo-second-order kinetics model.

Xiao et al. studied adsorption of octyltriethylammonium bromide with sodium dodecylbenzenesulfonate and dodecylpyridinium chloride with sodium
octanesulfonate mixed systems at activated carbon. The authors reported that hydrophobic interactions between the surfactants and activated carbon are mainly responsible for the adsorption of these compounds at the sorbent. It was shown synergetic adsorption of the surfactants due to electrostatic attraction of oppositely charged ions of the anionic and cationic surfactants.

In this work, the adsorption of 1-hexadecylpyridinium bromide (HDPB) and p-(1,1,3,3-tetramethylbutyl)-phenoxypropoxyethylene glycols of the Triton X series 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 has been studied to reveal the main features of the mixed adsorption of cationic and non-ionic surfactants on the hydrophobic solid surface.

MATERIALS AND METHODS

Materials

The CB used in the adsorption studies was purchased from Degussa (Germany) under the brand name Printex XE2. To graphitize CB was thermally treated at 1300 °C for 24 h following the procedure described previously. Prior to use in experiments CB was washed with hexane in a Soxhlet apparatus at 68 °C for 24 h, then washed with ultrapure water until the UV absorbance of the water was less than 0.005 at 258 nm to remove any impurities, before being dried in the oven at 110 °C. The total surface area of the graphitized CB as was evaluated by BET method with nitrogen adsorption was 105 m² g⁻¹.

The cationic HDPB surfactant of the molecular formula C₂₁H₃₈NBr and non-ionic p-(1,1,3,3-tetramethylbutyl)-phenoxypropoxyethylene glycols surfactants of the Triton X series of the molecular formula C₆H₄-(O(CH₂CH₂)n 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 used as received. The chemical structures of the used surfactants are presented in Fig. 1. Distilled water was used for the preparation of the surfactant solutions.

![Chemical structures of HDPB (a) and Triton X surfactants (b)](image)

Methods

For adsorption experiments, 0.1 g of CB was added to 50 mL of the surfactant solutions. The prepared CB suspensions were left shaking for 24 h at 25 °C and then centrifuged at 4000 rpm for 10 min. The pH values of surfactant solutions were 6.0-6.5.

The adsorbed amount of the surfactant (A / mmol g⁻¹) was calculated from the change in the surfactant concentrations, according to the following equation:
where \( C_0 \) and \( C_e \) are the surfactant concentrations (mmol L\(^{-1}\)) in the initial solution and at the adsorption equilibrium, respectively, \( V \) is the volume of the solution (L) and \( m \) is the CB loading in the solution (g).

Based on the adsorption isotherms and BET surface area of the CB particles, the area per adsorbed surfactant molecule \((\omega / m^2)\) at the maximum adsorption was calculated using the equation\(^{24}\):

\[
\omega = \frac{S}{A_{\text{max}} N_A} \tag{2}
\]

where \( S \) is the CB surface area (m\(^2\) g\(^{-1}\)), \( N_A \) is the Avogadro number (mol\(^{-1}\)), and \( A_{\text{max}} \) is the adsorption value at saturation (mol g\(^{-1}\)).

The concentrations of the non-ionic surfactants in the probes were analyzed by spectrophotometric method by measuring the optical density of the solution at 274 nm using a Shimadzu UV310 spectrophotometer, while the contents of HDPB in the solutions were evaluated by two-phase titration method with sodium salt of tetraphenyl borate as titrant and tetrabromophenolphthalein ethyl ester as indicator.\(^{25}\) In our preliminary experiments it was found that each surfactant in the HDPB/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 \(10^{-5} - 2.0 \times 10^{-3}\) 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.

The mole fraction of Triton X surfactants in the aqueous solutions was evaluated using the following equation:

\[
\alpha_{TX} = \frac{C_{TX}}{C_{\text{HDPB}} + C_{TX}} \tag{3}
\]

where \( \alpha_{TX} \) is the mole fractions of Triton X in the mixed solutions, \( C_{TX} \) and \( C_{\text{HDPB}} \) are the concentrations of Triton X and HDPB surfactants in the mixed solutions, mol L\(^{-1}\).

The critical micelle concentration (CMC) values in the surfactant solutions were evaluated by plotting the values of solution surface tension (\(\sigma\)) versus the equilibrium surfactant concentration (\(C\)) values.\(^{26}\) The CMC value is defined as the concentration, which related to the break point on the \(\sigma\) (ln \(C\)) plot. Measurement of the surface tension (\(\sigma\)) was carried out by Wilhelmy method by balancing a platinum plate by using the tensiometer BT-500 (Analytpryld, Ukraine). The experimental error of the surface tension measurement was \(\pm 0.5\) mJ m\(^{-2}\).

The surface charge of the 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 (\(\mu\)) of the dispersed particles and converting it in zeta potential values using the Smoluchowski equation\(^{27}\):

\[
\zeta = \frac{\mu \eta}{\varepsilon} \tag{4}
\]
where $\zeta$ is the zeta potential (mV), $\eta$ is dynamic viscosity (Pa s) and $\varepsilon$ is dielectric constant.

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 %.

RESULTS AND DISCUSSION

Adsorption of HDPB at CB from the single aqueous solution

The adsorption isotherm of HDPB at the CB surface is shown in Fig. 2. The HDPB amount adsorbed at the CB surface increases sharply in the range of equilibrium surfactant concentrations up to $2 \times 10^{-4}$ mol L$^{-1}$ and attaining a quasi-plateau region at the equilibrium concentration of approximately $7 \times 10^{-4}$ mol L$^{-1}$ (Fig. 2, curve 1).

Fig. 2. Adsorption isotherms of HDPB (1) at CB and zeta potential ($\zeta$) of CB particles in aqueous HDPB solutions (2), pH 6.5

Adsorption of HDPB is mainly due to the hydrophobic interactions between the alkyl chains of the surfactant molecules and the CB surface. It might be also assumed that interactions between the positively charged HDPB$^+$ ions and $\pi$ electrons of the graphite lattice of the CB surface also contribute to the adsorption of the cationic surfactant, similarly as it was suggested previously for adsorption of cationic cetyltrimethylammonium bromide on the CB particles in aqueous solutions. As seen in Fig. 2, the maximum adsorbed amount of the cationic surfactant is approximately 0.46 mmol g$^{-1}$, which corresponds, as per equation 2, to the limiting area of 0.38 nm$^2$ per HDPB molecule adsorbed at the CB surface.

It was shown that the zeta potential value of CB particles is very low (0.2 mV) in the aqueous solution without the cationic surfactant (Fig. 2, curve 2). Similarly,
Julien et al.\textsuperscript{29} 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 of activated carbon particles in water at different pH values of 2-8 were in the range between +0.18 mV to -0.27 mV.\textsuperscript{22} Such low values of zeta potential indicate a practical lack of chargeable active sites at the sorbent surface.\textsuperscript{30} Adsorption of HDPB molecules essentially changes zeta potential of the CB particles even at low surfactant concentrations. Zeta potential values were observed to increase with raising HDPB concentration in the solutions, reaching a plateau value of about +48 mV (Fig. 2, curve 2). These findings prove that HDPB molecules adsorb by their hydrophobic alkyl parts at the CB surfaces while the cationic groups protrude into the aqueous phase.

\textit{Adsorption of Triton X surfactants at CB from single aqueous solutions}

Figure 3 depicts the adsorption isotherm 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 HDPB.\textsuperscript{2,31}

![Fig. 3. Adsorption isotherms of Triton X surfactants at CB and zeta potentials of CB particles in aqueous Triton X solutions, pH 6.5](image)

As seen in Fig. 3, adsorption of non-ionic TX-45 at the CB surface had little effect on the magnitude of \( \zeta \)-potential of CB particles. Similar zeta potential values were also observed for CB particles after the adsorption of TX-100 and TX-305 surfactants (Fig. 3).
The maximal adsorption values and the limiting area per adsorbed molecule for the Triton X surfactants are presented in Table 1.

**TABLE I. Adsorption parameters of Triton X surfactants at CB surface**

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$A_{\text{max}}$ / mmol g$^{-1}$</th>
<th>$\omega$ / nm$^2$</th>
<th>CMC, mmol L$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TX-45</td>
<td>0.43±0.03</td>
<td>0.41±0.02</td>
<td>0.16±0.02</td>
</tr>
<tr>
<td>TX-100</td>
<td>0.28±0.02</td>
<td>0.62±0.02</td>
<td>0.24±0.02</td>
</tr>
<tr>
<td>TX-305</td>
<td>0.11±0.01</td>
<td>1.59±0.04</td>
<td>0.30±0.02</td>
</tr>
</tbody>
</table>

As can be seen in Fig. 3 and Table 1, the adsorption value for the non-ionic surfactants essentially decreases when the length of the polyoxyethylene chain in the surfactant molecules increases. In accordance, the limiting area per the adsorbed non-ionic surfactant molecule increases with increasing the length of the polyoxyethylene chain (Table 1). 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. The conformation of polyoxyethylene chain depend on its length and the long chains could possibly assume a coil conformation in the solution.

*Mixed adsorption of HDPB and Triton X surfactants at CB surface*

Figure 4 shows the experimental isotherms of total surfactant adsorption of HDPB/Triton X mixtures at CB surface and the isotherms of total adsorption of the surfactant mixtures calculated from the additivity assumption, as was previously described:

![Adsorption isotherms of single HDPB and Triton X surfactants as well as the isotherms of total adsorption (experimental and calculated from equation 6) of HDPB/Triton X mixtures at CB; $\alpha_{\text{TX}} = 0.6$.](image)

Fig. 4. Adsorption isotherms of single HDPB and Triton X surfactants as well as the isotherms of total adsorption (experimental and calculated from equation 6) of HDPB/Triton X mixtures at CB; $\alpha_{\text{TX}} = 0.6$. 

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*On Line First*
\[ A_{\text{calc}} = \alpha_{\text{TX}} A_{\text{TX}} + (1 - \alpha_{\text{TX}}) A_{\text{HDPB}} \] (5)

where \( A_{\text{calc}} \) is calculated value of total ideal adsorption from the surfactant mixtures, \( \alpha_{\text{TX}} \) is the mole fractions of Triton X in the mixed solutions, \( A_{\text{TX}} \) and \( A_{\text{HDPB}} \) are the adsorption values for Triton X and HDPB surfactants from their single solutions at CB surface.

As seen in Fig. 4, in the studied concentration region the experimental values of total adsorption of the surfactants in HDPB/Triton X mixtures, are higher than the calculated values for ideal adsorption. These findings might be explained by increasing in electrostatic repulsion between the adsorbed HDPB ions because of incorporation of the non-ionic surfactant molecules into the mixed HDPB/Triton X adsorption layer. Previously Zhou and Rosen\(^3\)\(^4\) reported higher adsorption of ionic \( \text{C}_4\text{H}_9\text{OPhSO}_3\text{Na} \) surfactant from the mixture with the non-ionic \( \text{C}_{12}\text{H}_{25}\text{N-pyrrolidone} \) at hydrophobic polyethylene surface compared with the anionic surfactant adsorption from its single solution. Schwuger and Smolka\(^3\)\(^5\) also showed that adsorption of ionic sodium dodecylsulfate at activated carbon surface increased in the presence of non-ionic \( p\)-octylphenol-polyglycol ethers at low surfactants concentration.

Also, adsorption of the non-ionic surfactant might increase due to decreasing in steric repulsion between the hydrophilic groups of Triton X molecules in the mixed adsorption layer after inclusion of the ionic surfactant. Zhou and Rosen\(^3\)\(^7\) previously reported that in a single component solution there is electrostatic self-repulsion of the molecules of the ionic surfactant and steric self-repulsion of the molecules of the non-ionic surfactant, whose magnitude depends on the size of its hydrophilic group. These interactions are attenuated by the dilution effect upon mixing the ionic and non-ionic surfactants.\(^3\)\(^5\) Ivanova \textit{et al.}\(^3\)\(^8\) also reported increasing of the adsorption values in the mixtures of cationic dodecylpyridinium bromide with TX-100 surfactant at hydrophobized SiO\(_2\) both before adsorption saturation and when the saturated adsorption layer was formed.

As seen in Fig. 4, higher total adsorption values were observed in HDPB/TX-45 mixture compare to HDPB/TX-100 and HDPB/TX-305 ones. Since Triton X surfactants differ only in the length of the polyoxyethylene chain, it is obvious that its size and macromolecular configuration affect the adsorption value. It might be assumed that the lowest adsorption values in HDPB/TX-305 mixture are associated with the larger size of polyoxyethylene chain of TX-305 surfactant compare to TX-45 and TX-100. The increased spatial requirements for the lengthy polyoxyethylene chain increase the average surface area occupied by the surfactant molecule\(^3\)\(^2\) and thus reduce the total adsorption value.

To have better insight into the adsorption data in HDPB/Triton X mixtures, the calculation of intermolecular interactions between the components at the CB surface/solution interface was performed.
One of the most widely accepted and used to study the intermolecular interactions in surfactant mixtures, is the Rubin-Rosen model, which is based on the theory of regular solutions.\textsuperscript{39,40} In this model the interaction between the two different molecules of surfactants can be evaluated by the dimensionless parameter $\beta$, which can be calculated as:

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

(6)

where $E_{11}$, $E_{22}$, $E_{12}$ are the interaction energies between the single molecules of surfactant 1, surfactant 2, and molecules of surfactant 1 and surfactant 2, respectively. Negative $\beta$ values indicate attractive interaction, while positive values indicate repulsive interaction between the different surfactants molecules.

Previously it was shown\textsuperscript{36,41} that mixed adsorption layers are formed at solid surface at adsorption of the surfactants mixture. According to the Rubin-Rosen approach, the interaction parameter $\beta$ in a mixed adsorption layer can be calculated by using the following equations\textsuperscript{41}:

$$\chi_1^2 \ln \left( \frac{\alpha_1 C_{12}^0}{C_1^0 \chi_1} \right) = (1-\chi_1)^2 \ln \left( \frac{(1-\alpha_1) C_{12}^0}{C_2^0 (1-\chi_1)} \right)$$

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

(7) \quad (8)

where $\alpha_1$ is the molar fraction of Triton X in the solution, $\chi_1$ is the molar fraction of Triton X in a mixed adsorption layer at the solid/liquid interface, $C_1^0$, $C_2^0$ and $C_{12}$ are the molar concentrations of Triton X, HDPB and their mixtures, respectively, which are evaluated by using the experimental adsorption isotherms from the single and mixed surfactant solutions, respectively. The calculations were conducted as previously described\textsuperscript{34}.

Equation 7 is solved numerically to receive $\chi_1$ value, which is then substituted in equation 8 to calculate the interaction parameter $\beta^s$ between the molecules of Triton X and HDPB in the mixed adsorption layer. The results show (Table 2) that the composition of the adsorption layer at the CB surface differs essentially from the bulk composition of the surfactants in the solution. Data presented in Table 2 indicate that, the mixed HDPB/Triton X adsorption layer at CB surface is enriched with the molecules of the non-ionic surfactant. The parameter of intermolecular interaction $\beta^s$ has negative meanings, which indicate attractive intermolecular interactions between the components in the mixed adsorption layer. This can be explained by the presence of hydrophobic interactions between the alkyl groups of HDPB and Triton X molecules, as well as by ion dipole interactions between the head groups of the non-ionic and cationic surfactants. It is known that the attractive dispersion forces between hydrophobic parts of the surfactants molecules largely contribute to their intermolecular interactions.\textsuperscript{2} Also, the possibility of ion-dipole
interactions between the hydrophilic groups of cationic and nonionic surfactants was previously reported. Oxygen atoms in polyoxyethylene chains of the non-ionic surfactants possess unpaired electrons, which can coloumbically interact with the ions of the cationic surfactant.41

TABLE II. Parameter $\beta^*$ and mole fractions of TX-45 in the bulk solution ($\alpha_{TX,45}$) and in the mixed adsorption layer at CB surface ($\chi_{TX,45}$)

<table>
<thead>
<tr>
<th>$\alpha_{TX,45}$</th>
<th>$\beta^*$</th>
<th>$\chi_{TX,45}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>-</td>
<td>0.00</td>
</tr>
<tr>
<td>0.2±0.01</td>
<td>-6.47±0.20</td>
<td>0.40±0.02</td>
</tr>
<tr>
<td>0.4±0.02</td>
<td>-6.75±0.20</td>
<td>0.67±0.03</td>
</tr>
<tr>
<td>0.6±0.03</td>
<td>-8.28±0.30</td>
<td>0.85±0.04</td>
</tr>
<tr>
<td>0.8±0.04</td>
<td>-5.43±0.20</td>
<td>0.90±0.04</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Triton X mole fractions both in the mixed adsorption layer ($\chi_{TX}$) and in the mixed solutions ($\alpha_{TX}$) are shown in Fig. 5. If the surfactant composition at the CB surface were the same as in the solution, the experimental data would fall in the dashed line in this Figure. As seen for all non-ionic surfactants $\chi_{TX}$ values are larger than $\alpha_{TX}$, hence the molecules of non-ionic surfactants are present in excess at the CB surface. At the same $\alpha_{TX}$ values the mole fraction of Triton X surfactants in the mixed adsorption layer decreases in the following order: TX-45>TX-100>TX-305. These findings indicates that the mole fraction of Triton X surfactant in the mixed HDPB/Triton X adsorption layer decreases with increasing in ethoxylation degree of the non-ionic surfactant molecules.

![Fig. 5. Mole fractions of Triton X in the mixed adsorption layer ($\chi_{TX}$) at the CB surface versus Triton X mole fractions ($\alpha_{TX}$) in the mixed solution with HDPB](image-url)
As seen in Fig. 6, the positive zeta potential value of +46 mV of CB particles in the single HDPB solution decreases in the mixed solutions in the presence of the non-ionic surfactants. This effect might be explained by formation of the mixed adsorption layer, which consist of HDPB and Triton-X molecules at the sorbent surface that reduces the zeta potential values of CB particles. Adsorption of TX-45 surfactant at CB resulted in the most pronounced decreasing in zeta potential values of the sorbent particles (Fig. 6). This finding might be due to higher amount of TX-45 adsorbed at CB surface compared to TX-100 and TX-305 surfactants.

CONCLUSION

Adsorption of cationic HDPB and non-ionic surfactants of Triton X series with different ethoxylation degree: TX-45, TX-100 and TX-305 from their single and mixed aqueous solutions at thermally graphitized CB surface has been studied. It has been found that addition of the non-ionic surfactant increases the value of HDPB adsorption from HDPB/Triton X mixtures compared to HDPB adsorption from its single solution. It is shown that at low solution concentrations the experimental values of total surfactant adsorption in HDPB/Triton X mixtures at CB are higher than the calculated values for total ideal adsorption in the surfactants mixtures. This is obviously due to decreasing in electrostatic repulsion between the HDPB ions, as well as to reducing in steric repulsion between the polyoxyethylene chains of Triton X molecules in the mixed HDPB/Triton X adsorption layer because of inclusion of the molecules of the counterpart surfactant. Using the Rubingh-Rosen approach, the composition of
mixed HDPB/Triton X adsorption layer and the parameters of intermolecular interaction between the components ($\beta$) in this layer were calculated. It is shown that the $\beta$ parameters have negative values, which indicate notable interactions between Triton X molecules and HDPB ions in the mixed adsorption layer. It was found that the surfactants composition in the bulk solution is notably different from the composition of the mixed HDPB/Triton X adsorption layer at CB surface. The mixed adsorption layer is enriched with Triton X molecules and the molar fraction of the non-ionic surfactant decreases in a row: TX-45>TX-100>TX-305. Therefore, the more hydrophobic is the molecule of the non-ionic surfactant the higher its molar fraction in the mixed HDPB/Triton X adsorption layer at CB surface.

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