Surface modification of activated carbon by surfactants mixtures

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Abstract. Adsorption of surfactants is widely used for surface modification of different materials. Using of the mixtures of the surfactants in many cases is more attractive compared with single surfactants, however composition of mixed adsorption layers at solid surface was not sufficiently studied yet. In this work, the mutual effect of anionic and nonionic surfactants on the composition of the mixed adsorption layer on the surface of activated carbon (AC) was studied. Sodium hexadecyl sulphate (SHS) and oxyethylated octylphenol Triton X100 (TX-100) were used as anionic and nonionic surfactants, respectively. Mixed SHS/TX-100 systems have been studied over a concentration range of 0.1 -8.0 mmol/L and the molar fractions of SHS in the mixtures were within 0.2-0.8. It was shown that the adsorption isotherms of SHS or TX-100 surfactants at AC could be described by the Langmuir equation. For surfactants mixtures at low equilibrium concentrations, it was found that adsorption of SHS increases when TX-100 is present in the solution. This might be explained by the decreasing of electrostatic interactions between the head groups of SHS molecules in the mixed adsorption layers due to incorporation of the molecules of the nonionic surfactant. At higher total surfactant concentrations, SDS adsorbed at AC surface is replaced by TX-100 molecules and as result the nonionic surfactants is preferentially adsorbed on AC.

Keywords: Activated carbon; surface layer; sodium hexadecyl sulphate; Triton X100

1. Introduction
Adsorption of surfactants is widely used for surface modification of different materials in numerous industrial processes such as flotation, enhanced oil recovery, lubrication [1]. In many cases the surfactants mixtures are more beneficial than the single surfactants [1,2]. Because of broad usage, about 10 million ton of surfactants are produced annually [3]. As a result of the massive production the surfactants could enter and pollute surface and ground waters negatively affecting the environment [4]. To optimize the practical application of the surfactants and their removal from water it is important to investigate the processes, which occur at the solid-liquid interface in the surfactants mixtures. Activated carbon (AC) is widely used in different application and it is the most important sorbent for adsorptive removal of toxic pollutants from water [5]. Surface modification of the AC with surfactants, which is widely used to enhance removal of the contaminants, is based on deposition of surfactants nanolayers at AC [6]. The properties of the prepared composite AC/surfactants materials largely
depends on the structure of the adsorbed surfactants layers [1,6]. It should be mentioned that numerous studies on adsorption of different types of the surfactants from single surfactant aqueous solutions on AC and features of the adsorbed layers of single surfactants are available in the literature [1, 7-10], however only few papers are related to mixed surfactants systems on AC [11, 12]. Xiao et al. [11] studied adsorption of octyltriethylammonium bromide with sodium dodecylbenzenesulfonate and dodecylpyridinium chloride with sodium octanesulfonate mixed systems at AC. The authors reported that hydrophobic interactions between the surfactants and AC are mainly responsible for the adsorption of these compounds at the sorbent. It was also shown synergetic adsorption of the surfactants due to the electrostatic interaction between oppositely charged ions of the anionic and cationic surfactants [11]. On the other hand, Gao at al. [12] found that adsorption of the nonionic surfactant on AC decrease in the presence of cationic cetyltrimethylammonium bromide.

In this work, the adsorption of anionic sodium hexadecyl sulfate (SHS) and nonionic octylphenol ethoxylate Triton X100 (TX-100) surfactants from their mixed solutions has been studied. This work aims to provide better understanding of surfactant interactions at the surface of AC to optimize such interactions.

2. Materials and methods

AC of AG-3 type was used as a sorbent. To remove inorganic impurities AC was treated with 2M solutions of HNO
3
 and with concentrated HF. Then the samples were washed with distilled water and dried at 105 °C. The total pore volume, volume of micropores, volume of mezopores and total surface area of AC were 2.9×10
-4
 m
3
/kg, 2.6×10
-4
 m
3
/kg, 3.0×10
-5
 m
3
/kg and 6.7×10
-5
 m
2
/kg, respectively, as was evaluated by benzol adsorption. AC with a grain size of 0.50-0.63 mm was used in the experiments. SHS and TX-100 surfactants were obtained from Sigma-Aldrich (USA).

For adsorption experiments, weighted amounts (0.1-0.3 g) of AC were added to surfactant solutions. The prepared AC dispersions were left shaking for 40 h at 25 °C and then centrifuged at 4000 rpm for 10 min. The surfactant solutions were prepared at pH 6.0-6.5.

The adsorbed amount of the surfactant (A, mmol/g) was evaluated from the change in the surfactant concentrations as follows:

\[
A = \frac{(C_0 - C_e)V}{m}
\]  

where \(C_0\) and \(C_e\) are the surfactant concentrations (mmol/L) in the initial solution and in the equilibrium solution, respectively, \(V\) is the volume of the solution (L) and \(m\) is the AC loading in the solution (g).

TX-100 concentration in the solutions was analyzed spectrophotometrically by measuring the optical density of the solutions at 274 nm, while SDS content in the probes was evaluated by two-phase titration method [13].

The mole fractions of SHS surfactant on the AC surface and in the aqueous solutions were evaluated using the following equations:

\[
\chi = \frac{A_{SHS}}{A_{SHS} + A_{TX-100}} 
\]

\[
\alpha = \frac{C_{SHS}}{C_{SHS} + C_{TX-100}} 
\]

where, \(\chi\) and \(\alpha\) are the mole fractions of SHS on AC surface and in the mixed equilibrium solution, respectively, \(A_{TX-100}\) and \(A_{SHS}\) are the adsorption values for TX-100 and SHS surfactants at AC surface, \(C_{TX-100}\) and \(C_{SHS}\) are the concentrations of TX-100 and SHS surfactants in the mixed equilibrium solution.
The surface charge of the AC particles was evaluated with a Zeta-Meter System 3.0+ by using the Smoluchowski equation:

\[ \zeta = \frac{M \eta}{\varepsilon} \]  

(4)

where \( \eta \) is the zeta potential (mV), \( \eta \) is dynamic viscosity (Pa s) and \( \varepsilon \) is dielectric constant. The measurements were performed at the solution pH values of 6.0-6.5.

3. Results and discussions

3.1. Adsorption of SHS and TX-100 from their single aqueous solutions

As seen in Fig. 1, the adsorption isotherm of SHS and TX-100 on AC surface follows the Langmuir type with a well-defined horizontal plateau in the neighborhood of their respective critical micelle formation concentration values. The amounts of the adsorbed surfactants increase sharply with the surfactant concentration attaining at the equilibrium concentration of approximately 0.6 mmol/L for SHS (Fig. 1a) and 0.35 mmol/L for TX-100 (Fig. 1b). The strong adsorption of SHS and TX-100 is due to the hydrophobic interactions between the alkyl residue of the surfactants molecules and graphite lattice at AC surface, which are recognized as the main force involved in the surfactant adsorption at AC [7-9]. The maximum adsorbed amounts of SHS and TX-100 on AC are approximately 0.28 and 0.45 mmol/g, respectively.

![Figure 1](image_url)  

Figure 1. Adsorption isotherms and zeta potentials of AC particles in single SHS (a) and TX-100 (b) surfactants solutions. pH 6.5.

As seen in Fig. 1, zeta potential of AC particles is very low (-0.4 mV) in an aqueous solution without the anionic surfactant. Similarly, Julien et al. [14] showed that the zeta potential of AC treated at 700 °C was close to zero. Adsorption of SHS molecules essentially changes zeta potential of AC particles even at low surfactant concentrations. Zeta potential values were observed to decrease steadily with the SHS concentration in the solutions, reaching a plateau value of about -45 mV (Fig. 1a). The change in the values of zeta potential of AC particles in SHS presence clearly indicates that significant adsorption of the surfactant at the AC surface take place. There is also a good correlation between the adsorbed amount of the anionic surfactant and values of zeta potential of the AC particles (Fig 1a). It might be assumed that SHS molecules adsorb with their hydrophobic residues oriented towards the AC surfaces while the anionic groups of the surfactant protrude into the aqueous phase. In contrast, as TX-100 is a nonionic surfactant its adsorption at the AC surface has practically no effect on \( \zeta \)-potential of AC particles (Fig. 1b).
3.2. Mixed adsorption of SHS and TX-100 at AC

Figure 2 presents the adsorption values of SHS on AC surface in the mixed surfactant solutions at different mole fraction of SHS in the solutions. It should be noted that at low total solution concentrations the values of SHS adsorbed from the binary mixtures are higher compare to SHS adsorption from its single solution. It means that SHS adsorption increase in the presence of TX-100. The larger SHS mole fraction in the mixture, the higher SHS adsorption and the larger is the total surfactant concentration at which this effect happen. These findings might be explained by that fact that the embedding of the molecules of the nonionic surfactant in the adsorption SHS layer reduce the electrochemical repulsion between the negatively charged head groups of SHS molecules. This results in higher adsorption of the anionic surfactant from SHS/TX-100 mixture, than that observed in single SHS solution.

In contrast, at higher total surfactants concentration, the amount of SHS adsorbed from the binary mixtures is lower compare to SHS adsorption from its single solution. At higher total concentration the ionic surfactant is possibly displaced by the nonionic on AC surface. The displacement is higher at larger mole fraction of nonionic surfactants in the solution (Figure 2). This means that interaction of the nonionic surfactant to AC surface is stronger compare to that one for SHS.

Figure 2. Adsorption of SHS on AC from mixed surfactants solutions at different mole fraction (α) of SHS in the mixture.

Figure 3. SHS mole fraction on AC surface versus SHS mole fraction in the solution at different total concentration of the surfactants mixture.

Figure 3 shows that, a mole fraction of SHS at AC surface essentially varies at different concentrations of the surfactants mixture. If the surfactant composition on AC surface were the same as that in the bulk solution, the experimental points would fall in the median line in the Figure 3. It seems that at low total concentration of SHS/TX-100 mixture (0.1 mmol/L) and at a high SHS mole fraction in the solution (α> 0.5) the adsorption layer is enriched with SHS molecules. This might be due to smaller electrostatic repulsion between the negatively charged head groups of SHS owing to incorporation of nonionic TX-100 molecules in the mixed adsorbed layer. As was discussed above, an increase of the concentration of nonionic surfactants in the mixture leads to displacement of anionic surfactant from AC surface and this will reduce SDS mole fraction in the mixed adsorption layer. For relatively low total surfactants concentration (0.1 mmol/L) and at the SHS mole fraction in the solution of 0.5, the mixed adsorption layer is formed from equal amounts of both surfactants. At higher surfactant concentration (0.3 mmol/L), SHS adsorbed at AC is more efficiently replaced by TX-100 molecules and as a result the mixed adsorption layer is enriched with the molecules of the nonionic surfactant.

4. Conclusions

Composition of the adsorption layers on AC surface in single and mixed solutions of SHS and TX-100 surfactants have been studied. The presented data indicates that the surfactants adsorption from their single solutions is of Langmuir type. The results show that the surfactants composition at the AC surface differs essentially from the solution composition of the surfactants. At low concentrations of
the surfactants mixture, SHS adsorption is higher in the presence of nonionic surfactant compare to SHS adsorption in the single solution. Obviously, incorporation of the molecules of the nonionic surfactant in the mixed adsorption layer will reduce electrochemical repulsion between the charged hydrophilic groups of the anionic surfactant and thus promoting SHS adsorption. At higher total surfactants concentration in the solution, the amount of the adsorbed SHS from the binary mixtures is lower compare to SHS adsorption from its single solutions due to displacement of the ionic surfactant from AC surface by the nonionic counter partner.

Acknowledgement
O. Kochkodan, N. Antraptseva and V. Maksin gratefully acknowledge the support of Ministry of Education and Science of Ukraine (Grant No. 110/103-F).

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