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Effect of inorganic electrolyte concentration on anionic-cationic adsorption films.
Part 3: Dodecylpyridinium chloride + sodium octylsulfonate + sodium chloride

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Abstract: The effect of sodium chloride concentration on the simultaneous adsorption of dodecylpyridinium chloride ($R_{12}PyCl$) and sodium octylsulfonate (R_8SO_3Na) on the free surface of their aqueous solutions has been examined. The composition of mixed films adsorbed from equimolar solutions has been determined on the basis of the Gibbs adsorption equation as well as by using the regular solution model. It has been stated that this composition is dependent on the surface tension value (the degree of the surface coverage) as well as on the concentration of added inorganic electrolyte. The same factors influence the value of the interaction parameter β, which negative values indicate a strong attraction between the components in the mixed monolayer.

Key words: Dodecylpyridinium chloride – sodium octylsulfonate – anionic-cationic adsorption films – composition of mixed films – regular solution model

Introduction

The surfactants used in practical applications are usually mixtures of surface active components. This is due, not only to very high costs of pure substances production, but also to the fact that the surfactant mixtures show in many practical applications much better properties than those of their individual components. Therefore, investigations of the surface properties of surfactant mixtures are very important. The mixtures of anionic and cationic surfactants show most interesting surface behavior among mixtures of different types of surfactants. These mixtures distinguish a large synergism in surface tension reduction [1–5, 7–9] and they form mixed adsorption films showing strong deviations from ideality [3–9]. Behavior of these films is well described by a regular solution model, according to which the activity coefficients of the components in the mixed monolayer are given by the following equations [3–5, 7–11]:

$$f_1 = \exp(\beta x_2^2), \quad f_2 = \exp(\beta x_1^2) , \qquad (1)$$

where x_1, x_2 are the surface mole fractions of the components and β is a parameter characterizing mutual interactions of the components in the mixed monolayer. If the interactions between monolayer components are attractive, the value of β is negative, whereas in the case of repulsive interactions, the value of β is positive. The stronger the components interaction the larger is the absolute value of β ($\beta = 0$ in the case of the ideal mixed monolayer).

By using the regular solution model of the mixed monolayer its composition may also be determined on the basis of the equation [4, 5, 9–11]:

$$\beta = \frac{\ln(\alpha_1 c_{12}/x_1 c_1^0)}{x_2^2} = \frac{\ln(\alpha_2 c_{12}/x_2 c_2^0)}{x_1^2} , \qquad (2)$$

where α_1, α_2 are the mole fractions of the components in the solutions and c_1^0, c_2^0, c_{12} are the concentrations of the individual surfactants and their mixture, respectively, required to produce a given value of the surface tension. The surface mole fractions determined in this way are usually in good agreement with those obtained on the basis of the Gibbs surface excesses [5, 10, 12].

Owing to electrostatic interactions between adsorbed components the properties of anionic-cationic films are dependent on the concentration and type of inorganic electrolyte present in the solution [5, 13–18]. In this paper the effect of sodium chloride concentration on the composition and mutual interactions in mixed films adsorbed from solutions containing equimolar amounts of dodecylpyridinium and octylsulfonate ions has been investigated. The present results are compared with those obtained previously [5, 13, 15] for other mixtures of anionic and cationic surfactants. The composition of mixed monolayers is determined on the basis of the Gibbs adsorption equation as well as by using the regular solution model.

Experimental

The solutions investigated contained dodecylpyridinium chloride ($R_{12}PyCl$) as a cationic substance and sodium octylsulfonate (R_8SO_3Na) as an anionic surfactant. The methods of purification of these substances have been described in previous papers [19, 20]. In order to prepare the solutions, four times distilled water was used, which was boiled down to two-thirds of its volume immediately before being used in order to remove CO_2 and any other volatile contaminations which might be present.

In order to obtain a definite value of the ionic strength, suitable quantities of sodium chloride were added to the solutions. This inorganic electrolyte contains ions common with the examined cationic (Cl^-) as well as anionic (Na^+) surfactants.

The surface tension of the solutions was measured by using the drop weight method at constant temperature (25 °C). The time of the drop formation (1 min) was chosen empirically so as to attain the equilibrium value of the surface tension. The measurement's accuracy was ± 0.1 mN/m.

Results and discussion

Determination of the composition of anionic-cationic adsorption films on the basis of the Gibbs adsorption equation

The composition of monolayers adsorbed from solutions containing anionic and cationic surfactant may be determined by calculation of the values of surface excesses for both types of surface-active ions on the basis of the Gibbs adsorption equation. For this purpose the surface tension measurements were carried out for each ionic strength value (0.003, 0.01 and 0.03 M NaCl) for seven series of solutions with fixed concentrations of the cationic substance ($R_{12}PyCl$). Each series consisted of seven solutions differing in their concentration of the anionic substance (R_8SO_3Na). The concentrations have been selected in such a way that the *i*-th solution in the *i*-th series contains equimolar amounts of both surfactants. Previously [21] the same measurements were carried out for the concentration of NaCl equal to 0.1 M. The obtained results are presented, as an example, for the ionic strength equal to 0.003 M in Figs. 1a, b.

For systems investigated the Gibbs adsorption equation may be written in the following form:

$$d\pi = RT(\Gamma_{R_{12}Py^+}\, d\ln a_{R_{12}Py^+} + \Gamma_{R_8SO_3^-} d\ln a_{R_8SO_3^-} + \Gamma_{Na^+}\, d\ln a_{Na^+} + \Gamma_{Cl^-}\, d\ln a_{Cl^-})\,, \qquad (3)$$

where $\pi = \sigma^0 - \sigma$ is the surface pressure, Γ_i is the Gibbs surface excess of the *i*-th component, a_i is its activity in the solution, R is the universal gas constant and T is the absolute temperature.

The complex formed by long-chain anions and cations has not been taken into consideration because the results of measurements of the electrical conductivity of the mixed solutions indicate that the formation of such complex may be neglected even at higher concentrations than those now considered [22].

In the solutions examined the ionic strength was constant and the sodium chloride concentrations considerably exceeded the concentration of both ionic surfactants. For that reason $c_{Na^+} = c_{Cl^-} = \text{const.}$ and, moreover, the ionic

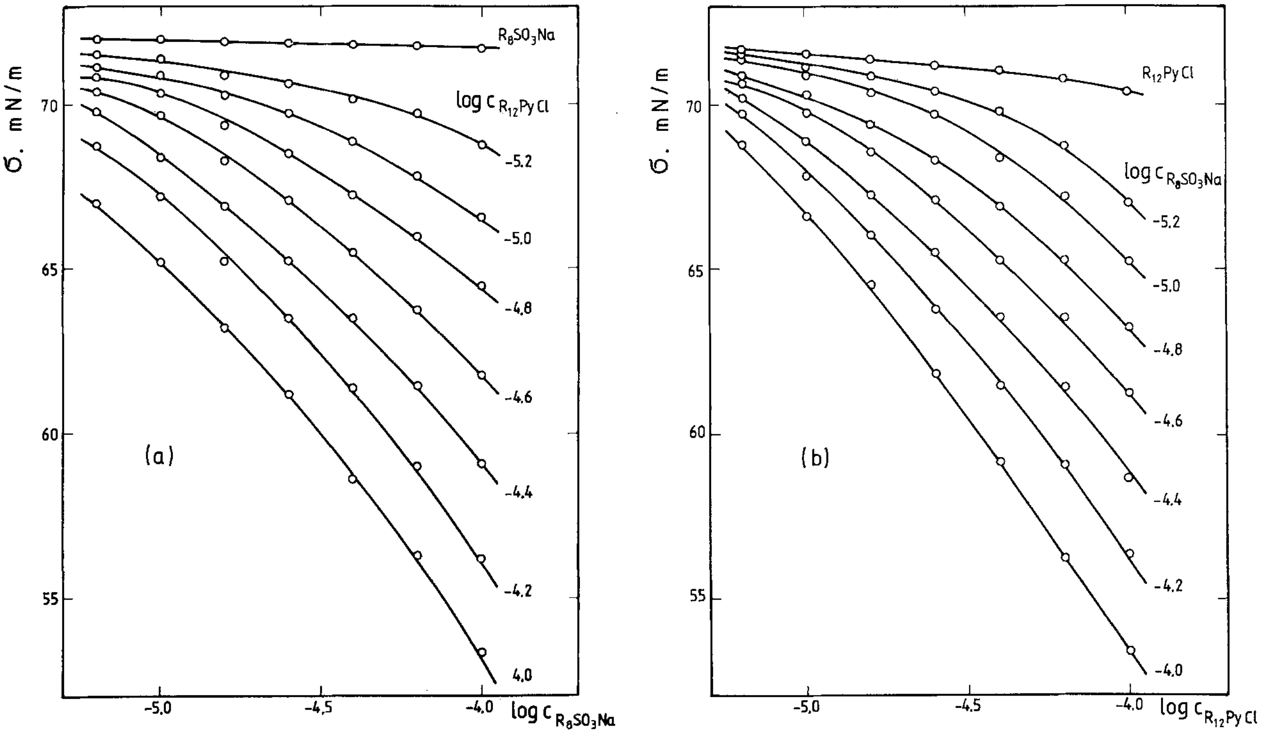

Fig. 1. Dependence of the surface tension σ on: (a) the logarithm of R_8SO_3Na concentration for solutions of fixed $R_{12}PyCl$ concentration, (b) the logarithm of $R_{12}PyCl$ concentration for solutions of fixed R_8SO_3Na concentration. Ionic strength: 0.003 M NaCl.

activity coefficients have a constant value. Thus, $da_i = dc_i$ and furthermore, $da_{\mathrm{Na}^+} = da_{\mathrm{Cl}^-} = 0$. Consequently, Eq. (3) simplifies to:

$$d\pi = RT(\Gamma_{R_{12}Py^+}\, d\ln c_{R_{12}Py^+} + \Gamma_{R_8SO_3^-} d\ln c_{R_8SO_3^-}) \tag{4}$$

and the surface excesses of individual components may be calculated as:

$$\Gamma_{R_8SO_3^-} = \frac{1}{RT}\left(\frac{d\pi}{d\ln c_{R_8SO_3^-}}\right) \quad \text{for } c_{R_{12}Py^+} = \text{const.} \tag{5a}$$

$$\Gamma_{R_{12}Py^+} = \frac{1}{RT}\left(\frac{d\pi}{d\ln c_{R_{12}Py^+}}\right) \quad \text{for } c_{R_8SO_3^-} = \text{const.} \tag{5b}$$

Values of derivatives of the surface pressure π relative to the concentration logarithm have been determined analytically, describing the experimental results by means of third-order polynomials.

Results of surface excess calculations for both surface-active ion types are shown in Figs. 2a, b for the ionic strength equal to 0.003 M in form of adsorption isotherms: $\Gamma_{R_8SO_3^-}$ vs. $c_{R_8SO_3^-}$ (Fig. 2a) and $\Gamma_{R_{12}Py^+}$ vs. $c_{R_{12}Py^+}$ (Fig. 2b). For comparison, adsorption isotherm is also shown in each figure for solutions containing a single anionic or cationic surfactant.

On the basis of presented results it can be stated that the cationic (anionic) substance addition more greatly increases the anionic (cationic) substance adsorption the greater this addition is. Similar effect may be also observed for other ionic strengths; it is result of a strong attraction between adsorbed long-chain anions and cations.

The increase of inorganic electrolyte concentration in the solution increases the cationic surfactant adsorption (Fig. 3) owing to suppression of electrostatic repulsion of adsorbed ions. This effect appears for single cationic surfactant solutions (Fig. 3a) as well as for those containing the anionic substance addition (Fig. 3b). However, in the latter case it is much less pronounced and becomes smaller as the anionic surfactant content

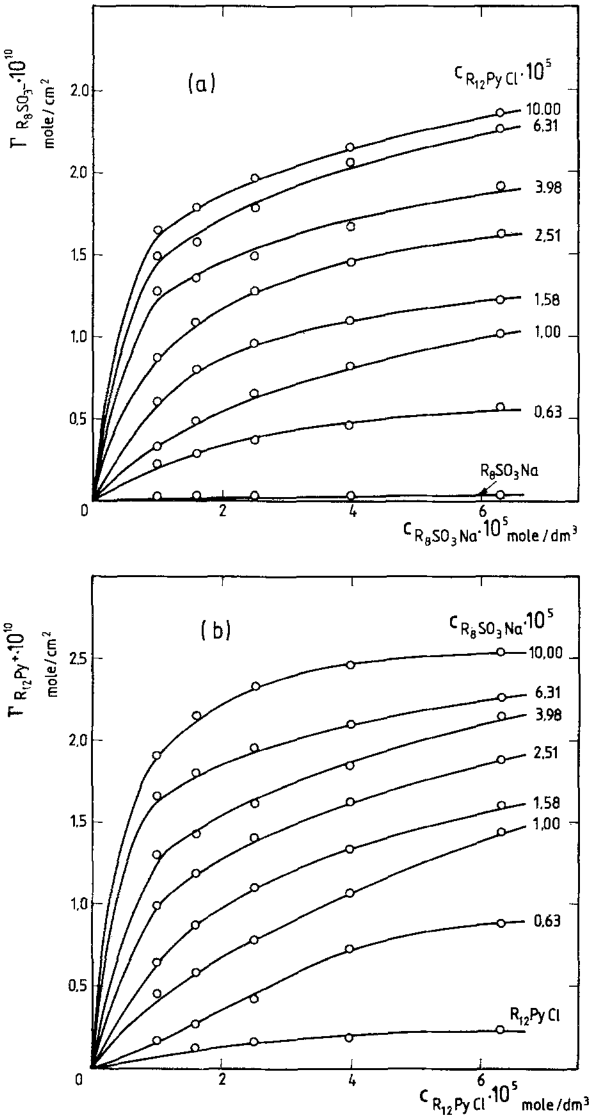

Fig. 2. Adsorption isotherms of: (a) anionic substance at constant cationic surfactant concentration, (b) cationic substance at constant anionic surfactant concentration. Ionic strength: 0.003 M NaCl.

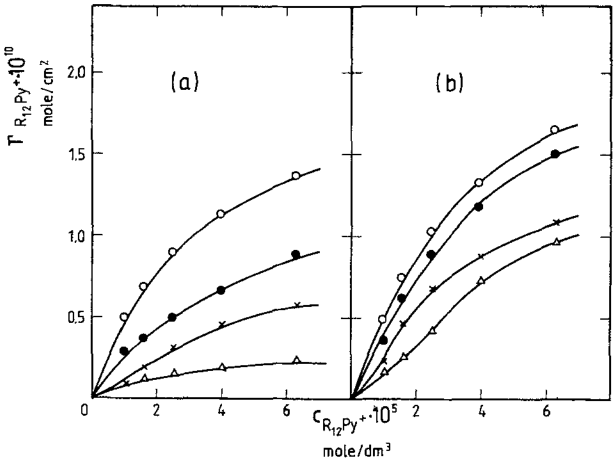

Fig. 3. Effect of NaCl concentration on the course of adsorption isotherms of cationic surfactant from solutions: (a) without the anionic substance addition, (b) containing a constant anionic substance addition ($0.63 \cdot 10^{-5}$ M). Ionic strength: △ – 0.003 M, × – 0.01 M, ● – 0.03 M, ○ – 0.1 M.

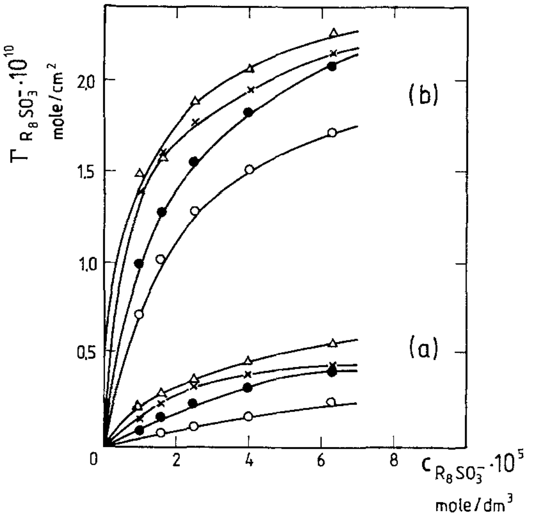

Fig. 4. Effect of NaCl concentration on the course of adsorption isotherms of anionic surfactant from solutions containing a constant cationic substance addition (a – $0.63 \cdot 10^{-5}$ M, b – $6.31 \cdot 10^{-5}$ M).

in the solution is increased. This is probably due to the weaker ionic nature of the mixed monolayer. On the other hand, the effect of NaCl concentration on the anionic surfactant adsorption from mixed solutions is of the opposite direction compared to the case of cationic surfactant. Namely, the increase of inorganic electrolyte concentration results in reduction of the anionic substance adsorption (Fig. 4). This effect becomes larger as the cationic substance content in the solution increases. Such behavior is due to an enlargement of the asymmetry of the surface layer composition by NaCl addition, which is related to a decrease of adsorption of the ions with the shorter alkyl chain ($R_8SO_3^-$).

Figure 5 shows the effect of the solution ionic strength on the composition of mixed films

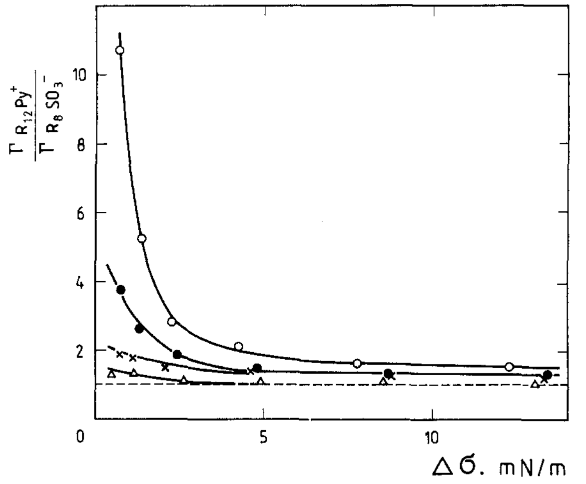

Fig. 5. Effect of NaCl concentration on the composition of films adsorbed from solutions containing equimolar amounts of $R_{12}PyCl$ and R_8SO_3Na. Ionic strength: as on Fig. 3.

adsorbed from solutions containing equimolar amount of both surfactants. Mixed adsorption films formed at low ionic strength (0.003 M NaCl) contain almost equal amounts of both types of surface active ions. On the other hand, the increase of inorganic electrolyte concentration in the solution results in the appearance in the adsorption layer of an increasingly larger excess of more surface active ions with longer alkyl chain ($R_{12}Py^+$). The increase of the solution ionic strength allows the surface electroneutrality to be maintained in spite of the asymmetry of its composition.

In the system now investigated the asymmetry of mixed adsorption films composition is much greater than it was in the previously studied $R_{10}PyCl + R_8SO_3Na + NaCl$ system [15], which contains surfactants less differing in their surface activity. On the other hand, the behavior of $R_8PyCl + R_{12}SO_3Na + NaCl$ system [13] is similar to the one now under consideration.

Application of the regular solution model to anionic-cationic adsorption films

Dependencies of the surface tension on the logarithm of the concentration for solutions containing individual ionic surfactants and their equimolar mixtures (concentration ratio of the components is constant and equal to 1 : 1) in pure water, as well as in solutions of different NaCl concentrations, are shown in Fig. 6. From these plots the values of the individual surfactants concentrations (c_1^0, c_2^0) and their mixture concentration (c_{12}) required to produce a given surface tension value have been read. The composition of mixed monolayers (x_1, x_2) and the values of the interaction parameter β have been calculated on the basis of Eq. (2) and the surface activity coefficients of the components have been calculated on the basis of Eq. (1). For systems under consideration $\alpha_1 = \alpha_2 = 0.5$ (equimolar mixtures) which

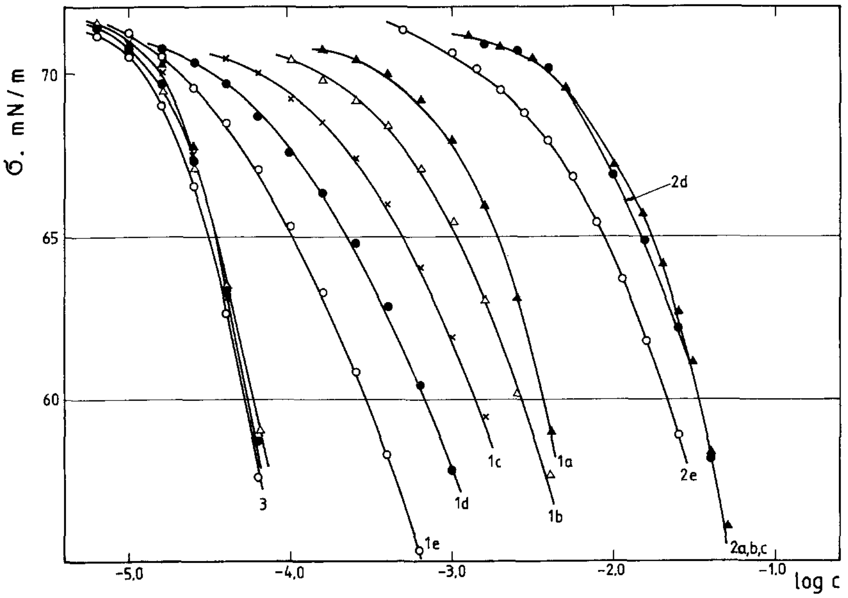

Fig. 6. Dependence of the surface tension on the logarithm of the concentration for solutions containing individual ionic surfactants ($R_{12}PyCl$ – curves 1, R_8SO_3Na – curves 2) and their equimolar mixtures (curves 3) at different NaCl concentrations: a – 0, b – 0.003 M, c – 0.01 M, d – 0.03 M, e – 0.1 M.

Table 1. Influence of the inorganic electrolyte concentration on anionic-cationic adsorption films properties
System: $R_{12}PyCl$ (1) + R_8SO_3Na (2) + NaCl

Inorganic electrolyte	σ = 65 mN/m					σ = 60 mN/m				
	x'_1	x_1	β	f_1	f_2	x'_1	x_1	β	f_1	f_2
H_2O	–	0.551	– 20.10	0.017	0.002	–	0.550	– 20.91	0.014	0.002
0.003 M NaCl	0.52	0.556	– 19.08	0.028	0.002	0.51	0.559	– 20.13	0.020	0.002
0.01 M NaCl	0.58	0.592	– 17.28	0.056	0.002	0.56	0.576	– 18.98	0.033	0.002
0.03 M NaCl	0.58	0.623	– 15.01	0.102	0.003	0.56	0.603	– 17.07	0.068	0.002
0.1 M NaCl	0.62	0.649	– 12.73	0.208	0.005	0.58	0.630	– 14.31	0.141	0.003

simplifies the calculations considerably. The calculation results obtained for two surface tension values (65 and 60 mN/m) are collected in Table 1. For comparison, the values of the surface mole fractions x'_1, calculated on the basis of the Gibbs surface excesses: $x'_1 = \Gamma_1/(\Gamma_1 + \Gamma_2)$ have been also placed in this table. Owing to an error of the Γ_i calculation the values of x'_1 are much less precise than those obtained on the basis of Eq. (2), but they change with the surface tension decrease and with the inorganic electrolyte concentration increase in a similar way.

The values of the interaction parameter β are strongly negative, which demonstrates a powerful attraction between components in the mixed monolayer. The values of β are dependent on the surface tension value as well as on the concentration of added inorganic electrolyte.

In the systems investigated the values of the surface activity coefficients are much less than unity, which demonstrates great deviations of the anionic-cationic adsorption films from ideal behavior. These deviations are larger the more negative the value of the interaction parameter β and they are greater for the component for which the surface mole fraction is smaller (R_8SO_3Na).

Conclusions

The regular solution model applied to anionic-cationic adsorption films is only a rough approximation of what is happening at the interface. Nevertheless, it gives some information on the properties of these mixed films. The surface composition calculated by using this model is in reasonable agreement with that obtained on the basis of the Gibbs surface excesses. The mixed monolayers formed in the system investigated contain a predominance of dodecylpyridinium ions of larger surface activity. The asymmetry of the surface layer composition is greater the higher the surface tension value (the degree of the surface coverage is then lower) and the inorganic electrolyte concentration in the solution is larger.

The negative values of the interaction parameter β indicate a strong attractive interaction between adsorbed components. There are electrostatic attractions of oppositely charged head groups and van der Waals attractions of hydrocarbon chains. The absolute value of β decreases when the surface tension increases. The reason is a reduction of interactions between adsorbed long-chain ions as their mutual distances at the surface grow when the adsorption decreases. The increase in the inorganic electrolyte concentration results in reduction of the absolute value of β because the rise in the ionic strength of the solution weakens the electrostatic attractions between the adsorbed long-chain anions and cations.

The similar effect of the surface tension value (the degree of the surface coverage) and the concentration of added inorganic electrolyte on the adsorption films composition and the mutual components interaction has been stated for other mixtures of anionic and cationic surfactants previously investigated [5].

For reason of approximate character of the applied approach all presented conclusions are only qualitative, but they seem quite reasonable and they are in accordance with the expectations.

Additional information about mutual interactions of mixed monolayers components could be obtained from analysis of molecular areas as a function of molar ratios of the components at constant π. Such approach to the problem of mixed monolayers will be adapted in future papers.

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