

# The adsorption at solution–air interface and volumetric properties of mixtures of cationic and nonionic surfactants

Katarzyna Szymczyk, Bronisław Jańczuk\*

*Department of Interfacial Phenomena, Faculty of Chemistry, Maria Curie-Skłodowska University,  
Maria Curie-Skłodowska Sq. 3, 20-031 Lublin, Poland*

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## Abstract

Surface tension, density and conductivity measurements were carried out for systems containing mixtures of cetyltrimethylammonium bromide (CTAB) and *p*-(1,1,3,3-tetramethylbutyl)phenoxy poly(ethylene glycol), Triton X-100 (TX100). The obtained results of the surface tension measurements were compared with those calculated from the relations derived by Joos, Miller and co-workers. From the comparison it appeared that using the modified adsorption isotherm derived by Joos the adsorption behaviour of CTAB and TX100 mixture can be predicted satisfactorily; however, the values of the surface tension of aqueous solutions of these mixtures calculated on the basis of the simple relationships of Miller et al. are a little higher than those measured in contrast to many two component systems of surfactants studied earlier. On the basis of the results obtained from the measurements and calculations it was found that there is a linear relationship between the surface tension and composition of CTAB and TX100 mixtures at their low concentration; however, in the concentration range corresponding to that of the saturated monolayer at the interface a negative deviation from the linear relationship is observed. This fact and the values of the parameters of molecular interactions in the mixed monolayer suggest that there is synergism in the reduction of the surface tension of aqueous solutions of CTAB and TX100 mixture when saturation of the monolayer is achieved. The negative parameters of intermolecular interaction in the mixed micelle and calculations based on MT theory of Blankshtein indicate that there is also synergism in the micelle formation for CTAB and TX100 mixture. It was also found that the values of the standard free energy of micellization for the mixture of CTAB and TX100 are somewhat lower than for individual components and they can be predicted on the basis of Maeda equation and the mole fraction of surfactant and free enthalpy of mixing CTAB and TX100 in the micelle. Our measurements and calculations indicate that the volume both of the individual surfactants and mixture studied decreases during the micellization process; however, at the concentration of the surfactants higher than CMC an increase of this volume is observed.  
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## 1. Introduction

The tendency of surfactants to adsorb at interfaces in an oriented fashion and micelle formation are their two fundamental properties [1–3].

The adsorption of surfactants at air–water interface controls the dynamic behavior of many important systems [4,5]. The surfactants adsorption influence the stability of foams, the droplet size in jets and sprays, the spreading of drops on solid surfaces, and the smooth coating of multiple layers [6].

The micelle formation affects such interfacial phenomena as surface or interfacial tension reduction that do not directly involve micelles. Some of the micelles have the structure similar to that of the biological membranes and globular protein and catalytical properties [7–9].

Because of the specific surface and volumetric properties of the surfactants they are employed by organic chemists and biochemists in different industrial processes such as: ore flotation [10], coal transport [11], firefighting [12], emulsion polymerization [13], corrosion inhibition [14], oil recovery [15], cement hardening [16] and commercial laundering [17].

However, the systems employed in these applications almost always consist of mixtures of surfactants, because technical-grade surfactants are themselves mixtures, and the purification process may be difficult or excessively expensive, and the mixed

\* Corresponding author. Tel.: +48 81 537 5649; fax: +48 81 533 3348.  
E-mail address: [Bronek@hermes.umcs.lublin.pl](mailto:Bronek@hermes.umcs.lublin.pl) (B. Jańczuk).

systems often behave better than a single surfactant [18–20]. The widespread use of surfactant mixtures for industrial purposes has stimulated the interest of researchers, and in the last decade many papers have been published on the solution properties of mixed surfactant systems [21–25].

In these papers it is possible to find that the micelle and monolayer at water–air interface and the composition of two surfactant mixtures can be substantially different than the equilibrium composition in the bulk phase [2,26]. Because of these differences a deviation from linear relationships between such parameters as surface or interfacial tension, wettability, CMC, standard free energy of adsorption and micellization and composition of surfactants is observed. Sometimes, the above mentioned parameters show a maximum or minimum at a given composition of the parameters. Our earlier studies showed that even for mixtures of two anionic surfactants, having different hydrophilic heads and a different length of hydrophobic alkyl tails, there is no linear relationship between the concentration excess at water–air and hydrophobic solid–water interfaces, the surface tension, critical micelle concentration and wettability of hydrophobic low energetic solids and the composition of the mixtures [3].

From the fundamental point of view mixtures of ionic–nonionic surfactants are more interesting because they often exhibit a highly nonideal behavior. Addition of a nonionic surfactant to an ionic surfactant micelle can reduce the electrostatic repulsions between the charged surfactant heads and greatly facilitate mixed micelle formation. Nonideal behavior of an ionic/nonionic surfactant mixture can also be influenced by other structural characteristics of the two surfactants, such as differences in the sizes of the surfactants heads or the lengths of the surfactants tails [27].

In the literature it is possible to find data concerning rather the anionic/nonionic mixtures of two surfactants than those of cationic/nonionic ones which are also used in many processes, for example as detergents for some materials.

Thus, the purpose of our studies was to determine the adsorption behavior of mixed layers basing on the equations of Gibbs, Joos, Miller and co-workers [2,28–31] as well as interactions between cationic and nonionic surfactants in the surface layers and micelles.

For this purpose the surface tension, density and conductivity of aqueous solutions of cetyltrimethylammonium bromide (CTAB) and *p*-(1,1,3,3-tetramethylbutyl)phenoxy poly(ethylene glycol), Triton X 100 (TX100) mixtures were measured.

## 2. Experimental

### 2.1. Materials

Cetyltrimethylammonium bromide (CTAB) (Sigma) and Triton X-100 (TX100), *p*-(1,1,3,3-tetramethylbutyl)phenoxy poly(ethylene glycol) (Sigma) were used for preparation of aqueous solutions. Aqueous solutions of individual surfactants and CTAB and TX100 mixtures at different ratios of CTAB to TX100 were prepared using doubly distilled and deionized water (Destamat B118E). The surface tension of water was always controlled before the solution preparation.

## 3. Methods

### 3.1. Surface tension measurements

Surface tension measurements were made at 293 K with Krüss K9 tensiometer under atmospheric pressure by the ring method. The platinum ring was thoroughly cleaned, and the flame dried before each measurement. The measurements were done in such a way that the vertically hung ring was dipped into the liquid to measure its surface tension.

It was then subsequently pulled out. The maximum force needed to pull the ring through the interface was then expressed as the surface tension,  $\gamma$  (mN/m). Measurements of the surface tension of pure water at 293 K were performed to calibrate the tensiometer and to check the cleanliness of the glassware. In all cases more than 10 successive measurements were carried out, and the standard deviation did not exceed  $\pm 0.2$  mN/m. The temperature was controlled within  $\pm 0.1$  K.

### 3.2. Density measurements

We have measured the densities of water and aqueous solutions of the individual surfactants and CTAB and TX100 mixtures using a vibrating tube densimeter Anton Paar, model DMA 5000. The apparatus consists of a glass U tube with a platinum resistance thermometer inside a thermostatic jacket. The sample density is a function of the oscillation frequency when the tube vibrates under the assumption that the sample volume trapped between the oscillation nodes is constant. The accuracy of the thermometer and the density measurements are  $\pm 0.01$  K and  $\pm 0.005$  kg/m<sup>3</sup>, respectively. The precision of the density and temperature measurements given by the manufacturer is  $\pm 0.001$  kg/m<sup>3</sup> and  $\pm 0.001$  K.

The densimeter is calibrated regularly with distilled and deionized water. After measuring the density of water more than three measurements of density were carried out at constant temperature equal 293 K.

### 3.3. Conductivity measurements

Conductivity measurements of surfactant solutions were made by a conductivity meter model, Elmetron CX-731. After measuring the conductivity of the solvent three successive conductivity measurements of the surfactant solutions were carried out under controlled constant temperature. The accuracy of the measurements was  $\pm 0.01$   $\mu$ S.

The break point in the plot of either the equivalent conductivity versus the square root of the total surfactant concentration or the molar conductivity versus the total surfactant concentration was taken as CMC at the mole fraction.

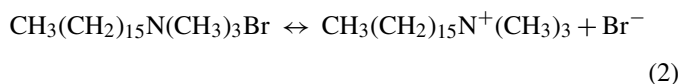
### 3.4. Evaluation of the surface excess concentration of surfactant at interface

The surface excess concentration of surfactants at water–air interface can be determined on the basis of the adsorption isotherms using the Gibbs equation [2,3].

For dilute solution ( $10^{-2}$  mol/dm<sup>3</sup> or less) containing only TX100 (nonionic surfactant) the Gibbs equation can be written in the form:

$$\Gamma = -\frac{Cd\gamma}{RTdC} = -\frac{1}{RT} \frac{d\gamma}{d \ln C} = -\frac{1}{2.303RT} \frac{d\gamma}{d \log C} \quad (1)$$

In the case of cationic surfactant, considering CTAB as a strong electrolyte, which is dissociated in aqueous solution into organic cation cetyltrimethylammonium (CTA<sup>+</sup>) and bromide counterion (B<sup>-</sup>) according to:



the appropriate form of the Gibbs equation is [2]:

$$d\gamma = -RT(\Gamma_{A^+}d \ln a_{A^+} + \Gamma_{B^-}d \ln a_{B^-}) \quad (3)$$

where  $\Gamma_{A^+}$  and  $\Gamma_{B^-}$  is the surface excess concentration of ion A<sup>+</sup> and B<sup>-</sup>, respectively, and  $a_{A^+}$  and  $a_{B^-}$  are the activity of ion A<sup>+</sup> and B<sup>-</sup>, respectively.

Since  $\Gamma_{A^+} = \Gamma_{B^-} = \Gamma$  to maintain electro neutrality and  $a_{A^+} = a_{B^-} = C \times f_{AB}$  without a significant error, then

$$d\gamma = -2RT\Gamma d \ln(C \times f_{AB}) \quad (4)$$

where  $f_{AB}$  is the mean activity coefficient of the surfactant.

For dilute solutions ( $f_{A^+} \approx f_{B^-} \approx 1$  and then  $f_{AB} \approx 1$ ), Eq. (4) assumes the form:

$$\Gamma = -\frac{Cd\gamma}{2RTdC} = -\frac{1}{2RT} \frac{d\gamma}{d \ln C} = -\frac{1}{4.606RT} \frac{d\gamma}{d \log C} \quad (5)$$

The concentration of each surfactant at the interface can be calculated from the slope of  $\gamma$ - $\log C$  plot (Table 1 – maximal values). It is convenient if the dependence between the surface tension and concentration of aqueous surfactant solution can be expressed by the known mathematical function.

### 3.5. Equation of state described mixed adsorption behavior

Using the adsorption isotherm derived by Joos [28] and modified by us [26] for the systems including ionic and non-ionic surfactants, the surface adsorption behavior of the mixture of these surfactants can be predicted in a quite accurate way. The equation for the mixture of CTAB and TX100 in which one is non-ionic surfactant (TX100) and the other ionic being the 1:1

electrolyte type (A<sup>+</sup> and B<sup>-</sup>) can be written in the form [26,28]:

$$\exp\left(\frac{-\Pi}{RT\Gamma_1^\infty}\right) + \exp\left(\frac{-\Pi}{RT\Gamma_2^\infty}\right) \frac{C_1}{a_1} + \exp\left(\frac{-\Pi}{2RT\Gamma_2^\infty}\right) \frac{C_2}{a_2} = 1 \quad (6)$$

if their activity is close to  $C$  (for  $C < 10^{-2}$  M), where  $\Gamma_1^\infty$ ,  $\Gamma_2^\infty$  and  $\Gamma_2^\infty$  are the maximum of the solvent adsorption, and surfactants 1 and 2, respectively.  $\Pi$  is the surface pressure. The parameters  $a_1$  and  $a_2$  can be expressed as:

$$a_1 = \exp\left(\frac{\mu_1^S - \mu_1^B}{2RT}\right) \omega, \quad a_2 = \exp\left(\frac{\mu_2^S - \mu_2^B}{2RT}\right) \omega \quad (7)$$

where  $\mu^S$  is the chemical potential in the surface under standard conditions,  $\mu^B$  the chemical potential in the bulk under standard conditions, and  $\omega$  the number of molecules of water per litre.

Assuming that  $C_2/C_1 = b = \text{const.}$ , and  $C_{\text{tot}} = C_1 + C_2 = C_1(1+b)$ , gives:

$$\exp\left(\frac{-\Pi}{RT\Gamma_1^\infty}\right) + \left[\exp\left(\frac{-\Pi}{RT\Gamma_1^\infty}\right) \frac{1}{a_1} + \exp\left(\frac{-\Pi}{2RT\Gamma_2^\infty}\right) \frac{b}{a_2}\right] \frac{C_{\text{tot}}}{1+b} = 1 \quad (8)$$

Miller et al. [29–31], taking into account the assumption that for an ideal mixture of homologues  $a_1 = a_2 = a_{12} = 0$  and  $\omega = \omega_1 = \omega_2$  as well as  $\bar{\Pi} = (\Pi\omega)/(RT)$ ,  $\bar{\Pi}_1 = (\Pi_1\omega)/(RT)$  and  $\bar{\Pi}_2 = (\Pi_2\omega)/(RT)$ , have derived the equation of state which relates the surface pressure of a surfactant mixture with the surface pressure of individual solutions. This equation can be expressed in the form:

$$\exp \bar{\Pi} = \exp \bar{\Pi}_1 + \exp \bar{\Pi}_2 - 1 \quad (9)$$

where  $a_1$ ,  $a_2$  and  $a_{12}$  are the constants of intermolecular interactions,  $\omega_1$  and  $\omega_2$  are the partial molar surface areas of surfactant 1 and 2, respectively, and  $\Pi_1$ ,  $\Pi_2$  and  $\Pi$  are the surface pressures of solutions of the individual surfactants and their mixture, respectively, equal to the difference between surface tension of the solvent and solution ( $\gamma_o - \gamma$ ).

### 3.6. Evaluation of the molecular interaction parameters

For surfactant mixtures the characteristic phenomena are the formation of mixed monolayers at the interface and mixed micelles in the bulk solution. Most of the theories are based on

Table 1

Values of the maximal excess of surfactant concentration at water–air interface,  $\Gamma_m$ , minimal area per molecule,  $A_m$ , standard free energy of adsorption,  $\Delta G^\circ_{\text{ad}}$ , and micellization,  $\Delta G^\circ_{\text{mic}}$

Surfactant	$\Gamma_m$ (mol/m <sup>2</sup> ) Eqs. (1) or (5)	$A_m$ (nm <sup>2</sup> )	$\Delta G^\circ_{\text{ad}}$ (kJ/mol) Eq. (19)	$\Delta G^\circ_{\text{mic}}$ (kJ/mol) Eq. (30)
TX100	$2.83 \times 10^{-6}$	0.587	-40.87	-19.843
CTAB	$3.10 \times 10^{-6}$	0.536	-28.86	-17.044

the regular solution theory and they have been applied to the phase separation model for the micelles and to the monolayer model for the adsorbed films in order to estimate the interaction parameter  $\beta$  in various binary surfactant systems [2]. The molecular interaction parameter,  $\beta$ , for monolayer can be evaluated, among other things, using the equation derived by Rubingh and Rosen [2,32,33]:

$$\beta^\delta = \frac{\ln(\alpha C_{12}/X_1 C_1^0)}{(1 - X_1)^2} \quad (10)$$

where  $\alpha$  is the mole fraction of surfactant 1 in the mixture of two surfactants,  $X_1$  the mole fraction of surfactant 1 in the mixed monolayer,  $C_1^0$  and  $C_{12}$  are the molar concentrations in the bulk of surfactant 1 and of the mixture of surfactant 1 and 2, respectively, required to produce a given surface tension value.  $X_1$  can be obtained from:

$$\frac{(X_1)^2 \ln(\alpha C_{12}/X_1 C_1^0)}{(1 - X_1)^2 \ln[(1 - \alpha)C_{12}/(1 - X_1)C_2^0]} = 1 \quad (11)$$

where  $C_2^0$  is the molecular concentration of surfactant 2 in the bulk required to produce a given surface tension.

In the case of mixed micelles it is possible to calculate the molecular interaction parameter,  $\beta^M$ , from the relation of Rubingh and Rosen in the form [2,32,33]:

$$\beta^M = \frac{\ln(\alpha C_{12}^M/X_1^M C_1^M)}{(1 - X_1^M)^2} \quad (12)$$

where  $C_1^M$ ,  $C_{12}^M$  are the critical micelle concentrations (CMC) of the individual surfactant 1, and mixture of surfactants 1 and 2, respectively, and  $X_1^M$  is the mole fraction of surfactant 1 in the mixed micelle.

$X_1^M$  can be evaluated from the equation:

$$\frac{(X_1^M)^2 \ln(\alpha C_{12}^M/X_1^M C_1^M)}{(1 - X_1^M)^2 \ln[(1 - \alpha)C_{12}^M/(1 - X_1^M)C_2^M]} = 1 \quad (13)$$

where  $C_2^M$  is the CMC of the individual surfactant 2.

Knowing the interaction parameters for the mixed monolayer and micelles it is possible to determine the activity coefficient of the surfactants in the mixtures. From the nonideal solution theory it results that the activity coefficients of the surfactants 1 and 2 in the mixed film ( $f_1$  and  $f_2$ ) and mixed micelle ( $f_1^M$  and  $f_2^M$ ) fulfil the conditions, respectively:

$$\ln f_1 = \beta^\delta (1 - X_1)^2, \quad (14)$$

$$\ln f_2 = \beta^\delta (X_1)^2, \quad (15)$$

$$\ln f_1^M = \beta^M (1 - X_1^M)^2 \quad (16)$$

and

$$\ln f_2^M = \beta^M (X_1^M)^2 \quad (17)$$

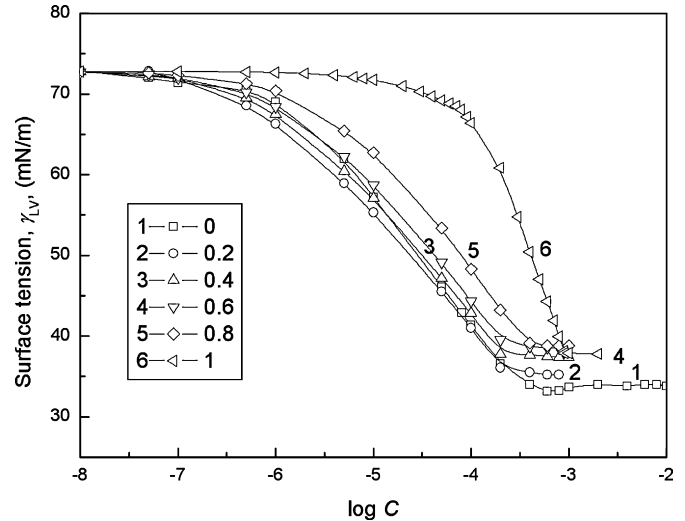


Fig. 1. Dependence of the surface tension of aqueous TX100 (curve 1) and CTAB (curve 6) solutions and their mixture at monomer mole fraction of CTAB equal 0.2, 0.4, 0.6, 0.8 on log C.

## 4. Results and discussion

### 4.1. Adsorption isotherms

The measured values of the surface tension ( $\gamma$ ) of aqueous solutions of TX100 and CTAB and their mixtures are presented in Fig. 1. This figure shows the dependence between  $\gamma$  and log C ( $C$  represents the concentration of TX100, CTAB, and their mixtures at a given  $\alpha$ ) for aqueous solution of TX100 (curve 1) and CTAB (curve 6) and their mixtures (curves 2–4). From this figure it appears that the shape of curve 6 is somewhat different from the others; however, for all surfactants a linear dependence exists between  $\gamma$  and log C near the critical micelle concentration (CMC). In the case of TX100 the values of  $\gamma$  at a given concentration are smaller than for CTAB. Thus, the value of the maximal reduction of water surface tension by TX100 is higher than for CTAB. In the case of the mixtures of CTAB and TX100 the shape of the  $\gamma$ –log C curves is closer to that of TX100 than for CTAB.

To show the influence of the mixtures composition on the water surface tension in Fig. 2, the dependence between surface tension and monomer mole fraction of CTAB,  $\alpha$ , in the mixture is plotted. From this figure it is seen that at only a very low concentration of surfactant mixtures there is almost a linear dependence between the surface tension and mole fraction of CTAB in the mixture. However, at the concentration close to  $5 \times 10^{-6}$  and higher there is a negative deviation from the linear relationship between  $\gamma$  and  $\alpha$ . In other words, at concentrations corresponding to the beginning of the saturation monolayer formation nonideal mixing of surfactants is evident. In some cases the minimum on the curve  $\gamma$ –log C is observed. It suggests that the composition of the saturated monolayer at water–air interface should be different than that of the surfactant in the bulk phase. This suggestion is confirmed by the data presented the relationship between the mole fraction of CTAB in the mixed monolayer for each  $\alpha$  and surface tension of the solution. It

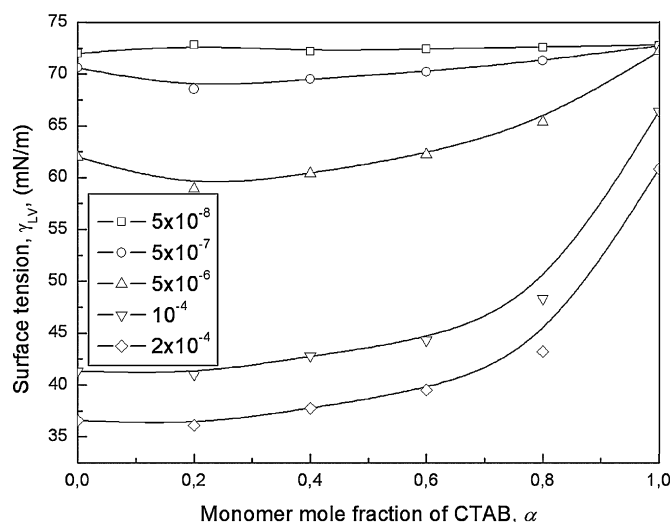


Fig. 2. Dependence of the surface tension of aqueous solutions of TX100 and CTAB mixtures on the monomer fraction of CTAB,  $\alpha$  at total concentration of surfactants,  $C$ , equal  $5 \times 10^{-8}$ ,  $5 \times 10^{-7}$ ,  $5 \times 10^{-6}$ ,  $10^{-4}$  and  $2 \times 10^{-4}$  M, respectively.

results that for all  $\alpha$  at a given  $\gamma$  the mole fraction of CTAB in the mixed monolayer is smaller than in the bulk phase, but we observe different shapes of  $X_1-\gamma$  curves for the same  $\alpha$ . The biggest changes of  $X_1$  as a function of  $\gamma$  appear for  $\alpha$  equal 0.2 and 0.8; however, the direction of the  $X_1$  changes for  $\alpha$  equal 0.2 is different than for  $\alpha$  equal 0.8, and the smallest changes appear for  $\alpha$  equal 0.6. The shapes of  $X_1-\gamma$  curves probably result from the tendency of CTAB and TX100 to adsorb at water–air interface and from the intermolecular interactions in the mixed monolayer, which represent the  $\beta^\delta$  parameter presented in Fig. 3. For all  $\alpha$  this parameter has a negative value and decrease with surface tension increase of the aqueous solution of the surfactant mixtures.

The negative values of  $\beta^\delta$  parameter suggest that there is synergism in the surface tension reduction efficiency. However,

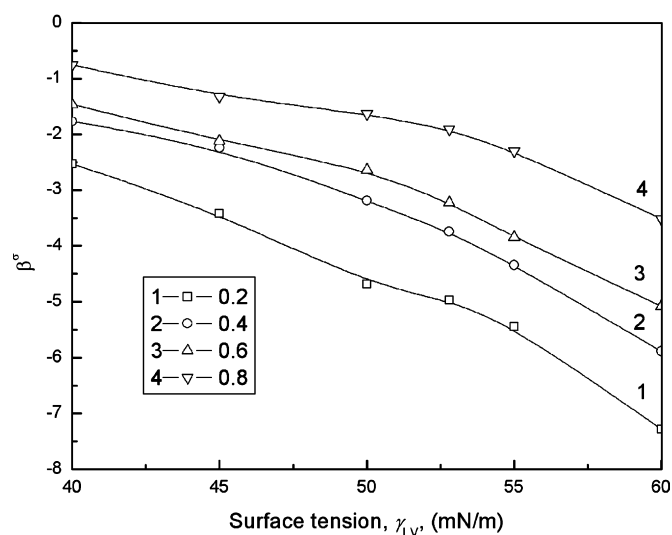


Fig. 3. Dependence of the molecular interaction parameter,  $\beta^\delta$ , on surface tension of aqueous solution of surfactant mixtures at different monomer mole fraction of CTAB,  $\alpha$ .

the second condition for the existence of negative synergism must be fulfilled. The condition is that the  $\beta^\delta$  parameter should be greater than  $|\ln((C_1^0)/(C_2^0))|$  [2]. This parameter is greater than  $|\ln((C_1^0)/(C_2^0))|$  at  $\alpha = 0.2$  for each value of the surface tension. Thus, it can be concluded that there is a negative synergism in the surface tension reduction in the whole concentration range corresponding to the mixed saturated monolayer at water–air interface for  $\alpha = 0.2$ . In the case of a mixture in which  $\alpha = 0.4$  the second condition of the existing synergism is fulfilled for surface tension equal 60, 55, 52.8, 50 mN/m, but for  $\alpha = 0.6$  and 0.8 only for  $\gamma = 60$  mN/m. On the basis of these results we can state that in the mixtures of TX100 and CTAB of a monomer mole fraction of CTAB equal 0.4, 0.6, 0.8 synergism exists only at concentrations of the mixtures in which the saturated monolayer begins to form at water–air interface and when the intermolecular interaction in the monolayer plays an important role.

As we can see in this study, the surface tension reduction efficiency has been determined as the surfactant giving a surface tension reduction by 20 mN/m, i.e.  $C_{20}$ . The concentration values are: TX100- $1.91 \times 10^{-5}$ ,  $0.2-1.51 \times 10^{-5}$ ,  $0.4-2.0 \times 10^{-5}$ ,  $0.6-2.7 \times 10^{-5}$ ,  $0.8-5.3 \times 10^{-5}$ ; CTAB- $3.41 \times 10^{-4}$ . All these values for the surfactant mixtures are lower than for the individual surfactants and the lowest value appears for  $\alpha = 0.2$ .

#### 4.2. Adsorption isotherms of Joos and Miller et al.

It is interesting whether on the basis of the theoretical isotherms of adsorption it is possible to predict the surface tension for the mixtures of CTAB and TX100 for which synergism in reduction of the surface tension cannot be excluded. Therefore, in Fig. 4 the isotherms of Joos and Miller et al. are presented for  $\alpha = 0.2$ .

The line 2 in Fig. 4 reflects the function of  $\gamma$  versus  $\log C$  calculated from Eq. (9). The value of  $\omega$  used for calculations in this equation, at first approximation, was assumed as equal to  $2 \times 10^5$  m<sup>2</sup>/mol [31].

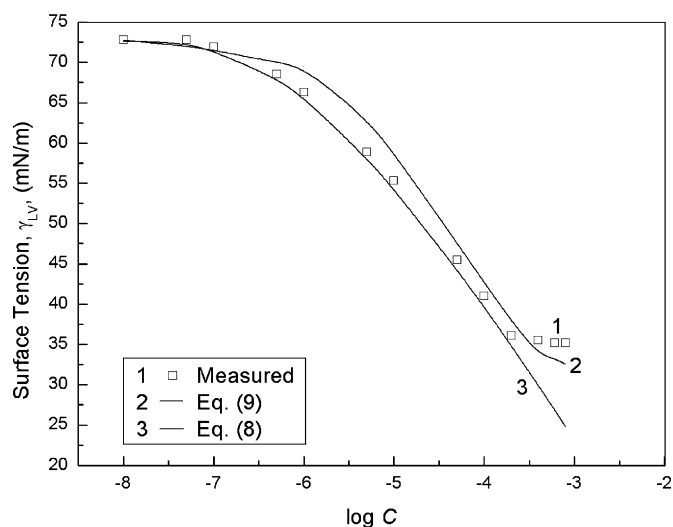


Fig. 4. Dependence of the surface tension of aqueous solutions of TX100 and CTAB surfactants mixture on  $\log C$  for  $\alpha$  equal 0.2. Point 1 represent the measured values of surface tensions, and curves 2 and 3 represent the values of the surface tension calculated from Eqs. (9) and (8), respectively.

Table 2  
Parameters in Eq. (8) for water, TX100 and CTAB

Substance	$\Gamma^\infty$ (mol/m <sup>2</sup> )	$a$ (mol/l)	$A$ (nm <sup>2</sup> )
Water	$16.6 \times 10^{-6}$		0.10
CTAB	$5.45 \times 10^{-6}$	$4.05 \times 10^{-4}$	0.3046
TX100	$3.15 \times 10^{-6}$	$1.95 \times 10^{-6}$	0.5270

Line 3 in this figure reflects the dependence of the surface tension ( $\gamma$ ) of aqueous solution of TX100 and CTAB mixtures on the total concentration of surfactants ( $\log C$ ) for  $\alpha$  ( $\alpha$  is the mole fraction of CTAB) equal 0.2 calculated from Eq. (8) using the values of  $\Gamma^\infty$  and  $a$  of the individual components.

The values of  $\Gamma_0^\infty$ ,  $\Gamma_1^\infty$ ,  $\Gamma_2^\infty$ ,  $a_1$  and  $a_2$  used in Eq. (8) were determined from Eq. (7) from the data for individual surfactants (TX100 and CTAB) on the assumption that  $C_1=0$  or  $C_2=0$  and are listed in Table 2. In all cases it was assumed that the area occupied by water is close to  $0.10 \text{ nm}^2$  and thus  $\Gamma_0^\infty = 16.6 \times 10^{-6} \text{ mol/m}^2$ .

The results presented in Fig. 4 and calculated for other mixtures show that the changes of  $\gamma$  as a function of  $\log C$ , for a given  $\alpha$ , have the same shape. Of course, near CMC there is a linear dependence of  $\gamma$  on  $\log C$ . From Fig. 4 and other calculations it also appear that at low concentrations of surfactant mixtures there is a good agreement between the values of the surface tensions of the solution measured and calculated from Eq. (8) (curve 3), which is better than between those calculated from Eq. (9) (curve 2).

Practically the experimental points (point 1) are between the theoretical curves (curves 2 and 3) for all values of  $\alpha$ , but curve 3 is a better approximation for the measured values of the surface tension of solutions. These facts indicate that using the equation of state derived by Joos [28], and next modified by us [26], it is possible to predict the surface tension of aqueous solution of TX100 and CTAB mixtures almost in the whole range of their concentrations from 0 to CMC. Of course, it is impossible to predict the surface tension of the solution of TX100 and CTAB at the concentration close to CMC or higher than CMC.

Some differences between the theoretical values of  $\gamma$  obtained from Miller equation, particularly at  $C$  close to that of the saturated monolayer and measured (curve 2 and point 1), probably results from synergism in the surface tension reduction. This conclusion is confirmed by the data presented in Fig. 3.

#### 4.3. The standard free energy of adsorption

Because there are differences between slopes of the linear part of curves 1 and 6 (Fig. 1), which represent the dependences between  $\gamma$  and  $\log C$ , and differences between values  $\gamma$  at the same concentration for TX100 and CTAB, respectively, it suggests that “efficiency” and “effectiveness” of the adsorption of TX100 is different than of CTAB.

The surface excess concentration at surface saturation,  $\Gamma_m$ , is a useful measure of the adsorption effectiveness of the surfactant at water–air interface, since it is the maximum value to which adsorption can attain. However, the adsorption efficiency

is related to the standard free energy of the adsorption,  $\Delta G^\circ_{\text{ad}}$  [2].

Table 1 presents the values of the surface access concentration and minimal area ( $A_m$ ) per TX100 and CTAB molecule at air–water interface determined from Eqs. (1) and (5). From this Table it is seen that  $\Gamma_m$  for TX100 is lower, and  $A_m$  higher than for CTAB. It means that the effectiveness of TX100 adsorption at water–air interface is lower than CTAB.

The standard free energy of adsorption,  $\Delta G^\circ_{\text{ad}}$ , can be determined by different methods. If the adsorbed molecules are immobile and adsorb on ‘sites’ at the interface, the area  $A$  per adsorbed molecule will be related to the bulk concentration of surfactant by means of the modified Langmuir equation [34]:

$$\frac{A_0}{A - A_0} = \frac{C}{\omega} \exp\left(\frac{-\Delta G^\circ_{\text{ad}}}{RT}\right) \quad (18)$$

where  $\omega$  is the number of moles of water per liter of water and  $A_0$  the ‘excluded area’, that is the area of the interface unavailable to one molecule by the presence of another.

On the other hand if mobile adsorption isotherms are considered a statistical correction to Eq. (18) has been introduced by de Boer [35]:

$$\frac{A_0}{A - A_0} \exp\left(\frac{A_0}{A - A_0}\right) = \frac{C}{\omega} \exp\left(\frac{-\Delta G^\circ_{\text{ad}}}{RT}\right) \quad (19)$$

The standard free energies of adsorption,  $\Delta G^\circ_{\text{ad}}$ , of TX100 and CTAB were calculated from Eq. (19) using  $A_0$  equal  $0.527 \text{ nm}^2$  and  $0.305 \text{ nm}^2$ , respectively, and are given in Fig. 5. The values of  $A_0$  were obtained from Eq. (5). In the range of low concentrations  $\Delta G^\circ_{\text{ad}}$  is constant for both surfactants, but for TX100 is equal  $-40.87 \text{ kJ/mol}$  and CTAB is equal  $-28.86 \text{ kJ/mol}$ . For both surfactants this relationship has a wide minimum, which in the case of CTAB increases with the concentration up to the CMC of the surfactant and is related with the region of  $C$ , where the attractive and repulsive forces act strongly between the ions in the adsorbed monolayers at air–water interface. For TX100

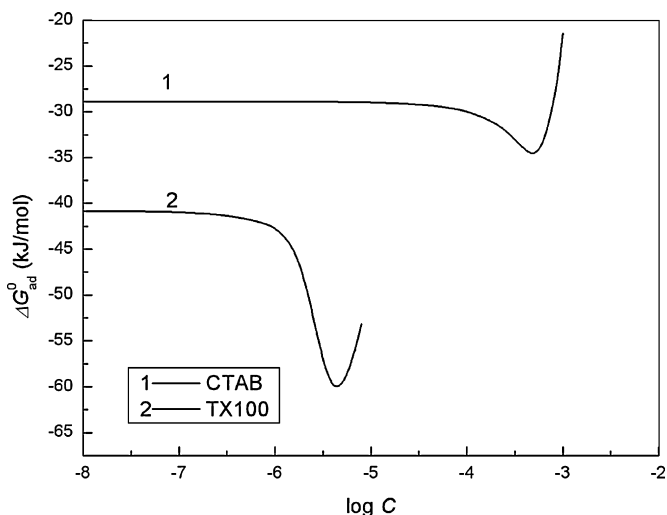


Fig. 5. Dependence between the free energy of adsorption,  $\Delta G^\circ_{\text{ads}}$ , calculated from Eq. (19) and  $\log C$  for CTAB (curve 1) and TX100 (curve 2).

the minimum occurs in the concentration range corresponding to saturated monolayer at water–air interface.

The standard free energy of adsorption of TX100 and CTAB at water–air interface, which is related to their efficiency of adsorption was also determined from the equation derived by Rosen and Aronson [2,36]. If the surfactant concentration corresponding to the saturated monolayer at interface is lower than  $1 \times 10^{-2}$  M, the Rosen and Aronson equation can be expressed in the form:

$$\Delta G_{\text{ad}}^{\circ} = 2.303RT \log \frac{C}{\omega} - N\pi A_{\text{m}} \quad (20)$$

where  $\omega$  is the number of water moles per  $\text{dm}^3$  and  $\pi$  the surface pressure corresponding to the surfactant concentration,  $C$ , at which  $A_{\text{m}}$  is achieved.

Eq. (20) is fulfilled for nonionic surfactant and ionic AB electrolyte type (1:1) in the presence of neutral salt in solution having the same ion as counterion at a high concentration. However, assuming that CTAB at its high concentration is not completely dissociated on ions, we calculated from Eq. (20) the values of the standard free energy of adsorption for both TX100 and CTAB, which are equal  $-43.99$  kJ/mol and  $-36.37$  kJ/mol, respectively. It appears that the value of the standard free energy of adsorption of TX100 determined in such is lower than for CTAB. It means that TX100 way has a higher adsorption efficiency than CTAB.

From Eq. (20) the values of the standard free energy of CTAB and TX100 mixtures were also calculated. For these calculations the values of  $C$  at  $\gamma$  equal 50 mN/m were used, and values of  $A_{\text{m}}$  were determined from the following equation:

$$A_{\text{m}} = X_1 A_{\text{m}}^1 + X_2 A_{\text{m}}^2 \quad (21)$$

where  $A_{\text{m}}^1$  and  $A_{\text{m}}^2$  are the values of minimal area per molecule for CTAB and TX100 equal  $0.536$   $\text{nm}^2$  and  $0.587$   $\text{nm}^2$ , respectively, and  $X_1$ ,  $X_2$  are the mole fractions of surfactants 1 and 2 in the mixed monolayer calculated from Eq. (11).

The calculated values of the standard free energy of CTAB and TX100 mixtures are presented in Fig. 6 (curve 1). Curve 2

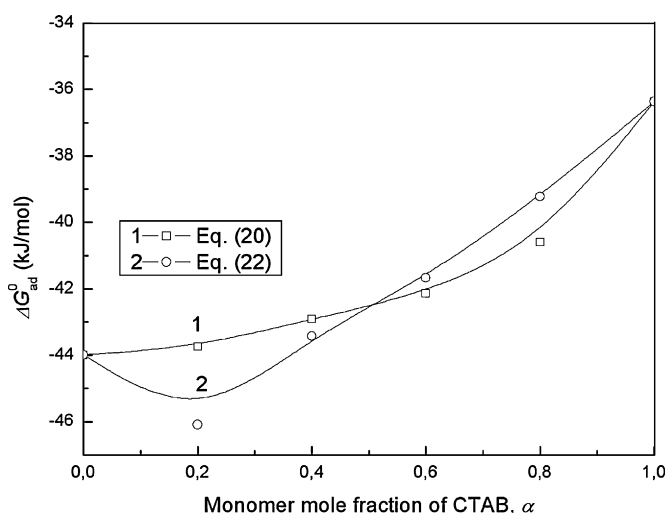


Fig. 6. Dependence between the free energy of adsorption,  $\Delta G_{\text{ads}}^{\circ}$ , calculated from Eqs. (20) and (22) and monomer mole fraction of CTAB,  $\alpha$ .

in this figure represents the values of  $\Delta G_{\text{ad}}^{\circ}$  calculated from the relation:

$$\Delta G_{\text{ad}}^{\circ} = X_1 \Delta G_{\text{ad}1}^{\circ} + X_2 \Delta G_{\text{ad}2}^{\circ} + G_{\text{mix}} \quad (22)$$

where

$$G_{\text{mix}} = RT(X_1 \ln f_1 + X_2 \ln f_2) \quad (23)$$

From this figure it appears that  $\Delta G_{\text{ad}}^{\circ}$  values calculated from Eq. (22) are somewhat higher than those calculated from Eq. (20) for  $\alpha = 0.6, 0.8$ , but at  $\alpha = 0.2$  we obtained a clear minimum. This minimum confirmed a negative synergism in the surface tension reduction in the whole concentration range corresponding to the mixed saturated monolayer at water–air interface for  $\alpha = 0.2$ .

From comparison of curve 1 to curve 2 in Fig. 6 we can state that it is possible to predict the tendency to adsorb the mixture of CTAB and TX100 only on the basis of standard free energy of adsorption of individual surfactant if we know the monolayer composition at water–air interface.

#### 4.4. CMC

Another characteristic property of surfactants is their ability to form micelles. The concentration at which the micelization process takes place is called critical micelle concentration (CMC).

The values of CMC for TX100 and CTAB mixtures were determined from isotherms of adsorption (Fig. 1), density and conductivity measurements presented in Fig. 7 (curves 1–3).

Conductometric determination of CMC was carried out through the change in the slope when the specific conductivity versus surfactant concentration for surfactant solutions is plotted. The values of CMC determined from conductivity measurements for CTAB and mixtures of CTAB and TX100 (Fig. 7, curve 3) are somewhat smaller than those obtained from

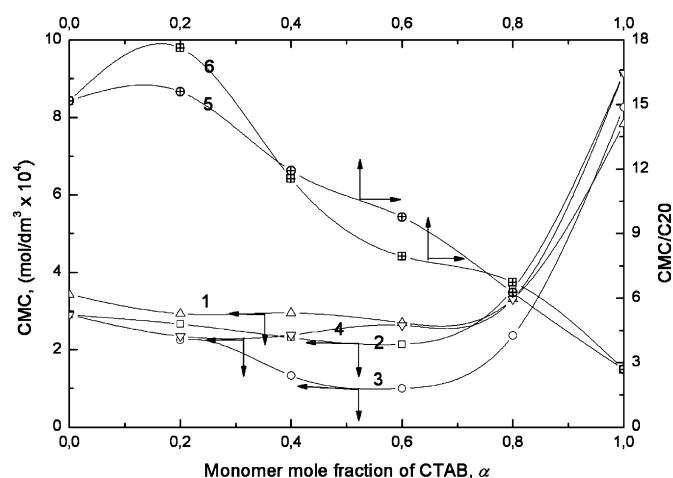


Fig. 7. Dependence of the critical micelle concentration (CMC) determined from the density measurements (curve 1), adsorption isotherms (Fig. 1) (curve 2), conductivity measurements (curve 3), and calculated from Eq. (24) (curve 4) on the monomer mole fraction of CTAB,  $\alpha$ , as well as between the values of the ratio of  $\text{CMC}/\text{C}_{20}$  calculated on the basis of the values of CMC calculated from Eq. (24) (curve 5) and determined from the surface tension measurements (curve 6).

surface tension (curve 2), but those determined from density measurements (curve 1) for  $\alpha$  in the range from 0 to 0.6 are higher than those obtained for  $\gamma$ . The determined values of CMC for an individual surfactants, TX100 and CTAB, are close to those obtained by other researchers, especially for CTAB:  $9.15 \times 10^{-4} \text{ mol/dm}^3$  [37]. In the case of TX100 the values of CMC measured:  $2.9 \times 10^{-4} \text{ mol/dm}^3$  are a little different from those in literature:  $2.38 \times 10^{-4} \text{ mol/dm}^3$  [38].

It is well known that the various methods used for detection of the CMC often lead to different numerical estimates, not only because of measurement errors but also because the CMC is the range rather than a single pinpointed value [39].

The changes of the CMC values as a function of  $\alpha$  determined by all three methods are going through a minimum at  $\alpha$  equal 0.6. It should be noted that at minimum the surface tension reduction was appeared at  $\alpha$  equal 0.2. For explanation of these differences we employed the molecular-thermodynamic theory of mixed surfactant solutions [20,40,41]. This theory allows us to predict the critical micelle concentration of nonideal binary surfactant mixtures in aqueous solution.

The CMC of a binary mixture of surfactants 1 and 2 can be expressed as a function of the CMCs of the constituent pure surfactants as follows:

$$\frac{1}{\text{CMC}_{12}} = \frac{\alpha}{f_1^* \text{CMC}_1} + \frac{1-\alpha}{f_2^* \text{CMC}_2} \quad (24)$$

where  $\text{CMC}_{12}$ ,  $\text{CMC}_1$ ,  $\text{CMC}_2$  are the critical micelle concentrations of the mixture, pure surfactant 1, and pure surfactant 2, respectively,  $\alpha$  the solution monomer composition, and the variables  $f_1$  and  $f_2$  are the micellar activity coefficients, which can be computed from:

$$f_1^* = \exp\left(\frac{\beta_{12}(1-\alpha^*)^2}{kT}\right) \quad (25)$$

$$f_2^* = \exp\left(\frac{\beta_{12}(\alpha^*)^2}{kT}\right) \quad (26)$$

where  $\beta_{12}$  is the parameter that reflects specific interactions between surfactants 1 and 2,  $\alpha^*$  the optimal micellar composition, i.e. the composition at which the free energy of mixed micellization attains its minimal value,  $k$  the Boltzmann constant, and  $T$  the absolute temperature.

The value of  $\alpha^*$  can be obtained from the molecular thermodynamic theory from the relation:

$$\frac{\beta_{12}}{kT}(1-2\alpha^*) + \ln\left(\frac{\alpha^*}{1-\alpha^*}\right) = \ln\left(\frac{\alpha}{1-\alpha} \frac{\text{CMC}_2}{\text{CMC}_1}\right) \quad (27)$$

The calculated values of CMC from Eq. (24) are presented in Fig. 7 (curve 4). From this figure it appears that the changes of the CMC values as a function of  $\alpha$  are somewhat similar to those obtained from the adsorption isotherm; however, the minimal value is obtained at  $\alpha=0.2$ . It means that the theoretical minimal value of CMC for the mixture of CTAB and TX100 appears at the same composition of the mixture at which the maximal reduction of the surface tension of solutions takes place (Fig. 4). Surface tension reduction of water by surfactants is con-

Table 3

Values of the mole fraction of surfactant 1 in the mixed micelle,  $X_1^M$ , molecular interaction parameter in the mixed micelle,  $\beta^M$ , activity coefficients of the surfactants 1 and 2 in and mixed micelle ( $f_1^M$  and  $f_2^M$ )

	$X_1^M$	$\beta_1^M$	$f_1^M$	$f_2^M$
0.2	0.2036	-1.9758	0.2856	0.9213
0.4	0.3401	-2.7887	0.2969	0.7242
0.6	0.4325	-3.4948	0.3245	0.5201
0.8	0.5273	-2.3463	0.5920	0.5208

nected with their tendency to adsorb at water–air interface, and the decrease of this surface tension by 20 mN/m is a good measure of this tendency; therefore, for comparison of the influence of CTAB and TX100 mixtures composition on the tendency to adsorb and to form micelles, the ratio of  $\text{CMC}/C_{20}$  was calculated, which is shown in Fig. 7 (curves 5 and 6). From this figure it is seen that there is the maximum of  $\text{CMC}/C_{20}$  for CMC values obtained from the adsorption isotherm and calculated from Eq. (24) at  $\alpha=0.2$ . It means that for this composition of the surfactant mixture the tendency to adsorb is higher than that to form micelles. It is interesting that at  $\alpha=0.2$  the composition of the mixed monolayer at  $C_{20}$  (determined from Eq. (11)) and mixed micelles (calculated from Eq. (13) (Table 3) is nearly the same as the composition of CTAB and TX100 in the bulk phase, but at  $\alpha=0.4, 0.6$  and  $0.8$ , the mole fraction of CTAB ( $X_1$ ) in the mixed monolayer and mixed micelles is lower than in bulk phase.

According to Liljekvist and Kronberg [42] the minimum of CMC appears if the composition of the mixed micelle is almost the same as the bulk phase and is in accordance with our CMC determined theoretically, but a minimum of CMC determined experimentally by three different methods appears at  $\alpha=0.6$ , where the molecular mole fraction of CTAB is lower in the mixed micelle than in the bulk phase. At  $\alpha=0.6$  the molecular interaction parameter in the mixed micelle,  $\beta^M$ , calculated from Eq. (12) (Table 3) has also the lowest value.

Because the values of  $\beta^M$  for all mixtures are negative and their absolute values are higher than  $|\ln((C_1^M)/(C_2^M))|$ , we can state that synergism exists in mixed micelle formation in the solution of all examined mixtures. However, taking into account the lowest value of  $\beta^M$  the best synergism exists at  $\alpha=0.6$ .

On the basis of the data presented above it is difficult to explain exactly why the minimum of CMC calculated theoretically appears at a different composition of the mixed micelle than that obtained from measurements of the surface tension, density and conductivity of CTAB and TX100 mixtures of aqueous solution. It is possible, as suggested by Ysambertt et al. [39], the CMC is rather the concentration range than one point value, and this range depends on the composition of CTAB and TX100 mixture. It is interesting that at  $\alpha=0.6$ . The highest difference between the CMC values determined by three methods is observed among of all studied compositions, but at  $\alpha=0.2$  the values obtained from surface tension, density and conductivity measurements are close to one another. This fact confirms to some extent our suggestion.



#### 4.5. The standard free energy of micellization

The tendency of surfactants to form micelles can be established on the basis of standard free energy of micellization ( $\Delta G^\circ_{\text{mic}}$ ). In the literature there are many different ways for determination of this energy. Recently, Maeda [27,43] has proposed a new approach of standard free energy determination for mixed micelles involving ionic species. In this approach  $\Delta G^\circ_{\text{mic}}$  for mixtures of two surfactants including one nonionic and one ionic are given as a function of the ionic surfactant in the mixed micelle by:

$$\frac{\Delta G^\circ_{\text{mic}}}{RT} = B_0 + B_1x_1 + B_2x_1^2 \quad (28)$$

where  $B_0$  is the independent term related to CMC of nonionic surfactant by  $B_0 = \ln C_2$ . The other parameter,  $B_1$ , is related to the standard free energy change upon replacement of a nonionic monomer in the nonionic pure micelle with an ionic monomer and  $B_2$  is equivalent to  $\beta^M$  calculated from Eq. (12). Finally, the parameters  $B_1$  and  $B_2$  are related to the CMC values of pure systems by the equation:

$$\ln \left( \frac{C_1}{C_2} \right) = B_1 + B_2 \quad (29)$$

The calculated values of  $B_1$  are negative and equal:  $-0.826$ ,  $-1.640$ ,  $-2.3458$ ,  $-1.1974$  for  $\alpha = 0.2, 0.4, 0.6, 0.8$ , respectively. According to Maeda [43] parameter  $B_1$  is related to the standard free energy change associated with the introduction of one ionic species into a nonionic micelle coupled with the release of one nonionic species from the micelle. The change of this standard free energy is associated with the transfer process consisting of two contributions: interaction between the head groups and between the hydrocarbon chains. When the hydrocarbon chains are of the same kind, the first contribution is predominant; however, when there is dissimilarity between the hydrocarbon tails the interaction between these tails becomes more significant and makes the values of  $B_1$  negative. In our case not only the interactions between hydrocarbon chain affected the values of  $B_1$  but also the steric factor due to the presence of phenyl group of TX100, which interact with the quaternary ammonium group of CTAB.

According to Robson and Dennis [44] the TX100 micelle has a prolate ellipsoid shape with a semiaxis of 52 and 27 Å for the long and short dimension and its structure consisting of a hydrated POE mantle and a hydrocarbon core. Ruiz and Aguiar [27] determined the length of the whole molecule of CTAB-21.5 Å. This value compared with the dimensions of TX100 micelles indicates that, from the steric point of view, the incorporation of CTAB monomers in the TX100 micelle produces a minor distortion in their micellar structure.

On the basis of the values of  $B_1$ ,  $B_2$  and the molecular interaction parameter in the mixed micelle,  $\beta^M$ , we determined the values of the standard free energy of micellization of TX100 and CTAB mixtures from Eq. (28) which are presented in Fig. 8 (curve 3). The points in curve 3 (Fig. 8) corresponding to the values of the standard free energy of micellization of individual

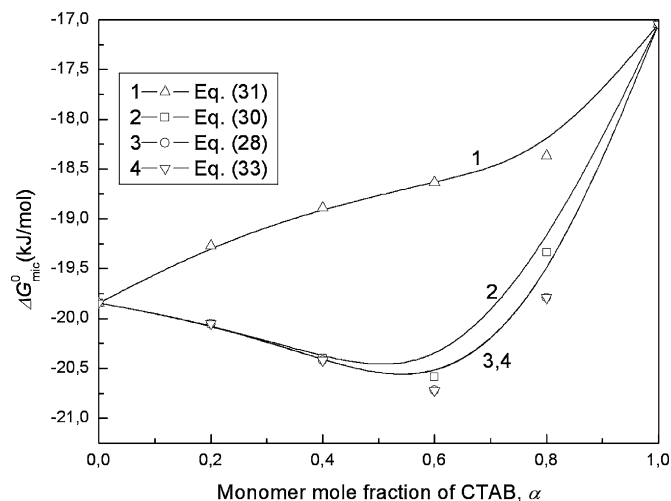


Fig. 8. Dependence of the free energy of micellization  $\Delta G^\circ_{\text{mic}}$  determined from Eq. (31) (curve 1), Eq. (30) (curve 2), Eq. (28) (curve 3) and Eq. (33) (curve 4) on the monomer mole fraction of CTAB,  $\alpha$ .

surfactants were determined from the following equation [38]:

$$\Delta G^\circ_{\text{mic}} = RT \ln \text{CMC} \quad (30)$$

These values of standard free energy of micellization for TX100 and CTAB are equal  $-19.843$  kJ/mol and  $-17.044$  kJ/mol, respectively.

In Fig. 8 there are also presented the values of standard free energy of micellization of TX100 and CTAB mixtures estimated by other two different ways. Curve 2 presents the values of  $\Delta G^\circ_{\text{mic}}$  calculated from the same equations as in the case of individual surfactants (Eq. (30)). From Fig. 8 it is seen that for the mixture of TX100 and CTAB at  $\alpha = 0.2$  and  $0.4$  there is a very good agreement between the values calculated from Eqs. (28) and (30). For mixtures of monomer mole fraction of CTAB higher than  $0.4$  the values of  $\Delta G^\circ_{\text{mic}}$  calculated from Eq. (30) are somewhat higher.

Curve 1 in Fig. 8 represents the values of the standard free energy of micellization for mixtures of two surfactants defined as:

$$\Delta G_{\text{mic}} = X_1^M \Delta G_{\text{mic}1} + X_2^M \Delta G_{\text{mic}2} \quad (31)$$

The values determined in this way are higher than those obtained from Eqs. (28) and (30). It is possible that we can obtain the same values of  $\Delta G_{\text{mic}}$  as those determined from Eqs. (28) and (30) if we add to the right side of Eq. (31) the term of the free energy of micellization resulting from the mixing process of the surfactants in the micelles. This term should fulfil the equation:

$$G^M = RT(X_1^M \ln f_1^M + X_2^M \ln f_2^M) \quad (32)$$

where the  $X_1^M$ ,  $X_2^M$  are the mole fractions of surfactants 1 and 2 in the mixed micelle and  $f_1^M$ ,  $f_2^M$  are the activity coefficients of the surfactants 1 and 2 in the mixed micelle. Adding the Eqs. (31) to (32) we have:

$$\Delta G_{\text{mic}} = X_1^M \Delta G_{\text{mic}1} + X_2^M \Delta G_{\text{mic}2} + G^M \quad (33)$$

The values calculated from Eq. (33) are presented in Fig. 8 (curve 4). From Fig. 8 it appears that the values of the standard free

energy calculated from Eq. (33) are identical as those determined from Eq. (28) and nearly the same as those determined from Eq. (30) (curve 2). In these three relationships presented above there are minimum values of  $\Delta G_{\text{mic}}$  at  $\alpha$  equal 0.6.

These calculations indicate that using Eq. (32) it is possible in a simple way to obtain the values of the standard free energy of micellization for mixtures of two surfactants identical as those proposed by Maeda [43].

#### 4.6. Volumetric properties

Aggregation of the surface active agents into micelles is related to a change of the apparent molal and the partial molar volumes. In the literature there are many works dealing with the apparent molar volume of surfactants,  $\phi_v$ , and the volume change,  $\Delta V$ , upon micelle formation [45,46]. Kale and Zana [47] presented for simple mixture a law for evaluation of  $\phi_v$  and  $\Delta V$  on the basis of density measurements.

The  $\phi_v$  can be evaluated from the following expressions:

$$\phi_v = \frac{M_S}{\rho_0} + \frac{1000(\rho_0 - \rho)}{C\rho\rho_0} \quad (34)$$

where  $M_S$  is the molecular weight of surfactant,  $C$  its concentration (in mol/cm<sup>3</sup>),  $\rho$  and  $\rho_0$  are the density of solution and pure solvent, respectively.

However,

$$\Delta V = \bar{V}_M - \bar{V}_m \quad (35)$$

where  $\bar{V}_M$  and  $\bar{V}_m$  are the partial molal volumes in the micellized and dispersed states, respectively. Usually it is assumed that  $\bar{V}_m$  is equal to the apparent molal volume at infinite dilution.  $\bar{V}_m$  can be calculated from the density by equation [45]:

$$\bar{V}_M = \frac{M_S}{\rho} \left[ 1 - \frac{(100 - c_p)}{\rho} \frac{d\rho}{dc_p} \right] \quad (36)$$

where  $c_p$  is the solution concentration in % by weight.

The values of  $\phi_v$  calculated from Eq. (34) are presented in Fig. 9.

In the case of the surfactant mixtures for calculations of  $\phi_v$  and  $\bar{V}_M$ , average values of  $M_S$  for TX100 and CTAB were used [ $M_S = M_S(1)\alpha + (1 - \alpha)M_S(2)$ ].

From Fig. 9 it appears that the biggest values of  $\phi_v$  are for the TX100 (curve 1) and the smallest for CTAB (curve 6). In the case of mixture of these two surfactants the values become smaller from  $\alpha = 0.8$  to 0.2 (curves 2, 3, 4, 5). For both pure surfactants and each mixture of the lowest concentrations the values of  $\phi_v$  clearly become smaller. After a specific concentration, lower than CMC, the values of  $\phi_v$  are the same. These leveling of the values of  $\phi_v$  before CMC indicate that at these concentrations, dimers or trimers are begging to form.

Fig. 10 shows the values of  $\Delta V$  at CMC determined in different ways. Curve 1 in this figure presents the values calculated from Eq. (35). It appears that there is a small deviation from linear relationship between two points representing the values of  $\Delta V$  for a single surfactant. The linear relationship between

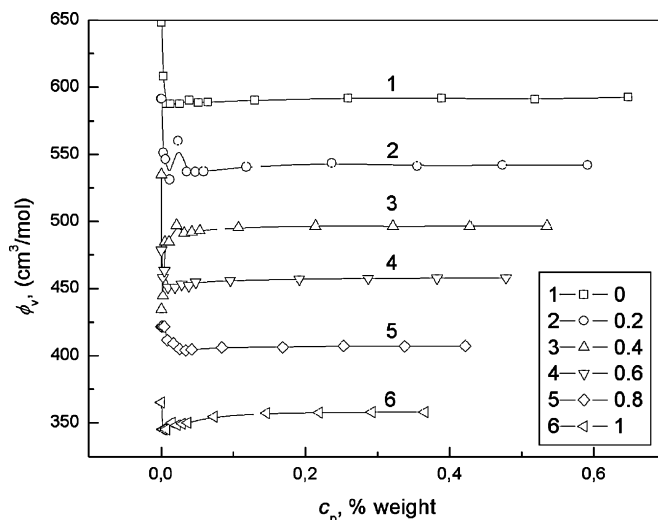


Fig. 9. The relationship between the apparent molar volume of surfactants,  $\phi_v$ , and concentration of solution, in % by weight,  $c_p$ , for mixtures of TX100 and CTAB at different value of monomer mole fraction of CTAB,  $\alpha$ .

these two points (curve 2) is obtained from equation:

$$\Delta V = \Delta V_1\alpha + \Delta V_2(1 - \alpha) \quad (37)$$

Because we proved that in mixture at  $\alpha = 0.2$  the mole fraction of surfactant 1 in the mixed micelle was the same as in the mole fraction in the bulk solution, but for  $\alpha$  in the range from 0.2 to 0.8 the values of  $X_1^M$  are smaller than appropriate  $\alpha$ , we calculate the values of  $\Delta V$  (curve 3) from the equation:

$$\Delta V = \Delta V_1 X_1^M + \Delta V_2(1 - X_1^M) \quad (38)$$

As it is seen in Fig. 10 (curve 3), there is a negative deviation from the linear relationship between  $\Delta V$  at CMC and monomer mole fraction of CTAB in mixture, which confirms the synergism in mixed micelle formation in solution.

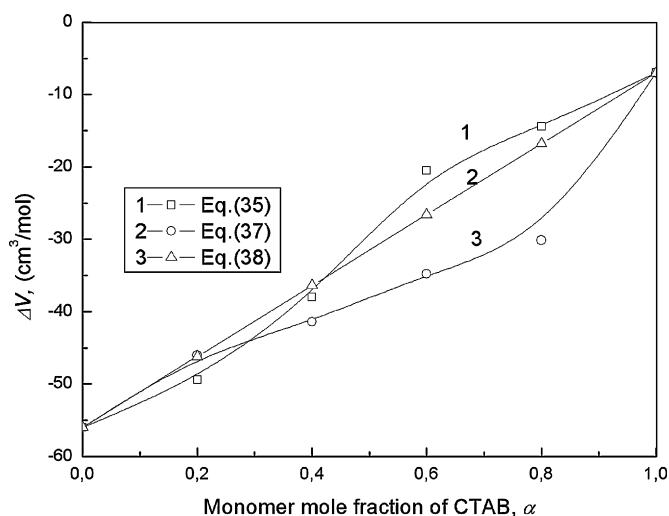


Fig. 10. Dependence between the volume change upon micelle formation,  $\Delta V$ , calculated from Eq. (35) (curve 1), Eq. (37) (curve 2) and Eq. (38) (curve 3) for mixtures of TX100 and CTAB at different value of monomer mole fraction of CTAB,  $\alpha$ .

## 5. Conclusion

The results of the measurements of the surface tension and the calculations of the standard free energy of adsorption and micellization of aqueous solution of CTAB and TX100 suggest that:

- (a) the surface tension depends on the concentration and composition of aqueous solution of CTAB and TX100 mixture and at the concentration close to  $5 \times 10^{-6}$  and higher there is a negative deviation from the linear relationship between  $\gamma$  and  $\alpha$ ;
- (b) for all  $\alpha$  values the parameter of intermolecular interaction in mixed monolayer;  $\beta^\delta$  has a negative value and decreases with surface tension increases of solution of surfactant mixtures solutions;
- (c) using the equation of state derived by Joos [17] and next modified by us [15], it is possible to predict the surface tension of aqueous solution of TX100 and CTAB mixtures almost in the whole range of their concentrations from 0 to CMC;
- (d) it is possible to predict the tendency to adsorb the mixture of CTAB and TX100 only on the basis of standard free energy of adsorption of individual surfactants if we know the monolayer composition at water–air interface.
- (e) on the basis of MT theory of Blankshtein it is possible to predict the CMC of CTAB and TX100 mixtures. The values of CMC calculated are close to those determined from the adsorption isotherms;
- (f) there is a synergism in the surface tension reduction and micelle formation at  $\alpha = 0.2$ ;
- (g) knowing the composition of the mixed micelle it is possible to determine in a simple way the standard free energy of micellization process of CTAB and TX100 surfactant mixtures;
- (h) there is a negative deviation from the linear relationship between  $\Delta V$  at CMC and monomer mole fraction of CTAB in mixture.

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## References

- [1] J.F. Scamehorn, D.A. Sabatini, J.H. Harwell, Encyclopedia of Surface and Colloid Science, Marcel Dekker, New York, 2004, pp. 1458–1469.
- [2] J.M. Rosen, Surfactants and Interfacial Phenomena, Wiley-Interscience, New York, 2004.
- [3] D.C. McDermott, D. Kanelleas, R.K. Thomas, Study of the adsorption from aqueous solution of mixtures of nonionic and cationic surfactants on crystalline quartz using the technique of neutron reflection, Langmuir 9 (1993) 2404–2407.
- [4] Ch. Chien-Hsiang, I.F. Elias, Adsorption dynamics of surfactants at the air/water interface: a critical review of mathematical models, data, and mechanisms, Coll. Surf. A 100 (1995) 1–45.
- [5] K.R. Lange, Surfactants, A Practical Handbook, Hanser Publisher, 1999, pp. 144–169.
- [6] R.A. Campbell, S.R.W. Parker, J.P.R. Day, C.D. Bain, External reflection FTIR spectroscopy of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) on an overflowing cylinder, Langmuir 20 (2004) 8740–8753.
- [7] A.N. Lukyanov, C.P. Torchilin, Micelles from lipid derivatives of water-soluble polymers as delivery systems for poorly soluble drugs, Adv. Drug Deliv. Rev. 56 (9) (2004) 1273–1289.
- [8] L.Ch. Liu, Cholesterol binding to simple micelles in aqueous bile-salt-cholesterol solutions, J. Coll. Interf. Sci. 190 (1997) 261–268.
- [9] P.T. Campana, L.M. Beltrami, A.J. Costa-Filho, G. Tonarelli, Conformation of a synthetic antigenic peptide from HIV-1 p24 protein induced by ionic micelles, Biophys. Chem. 113 (2005) 175–182.
- [10] J. Leja, Surface Chemistry of Froth Flotation, Plenum Press, New York, 1982.
- [11] A.V. Gross, N.H. Cherry, U.S. Patent 4392865, 1983.
- [12] Foams: Physics, Chemistry and Structure, Springer Verlag, 1989, pp. 1–40.
- [13] M.J. Comstock, Emulsion polymers and emulsion polymerization, ACS Symposium Series #165, Washington, 1981.
- [14] N. Hackerman, E.S. Snavely, Corrosion Basic, an Introduction, NACE, Houston TX, 1984.
- [15] J.C. Estes, U.S. Patent 3575855, 1971.
- [16] P.C. Hewlett, Superplasticizers in concrete, Am. Concrete Inst., Detroit, Mich. (1979).
- [17] A.J. Sabia, Text. Chem. Color. 12 (1980) 22–29.
- [18] D. Lopez-Diaz, I. Garcia-Mateos, M.M. Velaques, Synergism in mixtures of zwitterionic and ionic surfactants, Coll. Surf. A 1 (2005) 153–162.
- [19] T.R. Desai, S.G. Dixit, Interaction and viscous properties of aqueous solutions of mixed cationic and nonionic surfactants, J. Coll. Interf. Sci. 177 (1996) 471–477.
- [20] A. Shiloach, D. Blankshtein, Measurements and prediction of ionic/nonionic mixed micelle formation and growth, Langmuir 14 (1998) 7166–7182.
- [21] F.A. Siddiqui, E.I. Franses, Equilibrium adsorption and tension of binary surfactant mixtures at the air/water interface, Langmuir 12 (1996) 354–362.
- [22] J.A. McDonald, A.R. Rennie, A structural study of mixed micelles containing C<sub>16</sub>TAB and C<sub>12</sub>E<sub>6</sub> surfactants, Langmuir 11 (1995) 1493–1499.
- [23] M. Bujan, N. Vdović, N. Filipović-Vinceković, Phase transitions in cationic and anionic surfactant mixtures, Coll. Surf. 118 (1996) 121–126.
- [24] F. Li, G.Z. Li, J.B. Chen, Synergism in mixed zwitterionic–anionic surfactant solutions and the aggregation numbers of mixed micelles, Coll. Surf. A 145 (1998) 167–174.
- [25] A. Murphy, G. Taggart, A comparison of predicted and experimental critical micelle concentration values of cationic and anionic ternary surfactant mixtures using molecular-thermodynamic theory and Pseudophase Separation Theory, Coll. Surf. A 205 (2002) 237–248.
- [26] B. Jańczuk, A. Zdziennicka, W. Wójcik, The properties of mixtures of two anionic surfactants in water at the water–air interface, Coll. Surf. A 220 (2003) 61–68.
- [27] C.C. Ruiz, J. Aguiar, Interaction, stability, and microenvironmental properties of mixed micelles of Triton X100 and *n*-alkyltrimethylammonium bromides: influence of alkyl chain length, Langmuir 21 (2000) 7946–7953.
- [28] P. Joos, Thermodynamics of mixed monolayers, Bull. Soc. Chim. Belg. 76 (1967) 591–600.
- [29] R. Miller, V.B. Fainerman, A.V. Makievski, G. Czichocki, Temperature dependence of the equilibrium and dynamic surface tension of oxyethylated *p*-tert-butyl phenol solutions, Tenside Surf. Det. 38 (2001) 3–8.
- [30] V.B. Fainerman, R. Miller, Simple method to estimate surface tension of mixed surfactant solutions, J. Phys. Chem. B 105 (2001) 11432–11438.
- [31] V.B. Fainerman, R. Miller, E.V. Aksenenko, Simple model for prediction of surface tension of mixed surfactant solutions, Adv. Coll. Interf. Sci. 96 (2002) 339–359.

- [32] X.Y. Hua, M.J. Rosen, Calculation of the coefficient in the Gibbs equation for the adsorption of ionic surfactants from aqueous binary mixtures with nonionic surfactants, *J. Coll. Interf. Sci.* 87 (1982) 469–477.
- [33] D.N. Rubingh, in: K. Mittal (Ed.), *Solution Chemistry of Surfactants*, Plenum Press, New York, 1979, p. 337.
- [34] D.K. Chataraj, K.S. Birdi, *Adsorption and Gibbs Surface Excess*, Plenum Press, New York, 1984, pp. 167–168.
- [35] J.H. de Boer, *The Dynamic Character of Adsorption*, Oxford University Press, Oxford, 1953.
- [36] S. Rosen, Aronson, Standard free energies of adsorption of surfactants at the aqueous solution/air interface from surface tension data in the vicinity of the critical micelle concentration, *Coll. Surf.* 3 (1981) 201–208.
- [37] M. Czerniawski, A study of double layer structure of colloidal electrolytes. IV. Determination of thermodynamic charge on the micelles surface of CTAB, CpyB and DDNH<sub>3</sub>Cl, *Roczniki Chem.* 40 (1966) 1265–1271 (in polish).
- [38] C. Carnero Ruiz, J.A. Molina-Bolivar, J. Aguiar, Thermodynamic and structural studies of Triton X-100 micelles in ethylene glycol-water mixed solvents, *Langmuir* 17 (2001) 6831–6840.
- [39] F. Ysambertt, F. Vejar, J. Paredes, J.-L. Salager, The absorbance deviation method: a spectrophotometric estimation of the critical micelle concentration (CMC) of ethoxylated alkylphenol surfactants, *Coll. Surf. A* 137 (1998) 189–196.
- [40] C. Sarmoria, S. Puvvada, D. Blankschtein, Prediction of critical micelle concentration of nonideal binary surfactant mixtures, *Langmuir* 8 (1992) 2690–2697.
- [41] A. Shiloach, D. Blankschtein, Prediction of critical micelle concentrations and synergism of binary surfactant mixtures containing zwitterionic surfactants, *Langmuir* 13 (1997) 3968–3981.
- [42] P. Liljekvist, B. Kronberg, Comparing decyl- $\beta$ -maltoside and octaethyleneglycol mono *n*-decyl ether in mixed micelles with dodecyl benzenesulfonate, *J. Coll. Interf. Sci.* 222 (2000) 159–164.
- [43] H.J. Maeda, A simple thermodynamic analysis of the stability of ionic/nonionic mixed micelles, *J. Coll. Interf. Sci.* 172 (1995) 98–105.
- [44] R.J. Robson, E.A. Dennis, The size, shape, and hydration of nonionic surfactant micelle. TX100, *J. Phys. Chem.* 81 (1977) 1075–1078.
- [45] L. Benjamin, Partial molal volume changes during micellization and solution of nonionic surfactants and perfluorocarboxylates using a magnetic density balance, *J. Phys. Chem.* 70 (1966) 3790–3797.
- [46] S. Kato, S. Harada, H. Nakashima, H. Nomura, Ultrasonic relaxation and volumetric studies of micelle/monomer exchange process in aqueous solutions of sodium and cesium perfluorooctanates, *J. Coll. Interf. Sci.* 150 (1992) 305–313.
- [47] K.M. Kale, R. Zana, Effect of the nature of the counterion on the volume change upon micellization of ionic detergents in aqueous solutions, *J. Coll. Interf. Sci.* 61 (1977) 312–322.