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Ethanol behaviour at the solution-air interface in the presence of Triton X-100 and cetyltrimethylammonium bromide mixture

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On the basis of the surface tension (γ_{LV}) data of the aqueous solutions of p-(1,1,3,3-tetramethylbutyl)phenoxypoly(ethylene glycol) (Triton X-100 or TX-100) and cetyltrimethylammonium bromide (CTAB) mixture with ethanol published in our previous paper, the process of ethanol adsorption was investigated. For that reason, the values of Gibbs surface excess concentration of ethanol at the solution-air interface and Gibbs standard free energy of its adsorption at that interface were calculated and compared with those determined for the aqueous solutions of ethanol. The surface excess concentration of ethanol at the solution-air interface was calculated with two different methods. The standard free energy of alcohol adsorption was determined from both the Gu and Zhu and Langmuir equations.

1. INTRODUCTION

Short-chain alcohols are common additives used for improvement of surface and volumetric properties of the aqueous solutions of surfactants [1, 2]. Depending on their concentration, they can be regarded as cosurfactants or cosolvents and their behaviour at interfaces depends also on the number of carbon atoms in their molecules. Among the short-chain

alcohols, ethanol seems to possess one of the largest ranges of applica-tions, due to both its surface-active and also disinfecting properties [3, 4].

Despite numerous literature data concerning the surface and volumetric properties of the aqueous solutions of ethanol [5-8], its behaviour in the aqueous solutions of surfactants (especially in the surfactant mixtures in which the synergetic effect in the reduction of the solution surface tension or micelle formation is likely to occur) has not been sufficiently explained yet.

For that reason, we used the data obtained from the surface tension (γ_{LV}) measurements of the aqueous solutions of the mixture of two classical surfactants: nonionic Triton X-100 (TX-100) and cationic cetyltrimethylammonium bromide (CTAB) with ethanol (which were published in our previous paper [9]) and calculated a few thermodynamic parameters describing the process of ethanol adsorption at the solution-air interface at 293 K. The concentration of TX-100 and CTAB mixture (C_1) was in the range from $1 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M and the TX-100 mole fraction in that mixture (α) was equal to 0.2; 0.4; 0.6 and 0.8, respectively. Ethanol mole fraction in the solution (X_2) was in the range from 0 to 1.

2. RESULTS AND DISCUSSION

2.1 Gibbs surface excess concentration of ethanol

To determine the surface excess concentration of ethanol (Γ_2) at the solution-air interface, we applied the Gibbs adsorption isotherm in the following form [5, 10]:

$$\Gamma_2 = -\frac{a_2^v}{RT}\left(\frac{\partial\gamma_{LV}}{\partial a_2^v}\right)_{T,C_1} \tag{1}$$

where R is the gas constant, T is the absolute temperature and a_2^v is the alcohol activity in the bulk phase.

On the basis of the obtained results it can be stated that Gibbs surface excess concentration of ethanol (Figs. 1 and 2 as examples) depends largely on the composition and concentration of TX-100 and CTAB mixture. The maximal value of Γ_2 corresponds to the ethanol mole fraction in the bulk phase which is approximately equal to 0.16. This value of X_2 is close to the critical aggregation concentration of ethanol

(CAC) i.e. ethanol concentration at which its molecules start to form aggregates in the bulk phase [9]. Moreover, the value of this maximum decreases with the increasing concentration of the surfactant mixture (or more precisely with the TX-100 content in that mixture). For the studied solutions Γ_2 is much lower than that for the aqueous solutions of ethanol, especially when the value of surfactant mixture concentration exceeds its critical micelle concentration in the absence of alcohol [5, 11]. It can be connected with the competitive adsorption of alcohol and surfactant molecules. However, it should be remembered that the Gibbs isotherms give real results only at low alcohol concentration because it should approach zero when alcohol content in the solution approaches unity.
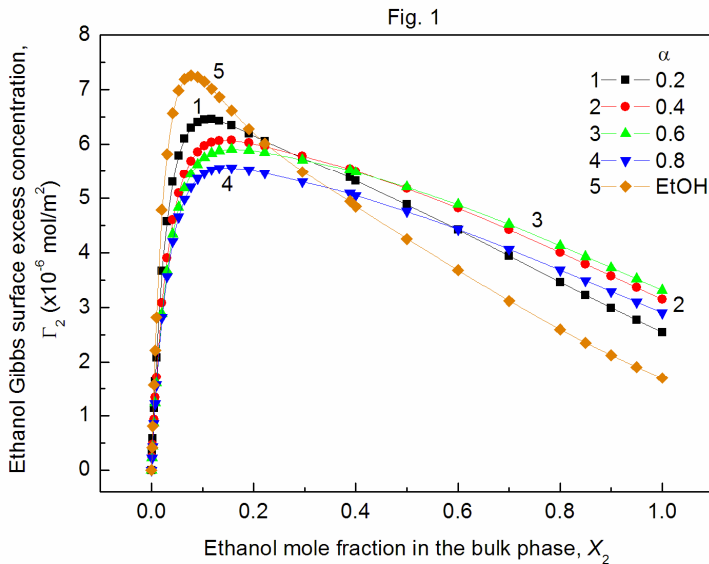

Fig. 1. A plot of the Gibbs surface excess concentration (Γ_2) of ethanol at the solution-air interface calculated from Eq. (1) vs. ethanol mole fraction in the bulk phase (X_2) in the presence of the TX-100 and CTAB mixture at the constant total concentration equal to $1 \cdot 10^{-5}$ M. Curves 1-4 correspond to the TX-100 mole fraction in the mixture with CTAB in the bulk phase (α) equal to 0.2; 0.4; 0.6 and 0.8, respectively. Curve 5 corresponds to the aqueous solutions of ethanol [5].

There is also another approach to calculate Gibbs surface excess concentration of ethanol (Γ_2), assuming that a given alcohol activity at the solution-air interface corresponds to a given value of its surface excess concentration and does not depend on the other constituents of the

solution. Thus, the surface activity of ethanol in the studied solutions was calculated from the Sprow and Prausnitz equation [12]:

$$\gamma_{LV} = \gamma_2 + \frac{RT}{\omega_2} \ln \frac{a_2^S}{a_2^B}$$

(2)

where γ_2 is the surface tension of the aqueous solution of ethanol, ω_2 is the molar area per one square meter of ethanol, a_2^S and a_2^B are the ethanol activities in the surface layer and in the bulk phase [5].
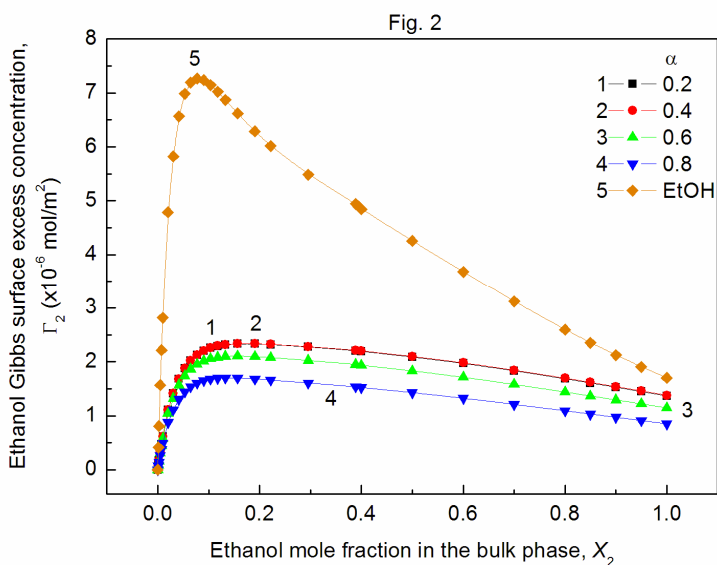

Fig. 2. A plot of the Gibbs surface excess concentration (Γ_2) of ethanol at the solution-air interface calculated from Eq. (1) vs. ethanol mole fraction in the bulk phase (X_2) in the presence of the TX-100 and CTAB mixture at the constant total concentration equal to $1 \cdot 10^{-3}$ M. Curves 1-4 correspond to the TX-100 mole fraction in the mixture with CTAB in the bulk phase (α) equal to 0.2; 0.4; 0.6 and 0.8, respectively. Curve 5 corresponds to the aqueous solutions of ethanol [5].

The Gibbs surface excess concentration of ethanol in its aqueous solution [5] was plotted as a function of its activity at the solution-air interface calculated from Eq. (2) and this plot was used as a 'calibration curve'. Then the Gibbs surface excess concentration of ethanol at the solution-air interface for the studied aqueous solutions of the TX-100 and CTAB mixture with ethanol was determined (Figs. 3 and 4 as examples).

The values of ethanol surface excess concentration obtained with this method depend only slightly on the concentration and composition of the surfactant mixture. They are more consistent with the surface tension (γ_{LV}) data [9] than those obtained directly from the equation of Gibbs adsorption isotherm (Figs. 1 and 2), because over the ethanol CAC the γ_{LV} values of the studied solutions are close to those obtained for the aqueous solutions of ethanol in the absence of surfactants [5]. Over the ethanol CAC, the adsorption of surfactants at the solution-air interface probably does not occur, therefore the maximal value of Γ_2 does not differ considerably from that for the aqueous solutions of ethanol [5]. However, the value of ethanol mole fraction corresponding to its maximal surface excess concentration increases with the increasing concentration of TX-100 and CTAB mixture in the bulk phase (Figs. 3 and 4). It may result from the presence of some alcohol molecules in the micellar phase of surfactants.
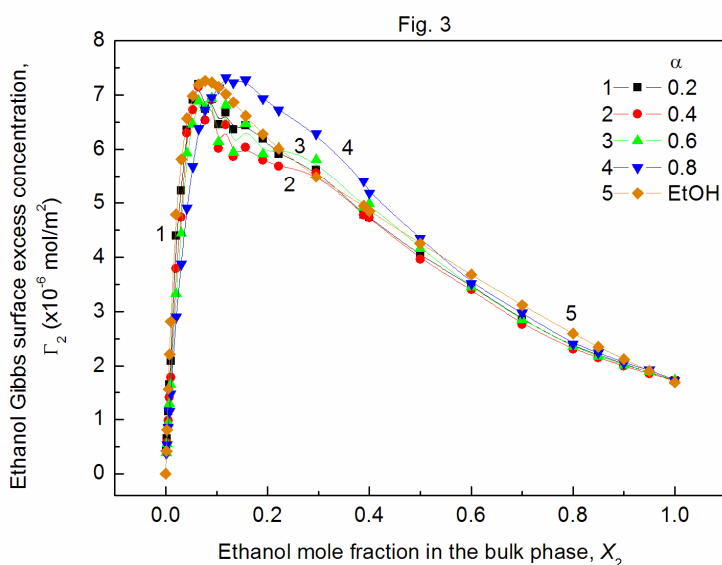

Fig. 3. A plot of the Gibbs surface excess concentration (Γ_2) of ethanol at the solution-air interface calculated on the basis of its activity in the surface layer vs. ethanol mole fraction in the bulk phase (X_2) in the presence of the TX-100 and CTAB mixture at the constant total concentration equal to $1 \cdot 10^{-5}$ M. Curves 1-4 correspond to the TX-100 mole fraction in the mixture with CTAB in the bulk phase (α) equal to 0.2; 0.4; 0.6 and 0.8, respectively. Curve 5 corresponds to the aqueous solutions of ethanol [5].
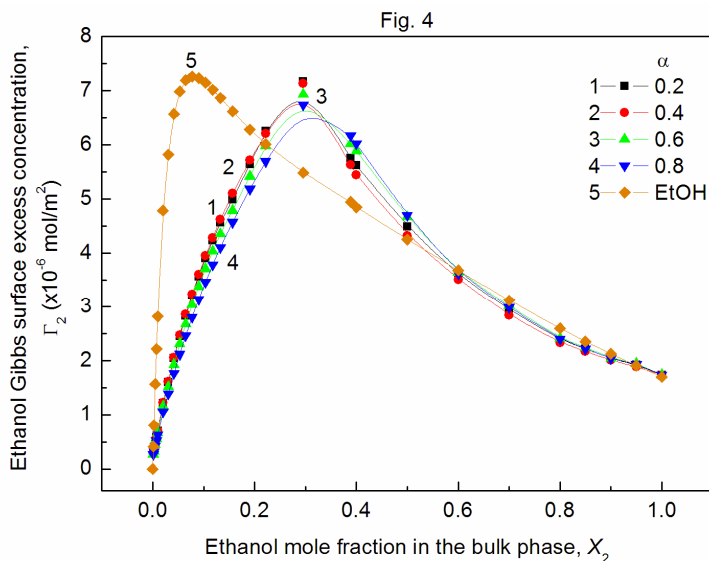
Fig. 4. A plot of the Gibbs surface excess concentration (Γ_2) of ethanol at the solution-air interface calculated on the basis of its activity in the surface layer vs. ethanol mole fraction in the bulk phase (X_2) in the presence of the TX-100 and CTAB mixture at the constant total concentration equal to $1 \cdot 10^{-3}$ M. Curves 1-4 correspond to the TX-100 mole fraction in the mixture with CTAB in the bulk phase (α) equal to 0.2; 0.4; 0.6 and 0.8, respectively. Curve 5 corresponds to the aqueous solutions of ethanol [5].

2.2 Gibbs standard free energy of ethanol adsorption at the solution-air interface

A convenient measure of alcohol tendency to adsorb at the solution-air interface is the Gibbs standard free energy of its adsorption (ΔG_{ads}^0). It can be determined with different methods, but for our calculations the Gu and Zhu adsorption isotherm equation [13-15] as well as the Langmuir equation modified by de Boer [1, 16] were chosen.

The Gu and Zhu adsorption isotherm equation [13-15] was developed for the hydrophilic high-energy solids, but it turned out that it can be also useful for the investigation of adsorption process of ethanol at the solution-air interface. It has the following form:

$$\Gamma_2 = \frac{\Gamma_2^\infty K C_2^n}{1 + K C_2^n} \tag{3}$$

where $K = k_1 k_2$ (k_1 and k_2 are the equilibrium constants of the surface monolayer and aggregate formation, respectively, n is the aggregation number of ethanol surface aggregates, C_2 is the molar concentration of ethanol and Γ_2^∞ is the maximal surface excess concentration of ethanol).

It should be mentioned that free and adsorbed species of the solution are in equilibrium.

Equation (3) can be transformed into the logarithmic form:

$$\log\left(\frac{\Gamma_2}{\Gamma_2^\infty - \Gamma_2}\right) = \log K + n \log C_2 \tag{4}$$

If the plot of $\log\left(\dfrac{\Gamma_2}{\Gamma_2^\infty - \Gamma_2}\right)$ versus $\log C_2$ is linear, the K and n constants can be determined from Eq. (4). If $n = 1$, then $K = 1/a$ where a is the constant in the Langmuir equation which at 293 K fulfils the condition [1]:

$$a = 55.4 \exp \frac{\Delta G_{ads}^0}{RT} \tag{5}$$

When the value of Γ_2^∞ equal to 7.91 x 10^{-6} mol/m^2 (which is related to the minimal surface area of adsorbed ethanol molecule arranged perpendicularly to the solution-air interface equal to 21 Å^2) [17] was applied in Eq. (4), it occurred that the dependence between $\log\left(\dfrac{\Gamma_2}{\Gamma_2^\infty - \Gamma_2}\right)$ and $\log C_2$ is a straight line in the range of low alcohol concentration and the value of its slope is close to 1, so the standard Gibbs free energy of ethanol adsorption (ΔG_{ads}^0) could be determined from Eq. (5) (Table 1).

The second approach used to determine ΔG_{ads}^0 of ethanol was the Langmuir equation modified by de Boer [16] which has the following form:

$$\frac{A_0}{A - A_0} \exp \frac{A_0}{A - A_0} = \frac{C_2}{\omega} \exp\left(\frac{-\Delta G_{ads}^0}{RT}\right) \tag{6}$$

where A is the occupied area per molecule at the interface, A_0 is the limiting co-area per molecule of the adsorbed ethanol molecules and ω is the number of water moles in 1 dm^3.

Table 1. Standard Gibbs free energy of ethanol adsorption (ΔG_{ads}^0) calculated from equations (5) and (6).

$C_1(M)$[a]	α[b]	ΔG_{ads}^0 (kJ/mol)			
		Eq. (5)[c]	Eq. (6)[c]	Eq. (5)[d]	Eq. (6)[d]
$1 \cdot 10^{-6}$	0.2	−9.83	−9.55	−9.75	−10.72
	0.4	−9.72	−9.45	−9.60	−10.41
	0.6	−9.67	−9.41	−9.56	−10.41
	0.8	−9.49	−9.26	−9.53	−10.28
$1 \cdot 10^{-5}$	0.2	−8.86	−8.7	−8.77	−9.38
	0.4	−8.23	−8.12	−8.36	−8.75
	0.6	−8.00	−7.91	−8.01	−8.44
	0.8	−7.94	−7.88	−7.52	−8.06
$1 \cdot 10^{-4}$	0.2	−7.25	−7.23	−6.95	−7.48
	0.4	−6.18	−6.24	−6.37	−6.61
	0.6	−6.04	−6.12	−6.13	−6.45
	0.8	−5.95	−6.07	−5.86	−6.23
$1 \cdot 10^{-3}$	0.2	−5.27	−5.41	−5.53	−6.00
	0.4	−5.26	−5.39	−5.50	−6.01
	0.6	−5.11	−5.27	−5.18	−5.88
	0.8	−4.66	−4.86	−4.85	−5.71

[a] C_1 – the TX-100 and CTAB mixture concentration in the bulk phase
[b] α – the TX-100 mole fraction in the mixture with CTAB in the bulk phase
[c] Surface excess concentration of ethanol was calculated directly from the Gibbs adsorption isotherm equation (Eq. (1))
[d] Surface excess concentration of ethanol was calculated on the basis of its surface activity at the solution-air interface

To calculate ΔG_{ads}^{0} we used the Gibbs surface excess concentration of ethanol determined using both methods described previously. It appeared that if Γ_2 is determined directly from Eq. (1), the ΔG_{ads}^{0} values calculated from Eqs. (5) and (6) are almost the same for a given concentration and composition of TX-100 and CTAB mixture (Table 1). They increase with the increasing concentration of that mixture which indicates the decreasing tendency of ethanol to adsorb at the solution-air interface in the presence of surfactants. It should be also stated that at low concentration of the surfactant mixture, ΔG_{ads}^{0} values are close to that obtained for the aqueous solutions of ethanol [5]. If the Gibbs surface excess concentration of ethanol is obtained on the basis of its surface activity, ΔG_{ads}^{0} values evaluated from Eqs. (5) and (6) differ only slightly from each other (less than 1kJ/mol) and probably it results only from a more complex way of Γ_2 determination (Table 1).

3. CONCLUSIONS

Based on the obtained results and their analysis it can be stated that:
The values of Gibbs surface excess concentration of ethanol determined based on its activity at the solution-air interface are more consistent with the surface tension changes of the studied solutions than those obtained directly from the Gibbs adsorption equation.

The maximal values of this excess concentration correspond to the ethanol mole fraction at which its molecules start to form aggregates in the bulk phase and they are lower than that resulting from the maximal packing of ethanol molecules at the water-air interface.

The tendency of ethanol to adsorb at the solution-air interface decreases with the increasing concentration of the surfactant mixture. The values of Gibbs standard free energy of ethanol adsorption calculated from both the Gu and Zhu equation, and from the Langmuir one are almost the same.

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REFERENCES

[1] M. J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley-Interscience, New York, 2004.

[2] R. Zana, *Adv. Colloid Interface Sci*., **57**, 1-64, (1995).

[3] W. R. Moorer, *Int. J. Dent. Hyg.,* **1(3)**, 138-142, (2003).

[4] F. A. van Engelenburg, F. G. Terpstra, H. Schuitemaker, W. R. Moorer, *J. Hosp. Infect.,* **51(2)**, 121-5, (2002).

[5] A. Chodzińska, A. Zdziennicka, B. Jańczuk, *J. Sol. Chem.,* **41**, 2226-2245, (2012).

[6] Y. F. Yano, *J. Colloid Interface Sci.,* **284**, 255-259, (2005).

[7] R. Zana, M. J. Eljebari, *J. Phys. Chem*., **97**, 11134-11136, (1993).

[8] M. Kahlweit, G. Busse, J. Jen, *J. Phys. Chem*., **95**, 5580-5586, (1991).

[9] M. Bielawska, B. Jańczuk, A. Zdziennicka, *J. Surfactants Deterg*., **16**, 203-212, (2013).

[10] A. W. Adamson, A. P. Gast, *Physical Chemistry of Surfaces*, Wiley Interscience, New York, 1997.

[11] K. Szymczyk, B. Jańczuk*, Colloids Surf. A*, **293**, 39-50, (2007).

[12] F. B. Sprow, J. M. Prausnitz, *Can. J. Chem. Eng*., 45, 25-28, (1967).

[13] T. Gu, B-Y. Zhu, *Colloid Surf*., **44**, 81–87, (1990).

[14] T. Gu, B-Y. Zhu, H. Rupprecht, *Prog. Colloid Polym. Sci*., **88**, 74-85 (1992).

[15] B-Y. Zhu, T. Gu, *Colloid Surf*., **46**, 339-345, (1990).

[16] J. H. De Boer, *The dynamic character of adsorption*, Oxford University, Oxford, 1953.

[17] B. Jańczuk, W. Wójcik, T. Białopiotrowicz, *Polish J. Chem,*. **65**, 1333-1340, (1991).

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