Colloid Polym Sci 278:321–328 (2000)

ORIGINAL CONTRIBUTION

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Adsorption of TX100 and TX165 at the aqueous solution–air interface: free enthalpy of adsorption and equation of state

Received: 13 July 1999
Accepted in revised form: 20 October 1999

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Abstract Surface tension measurements of aqueous solutions of TX100 and TX165 were made at different temperatures. The thermodynamic parameters of the adsorption calculated from the surface tension measurements, using several methods, have given slightly different values. The equation of state for the TX100 and TX165 monolayers at the solution–air interface was analysed. There is excellent agreement between the modified Volmer equation of state and the experimental π–A isotherms.

Key words Surface tension · Nonionic surfactant · Adsorption · Equation of state · Free enthalpy of adsorption

Introduction

Nonionic surfactants play an important role in a number of bulk chemical applications. They are widely used in a variety of industrial and commercial applications and are largely exploited for their detergency, solubilisation, and surface wetting in diverse areas, such as mining, petroleum, chemical, and biochemical research [1, 2]. The physical phenomenon basic to these many applications of surfactants is their tendency to be preferentially adsorbed at interfaces of various types. Such adsorption will usually affect a system or process by altering the energetic or mechanical characteristics of the interface, for instance, by lowering the interfacial tension between two immiscible liquid phases, by altering the wetting properties of a solid surface, or by interposing between phases an electrical or physical barrier that inhibits or prevents close approach or contact between dispersed droplets or particles. These and several other properties of surfactants adsorbed at interfaces represent the important physical and chemical consequences of surface activity that make surfactants the foundation of so many modern technological innovations.

The mechanism of adsorption of nonionic surfactants at solid–liquid and liquid–vapour interfaces and the orientation and interaction of their molecules in the interface region have been the subject of several works [3, 4]. It is well established that surfactants form monolayer films at the liquid–vapour interface. At bulk solution concentrations well below the critical micelle concentration (cmc), the excess concentration of the surfactant at the interface is low and, at the air–water interface, the alkyl chains of the surfactants adsorbed probably lie mostly parallel to the surface. As the concentration is increased, adsorption increases and surfactant molecules adopt a vertical position at the interface. The surface excess reaches a constant value at bulk concentrations well below the cmc, often as low as 0.3 × cmc [5]. At this stage, the area occupied by the surfactant molecule is still much larger than the cross-sectional area of the molecule in the surfactant crystal because the headgroup solvation and mutual electrostatic repulsion keep the adsorbed alkyl chain ions apart. The further, usually quite large decrease in surface tension as the surfactant concentration is increased up to the cmc is accompanied by only small changes in surface composition. A neutron-reflection study at the solution–air interface recently provided experimental evidence that changes in surface structure occur at bulk concentrations up to and beyond the cmc [6].

The nature of the interfacial monolayer of the surfactant may also be elucidated by applying a rigorous thermodynamic treatment of the interfacial tension data, which are considered as a function of different thermodynamic variables. The thermodynamic study of aqueous solutions of surfactant is important for the knowledge of the interaction between the surfactant and water molecules. The standard thermodynamic parameters of the adsorption of the surfactant can be calculated from the surface tension measurements. These data can also be useful in the study of the equation of state for monolayer surfactant films at the air–liquid and liquid–liquid interfaces. In the two-dimensional approach, the kinetic and the various intermolecular forces operating on the molecules of the surfactant in the monolayer are assumed to give rise to a surface pressure, $\pi = \gamma_0 - \gamma$. This pressure is equal to the decrease in surface tension due to the presence of surfactant. An equation of state relating π to the area, A, occupied by the surfactant can be derived by considering the various types of forces contributing to the pressure in much the same way that the $PV = nRT$ relationships are obtained for three-dimensional gases. From the surface tension data, it is possible to establish the limiting value of the product πA and the region of A values where the intermolecular forces between surfactant molecules influence the surface tension of the solution.

Thus, the present investigation was to measure the surface tension of aqueous solutions of the nonionic surfactants TX100 and TX165 at different temperatures, particularly at low surfactant concentrations. From these measurements, the thermodynamic parameters of adsorption at the air–liquid interface have been calculated.

Experimental

The TX100 and TX165 surfactants are nonionic surfactants, containing an average of 9.5 and 16 oxyethylene units per molecule. They were manufactured and supplied by SEPPIC (France) with high grade of purity (the curve of surface tension, γ, versus the logarithm of the concentration, ln c, shows no minimum near the cmc region). The surfactant solutions were prepared with water, which was distilled after deionisation on ion-exchange resins. The surface tension of the water was always tested before preparing the solutions.

The surface tension of the aqueous solutions of TX100 and TX165 was measured at 15, 30, and 40 °C under atmospheric pressure, with a Kruss K12 processor tensiometer using the Wilhelmy-plate method. The apparatus was controlled by a computer, which also analysed the results. This allowed the measurement process to be repeated, once the maximum pull on the plate was reached, without taking the plate out of the solution. The temperature was maintained within ±0.1 °C with thermostated water, from a Haake-C thermostat, circulating through a jacket surrounding the vessel containing the surfactant solution. In all cases, more than 30 successive measurements were carried out. The standard deviation of the surface tension for 30 measurements of different samples at the same concentration was ±0.05 mN m^{-1}. However, for the same sample the standard deviation of 30 successive measurements of the surface tension from the maximum pull on the plate was ±0.01.

Results and discussion

The change in surface tension is shown as a function of the increase in surfactant concentration, at 15, 30, and 40 °C, in Figs. 1 and 2. The surface tension curves of TX100 and TX165, at different temperatures, have the same shape. At low surfactant concentration the surface tension decreases slightly. When the surfactant concentration increases and becomes equal to about 0.11 × cmc, the surface tension decreases strongly until the cmc is reached. Near the cmc region the relationship between the surface tension, γ, and ln c is linear. At a given concentration, γ decreases as the temperature increases. The cmc values determined from the γ-ln c curves are presented in Tables 1 and 2. For TX100 and TX165, the cmc decreases from 2.70×10^{-4} to 2.24×10^{-4} to 2.07×10^{-4} mol l^{-1} and from 6.37×10^{-4} to 5.02×10^{-4} to 4.33×10^{-4} mol l^{-1}

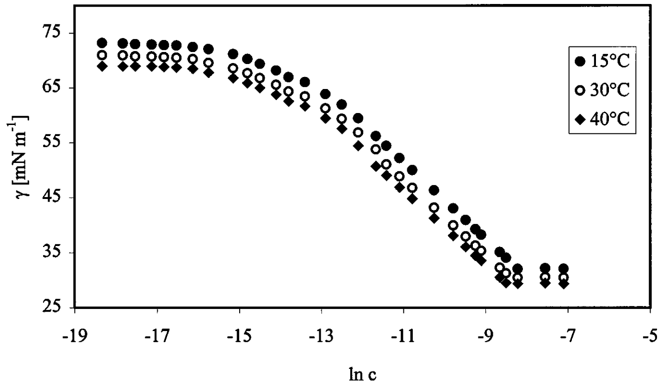

Fig. 1 Variation of the surface tension of TX100 at 15, 30, and 40 °C

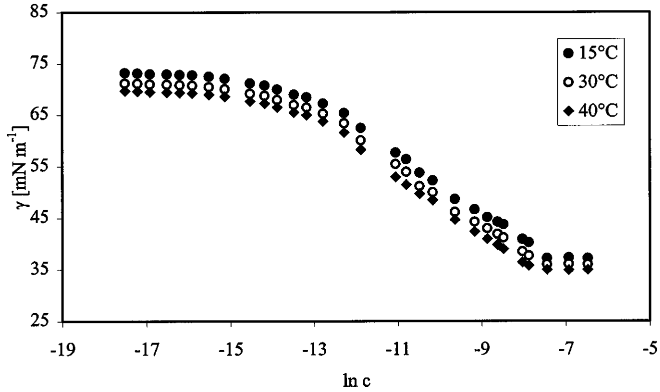

Fig. 2 Variation of the surface tension of TX165 at 15, 30, and 40 °C

Table 1 Values of the critical micelle concentration (*cmc*), Γ_m, A_m, and π_m for aqueous solutions of TX100 at 15, 30, and 40 °C

Temperature (°C)	cmc (mol l^{-1})	Γ_m (mol m^{-2})	A_m (Å^2)	π_m (mN m^{-1})
15	2.70×10^{-4}	2.92×10^{-6}	57	40.8
30	2.24×10^{-4}	2.75×10^{-6}	60	40.4
40	2.07×10^{-4}	2.57×10^{-6}	65	39.5

Table 2 Values of the critical micelle concentration (*cmc*), Γ_m, A_m, and π_m for aqueous solutions of TX165 at 15, 30, and 40 °C

Temperature (°C)	cmc (mol l^{-1})	Γ_m (mol m^{-2})	A_m (Å^2)	π_m (mN m^{-1})
15	6.37×10^{-4}	2.27×10^{-6}	73	36
30	5.02×10^{-4}	2.17×10^{-6}	77	35.2
40	4.33×10^{-4}	2.09×10^{-6}	79	34.7

when the temperature varies from 15 to 30 to 40 °C, respectively.

The decrease in the surface tension with surfactant concentration is a consequence of the surfactant adsorption at the solution–air interface. When interfacial adsorption occurs, the energy of the interface changes. To understand and predict the role of surfactant adsorption, it is necessary to know the number of surfactant molecules adsorbed at the interface of interest. The Gibbs equation, which relates the change in the interfacial energy of a system to the amount of surfactant adsorbed and the composition of the bulk phase, forms the basis for understanding the thermodynamics of the adsorption process. Under conditions of constant temperature and pressure, the basic equation is [7]

$$d\gamma_i = -\sum_i \Gamma_i \, d\mu_i \ . \tag{1}$$

In the simplest case, that of a two-component system, Eq. (1) becomes

$$d\gamma = -(\Gamma_1 \, d\mu_1 + \Gamma_2 \, d\mu_2) \ . \tag{2}$$

This equation describes how the surface tension of a solution of, say, component 2 in solvent 1 is changed as the activity of component 2 is altered, at constant temperature. If we choose the dividing surface so that $\Gamma_1 = 0$, then $\Gamma_2 = \Gamma_2^\sigma = \Gamma_{2,1}$ and so

$$d\gamma = -\Gamma_{2,1} \, d\mu_2 \ . \tag{3}$$

We can also write

$$\mu_2 = \mu_0 + RT \ln a_2 \ ; \tag{4}$$

so

$$d\mu_2 = RT d \ln a_2 \ , \tag{5}$$

where a_2 is the activity of component 2. It follows that

$$\Gamma_{2,1} = -\frac{1}{RT} \frac{d\gamma}{d \ \ln \ a_2} \ . \tag{6}$$

If the solution is fairly dilute, then

$$\Gamma_{2,1} = -\frac{1}{RT} \frac{d\gamma}{d \ \ln \ c_2} \ . \tag{7}$$

The values of $d\gamma/dc$ were determined by fitting the γ–ln c curve with the polynomial function

$$f(x) = a_n c^n + a_{n-1} c^{n-1} + \cdots + a_1 c + a_0 \ . \tag{8}$$

This function was used to fit the surface tension data only in the range of c from 0 up to the concentration corresponding to the first point of saturation at the air–solution interface (the point at which the curves become linear, before the cmc). At the cmc value the amount of TX100 and TX165 adsorbed is a maximum and it corresponds to the minimum value of the area occupied per surfactant molecule at the interface, A_m. From the amount adsorbed, Γ, it is possible to calculate the area per molecule, A,

$$A = \frac{1}{N_A \Gamma_{2,1}} \ , \tag{10}$$

where N_A is the Avogadro number. The maximum amount adsorbed, Γ_m, the minimum area per molecule, A_m, and the maximum surface pressure, π_m, are presented in Tables 1 and 2. The cmc, the amount adsorbed, and the surface pressure at saturation decrease, while the area per molecule at saturation increases as the temperature is raised. The effects of temperature changes on the cmc of aqueous solutions of surfactants is quite complex [8–10]. It has been shown that the cmc of most ionic and nonionic surfactants regularly decreases on increasing the temperature up to the critical solution temperature, passes through a minimum, and increases. The initial decrease in the cmc can be explained as a direct consequence of the decrease in the hydrophilicity of the surfactant molecules, which is due to a smaller probability of hydrogen-bond formation between the surfactant and water at higher temperature. It seems clear that the area of impact is in the degree of hydration of the headgroup of the surfactant, since the structuring of water molecules is known to be very temperature sensitive. As the temperature of the system is increased, the degree of hydration decreases. The net result will be a loss of energetic factor favouring dissolution and an increase in the tendency towards micelle formation; therefore, the onset of micellisation occurs at a lower concentration as the temperature increases. In contrast, while the surfactant dissolves in water, the alkyl tailgroup distorts the water structure. The increase in temperature also causes an increase in the breakdown of the structured water molecules surrounding the hydrophobic alkyl chain of the surfactant. The result from this scenario is a reduction in the magnitude of the free-energy component attributable to the hydrophobic effect. Such an effect increases the solubility of the alkyl chain in water and, consequently, the onset of micellisation tends to occur at higher concentration as the temperature is raised. The existence of a minimum cmc value in the cmc–temperature curve is thus an outcome of these two opposing effects.

The standard thermodynamic functions

There are different equations which may be used to calculate the free energy of adsorption, $\Delta G^0_{\mathrm{ads}}$, of TX100 and TX165 at the solution–air interface. According to the concept of Langmuir, if the adsorbed molecules are immobile and are adsorbed on sites at the interface, the area per adsorbed surfactant molecule, A, will be related to the bulk concentration. The free energy of adsorption will satisfy [11]

$$\frac{A_0}{A - A_0} = \frac{c}{\omega}\exp\left(-\frac{\Delta G^0_{\mathrm{ads}}}{RT}\right) \ , \tag{11}$$

where A_0 is the excluded area, i.e., the area of the solution–air interface inaccessible to one molecule due to the presence of another, c is the concentration of the surfactant in the bulk, and ω is the concentration of water. However, in the absence of intermolecular interactions between the surfactant molecules in the film, the adsorbed molecules at the solution–air interface become perfectly mobile. Then, any previously occupied site at the interface may be accessible. A statistical correction to Eq. (11) has been introduced by de Boer [12]. The modified equation may be written as follows:

$$\frac{A_0}{A - A_0}\exp\left(\frac{A_0}{A - A_0}\right) = \frac{c}{\omega}\exp\left(-\frac{\Delta G^0_{\mathrm{ads}}}{RT}\right) \ . \tag{12}$$

The free energies of adsorption (or the free energy of transfer) of TX100 and TX165 molecules at the interface, calculated from Eq. (12), are presented in Figs. 3 and 4. The free energy of adsorption decreases as the temperature is raised. All the curves can be divided into three parts:

1. In the region of low TX100 and TX165 concentrations (a), $\Delta G^0_{\mathrm{ads}}$ increases linearly with the logarithm of the concentration. This is obvious since at low concentration, the surface tension is almost constant; therefore, the area occupied per surfactant molecule does not vary. In this case Eq. (12) can be written

$$\begin{aligned}\Delta G^0_{\mathrm{ads}} &= RT\left[\ln\frac{c}{\omega} - \ln\left(\frac{A_0}{A - A_0}\right) - \left(\frac{A_0}{A - A_0}\right)\right] \\ &= RT\ \ln\frac{c}{\omega} + B \ , \end{aligned} \tag{13}$$

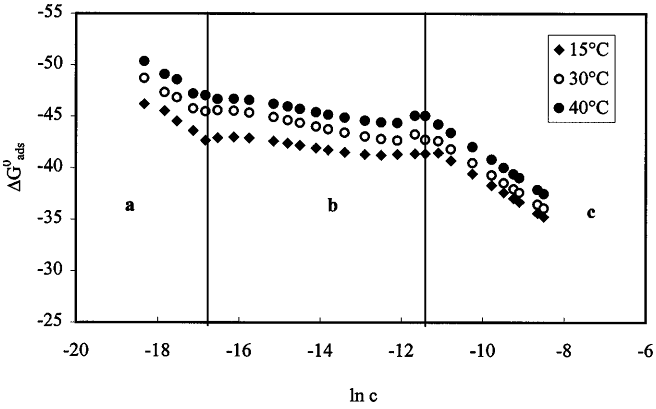

Fig. 3 Dependence of $\Delta G^0_{\mathrm{ads}}$ on ln c for TX100 calculated from Eq. (12) at 15, 30, and 40 °C

   where B is a constant. It appears from this equation that the free energy of adsorption is only a function of the logarithm of the concentration.
2. In the intermediate region (b) the free energy of adsorption increases very slightly and can be considered as constant.
3. The third part of the curves (c) shows a sharp increase in the free energy of adsorption. In this region, there is a linear relation between the free energy of adsorption and the logarithm of the concentration because the area per surfactant molecule remains constant and only the concentration of the surfactant varies.

It can be noted from these data that the $\Delta G^0_{\mathrm{ads}}$ values become more negative with increasing temperature. This indicates that micelle formation and adsorption of the surfactants at the solution–air interface is favoured: as the temperature increases, the hydration of the hydrophobic group of the surfactant decreases and hence the cmc is lower. For each temperature, the free energy of adsorption is more negative for TX100 than for TX165: when the length of the headgroup is raised, because of its polarity, the surfactant is more soluble in water. The hydrogen-bonding interaction between the headgroup and water has a major effect on the water structure at the surfactant hydrocarbon moiety–water interface, which is otherwise structured by a hydrophobic effect. The structured water around the hydrocarbon moiety of the surfactant is disrupted. In other words, the increase in the hydrogen bonding between water and the polar moiety of the surfactant leads to poorer contributions of the hydrophobic interactions, which are the driving forces for adsorption and micellisation. The solubility of the nonionic surfactants TX100 and TX165 depends on the hydrophilic/hydrophobic balance of the surfactant molecules; therefore, raising the number of oxyethylene group from 9.5 to 16 results in a better solubility of the surfactant and as a result the free energy of adsorption is less negative.

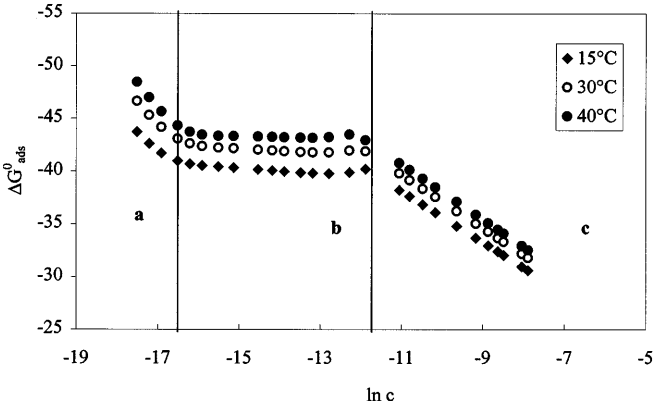

Fig. 4 Dependence of ΔG^0_{ads} on ln c for TX165 calculated from Eq. (12) at 15, 30, and 40 °C

For very dilute aqueous solutions of surfactant, the reduction in the surface tension versus the logarithm of the concentration is weak; therefore,

$$\left(\frac{\partial \pi}{\partial c}\right)_{c\to 0} = \alpha \ , \tag{14}$$

where α is the Traube constant. For this concentration range, the free energy of adsorption may be calculated using the following expression [13]:

$$\Delta G^0_{ads} = -2.303\,RT\,\log\left(\frac{\partial \pi}{\partial c}\right)_{c\to 0} \ . \tag{15}$$

Using the values of the surface tension determined from Eq. (8) in the region of concentrations less than $1 \cdot 10^{-7}$ mol l^{-1}, the standard free energies of adsorption were calculated from Eq. (15) and are presented in Table 3. These values are constant and about 4 kJ/mol lower than those calculated from Eq. (12) in the same range of the concentration (Figs. 3, 4).

Rosen and Aronson [14] have proposed a new method of calculating the standard free energy of adsorption of surfactant molecules at the solution–air interface. They only used the surface tension data in the vicinity of the cmc. Following their method, the standard free energy of adsorption can be calculated from the expression

$$\Delta G^0_{ads} = RT\ln\frac{c}{\omega} - 6.023\pi_m A_m \ . \tag{16}$$

Of course Eq. (15) is only valid in the region of low concentrations, while Eq. (16) is only valid in the vicinity of the cmc. The standard free energies of adsorption of TX100 and TX165 were calculated for each temperature, using Eq. (16) with c equal to the cmc. The results are presented in Table 3. One observes that the free energy of adsorption is negative and becomes more negative when the temperature is raised. A comparison of ΔG^0_{ads} calculated from Eq. (16) and those from Eq. (12) (Figs. 2, 3) shows that the former are 3–5 kJ/mol lower than the later. The weak disagreement between the ΔG^0_{ads} values calculated from the experimental data and using Eqs. (12), (15), and (16) is probably related to the nature and strength of the interactions between film-forming molecules at the solution–air interface. At the interface, the molecules are oriented with their hydrophilic parts directed towards the water phase, while their hydrocarbon tails are directed towards the air-side interface. Thus, two different effects influence the strength of the interactions existing in the monolayer. One of them is due to the attractive forces between the hydrocarbon moiety because of the van der Waals interactions. The second effect is due to the steric repulsion between the oxyethylene headgroup of the surfactant molecules at the interface. Both effects increase when the concentration of the surfactant at the solution–air interface is raised.

Table 3 Values of the standard free energy of adsorption at the solution–air interface for TX100 and TX165

Temperature (°C)	ΔG^0_{ads} (kJ/mol)			
	TX100		TX165	
	Calculated from		Calculated from	
	Eq. (15)	Eq. (16)	Eq. (15)	Eq. (16)
15	−38	−29.3	−36.4	−27.2
30	−40	−31.3	−38.3	−29.3
40	−41	−32.5	−39.6	−30.6

From the values of the standard free energy of adsorption at different temperatures, the standard entropy of adsorption of TX100 and TX165 may be obtained from the following relation:

$$\Delta S^0_{ads} = -\left(\frac{\partial \Delta G^0_{ads}}{\partial T}\right)_{P=\mathrm{cte}} \ . \tag{17}$$

The change in the standard enthalpy of adsorption of TX100 and TX165 may be calculated on the basis of the thermodynamic relation

$$\Delta H^0_{ads} = \Delta G^0_{ads} + T\Delta S^0_{ads} \ . \tag{18}$$

The ΔS^0_{ads} and ΔH^0_{ads} obtained calculated on the basis of the ΔG^0_{ads} values determined from Eq. (16) are presented in Table 4. They do not depend on the temperature and are both positive. On can note that the adsorption of TX100 and TX165 at the solution–air interface gives a negative change in the standard free energy of adsorption (ΔG^0_{ads}) and a positive change in ΔS^0_{ads} and ΔH^0_{ads}. This indicates that there has been an overall increase in molecular disorder, which implies that, despite the restrictions on translational motion imposed by the surface, the hydrocarbon moiety of the

Table 4 Values of $\Delta G^0_{\mathrm{ads}}$, $\Delta S^0_{\mathrm{ads}}$, and $\Delta H^0_{\mathrm{ads}}$ of TX100 and TX165

Temperature (°C)	TX100			TX165		
	$\Delta G^0_{\mathrm{ads}}$ (kJ/mol)	$\Delta S^0_{\mathrm{ads}}$ (kJ/mol)	$\Delta H^0_{\mathrm{ads}}$ (kJ/mol)	$\Delta G^0_{\mathrm{ads}}$ (kJ/mol)	$\Delta S^0_{\mathrm{ads}}$ (kJ/mol)	$\Delta H^0_{\mathrm{ads}}$ (kJ/mol)
15	−29.3	0.130	8.14	−27.2	0.136	12.00
30	−31.3	0.130	8.09	−29.3	0.136	11.91
40	−32.5	0.130	8.19	−30.6	0.136	11.97

surfactant is more mobile and fluidlike at the surface than in the bulk phase, where it is hindered by the solvent. It was pointed out that, in the process of dissolving a hydrocarbon compound in water, the water adjacent to the hydrocarbon moiety is more structured than that in the rest of the bulk phase. This structured water looks like microscopic icebergs around the apolar portion of the surfactant. This water is released when the surfactant is adsorbed at the interface, with a consequent gain in entropy. Whatever the correct explanation, it is clear that a significant component of the free energy of adsorption is entropic in nature, although whether the main driving force for adsorption comes from the van der Waals interactions or from the hydrogen-bonding structural forces in the solvent is still in debate.

Equation of state

The principal parameters which characterise the state of a monolayer of the surfactant compounds at the aqueous solution–air interface are the temperature (T), the surface pressure (π), and the surface area (A) occupied per molecule at the interface. An equation of the general form may, therefore, be referred to as an equation of state of the monolayer: $\pi = \pi(T, A)$. If, at constant temperature, the function $\pi = \pi(A)_{T=\mathrm{constant}}$ is expressed graphically, one may refer to it as the surface pressure–area (π–A) diagram of the monolayer [15–18].

The simplest model describing monolayer behaviour is the two-dimensional ideal–gas model. It can be derived either from the empirical equations of Traube and Szyszkowski or by applying kinetic molecular theory for three-dimensional gases. Traube [19], based on surface tension measurements of homologous carboxylic acids and alcohols, found that with dilute aqueous solutions the difference between the surface tension of pure solvent (γ_0) and that of a solution (γ_i) of the surfactant at a concentration c_i, called the surface pressure, π, is proportional to the concentration, c_i:

$$\pi = \gamma_0 - \gamma_i = kc_i \ , \tag{19}$$

where k is an empirical constant, which is positive when the surfactant molecules are non-ionised. Further investigations carried out by Szyszkowski [19] led to the semiempirical formula

$$\pi = \gamma_0 - \gamma_i = b \ln(1 + ac_i) \ , \tag{20}$$

where b is a constant characteristic of the homologous series of the organic compound and a is a constant of each compound. Differentiating Eq. (20) with respect to c_i and using the Gibbs adsorption equation, the following expression can be obtained:

$$\Gamma = \frac{b}{RT} \frac{ac}{(1 + ac)} \ . \tag{21}$$

From Eqs. (20) and (21) it is possible to show that for dilute solutions, when $ac \ll 1$, $(1/\Gamma)bac = RT$. Under these conditions, $b \ln(1 + ac) \approx bac$ and

$$\pi A = kT \ . \tag{22}$$

Equation (22) is analogous to the ideal-gas law. This leads to the conclusion that the adsorbed molecules at the solution–air interface obey the equation of state for a two-dimensional ideal gas. Figures 5 and 6 show the variation of πA versus the logarithm of the concentration of TX100 and TX165. From these figures, one observes that, in the region of low concentration, the film-forming monolayer at the interface obeys the equation of state for a two-dimensional ideal gas; however, when the concentration becomes greater than 3.05×10^{-7} and 2.26×10^{-6} mol l^{-1} for TX100 and TX165, respectively, πA increases with increasing concentration of the surfactant. Therefore, there is a discrepancy between the experimental data and Eq. (22). This equation may be used only for very dilute solutions where the surfactant molecules at the interface

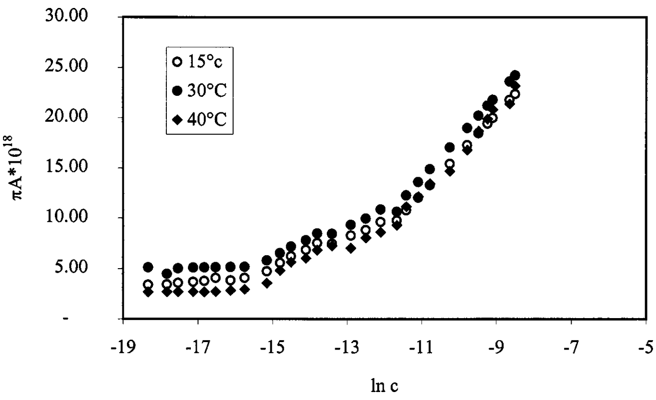

Fig. 5 Variation of πA with ln c for TX100 at 15, 30, and 40 °C

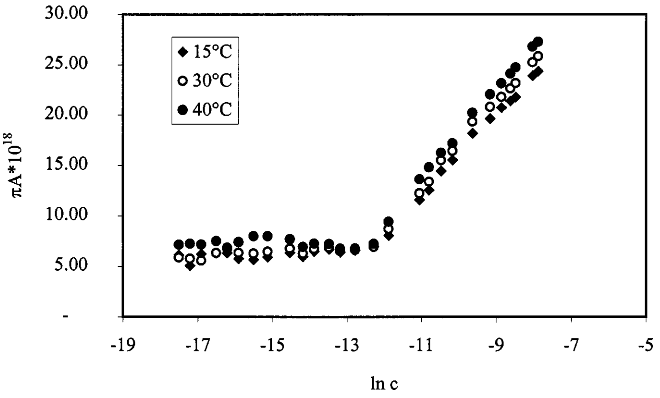

Fig. 6 Variation of πA with ln c for TX165 at 15, 30, and 40 °C

are widely separated; in this case, the intermolecular forces between the adsorbed molecules can be neglected in comparison to the thermal energy of translational motions and the dimension of the surfactant molecules is so small that it is negligible in relation to the area of the surface in which the molecules are confined. As the surfactant concentration is raised, intermolecular interactions between the surfactant molecules adsorbed at the interface must be taken into account.

Let us consider an aqueous solution of surfactant. The chemical potential of the surfactant at the surface monolayer, μ^{s}, can be expressed by the Buttler equation [20]:

$$\mu^{s} = \mu^{0s} + RT\ln(f^{s}x^{s}) - \gamma\omega \ , \tag{23}$$

where μ^{0s} is the standard chemical potential of the surfactant, T and R are the temperature and the ideal gas constant, f^{s} is the activity coefficient, x^{s} is the molar fraction, γ is the surface tension, and ω is the net molecular area. The Gibbs adsorption equation for this system is $d\pi = \Gamma d\mu^{s}$, where Γ is the amount of surfactant adsorbed and $\pi = \gamma_0 - \gamma$ is the surface pressure. If we introduce Eq. (23) into the Gibbs equation and take into account the dependence of f^{s} on $x^{s} = \Gamma\omega$ given by the relation

$$\ln f^{s} = a(1 - \Gamma\omega)^2 \ , \tag{24}$$

where a represents the intermolecular interaction constant, the following expression is obtained:

$$\frac{d\pi}{d\Gamma} = \frac{RT}{1 - \Gamma\omega} - 2aRT\Gamma\omega \ . \tag{25}$$

The approximate integration of Eq. (25) [the expression $1/(1 - \Gamma\omega)$ being taken out of the integral sign] [17] yields the van der Waals equation of state for a two-dimensional nonideal gas

$$\pi = -\frac{RT}{A - \omega} - \frac{aRT\omega}{A^2} \tag{26}$$

$$\pi = -\frac{RT}{A - \omega} - B \ . \tag{27}$$

For B = constant = π^* (cohesion pressure) this equation is the modified Volmer equation. The π–A isotherms, for TX100 and TX165 at 15 °C, calculated from the equation of state (Eq. 27) and those determined from the experimental surface tension measurements are presented in Figs. 7 and 8. The parameters of the theoretical π–A isotherms were determined using a fitting program which seeks the best correspondence between the theoretical and experimental curves. There is excellent agreement between the π–A isotherms. This is obvious since the equation takes into account the interaction between the molecules adsorbed at the interface: at low concentration the attractive forces due to van der Waals forces between the hydrophobic moiety of the surfactant are greater than the repulsive ones, but at higher concentration there is a strong repulsive force between the polar headgroup of the surfactant; the interpenetrating of two headgroups of the adsorbed

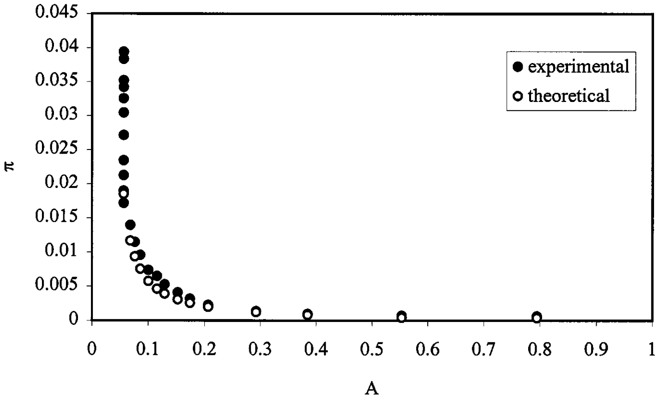

Fig. 7 Comparison between the experimental and theoretical π–A diagram for TX100 at 15 °C

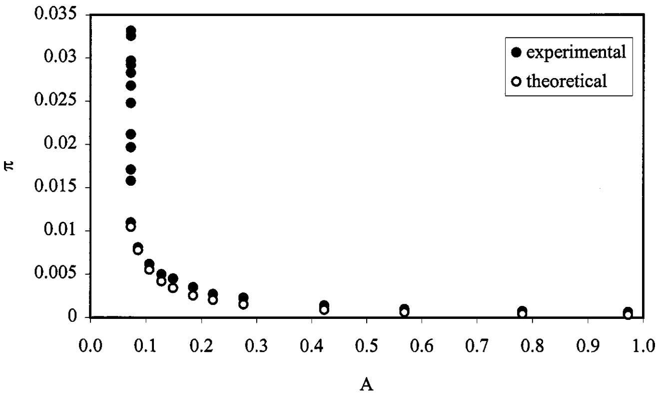

Fig. 8 Comparison between the experimental and theoretical π–A diagram for TX165 at 15 °C

surfactant molecules can result in a loss of translational freedom and, as a consequence, in a loss of entropy, and leads to repulsion between the surfactant molecules.

Conclusion

The surface tension measurements of aqueous solution of TX100 and TX165 allowed us to determine the thermodynamic parameters of adsorption. It can be noted from these data that the $\Delta G^0_{\mathrm{ads}}$ values become more negative when the temperature is raised. This indicates that micelle formation and adsorption of the surfactants at the solution–air interface is favoured with increasing temperature. As the temperature increases, the hydration of the hydrophobic group of the surfactant decreases and hence the cmc is lower. For each temperature, the free energy of adsorption is more negative for TX100 than for TX165: when the length of the headgroup is raised, because of its polarity, the surfactant is more soluble in water. The hydrogen-bonding interaction between the headgroup and water has a major effect on the water structure at the surfactant hydrocarbon moiety–water interface: the structured water around the hydrocarbon moiety of the surfactant is disrupted. In other words, an increase in the hydrogen-bonding between water and the polar moiety of the surfactant leads to poorer contributions of the hydrophobic interactions, which are the driving forces for adsorption and micellisation. The solubility of the nonionic surfactants TX100 and TX165 depends on the hydrophilic/hydrophobic balance of the surfactant molecules; therefore, raising the number of oxyethylene group from 9.5 to 16 results in a better solubility of the surfactant and as a result the free energy of adsorption is less negative. A comparison between the π–A isotherms, for TX100 and TX165, and the modified Volmer equation shows good agreement because this equation of state takes into account the interaction forces between the surfactant molecules adsorbed at the interface, while the two-dimensional ideal-gas model is not satisfactory for the description of the π–A isotherms of TX100 and TX165.

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