Effect of surfactant structure on the adsorption of carboxybetaines at the air–water interface

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Abstract

In order to study the effect of charge on the adsorption of surfactants at the air–water interface, two carboxybetaines have been synthesized with different number of separation methylenes between their charged groups. After purification and structure confirmation, the equilibrium and dynamic surface tensions were measured as a function of surfactant concentration for both the cationic and neutral forms of the surfactant molecules. The effect of ionic strength on the adsorption process was also studied. The equilibrium surface tension values were interpreted according to the Langmuir model and the dynamic surface tension data, converted to surface concentration by the Langmuir parameters, are consistent with the assumption of diffusion control over the range of surfactant concentrations studied. The diffusion coefficients show a progressive decrease in the rate of adsorption when the number of methylene units between the betaine charged groups increase.
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1. Introduction

The advance in the theory of adsorption from solutions of ionic and non-ionic surfactants allows a detailed analysis and computer modeling of the interfacial properties of adsorbed molecules. It is well known that the surfactant charge plays an important role in the adsorption properties. A great number of experimental results have been presented in the literature for the equilibrium isotherms of non-ionic surfactants [1] and for the ionic ones [2]; however, the adsorption process of the zwitterionic surfactants has received poor attention. In this context, zwitterionic surfactants such as carboxybetaines (with a positive charge over the nitrogen atom and a negative one over a carboxylate group) provide an excellent opportunity to study the effect of the charge on the adsorption processes because it is possible to work with the cationic, neutral or anionic surfactant forms by changing the pH of their aqueous solutions. In addition, these surfactants are widely employed in a variety of applications such as detergency, emulsification, and foaming, since they are less toxic than the ionic ones. Therefore, the proper utilization of these surfactants requires the knowledge of the properties of the monolayers adsorbed at the interface. On the other hand, several technological processes such as foam generation or emulsification employ surfactant solutions under non-equilibrium conditions. In these applications, the dynamic surface tension is an important property, which allows obtaining kinetic information of the surfactant adsorption at the interface.

Therefore, the aim of this work is to analyze the effect of the surfactant charge and the influence of ionic strength on the equilibrium surface properties and on the kinetics of adsorption at the air–water interface. The surfactants chosen are the neutral and cationic forms of dimethyl dodecyl betaines. We also studied the effect of surfactant structure on the adsorption process by studying the adsorption of two betaines with different distance between the charged groups. The molecular structure of carboxybetaines employed in this work is shown in Scheme 1.
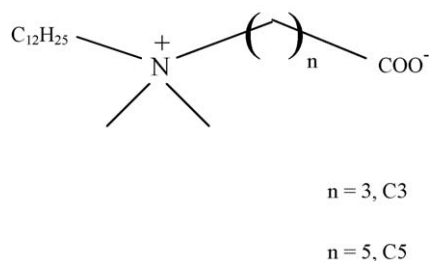
2. Experimental

2.1. Materials

The surfactants *N-N*-dimethyl, *N*-dodecyl, *N*-propane ammonium carboxylate and *N-N*-dimethyl, *N*-dodecyl, *N*-pentane

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Scheme 1. Molecular structure of carboxybetaines, *n* represents the number of methylene units between the charged groups.

ammonium carboxylate, C3 and C5 hereafter, were synthesized and purified according to a method published elsewhere [3], but with some critical adjustments. Modifications have been incorporated in the synthesis procedure to guarantee a degree of purity >99.9%. The high degree of surfactant purity is a prerequisite for the proper interpretation of surface experiments, because the interface properties are greatly affected by surface active impurities even if present in trace amounts [4].

Betaines were synthesized in two stages according to the procedure outlined in Scheme 2. In the first stage, we employ a tertiary amine, *N*,*N*-dimethyl-*N*-dodecyl amine, PS grade from Aldrich, and two ω-brominated esters: ethyl-4-bromobutyrate of PS grade from Merck for betaine C3 and ethyl-6-bromohexanoate of similar grade from Aldrich for C5. This reaction is refluxed with acetone for 12 h.

After acetone evaporation, the crude product of reaction is extracted with ethylic ether and purified water, so that the unreacted reagents remain in the organic phase and quaternary ammonium salt, the reaction product, goes to the aqueous phase. After this first step, we obtained a quaternary ammonium salt with a yield of >95%.

In the second step, the ammonium salt is treated in its own aqueous phase with an interchanging basic ion resin, AG 1-X8, biotechnology grade from Bio-Rad Laboratories [3]. Even though the original method indicated that the reaction could be carried out in methanol, ethanol, or isopropanol, the presence of alcohol leads to parallel reactions of transesterification, which then result in smaller reaction yields due to the production of other byproducts.

The resin employed allows the interchange of the anion bromide of the intermediate product with a hydroxyl group of the resin resulting in the formation of the final products. Resin is added until basic pH is reached and the reaction is carried out until all the ester has been hydrolyzed, which is verified by HPLC-MS. When 99.9% of reaction has been reached, the resin is filtered and the water is evaporated. Water evaporation is quite difficult because betaines are foaming agents. Therefore, we added some amount of toluene, which forms an azeotrope
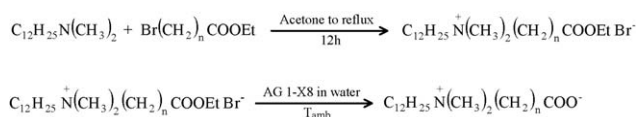
with the water that prevents foam formation. Moreover, it serves to dry products, which are very hygroscopic.

When the products were completely desiccated, they were dissolved in boiling acetone and crystallized by cooling. Finally, solids were filtered and desiccated at vacuum under inert atmosphere.

Betaines purity, 99.99%, is determined by MS, and ^{1}H NMR, ^{13}C NMR, and IR. NMR spectra also confirm the elimination of acetone employed for crystallization.

Solvents used in this investigation are acetone and toluene of PRS grade purchased from Panreac and diethyl ether, of similar grade from Carlo Erba. Water was purified with a combination of RiOs and Milli-Q systems from Millipore. This water was also used to prepare the solutions of C3 and C5 and to clean the glassware.

The cationic forms of the surfactants were obtained by addition of aqueous solutions of HCl, from Merck. As the pK_a of C3 and C5 are 3.96 and 4.37, respectively [3], the maximum pH to reach the 100% of cationic form was 1. The variation of ionic strength was achieved with NaCl from Merck. Sodium chloride was baked for 12 h in a porcelain casserole at 500 °C to remove traces of organic compounds.

2.2. Equilibrium surface tension measurements

The measurements of the equilibrium surface tension were carried out with a drop tensiometer TVT-1 from Lauda [5]. The inner radius of the steel capillary was 1.345 mm, and the employed syringe was of 5 ml.

TVT-1 drop tensiometer has three different measurement modes [5]: the dynamic measuring mode, which is the classic version of the drop volume method, applicable to the measurement of the static and dynamic surface tensions of pure liquids; and the standard and quasi-static modes for the measurement of the static and dynamic surface tensions of surface-active agents, respectively. In this work, equilibrium surface tension measurements were carried out with the so-called standard mode. It consists of a two-step process; in the first one, a drop with a certain volume is quickly formed at the capillary. This volume must be smaller than the critical volume according to the actual interfacial tension at the drop surface and in the beginning, the drop will remain at the tip of the capillary. After that, drop volume is increased more slowly to minimize hydrodynamic effects until it becomes large enough to detach. In order to reach the equilibrium surface tension, the standard method permits one to select the dosing rate. Thus, to ensure that the solutions do not show long time dependence, due to slow surfactant adsorption, we have applied the dynamic mode. The dosing rate at which no remarkable decrease of surface tension is observed can be used for the measurements with the standard mode. In our systems, the dosing rate employed was $0.07 \, s \, \mu l^{-1}$. In the dynamic mode, the time dependence is measured by progressive decrease of the drop volumes so that the detachment time becomes bigger and bigger.

All measurements (including the dynamic surface tension measurements) were carried out at 25.0 °C. Temperature in the tensiometer was controlled by means of thermostat/cryostat RM

$$C_{12}H_{25}N(CH_3)_2 + Br(CH_2)_nCOOEt \xrightarrow[12h]{Acetone\ to\ reflux} C_{12}H_{25}\overset{+}{N}(CH_3)_2(CH_2)_nCOOEt\ Br^-$$

$$C_{12}H_{25}\overset{+}{N}(CH_3)_2(CH_2)_nCOOEt\ Br^- \xrightarrow[T_{amb}]{AG\ 1-X8\ in\ water} C_{12}H_{25}\overset{+}{N}(CH_3)_2(CH_2)_nCOO^-$$

Scheme 2. Synthesis procedure of carboxybetaines.

6 from Lauda, and was measured with a contact thermometer Physics 2000. Reproducibility of surface tension measurements of surfactant solutions is within ± 0.1 mJ m^{-2}.

2.3. Dynamic surface tension measurements

Measurements of the dynamic surface tension were performed with: maximum bubble pressure tensiometer MPT-2 from Lauda [6], and drop tensiometer TVT-1 from Lauda, Germany [5], with the dynamic mode described elsewhere. Using these methods, it is possible to obtain dynamic curves for times ranging from milliseconds to hours.

In the case of MPT-2 tensiometer, air is blown into a surfactant solution to obtain bubbles. If the system volume is much larger than the bubble volume, the dynamic surface tension can be determined in the millisecond range taking into account the variation of the bubble pressure with the flow rate of air. Therefore, in all cases, a volume of 10 ml was used.

3. Results and discussion

3.1. Equilibrium surface tension measurements

Previously to obtain the dynamic adsorption properties of surfactants, we have obtained the adsorption isotherms. Figs. 1 and 2 show the equilibrium surface tensions for C3 and C5 surfactants in the cationic and zwitterionic forms. These figures also present values obtained in the presence and absence of electrolytes. For the sake of clarity, only two isotherms are shown for each surfactant. We can observe from the figures that the isotherm curves are not significantly influenced by electrolyte concentration or surfactant chemical form. Surface tension values decrease rapidly when increasing the surfactant concentration before reaching a plateau. The critical micellar concentration (c.m.c.) is estimated from the break point in the resulting curve. The c.m.c. values for C3 and C5 are displayed in Table 1. The values are in excellent agreement with data in the literature [7], which are also presented in the table.
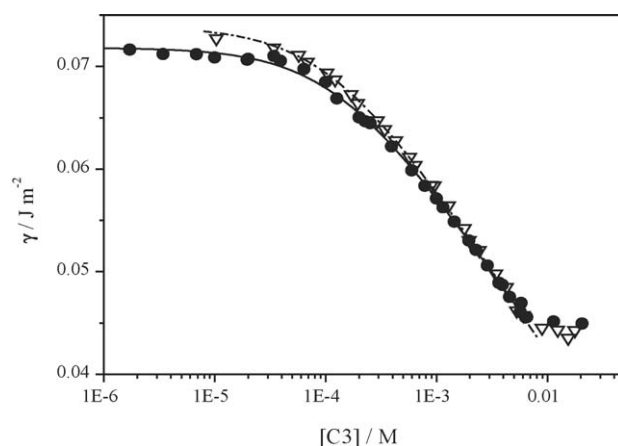

Fig. 1. Equilibrium surface tension data of C3 betaine surfactant dissolved in water ($\bullet$) and in NaCl 0.1 M ($\triangledown$). These measurements were performed at 25.0 °C. Lines are calculated from the Langmuir model, Eq. (1) and parameters in Table 1.
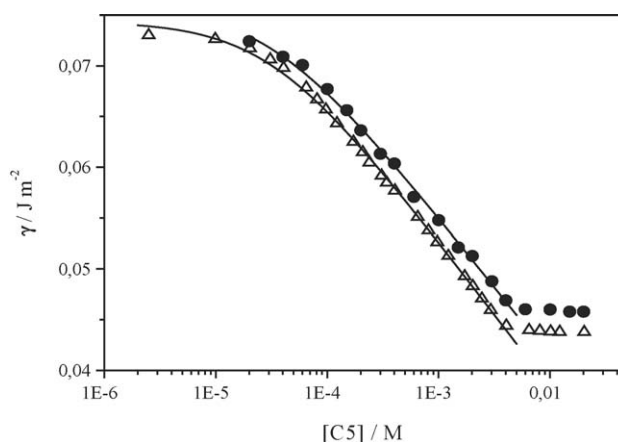

Fig. 2. Equilibrium surface tension data of C5 betaine surfactant in their neutral ($\bullet$), and cationic ($\triangle$), forms dissolved in aqueous solutions of 0.1 M ionic strength. All results were obtained at 25.0 °C Lines are calculated from the Langmuir model, Eq. (1) and parameters in Table 1.

Table 1

Values found in this work of c.m.c., maxima excess surface concentration obtained by Gibbs ratio, Γ_{Gibbs} and best-fit parameters of the surface tension isotherms to the Langmuir model for carboxybetaines C3 and C5

	I (M)	10^3 c.m.c. (M)	10^3 c.m.c.^{a} (M)	10^6 Γ_{Gibbs} (mol m^{-2})	10^6 Γ_{∞} (mol m^{-2})	10^3 a (M)
C3	0	6.4 ± 0.2	6.0	2.7 ± 0.8	2.71 ± 0.05	0.130 ± 0.001
	0.1	5.5 ± 0.1		2.8 ± 0.6	2.9 ± 0.1	0.13 ± 0.02
	0.5	4.4 ± 0.1		3.7 ± 1.0	3.0 ± 0.2	0.09 ± 0.02
C3$^+$	0.1	6.9 ± 0.2		2.8 ± 0.4	2.84 ± 0.06	0.11 ± 0.01
	0.5	3.0 ± 0.1		3.1 ± 0.5	3.4 ± 0.2	0.07 ± 0.02
C5	0	5.6 ± 0.2	5.1	2.4 ± 0.4	2.43 ± 0.05	0.060 ± 0.006
	0.1	4.7 ± 0.1		2.4 ± 0.3	2.41 ± 0.07	0.030 ± 0.007
	0.5	3.3 ± 0.1		2.5 ± 0.2	2.6 ± 0.2	0.03 ± 0.01
C5$^+$	0.1	4.3 ± 0.1		2.6 ± 0.5	2.53 ± 0.08	0.030 ± 0.003
	0.5	1.6 ± 0.1		2.9 ± 0.3	3.4 ± 0.2	0.07 ± 0.02

All results are referred to a temperature of 25.0 °C.
^{a} Data from ref. [7].

As expected, the c.m.c. values decrease more steeply with ionic strength for the cationic forms than for the zwitterionic ones. This can be attributed to the repulsions between the positive charges of the cationic forms always being greater than between dipoles of hydrophilic group of the zwitterionic surfactant. Consequently, the addition of electrolytes has greater influence in the micelle formation of cationic surfactants than the zwitterionic counterparts.

In all cases, c.m.c. values are minor for C5 betaine than for C3 betaine. The increase in hydrophobic interactions due to the increase in the number of methylene units in C5 could be responsible for this behavior.

Molecular adsorption of non-ionic surfactants on the fluid phases is usually interpreted by the Langmuir adsorption isotherm [8]. This model considers that the adsorption occurs on a particular site of the interface and that the energetic barrier for transferring the surfactant between sites is much larger than the thermal energy. In addition, the model assumes that the activation energies are independent of the surface coverage. Accordingly, the equilibrium surface tension of surfactant solutions, γ, is related to the bulk surfactant concentration by the following equation

$$\gamma_0 - \gamma = \Gamma_\infty RT \ln\left(1 + \frac{C}{a}\right) \qquad (1)$$

where γ_0 is the solvent surface tension value, Γ_∞ is the maximum excess surface concentration; C is the bulk surfactant concentration and a is the ratio of desorption and adsorption rate constants, respectively.

Figs. 1 and 2 show that the fit to the Langmuir equation for C3 and C5 surfactants is in good agreement with the experimental results. The best-fit parameters are reported in Table 1.

As can be seen in Figs. 1 and 2, the Langmuir model satisfactorily interprets even the equilibrium surface tension of the cationic forms. In the case of ionic surfactants, to interpret the surfactant adsorption, more realistic models that take into account the effect of the electrostatic surface potential are often necessary [2]. However, in our systems, we fitted the experimental results to the Davies model [9]. This adsorption isotherm is a two-parameter model, which considers that the bulk solution is ideal and that the surface is a charged monolayer in which the kinetic desorption coefficient is a function of the surface potential, ψ, expressed as the Boltzmann equation [9]. When ψ is equal to zero, the Davies isotherm reduces to the Langmuir equation. However, the values found for the electrostatic surface potential of these monolayers were too small, and the goodness of the fit, using the χ^2 indicator, is poor as compared with the Langmuir model. Therefore, we considered the Langmuir model as the most accurate state equation to interpret the adsorption of the betaines. In the case of the cationic forms of betaines, addition of HCl 0.1 M is necessary to obtain the charged form of the surfactant molecules. Therefore, the electrolyte molecules screen the electrical charge of the surfactant molecules adsorbed at the interface, decreasing the electrostatic surface potential [10] and the monolayer behaves like a non-ionic one. Consequently, the best fits are obtained with the Langmuir
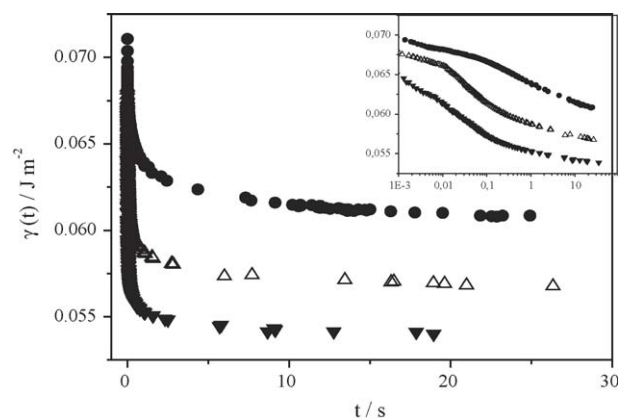

Fig. 3. Dynamic surface tension values for aqueous solutions of C3 obtained at different surfactant concentrations: 2.514 10^{-4} M (●); 5.98 10^{-4} M (△); and 9.97 10^{-4} M (▼). The inset presents results obtained at short time by maximum bubble pressure and drop volume tensiometers. All measurements were performed at 25.0 °C.

state equation. This analysis leads to adsorption values compatible with those obtained from Gibbs law, and these are also presented in Table 1.

Examination of the fitting parameters shows the following: (i) the maximum excess concentration does not present significant dependence on the molecular form; (ii) when some salt is added, a slight increase in the maximum excess concentration is observed, as is expected, since charges are screened; the effect is more pronounced in the cationic form of the surfactants because repulsions between cationic adsorbed molecules are greater than between the neutral ones; consequently, the screening effect becomes more important in cationic monolayers than in zwitterions counterparts; (iii) finally, the a parameter is practically independent of the ionic strength for each surfactant. However, it weakly decreases when the distance between the charged groups of the surfactant increases.

3.2. Dynamic surface tension measurements

The dynamic surface tensions of solutions containing different surfactant concentrations are presented in Figs. 3 and 4 for C3 and C5, respectively. In all cases, the surfactant concentration was below its c.m.c. to avoid the effect of the diffusion of micellar aggregates. Experimental curves were obtained at 25.0 °C. For the sake of clarity, only some of the DST curves are shown.

The dynamic surface tension obtained from both MPT-2 tensiometer (time ranging from 1 ms to 10 s) and TVT-1 tensiometer measurements agree very well with each other within the experimental error as seen in Figs. 3 and 4.

The main model to analyze the dynamic surface tension curves considers dynamic adsorption at the interface as a diffusion-controlled process [11] and it relates the excess surface concentration and the time by the Ward and Tordai equation

$$\Gamma(t) = 2C\left(\frac{Dt}{\pi}\right)^{1/2} - 2\left(\frac{D}{\pi}\right)^{1/2}\int_0^{t^{1/2}} C_s(t-\tau)d\tau^{1/2} \qquad (2)$$
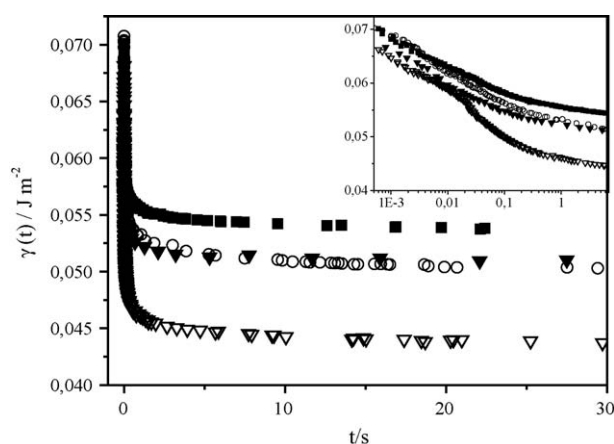
Fig. 4. Dynamic surface tension values obtained for aqueous solutions of 1.00×10^{-4} M the cationic and neutral forms of the C5 surfactant at different ionic strength. For the cationic form: $I = 0.1$ M (■); $I = 0.5$M (○); and for the zwitterionic one: $I = 0.1$ M (▼), and $I = 0.5$ M (▽). The inset presents results obtained at short time by maximum bubble pressure and drop volume tensiometers at 25.0 °C.

where D denotes the diffusion coefficient and $\Gamma(t)$ and C_s the surface and subsurface concentrations, respectively.

This equation cannot be solved analytically and therefore, asymptotic solutions have to be employed at short and long times [12]. The short time approximation is given by

$$\Gamma(t) = 2C \sqrt{\frac{Dt}{\pi}} \tag{3}$$

and the long time asymptotic solution is

$$\Gamma(t) = \Gamma_{eq} - \frac{\Gamma_\infty^2}{C} \sqrt{\frac{\pi}{Dt}} \tag{4}$$

where Γ_{eq} represents the surface excess concentration at equilibrium.

Since most experiments measure dynamic surface tensions and not surface concentrations, it is necessary to obtain a relation between these two variables in order to relate experimental to theoretical results. The Henry law isotherm is usually employed to transform surface concentrations to the corresponding surface tension values. This state equation is only valid at very dilute surfactant concentrations, whereas for more concentrated surfactant solutions, the use of the Henry law leads to ambiguous results for the diffusion coefficient, (lower results of the diffusion coefficient are obtained from the long time approximation). In several cases, a kinetic barrier has been postulated. Thus, the model introduces a renormalized diffusion coefficient that takes into account both the diffusion to the subsurface and then the crossing of the energetic barrier [13]. Although such an approach has been widely used, a more consistent treatment was proposed. This treatment considers the suitable isotherm to transform the dynamic surface tension values in excess concentration data [14]. Then, the dynamic surface coverage is fitted to Eqs. (3) and (4).

We employed the Langmuir isotherm to convert dynamic surface tension in surface coverage, $\Gamma(t)$. We then fitted $\Gamma(t)$ to Eqs. (3) and (4) to obtain the diffusion coefficients. The dynamic sur-

Table 2
Diffusion coefficients of C3 and C5 betaines obtained at 25.0 °C from the Ward and Tordai asymptotic solutions using the corresponding Langmuir isotherm

Surfactant	I (M)	$10^{10} \, D$ (m² s⁻¹)
C3	0	4.3 ± 0.4
	0.1	3.8 ± 0.3
	0.5	3.5 ± 0.4
C3⁺	0.1	5.4 ± 0.5
	0.5	3.4 ± 0.2
C5	0	2.1 ± 0.3
	0.1	1.5 ± 0.1
	0.5	1.3 ± 0.2
C5⁺	0.1	2.9 ± 0.2
	0.5	2.4 ± 0.3

face coverage fit very well to the asymptotic solutions of the Ward and Tordai model at both long and short time. The diffusion coefficients found from short and long time approximations are in excellent agreement, indicating that the kinetics of surfactant adsorption of cationic and neutral forms of carboxybetaines is a diffusion-controlled process. This is in agreement with theoretical predictions from the Andelman model [15] for non-ionic surfactants and ionic surfactants with added salt. The D values are also independent of the surfactant concentration; therefore, the results shown in Table 2 are the averages from at least five different surfactant solutions.

As can be seen in Table 2, the diffusion coefficient of the zwitterionic forms decreases slightly as the ionic strength increases. The effect is more marked in the cationic forms of these surfactants. In the latter case, one can analyze this behavior in terms of the Andelman model [15]. This model relates the relaxation time of the electrical double layer, τ_e, with both, the diffusion coefficient and the Debye Hückel screening length, κ^{-1}, by $\tau_e = (D\kappa^2)^{-1}$. According to this equation, using the D values obtained in this work and taking into account that the Debye Hückel screening length, κ^{-1} decreases when the ionic strength increases, the decay is faster in the case of cationic surfactant with low salt concentrations. This fact is consistent with experimental results in the literature [16].

Finally, the diffusion coefficients values are always smaller for C5 surfactant than for C3. This shows that the increase of separation between the charged groups of caboxybetaines retards the surfactant adsorption at the air–water interface.

4. Summary

The equilibrium surface tension of C3 and C5 carboxybetaines in their neutral and cationic forms and in the absence and presence of electrolytes were interpreted according to the Langmuir model. The dynamic surface tension data employing the Langmuir isotherm as the state equation are interpreted as a diffusion-controlled process.

Results found in this work indicate that whereas thermodynamic parameters, such as surface excess at saturation, are practically independent of both the ionic strength and the chemical surfactant form, the kinetic parameters, diffusion

coefficient and the *a* parameter, show a significant dependence on the surfactant structure. Thus, these parameters decrease sharply as the distance between the charged groups of betaines increases.

Acknowledgments

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