

The adsorption kinetics of 1-*N*-L-tryptophan–glycerol-ether surfactants at the air–liquid interface: effect of surfactant concentration and alkyl chain length

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Received 19 August 2003; accepted 24 November 2003

Abstract

Dynamic surface tension of aqueous alkaline solutions of 1-*N*-L-tryptophan–glycerol-ether surfactants, C_{*n*}-TEG, below its critical micelle concentration has been measured as a function of the surfactant concentration and over a temperature range of 19.7–31.5 °C. The static tension of the alkyl tryptophan–glycerol-ether surfactants with *n* = 9–11 is analyzed in terms of the combined Frumkin–Davies isotherm. By using this state equation the adsorption kinetics of these surfactants can be interpreted as a diffusion-controlled process.

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Keywords: 1-*N*-L-Tryptophan–glycerol-ether surfactants; Dynamic surface tension; Adsorption kinetics; Diffusion-controlled adsorption; Frumkin–Davies isotherm

1. Introduction

The equilibrium surface tension of a surfactant solution is not achieved instantaneously. When a fresh interface of an aqueous surfactant solution is formed, it initially has a surface tension close to that of water and over a period of time the surface tension decays to the equilibrium value. The period of time ranges from milliseconds to days and the decay curve is named as dynamic surface tension, $\gamma(t)$ or DST. The rate of surfactant adsorption at interfaces has crucial importance for processes such as foam generation, emulsification and several biological and technological applications because in some processes the interface may not attain equilibrium. Thus, the knowledge of the adsorption is not complete without the study of the kinetics of adsorption.

It is well known that monomer transport to the interface occurs in two steps, diffusion from the bulk to the subsurface and adsorption at the interface [1]. If the adsorption process is very fast then diffusion is the rate-controlling step

(*diffusion-controlled model* [2]). When the rates of the two processes are similar, an adsorption barrier is postulated and the model is referred as *mixed-kinetic model* [1]. The nature of this barrier has been related to potential energy barrier [3], monomer reorientation [4,5] or electrostatic barrier [6]. Although such an approach has been widely used, a more consistent and unified treatment of the dynamic results is warranted.

The main problem for interpreting DST is the application of an appropriate isotherm to relate surfactant concentration in the bulk to the adsorbed amount at the interface [7]. In most cases the Henry law isotherm is used. However, this isotherm is only valid at low surface concentrations and can be the main reason for the appearance of the activation barrier at high surfactant concentrations. In this context the aim of this work is to study the kinetics of adsorption of anionic surfactants of 1-*N*-L-tryptophan–glycerol-ethers (see Fig. 1). These surfactants were previously synthesized [8] and are used as wetting agents in cotton mercerization with caustic soda solutions. In order to study the effect of the surfactant structure on the adsorption process, we have studied the adsorption of the homologous series of monoalkyl

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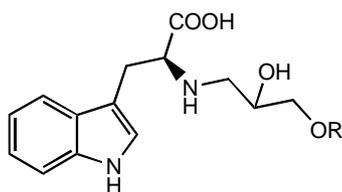


Fig. 1. The chemical structure of 1-*N*-L-tryptophan-glycerol-ether surfactants. R represents the alkyl chain.

glycerol ether surfactants with different alkyl chain lengths ($R = C_9$ – C_{11}). The effect of surfactant concentration and temperature has also been investigated and the results are reported in this article.

2. Experimental

2.1. Materials

The surfactants C_9 -TGE, C_{10} -TGE, C_{11} -TGE were synthesized and purified according to the published methods and the grade of purity was evaluated by HPLC [8]. The results indicate that the samples contains >99.5% of surfactant.

The solutions of C_9 -TGE, C_{10} -TGE, C_{11} -TGE were prepared with water purified with a combination of RiOs and Milli-Q systems from Millipore. The conductivity of the water was around $0.2 \mu\text{S cm}^{-1}$. This water was also used to clean the cell and other glassware. All surfactant solutions were dissolved at $\text{pH} \sim 13$ in 1 M of sodium hydroxide. The alkaline solutions were prepared in boiled water and stored in closed bottles of polypropylene.

2.2. Dynamic surface tension measurements

The measurements of the dynamic surface tensions were carried out with a drop tensiometer TVT-1 from Lauda, Germany [9]. The inner radius of the steel capillary was 1.345 mm, and the employed syringe was of 5 ml [10,11].

The drop tensiometer TVT-1 presents three different modes of measurements [9]: the dynamic measuring mode, 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 the dynamic surface tensions were carried out with the so-called quasi-static mode. The quasi-static mode consists of a two-step process; in the first, 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 at first the drop will remain at the tip of the capillary. While keeping the drop volume constant, the interfacial tension decreases as a result of adsorption and after some time, it reaches a value corresponding to the critical volume and the drop

detaches. The time interval between the drop formation and detachment is measured and the next drop is formed by the same principle. By this measuring mode, hydrodynamic influences are avoided.

The kinetic study was performed at different temperatures ranging from 19.7 to 31.5 °C. The temperature in the tensiometer was controlled by means of thermostat/cryostat RM 6 from Lauda, and was measured with a contact thermometer Physics 2000. Reproducibility of the surface tension measurements of surfactant solutions is less than $\pm 0.1 \text{ mN m}^{-1}$.

3. Results and discussion

The dynamic surface tensions of solutions containing different surfactant concentrations are presented in Fig. 2 for C_9 -TGE, C_{10} -TGE, and C_{11} -TGE, respectively. Experimental curves were obtained at 25 °C. For the sake of clarity only some of the DST curves are shown.

The main theoretical model to analyze the dynamic surface tension curves considers dynamic adsorption at the interface as a diffusion-controlled process [13]. The equation pertaining to this model is the classic equation of Ward and Tordai [13]:

$$\Gamma(t) = 2C \left(\frac{Dt}{\pi} \right)^{1/2} - 2 \left(\frac{D}{\pi} \right)^{1/2} \int_0^{t^{1/2}} C_s(t - \tau) d\tau^{1/2} \quad (1)$$

where D denotes the diffusion coefficient, $\Gamma(t)$ and C_s the surface and subsurface concentrations, which are a function of time and C is the surfactant concentration in bulk.

This equation cannot be solved analytically; as a consequence, the experimental results are not fitted to this equation. However, asymptotic solutions at long and at short times were obtained and have been successfully applied to surfactants [12]. These solutions in the form of derivatives are the following:

$$\left(\frac{d\Gamma(t)}{dt^{1/2}} \right)_{t \rightarrow 0} = 2C \left(\frac{D}{\pi} \right)^{1/2} \quad (2)$$

$$\left(\frac{d\Gamma(t)}{dt^{-1/2}} \right)_{t \rightarrow \infty} = -\frac{\Gamma_{\text{eq}}^2}{C} \left(\frac{4\pi}{D} \right)^{1/2} \quad (3)$$

By Henry law isotherm it is possible to transform the asymptotic solution at short times and to determine the diffusion coefficient from experimental data of dynamic surface tension:

$$D_{t \rightarrow 0} = \pi \left(-\frac{d\gamma(t)}{dt^{1/2}} \right)_{t \rightarrow 0}^2 \left(\frac{1}{4CRT} \right)^2 \quad (4)$$

and using the Gibbs equation the asymptotic solution at long times gives:

$$D_{t \rightarrow \infty} = \pi \left(\frac{d\gamma(t)}{dt^{-1/2}} \right)_{t \rightarrow \infty}^2 \left(\frac{C}{RT\Gamma_{\text{eq}}^2} \right)^2 \quad (5)$$

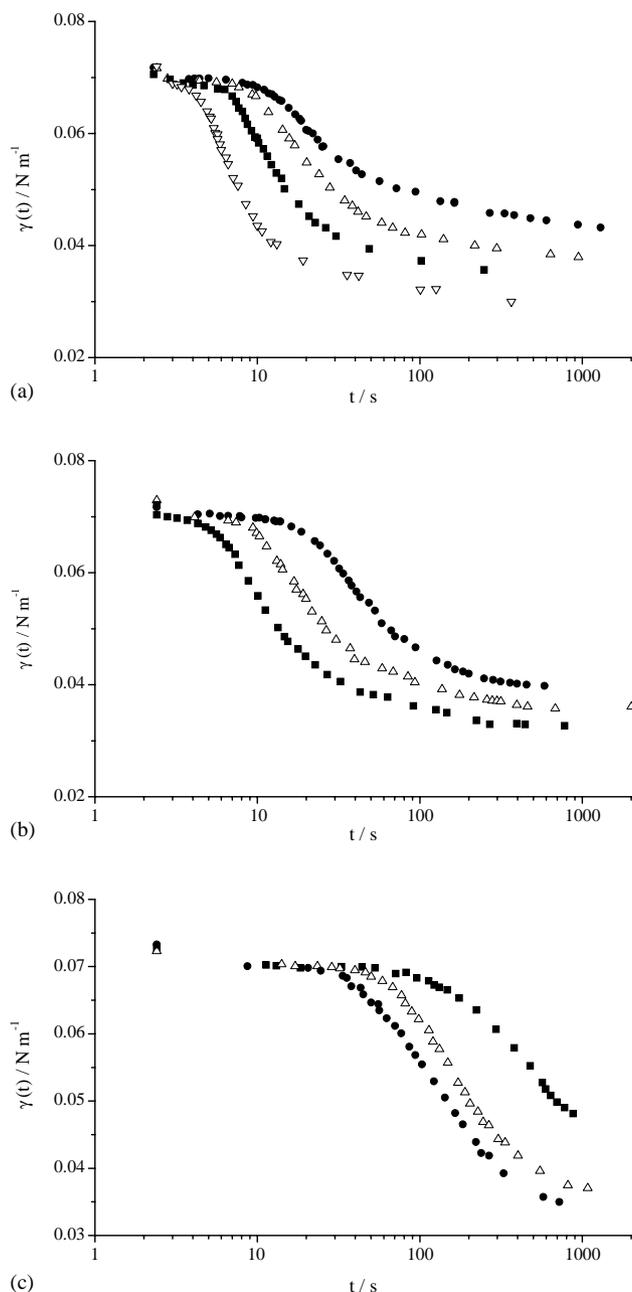


Fig. 2. Dynamic surface tension values for solutions of—(a) C₉-TEG obtained at different concentrations: (●) 2.60×10^{-5} M; (△) 3.02×10^{-5} M; (■) 3.40×10^{-5} M; (▽) 7.00×10^{-5} M; (b) C₁₀-TEG, the surfactant concentrations are: (●) 2.02×10^{-5} M; (△) 3.01×10^{-5} M; (■) 5.02×10^{-5} M and (c) C₁₁-TEG surfactant concentrations of: (■) 0.75×10^{-5} M; (△) 1.50×10^{-5} M; (●) 2.00×10^{-5} M. All results were obtained at 25 °C.

If pure Fickian diffusion is the only mechanism for mass transport to the interface, one finds $D_{t \rightarrow 0} = D_{t \rightarrow \infty} = D$, whereas in the *mixed-kinetic model*, the activated diffusion may be represented by an effective diffusion coefficient, D_{eff} . Liggieri et al. introduced this idea [14,15] and their calculations showed that at long times small barriers have significant effects on the $\Gamma(t)$ [15]. This mixed mechanism corresponds to renormalized diffusion kinetics with an ad-

sorption barrier E_{act} . Accordingly the effective diffusion coefficient, $D_{\text{eff}} = D_{t \rightarrow \infty}$, is given by:

$$D_{\text{eff}} = D \exp\left(\frac{-E_{\text{act}}}{RT}\right) \quad (6)$$

To test the validity of these equations the dynamic surface tension is plotted versus $t^{1/2}$ and $t^{-1/2}$, respectively. Figs. 3 and 4 show some of these results. For the sake of clarity the figures only present results corresponding to one concentration for each surfactant; analogous behavior is observed in the whole surfactant concentration range studied. As seen in the figures, results are linear at short and at long times as expected for a diffusion controlled process.

Diffusion coefficients are calculated from the slopes of the linear fit at long and short times, Eqs. (4) and (5). Fig. 5 shows the values of $D_{t \rightarrow 0}$ and $D_{t \rightarrow \infty}$ for C₉-TGE at 25 °C and its dependence with surfactant bulk concentration. As observed in the figure, for concentrations below 4.5×10^{-5} M, $D_{t \rightarrow 0} = D_{t \rightarrow \infty}$ and is independent of bulk surfactant concentration. The average value found in this work was $(1.1 \pm 0.1) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Above this surfactant concentration both asymptotic solutions do not give the same result [$D_{t \rightarrow 0} = (1.1 \pm 0.1) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, and $D_{t \rightarrow \infty} = (0.45 \pm 0.02) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$]. These diffusion coefficients are independent of concentration as well. The same behavior is observed for C₁₀-TGE. In this surfactant at bulk surfactant concentrations below of 4.7×10^{-5} M, $D_{t \rightarrow 0} = D_{t \rightarrow \infty} = (1.0 \pm 0.1) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, and above this concentration, $D_{t \rightarrow 0} > D_{t \rightarrow \infty}$ and the average value of $D_{t \rightarrow \infty}$ is $(0.68 \pm 0.02) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Similarly, for C₁₁-TGE, below 1.37×10^{-5} M the diffusion coefficients obtained from asymptotic solutions at short and long times are the same, [$(1.1 \pm 0.1) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$], but for concentrations higher than 1.37×10^{-5} M, $D_{t \rightarrow 0} > D_{t \rightarrow \infty} = (0.69 \pm 0.02) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

Analysis of this behavior results in the following conclusions: (i) the $D_{t \rightarrow 0}$ values seem to be independent of both the nature of the surfactant and the surfactant concentration; the average value is around $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$; (ii) the diffusion coefficient values show that in dilute surfactant concentrations, $D_{t \rightarrow \infty} \sim D_{t \rightarrow 0}$, while in more elevated bulk concentrations, $D_{t \rightarrow \infty} < D_{t \rightarrow 0}$, indicating the presence of an energy barrier. In the particular case of TGE derivatives, the barrier might be of electrostatic origin.

In order to obtain the activation energy values more accurately, we have studied the kinetics of the adsorption of the surfactant at different temperatures ranging from 19.7 to 31.5 °C. We have worked with surfactant concentrations in the range of mixed-kinetic model and using the same procedure described above we calculated the diffusion coefficients. We have observed that the trend is similar to the results at 25 °C, i.e. the diffusion coefficients at short times are close to $1.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, and are independent of both the nature of surfactant and the surfactant concentration, and diffusion coefficients obtained at long times are lower than those at short times and vary with the nature of surfactant.

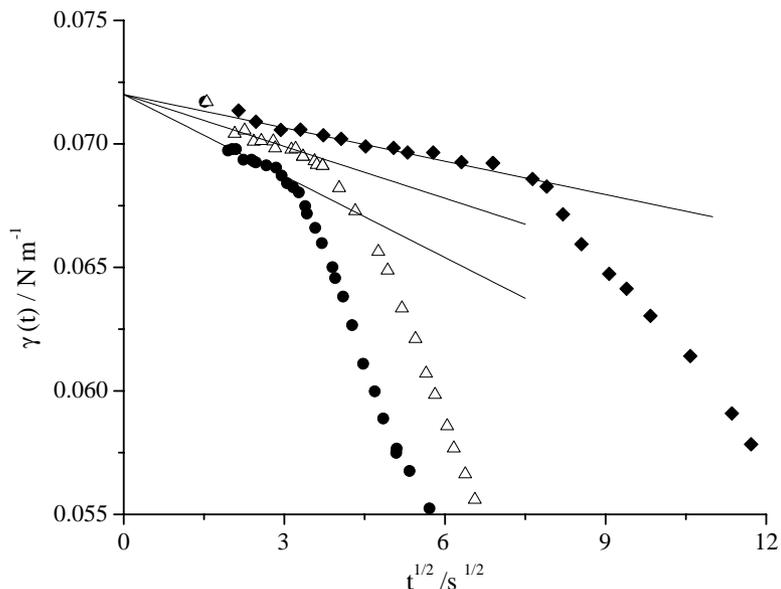


Fig. 3. Dynamic surface tension data plotted vs. $t^{1/2}$. The lines are least-squares fits to the data as $t \rightarrow 0$: (●) 2.60×10^{-5} M of C₉-TEG; (Δ) 2.02×10^{-5} M of C₁₀-TEG and (\blacklozenge) 1.22×10^{-5} M of C₁₁-TEG. Results are obtained at 25 °C.

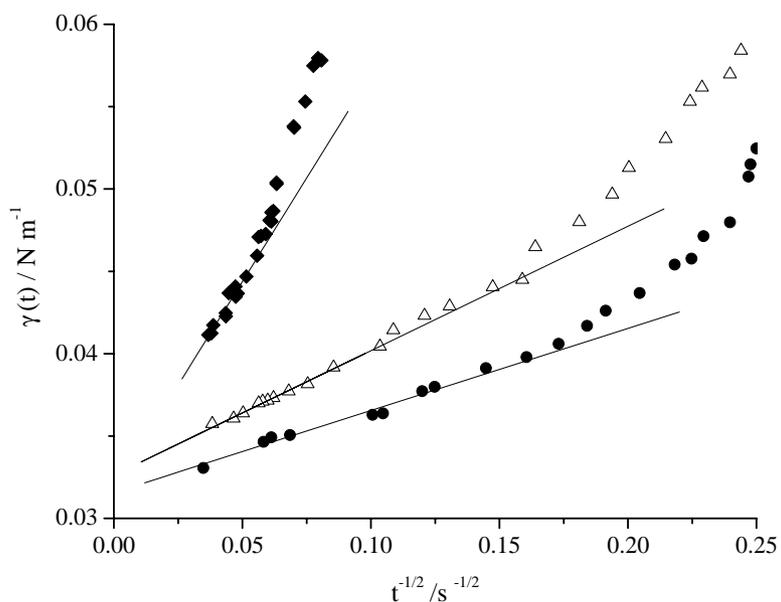


Fig. 4. Dynamic surface tension data plotted vs. $t^{-1/2}$. The lines are least-squares fits to the data as $t \rightarrow \infty$: (●) 3.96×10^{-5} M of C₉-TEG; (Δ) 3.01×10^{-5} M of C₁₀-TEG; (\blacklozenge) 1.58×10^{-5} M of C₁₁-TEG. Results are obtained at 25 °C.

Fig. 6 shows plots of $\ln(D_{\text{eff}}/D_0)$ versus $1/T$ in line with Eq. (6) for all three surfactants. It is interesting to note that the lines for C₁₀-TGE and C₁₁-TGE coincide whereas the plot for C₉-TGE has a different slope. The activation energy calculated according to Eq. (6) was (100 ± 3) kJ mol⁻¹ for C₉-TGE and (45 ± 2) kJ mol⁻¹ for C₁₀-TGE and C₁₁-TGE. The dependence found for the activation energy with the alkyl chain length is unexpected if one considers the adsorption process exclusively controlled by the electrostatic barrier. The maximum surface excess concentration calculated from the equilibrium sur-

face tension measurements increases as the chain length of the surfactant increases [8]. As a consequence one expects that the surface potential at the interface, electrostatic barrier, also increases with the surfactant chain length. However, the opposite behavior was observed. This behavior can be explained by the existence of attractive interactions between monomers adsorbed. These attractive interactions could counteract the electrostatic barrier. These effects operate at higher surfactant concentrations where the Henry law isotherm cannot be used to interpret the thermodynamics of the adsorption process. Therefore

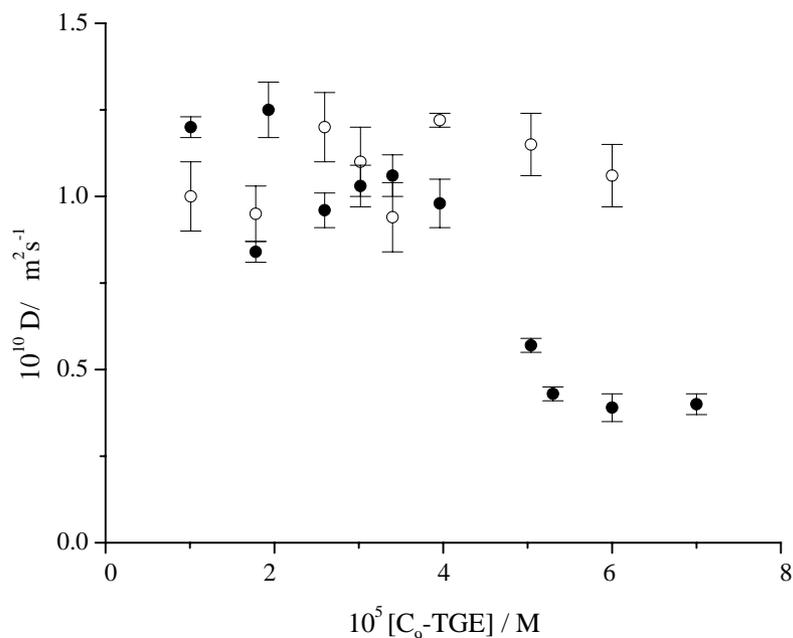


Fig. 5. Diffusion coefficients of C₉-TGE obtained from the Ward and Tordai asymptotic solutions at short and at long times using the Henry isotherm: (○) $D_{t \rightarrow 0}$; (●) $D_{t \rightarrow \infty}$. Results are obtained at 25 °C.

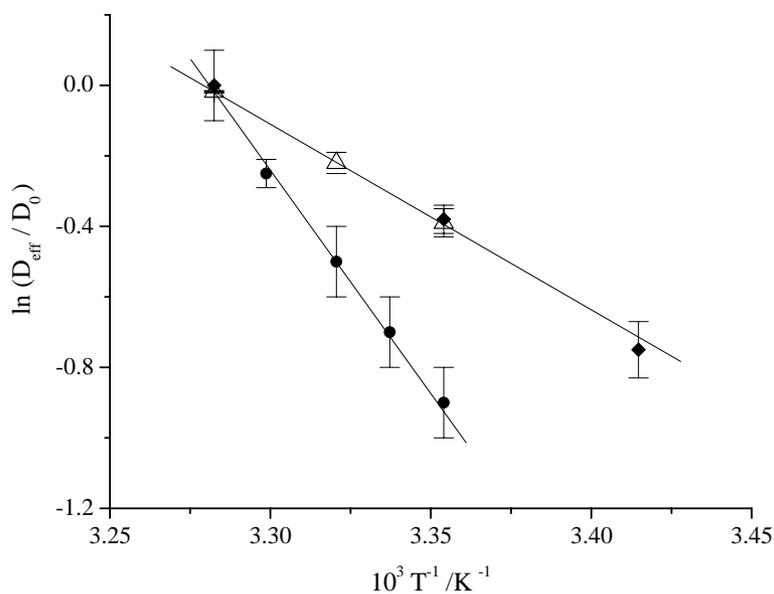


Fig. 6. Arrhenius-type plot for surfactant solutions of: (●) C₉-TEG; (△) C₁₀-TEG and (◆) C₁₁-TEG.

a more realistic isotherm that takes into account the effect of the electrostatic surface potential [16], ψ_0 , and the lateral attractive interactions between the hydrocarbon chains adsorbed at the interface it is necessary. We used the combined Frumkin–Davies isotherm [17] derived by Borwankar and Wasan [18] to interpret the equilibrium surface tension measurements. In this model, the charge on the surface produces a surface potential modeled by the Gouy–Chapman theory and intramonomolayer interactions are

incorporated according to the Frumkin model. Accordingly the fraction of surface occupied by the surface-active ion is given by:

$$\theta = \frac{\Gamma}{\Gamma_{\infty}} = \left(\frac{C}{a} \right) \frac{\exp(-H\theta) \exp(-zF\psi_0/RT)}{1 + (C/a) \exp(-H\theta) \exp(-zF\psi_0/RT)} \quad (7)$$

and the isotherm is then:

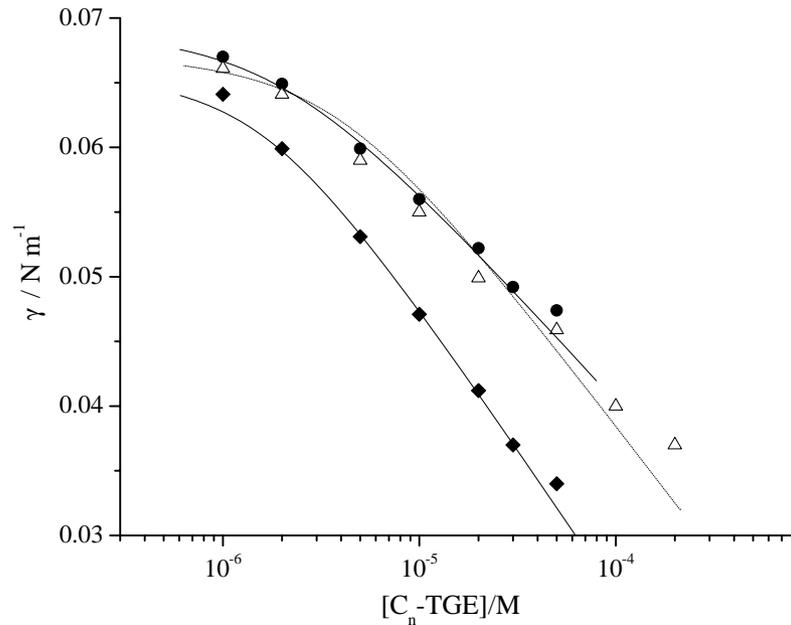


Fig. 7. Equilibrium surface tension data of C_n -TEG surfactants of Pegiadou [8] at 25 °C: (●) $n = 9$; (△) $n = 10$ and (◆) $n = 11$. Lines are calculated according to Frumkin–Davies model, Eqs. (7) and (8) and parameters in Table 1.

$$\frac{\gamma_0 - \gamma}{RT} = -\Gamma_\infty \left[\ln(1 - \theta) - H \frac{\theta^2}{2} \right] + \frac{1}{4N_A \kappa^{-1} \lambda} \left[\cosh \left(\frac{zF\psi_0}{RT} \right) - 1 \right] \quad (8)$$

In these equations κ^{-1} is the Debye length ($\sim 11 \text{ \AA}$ in this system), $\kappa^{-1} = F^{-1}(\epsilon_0 \epsilon RT/2I)^{1/2}$, where I is the ionic strength, F , N_A and k_B are the Faraday, Avogadro and the Boltzmann constants, respectively. z denotes the surfactant ion valence and γ_0 the solvent surface tension. λ denotes the length of Bjerrum, given by: $\lambda = e^2/4\pi\epsilon_0\epsilon k_B T$, where ϵ_0 is the permittivity of the vacuum and ϵ is the relative permittivity of the medium, water. The parameter “ $a = k_d/k_a$ ” is the ratio between the rate constants of desorption and adsorption processes. Finally, H is the Frumkin interaction parameter related with lateral interactions between the surfactant monomers adsorbed at the interface, $H < 0$ suggests net attractive interactions, while $H > 0$ suggests repulsive interactions [19]. The opposite sign convention is also used [20].

Equilibrium surface tension data of Pegiadou et al. [8], for C_9 -TGE C_{10} -TGE and C_{11} -TGE surfactants were fitted according to Eqs. (7) and (8). Fig. 7 shows the experimental data and the Frumkin–Davies simulation with the best-fit

parameters, which are displayed in Table 1. From Table 1, it can be observed that the interaction parameter H is always negative indicating attractive interactions between the adsorbed monomers at the interface. As expected, the absolute value of this parameter increases with the length of the hydrocarbon chain. Surface potential is negative and its absolute value increases with increasing chain length. According to Eq. (7), attractive interactions between adsorbed monomers increase the adsorption at the interface whereas the existence of a negative surface potential decreases it. The observed dependence of H and the electrostatic surface potential, ψ_0 , with the hydrophobic nature of surfactants is consistent with the increase of the surface concentration observed when the hydrocarbon chain length increases. The maximum surface concentration obtained from the fit agrees very well with the surface excess concentration value obtained at the cmc, Γ_{cmc} . The Γ_{cmc} values were calculated from the Gibbs’ adsorption equation that for the particular case of ionic surfactant in the presence of a second electrolyte is given by [21]:

$$\Gamma = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln C} \right) \quad (9)$$

The surface concentration in dynamic surface tension measurements $\Gamma(t)$ can be obtained by solving Eq. (8) according

Table 1
Best-fit parameter values to the combined Frumkin–Davies model

Surfactant	$10^6 \Gamma_\infty$ (mol m ⁻²)	Ψ_0 (V)	H	$10^6 \Gamma_{\text{cmc}}$ (mol m ⁻²)	$10^6 \chi^2$
C_9 -TGE	2.93 ± 0.01	-0.21 ± 0.01	-0.8 ± 0.6	2.91	10.00
C_{10} -TGE	3.51 ± 0.01	-0.23 ± 0.01	-1.1 ± 0.4	3.44	4.34
C_{11} -TGE	3.96 ± 0.01	-0.24 ± 0.01	-1.4 ± 0.4	3.81	10.00

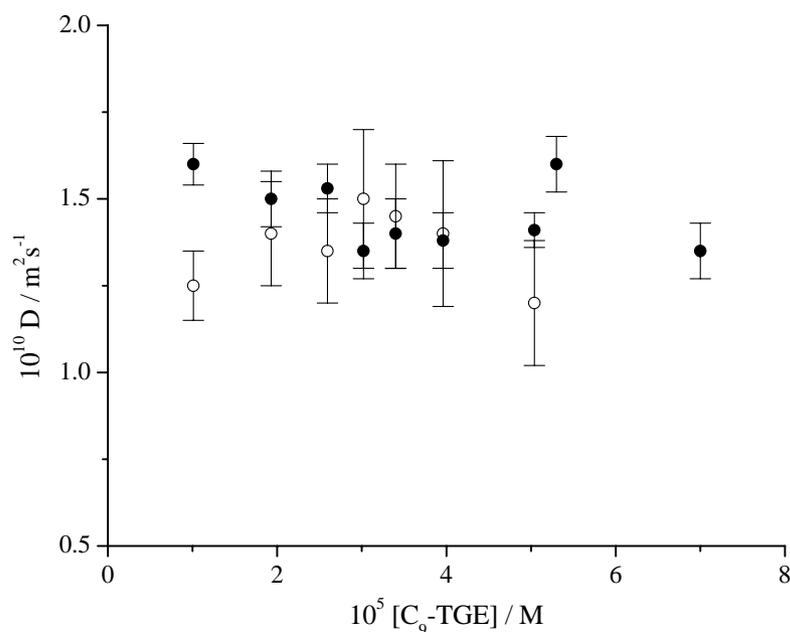


Fig. 8. Diffusion coefficients of C₉-TGE obtained from the Ward and Tordai asymptotic solutions at short and at long times using the Frumkin–Davies isotherm: (○) $D_{t \rightarrow 0}$; (●) $D_{t \rightarrow \infty}$. Results are obtained at 25 °C.

to the best-fit parameters of Table 1. According to Eqs. (2) and (3), both plots of $\Gamma(t)$ versus $t^{1/2}$ and $\Gamma(t)$ versus $t^{-1/2}$ are linear at short and at long times, and the diffusion coefficients were calculated from the slopes.

The values of the diffusion coefficients for C₉-TEG at 298.15 K are presented in Fig. 8. They were obtained from asymptotic solutions of Ward and Tordai in terms of surface concentration, Eqs. (2) and (3), and Frumkin–Davies isotherm. Similar results were obtained for C₁₀-TEG and C₁₁-TEG. Results show that for all three surfactants

$D_{t \rightarrow \infty} \sim D_{t \rightarrow 0}$. This fact indicates that the adsorption of these surfactants is exclusively diffusion-controlled when the appropriate equation of state (in this case the Frumkin–Davies isotherm) is used to related dynamic surface tension with surface concentration. We calculated an average value for the diffusion coefficient of $(1.5 \pm 0.2) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, in excellent agreement with the value obtained from the classic Ward and Tordai equation at short times along the Henry law isotherm. This proves that at low surface coverage (short times), the electrostatic

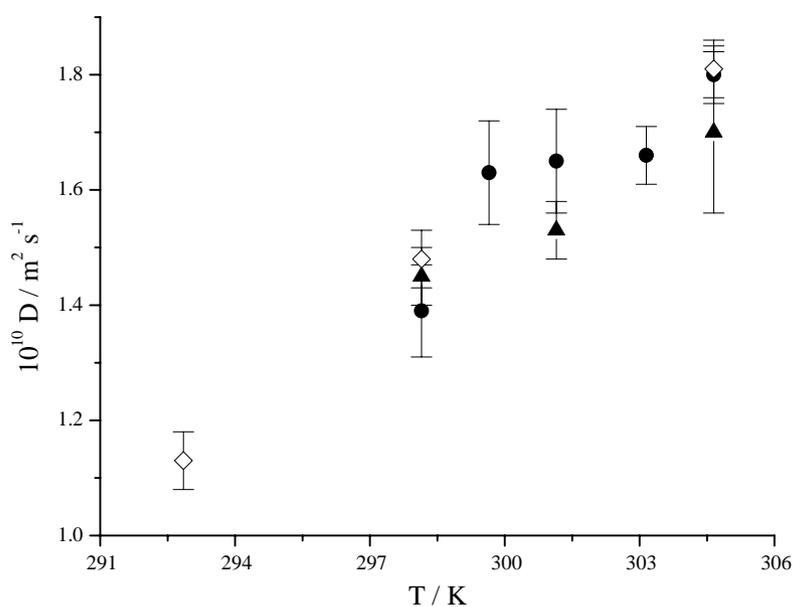


Fig. 9. Diffusion coefficients of C_n-TGE obtained from the Ward and Tordai equations and Frumkin–Davies model as function of the temperature: (●) $n = 9$; (△) $n = 10$ and (◇) $n = 11$.

and attractive interactions can be neglected, thus the diffusion coefficient calculated by Henry and Frumkin–Davies isotherms have the same values. However, when the surface coverage increases these effects became important and the accurate isotherms, FD in this case, must be used in order to interpret the dynamic of the adsorption process.

Finally, Fig. 9 shows the C_n -TGE average diffusion coefficients as a function of temperature obtained from same procedure. Examination of all these results shows the following: (i) the diffusion coefficient is independent of the length of the surfactant hydrocarbon chain. This fact has been observed elsewhere with *n*-alkyl sulfates [12], dialkyl phosphatidylcholines [21], and *n*-alkyl polyglycol ethers [22]; (ii) the diffusion coefficient increases with temperature as estimated from the Stokes–Einstein equation.

4. Summary

The dynamic surface tension of 1-*N*-L-tryptophan–glycerol-ether surfactants was analyzed according to the classic equation of Ward and Tordai using the Henry isotherm to relate the surface tension and the surfactant concentration in bulk. The controlling mechanism for mass transfer changes as a function of bulk surfactant concentration; it shifts from diffusion control at dilute concentration to mixed diffusion-kinetic control at elevated bulk surfactant concentrations.

We used the combined Frumkin–Davies isotherm as a more realistic surface equation of state, thus the equilibrium surface tension data obtained by Pegiadou et al. [8] were fitted to FD equation. This analysis leads to adsorption values compatible with those obtained from the Gibbs' law. The surface potential and the Frumkin interaction parameter H are negative and its absolute values increase with increasing surfactant chain length. The dynamic surface tension data obtained by Frumkin–Davies isotherm are consistent with the assumption of sole diffusion control even at high concentrations of surfactant solutions. Results presented in this work show the importance of the state equation in order to

interpret accurately the adsorption kinetics of the surfactant at the air–water interface.

Acknowledgements

The work was financially supported by Ministerio de Ciencia y Tecnología of Spain (BQU-2001-1507). C. Delgado wishes to thank Ministerio de Ciencia y Tecnología of Spain for the grant FP-2001-0479.

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