

Langmuir monolayers of the zwitterionic surfactant hexadecyl 1-*N*-L-tryptophan glycerol ether

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Received 16 December 2003; accepted 11 August 2004

Available online 9 December 2004

Abstract

We report the formation of Langmuir monolayers of pure zwitterionic hexadecyl 1-*N*-L-tryptophan glycerol ether (C₁₆-TGE) surfactant and mixed monolayers of cationic–zwitterionic surfactant obtained modifying the pH of the subphase. The pressure–area and surface potential–area isotherms and fluorescence microscopy measurements have been used to characterize the surface phase transitions in the monolayers. These transitions appeared at larger areas as the pH decreased from 6.0 to 2.0 and almost disappeared as the pH decreased further. The analysis of the surface potential and the infrared reflection–absorption spectroscopy data suggests that the phase transition is associated with a change of orientation of both the hydrocarbon chain and the aromatic group of the surfactant with respect to the air–water surface. The surface rheology of the monolayers was studied by quasielastic light scattering and by the oscillatory barrier technique. The results indicate that there is at least one relaxation process in the monolayer.

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Keywords: Langmuir monolayers; Hexadecyl 1-*N*-L-tryptophan glycerol ether; Surface potential; Fluorescence microscopy; Infrared reflection–absorption spectroscopy (IRRAS); Quasielastic light scattering (SQELS)

1. Introduction

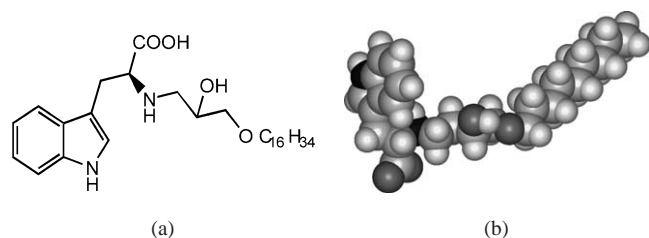
Langmuir monolayers at the liquid–air interface are well-defined interfacial systems and therefore are excellent models to study interactions in two-dimensional arrangements. In the last decades, optical microscopies such as fluorescence [1], Brewster angle [2], and ellipsometric microscopy [3] have been developed to obtain information on their structure. In addition, synchrotron X-ray diffraction provides information on the monolayer structures at molecular resolution [4]. The results from these techniques have pointed out that the structures of the monolayers are strongly dependent upon small changes of the physical variables. In effect, in the

case of monolayers of fatty acids, up to 10 different phases have been identified, and transitions from one phase to another can be driven by tiny changes in monolayer density and temperature or in the pH, ionic strength, or composition of the subphase [5].

Monoalkyl glycerol ether surfactants with different alkyl chain lengths (R = C₉ to C₁₆) in the hydrophobic part and tryptophan as the polar group are a novel family of lipoaminoacid compounds synthesized by the Department of Surfactant Technology in Barcelona [6]. Due to the presence of the glycerol group, these surfactants can be used as emulsifiers; in addition, the tryptophan group reduces the surfactant toxicity and therefore constitutes an interesting alternative to conventional synthetic surfactants in pharmaceutical and cosmetic applications [7,8]. The main advantage of these ether-type surfactants over glycerol ester derivatives is

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Scheme 1. Hexadecyl 1-*N*-L-tryptophan glycerol ether surfactant, C₁₆-TGE, molecular structure and the optimum conformation of the zwitterionic surfactant calculated within the AM1 approximation [14].

their stability against temperature and extreme pH values [6]. In these applications the structure of the interface plays an important role in the stabilization of the emulsions, foams, or bubbles; therefore we are interested in studying the structure and the properties of the monolayers of these surfactants. Thus we have studied the thermodynamic and dynamic properties of the Gibbs monolayers formed by the adsorption of the shorter chain-length surfactants at the air–water interface [9] and in the present work we have obtained information on the Langmuir monolayers formed by the longest chain-length compound hexadecyl 1-*N*-L-tryptophan glycerol ether (C₁₆-TGE, Scheme 1). Because the surfactant molecule contains one amino acid residue, tryptophan, it can exist in either a zwitterionic or a protonated form. We have also studied the structure and properties of mixed monolayers of the cationic–zwitterionic molecules modifying the pH of the aqueous subphase.

Pressure–area and potential surface–area isotherms and fluorescence microscopy measurements of pure zwitterionic and mixed zwitterionic–cationic monolayers provided evidence for the existence of a surface phase transition. On the other hand, the molecular orientation and the intermolecular interactions of surfactant molecules at the interface have been studied by infrared reflection–absorption spectroscopy. Finally, the viscoelastic properties of C₁₆-TGE monolayers studied by quasielastic light scattering, SQELS, and by oscillatory barriers indicate that there is at least one relaxation process in the monolayer. The amplitude of this relaxation process increases as the pH of the subphase decreases from 6 to 2.

2. Experimental

2.1. Chemicals

Hexadecyl 1-*N*-L-tryptophan glycerol ether, C₁₆-TGE, was synthesized as described in Ref. [6]. The surfactant was purified according to the published method, and the purity was evaluated using HPLC [6]. The purity of the compound is >99.5%. Ultrapure water (Milli Q) was used as subphase. Langmuir monolayers prepared by spreading aliquots of a chloroform (Carlo Erba, for analysis) surfactant solution (concentration around 0.1 mM) onto the air–water interface.

Subphase pH and ionic strength were adjusted by addition of HCl and NaCl (Fluka). Hydrochloric acid solutions (0.1 N) Normex were from Carlo Erba.

2.2. Langmuir trough

The monolayers were performed on a computer-controlled Teflon Langmuir minitrough (KSV, Finland). The surface pressure was measured with a Pt Wilhelmy plate connected to an electrobalance. The temperature control of water in the trough was carried out by passing thermostated water into the jacket at the bottom of the trough. The temperature near the surface was measured with a calibrated Pt-100 sensor and was maintained at 25.0 ± 0.1 °C.

From the equilibrium measurements, the spreading solution was applied with a Hamilton microsyringe at different parts onto the surface. To confirm the stability of the monolayer two different forms for preparing the monolayers were used. In the first one the surface concentration was changed by subsequent additions of the surfactant solution. The surface pressure was continuously measured, and the equilibrium value was taken when the surface pressure Π had remained constant at least 10 min. In the second way, the monolayers were symmetrically compressed by moving two barriers (Delrin) under computer control after the spreading of the surfactant solution. The maximum barrier speed was 10 mm/min. Both isotherms agreed with each other except in the cases of monolayers formed in acidic solutions of pH < 1.5. At this pH the cationic form of the surfactant predominates (>90%) and the monolayer becomes partially soluble; therefore we have not obtained results in acidic subphases of pH < 1.5.

The surface potential ΔV was measured simultaneously with the Π measurements. A Kelvin probe (Treck Inc.) located approximately 2 mm above the aqueous surface was used. The reference electrode, made of gold, was placed in the subphase. The surface potential measurements were reproducible to ± 20 mV.

2.3. Infrared spectroscopy (IRRAS)

The FT-IRRAS spectra have been recorded with a Nicolet Model 750 FT-IR spectrophotometer, with a resolution of 4 cm^{-1} . The spectra were obtained by accumulating 200 interferograms. The spectrophotometer was equipped with an external reflection attachment, a monolayer/grazing angle specular reflectance accessory (Specac P/N 19650), which has a removable Teflon Langmuir trough.

Optimal conditions for detection were obtained with an incident angle of about 70° relative to the normal to the water surface. In order to reduce the intense bands of air, a slow flow of dry nitrogen was introduced in the sample chamber for 3 h prior to the measurements. This method was introduced by Gericke et al. [10] to compensate for the water vapor bands. IRRAS data were reported as plots of reflectance–absorbance (R.A.) versus wavenumber. R.A. is

defined as $-\log(R/R_0)$, where R_0 and R are the reflectivity of the pure and film-covered aqueous surfaces, respectively.

In order to ensure that any possible effect of the bands of the residual CO_2 on the spectra was appropriately eliminated by the background subtraction, the spectra were repeated three times on different days. Only those features that were not affected by the purging process are discussed in this work.

2.4. Fluorescence microscopy

Fluorescence images were taken with a Leica inverted microscope equipped with a Hamamatsu SIT camera that was described in Ref. [11]. For film visualization 18 μM of 4-hexadecyl-amino-7-nitrobenzene-2-oxa-1,3-diazole (NBD-hexadecylamine) from Molecular Probes was admixed to the surfactant solution prior to spreading. The dye preferentially segregates to the less ordered regions of the monolayers and appears bright in the images [12].

2.5. Surface quasielastic light scattering (SQELS)

We have used a homemade SQELS setup, which has been described in detail in Ref. [11]. The spectrometer has been calibrated using ethanol, dimethyl ether, and water and can be used in the wavenumber range $100 < q < 900 \text{ cm}^{-1}$.

2.6. Oscillatory barrier measurements

These experiments were performed at constant barrier speed by oscillating the barrier of the trough [11]. The frequency was varied by changing the maximum area change ΔA . Care was taken in order to ensure that the experiments were performed in the linear region [13]. Also it was ensured that at each oscillation cycle, the values of Π corresponding to the maximum and minimum values of the monolayer area agreed with those of the corresponding equilibrium states.

3. Results

The surfactant C_{16} -TGE contains one amino acid residue, tryptophan, and can exist in either zwitterionic or protonated forms. Therefore changes in the subphase pH can induce changes on the zwitterionic/cationic proportion. Scheme 1 shows the optimum conformation of the zwitterionic surfactant calculated within the AM1 approximation [14]. The cationic form has a similar conformation; however, the main differences are related to the torsion angle of the atoms that link the N of the amine group with the aromatic carbon (39.9° for the cationic surfactant and 43.3° for the zwitterionic one) and to the distance between the amine and the carbonyl groups (2.56 and 2.21 \AA for the cationic and the zwitterionic molecules, respectively). For pH 6.0, the surfactant is expected to be in the zwitterionic form.

3.1. Pure zwitterionic surfactant monolayers

Fig. 1 shows the surface pressure, Π -, and electric surface potential, ΔV -, area, A , isotherms of the monolayer of the zwitterionic surfactant C_{16} -TGE. Although no plateau is observed in the pressure–area isotherm, it can be observed clearly on the surface potential isotherm. Epifluorescence microscopy shows that this plateau corresponds to a surface phase transition. Fig. 2a shows a homogeneous monolayer; it corresponds to states ranging from high values of A down to the region just preceding the plateau. Conversely, Fig. 2b corresponds to a state within the plateau region and shows different domains which are seen as stripes, and which disappear at the low-area end of the plateau. Hence the plateau can be interpreted as the liquid-expanded (LE) to liquid-condensed (LC) phase transition.

Taking into account that at the pH (6.03) of the subphase the surfactant molecule is in its zwitterionic form, it

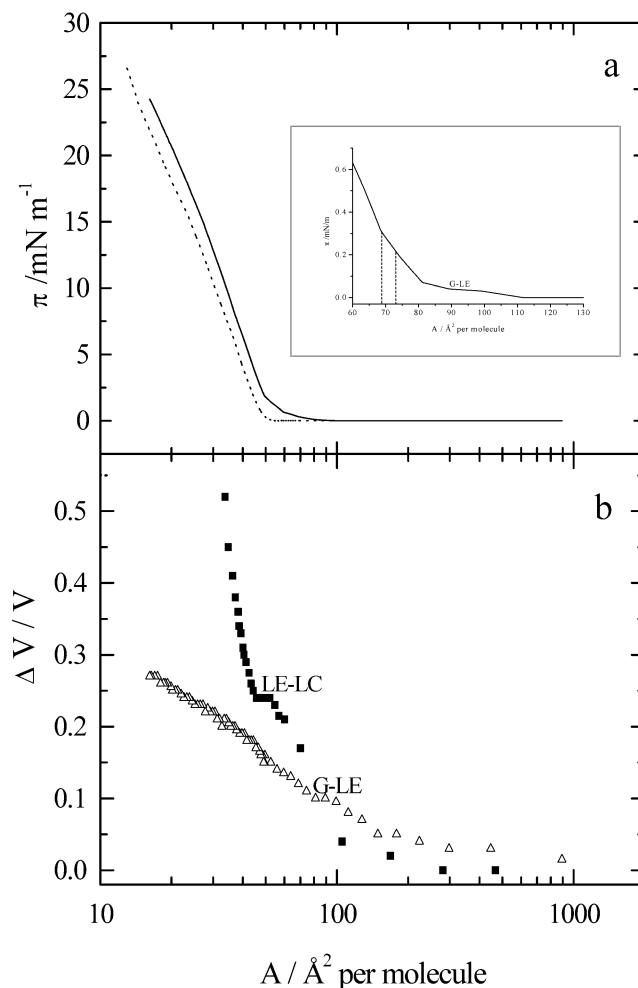


Fig. 1. (a) Surface pressure–area isotherms of films of C_{16} -TGE on water (dashed line) and on 0.01 M NaCl subphases (full line). (b) Surface potential–area isotherms of monolayers of C_{16} -TGE on water (squares) and on 0.01 M NaCl subphase (triangles). The insert corresponds to the isotherm adsorbed on saline solutions. Dashed lines mark the region of fluctuation stripe phase. Results were obtained at 25°C .

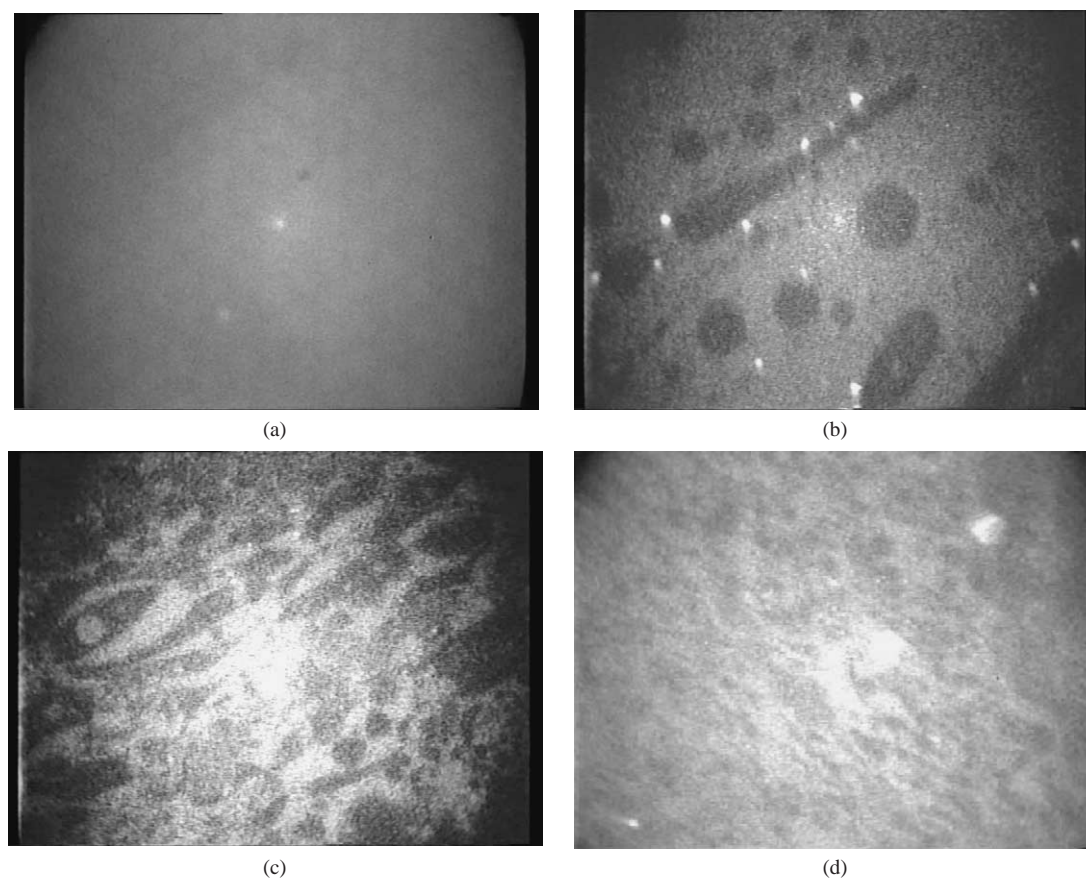


Fig. 2. Fluorescence images of C_{16} -TGE adsorbed on distinct subphases at different compression stages: (a) subphase: water and $\pi = 0.1$ mN/m; (b) subphase: water and $\pi = 1$ mN/m; (c) subphase: 0.01 M NaCl and $\pi = 0.02$ mN/m; (d) subphase: 0.01 M NaCl and $\pi = 0.3$ mN/m.

Table 1

Band positions (cm^{-1}) and assignment of bands corresponding to the IR-RAS spectra of monolayers of C_{16} -TGE

Mode description	Water subphase	0.01 M NaCl subphase	pH 2.02 subphase	pH 2.02/NaCl 0.09 M subphase	Ref.
CH_2 rock	887(↑)	887(↑)	899(↑)	864(↑)	[20]
ν_s (C–O–C) sym. stretch	1061(↑)	—	1050(↑)	1053(↑)	[21]
Ring vibration	1540(↓)	1540(↑)	1531(↑)	1538(↑)	[22]
Ring vibration	1585(↑)	1585(↓)	1587(↓)	1589(↓)	[22]
ν_s (C=O) sym. stretch	1746(↓)	1702(↑)	1697(↑)	1704(↑)	[18]

Note. Arrows indicate the orientation of IRRAS bands.

seems reasonable to assume that the interactions that drive the phase transition are mainly of an electrostatic character. In order to confirm this fact, we have studied the C_{16} -TGE monolayers on a water subphase containing NaCl 0.01 M (pH 5.90). The results are also presented in Fig. 1. Several changes are observed with respect to the unsalted subphase: (a) The whole Π -A isotherm is shifted to larger areas. (b) The values of ΔV are lower than those for the monolayer on pure water. (c) The plateau is shifted to larger areas. A similar shift of the plateau was already reported for monolayers of another zwitterionic surfactant, dipalmitoyl phosphatidyl glycerol [15,16]. Grigoriev et al. [16] have explained this effect in terms of the different populations

of protonated and dissociated forms of the surfactant. The protonated form of the surfactant results from the hydrolysis of the dissociated one [16]. This equilibrium depends on the electrolyte concentration in the subphase. According to Ref. [16], at large areas, the protonated surfactant forms condensed aggregates surrounded by less dense regions of the dissociated one. This is consistent with the epifluorescence image (Fig. 2c), which shows the stripelike domains ascribed to the G-LE transition. At the end of the plateau the stripes condense into the disorder fluctuation stripe phase [17] shown in Fig. 2d. The different domains disappear in the LE region at $\Pi > 0.3$ mN/m. At $\Pi \approx 2.3$ mN/m the monolayer exhibits an almost uniform distribution of dark domains of the LC phase.

In order to gain some insight into the orientation of the surfactant molecules on the interface, we have obtained the infrared internal reflection spectra, IRRAS, of the surfactant molecules on both monolayers. The position of the most intense bands is given in Table 1. The assignment of the bands was done according to Refs. [18–22]. From the data in Table 1 one observes that the wavenumber of bands corresponding to the IR spectra of the surfactant adsorbed on the two subphases are essentially coincident, except for the position of the band assigned to the symmetric stretching mode of the C=O group. The position of this band is very sensitive to the protonation state. Band positions of 1739, 1720, and

1704 cm^{-1} correspond to the stretching vibration of unprotonated, monoprotonated, and double protonated functional groups [18,19], respectively.

3.2. Monolayers of mixed cationic–zwitterionic surfactant molecules

In order to investigate the effect of zwitterionic/cationic ratio on C_{16} -TGE isotherms, aqueous solutions with different pH ranging from 6.0 to 1.5 were used as subphase. According to the pK values of the tryptophan's acid and amine groups, 2.38 and 9.4, respectively [23], the monolayers on subphases with $\text{pH} > 2.4$ are rich in the zwitterionic form of the surfactant. Conversely, when the subphase pH is lower than 2.4, the cationic species predominates on the monolayer. Even though differences are expected between the surface's degree of ionization of the surfactant head groups in the monolayer and in the bulk [24], this fact does not affect the qualitative conclusions of the present study.

The pressure–area isotherms as a function of pH are shown in Fig. 3. The trend of these isotherms is similar to that in pure water; however, the shape of these curves is quite sensitive to pH. The limiting area per molecule of the liquid-expanded and liquid-condensed phases are collected in Table 2. They point out that the isotherms become more

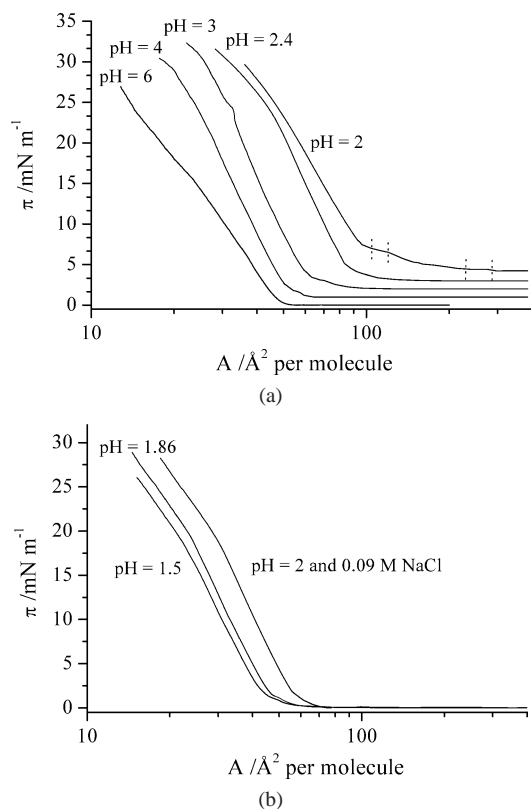


Fig. 3. Surface pressure–area isotherms of the mixed monolayers of zwitterionic and cationic C_{16} -TGE on aqueous subphase acidified at different pH values. For the sake of clarity, isotherms of (a) were each shifted 1 mN/m upward with respect to the previous one. Dashed lines mark the plateau regions.

expanded as the proportion of the cationic form of the surfactant increases ($2 \leq \text{pH} \leq 6$), and then become less expanded. It has to be noticed that in the immediate vicinity of pH 2 there is a sharp maximum in the limiting area of the LE–LC transition. This isotherm has been measured four times with results that were consistent within the experimental uncertainty and shows two plateaus around 100 and 200 Å^2 per molecule, respectively. The existence and position of these plateaus are clearly shown in the surface potential isotherm. The expansion of the isotherms may be caused by the electrostatic repulsion between cationic groups.

In order to confirm this hypothesis, the isotherm of C_{16} -TGE on pH 2 and 0.09 M of NaCl (ionic strength 0.1 M) has been measured. The results shown in Table 2 clearly point out that the monolayer becomes more compressed when the electrolyte is added to the subphase. This can be rationalized by considering that the positive charge of the cationic form of the surfactant is screened by the Cl^- ions. The screening of the positive charge can also be responsible of the decrease of the limit areas in the most acidic subphases of $\text{pH} < 2$.

We have also obtained the surface potential–area isotherms of mixed monolayers. For the sake of clarity Fig. 4 only presents some representative values. The figure shows that the surface potential increases as the cationic forms of the surfactant increases as is expected for monolayers charged positively. An exception to this behavior is the monolayer adsorbed on a subphase of pH 2. In this case the surface potential values are the smallest for the mixed monolayers studied (see below). Some ΔV vs A isotherms present a plateau, Fig. 4. The position of the plateau is shifted at longer areas as the pH decreases from 6.0 to 2.0, and almost disappears as the pH is further decreased. In agreement with the surface pressure measurements, the surface potential isotherm of pH 2 presents two plateaus, the first one between 250 and 300 Å^2 per molecule and the second one between 140 and 100 Å^2 per molecule. The plateaus correspond to two regions of phase coexistence, G–LE and LE–LC, respectively, observed by epifluorescence microscopy.

Finally, infrared reflection–absorption spectra of the surfactant molecules adsorbed at different compression stages on the subphase of pH 2 without and with 0.09 M of NaCl were recorded. The main feature of the IR surfactant spectrum for pH 2 is that $R.A. < 0$ for the whole wavelength

Table 2
Limit areas values of C_{16} -TGE surfactant monolayers depending on the subphase pH at 25 °C

Subphase pH	NaCl/M	A (Å^2 /molecule (LE))	A (Å^2 /molecule (LC))
1.50	0	49	58
1.86	0	47	65
2.04	0	107	196
2.06	0.09	59	68
2.40	0	64	90
3.03	0	60	75
4.06	0	51	62
6.03	0	35	48
5.90	0.02	54	67

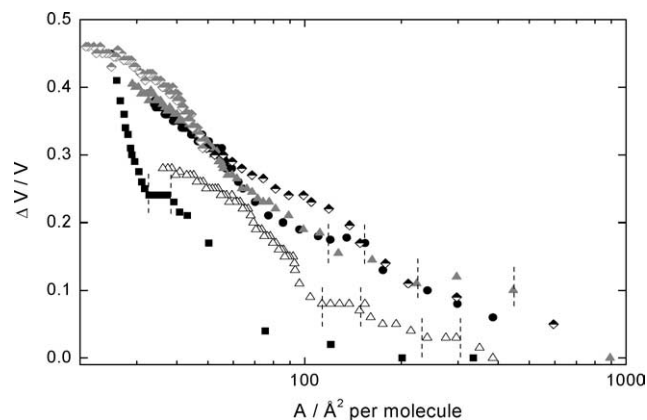


Fig. 4. Surface potential–area isotherms of the mixed monolayers of zwitterionic and cationic C_{16} -TGE on aqueous subphases acidified at different pH values. Squares: water. Circles: pH 3; open triangles: pH 2; diamonds: pH 1.5; triangles: pH 2 and 0.09 M of NaCl. Dashed lines mark the plateau regions.

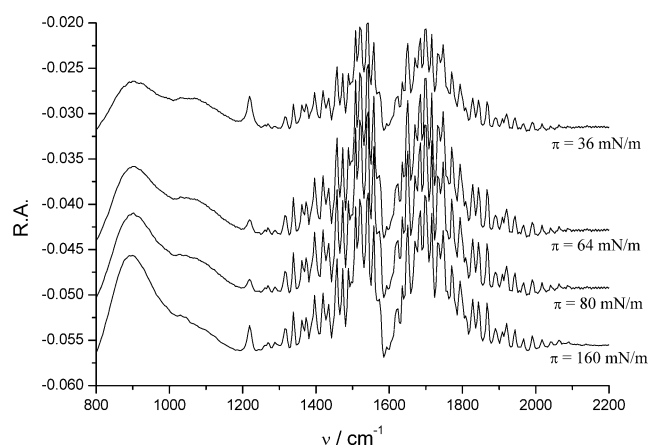


Fig. 5. Infrared reflection–absorption spectra in the range $2000\text{--}800\text{ cm}^{-1}$ for C_{16} -TGE on aqueous solutions subphases of acidified pH 2.

range and the R.A. values become more negative as the surface pressure increases, Fig. 5. Negative R.A. values have been associated with highly absorbing films [25]. In our case this behavior can be associated with the formation of the complex between cationic and zwitterionic surfactant species of great cross-sectional area. This complex disappears after the addition of NaCl to the subphase and as a consequence the R.A. values become positives. The existence of such a complex would be consistent with the fact that the limiting area for the isotherm at pH 2 is much higher than the cross-sectional area of the zwitterionic molecule as calculated by the AM1 method ($\approx 62\text{ \AA}^2$). It would also explain the low values of ΔV obtained for this isotherm.

3.3. Dilational rheology

We have calculated the dilational frequency for the constitutive parameters (γ , ε , and κ) that best fit the experimental SQELS spectra. For the sake of example, Fig. 6 shows the results for the dynamic elasticity ε of the monolayers on water as a function of the surface pressure and for five val-

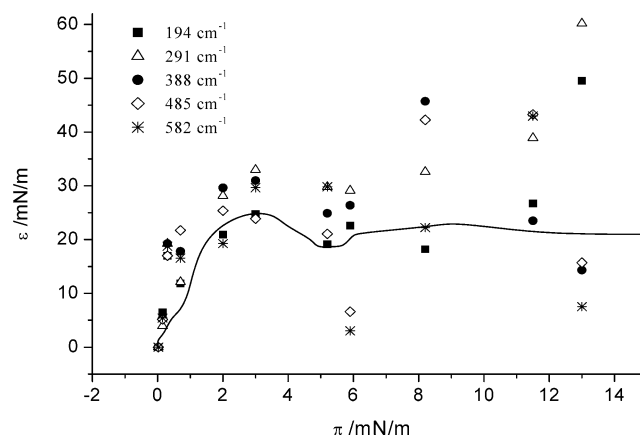


Fig. 6. Dynamic elasticity values, ε , of monolayers adsorbed in pure water at surface pressure. The values were obtained at five wave-vectors. The line represents the compressibility values obtained from the equilibrium Π vs A curve.

ues of the wavenumber. The compressibility obtained from the equilibrium Π vs A curves, $\varepsilon_{st} = -(\partial\Pi/(\partial\ln A))_T$, is also shown for comparison. As can be observed, both ε and ε_{st} present a maximum in the low- Π region. The minimum near $\Pi = 6\text{ mN/m}$ corresponds to the plateau region. It must be remarked that the uncertainty in ε for values of $\Pi > 10\text{ mN/m}$ is very high ($\approx 15\%$) because the monolayer is far from the resonance conditions between the capillary and the dilational modes [26]. The difference between ε and ε_{st} is an indication of the viscoelastic behavior of the monolayer [27].

Fig. 7 shows the frequency dependence of ε and κ for two of the systems studied. We have plotted at $\omega = 1\text{ mHz}$ the value that corresponds to the equilibrium value ε_{st} . It can be observed that, in spite of the experimental uncertainty, ε grows with ω . This tendency is confirmed by the values obtained from the oscillatory barrier (OB) experiments in the range $0.008\text{--}0.02\text{ Hz}$, which in most cases are also higher than ε_{st} .

The frequency dependence of ε points out the existence of, at least, a relaxation process in the monolayer. However, it would be necessary to have experimental data in the intermediate-frequency region ($10\text{ Hz--}1\text{ kHz}$) to be able to establish more clearly the exact nature of the relaxations.

4. Discussion

4.1. Pure zwitterionic surfactant monolayers

The analysis of surface pressure, the surface potential results, and the epifluorescence microscopy images show different features on the monolayers adsorbed in pure water and in 0.01 M NaCl . In addition, Table 1 points out that most of the frequencies of the bands of the IRRAS spectra are coincident on both subphases, except for those of the symmetric stretching of the carbonyl group, which is very sensitive to the protonation state [18,19]. As stated above, we only discuss the position of bands unaffected by both the purging

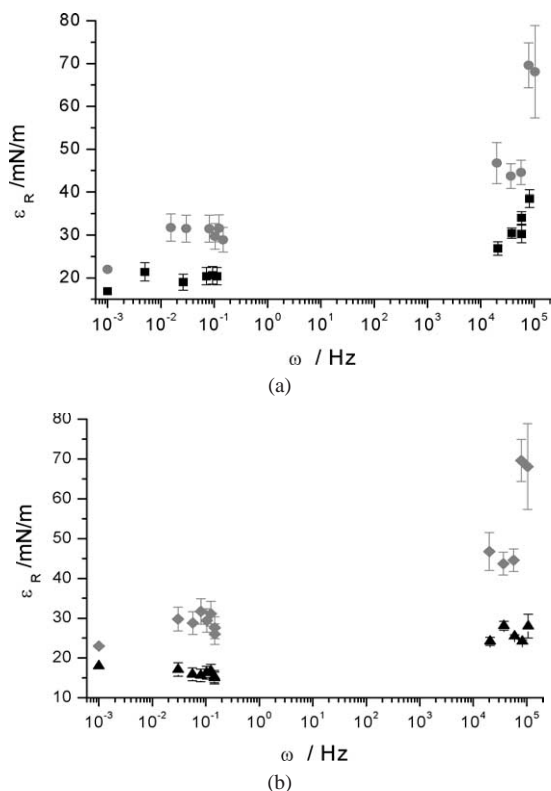


Fig. 7. Variation of the dilational elasticity with the frequency, for monolayers of C_{16} -TGE adsorbed (a) on aqueous solutions of 0.01 M of HCl and (b) on 0.01 M NaCl. Squares represent values at a surface pressure of 5 mN/m; circles of 9 mN/m; triangles 4 mN/m; and diamonds 8 mN/m. For comparison, points at $\omega = 1$ mHz represent the equilibrium value ε_{st} .

process and the water-vapor peaks. The position of the CO band corresponding to the surfactant molecule adsorbed on pure water, 1746 cm^{-1} , indicates that the carboxylic group of the surfactant is unprotonated [18]. The intensity of this band is very low. For the monolayers adsorbed on 0.01 M NaCl aqueous subphase, the CO stretching band is shifted at 1702 cm^{-1} . The position of this band indicates that the carboxylic group is double protonated [18].

The intensity of bands centered at 887 and 1061 cm^{-1} were assigned to CH_2 rocking [20] and C–O–C stretching [21]. Because the intensity of an IRRAS spectrum is related to both the orientation of the transition moment and to the concentration of molecules at the surface, it is necessary to eliminate the concentration effects. Multiplying the intensity by the area per molecule allow one to do this. Fig. 8 shows the dependence of the normalized intensity with the area in these monolayers. For large areas the intensity is small, and slightly increases with decreasing area until it reaches a certain value at which the intensity abruptly increases as the area decreases. This break point closely corresponds with the onset on pressure isotherms. The C–O–C stretching band disappears in the monolayer of NaCl aqueous subphase, which means that the transition moment is parallel to the air–water surface.

The behavior of the intensity of the CH_2 rocking band was studied in Ref. [20] for monolayers of small surfactant

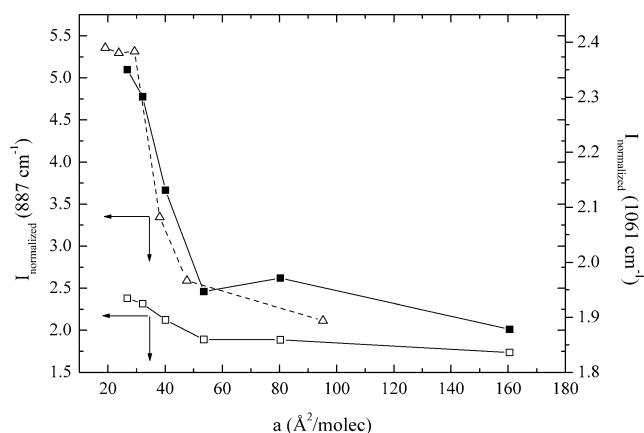


Fig. 8. Variation of the normalized intensity of IRRAS bands with the area per molecule of C_{16} -TGE monolayers on water (open and filled squares) and saline (triangles) aqueous subphases, respectively.

molecules. Upon compression, the intensity of this band increases, owing to an orientation of the hydrocarbon chain more perpendicular to the surface. The increase of intensity upon compression on the C–O–C stretching band can be interpreted on the same way. According to the surface selection rules for IRRAS, vibrational modes with their transition moments perpendicular to the surface are enhanced. Thus, the direction of the bands versus the baseline is an indication of the orientation of the transition moment at the water surface, and hence of that of the different functional groups [19]. The data in Table 1 allow one to conclude that the different orientations of the CO and of the ring bands on the two different subphases are related to distinct orientations of the molecules adsorbed on the two subphases. IRRAS spectra show that the transition moment associated with the CO vibration is more parallel to the interface in pure water subphase than in the saline monolayer, while the transition moment of either vibration is perpendicular to the interface in aqueous subphase and parallel in the saline one. Thus the IR bands corresponding to these vibrational modes have opposite orientation in each mode and also in each one of these monolayers. Analyzing these facts along with the optimum conformation of the surfactant, Scheme 1, it can be concluded that monomers adsorbed on saline subphase lie more flat to the surface than those adsorbed on pure water monolayer.

The different orientation of monomers in saline and pure aqueous subphases also explains the decrease of the surface potential in saline subphase. This further supports the idea that, in the lowest areas, the monomer is almost perpendicular to the air–pure water interface.

4.2. Monolayers of mixed cationic–zwitterionic surfactant molecules

As mentioned above, mixed monolayers of cationic and zwitterionic forms of C_{16} -TGE, become more expanded as concentration of the cationic form increases, goes through

a maximum at pH 2, and then decreases as the cationic form predominates. The expansion of the isotherms may be caused by the electrostatic repulsion between cationic groups. However, in the most expanded monolayer, subphase pH 2, the limiting area values and negative values of the R.A. of the IRRAS spectra seem to indicate the formation of a complex between the ammonium and acid groups of surfactant molecules. Differences between the complex refractive index of the intermolecular complexes and water or the independent surfactant molecules are responsible for the negative R.A. values [25]. This fact is also responsible for the more negative R.A. values found in dense monolayers of pH 2 than in the dilute ones. Thus, in the most concentrated monolayers, the infrared beam mostly reflects from the complexes adsorbed and little light reaches the water. Since water has a different complex refractive index than the complex adsorbed [25], changes in the reflectance are expected. In this case the reflectance spectrum is much stronger in surfaces occupied by complexes than by water. In diluted monolayers, most of the light is reflected from water and the absolute values of R.A. are lower than in dense monolayers. As discussed previously, complexes did not form when 0.09 M of NaCl was added to the subphase and consequently the R.A. is positive.

The IRRAS band corresponding to the CO group of monolayers formed in the acidic subphase of pH 2 in the absence and presence of electrolyte are centered on 1697 and 1704 cm^{-1} , respectively. These might be ascribed to the double protonated acid. However, in monolayers of pH 2 the frequency is around 7 cm^{-1} lower than that corresponding to that doubly protonated band reported in Ref. [18]. The shift of this band could be interpreted as due to the interaction between the CO and the ammonium group. It is well known that the hydrogen bonds affect the carbonyl frequencies by weakening of the C=O force constant, but the largest effects occur when the atom donating the hydrogen has a positive charge [28], as it is the case for the ammonium group of the surfactant. In contrast, the position of the CO band of surfactant adsorbed in subphase containing 0.01 M of HCl and 0.09 M of NaCl is the same than in saline aqueous solutions, confirming the breaking of the complex when the subphase contains NaCl.

The orientation and the variation of the intensity with the surface concentrations of bands ascribed to CH_2 rocking, C–O–C stretching, and ring vibrations, Table 1, are the same as on monolayers adsorbed on the saline aqueous subphase. This indicates that the position of the monomers adsorbed in the acid monolayers containing salt lies more parallel to the surface than in pure water.

4.3. Dilational rheology

It has already been pointed out that the elasticity results, obtained from the SQELS experiments, indicate that there is, at least, one relaxation process in the monolayer. Earnshaw et al. [27] found a similar behavior for monolayers of

n-decanoic acid. These authors analyzed their elasticity data by assuming that there was a single relaxation process at the frequencies characteristic of their SQELS experiments (for which the monolayer of *n*-decanoic acid behaves as insoluble). Within their experimental precision, their data could be described by a Maxwell relaxation mode with a characteristic relaxation time $\tau_R \approx 10 \mu\text{s}$. Earnshaw et al. [27] related the relaxation to a reorientation phase transition between two states in which the alkyl chains occupy different areas. It must be stressed that no phase transition was apparent in the pressure–surface concentration isotherm of *n*-decanoic acid. Sakai and Takagi [29] have found a similar relaxation for monolayers of tetradecanoic acid. They considered that this high-frequency process was related to the lateral association between neighboring molecules during the in-plane motion.

Fig. 9 shows clearly that the monolayers of C_{16} -TGE present a relaxation process in the high-frequency region. In all the monolayers studied in this work, the width of the loss modulus $\omega\kappa$ curves is too large to be fitted to a single Maxwell mode. The maximum of the $\omega\kappa$ curves correspond to relaxation times $\tau_R (= 1/\omega_{\text{max}}) \approx 10 \mu\text{s}$ for the monolayer on water and 20 μs for pH 2.0. These values are similar to those found in Ref. [27] for a single chain surfactant. It must be remarked that this relaxation is better defined for the monolayers on the subphase of pH 2.0 than for pure water and the other subphases. In effect, not only the width of the relaxation is smaller, but also its amplitude is signifi-

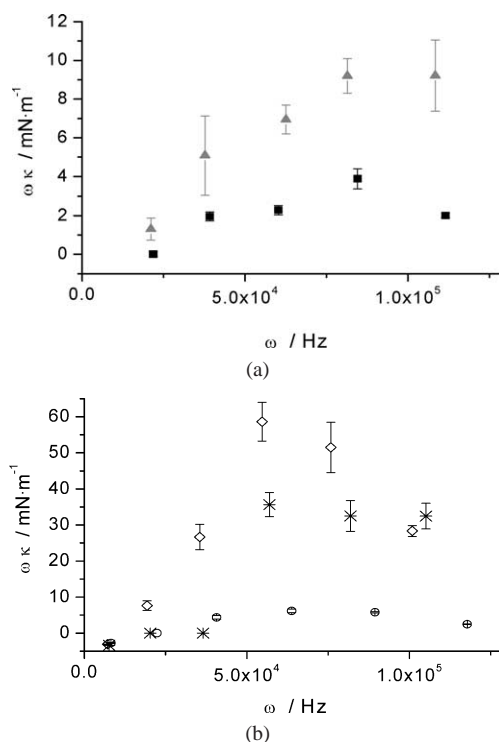


Fig. 9. Loss modulus values, $\omega\kappa$, obtained as a function of the frequency for C_{16} -TGE molecules adsorbed on (a) water subphase and surface pressures of (squares) 0.1 mN/m and (triangles) 5 mN/m and (b) on acidic aqueous subphase of pH 2 and surface pressure of (circles) 0.3 mN/m , (stars) 5.3 mN/m , and (diamonds) 10.4 mN/m .

cantly higher. The amplitude of the transition, measured by $(\omega\kappa)_{\max}$, increases as the pH decreases from 6 to 2.

The explanation of the fact that $\varepsilon > \varepsilon_{\text{st}}$ at high surface pressures for monolayers in which the molecules can coexist in two states with different areas per molecule goes back to an argument advanced by Scheludko [30] in 1966. For $t \ll \tau_{\text{R}}$ the free area available must be smaller than for $t \gg \tau_{\text{R}}$; if the molecules do not have time to reorient at the frequency characteristic of the capillary wave, the rarefaction and concentration of the molecules that take place at the peak and the trough of the wave will not lead to the changes of area per molecule that would correspond to ε_{st} .

It remains unexplained that $\varepsilon < \varepsilon_{\text{st}}$ at frequencies characteristic of the oscillatory barrier experiments (1 mHz–0.1 Hz). Although for soluble monolayers this frequency range may be characteristic of the kinetics of adsorption–desorption processes, the present surfactant is highly insoluble, and such a process can be safely ruled out.

5. Conclusions

The surfactant C₁₆-TGE forms stable insoluble monolayers in aqueous subphases at pH ranging from 1.5 to 6. The pressure–area and surface potential–area isotherms and fluorescence microscopy show the existence of surface phase transitions. The surface phase transition appears at longer areas as the pH is decreased from 6.0 to 2.0 and almost disappears as the pH is further decreased. The most expanded monolayer is formed in acidic subphase of pH 2. The results presented in this work seem to indicate that the strong electrostatic interactions between the carboxylic and ammonium groups of the contiguous surfactant molecules adsorbed at the interface are responsible of this behavior. This interaction disappears with the addition of NaCl. Infrared spectra of the surfactant adsorbed at the interface also showed that the position of acid monolayers lies more parallel to the surface than that in pure water. This trend is enhanced in air–brine surfaces.

Finally, using quasielastic light scattering, SQELS, and by oscillatory barriers the surface rheology of the monolayers was studied. The results indicate that there is at least one relaxation process in the monolayer and the amplitude of the relaxation process increases as the pH of the subphase decreases from 6 to 2.

Acknowledgments

The work was financially supported by two projects of the Ministerio de Ciencia y Tecnología of Spain (MAT-2003-1517 and BQU-2001-1507) and of the Comunidad de

Madrid (07N/0028/2002). M.M. Velázquez is grateful to the Universidad de Salamanca for the partial support of her stay in Madrid. The authors acknowledge the C.A.I. of Spectroscopy for making available the infrared facilities and the Aula Multimedia del Centro de Cálculo for performing the digitization of fluorescence images.

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