

Dynamic Surface Activity of Phenylalanine Glycerol–Ether Surfactant Solutions Measured by a Differential Maximum Bubble Pressure Tensiometer

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A refined differential maximum bubble pressure tensiometer was used for measuring the dynamic surface tension at various concentrations of a nonconventional surfactant, a member of a new homologous series of phenylalanine glycerol–ether amphiphiles, with 10 carbon atoms to the hydrophobic alkyl chain (C₁₀-PhGE). The effective bubble formation frequency for the examined surfactant concentrations was varied from 2 bubbles per second to 1 bubble per 20 s. The variation of equilibrium surface tension with concentration as well as the critical micelle concentration were determined by a Wilhelmy plate technique. Comparisons between dynamic and equilibrium surface tension values demonstrate that, under the employed surface deformation rates, the equilibrium surface tension is a misleading indicator of surface activity. This is also supported by simple surface rheology considerations. Results based on a diffusion-controlled kinetic analysis provide further evidence on the strong dependence of surface activity on the particular time scale of deformation.

1. Introduction

Surface tension of liquids plays a critical role in many applications such as production of detergents, emulsification of pharmaceuticals, cosmetics, foods, and electronics. Surface tension measurements refer to either equilibrium (static) or dynamic values, depending on the time scale of measurement.¹ Static surface tension reflects the thermodynamic status of an interface and refers to measurements obtained at sufficiently long times where both surface activity and interactions between the surface and the bulk are relaxed. On the other hand, many applications involve mass transfer rate-limited effects of surface tension, where equilibrium values of surface tension are not reached and where equilibrium measurements would not reveal a time factor on the process. Any interfacial measurement that detects changes over time can be considered to be dynamic.²

The dynamic surface tension of a fluid is simply a measurement of the surface tension at a significant rate of surface deformation. The equilibrium and dynamic surface tension values are the same for pure fluids, such as water. Yet the values of dynamic surface tension for solutions containing surfactants may be much higher than the corresponding equilibrium surface tension values.³ This is so because, under dynamic conditions, insufficient time may exist for the migration of surfactant molecules from the bulk solution to the interface and further alignment with adjacent molecules until minimum surface energy is reached. Apparently, the difference between the two surface tension values enlarges at higher shear rates. Nevertheless, in practice, it is often believed that equilibrium surface tension can represent the surface characteristics of surfactant solutions, even under the high shear

rates encountered in industrial applications.⁴ It is the contention of the present work that the dynamic surface tension, rather than the equilibrium one, is a more appropriate measure in accessing the interfacial characteristics at high shear rates.

One should further note that the determination of equilibrium surface tension in surfactant solutions is by itself a rather difficult task.³ This is mainly due to inevitable impurities that are almost always present in surfactant solutions with higher surface activity than the main component. For this reason, equilibrium surface tensions in practice are often evaluated by extrapolation of the dynamic surface tension values to infinity, assuming negligible adsorption of impurities in the time range of the extrapolation, e.g., see refs 5–7.

Recently,⁸ we synthesized and characterized a new nonconventional homologous series of surfactants having the skeleton of glycerol conjugated with a hydrophobic alkyl chain (with 10–16 carbon atoms) via an ether bond and with the amino acid phenylalanine via an NH bond. The carboxylic part of the amino acid is the hydrophilic moiety which, in alkaline solution used here, forms the sodium salt and, therefore, behaves as a real soap (Chart 1).

These surfactants are environmentally friendly compared to the conventional sulfates and sulfonates.^{9–12} Moreover, they possess better surface properties than the classic carboxylic soaps (lower cmc and σ_{cmc}), and high stability in water solutions of

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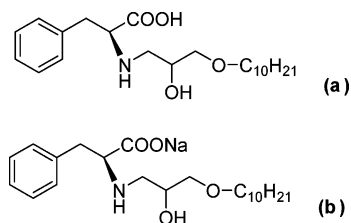
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Chart 1. Phenylalanine Glycerol–Ether with 10 Carbon Atoms to the Alkyl Chain Symbolized as C₁₀-PhGE, (a) in Solid State (b) in Alkaline Solution.



extreme pH values, due to the stable ether bond compared to the easily hydrolyzable ester bond of the widely used mono- and diglycerol ester surfactants, e.g., see refs 13–15. These surfactants, and the member of an analogous series with the amino acid tryptophan instead of phenylalanine previously synthesized and characterized,¹⁶ have already been tried as wetting agents in the mercerization process of cellulose, which takes place in high pH (12–14) solutions, and also as emulsifiers in personal care products, with very promising results (unpublished data).

A motivation for the present work is to show that, for the surface-active organic compounds of the above type, the appropriate concentration for the aforementioned applications should be judged chiefly on dynamic surface tension information. First, the equilibrium surface tension of all members is measured by the Wilhelmy plate technique in order to register variations with concentration and also identify the critical micelle concentration (cmc). Next, dynamic surface tension is measured by a differential maximum bubble pressure technique for alkaline solutions of the C₁₀-PhGE member at several concentrations, even beyond the cmc. Equilibrium and dynamic results are compared. Assuming diffusion-controlled adsorption kinetics, the diffusion coefficients for both short and long times are calculated and discussed. In addition, some simple surface rheology considerations are employed to shed a bit more light onto surface activity.

2. Materials and Methods

Materials. The synthesis and characterization of surfactants are described elsewhere.⁸

Equilibrium Surface Tension Measurements. The Wilhelmy plate technique (Sigma 701, KSV Inc.) was used to measure the equilibrium surface tension. This technique determines surface tension from the force required to pull a plate vertically away from the surface of the test solution. Measurements were taken at 30 min after the plate was immersed in the alkaline (pH = 12) solution, which was a time interval always adequate to reach a final steady value (± 0.5 mN/m). More details are given elsewhere.⁸

Dynamic Surface Tension Measurements. These measurements were conducted with a custom-made differential maximum bubble pressure tensiometer. The device was constructed according to the principles and specifications reported by Holcomb and Zollweg.¹⁷ A few key improvements and refinements allowed us to extend the range of effective operation beyond the limits set by those authors with regard to the bubble formation frequency and the size of bubbles; details can be found elsewhere.¹⁸ The technique employs differential

measurements from two firmly fixed capillaries to eliminate uncertainty due to hydrostatic pressure effects. Two capillary tubes, spaced 2 cm apart on the horizontal plane, were inserted vertically to the same depth (~ 1 cm) into the test solution. Glass capillaries and Teflon-coated capillaries (to make their surface nonwetttable) with radii of 0.125 and 0.635 mm, respectively, were used in the present study.

As bubbles grow and detach from the tubes, the bubbles' pressure varies due to changes in bubble radius. Very sensitive pressure transducers (measuring max 5" and 10" of water, respectively) were used to record the pressure signals from a succession of bubbles emerging from the two tubes. In accordance with the Young–Laplace (Y–L) equation, bubble inflation pressure reaches a maximum value when the bubble achieves a minimum radius of curvature. This occurs as the bubble assumes a hemispherical shape with a diameter equal to the tube diameter. The dynamic surface tension, σ_d , is calculated from measurements of the maximum bubble pressure and evaluating the differential Y–L relation over a range of bubble frequencies:¹⁷

$$P_{\max_2} - P_{\max_1} = 2\sigma_d \left(\frac{1}{R_2} \frac{(\alpha_0 + \alpha_1 E_{o2} + \alpha_2 E_{o2}^2)}{(1 + \alpha_3 E_{o2})} - \frac{1}{R_1} \frac{(\beta_0 + \beta_1 E_{o1} + \beta_2 E_{o1}^2)}{(1 + \beta_3 E_{o1})} \right) \quad (1)$$

where P_{\max_1} and P_{\max_2} are the maximum bubble pressure readings from the two capillaries, R_1 and R_2 are their respective radii, and E_o is the Eotvos number, $(\rho g R^2 / 2\sigma_d)$, which is the ratio of the buoyant force that distorts the bubble from sphericity over the surface tension force that acts to keep the bubble spherical.

Equation 1 is solved in an iterative manner. The numerical accuracy is much better than experimental errors (better than 0.1%). For $E_o < 0.5$ (which holds for most experimental conditions), $\alpha_0 = 1$, $\alpha_1 = 1.2257$, $\alpha_2 = 0.5983$, $\alpha_3 = 0.5746$, and $\beta_0 = 0.9198$, $\beta_1 = 1.259$, $\beta_2 = 0.05221$ and $\beta_3 = 0.1472$.¹⁷

For the examined surfactant solutions, the tensiometer proved to be effective in the range from 2 bubbles per second to 1 bubble per 20 s. Under certain conditions, it was possible to do measurements even up to 1 bubble per 80 s. Measurements were conducted at 25 °C. The accuracy of the tensiometer was tested by measuring the surface tension of some pure liquids (distilled water, carbon tetrachloride, acetone, ethylene glycol, and glycerin). For these liquids and for bubble formation frequencies (f) below 5 Hz, the results showed a deviation of less than $\pm 1\%$ from the surface tension values listed in the literature, e.g., in ref 19.

The dynamic surface tension measurements presented here are solely for solutions of the C₁₀-PhGE member, which is the smaller surfactant molecule of the developed homologous series. This is so because, for other longer molecules of the series, the dynamic surface tension approached that of the solvent (~ 73 mN/m at $T = 25$ °C and pH = 12) for most of the employed bubble formation frequencies and for surfactant concentrations even above cmc.

3. Adsorption Kinetic Analysis

Dynamic surface tension data can be used to analyze the adsorption mechanism of surfactants at gas/liquid interfaces. The most well-known adsorption model is the diffusion-controlled equation of Ward and Tordai, which is, in effect, the solution of the Fick diffusion equation under appropriate initial/boundary conditions and combined with an adsorption isotherm:⁴

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

where Γ is the excess surface concentration, C is the concentration in the bulk phase, C_s is the subsurface concentration, D is the diffusion coefficient, and t is the time.

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This nonlinear integral equation is amenable only to numerical solution for the general case. As the direct application of this model is rather complicated, asymptotic analytical solutions were derived and commonly used for both the regions of short and long surface lifetimes, e.g., see refs 7, 20, and 21.

To obtain information about the mechanism at the beginning of the adsorption process (short surface lifetimes), the diffusion-controlled adsorption theory yields the following relationship for ionic surfactants, e.g.,²¹

$$\left(\frac{d\sigma_d(t)}{dt^{1/2}}\right)_{t \rightarrow 0} = -4RTC \left(\frac{D_{t \rightarrow 0}}{\pi}\right) \quad (3)$$

where R is the universal gas constant, T is the temperature, and $D_{t \rightarrow 0}$ the diffusion coefficient at short times. At $t \rightarrow 0$ and for low surfactant concentrations, no special prerequisites (such as an adsorption isotherm) are necessary, and the diffusion coefficient $D_{t \rightarrow 0}$ can be determined directly from the slope of the data σ_d vs $t^{1/2}$.

On the contrary, at $t \rightarrow \infty$ (long time approximation), knowledge of the thermodynamic equilibrium state of the adsorption layer is needed in order to determine the diffusion coefficient $D_{t \rightarrow \infty}$. A common approximate expression used for long surface lifetimes is:⁷

$$\left(\frac{d\sigma_d(t)}{dt^{-1/2}}\right)_{t \rightarrow \infty} = \frac{RT\Gamma^2}{C} \left(\frac{1}{\pi D_{t \rightarrow \infty}}\right)^{1/2} \quad (4)$$

Despite its broad use by researchers, the above equation is valid only for a linear adsorption isotherm and gives an acceptable approximation for small surface coverage, i.e., in the range of the Henry isotherm ($\sigma = 2RT\Gamma$). This brings up two major difficulties. First, data so close to equilibrium rarely exist, and second, surface active impurities may absorb in this time region so that there is always the possibility of significant error in data interpretation.

Another often used approximate expression for the long time region is:²¹

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

where the excess surface concentration, Γ , is usually estimated through the Gibb's adsorption equation, ($d\sigma = -RT\Gamma d \ln C$). In some cases, the Langmuir and Frumkin isotherms have been used with success, e.g., in refs 22 and 23.

Equation 5 compares better than eq 4 with the linear part of the rigorous theory of Ward and Tordai when analyzing data acquired at realistic long times, yet not so close to equilibrium, e.g., in ref 24. It must be noted that eq 5 is not a rigorous asymptotic expression for the Ward and Tordai equation, as it is derived on the premise that $C(t - \tau) = \text{constant}$ for $0 < \tau < t$, and this is not a realistic condition for usual dynamic adsorption processes. However, eq 5 offers reasonable accuracy compared to that of the Ward and Tordai model for applications of small surface coverage and when the data lie in the region $50 \geq t/t_d \geq 1$,⁷ where t_d is the characteristic time of a diffusion-controlled adsorption

process defined as:

$$t_d = \frac{1}{D} \left(\frac{\Gamma}{C}\right)^2 \quad (6)$$

4. Surface Rheology Considerations

The ability of surface-active molecules to relieve excess surface tension when the surface area is expanded or compressed was originally described by Gibbs³ as a surface elasticity effect. Furthermore, for changes of surface area occurring at moderate rates of deformation, the ability of a surfactant to relieve stress is limited by adsorption or desorption from or to the bulk solution, and as a result, relaxation processes come into play, leading to gradual reequilibration of the system. Thus, in the most general case, any disturbance of an interface initiates both elastic and viscous effects that can be described by a complex surface dilatational modulus, e.g.:²⁵

$$\epsilon = \frac{d\sigma_d}{d \ln A} = A \frac{d\sigma_d}{dA} = \epsilon_r + i\epsilon_i \quad (7)$$

where A is the area of the surface, the real part ϵ_r accounts for the recoverable elastic energy stored in the surface, and the imaginary part ϵ_i reflects the viscous dissipation of energy through any relaxation (time-dependent) processes at or near the surface.

Apart from the above definition of dynamic viscosity, there is yet another "operational" definition based on the analogy between three- and two-dimensional systems relating the rate of yielding of a medium to applied isotropic pressure.¹ If $\gamma = (dA/dt)/A$ is the surface expansion rate, then:

$$\kappa = \frac{d\sigma_d}{d(\ln A/dt)} = \frac{d\sigma_d}{d\gamma} \quad (8)$$

The viscosity coefficient κ in eq 8 can be shown to be similar to the dynamic viscosity ϵ_i/γ in eq 7 at small rates of deformation, γ , e.g., in ref 26. The slope of dynamic surface tension with bubble frequency can be related to a surface dilatation modulus or a surface viscosity coefficient, as this is a measure of the rate of change of surface area, e.g., Karapantsios and Kostoglou.²⁷

It bears noting that the bubble formation frequency at the tip of a capillary is associated with the bubble surface expansion rate:²⁸

$$\gamma = \frac{Q}{2\pi R_i^3} \quad (9)$$

where γ is in s^{-1} , Q represents the volume flow rate of the injected gas, and R_i denotes the capillary radius. The surface expansion rate is a quantity proportional to the rate of shear strain. Sample calculations show that the expansion rate has values that are roughly 3 orders of magnitude higher than the bubble frequency because detached bubble radii are larger approximately by an order of magnitude from the tube radius. Such considerations are important when assessing the dynamic performance of a surfactant system in real applications.

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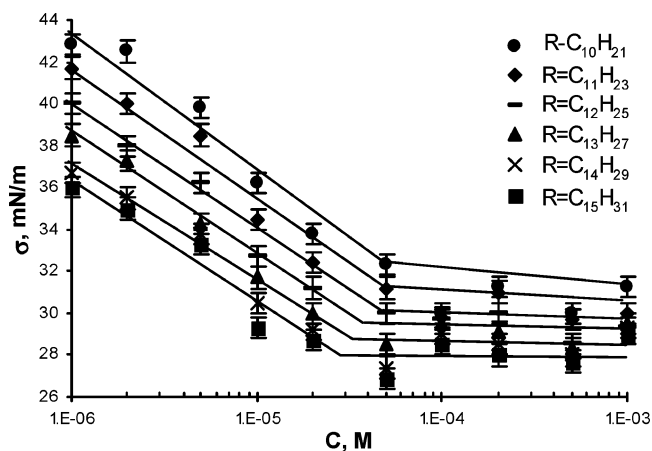


Figure 1. Static surface tension (σ) vs log of concentration (C) for all the compounds of the homologous series PhGE with 10, 11, 12, 13, 14, and 15 carbon atoms to the hydrophobic alkyl chain in alkaline aqueous solutions (pH = 12) showing critical micelle concentration (cmc). Error bars stand for standard deviation, including repetitions.

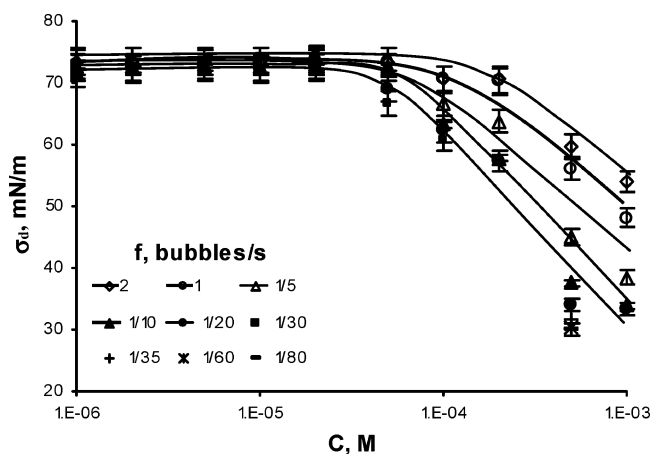


Figure 2. Dynamic surface tension (σ_d) of C_{10} -PhGE solutions vs concentration (C) with bubble formation frequency (f) as a parameter. Error bars stand for standard deviation, including repetitions.

5. Results and Discussion

Figure 1 presents measurements of the equilibrium surface tension vs concentration for all the members of the developed surfactant homologous series. It is well-known that, for solutions of organic compounds belonging to the same homologous series, the surface tension variation with concentration obeys a certain pattern: as the hydrophobic alkyl chain increases (by a CH_2 group), the equilibrium surface tension (for equal concentrations) decreases.¹ As the concentration of each solution increases, the equilibrium surface tension decreases approximately linearly (on the semilog plot), reflecting the gradual coverage of the liquid surface with surfactant molecules.¹ The decline of surface tension continues down to a concentration where the surface becomes saturated with surfactant molecules. This value is the critical micelle concentration (cmc) of the surfactant. Concentrations greater than the cmc practically do not cause any further decrease in the equilibrium surface tension.^{1,3}

Dynamic surface tension measurements for C_{10} -PhGE solutions at various bubble frequencies are presented in Figure 2. The values of the dynamic surface tension are noticeably higher than its equilibrium surface tension counterpart. Interestingly, for concentrations less than the cmc, the dynamic surface tension takes values pretty close to the surface tension of the solvent. It appears that, for the employed bubble formation frequencies,

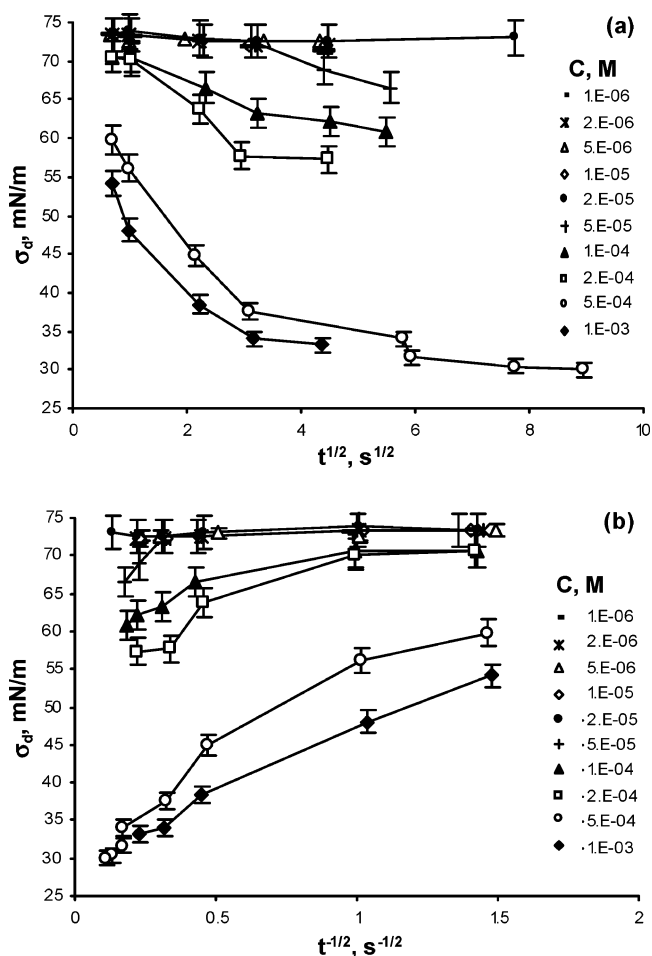


Figure 3. Dependence of dynamic surface tension of C_{10} -PhGE solutions on (a) $t^{1/2}$ (short times) and (b) $t^{-1/2}$ (long times). Error bars stand for standard deviation, including repetitions.

insufficient surfactant molecules manage to reach the surface to lower its surface tension. This indicates that the surfactant may not be as effective in reducing surface tension in processes where fresh interfaces are produced rapidly, such as removal of oil during washing, hard surface cleaning, or foaming.

It is only above cmc that the dynamic surface tension decreases from the value of the solvent. In this, there is a distinct frequency dependence; for decreasing bubble frequency, the surface tension becomes gradually lower, departing from the value of the solvent. This is due to the slower expansion rates (longer bubble lifetime) at lower frequencies, which allows more surfactant molecules to migrate to the bubble surface.

It would be expected that, in a solution of neutral pH, a typical anionic surfactant like C_{10} -PhGE should show little change of surface tension with bubble frequency. However, the above surfactants are carboxylic acids such as classic soaps and, consequently, are sparingly soluble in neutral water while absolutely soluble in alkaline media. So, the strong frequency dependence displayed in Figure 2 is due to the high ionic strength of the employed alkali solution. The presence of ions in the solution drives "free" surfactant molecules to the interface and also into more micelles, thereby depleting their availability to reduce the surface tension. This produces a diffusion-limited (frequency dependent) dynamic surface tension.

Figure 3a and b present dynamic surface tension, σ_d , vs $t^{1/2}$ and $t^{-1/2}$, respectively, where t is the effective lifetime of the bubble surface. This effective lifetime (time for migration of molecules to the surface) is considered to last up to the moment

Table 1. Estimated Diffusion Coefficient at Short and Long Adsorption Times

| $C \times 10^{-3}$ (M) | $D_{t \rightarrow 0} \times 10^{-11}$ ($\text{m}^2 \text{s}^{-1}$) | $D_{t \rightarrow \infty} \times 10^{-13}$ ($\text{m}^2 \text{s}^{-1}$) |
|---------------------------|---|--|
| 0.1 | 6.4 | |
| 0.2 | 2.2 | |
| 0.5 | 9.1 | 2.7 |
| 1 | 3.6 | 4.8 |

that a growing bubble reaches the hemispherical shape. The time interval after this instant up to the moment of bubble departure from the capillary is, in fact, a dead time for surface tension measurement.²¹

In Figure 3a and b, the data that deviate from the surface tension of the solvent follow an approximately linear variation at both *short* and *long* times. Diffusion coefficients are calculated from the slopes of the linear fits by using eqs 3 and 5. For short times, diffusion coefficients are derived for $C \geq 10^{-4}$ M; for lower concentrations, there is no reliable dependence of σ_d on $t^{1/2}$, indicating a short diffusion time with respect to the applied rate of deformation. For long times, diffusion coefficients are derived just for C : 5×10^{-4} and 10^{-3} M because, only for these two concentrations, the extrapolation of the data tends to a reasonable equilibrium surface tension value, ~ 29.5 mN/m; this value is the average of the intercepts for the two concentrations obtained for $t^{1/2} < 0.4$. Longer bubble lifetimes are required to produce coefficients at lower concentrations. The equilibrium surface tension value obtained by the dynamic measurements is lower than the value obtained by the Wilhelmy technique, ~ 30.5 mN/m, but deviations of this extent are not unusual for extrapolated predictions of the equilibrium surface tension.²⁴

For cases of low molar surfactant concentrations, there is a chance that molecules in the bulk are depleted during the adsorption at the surface of the bubble. To account for this effect in the determination of diffusion coefficients, the bulk concentration must be corrected according to the formula:^{22,23}

$$C_{\text{corr}} = C \left(1 - \frac{A}{V} \Gamma \right) \quad (10)$$

where A and V are the bubble surface area and volume, respectively. For the two capillary tubes of the employed tensiometer, the average correction is of the order 10^{-6} M, which is very small compared to the useful concentrations of this work that are above 10^{-4} M.

Table 1 presents the estimated values of diffusion coefficients at different concentrations by using the data in Figure 3a and b. For short times, diffusion coefficients $D_{t \rightarrow 0}$ are in the range of $2.2\text{--}9.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ with no statistically significant dependence regarding the solution concentration. Calculations are made for $t^{1/2}$ less than 1.0. The $D_{t \rightarrow 0}$ values lie in a physically reasonable range, e.g., in refs 23 and 29, indicating that the adsorption of C_{10} -PhGE at the freshly formed bubble surface may indeed follow a diffusion mechanism. At first glance, one might see with reservation the application of short time approximations on the data for the two highest surfactant concentrations C : 5×10^{-4} and 10^{-3} M. However, if one extrapolates the line through the data points for the shortest bubble lifetimes for these two concentrations, they intersect the y -axis at about the same value with the lines extrapolating from the other two useful concentrations (10^{-4} M and 2×10^{-4} M). Besides, the diffusion coefficients estimated from all four concentrations are in close proximity. Evidently, data over a

broader range of parameters and, particularly, at shorter times, are required in order to make definitive statements.

By taking into account the value for $\Gamma = 1.7 \times 10^{-6} \text{ mol m}^{-2}$ at the concentration range of interest (above the cmc in all cases),⁸ we obtain from Figure 3b the $D_{t \rightarrow \infty}$ values for the two concentrations 5×10^{-4} M and 10^{-3} M, $2.7 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ and $4.8 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, respectively, Table 1. Calculations are made for $t^{-1/2}$ less than 0.4 because the $(t_d)^{-1/2}$ and $(50t_d)^{-1/2}$ values for the two concentrations are 0.15 and 0.02 and 0.41 and 0.06, respectively. The estimated $D_{t \rightarrow \infty}$ values are unusually lower than the physically expected ones for such systems (low-molecular-weight surfactants), e.g., $10^{-8}\text{--}10^{-11} \text{ m}^2 \text{ s}^{-1}$, and imply that, at long adsorption times, the diffusion of surfactant is not the controlling mechanism, but an adsorption barrier retards the process.^{24,30} One may argue at this point that the application of eq 5 to cases with high surface coverage (such as the present ones) can introduce a significant error in the determination of the diffusion coefficient. However, the surface tension slopes described by eqs 4 and 5 differ only by a factor of $2/\pi$,⁷ and this difference does not change the order of magnitude of the estimated $D_{t \rightarrow \infty}$ values. So, it still appears that diffusion transport of molecules is not the dominant mechanism for long adsorption times.

Several ideas have been advanced in the literature to describe adsorption barriers, but for our ionic C_{10} -PhGE surfactant with only a moderate chain length, the existence of an electrostatic barrier is more probable than a rearrangement of the molecules at the interface in the sense that, as the molecules pack at the interface, surface potential increases and this can resist further adsorption of molecules.³¹ Apparently, further work, e.g., ζ potential, activation energy studies, etc., is required in order to reach conclusions.

Comparison of our results with those of Delgado et al.³² for an anionic surfactant of a similar glycerol-ether skeleton but a different conjugated amino acid (tryptophan), shows that the presence of the phenylalanine headgroup in our molecule yields diffusion coefficients smaller by approximately 1 order of magnitude for short adsorption times. At first glance, this is peculiar because the members of the tryptophan series of Delgado et al. are more hydrophilic due to the possible hydrogen bonding of the indole-NH group with water. This is reflected in the higher cmc and σ_{cmc} values of all the tryptophan members compared to those of phenylalanine members.⁸ So, one might intuitively expect a higher diffusion coefficient for our molecules. Nevertheless, this phenomenal inconsequence could be explained by the estimated area per molecule, A_{min} (minimum occupancy), of the members of both series determined from Γ_{max} . It was found that all the tryptophan members had A_{min} much lower than the phenylalanine members, indicating an increased packing of the molecules of tryptophan at the interface.⁸ This might be due to the higher intramolecular attractions among tryptophan molecules but also due to the extended 3D geometrical configuration of the phenylalanine molecule, which can create higher drag as it moves in the bulk solution and slip past other molecules, giving rise to slower diffusion transport.

The situation is even worse for phenylalanine molecules for long adsorption times, but from the standpoint of intense (rapid) industrial processing, the latter is not important. On the whole, despite the proximity between the equilibrium surface tension of Delgado et al.³² solutions and the equilibrium surface tension

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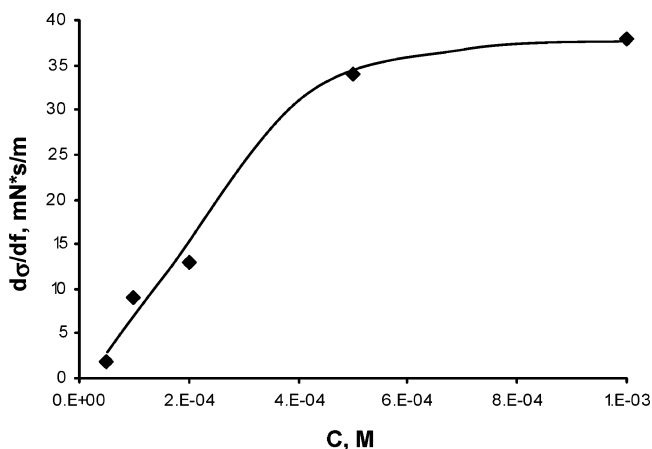


Figure 4. Surface rheological behavior of C₁₀-PhGE solutions at various concentrations (C).

measured for the present C₁₀-PhGE solutions,⁸ their dynamic surface behavior is markedly different. Therefore, to synthesize surfactants for rapid industrial applications, the dynamic (and not the static) surface activity of the molecules at short times must be taken into account.

Figure 4 is a plot of the dynamic surface tension slope with respect to bubble frequency vs C₁₀-PhGE concentration. To evaluate the value of this slope, it is assumed that the variation of surface tension with frequency is approximately linear over the range of the employed frequencies. This is particularly true for concentrations between 10⁻³ and 5 × 10⁻⁵ M and bubble formation frequencies between 0.1 and 2 Hz. For lower concentrations, the dynamic surface tension is roughly that of the solvent and so no meaningful calculation can be made. Recalling eq 9, it might be more appropriate to estimate the dynamic surface tension slope with respect to the bubble surface expansion rate rather than the bubble frequency. Yet, this is not possible at the present stage because the measured mean gas flow rate is not equal to the flow rate at the precise moment of the maximum bubble pressure, which would require measuring transducers with extremely fast response.

Although the analysis presented in Figure 4 is a preliminary step and only indicative arguments can be made out of it, it still has merit because this is the first time that the rheological behavior of this newly synthesized surfactant is examined. The ascending part of the curve in Figure 4 indicates a relatively inelastic surface where relaxation phenomena dominate. On the contrary, the gradual leveling off toward a final plateau (constant slope) for the highest surfactant concentrations implies a more elastic surface. Such interpretation of dynamic surface tension curves are common in the literature, e.g., in ref 33. From the practical standpoint, a more elastic surface would be more effective in

stabilizing dynamic interfaces. The behavior observed in Figure 4 might be the result of a number of parameters, such as the existence of an apparent adsorption barrier for mass transfer between the subsurface and the surface, a convective liquid flow caused by surface tension gradients (Marangoni effects), etc.²⁵

6. Conclusions

This experimental study aimed to shed some light onto the interfacial characteristics of C₁₀-PhGE aqueous solutions by comparing equilibrium with dynamic surface tension values and analyzing the dynamic measurements with respect to mass transport and rheological principles. The fundamental conclusions reached are:

The Wilhelmy plate technique measurements showed a distinct behavior among the examined surfactant compounds regarding the equilibrium surface tension variation with concentration and the appearance of the critical micelle concentration.

The differential maximum bubble pressure technique (MBPT) has been successfully applied to measure the dynamic surface tension of C₁₀-PhGE solutions.

The values of dynamic surface tension for most surfactant concentrations were significantly higher than their equilibrium surface tension values, increasing with increasing bubble frequency. Mass transport limitations between the molecules in the bulk solution and the freshly created interface of the bubbles are deemed responsible for this effect.

The critical micelle concentration (cmc) of C₁₀-PhGE solutions (determined by equilibrium surface tension measurements) was not detected by MBPT at the employed bubble formation frequencies. This is again due to the limited available time for mass exchange between bulk solution and surface.

The dynamic surface tension approached the static surface tension value of cmc only for concentrations above 5 × 10⁻⁴ M and for the slower bubble formation frequencies (<1 bubble per 20 s).

By using a diffusion-controlled adsorption kinetic analysis, it was shown that, for short adsorption times, diffusion controls surfactant migration, whereas for long times, an adsorption barrier prevails. The effect of the amino acid headgroup of the surfactant molecule in the surface activity was demonstrated by comparison with other data from the literature.³²

Surface rheology considerations indicate the existence of an upper surfactant concentration, where the response of the surface reaches a limiting state in terms of dynamic surface tension variation with respect to bubble frequency.

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