Correlation between Electric Potential and Interfacial Tension Oscillations in a Water−Oil−Water System

Véronique Pimienta,*,[†] Dominique Lavabre,[†] Thomas Buhse,[‡] and Jean-Claude Micheau[†]

Laboratoire des IMRCP, UMR au CNRS No. 5623, Université Paul Sabatier, 118, route de Narbonne, F-31062 Toulouse Cedex, France, and Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos, Avenida Universidad No. 1001, Col. Chamilpa, 62210 Cuernavaca, Morelos, México

Oscillations of the electric potential and of the interfacial tension were simultaneously recorded in a water−oil−water system (cetyltrimethylammonium bromide (CTAB) in water/picric acid in dichloromethane/water). Both types of oscillations were perfectly correlated in time and shape. In each oscillatory cycle, the fast jumps in the electric potential are related to a rapid adsorption of the surfactant at the interface while the slow motion relaxations correspond to the liberation of the interface from the surfactant by the formation of hydrophobic cetyltrimethylammonium picrate ion pairs that diffuse into the CH_2Cl_2 phase. The fast inflow of CTAB to the interface is probably caused by periodically occurring convective Marangoni instabilities. The transitions to the convective regime are assumed to be controlled by the fractional surfactant coverage of the interface.

I. Introduction

Spontaneous oscillations of the interfacial electric potential and/or the surface tension have been observed in several systems involving surfactant molecules submitted to transport processes. For instance, the solubilization of a surfactant of low solubility in water is at the origin of the periodic surface tension oscillations observed by Kovalchuk et al.[1−4] In their experiment, a drop of a neat liquid surfactant (diethyl phthalate or a long chain aliphatic alcohol) is formed at the tip of a capillary immersed in an aqueous phase (see Scheme 1a). Periodic oscillations of the surface tension at the water/air interface were detected for at least 8 h. The oscillations were attributed to transient convective fluxes due to the Marangoni instability. This instability, which is triggered by surface tension gradients appearing in systems submitted to heat (thermal Marangoni) or mass transfer (solutal Marangoni), has been widely studied in both experimental and theoretical aspects because of its important implication in many industrial applications. In the case of the solutal Marangoni instability, convective patterns increase significantly the rate of mass exchange in processes such as liquid/liquid extraction[5] and surface chemical reactions.[6]

In the experiments described by Kovalchuk et al., diffusion is preponderant in the first stage of the solubilization process. The solubilization of the surface-active solute from the droplet gives rise to a nonuniform distribution of the surfactant concentration near and at the interface. Because of the increasing concentration gradients, the system becomes unstable; convection develops and accelerates the transfer of surfactant from the bulk solution to the interface and results in an abrupt decrease of the surface tension. The high amount of surfactant supplied at the interface and the mixing due to the convective fluxes reduces the concentration gradients, bringing the system back to the stable diffusive regime.

* Corresponding author: Telephone: +33 5 61 55 62 75. Fax: +33 5 61 55 81 55. E-mail: pimienta@chimie.ups-tlse.fr.
† Université Paul Sabatier.
‡ Universidad Autónoma del Estado de Morelos.

SCHEME 1: Experimental Systems Used for the Observation of Artificial Water/Oil Membrane Oscillations[a]
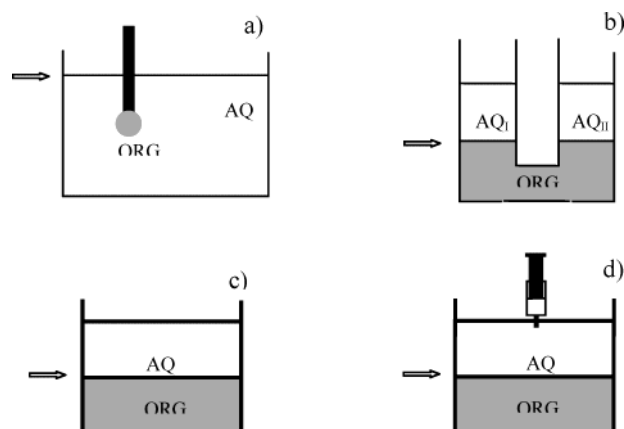
[a] (a) Kovalchuk and co-workers.[1] AQ, pure water; ORG, drop of neat surfactant (diethyl phthalate or aliphatic alcohol). (b) Suzuki and co-workers.[7] AQ_I, aqueous solution of sodium oleate and 1-propanol; ORG, nitrobenzene; AQ_II, aqueous solution of NaCl. (c) Nakache and Dupeyrat.[8] AQ, CTAB in water; ORG, picric acid in nitrobenzene. (d) Takahashi and co-workers.[20] Injection of SDS in AQ (pure water). ORG, nitrobenzene. Interfaces where the instabilities are observed are indicated by the arrows.

Such spontaneous periodic transitions between diffusive and convective regimes were also observed in systems implying liquid/liquid mass transfer of a surfactant. In 1992, Suzuki and Kawakubo[7] observed the transient formation of convective rolls during the transfer of sodium oleate between water and nitrobenzene (Scheme 1b); the convective instability was shown to be correlated to the oscillation of the electric potential at the interface.

Our work refers to a system that was initially described by Nakache and Dupeyrat[8] and in which mass transfer of a surfactant is coupled to a chemical reaction. The authors

observed periodic interfacial movements as well as potential and surface tension variations at the interface of a biphasic system (Scheme 1c) composed of an organic phase containing picric acid dissolved in nitrobenzene and an aqueous phase containing a cationic surfactant cetyltrimethylammonium bromide (CTAB). Initially, the two compounds are out of their partition equilibrium and tend to travel to the opposite phase. Mass transfer of the two compounds is accompanied by an interfacial reaction between the CTA^+ cations and the picrate (P^-) anions that leads to the formation of cetyltrimethylammonium picrate ion pairs (CTAP).

The experimental setup to observe potential oscillations was improved by Yoshikawa and co-workers[9] by using a three-phase (U-tube) reactor geometry. The organic phase (ORG) containing picric acid was placed in the bottom of a U-formed glass tube with two aqueous solutions on each side of the tube and located on top of the organic phase. One aqueous layer (AQ_I) contained the surfactant and an aliphatic alcohol that was reported to be essential to observing oscillations by this geometry.[10] The second aqueous layer (AQ_{II}) was a KCl or a sucrose solution. The electric potential was measured between the two aqueous phases and showed quasi-periodic oscillations for several hours with a period of several minutes.

Since then, many systems with similar behavior have been described[11] that generally involve a cationic, or an anionic, surfactant in an aqueous phase that is brought in contact with an organic phase containing an hydrophilic acid or base, respectively. A common feature of all these systems (including the systems previously described by Kovalchuk[1−4] and Suzuki[7]) is the shape of the observed oscillations that shows a fast accelerating stage followed by a slower relaxation.

Until now, no movements of the interface could be clearly observed for the CTAB/picric acid system in the U-tube geometry,[12] and the interpretations proposed do not take into account the Marangoni hydrodynamic instability. The most frequently cited interpretation[13] was proposed by Yoshikawa and Matsubara in ref 9. According to the authors, the fast variation in the electric potential would be related to the sudden release of reverse micelles of ion pairs from the interface into the organic phase. This fast desorption process was assumed to take place when a critical surfactant concentration was reached at the interface. Later, Toko et al.[14] proposed a different interpretation based on the autocatalytic (cooperative) formation of a tightly packed monolayer of ion pairs at the liquid−liquid interface and their subsequent release into the organic phase. More recently, Pimienta et al.[15] proposed a model in which the alcohol that is added to the surfactant solution in the U-tube geometry was assumed to induce an accelerated release of the ion pairs in the organic phase during the fast stage of the process.

In this paper we present experimental results, based on the simultaneous measurement of the electric potential and interfacial tension in the U-tube geometry. First attempts to correlate the electric potential and the surface tension were reported by Nakache et al.[16] in a two-phase system (water/oil in a beaker) and more recently by Takahashi et al.[17] using quasielastic light scattering in a three-phase geometry (water/oil/water in a U-tube). However, in both studies the signals did not show obvious synchronization that could allow clear mechanistic conclusions. Our results, together with the analysis of the equilibrium interfacial tension properties of the chemical compounds involved in the interfacial reaction, show that the former interpretations, based on an instability arising from a chemical interaction, do not account for the newly obtained experiments. In fact, the results gathered in this study support

the previous hypothesis proposed by Nakache and Dupeyrat based on hydrodynamic instability.

II. Experimental Section

1. Chemicals. All chemicals used were of analytical grade. Picric acid (Aldrich, ACS), CH_2Cl_2 (Aldrich, HPLC grade), cetyltrimethylammonium bromide, CTAB, (Aldrich, ≥99%), sucrose (Aldrich, ACS), and 1-butanol (Baker, analyzed) were used as purchased. The water was double-distilled.

2. Oscillations in the U-Tube. Oscillations of the electric potential were recorded in a U-shaped glass tube of 15.2 mm inner diameter at 25 ± 2 °C without stirring. The organic solution (13 mL) of CH_2Cl_2 containing 3×10^{-3} mol·L^{-1} picric acid was placed in the bottom of the U-tube. Then the two aqueous solutions (6 mL each)—AQ_I containing 5×10^{-3} mol·L^{-1} CTAB and 0.4 mol·L^{-1} 1-butanol and AQ_{II} containing 0.1 mol·L^{-1} sucrose—were carefully and simultaneously introduced into the two arms of the tube.

The potential was measured with two Hg/Hg_2Cl_2 electrodes placed in beakers containing saturated KCl solution and connected by two salt bridges to the two aqueous phases (see Scheme 2A). Data were recorded using a high impedance multimeter (Agilent 34970A), with an input resistance superior to 10 GΩ, connected to a personal computer.

Surface tension measurements were performed using a small glass cylinder (outer diameter 5.5 mm, inner diameter 4 mm, and height 4 mm) placed at the water/oil interface and connected to a microbalance (Scheme 2B). The small cylinder was placed at the interface and pulled at its maximum before breakage of the interfacial film. The strength exerted by the liquid film results in a variation of the weight measured by the microbalance. The whole system was placed in a Faraday cage. Prior to each use, the glass devices were cleaned with a sulfochromic solution and then rinsed with water and ethanol and dried under vacuum.

3. UV−Visible Experiment. An Ocean Optics SD 2000 miniature fiber optic spectrophotometer was used for the recording of time-resolved absorption spectra under biphasic conditions: 1.5 mL of picric acid in dichloromethane (2×10^{-5} mol·L^{-1}) was placed in a cuvette and carefully overlaid by 1.5 mL of an aqueous solution of CTAB (5×10^{-5} mol·L^{-1}). Detection was performed simultaneously in the two phases by using a bifurcated optical fiber. The lower organic phase and the upper aqueous phase were gently stirred by a small magnetic bar and a paddle stirrer, respectively, with the two phases kept separated.

4. Synthesis of CTAP Ion Pairs. Cetyltrimethylammonium picrate (ion pair) was synthesized by mixing equimolar amounts of picric acid (MW = 229.11) and cetyltrimethylammonium bromide (MW = 364.46) in double-distilled water. The yellow precipitate extracted by CH_2Cl_2 was dried over anhydrous sodium sulfate and evaporated. The yellow solid was recrystallized in hot methanol (yield > 96%).

5. Measurements of Equilibrium Interfacial Tension. Equilibrium interfacial tension measurements at the CH_2Cl_2/water interface were performed using the stir-up technique at 25 °C. In this case, a small cylinder (diameter 2.8 mm, height 10 mm) made of high-density polyethylene was connected to the microbalance. The cylinder was lowered to the liquid interface, immersed, and withdrawn until the maximum pull on the cylinder was found. Measurements were performed for the three compounds picric acid, CTAB, and CTAP in the range of 10^{-5}−10^{-2} mol·L^{-1}. Equal volumes (13 mL) of each phase were used in every case. Each compound was initially dissolved

Oscillations in a Water−Oil−Water System

J. Phys. Chem. B, Vol. 108, No. 22, 2004 **7333**

SCHEME 2: Experimental Setup for Potential and Surface Tension Measurements[a]
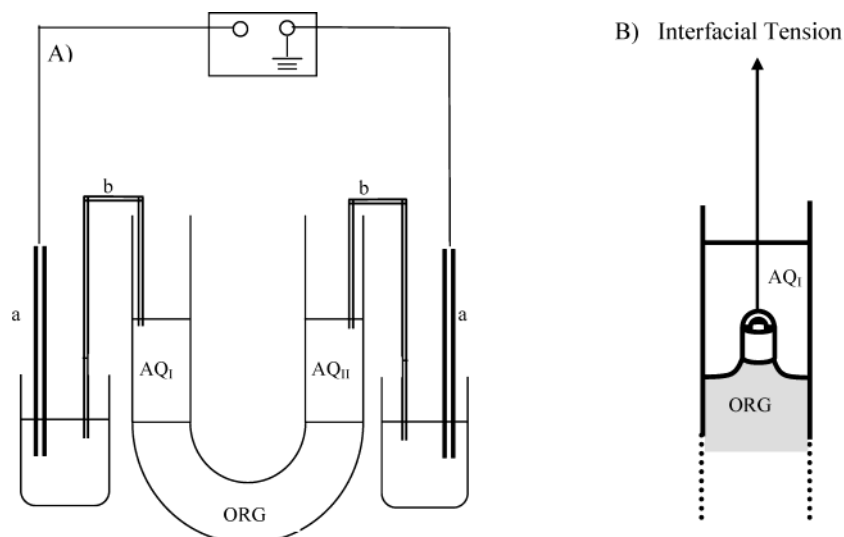
[a] (A) Device used for potential measurements in the three-phase (U-tube) geometry water/oil/water. (a) Electrodes; (b) salt bridges. AQ_I, 6 mL of aqueous solution of CTAB (5×10^{-3} mol·L^{-1}) and butanol (0.4 mol·L^{-1}); ORG, 13 mL of picric acid (3×10^{-3} mol·L^{-1}) in CH_2Cl_2; AQ_{II}, 6 mL of aqueous solution of sucrose (0.1 mol·L^{-1}). (B) Left side of the U-tube (AQ_I/ORG): small glass cylinder connected to a microbalance for surface tension measurements.
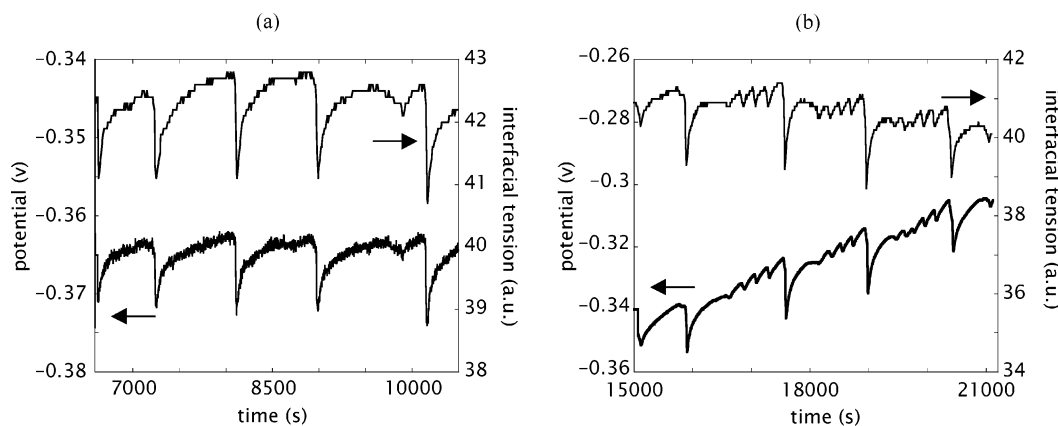

Figure 1. Simultaneous measurement of the potential and the interfacial tension oscillations in the three-phase (U-tube) geometry taken from one experiment: (a) between 6500 and 10 500 s; (b) between 15 000 and 21 000 s. Lower curve: electric potential (left axis). Upper curve: interfacial tension in arbitrary units (right axis).

in one phase: picric acid and CTAB in water and CTAP in dichloromethane (because of its low solubility in water). Before the measurements all samples were left overnight for equilibration; partition was accelerated by stirring the organic phase at slow rate, avoiding any emulsification of the phases.

III. Experimental Results

1. Simultaneous Measurement of Electric Potential and Interfacial Tension. Using the experimental setup described in Scheme 2, we have recorded oscillations of both electric potential and interfacial tension. These oscillations started after a short induction period of about 10 min and lasted for more than 8 h with a period increasing with time, from 500 s at the beginning to 1800 s at the end of the experiment. Parts of the recording showing a particularly regular oscillation pattern are presented in Figure 1.

The two signals showed a perfect correlation, indicating that the potential variations were directly related to the interfacial adsorption state. Even at the end of the experiment when we observed a particular regime in which small and high amplitude oscillations alternate, every variation of the potential was

reflected in synchronization by a change in the interfacial tension (see Figure 1b).

The drop of the potential corresponds to a fast decrease of the interfacial tension that indicates a fast increase of the concentration of the adsorbed surfactant. This observation is in agreement with the assumption that the interfacial potential is related to the electrical double layer[18] formed at the interface by the adsorbed surfactants, which are positively charged, and the negative counterions that accumulate in the aqueous phase near the interface. When the interfacial tension decreases, the absolute value of the difference of potential increases (the potential $V = V_{AQ_I} - V_{AQ_{II}}$ decreases) because of the formation of a denser electrical double layer. The globally negative sign of the potential can be related to the charge distribution at the interface; however, junction potentials, which vary with mass transfer, also contribute to the global value of the potential.

In summary, both signals account for the same process: a fast accelerated adsorption step followed by a slower relaxing desorption step.

2. Interfacial Reaction. During the oscillation experiment, the organic phase in contact with AQ_I in the U-tube became yellow while the aqueous phase stayed perfectly uncolored.[19]
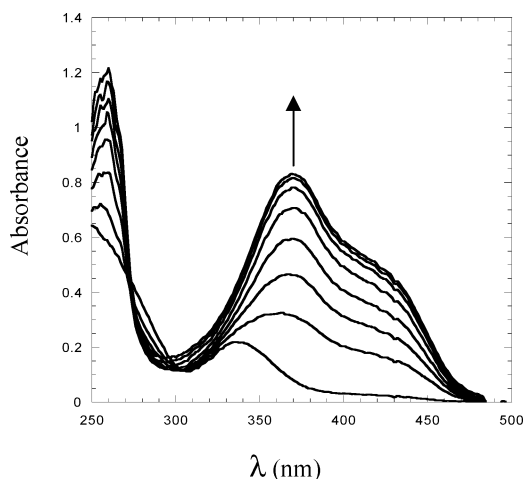
Figure 2. Time-resolved absorption spectra detected in the organic phase under biphasic conditions indicating the formation of ion pairs in the lower organic phase. Initial concentrations: $[CTAB]_0$ in the aqueous phase $= 5 \times 10^{-5}$ mol·L^{-1}; picric acid $[PH]_0$ in $CH_2Cl_2 = 2 \times 10^{-5}$ mol·L^{-1}. Δt between two spectra $= 1200$ s.

This indicates that picric acid does not enter the aqueous phase but reacts at the interface and is brought back into the organic phase. We have reproduced the two-phase system in a quartz cuvette with picric acid in the organic phase and CTAB in the aqueous phase. Absorbance was detected simultaneously in both phases.

After contact between the two phases, the reaction started and the time-resolved absorption spectra in the organic phase showed an increase of absorbance together with a shift of the absorption maximum from 336 nm (λ_{max} of picric acid in dichloromethane) to 370 nm (Figure 2). The spectrum with λ_{max} $= 370$ nm corresponds to the spectrum obtained when analyzing a sample of the organic phase from the vicinity of the AQ_I/ ORG interface at the end of an oscillatory experiment. It also matches the spectrum of the cetyltrimethylammonium picrate (CTAP) ion pairs synthesized as described in the Experimental Section. In the aqueous phase no absorption was detected indicating the absence and consequently a high hydrophobicity of these species.

The interfacial reaction can be described as follows: CTAB and picric acid, which are initially out of their partition equilibrium, travel from opposite directions toward the liquid/ liquid interface. When picric acid reaches the aqueous phase, it quickly dissociates and reacts with the adsorbed surfactant (CTA^+), which is present in excess at the interface. Subsequently, the counterion exchange, which is certainly a fast process, leads to the formation of the CTAP ion pairs.

As the oscillatory process leads to important variations of the interfacial tension measurements of equilibrium interfacial tensions of the three compounds involved in the interfacial reaction (picric acid, CTAB, and CTAP) were performed in the concentration domain of the oscillatory experiment. In the U-tube, the initial concentration was 5×10^{-3} mol·L^{-1} for CTAB and 2×10^{-3} mol·L^{-1} for picric acid. Concerning CTAP, its concentration near the AQ_I/ORG interface varies from 0 at the beginning of the experiment to approximately 10^{-3} mol·L^{-1}, which is the concentration measured typically near the interface when oscillations have stopped.

As shown in Figure 3, picric acid has no measurable effect on the interfacial tension. The CTAP ion pairs showed a slight surface activity, but only after exceeding a concentration of 10^{-3} mol·L^{-1}, which is the maximum concentration reached in the U-tube at the end of an oscillatory experiment. For lower
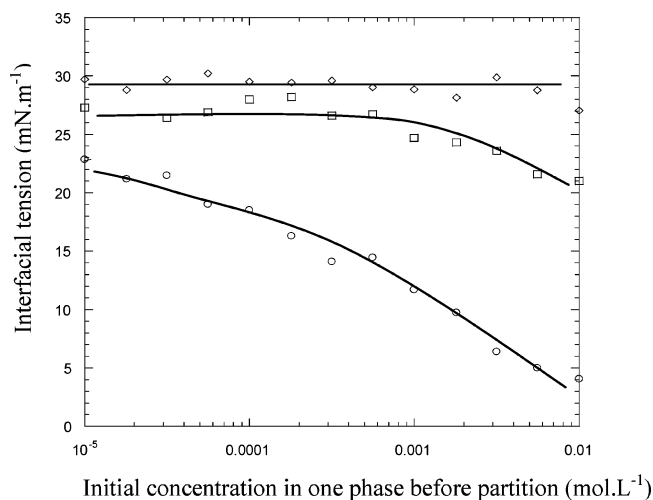

Figure 3. Equilibrium interfacial tension measurements at the water/ CH_2Cl_2 interface as a function of the initial concentration in one of the phases before partition. ◇, picric acid; □, CTAP; ○, CTAB. Lines joining the data points are a visual guide.

concentrations the effect on the interfacial tension was negligible. CTAB appears to be the only compound involved in the oscillatory process with significant activity. Hence, the fast drop of the interfacial tension must be related to the adsorption of the surfactant.

We have also compared the hydrophobicity of CTAB and CTAP by analyzing the concentration in each phase after partition. For instance, for an initial concentration of 10^{-3} mol·L^{-1}, the ratio between the concentrations in the organic phase and the aqueous phase is about 30 times higher for CTAP ion pairs than for CTAB. Thus, the product of the interfacial reaction CTAP is not surface active (at least in the concentration domain of the U-tube experiment) and it is also more hydrophobic than CTAB.

IV. Discussion

In this section, we discuss the interpretations proposed in the literature in regard to our experimental results. These models may be classified in two categories: on one hand, models in which the accelerating process leading to the instability is due to a chemical interaction; and, on the other hand, the hydrodynamic interpretation implying the Marangoni instability.

1. Chemical Interactions at the Origin of the Instability. A simple qualitative analysis shows that the models reported at the end of the Introduction stand in contradiction to our experimental results. In the interpretation proposed by Yoshikawa et al.,[9] the fast drop of the potential was attributed to a sudden cooperative release of inverse micelles in the organic phase. This means a desorption process, which would lead to a fast increase of the interfacial tension rather than to a decrease as has been established by our experiments. In the same way, the formation of a highly packed monolayer of ion pairs at the interface, as proposed in ref 14, is very unlikely because of the low surface activity of these species. In our previous work,[15] we assumed that the alcohol was at the origin of the accelerated desorption of the surfactant from the interface after formation of the hydrophobic ion pairs. However, to account for the new experimental observations, the accelerating process at the origin of the instability should correspond to the adsorption and not to the desorption of the surface-active compound.

This was also the conclusion of Takahashi and co-workers,[20] who proceeded, like us, to the simultaneous measurement of

Oscillations in a Water−Oil−Water System

J. Phys. Chem. B, Vol. 108, No. 22, 2004 **7335**

the electric potential and interfacial tension in a system in which a local continuous injection of an anionic surfactant (SDS) was realized in a water phase overlying an organic phase (Scheme 1d). The pattern of the observed oscillations is similar to our recordings, and the authors proposed an interpretation that associates a hindrance effect to adsorption and the Marangoni instability. In our case, dynamic surface tension studies on CTAB, based on the pendant drop technique,[21] showed that, at the concentration used in our experimental setup, no delay to adsorption can be detected and that a classical diffusion-controlled process can be assumed. Hence, to account for the sudden inflow of surfactant at the interface, we will now consider the possibility of occurrence of purely hydrodynamic instabilities.

2. The Marangoni Instability. *The Convective Regime.* Concerning the system under study, the Marangoni instability played an important role in the interpretation proposed for the two-phase system by Nakache and Dupeyrat.[22] In this case, interfacial movements were clearly visible to the eye and, according to the authors, related to the sudden supply of surfactant resulting from convective movements induced in the aqueous phase by the formation of interfacial tension gradients. The growing convective cells[23] formed tend to oppose the surface tension gradients by a fast, accelerated supply of surfactant at the interface.

In the past, surfactant molecules were believed to dampen the Marangoni convection because of their ability to form a monolayer at the interface, which renders the interface less flexible.[24] More recently it was shown[25] that under mass transfer conditions and at low concentrations surfactant molecules can indeed induce the instability. The accelerated inflow of surfactant, due to the growing instability, would then vanish when a relatively packed monolayer is formed at the interface. Because of this negative feedback, the system would switch to a diffusive regime, during which the gradients at the interface could be restored.

The Diffusive Regime. Let us now focus on the slower stage of the oscillatory process. The hypothesis proposed by Nakache et al.[22] for this stage is rather complicated and involves a quite hypothetical proton transfer, from the aqueous to the organic phase, that would inhibit the interfacial reaction by consuming picrate anions that were supposed to be present in this phase due to the dissociation of picric acid.

Our interpretation for the relaxing phase derives directly from our experimental observations. Surface tension gradients at the origin of the instability are promoted by concentration gradients in both tangential and normal directions to the interface.[4] Tangential gradients may appear when the concentration of the adsorbed surfactant is sufficiently low to allow the molecules to move on the surface, which may lead to locally nonhomogeneous surface concentration distribution. Normal gradients are always involved in mass transfer processes. Therefore, in the following, we will try to analyze the processes taking place at the interface with regard to their contribution to gradients in both directions.

The two main processes taking place at the interface are the adsorption of CTAB and the fast interfacial ion exchange. These two processes can be represented by

$$CTA^+ + I \rightleftarrows CTA-I \qquad (1)$$

$$CTA-I + P^- \rightarrow CTAP + I \qquad (2)$$

Process 1 represents the adsorption of CTA^+ at the interface using Langmuir formalism, where "I" represents the vacant site

and CTA−I the adsorbed surfactant. As already mentioned,[21] a diffusion-controlled transport of the surfactant can be assumed. In this case, diffusion is limiting and the concentration of CTA−I remains at a concentration below its equilibrium value.[26] This effect is raised by the fact that the surfactant diffuses more slowly in the feeding aqueous phase than in the receiving organic phase (diffusion constant in water for CTAB is 2.5 times smaller than in CH_2Cl_2 when calculated using the Wilke and Chang empirical correlation method[27]). This leads to the formation of steeper concentration gradients in the normal direction and also to a further decrease of the concentration of adsorbed surfactants.

Process 2 represents the fast interfacial reaction. This process takes place on the aqueous side of the interface, where the electrical double layer is formed.[28] The reaction involves the adsorbed surfactant CTA−I and picrate ions that result from fast dissociation of the molecular picric acid as soon as it reaches the aqueous phase. The counterion exchange leads to the formation of the CTAP ion pairs that−due to high hydrophobicity and low surface activity−desorb instantaneously and diffuse in the organic phase. This process results in the formation of vacant sites "I", i.e., to lower fractional coverage of the interface favoring an inhomogeneous distribution of the surfactant at the interface. Hence, the difference of surface activity between the reactant and the product contributes to the formation of tangential gradients, while the fast interfacial reaction of the transferred compound enhances normal gradients.

In summary, when gradients created at the interface reach a critical value, the system becomes unstable and switches to convection. Convective fluxes then lead to the accelerated supply of surfactants at the interface. When a sufficiently packed monolayer is formed, gradients vanish and the system switches back to diffusion. The interfacial reaction becomes dominant again and restores the gradients until they become critical.

If we analyze theoretical studies on the solutal Marangoni convection, and although none of these studies really corresponds to our system, many elements of the above discussion appear in several studies. Most of these studies are based on the pioneering work of Sterling and Scriven,[29] who gave several criteria to predict the occurrence of Marangoni instability in the case of mass transfer of a single solute. They found that the size of the convective cells could vary by a few orders of magnitude depending on the system properties. According to the authors, the formation of smaller cells would be favored by a strong variation of interfacial tension with concentration (which is the main property of surfactants), steeper concentration gradients near the interface (enhanced by the interfacial reaction in our case), and greater disparities of viscosity and diffusivity between the two phases. They also found that the instability would take place only, as in our system, when the solute is transferred from the phase of lower diffusivity (and higher viscosity) to the phase of higher diffusivity (and lower viscosity). This criterion was shown later to hold only under diffusion-controlled transfer,[30] and adsorption-controlled kinetics may lead to different criteria. More recently, the influence of an interfacial reaction on the onset of instability was also analyzed: under spontaneous mass transfer conditions in ref 31 and when mass transfer is caused by an interfacial reaction in ref 32. In ref 31 the authors predicted that oscillatory modes of the hydrodynamic instability could be expected when the two components of the reaction had opposite effects on the surface tension, while in the second study[32] instabilities were predicted when the transfer process was diffusion-controlled and when very fast interfacial reactions were involved.

V. Conclusion

We have shown that the electric potential and the surface tension oscillations in the U-tube configuration were perfectly correlated and synchronized. The fast motion drop of the electric potential corresponds to a decrease of the interfacial tension related to the fast adsorption of surfactant at the interface which would be induced by a convective transport driven by the Marangoni instability. The switches between the two hydrodynamic regimes (diffusion and convection) are governed by the surfactant interfacial concentration through the formation of hydrophobic and not surface-active ion pairs. In this framework, the system under study can be regarded to form part of a more general set of oscillatory phenomena observed in biphasic systems in the presence of surfactant molecules.

References and Notes

(1) Kovalchuk, M. N.; Vollhardt, D. *J. Phys. Chem. B* **2000**, *104*, 7987.

(2) Kovalchuk, V. I.; Kamusewitz, H.; Vollhardt, D.; Kovalchuk, N. M. *Phys. Rev. E* **1999**, *60*, 2029.

(3) Kovalchuk, V. I.; Kovalchuk, N. M.; Vollhardt, D. *Phys. Rev. E* **2001**, *63*, 031604.

(4) (a) Kovalchuk, M. N.; Vollhardt, D. *J. Phys. Chem. B* **2001**, *105*, 4709. (b) Kovalchuk, M. N.; Vollhardt, D. *J. Phys. Chem. B* **2003**, *107*, 8439.

(5) Bakker, C. A.; Van Buytenen, P. M.; Beek, W. J. *Chem. Eng. Sci.* **1966**, *21*, 1039.

(6) Buzek, J. *Chem. Eng. Sci.* **1983**, *38*, 155.

(7) Suzuki, H.; Kawakubo, T. *Biophys. Chem.* **1992**, *45*, 153.

(8) (a) Nakache, E.; Dupeyrat, M. *Bielectrochem. Bioenerg.* **1978**, *5*, 134. (b) Dupeyrat, M.; Nakache, E. *Synergetics Far From Equilibrium*; Pacault, A., Vidal, C., Eds.; Springer-Verlag: New York, 1979; p 156.

(9) (a) Yoshikawa, K.; Matsubara, Y. *J. Am. Chem. Soc.* **1983**, *105*, 5967. (b) Yoshikawa, K.; Matsubara, Y. *Biophys. Chem.* **1983**, *17*, 183.

(10) In fact, the presence of alcohol in AQ$_I$ turned out not to be essential as we could recently observe, although maybe not so regular, small but clear oscillations in the U-tube in the absence of alcohol.

(11) (a) Yoshikawa, K.; Masaru, S.; Satoshi, N.; Maeda, S. *Langmuir* **1988**, *4*, 759. (b) Kai, S.; Muller, S. C.; Mori, T.; Miki, M. *Physica D* **1991**, *50*, 412. (c) Arai, K.; Fukuyama, S.; Kusu, F.; Takamura, K. *Electrochim. Acta* **1995**, *40*, 2913. (d) Yoshidome, T.; Higashi, T.; Mitsushio, M.; Kamata, S. *Chem. Lett.* **1998**, 855. (e) Li, H.; Wang, M. *Chem. Phys. Lett.* **2000**, *330*, 503. (f) Shioi, A.; Sugiura, Y.; Nagaoka, R. *Langmuir* **2000**, *16*, 8383. (g) Maeda, K.; Hyogo, W.; Nagami, S.; Kihara, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1505. (h) Maeda, K.; Nagami, S.; Yoshida, Y.; Ohde, H.; Kihara, S. *J. Electroanal. Chem.* **2001**, *496*, 124. (i) Shioi, A.; Kumagai, H.; Sugiura, Y.; Kitayama, Y. *Langmuir* **2002**, *18*, 5516.

(12) Motion of particles spread on the interface were reported in ref 11i.

(13) (a) Larter, R. *Chem. Rev.* **1990**, *90*, 355. (b) Sutou, S.; Yoshihisa, H.; Miyamura, K.; Gohshi, Y. *J. Colloid Interface Sci.* **1997**, *187*, 544. (c) Suzuki, H.; Tsuchira, Y. *Physica D* **1995**, *84*, 276. (d) Rastogi, R. P.; Srivastava, R. C. *Adv. Colloid Interface Sci.* **2001**, *93*, 1.

(14) Toko, K.; Yoshikawa, K.; Tsukiji, M.; Yamafuji, K. *Biophys. Chem.* **1985**, *22*, 151−158.

(15) Pimienta, V.; Etchenique, R.; Buhse, T. *J. Phys. Chem. A* **2001**, *105*, 10037.

(16) Nakache, E.; Dupeyrat, M. *Bielectrochem. Bioenerg.* **1982**, *9*, 583.

(17) Takahashi, S.; Tsuyumoto, I.; Kitamori, T.; Sawada, T. *Electrochim. Acta* **1998**, *44*, 165.

(18) Yoshidome, T.; Takahama, J.; Mitsushio, M.; Higo, M. *Anal. Sci.* **2003**, *19*, 603.

(19) On the other side of the tube (ORG/AQ$_{II}$), on the contrary, the organic phase remained uncolored while the aqueous phase became yellow because of the partition of picric acid.

(20) Takahashi, T.; Yui, H.; Sawada, T. *J. Phys. Chem. B* **2002**, *106*, 2314.

(21) Deshikan, S. D.; Bush, D.; Eschenazi, E.; Papadopoulos, K. D. *Colloids Surf.* **1998**, *136*, 133.

(22) Nakache, E.; Dupeyrat, M.; Vignes-Adler, M. *J. Colloid Interface Sci.* **1983**, *94*, 189.

(23) Pertler, M.; Häberl, M.; Rommel, W.; Eckhart, B. *Chem. Eng. Proc.* **1995**, *34*, 269.

(24) (a) Garner, F. H.; Hale, A. R. *Chem. Eng. Sci.* **1953**, *2*, 157. (b) Mudge, L. K.; Heideger, W. J. *J. Am. Inst. Chem. Eng.* **1970**, *16*(4), 602.

(25) (a) Agble, M. A.; Mendes-Tatsis, M. A. *Int. J. Heat Mass Transfer* **2000**, *43*, 1025. (b) Agble, M. A.; Mendes-Tatsis, M. A. *Int. J. Heat Mass Transfer* **2001**, *44*, 1439.

(26) Joos, P. *Dynamic surface Phenomena*; VSP: Utrecht, The Netherlands, 1999.

(27) Reid, R.; Sherwood, T. K. *The Properties of Gases and Liquids*; McGraw-Hill: New York, 1958; p 549.

(28) Borwankar, R. P.; Wasan, D. T. *Chem. Eng. Sci.* **1988**, *43*, 1323.

(29) Sterling, C. V.; Scriven, L. E. *AIChE J.* **1959**, *5*, 514.

(30) Hennenberg, M.; Sanfeld, A.; Bisch, P. M. *AIChE J.* **1981**, *27*, 1002.

(31) Warmuzinski, K.; Tanczyk, M. *Chem. Eng. Sci.* **1991**, *46*, 2031.

(32) Mendes-Tatsis, M. A.; Perez de Ortiz, E. S. *Chem. Eng. Sci.* **1996**, *51*, 3755.