

Periodic Marangoni Instability in Surfactant (CTAB) Liquid/Liquid Mass Transfer

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Periodic Marangoni convective instability has been observed in a biphasic system during the mass transfer of cetyltrimethylammonium bromide (CTAB) from an aqueous to a dichloromethane organic phase. Visualization of the convective fluxes was possible thanks to the CTAB crystals that are formed in the aqueous phase at a temperature below the Krafft point. Surface tension and electrical potential oscillations have been shown to be correlated with the fluid motion. Surface tension measurements, representative of the adsorption state, showed fast adsorption during the convective stage, followed by a slower desorption process in the quiet stage. To account for the electrical potential data, two components need to be taken into account. In the quiet stage, the signal was comparable to surface tension, and the main contribution would result from the electrical double layer formed at the interface by charged surfactants. In the convective stage, the electrical potential was furthermore related to the velocity of the fluid in the aqueous layer. Perturbations of the charge distribution in the Gouy–Chapman layer due to tangential flows could be at the origin of the phenomenon.

Introduction

Surface tension driven convection, known as Marangoni instability, is widely observed in systems submitted to heat or mass transfer. Its accelerating effect on extraction processes has been of major interest in engineering science for many years.¹ Among the various convective patterns obtained,² a particular behavior is observed in systems involving surfactant molecules. The convective instability appears only transiently, and the system switches periodically between two transport regimes: a slower and a faster one.

For instance, when a droplet of a surface active substance, with limited solubility (diethylphthalate or long chain aliphatic alcohols), is placed at the tip of a capillary immersed in water, the surface tension oscillations are observed at the water/air interface.³ In this case, concentration gradients at the origin of the instability are induced by the dissymmetry of the system because of the local source of the surfactant in the droplet. Such dissymmetry could also be at the origin of the similar behavior that is observed at a water/oil interface when a local and continuous injection of SDS is performed in the water phase.⁴

In systems involving a homogeneous initial concentration in the water phase, the same oscillatory pattern was observed by Suzuki and Kawakubo⁵ during the transfer of sodium oleate in the presence of propanol from water to nitrobenzene. In this case, transient convective cells could be clearly observed using the Schlieren technique. Comparable transitions between two hydrodynamic regimes are also observed in systems in which mass transfer is coupled to a chemical reaction. On the basis of the well-known CTAB/picric acid system,⁶ several authors⁷ have reported oscillatory behavior of the interfacial surface tension or electrical potential when a cationic, or an anionic, surfactant initially solubilized in a water phase is brought into contact with an organic phase containing a hydrophilic acid or base, respectively. The reaction involved is the formation of ion pairs

resulting from counterion exchange in the water phase. These ion pairs are rather hydrophobic⁸ and similar to those involved in phase transfer catalysis (PTC). Indeed, Srivastava et al.⁹ observed electrical potential oscillations during the permanganate oxidation of water insoluble aldehydes or alcohols in phase transfer catalysis conditions. In such applications, the onset of the hydrodynamic instability, which has a great influence on the rate of mass transfer and so on the rate of production, could be an important criterion for the choice of the phase transfer catalyst.

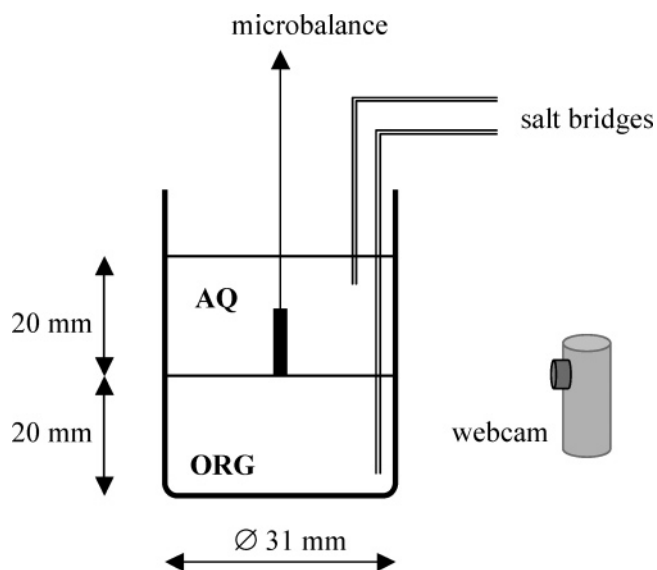
Because of its chemical properties, cetyltrimethylammonium bromide (CTAB), which is both a quaternary ammonium (family of compounds mostly used in PTC) and a surface active agent, appears in numerous studies.¹⁰ Until now, maybe because of the experimental conditions in which these studies were conducted, the occurrence of the chemical reaction (i.e., the formation of ion pairs) seemed to be essential to trigger the instability. In fact, in this work, we show that under mass transfer conditions, CTAB alone is able to induce the oscillatory behavior. We have used a particular property of this surfactant, which is the high value of the Krafft point, to visualize the convective cells in the aqueous phase. The periodical cells were of a large amplitude and resulted in fast fluid displacement. The correlation between observed movements, interfacial tension, and electrical potential measurements were also clearly established. These results will be interpreted in regard to our previous work¹¹ dedicated to the CTAB/picric acid system.

Experimental Procedures

All chemical reagents used were of analytical grade. Cetyltrimethylammonium bromide, CTAB (Aldrich, $\geq 99\%$), and CH_2Cl_2 (Aldrich, HPLC grade) were used. The water was ultrapure (resistivity $> 17 \text{ M}\Omega \text{ cm}$).

Oscillations were recorded in a glass beaker with a 31 mm inner diameter without stirring. The organic solution (15 mL) of CH_2Cl_2 ($\rho = 1.32 \text{ kg L}^{-1}$) was placed in the bottom of the beaker. Then, the aqueous solution (15 mL) containing CTAB

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SCHEME 1: Experimental Set-Up^a

^a AQ: aqueous solution of CTAB; ORG: dichloromethane.

was carefully introduced on top of the organic layer. When the CTAB solution was prepared, it was lightly heated to obtain a limpid phase (clarification is observed in a few seconds). For the experiments performed in the presence of crystals, the solution was then maintained at 18 °C for more than 18 h, time enough for the crystals to appear. The experiments in the absence of crystals were performed with freshly prepared solutions. Oscillations were observed for the CTAB initial concentration ranging from 10^{-3} to 2×10^{-2} mol L⁻¹.

Movies were recorded using a web cam (Phillips ToUcamII) placed in front of the beaker at the level of the interface and at a distance of around 5 cm; image distortion was not corrected.

Surface tension measurements were performed using a small cylinder (diameter 2.8 mm; 10 mm high) made of high-density polyethylene and connected to a microbalance. The cylinder was lowered to the liquid/liquid interface and pulled at its maximum before breakage of the interfacial film. The absolute error was about ± 1 mN m⁻¹; however, the error involved in the amplitude of the oscillations was estimated around ± 0.1 mN m⁻¹.

The potential was measured with two Hg/Hg₂Cl₂ electrodes placed in beakers containing saturated KCl solution and connected by two salt bridges to the two phases. Data were recorded using a high impedance multimeter (Agilent 34970A input resistance > 10 GΩ). The microbalance and multimeter were connected to a personal computer.

Although detection (the cylinder was placed at the interface for surface tension and bridges for electrical potential) certainly has an effect on the shape of the patterns formed, behavior was similar whenever the three detection techniques were used together or separately.

Prior to each use, the glass devices were cleaned with an ethanolic potassium hydroxide solution and then rinsed with water and ethanol and dried under vacuum.

Results and Discussion

Experimental Visualization of the Hydrodynamic Instability. The experimental set up, as described in Scheme 1, is very simple. The reactor is a beaker filled with an aqueous solution of CTAB overlaying an organic phase (dichloromethane). At the concentration used, the partition is in favor of the organic phase, and CTAB undergoes mass transfer. A particular property

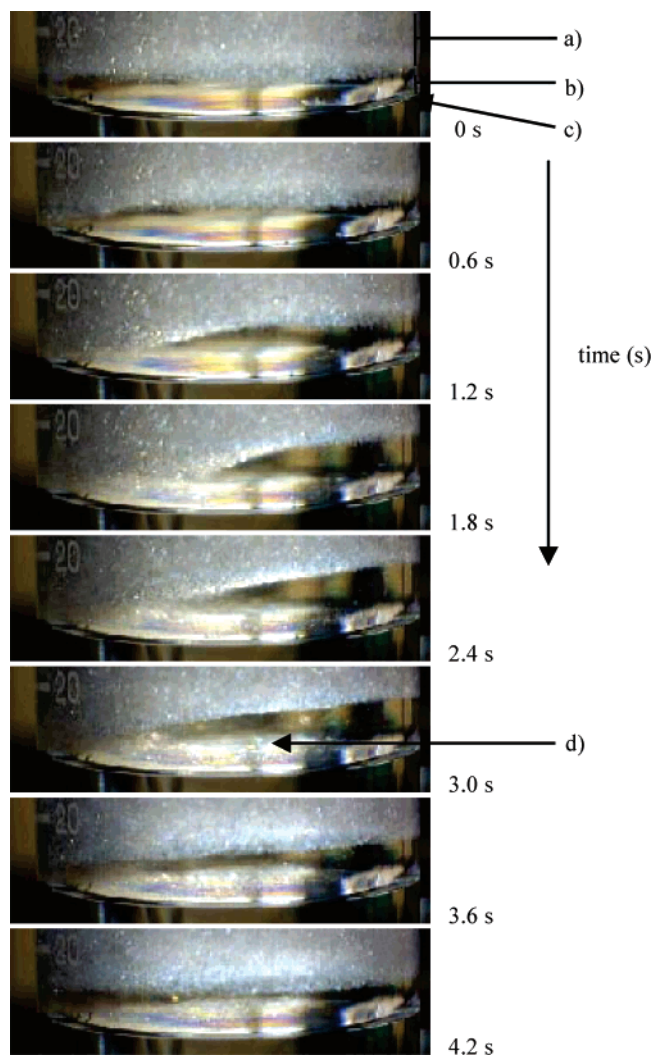


Figure 1. Images recorded during the convective stage. [CTAB]₀ = 3×10^{-3} mol L⁻¹, $T = 18$ °C, $\Delta t = 0.6$ s. (a) Aqueous phase containing CTAB crystals. (b) CH₂Cl₂ front in the aqueous phase. (c) Water/CH₂-Cl₂ interface. (d) Deposit of crystals at the water/oil interface.

of CTAB is the relatively high value of the temperature at the Krafft point (25 °C). Below this point, the solubility is limited, and surfactant monomers in solution are in equilibrium with hydrated surfactant crystalline particles (no micelles are formed in these conditions, although the CTAB concentration is over CMC). We have performed experiments at about 18 °C and profited from the presence of crystals to visualize the convective instability. The set of photographs in Figure 1 shows the moving stage of the process. The corresponding movie is provided as Supporting Information (S1).

When the two phases were put into contact, CTAB crystals were homogeneously distributed in the aqueous phase. Rather fast, a clear zone grew near the interface that could be attributed to the dichloromethane diffusion front. This is justified by the fact that if we add a drop of dichloromethane to a CTAB solution containing crystals, these crystals disappear in a few seconds under shaking, and the solution remains clear even after several hours in the fridge.

So, in the biphasic experiment, during the induction period before oscillations start, the only observation was the formation of the CH₂Cl₂ diffusion front. When the instability started, the first observation was a displacement of small bubbles trapped at the interface (from left to right in the experiment presented in Figure 1: 0 s). Simultaneously, CTAB crystals started to move

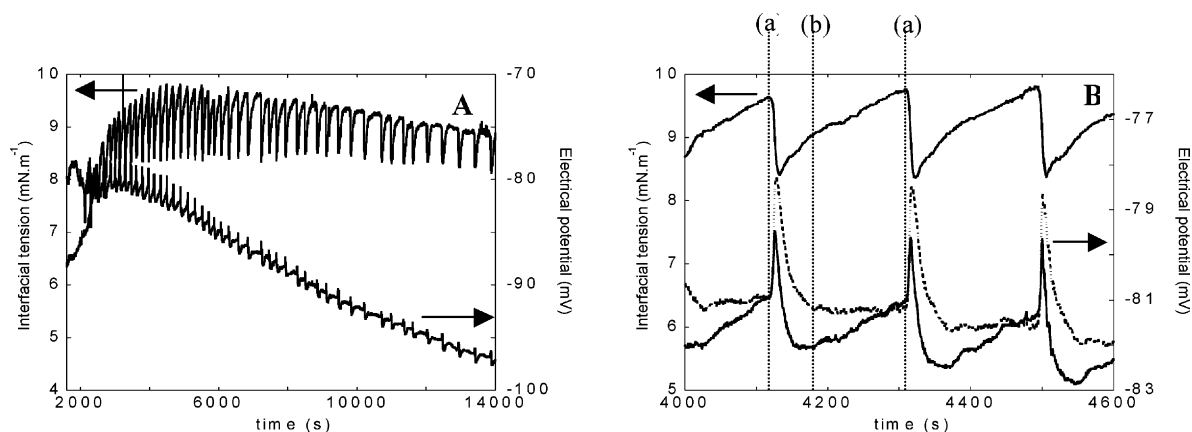


Figure 2. Simultaneous measurement of interfacial tension (γ) and electrical potential. $V = V_{\text{AQ}} - V_{\text{ORG}}$. $[\text{CTAB}]_0 = 5 \times 10^{-3} \text{ mol L}^{-1}$. (A) General view. (B) Zoom between 4000 and 4600 s; dotted line is $V + \alpha - \beta\gamma$.

laterally (from right to left) in the zone closest to the CH_2Cl_2 front. The movement seemed then to accelerate and was amplified until a sudden collapse of the clear zone occurred in the vicinity of the wall of the beaker (0.6–3 s). This violent effect resulted, in the beginning of experiment, in the deposit of some crystals at the water/oil interface (3.6–4.2 s). They disappeared rapidly while the system calmed down to its quiet stage again (6.6 s). This behavior was observed for several hours with a rather regular period of around 1 min. The sequence of images of Figure 1, where crystals were abundant, was chosen because of its visual quality. In this case, the movement was almost confined in the region close to the dichloromethane front, probably because of the higher viscosity of the layer containing crystals. When crystals were less abundant, a higher volume was involved in the movement (see movie S2 in Supporting Information). It is important to note that when the instability occurred, no deformation of the interface was observed.

We will see in the following that the data obtained using interfacial tension and electrical potential measurements in the presence of crystals showed a clear correlation between the visual observation of the convective stage and the oscillatory patterns recorded by both techniques. Furthermore, for the two techniques, the signal recorded in the presence or in the absence of crystals was similar, meaning that crystals are not at the origin of the instability but are only a means of visualization.

Surface Tension Measurements at the Water/Oil Interface.

Interfacial tension (γ) measurements are of particular interest as they give information on the adsorption state in the course of the oscillatory process. As observed in Figure 2A, during the induction period, interfacial tension increased monotonically. When the two phases were put into contact, CTAB was homogeneously distributed in the whole water volume. According to the literature,¹² at the concentrations used in this study, CTAB mass transfer can be considered as diffusion-controlled, and the initial value measured for interfacial tension (around 4 mN m^{-1}) corresponded to the value that we would obtain for the same water concentration in equilibrium conditions. Under mass transfer, concentration gradients build up in the diffusion layer, leading to a lower concentration of CTAB close to the interface. Then, adsorption of surfactant that is in fast equilibrium with the CTAB concentration in contact with the interface decreased (γ increased). When γ reached a value of about 8 mN m^{-1} , oscillations started and lasted for more than 4 h. The period of the oscillations increased with time from about 300 s at the beginning of the experiment to 800 s in the end. The amplitude decreased with time with a maximum of about 1.5 mN m^{-1} .

Looking closer at one cycle, the curve showed a fast accelerating decrease of the interfacial tension followed by a slower relaxing increase. It is interesting to note that the same pattern is observed in most of the studies cited in the Introduction even when experimental conditions are quite different.^{3,4,7} In particular, we have already analyzed similar surface tension data in our previous work¹¹ dedicated to the CTAB/picric acid system in the U-tube geometry. Although, in this geometry, the movement of fluid could not be observed, and we have attributed the fast drop of the interfacial tension to a convective inflow of surfactant due to Marangoni instability. Its periodical appearance could be linked to the fact that although surfactant molecules induce Marangoni convection under mass transfer conditions, it is known that their presence at the interface can, on the contrary, inhibit the instability.^{13,14} So, when the concentration of the adsorbed surfactant reached a sufficient value and because of intense mixing of the aqueous layer near the interface that destroys the normal gradients, the instability vanished, and the system switched to a slower transport process. During this phase, normal gradients, induced by CTAB mass transfer, appeared, and the concentration of surfactant at the interface decreased. This decrease was enhanced by the fact that diffusivity of the surfactant was higher in the receiving organic phase, leading to lower inflow than outflow at the interface. When the concentration of the adsorbed surfactant was sufficiently low, mobility of these ions was recovered, and tangential gradients could induce the instability again. In the case of the CTAB/picric acid system, the interfacial reaction that led to the formation of hydrophobic nonsurface active ion pairs cooperated also in this sense.

This interpretation seems to be confirmed by our visual observations in the present study. The decrease of the surface tension started just when movements were initiated (denoted (a) in Figure 2B); the amplification of the convective flux resulted in the drop of the signal, and the maximum of the movement intensity was observed toward the minimum of γ . Then, the surface tension started to increase again, and slow desorption took place while residual movements were still observed in the turbid layer containing crystals (marked (b)). Finally, the system went back to its initial quiet stage.

Interfacial tension oscillations were detected for CTAB initial concentration in the aqueous phase ranging from 10^{-3} to $2 \times 10^{-2} \text{ mol L}^{-1}$. No oscillations were observed in the absence of CTAB. The oscillations were not completely reproducible (the way the two phases are set into contact seemed to play an important role), but some qualitative features could be drawn up from our observations: the period became longer with

increasing initial concentration while the amplitude did not vary significantly with a typical value of about 1 mN m^{-1} . The value of γ at which the oscillations started seemed to decrease with a value of 12 mN m^{-1} for the lowest concentration to 8 mN m^{-1} for the highest. We have also tested the effect of a variation of the diameter of the beaker and found that for a larger interface size ($\varnothing = 62 \text{ mm}$), no clear difference was observed, but for a smaller size ($\varnothing = 21 \text{ mm}$), the period (60 s) and amplitude (0.12 mN m^{-1}) decreased.

We also performed one experiment in which CTAB was initially dissolved in the organic phase. In this case, we could observe very small oscillations (amplitude = 0.3 mN m^{-1}) with a very short period (30 s) that lasted only for about half an hour. However, the oscillatory pattern was very similar to the one observed in previous conditions.

Electrical Potential Measurements. Electrical potential, measured between the two phases ($V = V_{\text{AQ}} - V_{\text{ORG}}$), is a widely used technique⁷ to detect oscillatory behavior in such systems. Although the shape of the electrical signal is quite different than the one obtained by surface tension measurements, correlation between the two signals is obvious (Figure 2A). When the movements started, the potential increased very fast, passed through a maximum, and then dropped. This peak of potential was clearly correlated to the moving stage of the instability (from point a to b in Figure 2B). Then, when the quiet stage was reached, the electrical potential increased (absolute value of the difference of potential decreased) more slowly.

In our previous work¹¹ dedicated to the CTAB/picric acid system, we had already used the two techniques to follow the oscillatory process. As was already said, the convective cells could not be observed, and in this case, oscillations of the electrical potential were completely similar to the ones observed by surface tension. The electrical potential was then representative of the adsorption state due to the electrical double layer, formed by the adsorbed surfactants that are positively charged, and the negative counterions that accumulate in the aqueous phase at the vicinity of the interface. This interpretation was confirmed by the fact that if we used an anionic surfactant (SDS instead of CTAB) and a quaternary ammonium as a counterion, the recorded potential oscillations were similar but of opposite sign.

In the present work, to compare the two signals, the curve obtained by surface tension measurement was subtracted, after normalization to the same size, to the electrical potential data. The calculated curve represented by the dotted line in Figure 2B (dotted line = $V + \alpha - \beta\gamma$) showed horizontal parts (from line (b) to (a)) when adequate value of α (offset) and β (normalization coefficient) were chosen. This would mean that, during the quiet stage, the two signals would be identical and representative of the adsorption state. During the convective stage, the electrical potential would be furthermore related to the movement itself. The implication of hydrodynamics on the observed pick during the fast stage was confirmed by placing the two electrodes in the aqueous phase at some distance from each other.

The signal recorded in that case (dotted line Figure 3) was very similar to the calculated curve in Figure 2B,¹⁵ showing that the displacement of fluid in the aqueous layer was certainly at the origin of the fast variation of the electrical potential. The experimental conditions giving rise to this effect, in our system, can be compared to the experimental setup used in the tangential flow streaming potential technique¹⁷ that is used to measure the zeta (ζ) potential of a charged membrane. In the Gouy–Chapman–Stern–Graham model, the ζ potential is defined at

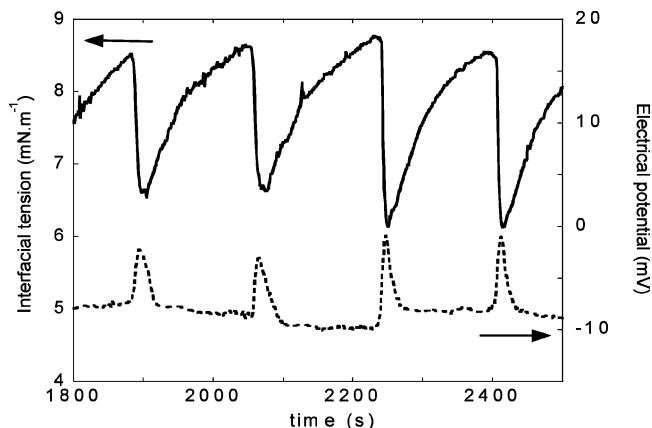


Figure 3. Interfacial tension and electrical potential $V = V_{\text{AQ1}} - V_{\text{AQ2}}$ measured with the two electrodes in the aqueous phase. $[\text{CTAB}]_0 = 5 \times 10^{-3} \text{ mol L}^{-1}$.

the shear plane between the electrical double layer (adsorbed and immobile) and the diffusive Gouy–Chapman layer. Under flow conditions, charge compensating ions are sheared off and accumulate downstream giving rise to a measurable potential along the membrane. In our system, the surfactant layer at the interface could play the role of the membrane, and spontaneous displacement of the fluid, parallel to the interface, would create the flow conditions.

Conclusion

This work constitutes the first experimental observation of periodic convective instability in a system involving, as a unique process, CTAB mass transfer. We have taken advantage of the relative high value of the temperature at the Krafft point to visualize the convective fluxes that give rise to movements of a high amplitude in the aqueous phase. A correlation between movements and surface tension and electrical potential oscillations has been clearly established. During the convective stage, surface tension data showed fast adsorption due to the fast inflow of surfactant at the interface. During the diffusive stage, desorption occurred, and gradients built up until the system became unstable again. To account for the electrical potential data, two components need to be taken into account. In the quiet stage, the signal is comparable to surface tension, and the main contribution would result from the electrical double layer formed at the interface by charged surfactants. In the convective stage, the electrical potential would be mostly related to the velocity of the fluid that disturbs the charge distribution in the Gouy–Chapman layer.

Supporting Information Available: Movies showing the experimental visualization of the hydrodynamic instability. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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