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Large Increase in the Heat Transfer through Monolayers Detected by Beam Deflection

Marcos Gugliotti,* Tiago S. Rodrigues, Mauricio S. Baptista, and Mario J. Politi

Departamento de Bioquímica, Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, cep 05508-000, São Paulo, Brasil

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We report the application of photothermal beam deflection for studying heat transfer across the liquid/gas interface covered with surfactant monolayers. Laser-induced Marangoni convection was generated on the surface of an absorbing aqueous solution with and without a monolayer. The change in heat transfer to the air was monitored by the deflection of a probe beam propagating close to the solution surface. A large increase in the deflection as well as in the air temperature for monolayer-covered surfaces was observed. A film-balance study showed that the magnitude of deflection increases as a function of monolayer compression.

Introduction

Surfactants and surface tension gradients play a fundamental role in heat and mass transfer. It is known that an insoluble surfactant monolayer enhances the superheating of water^{1,2} and that Marangoni convection³ near the surface of bubbles increases the rate of heat transfer at boiling conditions. These phenomena evoke attention due to the possibility of saving energy in industrial boilers, which may lead to a significant economy in some important applications, that is, to obtain desalinated water.⁴ Although surfactants have been largely used as additives in heat transfer processes, the mechanism of heat transfer enhancement is still not clear⁵ and a more detailed investigation is needed to understand the molecular basis of the phenomenon. To our knowledge, only the work of Fang and Shah⁶ attempted to elucidate the molecular mechanism of heat transfer across fluid/fluid interfaces in the presence of insoluble monolayers. They monitored the heat transfer through the air/water (a/w) and oil/water (o/w) interfaces with and without monolayers by using an IR imaging technique. According to the authors, the change in heat transfer through the a/w interface in the presence of a film was too small to be detected by the instrumentation used, and the effects of convection currents were minimized by keeping the temperature gradient across the film as low as possible. However, because convection currents are considered a major factor in heat transfer,³ it is necessary to investigate the changes in heat transfer in a system where both Marangoni convection and surfactants are present.

Recently,⁷ we studied the influence of insoluble surfactants on mass transfer by monitoring the effect of monolayers on Marangoni convection induced photothermally. Our previous results⁷ showed that tiny amounts of surfactants can suppress convection currents by the Gibbs–Marangoni effect. We now have extended this

investigation and detected changes in heat transfer across the liquid/gas interface associated with the suppression of convection currents by using photothermal beam deflection⁸ (PBD). The versatility of this technique allowed the determination of changes in heat transfer as a function of monolayer compression.

Experimental Section

PBD (also called “mirage effect”) is a powerful analytical technique based on the deflection of a probe beam by a refractive index gradient generated by local changes in temperature. A more detailed description of the PBD technique and its variations can be found elsewhere.⁹ This technique has been successfully employed for measuring heat transfer in liquids¹⁰ and for obtaining vibrational spectra of molecules deposited on solid surfaces.¹¹ However, there are no records on the use of PBD for studying monolayers on liquid surfaces. Our instrumental setup consisted of a pump laser (Nd:YAG, Uniphase, continuous wave, 532 nm, 50 mW), modulated by a shutter (Uniblitz) at intervals of 5 s for exposition and blocking and focused by a converging lens ($f = 5$ cm) perpendicularly on the surface of highly concentrated aqueous solutions of crystal violet (Aldrich). The absorbances of the solutions at 532 nm were measured on a Shimadzu spectrophotometer using a thin quartz cuvette (0.2 mm). A focused ($f = 20$ cm) probe laser (He–Ne, Oriel Instruments, 632.8, 10 mW) was allowed to propagate as close as possible to the solution surface and directed to a position detector (Hammamatsu). The instrumentation was aligned so that the beams intercepted each other at their focusing points. Voltages were acquisitioned by an analogic/digital converter (Computer Boards) and stored in a personal computer. Monolayers of hexadecanol (Aldrich) and phosphatidic acid (Avanti Polar Lipids) were formed on the surface of the solutions by depositing the surfactants with a microsyringe (chloroform solution) and in the form of small crystals. Some experiments were performed using a Petri dish (diameter 5 cm) filled to the brim with the absorbing solution making a liquid layer of ~ 1 -cm deep. A rough estimate of the increase in the air temperature was made by placing a conventional thermocouple (diameter 0.1 cm) at a distance of less than 0.2 cm above the solution surface, close to the pump beam spot. The experiments with the film balance (KSV 5000) were carried out in a cleanroom, with part of the instrumentation located outside (Figure 1).

* Corresponding author. Tel: + 55 11 3091-3877. Fax: +55 11 3815-5579. E-mail: marcosgugliotti@hotmail.com.

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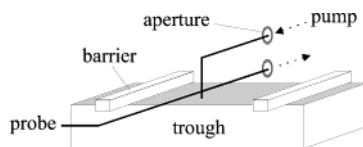


Figure 1. Schematic representation of the instrumental setup built on the film balance in the cleanroom. The lenses and mirrors were removed from the figure.

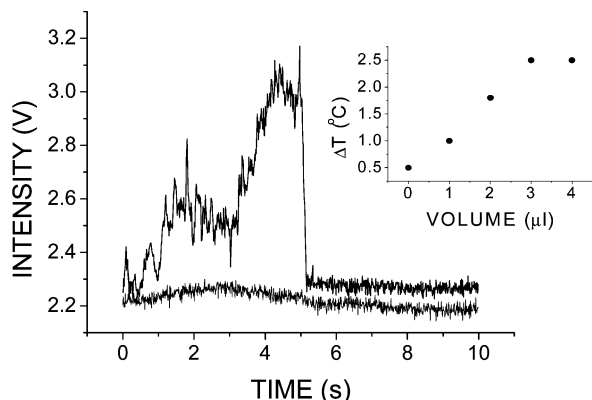


Figure 2. Deflection signals as a function of time obtained from a clean surface (smaller signal) and from a surface covered with a hexadecanol monolayer (larger signal). The inset shows the results of an independent experiment where the variation in the air temperature (ΔT) was measured as a function of the volume of hexadecanol solution deposited on the surface. The absorbances of the subphases are indicated in the text.

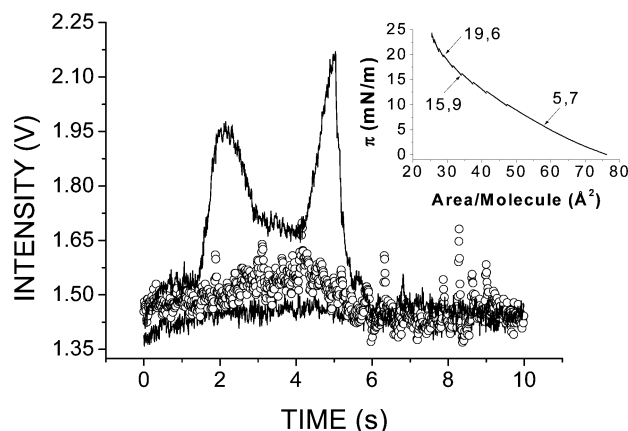


Figure 3. Deflection signals as a function of time at different surface pressures: 5.7 (lower solid curve), 15.9 (open circles), and 19.6 mN/m (upper solid curve). The inset shows the isotherm of hexadecanol against the concentrated solution of crystal violet used as the subphase ($\text{ABS}_{532} = 0.38$).

The probe laser was mounted on an *XY* micrometric stage and placed inside the room, beside the trough. Using only one mirror, the probe beam was propagated close to the solution surface and directed through a small aperture (3 cm) on the cleanroom wall to reach the position detector located outside. In the opposite direction, the pump beam was directed from outside and entered the cleanroom by a second aperture on the wall. After reflecting on the mirror placed above the trough, the beam was focused on the solution surface at a distance of ~ 6 cm from the Wilhelmy plate. The air circulation inside the room was turned off during data acquisition to minimize the noise in the signals.

Results and Discussions

In the results of Figures 2 and 3, the pump beam illuminated the surface of the absorbing solutions of crystal violet from $t = 0$ to $t = 5$ s, when the shutter was opened and closed, respectively. The changes in voltage represent the displacement of the probe beam on the position detector

(deflection). The increase in the deflection signal after placing two small crystals of hexadecanol on the surface of an absorbing solution that filled the Petri dish is shown in Figure 2.

Despite the noise in the signals, in part attributed to the air circulation above the surface of the sample, a 15-fold increase in the magnitude of the deflection (at $t = 5$ s) was observed after spreading of the monolayer on the absorbing solution ($\text{ABS}_{532} = 0.25$). For both signals, the deflection of the probe beam was rapidly interrupted when the pump beam was blocked ($t = 5$ s). No signal was detected when pure water was used as the subphase. The results shown in the inset of Figure 2 were obtained from an independent experiment. Small volumes of a hexadecanol solution in chloroform (8.8 mM) were deposited on the surface of the sample ($\text{ABS}_{532} = 1.3$), and a conventional thermocouple was placed above the surface, close to the beam spot. For a clean surface, the air temperature increased 0.5°C , whereas after saturation of the surface (formation of stable lenses) with $3\ \mu\text{L}$ of the hexadecanol solution, the air temperature increased 2.5°C , remaining unchanged after this point. Although the temperature values are subestimated by the use of a conventional thermocouple, this result clearly shows the large influence of the film on the heat transfer to the adjacent phase (air). Deflection patterns similar to those shown in Figure 2 were also obtained with monolayers of phosphatidic acid and hexadecanol deposited from chloroform solutions (not shown). In such experiments, the magnitude of the deflection was independent of the surfactants used, increasing more than 100% for surface pressures (π) above 10 mN/m for both surfactants.^{12,13} Because the results were similar for monolayers spread from crystals and solutions, it is concluded that solvent evaporation does not affect the results, at least when small volumes are used for monolayer deposition.

In the experiments using the Petri dish (Figure 2), the film was not fully compressed, and a more accurate investigation was carried out on a film balance in a cleanroom. Before the experiments, two isotherms of hexadecanol were obtained on pure water to verify the possible influence of the apertures on the cleanroom wall. No significant changes were observed with the apertures open or closed, with the minimum area per molecule being around $20\ \text{\AA}^2$ for both runs.¹⁴ Figure 3 shows the time-dependent variation in the deflection signals as a function of monolayer compression. Data acquisition points are indicated by arrows in the isotherm (Figure 3, inset). The large difference in the shape of this isotherm when compared to that on pure water is assigned to the formation of surface aggregates of crystal violet¹⁵ and to the possible interactions with the hexadecanol molecules.

In Figure 3, the signals obtained at π below 15.6 mN/m presented the same magnitude of that corresponding to 5.7 mN/m. Above 15.9 mN/m, a sharp increase in the signal was observed, as can be seen for the deflection at 19.6 mN/m. At the end of this experiment, the monolayer was uncompressed and recompressed successively, with π varying from 16.4 to 20.9 mN/m (not shown). The intensity of the signals followed the changes in monolayer compression, and the magnitude of deflections varied up to 100% for differences in π between 0.9 and 4 mN/m.^{12,13}

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The sharp increase in the deflection signal after a certain degree of compression (corresponding to ~ 16 mN/m) might indicate the dependence of heat transfer on the monolayer state. Although we do not claim to have observed a phase transition in hexadecanol at such conditions (the subphase is a concentrated solution of crystal violet), a transition in a mixed monolayer at the o/w interface has already been detected by changes in heat transfer⁶ and it seems reasonable to think that the present methodology may also be capable of detecting phase transitions.

The observed increase in the heat transfer to the air, and, consequently, in the magnitude of deflection can be explained by the attenuation of the convection currents in the presence of a monolayer.¹⁶ Upon local heating, a vigorous Marangoni convection develops underneath the surface of the concentrated solution, draining liquid away from the heated area. For clean surfaces, the heat delivered in the region illuminated by the laser is transferred to the bulk by conduction and convection. For monolayer-covered surfaces, however, the surfactant molecules are swept outward with the movement of the substrate,⁷ and the local changes in surface concentration generate a second surface tension gradient in the monolayer. Such an effect has been successfully used for mechanical manipulation of monolayers in the micrometric scale^{17,18} and, more recently, for the modification of black film hydration.¹⁹ The surface tension gradient formed in the monolayer counterbalances the Marangoni convection induced by laser heating causing attenuation of the convection currents, which in turn decreases the rate of heat transfer to the bulk and leads to an additional rise in the local temperature. The heat transferred by conduction to the air phase is, thus, enhanced, increasing the temperature above the surface. Of course, heat conduction to the air also occurs without a film (deflections are also observed for clean surfaces), but it is augmented in the presence of a monolayer, which accounts for the larger deflection of the probe beam. The increase in the surface viscosity as a function of the monolayer compression may also suppress motions on the liquid surface. However, because changes in the deflection signals are also observed when small quantities of surfactants are added on the surface and when the monolayer is not compressed (Figure 2), we believe the formation of a second opposite surface tension gradient is the dominant effect for the attenuation of the convection currents.⁷

The results in Figures 2 and 3 show other interesting features. The deflection signals decreased at ~ 2 s and increased again until the pump laser had been blocked by the shutter ($t = 5$ s). We believe this effect occurs because the opposite surface tension gradient generated in the film at the beginning of heating is not enough to overcome the Marangoni convection. However, it is not clear why it occurred at ~ 2 s for subphases with different concentrations. Also, the magnitude of deflection was not always

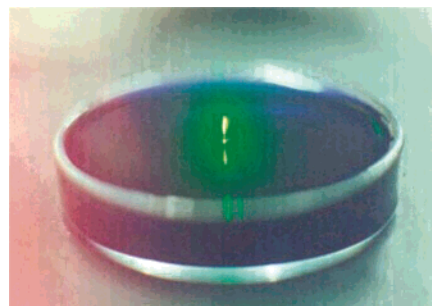


Figure 4. Intense light scattering and defocusing of the beam as a consequence of vaporization of the sample after saturation of the surface with monolayers of hexa- and octadecanol. The same effect was observed for monolayers spread from crystals.

proportional to the subphase absorbance, as it would be expected. For example, in the experiments of Figures 2 and 3, the subphase absorbances were 0.25 and 0.38, whereas the deflection peaks at 5 s were 15 and 7.3 times higher, respectively, in the presence of a monolayer (for Figure 3, considering the deflection peaks of the curves corresponding to 5.7 and 19.6 mN/m). These differences may be attributed to the experimental conditions, because for the same monolayer and subphase the deflection can be influenced by micrometric variations in the alignment of the beams and also by the normal air circulation at the moment of acquisition.

A striking example of the heat transfer enhancement was observed when the pump beam was precisely focused on the sample surface. A thin vapor steam was seen coming out of the solution surface (vaporization), which was accompanied by intense light scattering and strong defocusing of the beam, probably as a result of the thermal lens⁹ formed in the air phase. Figure 4 shows a picture of the observed effect after saturation of the surface with hexadecanol and octadecanol spread from chloroform solutions. For a clean surface, the energy threshold for vaporization was also achieved by using a laser beam focused by a lens of shorter focal distance ($f = 2.5$ cm, beam diameter = $14.7 \mu\text{m}$) and a highly concentrated subphase ($\text{ABS}_{532} = 0.5$). However, for subphases with lower absorbances and with the pump beam focused by a lens of $f = 5$ cm, vaporization was observed only after deposition of a monolayer.

The striking result in Figure 4, as well as the increase in the deflection signals, demonstrate that the mechanism of attenuation of convection currents by surfactant monolayers has a large influence in the heat transfer through the liquid/gas interface. The PBD technique showed that it is an alternative for studying heat transfer through fluid/fluid interfaces, and variations of this methodology (i.e., with pulsed lasers) could also be employed for the cases where the surfactant molecules or pure water are the absorbing media.

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