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Journal of Colloid and Interface Science 308 (2007) 249–253
JOURNAL OF Colloid and Interface Science
www.elsevier.com/locate/jcis

# Studies of the rate of water evaporation through adsorption layers using drop shape analysis tensiometry

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Received 9 October 2006; accepted 29 December 2006

Available online 24 January 2007

**Abstract**

With modified measuring procedure and measuring cell design in the drop profile tensiometer PAT, it became possible to study the rate of water evaporation through adsorbed or spread surface layers. This method was employed to measure the rate of water evaporation from drops covered by adsorbed layers of some proteins and surfactants, in particular *n*-dodecanol. It was shown that the formation of dense (double or condensed) adsorbed layers of protein and the formation of 2D-condensed *n*-dodecanol layer decrease the water evaporation rate by 20–25% as compared with pure water. At the same time, the adsorbed layers of ordinary surfactants (sodium dodecyl sulfate and nonionic ethoxylated surfactant $C_{14}EO_8$) do not affect the water evaporation rate remarkably.
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*Keywords:* Dynamic surface tensions; Drop profile analysis; Water evaporation; Surfactant adsorption layers

## 1. Introduction

Insoluble monolayers (e.g., *n*-heptadecanol) spread over aqueous substrate, in contrast to adsorption layers formed by ordinary surfactants, are capable to decrease the evaporation rate of water [1,2]. This fact indicates that insoluble monolayers possess dense (usually condensed) structures. Therefore, comparing the rate of evaporation from pure water drops and those covered by a spread or adsorbed surface layer one can estimate the surface layer contribution to the resistance against mass transfer, which also allows certain qualitative conclusions about the surface layer structure.

To study the rate of water evaporation through a monolayer, gravimetric devices are widely used, which measure the dynamics of liquid mass change during the evaporation process [2]. However, for such measurements also pendant drop tensiometers can be used, because these devices also determine the volume and surface area of the drop. In this case, the drop shape tensiometer has to be additionally equipped with a system that automatically controls the drop volume or area, and simultaneously monitors the volume of liquid which is pumped into the drop. The advantage of this technique as compared to gravimetric methods is the possibility to measure simultaneously the rate of water evaporation through adsorbed or spread monolayer, and the dynamic surface tension of the studied solution or the surface pressure of a spread monolayer. This method can be used also to study the mass transfer of a dissolved components across the interface between two immiscible liquid phases.

The target of the present work is to demonstrate the suitability of single drop experiments for studies of water evaporation through adsorbed layers of some surfactants and proteins. The measurements show that among various surfactants only the slightly soluble *n*-dodecanol is cable to decelerate water evaporation. On the other hand, proteins once they have formed a dense (condensed or double) adsorption layer, can retard the water evaporation essentially.

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doi:10.1016/j.jcis.2006.12.073

## 2. Experimental

The experiments were performed by drop profile analysis tensiometry (PAT-1 or modified PAT-2P, SINTERFACE Technologies, Germany) [3]. The temperature of the measuring glass cell (volume $V = 20$ ml) was controlled to be 25 or 20 °C. The cell was closed by a lid with an immersed capillary (the external diameter is equal 2.4 mm) at which the drop of studied liquid was formed. To stabilize and accelerate the water evaporation from the drop surface, up to 5 g of thin disperse $CaCl_2$ powder was distributed over the cell bottom and walls (kept by a metal grid). In this way, the $CaCl_2$ powder reduced the air humidity in the cell to almost zero. In the experiments, first the drop of studied solution was formed at the tip of a steel capillary using an automated pump. The surface area of the drop ($30 \pm 0.1$ mm$^2$) was controlled to be constant during the whole drop shape experiment (up to 20,000 s) by an automatic feed back action of the dosing system, and the volume added to the drop during the experiment was continuously monitored.

The rate of evaporation $dV/dt$ is a measure for the loss of volume per time at a given surface area. As we kept the area of the drops in all experiments constant, the slope of measured dependencies $V(t)$ give directly the evaporation rate for comparison between drops formed from different solutions.

When the drops were formed from a solution an increase of surfactant or protein concentration in the drop took place during the experiment due to evaporation of water. A second experimental method is the use of a so-called coaxial double capillary which allows to pump the pure solvent (water or buffer solution) into the drop through a second capillary located in the center of the measuring capillary [4]. However, this method when applied to weakly concentrated solutions can lead to a decrease of solute concentration in the drop as compared to the initial concentration due to the adsorption at the drop surface [5]. We have used here both described methods.

The substances studied were the anionic surfactant sodium dodecyl sulfate (SDS), and the nonionic surfactants *n*-dodecanol (from Fluka, puriss.) and ethoxylated surfactant $C_{14}EO_8$ (from Sigma Chemical). SDS was prepared and chemically purified as described previously [6]. The samples of $\beta$-lactoglobulin (BLG), human serum albumin (HSA) and $\beta$-casein were purchased from Sigma Chemical. The proteins were used without further purification. The protein solutions were prepared in the presence of phosphate buffer (0.01 M of $Na_2HPO_4$ and $NaH_2PO_4$, pH 7.0). All solutions were prepared using Milli-Q water.

## 3. Results and discussion

The dependence of dynamic surface tension of the studied protein solutions on the adsorption time at 25 °C is illustrated in Fig. 1, while Fig. 2 shows the same time dependence for the added drop volume. It should be noted that for all protein solutions studied the concentration was higher than a certain protein concentration $c^*$, above which the equilibrium surface tension remains almost constant, while the adsorption often further increases [7]. Such a constant surface tension level was explained

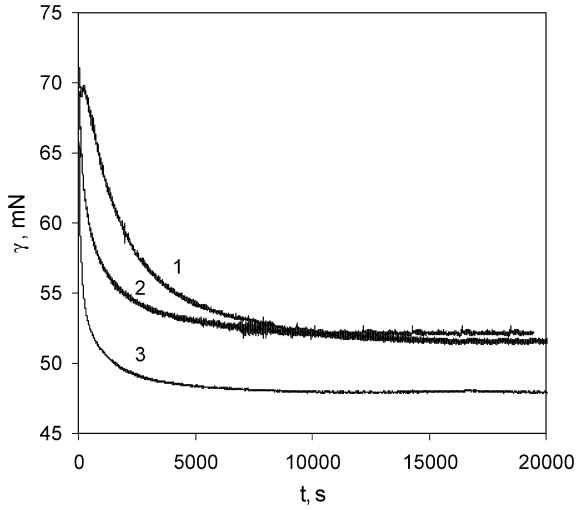


Fig. 1. Time dependence of dynamic surface pressure for: (1) HSA solutions, initial concentration 0.5 μmol/L; (2) BLG solutions, initial concentration 2.0 μmol/L; and (3) $\beta$-casein, initial concentration 0.5 μmol/L, measured by drop shape method with continuous control of drop surface area.

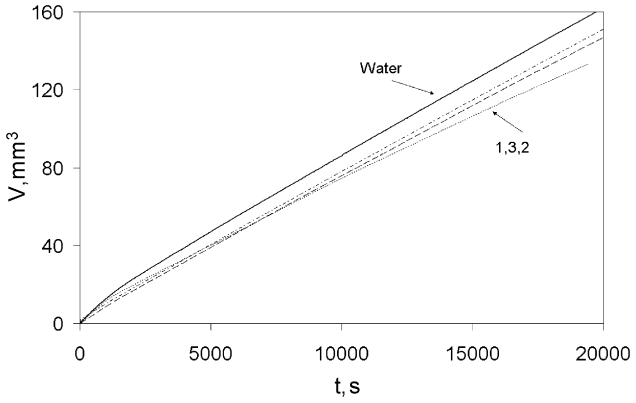


Fig. 2. Dependence of water or solution volume pumped into the drop with surface area 30 mm$^2$ on the time expired from the experiment start. Bold curve—experiments with pure water drops; (1) dotted line, (2) dot–dashed line, (3) dashed line (notation of curves as in Fig. 1).

by a two-dimensional condensation (aggregation) of the protein layer above a certain critical adsorption [7,8]. The significant increase in the adsorption without any changes in surface pressure can also be explained by the assumption that a bilayer (or multilayer) is formed [7,9–11]. It is seen from Fig. 1 that equilibrium surface tensions were attained with all studied protein solutions.

The results of evaporation of a pure water drop with the same surface area are shown in Fig. 2. It follows from Fig. 2 that for BLG and $\beta$-casein solutions the water evaporation rate is by 10% lower, while for HSA solution (the substance with the largest molecular mass among the studied proteins) the evaporation rate is decreased by even ca. 15%.

To determine the average rate of evaporation for protein solutions, the measuring procedure was somewhat modified. At a certain dynamic surface tension value, the automatic drop area control was temporarily suspended (for 100–110 s). This resulted in a decrease of the drop volume caused by evaporation. After this period, the control procedure was resumed to

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