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## Using Profile Analysis Tensiometry for Monitoring Auto-oscillations Caused by the Hydrolysis of 3-(Trimethoxysilyl)propyl Methacrylate when Contacting Water

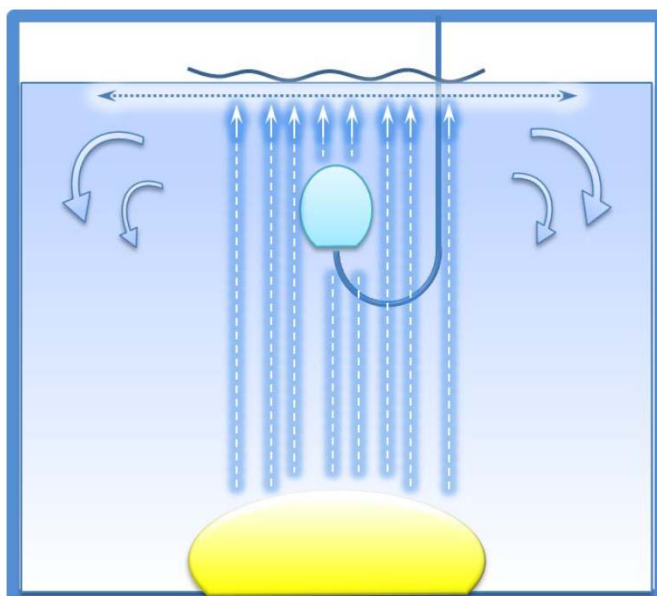
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### Graphical Abstract



### Highlights

**This work is the first step in study of reaction kinetics by using Profile Analysis Tensiometer. It allows to study different phenomena happening at interfaces.**

**Abstract**

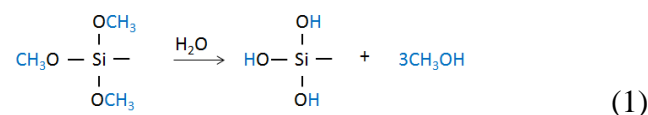
3-(Trimethoxysilyl)propyl methacrylate (TPM) hydrolyzes via the alkoxy groups attached to silicon when it comes into contact with an aqueous phase and forms surface active 3-(trihydroxysilyl)propyl methacrylate (THPM) molecules. Their formation and adsorption at the water/air interface, i.e. decrease in the surface tension, can be used as a sensor to follow the hydrolysis process and can help to explain the role of these molecules in the emulsion formation and stabilization process. The target of this contribution is to demonstrate the experimental details of a surface tension sensor using a bubble profile analysis tensiometer for monitoring the chemical reaction of TPM with water and to explain the peculiarities observed in the measured signal, i.e. irregularities in the dynamic surface tension. Auto-oscillations of the surface tension were observed during the measurements, which are connected to a complex of different types of flows in the volume of the aqueous phase. The kinetics of the reaction and hence of the surface tension can be controlled by changing the pH of the aqueous phase. It is also possible to prevent auto-oscillations by means of a continuous gentle stirring of the aqueous phase, which then allows a quantitative monitoring of the rate of the TPM/water reaction.

**Keywords:** TPM hydrolysis; Bubble profile analysis tensiometry; surface tension oscillations; Marangoni instabilities; reaction rate sensor

## Introduction

When 3-(Trimethoxysilyl)propyl methacrylate (TPM) comes into contact with an aqueous phase it starts to hydrolyze via the alkoxy groups attached to the silicon atom [1] according to the following reaction scheme (1). The resulting product of this hydrolysis, 3-(trihydroxysilyl)propyl methacrylate (THPM), is surface active due to the hydrophilic hydroxy-groups and the hydrophobic methacrylic groups. This reaction can be controlled by the pH value of the aqueous phase [2]. The resulting surface active product THPM and also methanol diffuse into the aqueous phase, and can adsorb at all available interfaces, such as the water/air and the water/oil interfaces.

The hydrolysis of TPM plays an important role in such processes like as for example modification of hydrophilic particles. After THPM adsorption on the surface of these particles and subsequent polycondensation via silanol groups they will become partially hydrophobic and can be used for the stabilization of Pickering emulsions [3], [4], [5].



The formation of surface active molecules and their adsorption at the water/air interface, i.e. decrease in the surface tension, can be used as sensor to follow the hydrolysis process and can help to explain the role of these molecules in the emulsion formation and stabilization process. The change in surface tension is a value directly related to the amount of a surface active substance adsorbed at the surface. Therefore, bubble profile analysis tensiometry seems to be a useful tool for monitoring the kinetics of TPM hydrolysis reaction. A direct monitoring of the hydrolysis reaction at a TPM drop surface immersed into water appears impossible due to the very fast reaction rate and the formation of a surface layer at the TPM/water interface. This interfacial layer changes quickly from a monomolecular adsorption layer into a multilayer and skin so that the shape of the TPM drop cannot be used to determine the interfacial tension [6-7].

The target of this contribution is to demonstrate the experimental details of a surface tension sensor using a bubble profile analysis tensiometer for monitoring the chemical reaction of TPM with water and to explain the peculiarities observed in the measured signal, i.e. irregularities in the dynamic surface tension.

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3-(Trimethoxysilyl)propyl methacrylate (TPM) was used as oil phase.. TPM with the purity of 98% was purchased from Sigma-Aldrich (Germany) and used without further purification. Water used was purified by a Milli-Q purification system. The water resistivity was  $18 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ . The surface purity of water was tested by interfacial tension measurements and was equal to  $72.5 \text{ mN/m}$  at  $25^\circ\text{C}$  and constant over at least 8 hours.

## Methods

To measure the dynamic and equilibrium interfacial tension ( $\gamma$ ) the Profile Analysis Tensiometer PAT-1 (SINTERFACE Technologies, Germany) was used. The principle of this method is based on an accurate determination of the drop profile and its analysis via the Gauss–Laplace equation. The principle of the pendant drop analysis technique is described in detail elsewhere [8], its use for studying the dilational rheology in [9] and for particle loaded interfaces in [10].

The experimental set-up is schematically shown in Fig.1. First an air bubble was formed at the tip of the capillary immersed into water. Then TPM was carefully injected on the bottom of the cuvette. The air bubble plays the role of a sensor, which shows a decrease in interfacial tension when hydrolyzed TPM molecules diffuse from the bottom through the volume of the solution, arrive at the bubble and adsorb at its surface. All measurements were performed at  $25^\circ\text{C}$ .

## Results and discussions

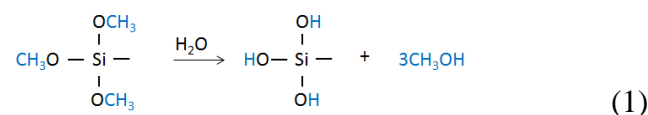
The surface tension of the air bubble in water is changing after the injection of TPM on the bottom of the cuvette according to the experimental curve shown in Fig.2. There is a first fast decreases with a number of irregularities, followed by an increase, and finally a slow decrease is observed over a very long period of time.

If we consider the first 30 min of the entire process with the higher time resolution we can distinguish some very fast decreases of the interfacial tension followed by slow increases again (Fig. 3). This phenomenon is repeated several times and is known as auto-oscillations of the surface tension [11]. In each graph two runs for the same system are shown. The curves seem to be more or less reproducible. The differences shown are due to the complicated geometry of the TPM drop at the bottom of the cuvette, the position of the bubble at the capillary in the cell and so on, so that it is difficult to maintain absolutely identical conditions for each experiment.

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## Materials

However, the strong vibration of the entire bubble at the capillary tip were observed several times simultaneously with the sharp drop in the surface tension what could be considered as an indirect indication of the presence of fluxes in the cuvette at this moment of time. Almost vertical periodical elongation and shaking of the bubble at that moment could roughly show the direction of these fluxes and confirm therefore that they were formed not in the proximity of the bubble but in the cuvette bulk.

The number of auto-oscillations can be controlled by the pH. For instance, at pH 9 (Fig. 3) the number of observed cycles is sufficiently higher than at pH 7. This is in line with the findings discussed in [1]. According to this work the hydrolysis rate is lowest at pH 7 and increases significantly in both acidic and basic conditions, in agreement with our data obtained via PAT measurements.

Higher rate of hydrolysis reaction at basic pH leads to higher concentration of products in the bulk and to the higher magnitude of autooscillations compared to pH 7. Also, the vortex movement in the bulk of the aqueous phase caused by this stronger oscillation needs more time to be damped. Therefore it can transport additional portions of solution enriched in hydrolysis products to upper surface of cuvette and induce further oscillation cycles. As a result, the number of oscillations during the same period of time is higher for pH 9.5 as shown in the figure 3.

The auto-oscillations observed here are much less regular as for example described by Kovalchuk et al. [12]. These oscillations can be completely prevented by homogenizing the concentration of the hydrolysis products in the aqueous phase done by a gentle stirring during the measurements (see scheme in Fig. 1).

In Fig. 5 the experimental results of surface tension measurements at exactly the same experimental condition as in Fig. 3a (pH 7) but with stirring and different pH of aqueous phase are shown. When using a stirrer the reaction products do not need to diffuse toward the bubble and the top water/air surface but they are homogeneously distributed in the aqueous phase. This forced convection enhances also the reaction by more than 10 times. In this way measurements of the dynamic surface tension allow recording the reaction kinetics at the water/TPM interface, which will be discussed in more detail in a forthcoming paper.

At the pH 3, silanol groups in the molecules of surface-active hydrolysis product THPM are almost fully protonated making it more hydrophobic. Due to this enhanced hydrophobicity, the

partition of THPM between oily TPM drop and aqueous bulk medium is strongly shifted to the oil phase. Therefore the working bulk concentration of THPM governing the adsorption kinetics is in this case essentially lower and leads to the slower decrease of the surface tension.

This accumulation of THPM in the TPM oily phase during the hydrolysis process at pH 3 can be observed visually by a gradual increase of its opacity (fig. 6). Therefore the effective concentration of THPM participating in decrease of dynamic surface tension is lower than at pH 7 and this is confirmed by kinetic curves for the surface tension given in the fig 6. This phenomenon will be discussed in more details in the forthcoming paper.

### **Conclusion**

It was shown that PAT measurements are suitable to monitor the hydrolysis process of TPM via changes in surface tension due to the surface active molecules produced in the hydrolysis process of TPM in contact with water and subsequently transported to the bubble surface.

Auto-oscillations of the surface tension were observed during the measurements, which are connected to a complex of different types of flows in the volume of the aqueous phase. These flows are consequences of forces caused by the products of the hydrolysis process. Firstly, the difference of densities between the aqueous phase and the hydrolysis products accumulated on the bottom cause a buoyancy force, which brings part of the surface active molecules to the air/water interface at the top; secondly, the adsorption of surfactants at the air/water interface leads to local surface tension gradients, which causes Marangoni effects, which in turn can generate vortexes of liquid in the cuvette. All these flows of the aqueous phase contribute to a transport of surfactants with a certain rate to the air bubble/water interface and lead to the changes in surface tension.

The kinetics of the reaction and hence of the surface tension can be controlled by changing the pH of the aqueous phase. For instance, at pH 7 the extent of auto-oscillations is less than at pH 9.

It is possible to prevent auto-oscillations by means of a continuous gentle stirring of the aqueous phase which helps to homogeneously distribute the formed surface active molecules in the entire aqueous phase in the cuvette. The increasing concentration of the formed surfactants can be detected more precisely and the hydrolysis reaction kinetics at the water/TPM interface becomes accelerated by more than 10 times.

## **Acknowledgements**

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Figure Captions

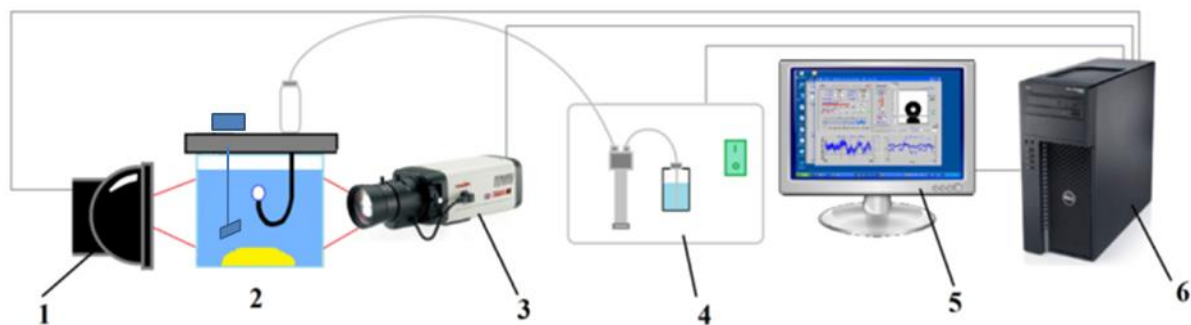
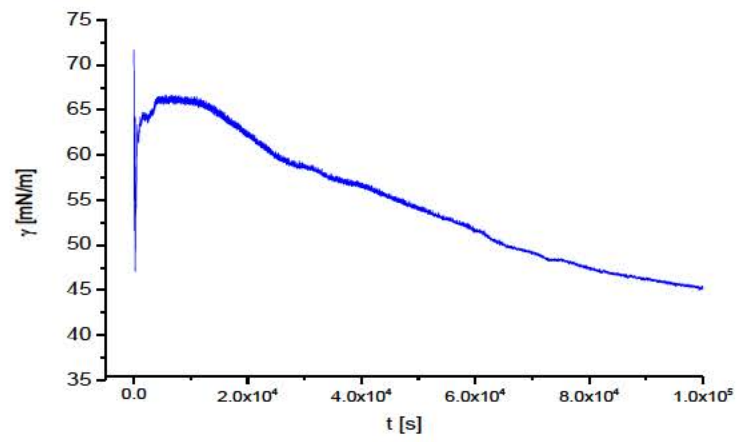
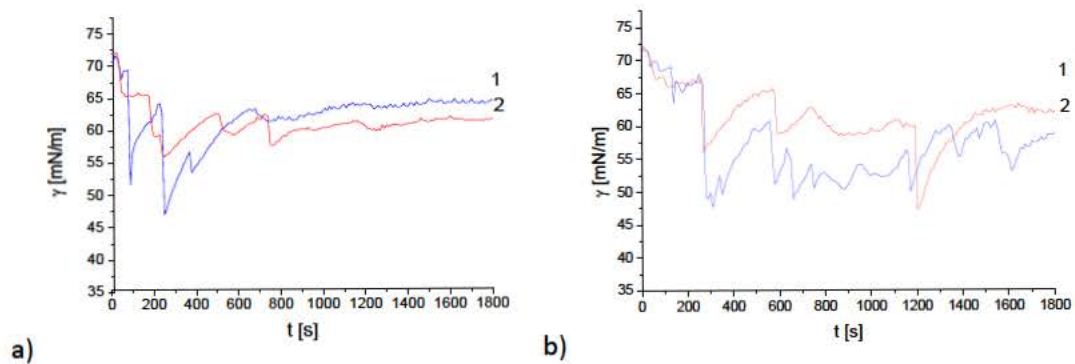


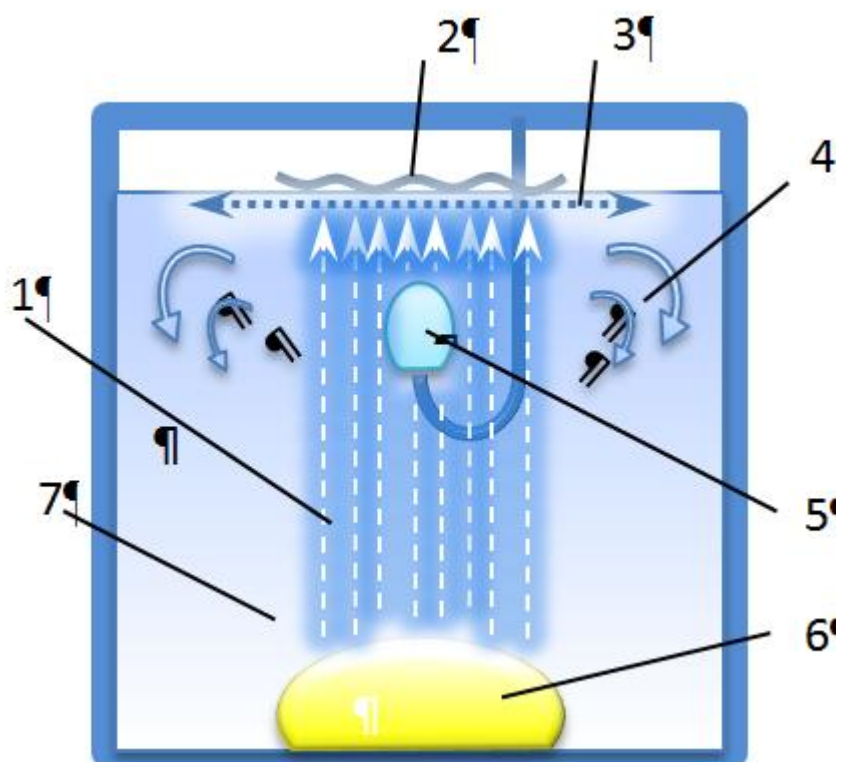
Fig. 1. - The experimental set-up for measurements of the dynamic interfacial tension: 1 – light source, 2 – cuvette filled with an aqueous buffer solution and a TPM drop at the bottom, 3 – video camera, 4 – dosing system, 5 – monitor, 6 – PC, 7 – stirrer (optional)



**Fig.2** – Dynamic surface tension of the water/air interface in presence of TPM at the bottom of the cuvette



**Fig. 3** – Irregularities of surface tension during the first 30 minutes after injection of TPM: a – at pH 7 of the aqueous phase, b – at pH 9,5 of the aqueous phase.



**Fig. 4** – TPM drop hydrolysis creates liquid flow in the cuvette: 1 – flow of TPM hydrolysis products, 2 – region on the surface of aqueous phase with low surface tension, 3 – flow of liquid due to Marangoni effect, 4 – vortex of liquid toward the bottom, 5 – air bubble at U-shape capillary, 6 – TPM oil drop, 7 – aqueous phase

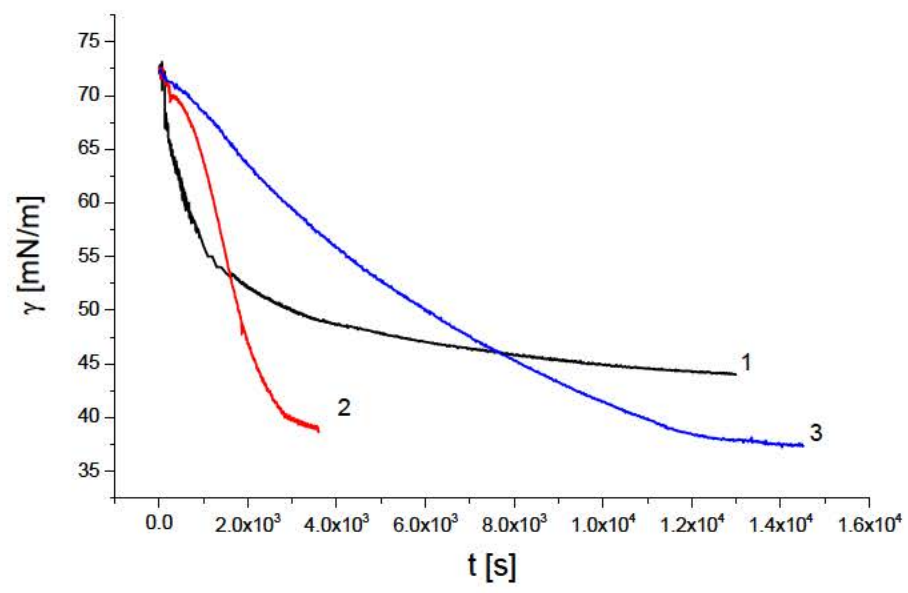
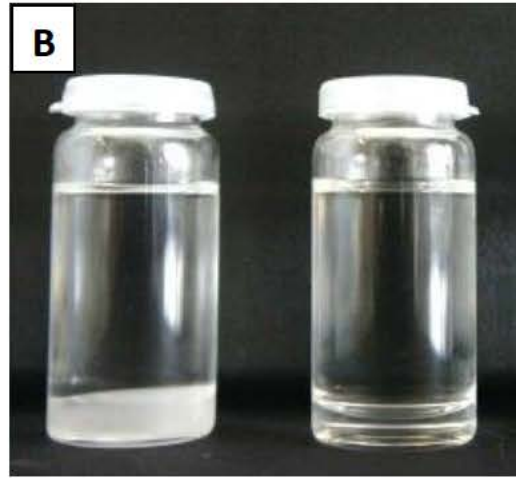
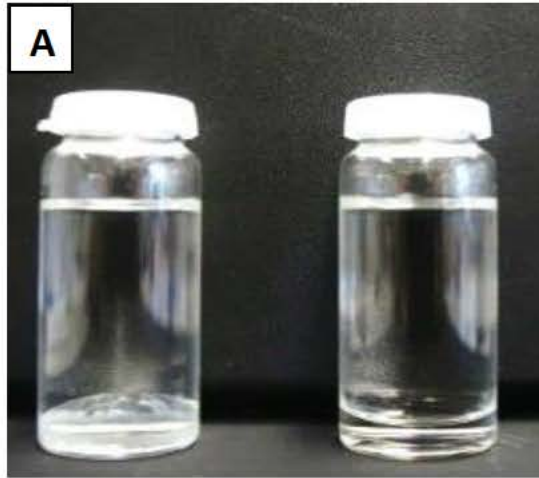


Fig. 5 – Dynamic surface tension under continuous gentle stirring at: 1 - pH 7, 2 – pH 9,5, 3 – pH 3.



**Fig. 6** – A: biphasic TPM/water system at pH 3 (left) and pH 7 (right), 5 minutes after formation; B: The same system but 60 minutes after formation.