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### Colloids and Surfaces A: Physicochemical and Engineering Aspects



journal homepage: www.elsevier.com/locate/colsurfa

# Dynamic surface tension of $C_{10}EO_8$ at the aqueous solution/hexane vapor interface as measured by bubble pressure tensiometry



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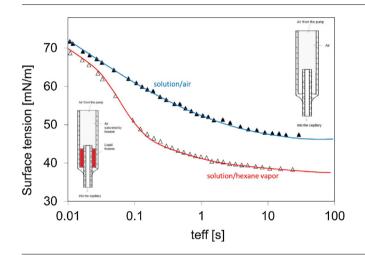
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#### HIGHLIGHTS

#### GRAPHICAL ABSTRACT

- The measuring cell of a bubble pressure analyser can be modified such that oil saturated gas bubbles can be used in measurements.
- The presence of hexane vapor in air bubbles changes the dynamic surface tension of surfactant solutions.
- The co-adsorption of hexane from the vapor phase increases the adsorption rate of surfactants.
- The co-adsorption of hexane molecules increases the surface activity of adsorbed surfactants.



#### ARTICLE INFO

Article history: Received 1 April 2015 Received in revised form 8 June 2015 Accepted 9 June 2015 Available online 19 June 2015

Keywords: Surfactant adsorption Dynamic surface tension Solution/hexane vapor interface Bubble pressure tensiometry Diffusion-controlled adsorption theory

Surfactant/alkane co-adsorption

Corresponding author.

#### The dynamic

ABSTRACT

The dynamic surface tension of aqueous solutions of  $C_{10}EO_8$  at the interfaces with air and saturated hexane vapor was measured by the maximum bubble pressure tensiometer BPA for adsorption times  $t \ge 0.01$  s. It can be shown that the dynamic surface pressure of  $C_{10}EO_8$  solutions in a saturated hexane atmosphere increases at short adsorption times with increasing surfactant concentration. The theory of diffusion controlled adsorption of two surfactants from the water and gas phases, respectively, was used for data analysis. The obtained experimental results agree with a model based on a reorientation of the  $C_{10}EO_8$  molecules, assuming a strong intermolecular interaction between hexane and  $C_{10}EO_8$  molecules in the surface layer. Alternatively, an additional enhancement of  $C_{10}EO_8$  adsorption activity can be assumed due to the presence of hexane molecules at the interface.

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#### 1. Introduction

Several studies have shown that alkanes adsorb from the gas vapor phase at the water surface [1-7] and reduce the surface

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http://dx.doi.org/10.1016/j.colsurfa.2015.06.015 0927-7757/© 2015 Elsevier B.V. All rights reserved. tension significantly. In these studies the drop profile analysis tensiometry turned out to be an excellent experimental tool and surface tension data were obtained for the adsorption of various alkanes (pentane, hexane, heptane, octane) at the water surface at room temperature [7]. In [8–13], the co-adsorption of surfactants from an aqueous solution phase and alkane from a gas vapor phase was investigated. In [11], the surface tensions of water and aqueous solutions of the non-ionic surfactant C<sub>10</sub>EO<sub>8</sub> (octaethylene glycol monodecyl ether) were measured at various concentrations in hexane saturated air by using the drop profile analysis tensiometry. For the analysis of the experimental data, an equation of state and a corresponding adsorption isotherm were derived. This theoretical model was based on the analysis of the chemical potentials of the solvent and of the surface active components in the solution bulk, in the gas phase and at the surface of the drop. The target of work presented in [12] was dedicated to the influence of the hexane partial vapor pressure on the surfactants and hexane co-adsorption. The study included cationic, anionic and non-ionic surfactants, each at different bulk concentrations and different hexane partial vapor pressures, respectively. On the basis of the model proposed in [11] the physics behind the co-adsorption was discussed.

An important field of application for the oil vapor co-adsorption from the gas phase is the simulation of the alveoli/air interface in the pulmonary system. In [13,14], the adsorption of fluorocarbon gases (FCs) to dipalmitoylphosphatidylcholine (DPPC) monolayers, taken as a simplified model of lung surfactant, and its impact on the structure and behavior of these monolayers upon compression and expansion was investigated. Overviews of the role of FCs in medicine were published in [13-18]. In particular, a discussion has been performed on the role of FCs in the treatment of acute respiratory distress syndrome, for alveolar environment of trauma patients and in pulmonary disease therapies [13,19]. In [19], the adsorption dynamics of a series of phospholipids (PLs) at the interface between aqueous solutions or dispersions of a series of phospholipids and a gas phase saturated with perfluorohexane gas (PFH) was studied by bubble profile analysis tensiometry. It was found that the PFH gas has an unexpectedly strong effect on both the adsorption rate and the equilibrium interfacial tension of the phospholipids. First, the presence of PFH in the gas phase lowered the surface tension significantly, i.e., by up to 10 mN/m. Second, the adsorption rates of all the PLs at the liquid/vapor interface were significantly accelerated up to five times in the presence of PFH at low PLs concentrations. Both effects, the surface tension reduction and the increased adsorption rate, caused by PFH point to a strong interaction of the latter with the PLs monolayer, which acts as a co-surfactant at the interface. This behavior is similar to that observed at the interface between alkane vapor and aqueous solutions of various surfactants [7-12]. PFH gas was also found to lower the kinetic barrier that opposes the displacement of albumin by dipalmitoylphosphatidylcholine at the air/water interface submitted to sinusoidal oscillations at frequencies in the range of those encountered in respiration [20].

In all studies on the adsorption of alkanes and fluorocarbons from the gas vapor phase at the surface of aqueous solutions, there is little work on the kinetics of lowering the surface tension at short adsorption times. This, however, would be especially important for investigations of respiratory systems, as in breathing the adsorption/desorption processes proceed at short times. The results in [19] indicate a high rate of the adsorption processes: for large phospholipids concentrations the results obtained by bubble profile analysis tensiometry are rather close to equilibrium at the shortest available time.

In the present work, studies were carried out by maximum bubble pressure tensiometry in the surface time range between 10 ms and several seconds. The bubble pressure experiments were performed with hexane saturated air, as it was done in [11]. It

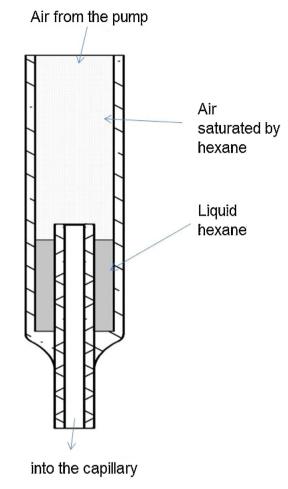


Fig. 1. Scheme of the measuring cell for BPA-1S to provide a hexane saturated atmosphere.

can be shown that the decrease in surface tension under dynamic conditions is larger at higher surfactant concentrations, and with increasing surfactant concentration the measured surface tension starts to decrease at shorter times. The results obtained are described theoretically by using a reorientation model and a diffusion mechanism for the adsorption of the surfactant  $C_{10}EO_8$ , and a non-diffusional mechanism for the adsorption of hexane. In addition a strong interaction between hexane and  $C_{10}EO_8$  molecules in the adsorption layer is assumed.

#### 2. Materials and methods

The dynamic surface tension was measured with the tensiometer BPA-1S (SINTERFACE Technologies, Germany). The instrument's design and measuring procedures were described in detail elsewhere [21–24]. For the saturation of air by hexane vapor a special measuring cell and capillary were used. The cell includes an additional chamber with liquid hexane as shown in Fig. 1, through which the air has to pass before forming bubbles at the capillary tip. To reach bubble lifetimes down to 10 ms, capillaries of 0.5 mm in diameter coupled with a bubble deflector were used. For bubble lifetimes of 10 ms the corresponding dead times were not longer than 20 ms with a bubble volume  $V_b$  of approximately 5 mm<sup>3</sup>. It was shown earlier [23,24] that such short dead times are required to measure the surface tension at times of 10 ms, since during this time the surface area of the bubble expands by approximately 20 times. Hence, the residual adsorption at the surface of a newly formed bubble corresponds to a lifetime of less than 1 ms. In addition,

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