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## Advances in Colloid and Interface Science

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# Influence of alkane and perfluorocarbon vapors on adsorbed surface layers and spread insoluble monolayers of surfactants, proteins and lipids

V.B. Fainerman<sup>a</sup>, E.V. Aksenenko<sup>b</sup>, R. Miller<sup>c,\*</sup><sup>a</sup> Medical University Donetsk, Donetsk, Ukraine<sup>b</sup> Institute of Colloid Chemistry and Chemistry of Water, Kyiv (Kiev), Ukraine<sup>c</sup> MPI Colloids and Interfaces, Potsdam, Germany

## ARTICLE INFO

Available online xxxx

## Keywords:

Surfactant adsorption  
 Protein adsorption  
 Water/hexane vapor interface  
 Effect of humidity of air  
 Hexane co-adsorption  
 Thermodynamic model

## ABSTRACT

The influence of hexane vapor in the air atmosphere on the surface tension of water and solutions of  $C_{10}EO_8$ ,  $C_nTAB$  and proteins are presented. For dry air, a fast and strong decrease of surface tension of water was observed. In humid air, the process is slower and the surface tension higher. There are differences between the results obtained by the maximum bubble pressure, pendant drop and emerging bubble methods, which are discussed in terms of depletion and initial surface load. The surface tension of aqueous solutions of  $\beta$ -casein (BCS),  $\beta$ -lactoglobulin (BLG) and human serum albumin (HSA) at the interfaces with air and air-saturated hexane vapor were measured. The results indicate that the equilibrium surface tension in the hexane vapor atmosphere is considerably lower (at 13–20 mN/m) as compared to the values at the interface with pure air.

A reorientation model is proposed assuming several states of adsorbed molecules with different molar area values. The newly developed theoretical model is used to describe the effect of alkane vapor in the gas phase on the surface tension. This model assumes that the first layer is composed of surfactant (or protein) molecules mixed with alkane, and the second layer is formed by alkane molecules only. The processing of the experimental data for the equilibrium surface tension for the  $C_{10}EO_8$  and BCS solutions results in a perfect agreement between the observed and calculated values. The co-adsorption mechanism of dipalmitoyl phosphatidyl choline (DPPC) and the fluorocarbon molecules leads to remarkable differences in the surface pressure term of cohesion  $\Pi_{coh}$ . This in turn leads to a very efficient fluidization of the monolayer. It was found that the adsorption equilibrium constant for dioctanoyl phosphatidyl choline is increased in the presence of perfluorohexane, and the intermolecular interaction of the components is strong.

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\* Corresponding author.

E-mail address: [miller@mpikg.mpg.de](mailto:miller@mpikg.mpg.de) (R. Miller).<http://dx.doi.org/10.1016/j.cis.2015.11.004>

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Please cite this article as: Fainerman VB, et al, Influence of alkane and perfluorocarbon vapors on adsorbed surface layers and spread insoluble monolayers of surfactants, proteins and lipids, Adv Colloid Interface Sci (2015), <http://dx.doi.org/10.1016/j.cis.2015.11.004>

## 1. Introduction

Adsorption of alkane vapor on water is related to a number of fundamental physical phenomena, such as intermolecular forces, wetting and oil recovery. The interactions between alkane and water molecules are determined by long-range van der Waals forces. Many results have shown that the behavior of alkane/water system is far from simple, and depends on a number of phenomena, for example, surface crystallization of alkanes. The adsorption of alkane vapor from the gas phase at the surface of a water drop was studied for alkanes of various chain lengths and for different partial pressures of alkanes in the gas phase [1–9]. In all these studies, the adsorption of alkane results in a significant decrease of the surface tension. In [6], the drop profile method was used to study the adsorption of different alkanes (pentane, hexane, heptane and octane) at the water surface. It was shown in particular that in the atmosphere saturated by hexane during a sufficiently long adsorption time, the surface tension decreases from 72 to 52–50 mN/m. Using X-ray reflectivity and neutron reflectivity methods, the thicknesses of the adsorbed alkane layers was determined in [8,9]. It was confirmed that these two methods produced identical results [8].

In [10–16], the co-adsorption of surfactants from an aqueous solution phase and alkane from a liquid and gas vapor phases was studied. In [14], the surface tension of water and aqueous solutions of the non-ionic surfactant  $C_{10}EO_8$  (octaethylene glycol monodecyl ether) was measured at various concentrations in hexane-saturated air 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 simultaneous adsorption of a soluble surfactant from an aqueous solution and a second compound from the vapor phase. The target of the work presented in [15] was 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 [14], the physics behind the co-adsorption was discussed. In [15], the dynamic surface of aqueous solutions of  $C_{10}EO_8$  at the interfaces with air and saturated hexane vapor was measured by the maximum bubble pressure method for the adsorption time interval  $t$  of 0.01 to 50 s. The theory of diffusion-controlled adsorption of two surfactants from the water and gas phases, respectively, was used. The obtained experimental results agree with a model based on a reorientation of the  $C_{10}EO_8$  molecules and intermolecular interaction between hexane and  $C_{10}EO_8$  molecules in the surface layer or an additional adsorption activity of  $C_{10}EO_8$  due to the presence of hexane molecules at the interface. The theory presented in [16] assumes the adsorption of protein molecules from the aqueous solution and a competitive adsorption of alkane molecules from the alkane phase. The dynamic surface tension of aqueous solutions of  $\beta$ -casein (BCS),  $\beta$ -lactoglobulin (BLG) and human serum albumin (HSA) at the interfaces with air and air-saturated hexane vapor was measured by drop profile analysis tensiometry [17]. The results indicate that the equilibrium surface tension in the hexane vapor atmosphere is considerably lower (by 13–20 mN/m) as compared to the values at the interface with pure air. A theoretical model is developed which assumes a double layer adsorption in these systems, with the first layer composed of protein mixed with hexane, and the second layer formed by hexane only. The experimental equilibrium surface tension data for the BCS solutions is in a perfect agreement with calculated values. The drop profile method is used in [18] to study the influence of hexane vapor in the air atmosphere on the surface tension of water. It was shown that the results of the experiments depend essentially on the air humidity. The reorientation model which assumes several states of adsorbed molecules with different molar area values is proposed. A new theoretical model is developed to describe the influence of alkane vapor on the surface tension of the solution of surfactant with variable molar area in the adsorption layer. This model assumes that the first layer is composed of

a surfactant mixed with alkane, and the second layer is formed by the alkane only, adsorbed on the alkane and the surfactant in the first layer. The processing of the experimental data for the equilibrium surface tension of  $C_{10}EO_8$  resulted in a perfect agreement between the observed and calculated values. It is essential that the model parameters involved in the calculations were exactly the same as those found for the individual  $C_{10}EO_8$  solution and hexane vapor at the interface with pure water.

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 [19,20], the adsorption of fluorocarbon gases (FCs) to dipalmitoyl phosphatidyl choline (DPPC) monolayers, taken as a simplified model of lung surfactant, and its impact on the behavior of these monolayers upon compression and expansion was studied. The role of FCs in medicine was presented in [19–24]. In particular, the role of FCs in the treatment of acute respiratory distress syndrome, for the alveolar environment of trauma patients and in pulmonary disease therapies was discussed. In [25], the adsorption dynamics at the interface between aqueous solutions or dispersions of a series of phospholipids (PLs) 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 [10–18]. PFH gas was also found to lower the kinetic barrier that opposes the displacement of albumin by dipalmitoyl phosphatidyl choline at the air/water interface subjected to sinusoidal oscillations at frequencies in the range of those encountered in respiration [26]. It should be noted that the results obtained for fluorocarbon gases [25] using the bubble profile method appear much more stable as compared to those obtained by the drop profile method [6].

In [27], an equation of state for insoluble monolayers was applied to describe the isotherms of DPPC in the presence of fluorocarbons in the gas phase (data taken from [19]). The co-adsorption mechanism of DPPC and the fluorocarbons molecules manifests itself in remarkable differences of the cohesion surface pressure  $\Pi_{coh}$ . When fluorocarbon molecules are adsorbed and interact with DPPC, the interaction energy between DPPC molecules is reduced. This leads to a very effective fluidization of the monolayer. The data on equilibrium and dynamic surface tension for phospholipids adsorbed from an aqueous solution (or dispersion) in the absence and presence of perfluorohexane (PFH) in the adjacent vapor phase (data taken from [25]) have been analyzed theoretically in [27]. It was found that the adsorption equilibrium constant for DiC8-PC (dioctanoyl phosphatidyl choline) is increased in the presence of PFH and the dynamic surface tensions of the given systems at low DiC8-PC concentrations are described by the diffusion-controlled adsorption mechanism.

This review starts with the theoretical description of the influence of oil vapor on the thermodynamics of the co-adsorption of surfactants and proteins from an aqueous solution phase and oil molecules from a gas vapor phase. The experimental results regarding the co-adsorption of surfactants and proteins from solutions and gaseous alkanes are analyzed. An equation of state for insoluble monolayers is applied to describe the isotherms of DPPC in the presence of fluorocarbon gas. The data on surface tensions for phospholipids adsorbed from an aqueous solution (or dispersion) in the absence and presence of perfluorohexane in the adjacent vapor phase are analyzed.

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