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Effect of partial vapor pressure on the co-adsorption of surfactants and hexane at the water/hexane vapor interface

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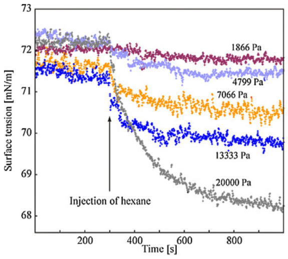
HIGHLIGHTS

- The adsorption of surfactants at the water/air interface is enhanced due to the presence of alkane vapor in the air phase.
- The alkane vapor effect can be described in terms of a co-adsorption of alkane molecules.
- The alkane vapor effect depends on the partial vapor pressure.
- A thermodynamic model developed for surfactant mixtures described the co-adsorption process.
- The alkane vapor co-adsorption effect depends on the surface activity and type of the surfactant.

GRAPHICAL ABSTRACT



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ABSTRACT

The adsorption of surfactants from aqueous solution at the water/air interface is changed when the air phase contains hexane vapor. This co-adsorption of surfactant and hexane depends on the hexane vapor pressure. A thermodynamic model developed for the adsorption of surfactant mixtures can be adapted to the present situation. The surfactants studied were SDS, C_{12}TAB and C_{12}DMPO, and the dependence of their adsorption characteristics on the partial hexane vapor pressure was determined. The co-adsorption of hexane from the vapor phase increases the surface activity of the adsorbing surfactants.

1. Introduction

Surfactants have been used for a long time in many processes and technologies, such as detergency, food processing, pharmaceutical and cosmetic industries. The importance of understanding the adsorption behavior of surfactants and the structure of their adsorption layers at liquid/air and liquid/liquid interfaces is the reason for the long time research [1–7]. However, besides liquid/air and liquid/liquid interfaces, recently it was found that the liquid/vapor interface represents an intermediate state [8]. The adsorption of surfactants at such water/oil vapor interfaces is governed by the mutual interaction between surfactants and oil

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molecules. The oil molecules enhance the surfactant's adsorption from the water bulk and, on the other side, the surfactant adsorption layer encourages the oil molecules to adsorb from the vapor phase [9,10]. In a recent paper describing surface tension studies at the water/oil vapor interface [10] it was managed to describe the physics of the simultaneous adsorption of C_nTAB from the aqueous solution and hexane from the vapor phase by using the theoretical model proposed for the co-adsorption of surfactants from adjacent liquid phases [11].

Surfactant adsorption layers at water/oil vapor interfaces are still insufficiently investigated and there are quite a number of pending questions. So far just few papers have been dedicated to the thermodynamics of adsorption at water/oil vapor interfaces. However, up to now there is a lack of systematic work on the kinetics and dilational rheology of such adsorption layers. The reason for this might be the difficulties in performing the experiments and the peculiarities to be considered for the experimental set-up for studies at the water/vapor interface. Moreover, the effect of surfactant concentration on the co-adsorption at water/vapor interfaces has been investigated just for a small number of particular surfactants. Understanding of the molecular structure of the surfactant adsorption layer requires suitable theoretical models as proposed recently in [10].

The target of this paper is to study the influence of the partial oil vapor pressure on the thermodynamics of the co-adsorption of surfactants and oil (hexane) molecules. We investigated one cationic, anionic and non-ionic surfactant, each at different bulk concentrations and different partial hexane vapor pressures, respectively. In order to better understand the physics behind the co-adsorption the experimental results were discussed on the basis of the model proposed in [11] for the competitive adsorption of a surfactant from the solution, and of alkane from the gaseous phase.

2. Materials and methods

In this work we studied the following surface active agents: SDS (sodium dodecyl sulphate, $M_w = 288.37$ g/mol), $C_{12}TAB$ (dodecyl trimethylammonium bromide, $M_w = 308.35$ g/mol) and $C_{12}DMPO$ (dodecyl dimethylphosphine oxide, $M_w = 246.37$ g/mol). All substances were purchased from Fluka (Switzerland) with a purity of >99%. Before use, the substances were additionally purified by a triple recrystallization from an ethanol/acetone mixture. All solutions were prepared with ultrapure Milli-Q water (resistivity = 18.2 MΩ cm). Hexane was purchased from Fluka, distilled, purified with alumina oxide and subsequently saturated with ultrapure Milli-Q water. Squalene was purchased from Sigma Aldrich. Mixing hexane and squalene in a certain ratio enables to control the partial hexane vapor pressure. In this work we used hexane and squalene in the mixing ratios $M_f = 0.14$, 0.26, 0.34, 0.48, 0.64, 0.76 and 0.87, which produce the partial hexane vapor pressures P_1 of 14, 25, 36, 53, 80, 100 and 120 mmHg, respectively, according to [12]. All experiments were performed at room temperature (23–24 °C).

For the surface tension measurements the drop profile analysis tensiometer PAT-1 (SINTERFACE Technologies, Germany) was applied [13,14]. A drop of the aqueous surfactant solution was formed at the tip of a capillary in a closed cuvette (3 cm × 3 cm × 3 cm). At the bottom of this cuvette about 1 ml of the hexane/squalene mixture was deposited and an equilibrium hexane vapor pressure was established within less than 5 min. In some experiments the hexane/squalene mixture was injected into the cell after a certain time, in general after 5 min of drop pre-ageing. Any further experimental details were explained elsewhere [8,10].

3. Thermodynamic model for the co-adsorption of surfactants and alkanes

The model approach to the description of the co-adsorption of alkane from the gaseous phase and the surfactant from the solution was developed in [11]. In the present publication a simplified version of the theory is used, which disregards the surfactant's influence on the adsorption of alkane vapor, previously accounted for by the introduction of the model parameter k_1. The mutual influence of the solution components on their adsorption is described in the model [11] by the cross-interaction constant a_{12}, which corresponds to the attraction between the alkane and surfactant molecules. It should be noted that the alkane influence on the surfactant adsorption could be accounted for either by the correction of the values of the surfactant adsorption equilibrium constant assuming it to depend on the partial alkane vapor pressure, or by the dependence of the alkane equilibrium adsorption constant on the surfactant concentration, or the dependence of the alkane/surfactant cross-interaction constant on the alkane vapor pressure.

The model equations which govern the system behavior are briefly summarized below. The equation of state for the mixed surface layer reads

$$-\frac{\Pi\omega_0^*}{RT} = \ln\left(1-\theta_1-\theta_2\right) + a_1\theta_1^2 + a_2\theta_2^2 + 2a_{12}\theta_1\theta_2 \tag{1}$$

with

$$\omega_0^* = \frac{\omega_{10}\theta_1 + \omega_{20}\theta_2}{\theta_1+\theta_2}, \tag{2}$$

here Π is the surface pressure, R is the gas law constant, T is the temperature, $\theta_i = \omega_i \cdot \Gamma_i$ is the surface coverage, Γ_i is the adsorption, ω_{i0} is the molar area at zero surface pressure by molecules of component i ($i = 1$ or 2 for the alkane and the surfactant, respectively). The coefficients a_1, a_2 and a_{12} are the Frumkin interaction constants. The molar area of the component 2 (surfactant) can be approximated by a linear dependence on surface pressure Π and the total surface coverage $\theta = \theta_1 + \theta_2$:

$$\omega_{21} = \omega_{20}\left(1-\varepsilon_2\Pi\theta\right), \tag{3}$$

The coefficient ε_2 is the two-dimensional relative surface layer compressibility which characterizes the intrinsic compressibility of molecules in the surface layer.

For the alkane molecules the adsorption isotherm reads

$$d_1P_1 = \frac{\theta_1}{\left(1-\theta_1-\theta_2\right)}\exp\left[-2a_1\theta_1 - 2a_{12}\theta_2\right], \tag{4}$$

and for the water-soluble surfactant

$$b_2c_2 = \frac{\theta_2}{\left(1-\theta_1-\theta_2\right)}\exp\left[-2a_2\theta_2 - 2a_{12}\theta_1\right] \tag{5}$$

here d_1 and b_2 are the corresponding model parameters referring to the surface activity of the two adsorbing components, P_1 is the partial pressure of the alkane vapors, and c_2 is the surfactant concentration in the aqueous solution bulk.

4. Results and discussion

4.1. Hexane adsorption at the water/vapor interface

The mechanism of the adsorption of hexane molecules from the vapor phase at the pure water surface cannot yet be fully explained. However, one of the driving forces is the partial vapor pressure of the hexane. In Fig. 1 the surface tension of a pure water drop in a hexane vapor atmosphere is shown for different hexane vapor pressures.