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

N. Mucic, N. Moradi, A. Javadi, E.V. Aksenenko, V.B. Fainerman, R. Miller

**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.

**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.

**KEYWORDS**
Adsorption of surfactants
Hexane co-adsorption
Drop profile tensiometry
Thermodynamic model
Water/vapor interface

**ARTICLE INFO**
Article history:
Received 30 August 2014
Received in revised form 31 December 2014
Accepted 2 January 2015
Available online 9 January 2015

**GRAPHICAL ABSTRACT**

**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
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 C20TAB 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, to up 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, $M_w = 288.37\text{ g/mol}$), C12TAB (dodecyl trimethylammonium bromide, $M_w = 308.35\text{ g/mol}$) and C12DMPO (dodecyl dimethylphosphine oxide, $M_w = 246.37\text{ g/mol}$). 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 (resitivity = 18.2 MΩcm). 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

$$-\frac{\Pi_0\sigma_0}{RT} = \ln \left(1 - \theta_1 - \theta_2\right) + a_1\theta_1^2 + a_2\theta_2^2 + 2a_{12}\theta_1\theta_2$$

(1)

with

$$\omega_0 = \frac{\omega_{10}\theta_1 + \omega_{20}\theta_2}{\theta_1 + \theta_2}.$$  

(2)

here $\Pi$ is the surface pressure, $R$ is the gas law constant, $T$ is the temperature, $\theta_i = \omega_i\Gamma_i$ is the surface coverage, $\Gamma_i$ is the adsorption, $\omega_{0i}$ 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 $\Pi$ and the total surface coverage $\theta = \theta_1 + \theta_2$:

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

(3)

The coefficient $\varepsilon_2$ 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

$$d_1P_1 = \frac{\theta_1}{\left(1 - \theta_1 - \theta_2\right)} \exp \left[-2a_1\theta_1 - 2a_2\theta_2\right].$$  

(4)

and for the water-soluble surfactant

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

(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.
A dynamic surface tension γ of the pure water/hexane interface at different partial hexane vapor pressures P1 is shown in Fig. 1. After 300 s the hexane/squalene mixture was injected into the cuvette to form the vapor phase. It is seen from Fig. 1 that the surface tension starts decreasing immediately. After about 700 s a quasi-equilibrium is reached. The term “quasi-equilibrium” used for the present experiments was explained elsewhere [10]. At longer surface ages the hexane starts to condensate at the water surface, which drastically changes the shape of the water drop. Once the hexane condensation sets in it became impossible to measure real surface tension values due to the thick hexane layer at the drop surface, which due to gravity subsequently drains down and forms a liquid lens at the drop apex (see details in [10]). Therefore, in Fig. 2 we present the surface tension values as a function of the hexane vapor pressure taken after 1000 s, at adsorption equilibrium but yet without any impact of a condensed hexane film on the drop surface. We can see that with increasing vapor pressure the quasi-equilibrium surface tension of the water/hexane vapor interface decreases. This means the higher the pressure the more hexane molecules adsorb at the water drop surface. The theoretical curve in Fig. 2 was calculated using Eqs. (1) and (4) with β2 = 0; the hexane adsorption parameters obtained from the best fit of the theoretical values are: d1 = 1.4 × 10−5 1/Pa, ω10 = 2.0 × 105 m2/mol, a1 = 0.7, ε1 = 0. Note that the d1 value is lower than that obtained in [11]; this can possibly be ascribed to the fact that the adsorption time in [11] was 8000 s, and therefore the condensation of the alkane could occur on the drop surface leading to the formation of liquid lenses.

4.2. Co-adsorption of SDS at the water/vapor interface

To study the behavior of anionic surfactants at the water/hexane vapor interface we have performed experiments with SDS solutions in the same way like those for the pure water/hexane vapor interface. For the studied concentrations the SDS molecules adsorb at the water surface within 300 s and the measured surface tensions are equilibrium values [8,15]. After 300 s the SDS solution drops were exposed to the hexane vapor at a certain partial pressure. The interfacial tension started decreasing immediately due to the co-adsorption of hexane molecules. When the surface tension equilibrates, the hexane adsorption attains the equilibrium. In Fig. 3 we plotted these values against the partial vapor pressure for four different SDS concentrations. As one can see, with increasing surfactant concentration the surface tension decreases, and with increasing partial hexane vapor pressure the surface tension decreases further. The reason for this is the co-adsorption of hexane and SDS molecules in the adsorption layer.

The surface tension isotherms in Fig. 3 are fitted with the adsorption model given by Eqs. (1)–(5) for a competitive adsorption. The values of the hexane adsorption parameters are listed above; the model parameters for SDS were taken from [9] to be ω20 = 3.5 × 105 m2/mol, a2 = 0 and ε2 = 0.005 mN/m. The values of b2 and a12 are obtained by fitting the theoretical dependencies to the experimental data and summarized in Table 1.

The value of the vapor pressure influences the SDS adsorption. This is shown by the trend of the SDS adsorption coefficient b2 with increasing hexane vapor pressure. It is seen from Table 1 that for mixed SDS/hexane adsorption layers the intermolecular SDS interaction with hexane is relatively weak (a12 = 0.2); however, the constant b2 becomes significantly higher (by a factor of 3 in the studied range of hexane partial pressures). Note that the account for the mutual enhancement of adsorptions due to the coefficient a12 is essential when the adsorptions of the components are close.
to each other, while the variation of the coefficient \( b_2 \) does not depend on the hexane and surfactant adsorption throughout the entire range of concentrations and partial pressures.

4.3. Co-adsorption of C\(_{12}\)TAB at the water/vapor interface

The behavior of C\(_{12}\)TAB adsorption layers exposed to hexane vapor was studied in the similar way like that for SDS (see Fig. 4). After equilibration of the C\(_{12}\)TAB adsorption layer the respective hexane/squalene mixture was injected into the cell in order to establish the required partial pressure. Shortly after the injection, the surface tension started decreasing, again due to the co-adsorption of hexane molecules. From Fig. 4 it is seen that with increasing hexane vapor pressure the surface tension decreases due to the co-adsorption of hexane.

The curves show the theoretical dependencies calculated using the adsorption model expressed by Eqs. (1)–(5). The model parameters for C\(_{12}\)TAB solutions are: \( \omega_2 = 2.5 \times 10^3 \text{ m}^2/\text{mol}, \beta_2 = 0 \) and \( \epsilon_2 = 0.005 \text{ mN} \) for all \( P_1 \) values, as reported in [9]. The values of the model parameters for hexane were listed above in the text, and the optimized \( b_2 \) and \( \alpha_12 \) values are shown in Table 1.

The value of the hexane vapor pressure influences the C\(_{12}\)TAB adsorption. For C\(_{12}\)TAB solutions the optimum way to account for this influence is to increase the \( \alpha_12 \) value (which only slightly depends on the partial hexane vapor pressure) to within the range of 0.6 to 1.0, and by the variation of \( b_2 \) value which becomes by a factor of 1.8 higher in the studied range of the hexane vapors partial pressure.

4.4. Co-adsorption of C\(_{12}\)DMPO at the water/vapor interface

C\(_{12}\)DMPO is a non-ionic surfactant with the same hydrophobic alkyl chain length like SDS and C\(_{12}\)TAB, however, it possesses much stronger surface activity than the two ionic surfactants above. Therefore, C\(_{12}\)DMPO adsorbs at much lower bulk concentrations. The experiments were performed in the similar way as described above and the results are shown in Fig. 5. Again, when the surfactant adsorption layer is exposed to hexane vapor, the surface tension additionally decreases.

The experimental results in Fig. 5 are fitted with the competitive adsorption model given by Eqs. (1)–(5). The model parameters taken for C\(_{12}\)DMPO solutions were identical to those reported in [16]: \( \omega_2 = 2.45 \times 10^3 \text{ m}^2/\text{mol}, \beta_2 = 0.35 \) and \( \epsilon_2 = 0.003 \text{ mN} \) for all \( P_1 \) values. The values of model parameters for hexane were listed above in the text, and the optimized \( b_2 \) and \( \alpha_12 \) values are shown in Table 1.

It is seen from Table 1 that for the non-ionic surfactant C\(_{12}\)DMPO the enhancement of the adsorption of both substances is best described by the intermolecular interaction between the hexane and C\(_{12}\)DMPO, \( \alpha_{12} = 2.5 \). This high value obtained from the fitting is due to the significant decrease of surface tension at low surfactant concentrations. The \( b_2 \) values are virtually the same for different partial pressures of hexane. Thus, the model expressed by Eqs. (1)–(5) for fixed \( b_2 \) and \( \alpha_12 \) values provides a good description for the adsorption of the hexane/C\(_{12}\)DMPO mixtures within the entire range of partial hexane pressure and C\(_{12}\)DMPO concentrations.

<table>
<thead>
<tr>
<th>( P_1 ) (Pa)</th>
<th>SDS</th>
<th>C(_{12})TAB</th>
<th>C(_{12})DMPO</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha_{12} )</td>
<td>( b_2 \text{ (m}^2/\text{mol}) )</td>
<td>( \alpha_{12} )</td>
<td>( b_2 \text{ (m}^2/\text{mol}) )</td>
</tr>
<tr>
<td>1866</td>
<td>0.2</td>
<td>20.0</td>
<td>0.6</td>
</tr>
<tr>
<td>3466</td>
<td>0.2</td>
<td>22.0</td>
<td>0.9</td>
</tr>
<tr>
<td>4799</td>
<td>0.2</td>
<td>26.3</td>
<td>1.0</td>
</tr>
<tr>
<td>7066</td>
<td>0.2</td>
<td>33.3</td>
<td>1.0</td>
</tr>
<tr>
<td>10,666</td>
<td>0.2</td>
<td>47.3</td>
<td>0.7</td>
</tr>
<tr>
<td>13,333</td>
<td>0.2</td>
<td>61.3</td>
<td>1.0</td>
</tr>
<tr>
<td>16,000</td>
<td>–</td>
<td>–</td>
<td>0.8</td>
</tr>
</tbody>
</table>
5. Discussion

In the present study we measured the surface tension of aqueous surfactant solutions against hexane vapor and it was shown that the partial vapor pressure has a significant effect on the surface tension. The hexane molecules interact with the hydrophobic parts of the surfactant molecules in the adsorbed layer, which results in an additional decrease in surface tension. In order to analyze the experimental results, we compared the difference $\Delta \Pi$ of the equilibrium surface tension before and after hexane vapor release, respectively. For each surfactant concentration, with increasing vapor pressure, this surface pressure difference increases. The surface activity of the studied surfactants has the following order: $C_{12}$TAB < SDS < $C_{12}$DMPO. The presence of the vapor phase does not change the order of the surface activity of the surfactants as it can be seen from Table 1 by comparing the adsorption coefficients $b_2$. For each surfactant concentration with increasing hexane vapor pressure the difference $\Delta \Pi$ increases more for the stronger surface active surfactants. For example, one can compare this difference for aqueous solutions of surfactants with the addition of hexane with the difference measured without the presence of hexane. While the surface tension decrease without the addition of hexane is approximately the same for $C_{12}$DMPO and $C_{12}$TAB, with the addition of hexane this difference $\Delta \Pi$ for the $C_{12}$DMPO solutions is approximately by a factor of 1.5 higher than that for the $C_{12}$TAB solutions. On the other hand, the hexane adsorption properties ($b_1$ and $\alpha_1$) for the different surfactant adsorption layers have the same values, i.e. there is not any order in the surface activity of hexane molecules.

It should be noted that there is a good agreement between the experimental data and theoretical results for all the systems studied. The theoretical model used here [11] assumes the alkane adsorption from the gaseous phase and the surfactant compressibility in the surface layer. These effects were not accounted for in the model of mixed monolayers which assumes the ideal entropy of the surface layer [17–20]. This theory, in turn, is the extension of the Frumkin model for solutions of individual surfactants.

Figs. 6–8 illustrate the dependence of the adsorption layer coverage by hexane and surfactants molecules on the surfactant concentration and the partial hexane vapor pressure. The model parameters used for the calculations are the same that were used to calculate the theoretical curves shown in Figs. 3–5.

It is seen from Fig. 6 that for mixed SDS solutions the hexane adsorption is insignificant throughout the whole concentrations range, and for the SDS concentration $10^{-5}$ M it is similar to that at the water/hexane interface. This fact can be attributed to a low $\alpha_1$ value; however the presence of hexane in the surface layer results in a significant increase of the $b_2$ value (see Table 1).

Fig. 7 illustrates the dependence of the adsorption layer coverage by $C_{12}$TAB and hexane molecules on the $C_{12}$TAB concentration. It is seen that with the increase of the hexane partial pressure its adsorption becomes higher, while the increase of the $C_{12}$TAB is rather insignificant, rather unlike the results shown in Fig. 6 for the SDS-hexane system. This result corresponds to the parameters shown in Table 1: the intermolecular interaction for the $C_{12}$TAB-hexane system is stronger, while the increase of the surfactant equilibrium adsorption constant is less pronounced.

The most interesting results were obtained for $C_{12}$DMPO solutions, as shown in Fig. 8. Strong intermolecular attraction (see Table 1) leads to a significant increase of hexane adsorption at low surfactant concentrations. It should be noted that in the framework of the theoretical model used here, the significant increase of $\Delta \Pi$ for $C_{12}$DMPO solutions at surface pressure values below 20 mN/m (without the hexane addition) could be reproduced only by the...
increase of the model parameter $a_{12}$. Therefore, the strong increase of $C_{12}$DMPO adsorption with increasing partial hexane vapor pressure occurs only at low $C_{12}$DMPO concentrations. With increasing surfactant concentration its adsorption becomes virtually independent of the hexane partial pressure, and at a pressure of 16,000 Pa even becomes smaller due to large adsorption of hexane.

6. Conclusions

Our results demonstrate the influence of the partial hexane vapor pressure on the surface tension behavior of pure water and surfactant solutions. It was shown that the exposition of a surfactant adsorption layer to a hexane vapor atmosphere leads to a co-adsorption of hexane molecules. The amount of co-adsorbed hexane depends directly on the partial vapor pressure, leading to an increased surface pressure. Moreover, it was found that the co-adsorption of hexane molecules in a surfactant adsorption layer does depend on the surfactant’s surface concentration and on the partial hexane vapor pressure. The co-adsorption of hexane molecules does not change the order of the surface activity of the surfactants. In surfactant adsorption layers, the surfactant molecules determine the surface properties while the hexane molecules co-adsorb from the vapor phase and enhance the surfactants’ adsorption by providing a hydrophobic environment for the hydrophobic alkyl chains. The theoretical model used provides good description of experimental results and is capable to determine the adsorption characteristics which govern the adsorption of hexane and surfactant. At the present state there are yet several open questions regarding the water/alkane vapor interfaces. Additional work is required on the dynamics and surface rheology of the co-adsorption of hexane and other alkanes from the vapor phase and its theoretical understanding. Also, the influence of hexane (alkane) vapor on the adsorption of surfactants at very low bulk concentrations is an exciting subject of further investigations.

Acknowledgements

The work was financially supported by projects of the DFG SPP 1506 (Mi1418/18-2), and the DLR (50WM1129).

References


