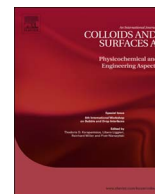




Contents lists available at ScienceDirect

Colloids and Surfaces A

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

Adsorption of alkane vapor at water drop surfaces

T. Kairaliyeva^{a,b}, V.B. Fainerman^c, E.V. Aksenenko^d, V.I. Kovalchuk^e, Yu. I. Tarasevich^d,
R. Miller^{a,*}

^a Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

^b Kazakh National Research Technical University K.I. Satpayev, Almaty, Kazakhstan

^c SINTERFACE Technologies, Berlin, Germany

^d Institute of Colloid Chemistry and Chemistry of Water, Kyiv (Kiev), Ukraine

^e Institute of Biocolloid Chemistry, Kyiv (Kiev), Ukraine

ARTICLE INFO

Keywords:

Water/heptane vapor interface
Drop profile analysis tensiometry
Dynamic surface tensions
Adsorption kinetics
Effect of temperature

ABSTRACT

The influence of temperature on the dynamic surface tension of water in heptane vapour is studied using drop profile analysis tensiometry. The water drops are formed in air saturated by heptane and water vapours. For long life times a new phenomenon is found: a sharp decrease of surface tension from about 60 mN/m down to 30 mN/m. The time until this sharp surface tension sets in decreases with increasing temperature. This phenomenon is attributed to the formation of heptane adsorption layers with a significant thickness.

To ensure that the sharp surface tension decrease is not an artefact, the experimental error (deviation of drop profiles from the Young-Gauss-Laplace equation) was determined using harmonic oscillations imposed to the surface of pure heptane drops. It was shown that fitting errors below 10 μm in the determination of the drop radius do not affect the calculated surface tension value. The sharp surface tension decrease was observed with fitting errors below 5 μm , so that this phenomenon was explained to be caused by the formation of multilayers. The surface tensions and adsorbed amounts are described by a model developed earlier.

The experimental results depend essentially on the experimental method used. In another experiment the atmosphere in the measuring cell was pre-saturated only by water vapour, and heptane (pentane) was added onto the cell bottom just immediately before the water drop was formed. The increase of temperature results in a slower adsorption process which is opposite to the case where the composition of the mixed atmosphere inside the cell was established prior to the experiments.

1. Introduction

The experimental results and theoretical models for the adsorption of alkanes from the gas phase at the surface of water drops, also the competitive adsorption of alkanes from the gas phase and surfactants (or proteins) from aqueous solution drops were studied recently [1–11]. It was shown that the adsorption of alkanes from the gas phase results in an essential decrease of the surface tension of water or aqueous protein (surfactant) solutions. Moreover, measurements presented in [1] demonstrate that the adsorption of alkanes on the surface of water drops results in a condensation of the alkane molecules at the water drop surface and the formation of liquid films. It should be noted that the experimental results are quite unstable (the deviation between the parallel experiments amounts to as much as ± 2 mN/m), which could possibly be ascribed to the instable humidity of the air in the measuring cell. It was shown in [10] that the influence of hexane vapor on the surface tension of water depends essentially on the air humidity. At the

interface with dry air a fast and strong decrease of surface tension was observed but in humid air the process was found to be slower and the surface tension higher.

In [11] the dynamic surface tension for water and aqueous C_{14}EO_8 solution drops at the interface to air saturated by pentane, hexane, heptane and toluene, respectively, were presented. The experimental results are best described by a model which implies a diffusion control for the C_{14}EO_8 molecules and the existence of a kinetic barrier for the alkane molecules. The desorption of alkanes from the surface layer after equilibration and their subsequent removal from the measuring cell was studied in [11] as well. The desorption process was shown to be slow for heptane and hexane. However, for the pentane vapor the desorption is quite rapid, and after the desorption commences the surface tension becomes equal to that for the interface with pure air.

The fundamental experimental and theoretical studies of adsorption of alkanes from the gas phase at a water surface by Pethica and co-workers [12–16] should be noted here. The thickness of such adsorbed

* Corresponding author.

E-mail address: rup_miller@gmx.de (R. Miller).

<http://dx.doi.org/10.1016/j.colsurfa.2017.04.002>

Received 30 January 2017; Received in revised form 28 March 2017; Accepted 1 April 2017
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alkane layers was determined in [17,18] using X-ray and neutron reflection and it was found to be up to 4–5 nm. The process of thickness increase is extremely slow: it needs 200 h to attain the final value. For the adsorption process during 10 h the layer thickness for heptane was 1.5 nm. The co-adsorption of alkane from the vapor phase at interfaces covered by ionic and non-ionic surfactants at different temperatures was studied in [19,20], and a packing model for both the oil and surfactant chains in the mixed layer was proposed. The adsorption of fluorocarbon gases on the surface of insoluble adsorbed monolayers can lead to a very efficient fluidization of the monolayer [7,21–24].

In the present work, we study the influence of temperature (in the range of 20–50 °C) on the dynamic surface tension of water drops (as measured by the drop shape method) in air saturated by heptane and pentane vapour, respectively. It is shown that at long drop ageing times in heptane vapor, a sharp decrease of surface tension (from 55–60 mN/m to 30–40 mN/m) occurs. The time at which this sharp decrease sets in becomes shorter with increasing temperature: 10000–15000 s at 20 °C, and 500–700 s at 50 °C. This phenomenon could be attributed to the formation of heptane adsorption layers of a significant thickness. The experimental error was estimated in a model experiment by imposing harmonic oscillations with a frequency of 0.5 Hz and an area amplitude of 15–30 % of the surface of a water drop in pure hexane vapour. This high magnitude was chosen to maximize possible errors. It was shown that errors in drop radius measurements below 10 μm do not affect the surface tension values. The sharp surface tension decrease was observed with fitting errors below 5 μm; therefore, the sharp surface tension decrease caused by the formation of multilayers is real.

2. Theory

A theoretical model of co-adsorption of surfactant molecules from the solution bulk and alkane molecules from the ambient gaseous phase at a drop surface was developed in [11]. The thermodynamic model for the adsorption of surfactants from solutions implies that the adsorbed molecules can exist in different states (conformations) with different molar areas [25]. The equation of state and adsorption isotherms for the mixed (surfactant + alkane) first adsorption layer and the second layer of alkane molecules adsorbed on this first mixed layer were derived in [8]. The model assumes an intermolecular interaction between the alkane molecules [26]. In absence of surfactant, only the alkane is adsorbed from the gas phase at the drop surface. Then, the equation of state for this model reads:

$$-\frac{\Pi\omega_A}{RT} = \ln(1 - \theta_{A1}) + \ln(1 - \theta_{A2}\theta_{A1}) + a_A(\theta_{A1}^2 + \theta_{A2}^2) \quad (1)$$

Here R is the gas law constant, T is the temperature, Π is the surface pressure ($\Pi = \gamma_0 - \gamma$), and γ and γ_0 are the surface tensions of the solution and the solvent, respectively. The subscripts A1 and A2 refer to the alkane in the first and second adsorption layer, respectively; $\theta_{A1} = \Gamma_{A1}\omega_A$ and $\theta_{A2} = \Gamma_{A2}\omega_A$ are the corresponding surface coverages by alkane; Γ_{A1} and Γ_{A2} are the corresponding adsorptions, ω_A is the molar area of alkane, a_A is the interaction constant between alkane molecules.

For the first layer the adsorption isotherm for the alkane molecules reads:

$$b_{A1}c_A = \frac{\theta_{A1}}{(1 - \theta_{A1})} \exp[-2a_A\theta_{A1}] \quad (2)$$

while for the second layer the adsorption isotherm we get:

$$b_{A2}c_A = \frac{\theta_{A2}}{(1 - \theta_{A2})} \exp[-2a_A\theta_{A2}]. \quad (3)$$

In Eqs. (2) and (3), b_{A1} and b_{A2} are the alkane adsorption equilibrium constants in the first and second layer, respectively, and c_A is the alkane concentration.

A more general adsorption isotherm for alkane multilayers given by

Eqs. (2) and (3) was derived recently in [8]. The adsorption in any additional layers ($2 < j \leq L_A$) does not affect the equilibrium surface tension remarkably, but it influences the kinetics and rheology of the mixed surface layer. A generalised model which assumes the influence of all alkane adsorption layers on the surface tension is the subject of future work.

The adsorption/desorption kinetics from individual and mixed solutions was discussed in a number of publications [27–36]. A theoretical description of the kinetics of the concurrent adsorption of alkanes from the gas phase and surfactants from the aqueous drop bulk phase at the drop surface was derived in [8,26]. For the adsorption of alkanes from the gas phase the assumption of a diffusion mechanism results in unrealistically low diffusion coefficients, which are by 7–8 orders of magnitude lower than the physically reasonable values. In a model assuming an adsorption barrier for the alkane molecules in the first and second layer, respectively, the kinetic equations are given by:

$$\frac{d\Gamma_{A1}}{dt} = \beta_A c_A \left(1 - \frac{\Gamma_{A1}}{\Gamma_A^\infty}\right) - \alpha_{A1} \frac{\Gamma_{A1}}{\Gamma_A^\infty}, \quad (4)$$

$$\frac{d\Gamma_{A2}}{dt} = \beta_A c_A \left(1 - \frac{\Gamma_{A2}}{\Gamma_A^\infty}\right) - \alpha_{A2} \frac{\Gamma_{A2}}{\Gamma_A^\infty}, \quad (5)$$

where $\Gamma_A^\infty = 1/\omega_A$, $\alpha_{A1} = \beta_A/b_{A1}$, $\alpha_{A2} = \beta_A/b_{A2}$, and β_A is the alkane adsorption rate coefficient. In an up-coming work, a more rigorous approach will be derived which involves the alkane adsorption kinetics equations for all layers $j > 2$.

3. Experimental

The procedure to measure the surface tension using the profile analysis tensiometry for a water drop in heptane vapor is similar to that described earlier elsewhere [2,8]. The experiments were performed with the tensiometers PAT-1 and PAT-2P (SINTERFACE Technologies, Germany), the operation principles of which are described in detail in [37]. The surface tension in these instruments is determined by fitting the experimentally measured drop profiles with theoretically predicted profiles calculated from the Young-Gauss-Laplace equation. The fitting procedure provides also a standard deviation in μm (fitting error), which is a measure for the quality of matching the measured drop profiles by the calculated profiles.

The temperature of the measuring cell with a volume of 30 ml was kept constant at 20, 30, 40 and 50 °C, respectively. The amount of 1 cm³ heptane was placed at the bottom of the measuring cell. To saturate the air in the cell by water vapor a vessel containing 2 cm³ of water was additionally placed at the cell bottom. To measure the dynamic surface tension of water drops in air saturated with alkane and water, the closed cell with heptane and water was aged at the experimental temperature over at least 30 min prior to the formation of the drop. Also, some experiments with heptane and pentane were performed with a cell preliminary saturated with water vapour: the alkane was injected into the cell already pre-saturated with water vapour and the water drop was then formed immediately. Also, using the drop profile method the surface tension of pure heptane at the interface with air was measured. To estimate the influence of the error caused by the determination of the drop radius on the calculated surface tension value, experiments with harmonic oscillations imposed on a heptane drop were performed. In these experiments the oscillation frequency of 0.5 Hz and surface area amplitudes between ± 5 % and ± 30 % were used.

The heptane and pentane were of spectroscopic grade and purchased from Fluka. All experiments were performed with Milli-Q water, the surface tension of which was 72.0 ± 0.2 mN/m at 25 °C during a time interval of up to 30000 s.

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