



## Influence of solubilised dodecane on the dynamic surface tension and dilational rheology of micellar Triton X-45 and SDS solutions

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### ABSTRACT

Maximum bubble pressure tensiometry is used to measure the dynamic surface tensions of micellar solutions of TX45 and mixtures of SDS/TX45 at the solution/air interface. For measurements of the dilational visco-elasticity of the micellar solutions the buoyant bubble profile tensiometry with harmonic bubble surface area oscillations is applied. The influence of dodecane solubilised in TX45 and mixed SDS/TX45 micelles, respectively, on the dynamic surface tension and dilational characteristics of these micellar solutions is determined. It is shown that the solubilisation of dodecane by micelles leads to a slowdown in the dynamic surface tension change and an increase in the visco-elasticity of the micellar solutions. Theoretical models proposed earlier are used for the description of the influence of solubilised dodecane on the dynamic surface tension and visco-elasticity of micellar TX45 solutions. It is shown that the presence of solubilised dodecane leads to a decrease of the CMC value, and to a decrease of the micelles diffusion coefficient.

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### 1. Introduction

Long-chain alkanes (or other hydrocarbons) are practically insoluble in water. In the presence of surfactant micelles, alkane molecules can transfer into the hydrophobic core of the micelles (solubilisation), and by this the oil solubility is increased significantly. This process is important in many industrial and biological applications. The solubilisation process was considered in a number of publications [1–9]. The main issues studied in these papers were the determination of molar solubilisation capacity of micelles and the solubilisation mechanism. The molar solubilisation ratio ( $S$ ), which is the number of moles of hydrocarbon solubilised per number of moles of surfactant in a micelle (aggregation number), can be calculated as follows:

$$S = \frac{c_{\text{sol}} - c_{\text{sat}}}{c_0 - c_k} \quad (1)$$

where  $c_{\text{sol}}$  is the concentration of solubilised hydrocarbon,  $c_{\text{sat}}$  is the hydrocarbon solubility in water,  $c_0$  is the total surfactant

concentration, and  $c_k$  is the critical micelle concentration (CMC).

In particular, the solubilisation of dodecane by micellar aqueous solutions of non-ionic ethoxylated dodecyl alcohol of various degrees of oxyethylation was studied in [1]. It was shown that  $S$  depends on the hydrophilic-lipophilic balance (HLB) of the studied surfactants within the HLB range of 12–18. The increase in HLB results in a decrease of  $S$ . For example, at HLB = 12 the micelles of ethoxylated dodecyl alcohol are able for the solubilisation of quite significant amounts of dodecane,  $S = 0.7$ – $0.8$ .

The dynamic tension at the interface between solubilised hydrocarbon (residual perchloroethylene) and the aqueous solution of Triton X-100 (both for sub-micellar and super-micellar Triton X-100 concentrations) was studied in [3]. The data thus obtained were used to study the diffusion and interfacial adsorption of surfactants, and also to obtain independent quantitative data on the distribution of the surfactants between the two phases.

However, to the best of our knowledge, among the studies devoted to the solubilisation there are no data on the surface or interfacial tension of micellar solutions of surfactants in the presence of solubilised hydrocarbons.

In the present publication we report on dynamic surface tension and dilation rheology studies of micellar Triton X-45 solutions in the presence of solubilised dodecane. The results

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provide a deeper insight into the influence of solubilisates on the dynamic characteristics of micellar surfactant. Equivalent experiments are also performed for aqueous SDS/TX45 mixed solutions.

## 2. Experimental

The experiments on surface tension and dilational elasticity were performed with the bubble/drop profile analysis tensiometry (PAT-1, SINTERFACE Technologies, Germany), the principle of which was described in detail elsewhere [10,11]. The temperature of the measuring glass cell (volume  $V = 20$  ml) was kept constant at  $25^\circ\text{C}$ . In this study we used the configuration of buoyant (oblate) bubbles formed at a Teflon capillary with a tip diameter of 3 mm. To study the dilational visco-elasticity  $E$ , after having reached the adsorption equilibrium the bubble was subjected to harmonic oscillations with frequencies  $f$  between 0.005 Hz and 0.2 Hz with a surface area oscillation amplitude of 5–7%. The results of oscillation experiments were analysed using the Fourier transformation [10]:

$$E(i\omega) = A_0 \frac{F[\Delta\gamma]}{F[\Delta A]} \quad (2)$$

where  $A_0$  is the initial area of the bubble surface,  $\gamma$  is the surface tension,  $A$  is the bubble surface area,  $\omega = 2\pi f$  is the angular frequency of oscillations.

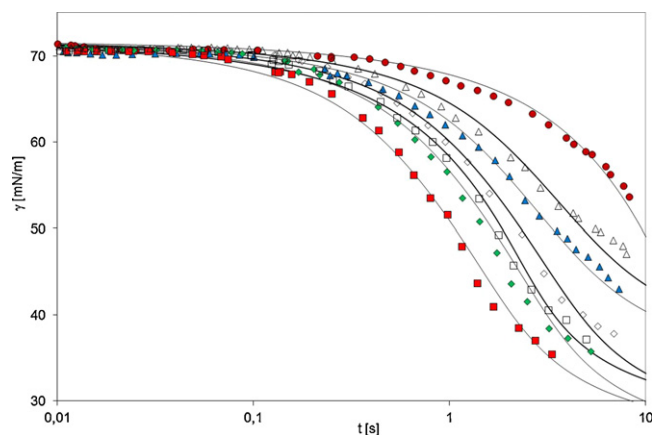
The maximum bubble pressure method (BPA-1S from SINTERFACE Technologies, Germany) was used here to measure the dynamic surface tension [12]. Steel capillaries of 0.25 mm in diameter coupled with a special bubble deflector have been used in order to reach extra short adsorption times. The volume of the separating bubble, and thereby the dead time of the bubble formation process, can be adjusted by the variation of the distance between the capillary tip and the deflector located opposite to it. A dead time of 5–10 ms is obtained for a bubble volume of approximately 2–3 mm<sup>3</sup>.

The substances studied were the polyethylene glycol octylphenyl ethers Triton X-45 (TX45), and dodecane from Sigma Chemical, which were used without further purification. The average number of EO groups in the studied TX45 was 4.5. All solutions were prepared with Milli-Q water. Similarly to [13], the solutions were prepared using aqueous 0.01 M NaCl solution. From equilibrium surface tension studies [13], the CMC for TX45 was determined as 0.1 mmol/l.

The solutions were prepared as follows. First, the micellar solution of TX45 was prepared. Then, the dodecane was added to this solution subject to the condition  $S = 1$ . As for TX45 the HLB = 10.4, then according to the data presented in [1] the  $S$  value should slightly exceed 1. The solution was stirred first in the magnetic stirrer during 6 h, and subsequently in a ultrasonic homogeniser (Sonorex Super from Bandelin Electronic, Germany) during 4 h. After any dilution of the concentrated solution (to decrease the dodecane concentration) by similar super-micellar TX45 solutions, the obtained solution was ultrasonically homogenised during at least 2 h. Solutions with the anionic surfactant SDS were prepared as described further below.

## 3. Results and discussion

Let us consider the results of dynamic surface tension studies performed by the bubble pressure tensiometry. Fig. 1 illustrates the time dependencies of the dynamic surface tension  $\gamma(t)$  of TX45 solutions at the CMC (0.1 mmol/l) and above the CMC: 0.2, 0.3 and 0.4 mmol/l (filled points). One can see that with increasing concentration, the rate of surface tension decrease becomes faster than exactly at the CMC. As the monomer concentration remains



**Fig. 1.** Dynamic surface tensions of TX45 solution measured by maximum bubble pressure method at the concentrations 0.1 (●, CMC), 0.2 (▲), 0.3 (◆), and 0.4 mmol/l (■); open points correspond to the same TX45 concentrations in the solution with the addition of solubilised dodecane ( $S = 1$ ) at concentrations 0.1 (△), 0.2 (◇) and 0.3 mmol/l (□); curves are calculated using the theoretical models: thin curves – pure TX45 solutions; bold curves – TX45 solutions with the additions of dodecane.

constant in this range of concentration and micelles do not adsorb, the disintegration process of micelles contributes essentially to the adsorption dynamics. The results in Fig. 1 agree well with those obtained earlier in [14] for TX45 solutions using the same method at CMC and at the concentration of 0.2 mmol/l. In this figure the results obtained for super-micellar solutions in the presence of dodecane ( $S = 1$ ) (i.e. for dodecane concentrations of 0.1, 0.2 and 0.3 mmol/l) are also shown by open symbols. It is clearly seen that the presence of solubilised dodecane results in a significant slowing down of the dynamic surface tension of the solution, obviously due to the decreased flux of TX45 monomers towards the bubble surface. This phenomenon is in more detail discussed further below.

Fig. 1 illustrates also the attempt to describe these experimental results in the framework of theoretical models. Thin lines correspond to the CMC and super-micellar TX45 solutions without any dodecane additions. These theoretical dependencies agree well with the experimental data. To calculate the dynamical surface tension at CMC the reorientation adsorption model with the parameters listed in Tables 2 and 3 of [13], and the diffusion model described in [15] were used. The theoretical approach is based on the numerical solution of the differential equations for a diffusion controlled surfactant adsorption at the bubble surface (assuming the actual geometry of the cell and accounting for the surfactant material balance) and involves the equations of state and adsorption isotherm [13]. The diffusion coefficient  $D$  for TX45 monomers at CMC was taken to be  $8 \times 10^{-11}$  m<sup>2</sup>/s, in agreement with the dependence of  $D$  on TX45 concentration as shown in Fig. 5 of [15]. The theoretical curves shown in Fig. 1 for the super-micellar TX45 solutions without the addition of dodecane were calculated using the same model, however, in these cases the effective diffusion coefficient of monomers was used [14]. More specifically, the effective diffusion coefficient  $D^*$  of monomers was calculated from the theory proposed by Joos and van Hunsel [16] as:

$$D^* = D(1 + \beta)(1 + \alpha\beta), \quad (3)$$

where  $\alpha = D_m/D \approx 0.25$ ,  $\beta = (c_0 - c_k)/c_k$ ,  $c_k = \text{CMC}$ ,  $c_0$  is the total surfactant concentration,  $D$  and  $D_m$  are the diffusion coefficients of surfactant monomers and micelles, respectively. As it was shown in [17], Eq. (3) describes the diffusion processes in micellar solutions for a time range exceeding the relaxation time of fast micelles dissociation. Here the influence of the slow micelle dissociation process (total decomposition of micelles) was neglected, because in our experiments the time range is probably significantly shorter than

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