Adsorption kinetics of nonionic surfactants using the drop volume method

R. Miller and K.-H. Schano

Central Institute of Organic Chemistry of the Academy of Sciences of the GDR, Berlin-Adlershof, G.D.R.

Abstract: The kinetic results obtained for the nonionic surfactants n-octyl, n-decyl, and n-dodecyl dimethyl and n-octyl, and n-decyl diethyl phosphine oxide show purely diffusion controlled adsorption. The drop volume technique applied in a static and dynamic version proves to be useful to measure the adsorption kinetics in the form of surface tensions in function of time. Comparisons of the results obtained from both the static and the dynamic measuring procedure confirm the validity of a theory applied to interpret the kinetic data.

Key words: Dynamic surface tension, drop volume method, nonionic surfactants, diffusion controlled adsorption kinetics.

Nomenclature

- $a$ – Langmuir parameter
- $c_0$ – surfactant bulk concentration
- $D$ – diffusion coefficient
- $\Gamma$ – surface concentration
- $\Gamma_0$ – equilibrium surface concentration
- $\bar{\Gamma} = \Gamma(t)/\Gamma_0$ – reduced surface concentration
- $\Gamma_m$ – maximum value of $\bar{\Gamma}$
- $R$ – gas law constant
- $\sigma$ – surface tension
- $\sigma_0$ – surface tension of pure water
- $t$ – time
- $T$ – absolute temperature

Introduction

Investigating the adsorption kinetics of surfactants at fluid interfaces static methods have the advantage of a simple theoretical description. But often there is the problem of creating a fresh interface in a reproducible way and to obtain accurate values in a time scale of seconds.

In contrast dynamic methods have the advantage that fresh interfaces can be created very simply and reproducibly but the theoretical description of adsorption kinetics is much more complicated, and also has to consider hydrodynamic flows in the solution bulk and flows at the surface. But because of the possibility that measurements can be performed in a time scale of milliseconds (oscillating jet) and seconds (maximum bubble pressure; drop volume method) these dynamic methods are often applied. The present paper is an experimental study on the adsorption kinetics of two homologous series of nonionic surfactants based on the drop volume technique. The surfactants used are of special, surface-chemical purity and the aim of the study is to discover the adsorption mechanism of these nonionic surfactants without any disturbances by surface-active impurities. Additionally the experiments performed are useful for checking the applicability of elaborated theories in the literature.

Experimental method and materials

The apparatus of the drop volume method applied offers two possibilities of measuring the time dependence of surface tension. The classical procedure works in a dynamic way by forming continuously growing drops at the tip of a capillary with a definite diameter. Reaching a critical volume the drop falls down and a new one will be created. The flow of solution is constant during the whole measuring procedure which is realized by a micrometer syringe. The result of these measurements is a dependence of surface tension on drop time. In the second measuring procedure first applied by Addison [1] a drop of a definite volume is formed very quickly at the tip of the capillary. The volume used is smaller than the critical one concerning the acting surface tension at that time. Although the drop volume remains constant the drop will fall down in that moment when the initial volume of the drop chosen corresponds to the critical volume due to the decrease of surface tension.
tension in the meantime. If the initial volume used was too small with regard to the limiting surface tension of adsorption equilibrium the drop will not fall down. During the whole procedure, excluding the initial phase, the drop surface remains nearly constant, there will be no flow into the drop and the classical theory of adsorption kinetics can be applied to interpret the results of the static procedure provided any circular flow is negligible.

To calculate the surface tension values from the drop volume the correction factors of Harkins and Brown [2] tabulated by Wilkinson [3] were used.

Surfactants used were members of the homologous series of dimethyl and diethyl alkyl phosphine oxides and are prepared in the laboratories of the Central Institute of Organic Chemistry of the Academy of Sciences of the GDR. Their surface-chemical purity was obtained by a purification procedure described elsewhere [4]. The equilibrium adsorption properties of all substances under investigation were published previously [5], where the necessary grade of purity ("surface-chemically pure") was checked applying the criterion elaborated by Lunkenheimer and Miller [6, 7].

### Theoretical basis

The first model on adsorption kinetics processes at the surface of a growing drop was proposed by Ilkovic [8]. Later works specifying the boundary conditions of the model for adsorption processes occurring at the drop surface during the application of the drop volume method found a simple relation to describe the initial period of adsorption [9].

\[ \Gamma(t) = 2 c_0 \sqrt{\frac{3Dt}{7\pi}}. \]  

(1)

The first complete initial and boundary value problem taking into account bulk and surface flow was formulated by Pierson and Whitaker [10], and solved numerically using an explicit difference method. The solution obtained from these calculations was not in good agreement with experimental findings because it suggests that adsorption at a static as well as at a continuously growing drop surface can be described by one and the same relation, the classical theory at static surfaces formulated by Ward and Tordai [11]. But experimental results showed that the time necessary to obtain the same surface tension or surface concentration at the surface of a growing drop is 2.5 times greater than the time at a static surface [12, 13].

A model of a purely kinetics-controlled adsorption at a growing drop surface was derived by Krotov and Rusanov [14] which reflects the factor of about 2.5 found experimentally, but the model does not describe the real adsorption mechanism of simple surfactants. The solution of the diffusion controlled model proposed by Pierson and Whitaker [10] was obtained by transforming the partial differential Equation into an integral Equation [15]

\[ \Gamma(t) = 2 c_0 - \sqrt{\frac{3Dt}{7\pi}} - \sqrt{\frac{D}{\pi}} t^{-2/3} \]

\[ + \int_0^\tau \frac{c_0}{(\tau - \lambda)^{1/2}} d\lambda \]

(2)

with

\[ \tau = \frac{3}{7} t^{7/5}. \]

(3)

This Equation was solved numerically [15]. Equation (1) results from Equation (2) as the simplest approximation at small t-values. The numerical results obtained from Equation (2) predict that there is a factor between 7/3 and 4.0 for the drop time at a growing drop surface compared with the time necessary to establish the same adsorption state at a static surface. This theoretical result is in agreement with the experimental findings. On the basis of the following experimental data the theory will be checked quantitatively.

### Experimental results

Using the static and dynamic procedure of the drop volume method dynamic surface tensions of aqueous solutions of n-decyl, and n-dodecyl dimethyl phosphine oxide (C_{10}DMPO and C_{12}DMPO) and n-octyl,