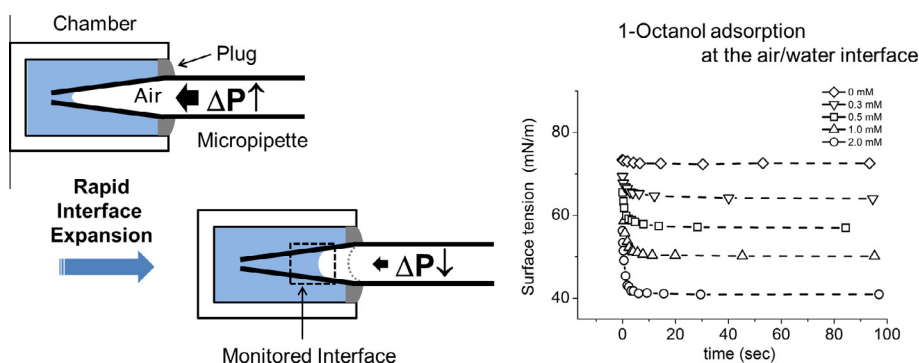Regular Article

New sensitive micro-measurements of dynamic surface tension and diffusion coefficients: Validated and tested for the adsorption of 1-Octanol at a microscopic air-water interface and its dissolution into water

Koji Kinoshita [a,*], Elisa Parra [a], David Needham [a,b]

[a] Center for Single Particle Science and Engineering (SPSE), Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, DK-5230 Odense, Denmark
[b] Department of Mechanical Engineering and Material Science, Duke University, Durham, NC 27708, USA

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Currently available dynamic surface tension (DST) measurement methods, such as Wilhelmy plate, droplet- or bubble-based methods, still have various experimental limitations such as the large size of the interface, convection in the solution, or a certain "dead time" at initial measurement. These limitations create inconsistencies for the kinetic analysis of surfactant adsorption/desorption, especially significant for ionic surfactants. Here, the "*micropipette interfacial area-expansion method*" was introduced and validated as a new DST measurement having a high enough sensitivity to detect diffusion controlled molecular adsorption at the air-water interfaces. To validate the new technique, the diffusion coefficient of 1-Octanol in water was investigated with existing models: the Ward Tordai model for the *long time adsorption regime* (1–100 s), and the Langmuir and Frumkin adsorption isotherm models for surface excess concentration. We found that the measured diffusion coefficient of 1-Octanol, $7.2 \pm 0.8 \times 10^{-6}$ cm^2/s, showed excellent agreement with the result from an alternative method, "*single microdroplet catching method*", to measure the diffusion coefficient from diffusion-controlled microdroplet dissolution, $7.3 \pm 0.1 \times 10^{-6}$ cm^2/s. These new techniques for determining adsorption and diffusion coefficients can apply for a range of surface active molecules, especially the less-characterized ionic surfactants, and biological compounds such as lipids, peptides, and proteins.

© 2016 Elsevier Inc. All rights reserved.

* Corresponding author.
  E-mail addresses: koji@sdu.dk (K. Kinoshita), parra@sdu.dk (E. Parra), needham@sdu.dk (D. Needham).

1. Introduction

Currently, there are a host of well-established techniques to measure the equilibrium and dynamic surface tension of liquid surfaces [1–3]. In general, the techniques are separated into three different groups by their method type: force method (Wilhelmy plate and Du Noüy ring), shape method (pendant or tensile droplet, sessile or captive bubble, spinning drop or bubble, and oscillating jet), and pressure method (maximum bubble pressure, and growing bubble and droplet). The subject of many of the studies that used, and still uses these techniques, has been to study the adsorption of a whole range of surface-active materials. In classical surfactant (or as in the case of molecules like 1-Octanol: surface-active compound) research, surfactants are mainly grouped by two characteristics, i.e. ionic and non-ionic surfactants. Their adsorption and desorption kinetics have been analysed theoretically with various kinetic and/or thermodynamic models [4–6]. Commonly used models for non-ionic surfactants are the Langmuir [7] and Frumkin adsorption isotherm [8] models and interpretations of dynamic adsorption have been based on the Ward-Tordai model of the 1940s [9].

One of the key steps of these experiments is the determination of dynamic surface excess concentration, $\Gamma(t)$, from the fitting analysis of surface tension data to the adsorption isotherm models. Although direct measurements of equilibrium $\Gamma(t = \infty)$ have been made, for instance using neutron reflection, a further development for direct dynamic $\Gamma(t)$ measurement is still needed [10–12]. High consistency of $\Gamma(t)$ derived from fitting analysis models requires high sensitivity and accuracy for DST measurement. For instance, important parameters such as the energy barrier for adsorption at the surface critically depend on $\Gamma(t)$. Here, to bring new insights for this, we introduce a new dynamic surface tension measurement called *Micropipette interfacial area-expansion method,* based on the surface tension measurements made previously with the tapered-micropipette manipulation technique [13,14]. In 2001, our group introduced a new pressure measurement –the "tapered pipette method", that used controlled micropipette pressure for the manipulation of a microscopic interface that allowed the measurement of liquid-gas and liquid-liquid interfacial tension [13,14]. The design was based on the Young–Laplace equation, where the radius of curvature of an interface is related to the surface tension via the pressure across the interface. By monitoring this applied pressure inside the tapered micropipette, both the equilibrium and the dynamic change in interfacial tension when surfactants and lipids adsorbed to the interface from solution could be measured. The optimized technique presented here allows us now to make more rapid dynamic surface tension measurements after an exposure of a clean interface to a surfactant solution, registering initial adsorption events in less than 1 s, where previously it took about 15 s.

In order to establish the new technique for equilibrium and dynamic surface tensions, we chose to make the new measurements on one of the most well-known soluble non-ionic, surface-active compounds, 1-Octanol [15–18], because it is a surface-active material, can be a soluble and so rapidly exchanging material, and also, it lent itself to a second check on measuring the diffusion coefficient because it is immiscible but soluble in water. The data is interpreted in terms of, and indeed provides further tests of, current models for interfacial transport, monolayer formation, and the ideality of adsorption isotherms for this class of molecules. This work also makes comparisons with existing data from the few pendant bubble, pulsating-bubble method, and oscillating jet technique [15,16,19,20] studies that have been published. The result of these analyses is not only surface tension measurements, but also their application to obtain new values for the diffusion coefficient of 1-Octanol in aqueous solution as it adsorbs and comes to equilibrium surface excess.

1.1. Dynamic surface tension measurements

The ability to make a short-time adsorption measurement (initial surfactant molecules adsorption measurement at a clean interface) is one of the key factors for obtaining highly accurate information of $\Gamma(t)$. As illustrated and reviewed again by Eastoe and Dalton [4] in their seminal paper, the manufacture and availability of commercial set-ups of surface chemical techniques has provided a range of time scales for dynamic surface tension measurements [2]. Currently, it is known that the maximum-bubble-pressure method (MBPM) [21,22], oscillating jet [19,23], growing-drop [24,25] and pendant bubble methods (PBM) [15] can give dynamic surface tension measurements in an initial time range of 100 ms or below (submillisecond). As we present in this paper, this very (ultra) short time range is actually not within the range available with our micropipette method, but we still have access to the long-time range which the diffusion coefficient can be obtained. In any event, as Franses et al. mentioned, there is still a major concern of the initial convection derived by flows during the formation of an initial interface at "time 0", especially for the adsorption-surface-area-change methods [1]. The convective flow can affect the initial adsorption and bring estimation errors for dynamic adsorption analyses that are focused on diffusion-limited measurements to obtain diffusion coefficients [26]. Therefore, any measurements and adsorption-rate analysis at these very early initial times will always need careful treatments such as those outlined by Casandra et al. [27]. Even if short-time adsorption measurements can be made, the size of the interface for dynamic adsorption measurements will also be an important factor in achieving high-sensitivity results. For example, the Wilhelmy plate and Du Noüy ring methods involve a relatively large surface area ($\sim cm^2 - m^2$) for the measurement. If there are any local effects, such as non-uniform surface tension derived by inhomogeneous surface concentration, it will take a longer time to return to a uniform condition compared with other methods that have much smaller interface area. Thus, while these techniques are good for the equilibrium surface tension measurement, they do not lend themselves so well to the rapid dynamic surface tension measurements. By using a bubble of just a few mm diameter, PBM does provide quite a small interfacial area, but this is still a relatively large interface of $10^7 \ \mu m^2$ [15]. It would therefore be an advantage to have even smaller interfaces, where diffusion distances are matched by practical times for observation. The MBPM [28] reduces the interface by another factor of 100, to about $10^5 \ \mu m^2$, and is more suitable for obtaining more high-sensitivity results of the dynamic surface tension measurement.

However, a truly high-sensitivity dynamic adsorption measurement is not yet totally established, because dynamic adsorption has so far been less well studied than the more easily measured state of equilibrium. As such, being able to make relatively rapid DST measurements with high-sensitivity is still in demand. Although the new micropipette technique we introduce here is not well-specified for the rapid adsorption in the short-time submillisecond range as yet, combining the relatively rapid DST measurement that we can make with the fairly small adsorption area $10^3 - 10^5 \ \mu m^2$ can provide additional insights into the transport and adsorption mechanisms, especially the important parameter of the diffusion coefficient of surfactants during their transport phase to the interface and attainment of equilibrium [4,5].