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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

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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, \(7.2 \pm 0.8 \times 10^{-8} \text{ cm}^2/\text{s}\), showed excellent agreement with the result from an alternative method, “single microdroplet catching method”, to measure the diffusion coefficient from diffusion-controlled microdroplet dissolution, \(7.3 \pm 1 \times 10^{-8} \text{ cm}^2/\text{s}\). 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.

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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, $C(t)$, 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 $10^2$ μm$^2$ [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 $10^3$ μm$^2$, 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 $10^2–10^4$ μm$^2$ 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].
1.2. Microdroplet dissolution measurement

While the above techniques provide measures of surface tension, these data still have to be fit to adsorption isotherms in order to derive the important parameter of surface excess concentration, that is then used in a second dynamic model to obtain the diffusion coefficient. For an immiscible, yet water-soluble material like 1-Octanol, the micropipette technique offers another alternative method giving an independent measurement of the diffusion coefficient [29,30] of these surface-active molecules and offers an additional new check on the diffusion coefficient value measured from the surface tension. The microdroplet dissolution method measures the dissolution of single immiscible but soluble microdroplets into a second medium. Therefore, even though the surface-active molecule’s solubility is extremely low in bulk medium, the method can measure the diffusion coefficient value. In fact, such low-solubility molecules like 1-Octanol are not preferable materials for other diffusion coefficient measurement methods, such as spin-echo NMR and Taylor dispersion measurement [31,32]. Because of this, the droplet dissolution method has been used for the aqueous 1-Octanol system to support the diffusion coefficient measurement of the surface tension micropipette method.

In the droplet dissolution method too, there are initial timing issues associated with forming single microdroplets using a single pipette or having to use two chambers side by side [33,34]. Thus, we also now introduce an improved new technique, the “single microdroplet catching method”, developed in order to obtain more accurate dissolution profiles from the initial time of microdroplet formation. This new technique eliminates the previously needed surfactant stabilizer required to isolate the droplet on the end of the micropipette, and can account for any dissolution that occurs during the droplet formation process, and before the droplet diameter can start to be measured. The measured microdroplet dissolution rate then provides comparable diffusion data from the application of the modified solubility diffusion model [29,30] of Epstein-Plesset [35] (see Section 2).

This work, then, establishes a new, relatively simple method for making DST measurements that is now available for determining adsorption and diffusion coefficients for a range of air-water- and also oil-water-surfactant systems, and combines it with a dissolution droplet measurement. Having checked the techniques against known data from the literature for 1-Octanol, in a subsequent paper [36] we plan to apply the technique to investigate more complicated systems, including ionic surfactant adsorption creating a charged interface, and to extend it to other systems such as charged lipids, polymers, peptides and proteins where shorter time ranges can be accessed due to slower molecular diffusion and kinetic diffusion models can be applied.

2. Theory

In order to validate the new dynamic surface tension measurement technique, it is necessary to evaluate the obtained data against dynamic and equilibrium adsorption processes embodied in theoretical models for dynamic adsorption. The Ward-Tordai model [9] has been the most influential theoretical work in this field since it was published in 1946. Application of this model to the micropipette data then yields estimates of the diffusion coefficients of the surface-active molecules transporting to the interface. An important parameter that is required in deriving the diffusion coefficient from such dynamic models is the surface excess concentration of the surfactant at equilibrium, \( \Gamma_{eq} \) and with it the surface area/molecule at the interface, \( a_m \). This parameter is readily obtained from measurements of the equilibrium surface tension using the Langmuir [37,38] and Frumkin-isotherms [4,8,39].

In this theory section, the Ward-Tordai model [9] will be briefly presented as it has been used to analyse the experimental results from the micropipette technique for 1-Octanol. We also include here the modified Epstein-Plesset model [29] that was used to obtain the diffusion coefficient for the water-immiscible but soluble 1-Octanol from its dissolving microdroplet, as applied to the other systems in previous studies [29,30,33,34].

2.1. Dynamic behavior: The Ward-Tordai diffusion model

The Ward-Tordai diffusion model [9], subsequently developed as asymptotic solutions by Fainerman et al. [40], and presented as a numerical solution by Li et al. [41], describes how the adsorption kinetics of a non-ionic soluble surfactant is governed by a two-step process: (1) the diffusion of molecules from the bulk solution to the subsurface layer (i.e., the layer immediately below the surface layer, at a thickness of only a few molecular diameters); (2) the molecular diffusion and adsorption from the subsurface layer to the interface [4,5]. Thus, when, as in the “interfacial area-expansion method”, a new clean surface is created and presented to a surfactant solution, a finite time is required for the excess surface concentration \( \Gamma(t) \) to reach equilibrium with the bulk concentration, \( C_0 \), and attain its equilibrium value, \( \Gamma_{eq} \). This period of time can range from milliseconds to days depending on the surfactant type and its concentration in solution; in the case of 1-Octanol adsorbing from its aqueous solution at moderate (mM) concentrations, it occurs in only a few seconds. Each step in this process of diffusion and adsorption is respectively influenced by the molecule’s structure (size) – based on the Stokes theory, and any molecular reorientation and lateral interactions required to form and enter the monolayer.

Thus, kinetically two time regimes can be identified – an ultrafast Short-Time Adsorption Approximation (the initial approach of the surfactant to the interface in the absence of “back diffusion”) and a Long-Time Adsorption Approximation (the approach to equilibrium), where a balance between adsorption and desorption of the water-soluble surfactant eventually results in no net change, because the adsorbing flux of monomers to the surface is equal to its desorbing flux. Because of its widespread use in the determination of adsorption mechanisms and the estimation of surfactant diffusivity, Casandra et al. [27] provided a very specific range of time intervals or surface pressures over which the short-time approximation at the air-water interface should be applied. In applying the Ward Tordai model, it is therefore necessary to adhere to these rules of limiting surface pressure \( (\Gamma_{max}) \) and dimensionless time \( (\Gamma_{max}) \) as a function of their dimensionless surfactant concentration \( (C_0/a) \), – the ratio between the bulk concentration and the surfactant activity. For our system, this parameter is \( \sim 0.1-0.2 \) s \( ^{1/2} \), i.e, 0.01–0.04 s, which is borderline or just outside the Casandra criterion. Therefore, since with the micropipette technique, we cannot measure the surface tension at times less than 0.5 s, we mainly focus here on the relatively long-time regime that is, nevertheless, from 1 to 100 s and still provides a measure of the diffusion coefficient. In the Supplementary Materials section, the short-time adsorption events are discussed and the limits of the micropipette technique (and those of others) are considered.

2.1.1. Long-time adsorption approximation

Briefly then, the so-called long-time adsorption approximation \( (t \to \infty) \) consists of an approach to equilibrium interfacial tension, \( \gamma_{eq} \) given by the Gibbs adsorption equation,

\[
\Gamma_{eq} = -\frac{1}{nRT} \left( \frac{d\gamma}{d\ln(C_0)} \right)_T
\]

where \( C_0 \) is the bulk concentration, \( R \) is the gas constant of surfactant, and \( T \) is temperature. By taking a limit of subsurface
concentration to bulk concentration in this equation, the surface tension becomes proportional to \( t^{-1/2} \).

\[
\gamma(t) = \gamma_{eq} + \frac{nRT_{eq}}{c_0} \sqrt{\frac{\pi}{4Dt}} \tag{2}
\]

where \( D \) is the diffusion coefficient of monomer surfactant, and \( n \) is a constant factor, -for a non-ionic surfactant or surface active compound like 1-Octanol, it is equal to \( 1^{-1} \) [4]. Thus, the slope of a plot of \( t^{-1/2} \) vs. surface tension depends on the surface excess concentration at equilibrium \( \Gamma_{eq} \) and the aqueous phase diffusion coefficient \( D \) for the surface active compound. Fitting this kinetic model to dynamic surface tension data from the micropipette technique should therefore give a measure of \( D \) for 1-Octanol, which can be compared to the analogous microdroplet dissolution measurement described below.

2.2. Equilibrium surface tension with diffusion controlled reversible adsorption

In order to apply the Ward-Tordai model, the surface excess concentration needs to be determined at equilibrium, obtained by applying an appropriate adsorption isotherm. We therefore considered two main models presented in the literature, that are used to analyse the adsorption and attainment of equilibrium interfacial tension of non-ionic surfactants: (i) the diffusion-controlled adsorption model given by the Langmuir isotherm, developed further to provide a surface tension value from the Langmuir-Syszkowski equation [19,37]; and (ii) a diffusion-controlled model given by the Frumkin equilibrium isotherm [38], that takes into account any potential non-ideality of the monolayer. Using these Langmuir and Frumkin isotherm models, the proper \( \Gamma_{eq} \) of the 1-Octanol monolayer at the air-water interface was estimated from the results of micropipette equilibrium surface tension measurements. For the analysis, it is assumed that the adsorption of 1-Octanol at the air-water interface from bulk solution follows a diffusion-controlled adsorption mechanism. Therefore, the estimated \( \Gamma_{eq} \) values are applied for the measured dynamic surface tension slope as a function of reciprocal square root of the adsorption time, \( t^{-1/2} \), following the long-time approximation of the Ward-Tordai adsorption model (Eq. (2)).

Since these isotherms are well established and reviewed extensively in the literatures [4,5,20,38], the respective equations will only be given in Section 4 along with the analysis of the data.

2.3. Dynamic behavior: The Epstein-Plesset dissolution model

Because 1-Octanol is immiscible yet soluble in water, an independent measurement of the diffusion coefficient can be obtained from the dissolution rate of a single microdroplet of 1-Octanol into water. Originally derived for the dissolution and growth of gas bubbles in water, the applicability of the Epstein-Plesset model [35] has been confirmed by Duncan and Needham using the micropipette technique for gas microbubbles [29]. It was also successfully applied to the dissolution of liquid microdroplets for water-into-oil [30,33] and oil-into-water [30,34]. The basic equation used for the droplet dissolution relates the time-rate of radius change for a microdroplet to the diffusion coefficient and solubility, the square root of time, and geometric and saturation-concentration parameters,

\[
\frac{dR(t)}{dt} = - \frac{Dc_s(1-f)}{\rho} \left[ \frac{1}{R(t)^2} + \frac{1}{\sqrt{\pi Dt}} \right] \tag{3}
\]

where \( R(t) \) is the radius of microdroplet in immiscible bulk solution, \( \rho \) is the density of the solute, \( C_s \) is the solubility limit of the dissolving component into the surrounding medium, and \( f \) is the ratio of the initial dissolved concentration and \( C_s \) (in this present case, \( f = 0 \), since pure water was used for the bulk solution). The equation was simplified by neglecting the second term. After integrating the first term of the simplified model, there is then a more convenient linear relation of \( R^2 \) and time [29],

\[
R_0^2 - R(t)^2 = \frac{2Dc_s}{\rho}t \tag{4}
\]

A plot of \( R_0^2-R(t)^2 \) vs. time then gives the \( D \) value calculated from the best fitting slope.

3. Materials and methods

3.1. Materials

1-Octanol (purity \( \geq 99\% \)) was purchased from Sigma (St. Louis, MO). The sample was used without further purification. Deionized distilled water was made via a MilliQ water purification system, which had 18.2 M\( \Omega \) cm resistivity. During these entire experiments, MilliQ water was always used. 6\( \theta \) glass capillary (OD 0.75 mm \( \times \) ID 0.4 mm) used to fabricate the micropipettes and glass cuvettes for the microchambers (dimensions 20 \( \times \) 3 \( \times \) 2 mm) were purchased from A-M Systems (Carlsborg, WA) and VitroCom (Mountain Lakes, NJ), respectively.

3.2. Sample preparation

For the interfacial measurements, it is vitally important to ensure that the materials are clean and pure (some comments about purity of Octanol are presented in Supplementary Materials). It is also important to ensure that 1-Octanol is not lost to the wall of sample vial due to the well-known Marangoni effect during any sample preparation or solution measurement. To minimize material loss, a Teflon container was used for mixing. 3 mM aqueous stock solution of 1-Octanol was made in 5 ml Teflon container and diluted as necessary for the series of different concentrations, 0.3–2 mM. After the solution was well mixed, it was completely solubilized, the octanol inside the Teflon container, it was diluted into 500 \( \mu \)l aliquots in plastic vials just before starting the experiment. For each dynamic and static surface tension measurement, 100 \( \mu \)l of sample volume were injected in the glass microchamber and placed on the microscope stage.

3.3. Micropipette methods

Since its introduction in the early 1970s for mechanical studies of red blood cells [42–44], we have been developing the micropipette technique for new applications in the general field of intermolecular and colloid and surface science [45–48]. This unique and extremely versatile platform technology is now finding its place as an important tool for the measurements of interfacial tensions and diffusion of materials in solution.

The basic tapered-micropipette manipulation equipment is shown in Fig. 1A, as first established in the papers of Lee et al. in 2001 [13,14] to measure the surface tension of microscopic liquid-gas and liquid-liquid interfaces. It was used in this work with significant upgrade in measurement and analysis. The modifications included: using Newport mechanical manipulators instead of pneumatic manipulators to position the pipettes, which gives better stability and control; video was digitally recorded; and a new LabVIEW program was used to display and analyse the pipette pressure and images of the radius of curvature (previously recorded using video tape and analysed by manual video calipers [13,14]). It can now achieve a higher resolution and has the precision required to enable the analysis of molecular diffusion.
Briefly, a custom-made chamber, filled with the desired test-solution, was viewed on a bright-field microscope stage with Köhler illumination (Zeiss) at room temperature (20 °C). Tapered micropipettes (taper angle ~3–4°) were prepared by using a pipette puller (from Sutter Instrument, CA), and cut to the desired tip diameter (~10 μm) with a micro-forging machine (Narishige) [49]. To manipulate the pipettes in the chamber (Fig. 1B), they were mounted in 3D mechanical manipulators (Newport) bolted firmly to the stage. During the micropipette manipulation experiment, live-images were observed with a CCD camera (DAGE-MTI, IN), and the pipette pressure was provided and controlled by using a 10 ml gas-tight syringe and measured with an in-line pressure transducer (Validyne Engineering Corp., CA), all monitored in real-time and recorded on a computer using a home-built LabVIEW program. All digital image analysis was done with ImageJ software provided by National Institutes of Health [66].

3.4. Equilibrium surface tension measurement

The simplest measurement that can be made is a static, or equilibrium, surface tension measurement of the air-water interface. As described by Lee et al. [13,14] for the micropipette system, it is well known that the Young–Laplace equation [50–52] relates the pressure across a curved interface, $\Delta P$, to the interfacial tension, $\gamma$, and the radius of curvature at the interface, $R_c$.

$$\Delta P = \frac{2\gamma}{R_c}$$

In general, any air-water interface in a tapered micropipette has a contact angle, $\theta_c$, with the pipette wall. This angle for air-water is small (~5°) but is not zero, and, given the optical diffraction at the glass pipette wall, it is difficult to visualize (Fig. 2A).

However, by using the radius of curvature $R_c$ determined from a segment of the interface, as in Eq. (5), we can avoid having to try to measure directly the contact angle at the glass surface. That is, this segment-derived measurement of surface tension using Eqs. (5) and (6) does not require any factor of the contact angle at the surfactant/glass surface in the micropipette (for further interest, the contact angle measurement and effect of refractive index for the air-water interfacial image are described in Supplementary Materials).

As a check on the accuracy and reproducibility of the measurement, these equilibrium positions are measured for a range of applied micropipette pressures and their resulting positions in the tapered pipette. From the slope of a plot of applied micropipette pressure vs 2/$R_c$, the equilibrium surface tension for the water-air interfacial tension at 20 °C was measured to be, $\gamma = 72.6 \pm 0.2$ mN/m. This value is similar to the value measured by Lee et al. [13] of 72.4 ± 0.6 mN/m for the air-water interface at the 23 °C, and each of these values were in a good agreement with the reference data from the International Table of the Surface Tension of Water, compiled by Vargaftik and Voljak of, $\gamma = 72.8 \pm 0.36$ mN/m at 20 °C [53]. Therefore, the technique, measurement accuracy, and any experimental errors are meeting the highest standard of previously published measurements of the air-water interfacial tension.

3.5. The “Micropipette Interfacial Area-Expansion Method”: Dynamic Surface Tension (DST) measurement

To overcome the 15 s time-gap disadvantage of Lee’s earlier method [13,14], a new technique, the “micropipette interfacial area-expansion method” was developed here. Using the same conical-shaped pipette as Lee et al., a dynamic surface tension experiment for a surfactant solution involves rapidly expanding the smallest interface formed at the tip of the pipette to a much larger area further down the conical pipette and observing the recovery of the air-water meniscus as surfactant adsorbs to this essentially new clean interface. The new method consists of the following steps.

- First, the tapered micropipette was set in the microchamber containing the sample, and the size (diameter and area) of the air-water interface in equilibrium (Fig. 2B) inside of the pipette was minimized making the air-liquid meniscus coincident with the micropipette tip. This is achieved by setting an initial positive pipette pressure $\Delta P$, ~9 kPa, in order to oppose any capillary forces that would otherwise allow liquid to be drawn beyond just the pipette tip. The microchamber end was sealed with a small volume of hexadecane to avoid water evaporation during the experiment. During the DST measurement, the volume of solution flushing inside of the pipette is about 0.1 μl, which is 0.1% of the entire solution’s volume in the chamber (the small-volume movements did not affect the plugging).
• Then, ΔP was rapidly decreased from 9 kPa to 0 kPa in 0.1–0.3 s to provide a defined step of negative-pressure change of ~9 kPa inside the pipette. Because of this step change, the aqueous medium quickly flowed from the bathing microchamber into the pipette, thereby expanding the area of the air-water interface by 150 times (from an initial area close to the pipette tip at an interface radius of 16 μm, and area of 1600 μm², to an interfacial area of 240,000 μm² further down the taper at a radius of ~200 μm). This action created an essentially clean air-water surface in the micropipette, i.e., the initial area (and concomitantly any adsorbed material) was only 0.67% of this final new clean interfacial area.

• After the expansion, the micropipette pressure was quickly backed to a positive-pressure value ~1.0 kPa in order to start the measurement (Fig. 2C). If a surface-active agent is present in the aqueous phase, the DST measurement monitors the position of the air-water surface, and hence its decrease in radius of curvature, as it moves to smaller pipette radii at the constant applied pressure due to the adsorption of surfactant, that reduces the surface tension (see Video 1 and Supplementary Materials for further details of the pressure reset setup).

Thus, this method enabled us to monitor adsorption-induced changes to the surface tension starting at times of less than 1.0 s (minimum) after the new expanded clean air-water surface was created.

3.6. “Single Microdroplet Catching Method”: A New single microdroplet dissolution technique

We have introduced in previous studies the micropipette manipulation techniques for the measurement of single gas or liquid microdroplet dissolution in immiscible bulk media, allowing the determination of the diffusion coefficient of the dissolving gas or liquid into the dispersion medium [29,30]. Typically these experiments used just one pipette to first form, and then, rapidly catch and hold the ejected droplet of material. Forming and detaching a single microdroplet was sometimes unreliable and difficult to control, especially for large-tension interfaces and when small amounts of pipette-coating surfactants (such as SDS) could not be used. A two-chamber method was therefore introduced by Su et al. [33,34], which, while certainly effective, was rather difficult to use. Now these techniques are improved and use one pipette to rapidly form the droplet and a second one to catch it exactly upon formation and hold it for subsequent analysis, hence the name, “single microdroplet catching method”.

Fig. 3 shows a schematic image of the single microdroplet catching method, consisting of a two-sided open glass chamber and two pipettes: catching (left side) and sample loading pipette (right side). The microdroplet created at the loading pipette tip was caught and isolated by the catching pipette. In order to set up this new micropipette experiment and position the two pipettes that have to be close and axially aligned, the following steps should be taken. First, the water-filled open chamber was positioned on the sample stage. Then, the two tapered micropipettes were prepared. One of these pipettes (loading micropipette) was filled with the sample solution, ~about 1 μl volume loaded through the tip (off the microscope). The two pipettes were then inserted into each open end of the chamber, and axially-positioned at the same line and height. During the position adjustment, capillary suction brings the aqueous phase into the catching micropipette tip to make the same environment inside the pipette of bulk solution for holding an isolated microdroplet. After the setting of the two pipettes at a proper position, the two chamber ends were sealed by hexadecane to avoid water evaporation (otherwise this evaporation creates convection in the solution inside the chamber). It is necessary to avoid such convection, since it could enhance the droplet dissolution and would give an overestimate of the diffusion coefficient. Single microdrioplets were then created in less than few seconds by controlling the injection pressure and blowing a solution from the loading pipette tip.

Immediately after the microdroplet is blown out from the pipette tip, the catching pipette catches the droplet under low, controlled suction pressure applied to the catching pipette and isolates it from the source-solution. In this new method, the biggest advantage is that there is no requirement for an emulsifier or stabilizer in order to help form and isolate the microdroplet. The other advantages are: (1) the ability to make a certain size of
droplet each time by controlling the inter-tip distance between the two pipettes, and (2) measuring droplet dissolution from the exact time of emergence of the liquid from the micropipette tip, at time 0 (see Video 2 in Supplementary Materials).

4. Results and discussion

The new micropipette interfacial area-expansion method is now validated in the following order: (1) Equilibrium surface tension measurements for the range of 1-Octanol concentrations in order to establish the maximum surface excess concentration, $\Gamma_m$, for 1-Octanol at the air water interface; (2) dynamic surface tension of 1-Octanol, investigated by the micropipette interfacial area-expansion method, analysed by using the Ward-Tordai model, in order to obtain the diffusion coefficient of 1-Octanol in water from the long-time adsorption regime (the short-time adsorption regime and its our technique-limitations are discussed in Supplementary Materials); and (3) a second independent measurement of the diffusion coefficient of 1-Octanol, by using the single microdroplet catching method, in order to calculate an independent value for the diffusion coefficient and compare it with the DST-derived measurement and reference values.

4.1. Equilibrium surface tension measurements of 1-Octanol

The equilibrium air-water interfacial tensions of five different concentrations of 1-Octanol in water (0, 0.3, 0.5, 1, and 2 mM) were measured using the micropipette manipulation technique at 20 °C (Fig. 4); the average values of equilibrium interfacial tension were presented in Table 1. The value of $\gamma_{eq}$ was obtained for each 1-Octanol concentration from the slope of a plot of applied micropipette pressure $\Delta P$ vs $2/R_c$; least squares analysis gave the average value from the slope.

It was also possible to obtain the surface tension from a single absolute value of $R_c$ at each pressure (Eq. (5)). However, relying on these measurements introduces a larger error value compared with a slope calculation because the pixel size-limit of optical magnification was 0.45 µm and this could create an approximately ±0.5 mN/m error for the calculated surface tension. This is the reason why the slope average value was used to calculate the surface tension [13].

In order to test for reversibility, equilibration, and any hysteresis, both advancing and receding interfaces were measured. This was achieved by simply applying a series of increasing (the interface moves down the pipette to smaller radii) and decreasing (the interface moves up the pipette to larger radii) positive pipette pressures to find the equilibrium surface tension at each new applied pipette pressure. It was observed that the surface tension, even after compression of the interfacial area by a factor of 10, maintained the same values and that the direction of the area change had no influence on the values obtained. Therefore, with these tests seen in Fig. 4, the reversibility of adsorption-desorption with area change was demonstrated, revealing the dynamic nature of the surface monolayers of 1-Octanol as truly “soluble monolayers”. That is, the 1-Octanol monolayer at the
The surface tension, \( \gamma \), can be then obtained from the Gibbs adsorption equation and the Frumkin adsorption isotherm (Eq. (10)), the surface equation of state is given by the following relation\[38\],

\[
\gamma = \gamma_0 + n \Gamma_m \frac{mRT}{C_0} \ln \left( 1 - \frac{\Gamma_m}{\Gamma_m^{eq}} \right) - k \left( \frac{\Gamma_m^{eq}}{\Gamma_m} \right)^2
\]

These equations (Eqs. (8), (9) and (11)) were used to find the best fitting curve from the measured 1-Octanol equilibrium surface tension versus concentration plots next.

4.1.3. Langmuir and Frumkin adsorption isotherm model fitting

As shown in Fig. 5, the data obtained for the equilibrium surface tension of 1-Octanol at concentrations from 0 to 2.0 mM at 20 °C were well matched by both the Langmuir (thin solid line) and Frumkin (thick solid line) isotherm models. For comparison, literature values, that had been measured previously using the Du Noüy ring and Pulsating Bubble Surfactometer (PBS) methods, were extracted from Chang et al.\[16\] and are shown on the same plot. To find the best fitting curve shown in Fig. 5 for each model, the maximum surface excess value, \( \Gamma_m = 7.75 \times 10^{-6} \text{ mol/m}^2 \), was estimated for both models. Our value is in the same range found for the other different experiments, that are between \( \sim 6-9 \times 10^{-6} \text{ mol/m}^2 \) with \( K_L \sim 2-5 \text{ m}^2/\text{mol} \), such as PBS, Pendant Bubble/Wilhemly Plate and Oscillating Jet method as shown in Table 2\[15,16,19,54\].

High resolution synchrotron X-ray measurement by Berge et al. have shown the chain length-independent surface area per alkanol molecule was 0.215 nm\(^2\) in the solid phase\[56\]. In general, long chain neutral (or zwitterionic) alkyl surfactant or surface active compounds adsorbing at the air-water interface \( \Gamma_m \) can lead to a more tightly packed molecular conformation involving hydrogen bonded networks at the headgroups, with van der Waals interactions between chains\[57,58\]. Therefore, in order to derive the diffusion coefficient for octanol from the micropipette...
experiments, we simply selected a value for the molecularly-packed surface area of $\Gamma_m = 0.215 \, \text{nm}^2$/molecule measured for alkanol molecules (corresponding to $K_m = 7.75 \times 10^{-6} \, \text{mol/m}^2$) [56].

Using the selected value for $K_m$, the other parameters, $K_L (=2.4 \pm 0.2 \, \text{m}^3/\text{mol})$ and $K_F (=1.7 \, \text{m}^3/\text{mol})$ and $k (=1.0)$, were obtained from the best fitting curves of Eq. (8) for the Langmuir model, and Eqs. (10) and (11) for the Frumkin model, respectively. Each of the adsorption equilibrium parameters used or obtained from fittings of the Langmuir and Frumkin adsorption models are listed in Table 2. Comparing the isotherm constants, the measured $K_L$ value of 2.4 mol/m$^3$ from the micropipette technique was in excellent agreement with Chang and Fransen’s (1994) value of 2.5 mol/m$^3$, who used the PBS and Du Noüy ring technique [15,16]. As can be seen, the fitted curve of 7.75 $\times 10^{-6}$ mol/m$^2$ for $\Gamma_m$ was most closely in line with their values (Fig. 5). Both $K_L$ and $K_F$ values from the new micropipette technique were also similar to Lin et al’s (1997) parameters measured using the Pendant Bubble and Wilhelmy plate techniques, although they used a slightly different $\Gamma_m$ parameter of 8.96 $\times 10^{-6}$ mol/m$^2$ for the Langmuir model, and 5.91 $\times 10^{-6}$ mol/m$^2$ for the Frumkin model [15]. The only slight disagreement was with Bleys et al’s (1985) $K_F$ parameter of 1.8 mol/m$^2$, which was derived from the oscillating jet method in the short-time adsorption range (<=20 ms) and it showed a higher value compared to the others, since they used much smaller value of $\Gamma_m (\sim 6.0 \times 10^{-6} \, \text{mol/m}^2)$ having much bigger $\Gamma_m (\sim 0.27 \, \text{nm}^2$/molecule) [19].

4.2. Dynamic Surface Tension (DST) measurements of 1-Octanol

One of the main features of the micropipette interfacial area-expansion method for dynamic surface tension measurement is being able to observe and measure directly the synchronization of surface-area and surface-tension change due to the adsorption of surfactant or surface active compounds at a microscopic interface that is only 10$^5 \, \mu\text{m}^2$ in area. The sensitive micropipette system brings the ability to control the position of the interface (radius of curvature) with a balancing applied pressure (AP), and a purely diffusion-controlled transport-environment inside the micropipette. Because of this, for a given applied static pressure, the solution and interface quickly find their local equilibrium of adsorption or desorption between the interface and subsurface during any dynamic adsorption process without significant delay. The system then assures that the transfer of 1-Octanol molecules between the bulk solution and the interfacial monolayer at an air-water surface is completely controlled by the kinetics of monomer diffusion.

Next, we show how the data is treated using both the Langmuir- and Frumkin-isotherm models, and then how the Ward-Tordai model was followed to account for the diffusion of monomers from a bulk solution to the interface.

4.2.1. 1-Octanol DST profile after area expansion

Fig. 6A shows the interfacial area profiles including the initial rapid area expansion due to the reduction in pressure and applied pressure reset and their recovery due to adsorption of 1-Octanol versus time; and Fig. 6B shows the corresponding calculated surface tension based on Eqs. (5) and (6).

Each time course in Fig. 6A starts with an applied pressure drop from 9 kPa to 0 kPa and an immediate return to 1 kPa, pressure reset (see earlier in Methods and Supplementary Materials for more details), leading to a rapid interfacial area expansion and exposure of the essentially new clean interface to octanol solution. As shown in Fig. 6A, for the 0.3 mM solution (inverted triangles), the area of the interface fell from its peak of $170 \times 10^3 \, \mu\text{m}^2$ to $125 \times 10^3 \, \mu\text{m}^2$ in the first 15 s, and remained stable as it approached its equilibrium value. This reduction in interfacial area, from the same initial peak expansion, became greater and greater with increasing 1-Octanol concentration in the aqueous phase from 0.3 mM to 2 mM. For all concentrations, the fall in area occurred immediately and reached its equilibrium value in 15 s or less, attaining this equilibrium in shorter and shorter times, the higher the octanol concentration. Thus, the importance of the technical improvement achieved with the new micropipette interfacial area-expansion method becomes clear, –we can now measure dynamic surface tensions within the initial 1–15 s time range, compared to the previous micropipette technique [14].

The pure water control (0 mM, diamonds) showed an interesting effect that appears to be due to a transient heating of the air in the tube connecting the micropipette to the syringe pump, causing slight friction from a rapid plunging of the piston. As described in more detail in the Supplementary Materials section, this was nevertheless self-correcting.

Correspondingly, since this area reduction was carried out at a constant applied pipette pressure, these interfacial radii were converted to surface tensions by applying the Laplace equation (Eq. (5)). As shown in Fig. 6B, the surface tension concomitantly fell

<table>
<thead>
<tr>
<th>Method</th>
<th>$T$ (°C)</th>
<th>$\Gamma_m \times 10^{-5}$ (mol/m$^2$)</th>
<th>$K_L , \text{mol/m}^3$</th>
<th>$K_F , \text{mol/m}^3$</th>
<th>$\Gamma_m \times 10^{-5}$ (mol/m$^2$)</th>
<th>$K_L , \text{mol/m}^3$</th>
<th>$K_F , \text{mol/m}^3$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropipette interfacial area-expansion</td>
<td>20</td>
<td>7.75</td>
<td>2.4 ± 0.2</td>
<td>–</td>
<td>This work</td>
<td>–</td>
<td>Lin [15]</td>
<td></td>
</tr>
<tr>
<td>Micropipette interfacial area-expansion</td>
<td>20</td>
<td>7.75</td>
<td>–</td>
<td>3.0 ± 1.0</td>
<td>This work</td>
<td>–</td>
<td>Lin [15]</td>
<td></td>
</tr>
<tr>
<td>Pendant bubble/Wilhelmy plate</td>
<td>25</td>
<td>8.96</td>
<td>1.80</td>
<td>–</td>
<td>Bleys [19]</td>
<td>–</td>
<td>Chang [16]</td>
<td></td>
</tr>
<tr>
<td>Oscillating jet</td>
<td>22</td>
<td>5.91</td>
<td>6.0</td>
<td>4.8</td>
<td>Chang [16]</td>
<td>–</td>
<td>Chang [16]</td>
<td></td>
</tr>
<tr>
<td>PBS/Du Noüy’s ring</td>
<td>20–25</td>
<td>7.5</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>
very rapidly within the first few seconds upon exposure of the formed clean air-water surface (\( \gamma = 73 \) mN/m) to the solutions of 1-Octanol. The surface tension drop (Fig. 6B) therefore corresponded to 1-Octanol adsorption, resulting in the corresponding reduction in interfacial area and its surface tension. In the experiment, the approach to each equilibrium value was also monitored, showing that each tension at equilibrium attained the same values as obtained in the equilibrium surface tension measurements (see Fig. 4 and Table 1). In these surface tension plots (Fig. 6B), the transient heating effect of the air in the tube was shown to be irrelevant, since it was self-correcting and, for the clean 0 mM octanol water control (diamonds), the tension as expected was unchanged.

4.2.2. Diffusion coefficient of 1-Octanol from long-time range regime

Focusing on the analysis of the long-time range adsorption regime of the Ward-Tordai equation (Eq. (2)), in order to obtain the diffusion coefficient, \( D \), of 1-Octanol molecules diffusing to the interface, we must use the more-steady and reliable dynamic surface tension results beyond times of 1 s (Note: limitations of the measurement at the short-time range adsorption regime is discussed in the Supplementary Materials). Fig. 7 shows the dynamic surface tension results for the pure-water control and each aqueous concentration of 1-Octanol as a function of the reciprocal square root of the adsorption time, \( t^{-1/2} \) (Eq. (2)). The best linear fitting lines, predicted from a linear relationship between surface tension and \( t^{-1/2} \) of the Ward-Tordai model, were calculated from the slope derived by the Ward-Tordai model, Eq. (2), from at least three separate runs for each concentration. The \( y \)-axis intercept of each fitting line shows the equilibrium surface tension for each concentration.

In Fig. 7, three independent dynamic surface tension results were plotted together at each concentration. The pure water control showed the expected zero slope, signifying no measurable dynamic process for the air-water interface. To calculate the diffusion coefficient of 1-Octanol from the diffusion-controlled model requires the equilibrium surface excess, \( \Gamma_{\text{eq}} \), and the slope of the \( \gamma \) vs \( t^{-1/2} \) plot at each concentration. Using the Langmuir (Eqs. (7) and (8)) and Frumkin isotherm models (Eq. (11)), proper values of \( \Gamma_{\text{eq}} \) for the 1-Octanol monolayer at the air-water interface were estimated from the results of the micropipette equilibrium interfacial tension measurements in Fig. 5. Fig. 8 shows the plot of the \( \Gamma_{\text{eq}} \) values vs \( \gamma_{\text{eq}} \) values for each concentration of 1-Octanol applying the parameters in the equations for each model.

Here, we require two parameters, –the excess concentration \( \Gamma_{\text{eq}} \) and the diffusion coefficient \( D \), in order to investigate the isotherm models and their ideality or non-ideality. As shown in Fig. 8, when
no 1-Octanol is present, the surface tension was at its usual value of \(~73\) mN/m and the equilibrium surface excess, \(\Gamma_{eq}\), for both models was zero. However, with increasing 1-Octanol concentration, the Frumkin model curve showed a slightly higher \(\Gamma_{eq}\) over the whole range than the Langmuir model curve. The biggest difference of \(\Gamma_{eq}\) for the two model curves at the same \(\gamma_{eq}\) value of \(~50–56\) mN/m was around 0.5–1.0 mM 1-Octanol. This suggests that, with increasing 1-Octanol concentration, the rate of 1-Octanol adsorption reached its maximum value for its surface excess, \(\Gamma_{m}\), slightly faster according to the Frumkin isotherm model than that with Langmuir isotherm model. Therefore, the Frumkin model curve in Fig. 8 positioned slightly above the Langmuir model-curve.

Thus, the specific \(\Gamma_{eq}\) values were obtained for each concentration from these model curves, and used in the subsequent calculations for \(D\) (Table 3).

The analysed data showed a fairly constant \(D\) value for each independent measurement in the concentration range between 0.3 and 2.0 mM. This data supported the hypothesis that the mass transfer process of 1-Octanol was a simple diffusion controlled process, and we did not have to invoke the more complex and mixed kinetic-diffusion [15,18,19,59].

The average \(D\) values for the Langmuir isotherm model, \(4.6 \pm 0.9 \times 10^{-6} \text{cm}^2/\text{s}\), was similar to other different measurements in the literature, including, the pendant bubble method of \(3.0 \pm 1.7 \times 10^{-6} \text{cm}^2/\text{s}\) by Lin’s group (1997) and \(0.064 \pm 2.35 \times 10^{-6} \text{cm}^2/\text{s}\) by Phan et al. (2010) [15,60,61]. However, it was smaller than the value from the Taylor dispersion method, \(7.11 \times 10^{-6} \text{cm}^2/\text{s}\) [61,62], and spin-echo NMR measurement, \(6.5 \times 10^{-6} \text{cm}^2/\text{s}\) [31] (these values were prediction values since the low solubility of 1-Octanol in water compromised the limitation of the measurements). On the other hand, the \(D\) value for the Frumkin isotherm model, \(7.2 \pm 0.8 \times 10^{-6} \text{cm}^2/\text{s}\), was in excellent agreement with the data from the pendant bubble tensiometry method of Lin et al. [15] and the Taylor dispersion method [61]. Although the Langmuir model showed about a 1.5 times smaller \(D\) value, \(4.6 \pm 0.9 \times 10^{-6} \text{cm}^2/\text{s}\), this discrepancy could be explained in terms of the cohesive interaction between the adsorbed molecules at the air-water interface [15,60]. As it was discussed above, from the Frumkin model, the intermolecular interactions of 1-Octanol acted to increase their cohesive interactions with increasing the surface coverage, but not for the Langmuir model. The Langmuir model does not count the intermolecular interactions. Therefore, compared with the rate calculated from the Langmuir and Frumkin models in Fig. 8 showed a faster rate of adsorption of 1-Octanol as it reached its maximum \(\Gamma_{m}\) value with increasing 1-Octanol concentration. Since it was assumed that the adsorption of 1-Octanol followed a diffusion-controlled adsorption mechanism, the slower rate of 1-Octanol adsorption would underestimate the \(D\) value.

With regard to the intermolecular cohesive force for alcohol at the monolayer, Maldarelli’s group (1991) investigated the surface excess concentration and measured the DST of three different carbon chain alcohols, 1-Dodecanol, 1-Octanol and 1-Heptanol, with several different isotherm models including the Langmuir and Frumkin models [63]. 1-Dodecanol, having the longest carbon chain, showed a much more obvious disagreement between the Langmuir and Frumkin isotherm model-fittings in the low-concentration regime on the surface tension vs. concentration plot (Note: our 1-Octanol data only had a slight difference in low concentration regime (see Fig. 5)). Their large disagreement actually created more than a three-times underestimated \(D\) value for 1-Dodecanol from the Langmuir model analysis compared with that of the Frumkin model, which contrasted with the only 1.5 times difference for 1-Octanol found here and in Lin’s data [15]. Therefore, it assumes that longer-carbon chains could make a larger underestimated of the \(D\) value because of larger cohesive interaction at the interface monolayer (chain length and packing relations were already mentioned above in Section 4.1.3). In fact, a negatively decreasing \(k\) value from \(-3.9\) to \(-1.7\) was derived from the best-fitting of the Frumkin model with decreasing carbon chain length [63].

The Frumkin isotherm model parameter \(k\) is related to \(\Delta E\) in the following way shown in Eq. (12), consisting of the activation energy of adsorption, \(E_a\), and desorption, \(E_d\), according to the cohesive energy assumption [4,20,63,64],

\[
\Delta E = E_a - E_d = E_0^d - E_0^a + kRT \frac{\Gamma(t)}{\Gamma_m}
\]

(12)

where \(E_0^d\) and \(E_0^a\) are the initial activation energy constants before surface coverage occurs. Therefore, when \(k\) has a negative value, \(\Delta E\) decreases with increasing of surface excess concentration due to adsorption, i.e., leading to an effective increase in the rate of adsorption. The negatively decreasing \(k\) value also reflects the slowing rate of change of \(\Delta E\) with increasing \(\Gamma(t)\), i.e., for smaller carbon chain length alcohols there is a slowing down of the effective increase in the rate of adsorption. Maldarelli’s group concluded that, when a molecule had long and slender hydrophobic chain, it could make stronger intermolecular attractions upon reaching a critical value of surface coverage. The underestimation of the \(D\) value from the Langmuir isotherm model found by our method was also consistent with the literature, following the concept of an increase in cohesive interactions with increasing surface coverage.

### Table 3

<table>
<thead>
<tr>
<th>Conc. (mM)</th>
<th>Long-time approximation</th>
<th>Langmuir</th>
<th>Frumkin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(D \times 10^{-6} \text{cm}^2/\text{s})</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>4.0 ± 0.6</td>
<td>6.5 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>3.8 ± 0.2</td>
<td>7.4 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>5.5 ± 0.8</td>
<td>8.3 ± 1.2</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>5.2 ± 1.2</td>
<td>6.6 ± 1.5</td>
<td></td>
</tr>
<tr>
<td>Ave.</td>
<td>4.6 ± 0.9</td>
<td>7.2 ± 0.8</td>
<td></td>
</tr>
</tbody>
</table>
includes the non-ideal contributions of the interaction 1-Octanol molecules at the interface that are also embedded in the Frumkin isotherm.

Fig. 9B shows the measurements done to obtain the diffusion coefficient of 1-Octanol in water by this technique. As shown in Fig. 9A, the change of microdroplet radius over time was obtained for three separate droplets dissolving in water at 20 °C.

Each of the three 1-Octanol microdroplets, that were around 30 μm in radius, dissolved in water in ~1000–1100 s. Interestingly this method was so sensitive that it also detected the ~0.6 %v/v water-insoluble impurity material(s), that precipitated out as a water-insoluble microdroplet. As described more fully in Supplementary Materials we consider that this material(s) would not affect the 1-Octanol monolayer formation because it couldn’t solve in water and 1-Octanol is quite a strong surface active agent. The obtained diffusion coefficient of 1-Octanol by using the Frumkin model to estimate the D value. More details about the limitations of the short-time approximation were discussed in Supplementary Materials.

**5. Conclusions**

A new technique to measure dynamic surface tensions (DST), the *micropipette interfacial area-expansion method*, was introduced and validated with one of the most well-characterized non-ionic surface active compounds, 1-Octanol. The obtained diffusion coefficient of 1-Octanol by using the Frumkin model to estimate the surface tension-derived result from combining the Frumkin isotherm and Ward-Tordai models, 7.2 × 10⁻⁶ cm²/s, but not with the Langmuir isotherm model result, 4.6 × 10⁻⁶ cm²/s, which estimated a lower Γ_s as shown in Fig. 8. Diffusion coefficient values are summarized in Table 4 for each method including reference values using different dynamic surface tension measurements from the literature.

Interestingly, the oscillating jet method appears to have comparatively underestimated the D value, even though the adsorption data did not require any estimation of Γ_s to be made because of using the short-time adsorption approximation of the Ward-Tordai model (see Supplementary Materials, Eq. (S3)). Their dynamic surface tension measurement was less than 20 ms. As mentioned it above, there was probably some convective-induced uncertainty associated with the initial time range for such rapid area-growing methods, and so this could be the reason that this oscillating jet method gave a comparatively lower value for the D value. More details about the limitations of the short-time approximation were discussed in Supplementary Materials.

### Table 4

Comparison of 1-Octanol diffusion coefficient measured by different dynamic surface tension measurements and our new single microdroplet catching method. The oscillating jet method by Bley and Defay found the diffusion coefficient from the short-time adsorption approximation of the Ward-Tordai model [18,19]. The oscillating jet method measured 1-Octanol dynamic adsorption within 20 ms.

<table>
<thead>
<tr>
<th>Method</th>
<th>Model</th>
<th>D × 10⁻⁶ (cm²/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropipette interfacial area-expansion</td>
<td>Langmuir</td>
<td>4.6 ± 0.9 (0.3–2.0 mM)</td>
<td>This work</td>
</tr>
<tr>
<td>Micropipette interfacial area-expansion</td>
<td>Frumkin</td>
<td>7.2 ± 0.8 (0.3–2.0 mM)</td>
<td>This work</td>
</tr>
<tr>
<td>Single microdroplet catching</td>
<td>Epstein-Plesset</td>
<td>7.3 ± 0.1</td>
<td>This work</td>
</tr>
<tr>
<td>Pendant bubble/Withelmy plate</td>
<td>Langmuir</td>
<td>3.0 ± 1.7 (0.3–0.8 mM)</td>
<td>Lin [15]</td>
</tr>
<tr>
<td>Pendant bubble/Withelmy plate</td>
<td>Frumkin</td>
<td>7.3 ± 1.2 (0.3–0.8 mM)</td>
<td>Lin [15]</td>
</tr>
<tr>
<td>Oscillating jet</td>
<td>Short-time WT</td>
<td>5.0 (0.5 – 1.34 mM)</td>
<td>Bley [19]</td>
</tr>
<tr>
<td>Oscillating jet</td>
<td>Short-time WT</td>
<td>4.9 (3.44 mM)</td>
<td>Defay [18]</td>
</tr>
</tbody>
</table>
with cohesive energy assumptions [63]. These dynamic measurements require high sensitivity and accuracy in order to obtain a high consistency of the surface excess concentrations of the surfactant, \( \Gamma (t) \), and, in turn, to obtain accurate information about the dynamic properties of surfactant molecules, such as their diffusion coefficient. Therefore, in order to further validate our new micropipette technique for DST measurement, we employed a second micropipette-based method, the single microdroplet catching method, which can measure the diffusion coefficient for even highly water-insoluble materials. The values for the 1-Octanol diffusion coefficients obtained from both of these new methods were in excellent agreement with each other, being 7.2 ± 0.8 × 10^-7 cm²/s by applying the Frumkin isotherm model to the DST measurement, and 7.3 ± 0.1 × 10^-6 cm²/s using the Epstein-Plesset model for microdroplet dissolution. Thus, we concluded that the new micropipette interfacial area-expansion method provided highly sensitive and accurate dynamic surface tension measurements with the sufficient consistency.

We expect that, once developed and tested for other materials, especially for ionic surfactants, as well as lipids, peptides, and proteins, and other surface-active materials, these techniques will be able to provide new insights into both simple and ideal cases, as well as less ideal, diffusion-controlled adsorption and liquid-liquid dissolution.

Acknowledgment

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcis.2016.10.052.

References


