



The importance of experimental design on measurement of dynamic interfacial tension and interfacial rheology in diffusion-limited surfactant systems



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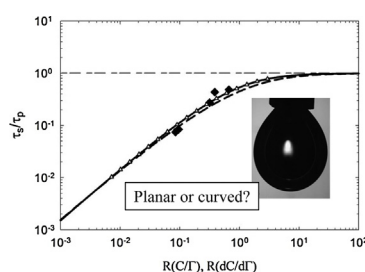
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HIGHLIGHTS

- Guidelines for design of interfacial rheology measurements that incorporate curvature and surfactant isotherm.
- Interfacial mechanics using a pendant drop/bubble.
- Scaling to design dynamic interfacial tension experiments on curved interfaces.
- Demonstration of scaling using experiments and simulations.

GRAPHICAL ABSTRACT



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ABSTRACT

Pendant bubble and drop devices are invaluable tools in understanding surfactant behavior at fluid–fluid interfaces. The simple instrumentation and analysis are used widely to determine adsorption isotherms, transport parameters, and interfacial rheology. However, much of the analysis performed is developed for planar interfaces. The application of a planar analysis to drops and bubbles (curved interfaces) can lead to erroneous and unphysical results. We revisit this analysis for a well-studied surfactant system at air–water interfaces over a wide range of curvatures as applied to both expansion/contraction experiments and interfacial elasticity measurements. The impact of curvature and transport on measured properties is quantified and compared to other scaling relationships in the literature. The results provide tools to design interfacial experiments for accurate determination of isotherm, transport and elastic properties.

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1. Introduction

Understanding the interfacial behavior of surfactants, or surface active agents, is vital to the design and optimization of commercial and consumer formulations involving these species. Interfacial

behavior is critical to the performance of coatings, emulsions, oil dispersants, and even commercial food products. Generally, the first step of any interfacial study on surfactants is to define an equilibrium isotherm that describes the mass coverage of surfactant on an interface as a function of bulk concentration. This can be performed by measuring the interfacial tension, γ , of a surfactant solution in contact with some other immiscible fluid phase (air, water or oil) for a range of surfactant concentrations. The interfacial tension, γ , is related to the mass coverage, Γ , via the

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Gibbs equation, $\Gamma = d\gamma/d \ln(C)$, where C is the bulk concentration.

For interfaces not at equilibrium, understanding of specific interfacial behavior requires characterization of the transport dynamics of surfactant to the interface. An equilibrium isotherm, combined with an equation of state (which relates the interfacial tension to the interfacial coverage), allows quantification of changes in interfacial coverage that arise either from normal equilibration processes (such as transport to an initially surfactant-free interface), or forced changes in interfacial area. Both the isotherm and mass transport problems are often complex and the goal of experiments is to parameterize the results with respect to a transport model. The isotherm and equation of state contain parameters including a maximum packing concentration, ratios of adsorption/desorption probabilities and other terms to capture intermolecular interactions and packing on the interface. Mass transport models include bulk diffusion coefficients, specific rate constants for adsorption or desorption, local flow or convection and geometry and incorporation of the isotherm as a boundary condition.

Digital imaging methods have allowed pendant bubble and pendant drop techniques to become core tools in the characterization of interfacial surfactant dynamics [1]. These techniques consist of forming a millimeter scale droplet or bubble pinned to the end of a capillary immersed in a volume of surfactant solution. Shape changes in the interface, which is distended by gravity or buoyancy, are analyzed and focus has been on the details of the fitting algorithms [2–4]. Since surfactant behavior is sensitive to the interfacial concentration, the contraction or expansion of an interface is used for both determining transport parameters and verifying equilibrium isotherm parameters [5–9]. A pendant bubble or drop is allowed to equilibrate, and is then compressed or expanded at a constant rate to extract isotherm parameters. As techniques using milliscala and microscale interfaces become more common, it is important to assess the relative impact of isotherm and transport properties on the measured interfacial/surface tension.

Surfactant adsorption to the interface is governed by diffusion and “reaction”, or adsorption/desorption, kinetics [10–12]. The scope of this study is focused on diffusion-limited systems where adsorption kinetics is assumed to not impact the observed behavior, and more specifically addresses the impact of interfacial curvature. And while discussions of curvature effects have long been present in the literature, their adaptation has been limited [13,14]. In a diffusion-limited surfactant system, the bulk concentration near the interface is assumed to be in equilibrium with the interface at all times. Applied surface deformations change the interfacial concentration, which simultaneously changes the concentration near the interface to maintain equilibrium. Concentration gradients between the fluid near the interface and the bulk then drive diffusion of molecules to or away from the interface.

The surface coverage of surfactant as a function of time is described with Fick’s law of diffusion, in spherical coordinates,

$$\frac{\partial C}{\partial t} + v_r \frac{\partial C}{\partial r} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right), \quad (1)$$

where v_r is the fluid radial velocity, r is the radius, t is time, D is the bulk diffusion coefficient, and $C(r,t)$ is the concentration as a function of radius and time. The use of this equation to model mass transport to a curved interface is well established [15,16]; in cases where the Peclet number is much greater than one, a planar assumption holds where the transport lengthscale is that of the fluid boundary layer. We will show that even in cases of high Pe cases for compression and expansion, it is still possible to need to account for curvature in elasticity measurements.

The mass balance at the interface, again in spherical coordinates, is given as

$$\frac{d\Gamma}{dt} + \frac{2\Gamma}{r} \frac{dr}{dt} = D \left(\frac{dC}{dr} \right)_{r=R}. \quad (2)$$

An isotherm is needed to define $\Gamma(C)$ and for this study, the Generalized Frumkin isotherm is used,

$$\frac{\Gamma}{\Gamma_\infty} = x = \frac{C}{a \cdot \exp(Kx^n + C)}, \quad (3)$$

as it describes the behavior of surfactant used in this work [1,17–19]. The parameters that are specific to the surfactant are D (the molecular diffusion coefficient) and the four isotherm parameters, K , which represents a surface van der Waals interaction term, n , a fitting parameter that adjusts the isotherm between the Frumkin ($n=1$) and Langmuir ($n=0$) equations, a , the ratio of the desorption to adsorption kinetic rate constants and, Γ_∞ , the surface coverage at its maximum value [20]. Note that none of these parameters should depend on the bulk concentration or the geometry of the interface. We define $x = \Gamma/\Gamma_\infty$ for convenience. The Gibbs equation using the Generalized Frumkin isotherm provides an equation of state to relate the measurable interfacial or surface tension to interfacial concentration,

$$\gamma - \gamma_0 = \Gamma_\infty RT \left[\ln(1-x) - \frac{Kn}{n+1} x^{n+1} \right]. \quad (4)$$

Solving Eqs. (1)–(4) allows the measurable dynamic interfacial tension to be related to the transport in these complex systems. This combination of the diffusion equation and isotherm provides a model that is used to predict the interfacial properties as a function of time or change in the interfacial area given the isotherm and transport parameters.

Dilatational elasticity measurements also provide a tool to determine mass transport properties of surfactants. Using pendant bubble or drop tensiometry, the interfacial response to an oscillatory area deformation is used to approximate dilatational rheology [21–25], and then extract diffusion coefficients from model fits to data. This is achieved by measuring the surface tension of a drop or bubble during an applied deformation, and characterizing the response as a function of deformation rate and the equation of state for the surfactant in question. The ratio of the response to the deformation is the complex modulus E^* , where the real and imaginary parts correspond to an elastic and viscous contribution. Using the Fourier transform of the deformation, it is possible to calculate E^* [5],

$$E^*(\omega) = \frac{\mathcal{F}\{\Delta\gamma(t)\}}{\mathcal{F}\{\Delta \ln(A(t))\}}, \quad (5)$$

where F is the Fourier transform function, $\Delta\gamma(t)$ is the change in surface tension as a function of time, $A(t)$ is the surface area as a function of time, and E^* is a function of angular frequency ω . For a small-amplitude single harmonic (i.e., sine wave) oscillation of the interfacial area, the modulus becomes,

$$E^* \approx A_0 \frac{d\gamma}{dA}, \quad (6)$$

where $d\gamma$ is the amplitude of the surface tension signal, dA is equal to the amplitude of the area signal, and A_0 is the median area of the applied oscillation. The origin of this stress–strain relationship is the focus of many publications [9,26–32].

For the simplest case of no mass transfer between the interface and the bulk and no interaction between adsorbed molecules on the interface, the elasticity is constant over small deformations, and is referred to as the Gibbs elasticity [33].

$$E_0 = - \frac{d\gamma}{d \ln(\Gamma)}, \quad (7)$$

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