

An examination on the validity of the assumptions commonly made in dynamic surface tension measurement using a pendant bubble

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Received 1 July 2007; accepted 24 October 2007

Available online 21 December 2007

Abstract

The assumptions commonly made in dynamic surface tension (DST) measurement using the pendant bubble method are examined. A pendant bubble changes its shape in response to DST due to surfactant adsorption. The shape change induces motion in the bulk fluid during the relaxation of surface tension. Three assumptions motivated by which are: (i) negligible influence of the bulk fluid motion, (ii) uniform surface concentration along the bubble surface, and (iii) negligible convective effects in surfactant mass transfer. The first two are related to the validity of the use of the Young–Laplace equation for DST measurement, so that DST measurement can be conducted under the conditions of keeping a bubble nearly hydrostatic and of a constant surface tension at each instant in time. The last assures the transport process to be diffusion-dominated, so that genuine kinetics can be examined without being mediated by the bulk convection. This study invokes a dimensional analysis to inspect these assumptions via identifying relative importance among relevant effects. Experimental data are provided for justification. Criteria are not only established in line for validating these assumptions, but also guide in the choice of appropriate experimental conditions for conducting DST measurement. © 2007 Elsevier B.V. All rights reserved.

Keywords: Air–water interface; Convection; Diffusion; Dimensional analysis; Dynamic surface tension; Pendant bubble; Surfactant; Young–Laplace equation

1. Introduction

As surfactant lands on an air–liquid interface, it reduces surface tension. The amount of surfactant on the interface determines surface tension, and the relaxation of surface tension depends on (i) the kinetic exchange of surfactant between the interface and the bulk phase and (ii) the surfactant diffusion in bulk phase.

This surfactant transport process is regulated by adsorption/desorption at the interface and diffusion through the bulk, which in turn causes the surface concentration to change with time, and hence the surface tension. The surface tension relaxes during this transport process and is termed the dynamic surface tension (DST). DST is often used to characterize the features of interfacial mass transport, providing a unique signature for a given aqueous–air system with surfactant.

The pendant bubble method is commonly employed to measure DST [1,2]. The working principle is to utilize the Young–Laplace equation that describes how the shape of a bubble adjusts in response to the change in surface tension. Using the image of the bubble shape at a given time, the surface tension can be obtained by fitting the Young–Laplace equation, and thereby DST can be monitored accordingly.

The purpose of this note is to revisit three assumptions commonly made in DST measurements using the pendant bubble method. First, as a bubble is changing its shape during DST, the induced fluid motion is assumed to be sufficiently slow so that its effects are negligible. Second, the surface concentration is assumed to be uniform along the surface so that the surface tension keeps constant at any instant during the relaxation. Third, by assuming the bulk fluid motion is weak, the mass transfer of surfactant thereof is further assumed to be dictated by diffusion. The first two assumptions are related to the validity of application of the Young–Laplace equation to DST measurement; they entail the system to stay nearly hydrostatic. The third offers a simplified way to assess the surfactant transport without the need in acquiring convective effects from the bulk.

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The validity of the first two assumptions has been established by Wong et al. [3] for an expanding or contracting bubble. Nevertheless, it stills lacks a justification for the pendant bubble method. The main difference between these two methods is that the motion of an expanding bubble is created by the displacement in response to an applied air flow while that of a pendant bubble is simply an adjustment due to DST.

In general, an expanding bubble creates a stronger flow field than a pendant bubble does. More importantly, the former has a definite velocity scale whereas there is no apparent velocity scale in the latter. While using an expanding bubble appears a useful method for DST measurements, the bulk convection could be critical to the surfactant mass transfer since it often depends on the conditions of applied flows. This could make the interpretation of DST masked by the influence of flow [4,5]. In this regard, the pendant bubble method might be more appealing to identify the genuine kinetics occurring in DST provided that the mass transfer of surfactant in the bulk can be indeed dominated by diffusion, which motivates the third assumption.

In this work, we shall devise a dimensional analysis to examine these assumptions, so that the relative importance among relevant effects can be identified. We then can derive the conditions under which the assumptions hold; hence the criteria established from which can furnish guidance in choosing appropriate conditions for conducting DST experiment.

2. Dimensional analysis

2.1. Fluid motions induced by bubble deformations

We first inspect the first assumption. Letting \mathbf{v} and p denote the velocity field and pressure in an incompressible liquid of density ρ and viscosity μ , the relevant equation involve the Navier–Stokes equation [4,6]:

$$\rho(\mathbf{v}_t + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + \rho g \mathbf{e}_g + \mu \nabla^2 \mathbf{v}, \quad (1)$$

and the normal stress condition at the interface,

$$p_{\text{air}} - p + \mu \mathbf{n} \cdot (\nabla \mathbf{v} + \nabla \mathbf{v}^T) \cdot \mathbf{n} = \gamma (\nabla_s \cdot \mathbf{n}) \quad (2)$$

Here, p_{air} is the gas pressure, \mathbf{n} is the unit normal along the interface, γ is the surface tension and g is the gravitational acceleration. In (2), $\nabla_s \cdot \mathbf{n}$ represents the mean curvature of the interface. To assess the influence of flow relative to the others, we estimate the scale of each effect. Since motions of a pendant bubble arise from DST in view of (2), the scale of p should be the capillary pressure γ_0/R_0 with γ_0 being the surface tension of a clean interface and R_0 being the typical size of a bubble. Thus, the pressure term in (1) has a scale γ_0/R_0^2 .

Assuming that the velocity scale is U , then the viscous term in (1) has a scale $\mu U/R_0^2$, and hence its effects relative to the capillary pressure can be reflected by $\mu U/\gamma_0$ which is usually referred to as the capillary number Ca . The inertia terms of (1) have a scale $\rho U^2/R_0$, so their effects relative to surface tension are $ReCa = \rho U^2 R_0/\gamma$, where $Re = \rho U R_0/\mu$ is the Reynolds number. The relative effect of buoyancy to surface tension is

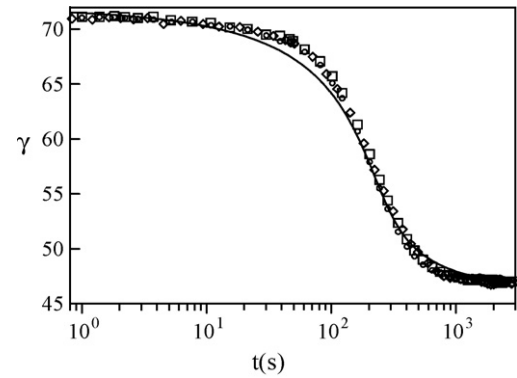


Fig. 1. DST data (symbol) for $C_{12}E_4$ adsorption onto a freshly created air–water interface. The line is the best-fit curve using Langmuir isotherm. $\Gamma_\infty = 3.90 \times 10^{-10}$ mol/cm², a (the ratio of desorption to adsorption rate constants) = 4.66×10^{-10} mol/cm³, $C_0 = 6 \times 10^{-9}$ mol/cm³.

represented by the Bond number $Bo = \rho g R_0^2/\gamma_0$. Similarly, in (2) viscous and buoyancy effects relative to surface tension are again reflected by Ca and Bo , respectively.

The effects of flow can be negligible if $Ca \ll 1$ and $ReCa \ll 1$, as we shall check *a posteriori* using DST data. In this case, (1) and (2) reduce to

$$0 = -\nabla p + \rho g \mathbf{e}_g, \quad (3)$$

$$p_{\text{air}} - p = \gamma (\nabla_s \cdot \mathbf{n}) \quad (4)$$

Accordingly, the system can be regarded as hydrostatic. That is, for a given γ , the interface reaches the equilibrium shape instantly; the influence of fluid motion relative to surface tension is $O(Ca)$.

Estimate of Ca entails the scale of U . It can be estimated from the temporal evolution of a bubble in response to DST. Since most of the systems are diffusion-controlled, DST can be analyzed through its relaxation behavior. Fig. 1 shows a typical temporal behavior of a DST and suggests that

$$\frac{\gamma_0 - \gamma}{\gamma_0 - \gamma_\infty} = f\left(\frac{t}{\tau}\right), \quad (5)$$

where f is a slow time-varying function with $f(t=0)=0$ and $f(t \rightarrow \infty) \rightarrow 1$. Here, $\gamma_\infty \equiv \gamma(t \rightarrow \infty)$ is the new equilibrium surface tension. τ is the relaxation time scale. For a diffusion-controlled process, $\tau \sim h^2/D$ with h being the adsorption depth and D being the diffusivity of surfactant.

Let R be the mean curvature of the interface, say at the bubble apex, and $R_0 \equiv R(t=0)$. Now inspecting (4), suppose that the hydrostatic pressure of the liquid does not change rapidly during the relaxation, R in response to the change in γ can be approximated via $\gamma/R \sim \gamma_0/R_0$. Thus,

$$R \sim R_0 \left(1 - \frac{\gamma_0 - \gamma_\infty}{\gamma_0} f\left(\frac{t}{\tau}\right)\right). \quad (6)$$

It follows that

$$U = \left| \frac{dR}{dt} \right| \sim R_0 \frac{(\gamma_0 - \gamma_\infty)}{\gamma_0 \tau}. \quad (7)$$

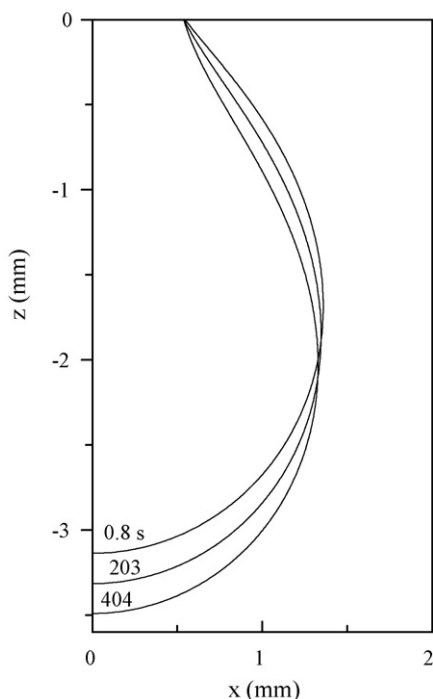


Fig. 2. An example of the relaxation of a pendant bubble for $C_{12}E_4$ adsorption onto a freshly created air–water interface. $C_0 = 6 \times 10^{-9}$ mol/cm³. Bubble age = 0.8, 203 and 404 s.

As such, we can estimate U based on both DST data and bubble dynamics. Fig. 2 is an example of the bubble evolution during a DST relaxation. The reduction of the surface tension makes R decreased, hence leading the bubble to be elongated as a consequence of mass conservation. For $R_0 \sim 0.1$ cm, $\gamma_0 = 70$ dyne/cm, $\gamma_\infty \sim 50$ dyne/cm, and $\tau \sim 10^3$ (for $h \sim 10^{-1}$ cm and $D \sim 10^{-5}$ cm²/s), these parameters give $U \sim 10^{-5}$ cm/s. Fig. 3 shows an example of the history of the bubble-apex movement. It reveals that both short ($t < 400$ s) and long ($600 \text{ s} < t < 3000$ s) time evolutions have speeds of 6.6×10^{-5} and 0.35×10^{-5} cm/s, respectively, which agree with the scale of U estimated above. Further evidence for supporting this velocity scale is also provided by examining bubble evolutions at different surfactant concentrations, as tabulated in

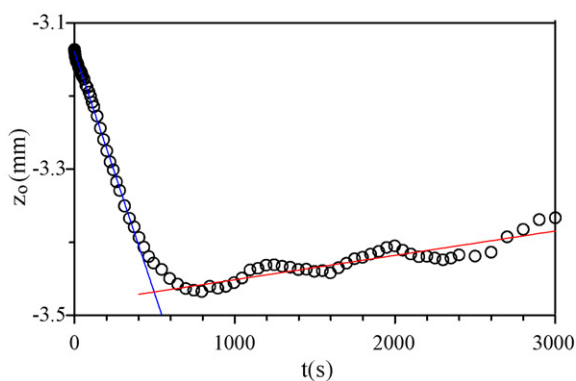


Fig. 3. A history of the bubble-apex movement. The short ($t < 400$ s) and long ($600 \text{ s} < t < 3000$ s) time evolutions have speeds of 6.6×10^{-5} and 0.35×10^{-5} cm/s, respectively.

Table 1

The speed (v) of the apex relaxation of a pendant bubble at different bulk concentrations of $C_{12}E_4$

C_0 ($\times 10^9$ mol/cm ³)	Time (s)	v (10^{-5} cm/s)
2	$50 < t < 450$	3.0, 1.1, 1.4, 1.4
	$1000 < t < 4000$	0.66, 0.73, 1.2, 0.58
6	$0 < t < 350$	6.6, 6.7, 6.6
	$600 < t < 3000$	−0.62, −0.045, −0.35
10	$10 < t < 150$	9.6, 7.1, 8.5, 10.6
	$350 < t < 3800$	−0.81, −0.59, −0.63, −0.65

Table 1. As such, the estimates of Ca and Re are $O(10^{-9})$ and $O(10^{-4})$, respectively, thus effects of the fluid motion are rather weak, and the bubble is virtually hydrostatic.

2.2. Uniformity of the surface concentration

We now turn our attention to the second assumption concerning if the Young–Laplace equation can be applied for DST measurement under the spatial-uniformity condition of surface tension. This requires examining the tangential stress condition. Let y and s denote the directions normal and tangential to the interface. We also let v be the tangential velocity. The tangential stress condition can be expressed in a simple form:

$$\mu \frac{\partial v}{\partial y} = -\frac{\partial \gamma}{\partial s} = \frac{RT}{1 - (\Gamma/\Gamma_\infty)} \frac{\partial \Gamma}{\partial s}. \quad (8)$$

Here we have invoked the equation of state: $\gamma - \gamma_0 = \Gamma_\infty R_g T \ln(1 - (\Gamma/\Gamma_\infty))$ where Γ_∞ is the maximum packing surface concentration, R_g the gas constant, and T the temperature. The left-hand side of (8) is the viscous stress of an order of $\mu U/R_0$; the right-hand side of (8) is the Marangoni stress of an order of $(\Gamma_\infty R_g T/R_0)/(1 - (\Gamma/\Gamma_\infty))$. The ratio of the former to the latter reflects the non-uniformity of Γ along the interface. It is Ca/E where $E = (\Gamma_\infty R_g T/\gamma_0)/(1 - (\Gamma/\Gamma_\infty))$ is the elasticity number. For $\Gamma_\infty \sim 10^{-10}$ mol/cm² at 25 °C, $E \sim O(10^{-2})$. Since $Ca \sim 10^{-9}$, we have $Ca/E \sim O(10^{-7})$. Consequently, the surface concentration is almost uniform, and the spatial uniformity of surface tension can be now justified.

2.3. Effects of convection on surfactant mass transfer

The last issue is concerning if the influence of convection can be neglected in surfactant mass transfer. Since convection can affect transports occurring in both the bulk and the interface, the corresponding effects are examined separately. We first inspect the mass transfer in the bulk. Consider the convective-diffusion equation [6]:

$$\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C = D \nabla^2 C. \quad (9)$$

To identify the relative effects of convection to diffusion, we consider both *far* field and *near* field behaviors below.

In the far field, suppose that one sees bubble dynamics in a distance of r away from the bubble, viz. $r \gg R_0$. As the bubble

grows, it looks like a nearly stationary point source in the far-field view, and induces an outward flow of a strength $\sim UR_0^2/r^2$. However, since the bubble is pinned at the needle, the bubble's necking near the rim also induces an inward flow that looks like a point sink of a strength $\sim UR_0^2/r^2$. Since the bubble volume remains almost unchanged during its evolution, a pair of source and sink works like a dipole having a strength $\sim UR_0^3/r^3$. As a result, the convective term has a scale $(UR_0^3/r^3)(1/R)C_0$ (C_0 the scale of the bulk concentration). Since the diffusive term is an order of $(D/r^2)C_0$, the relative effect of convection to diffusion is $Pe(R_0/r)^2$ where $Pe = UR_0/D$ is the Peclet number. For a sufficient large r , $Pe(R_0/r)^2$ is generally small for a typical pendant bubble with surfactant. The time scale in this region should be adjusted as r^2/D .

As in the near field, bubble deformations now become perceptible. Since we are interested in the mass transfer across the bubble surface, the convective flux should be viewed as a relative flux with respect to the moving surface. This modifies the time-derivative term $\partial C/\partial t$ in a frame reference to the bubble. Physically, as a bubble moves, it displaces the adjacent fluid material near the surface. Since this displaced material moves with an almost identical speed to the bubble, the associated convection is nearly offset by the moving surface. If diffusion is sufficiently fast across the displacement region, the influence of convection only manifests away from the bubble. But the flow also decays rapidly in the far field as discussed earlier; it therefore makes diffusion dominant throughout the entire fluid domain.

To illustrate the idea above, we consider a spherical bubble; so (9) can be written in the spherical coordinates (r, θ) with the corresponding velocity components (u, v) . Let $\eta = r/R$ be a variable in the moving coordinate where $R(t)$ is the bubble radius. Then the time-derivative term of (9) becomes

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial t} \Big|_{\eta} + \frac{\partial C}{\partial \eta} \frac{\partial \eta}{\partial t} = \frac{\partial C}{\partial t} \Big|_{\eta} + \frac{\partial C}{\partial \eta} \left(\frac{-\dot{R}}{R} \eta \right). \quad (10)$$

Lumping together with the convective term, we have

$$\frac{\partial C}{\partial t} \Big|_{\eta} + \left(\frac{u}{R} - \frac{\dot{R}}{R} \eta \right) \frac{\partial C}{\partial \eta} + \frac{v}{R\eta} \frac{\partial C}{\partial \theta} = \frac{D}{R^2 \eta^2} \frac{\partial}{\partial \eta} \left(\eta^2 \frac{\partial C}{\partial \eta} \right) \quad (11)$$

The second term of (11) reflects the convective flux relative to the moving bubble surface. Now consider the region near the bubble surface, we have $u \sim \dot{R}(1 + O(\delta/R_0))$ where δ is the scale of bubble displacements and R_0 is the scale of R . Since $\eta \sim 1 + O(\delta/R_0)$ near the bubble surface (so that $\partial/\partial \eta \sim \delta^{-1}$), the second term of (11) is $O(UC_0/R_0)$. Similarly, the third term is found to be $O(UC_0/R_0)$ as well. In comparison with the diffusive term of $O(DC_0/\delta^2)$, the relative effect of convection to diffusion is $O(U\delta^2/(R_0D))$. For $U \sim 10^{-5}$ cm/s, $R_0 \sim 10^{-1}$ cm, $\delta \sim 10^{-2}$ cm and $D \sim 10^{-5}$ cm²/s, these give $U\delta^2/(R_0D) \sim 10^{-3} \ll 1$. Thereby, diffusion dominates in the near field. The time scale in this region demands δ^2/D for capturing the change in the bulk concentration due to diffusion. As such, since diffusion prevails in both far and near fields, we conclude that diffusion dominates the mass transfer in the entire bulk region.

We now examine the surface transport of surfactant. For a uniform surface concentration as shown by (8), the transport along the interface is governed by

$$\frac{d\Gamma}{dt} + \frac{\Gamma}{r} \frac{\partial}{\partial s}(u_s r) + \Gamma u_n (\nabla_s \cdot \mathbf{n}) = -D\mathbf{n} \cdot \nabla C. \quad (12)$$

Here, we again assume that the surface kinetics is diffusion-controlled. The second and the third terms reflect the convective effects arising from surface convection and expansion, respectively. These convective terms are $O(U\Gamma_0/R_0)$. The diffusion term is $O(DC_0/\delta)$. The ratio of convection to diffusion is therefore $(UR_0/D)(\delta/R_0)^2(h/\delta)$. Here, we have invoked the adsorption depth $h = \Gamma_0/C_0$ for the diffusion term. The time scale for the surface transport becomes $h\delta/D$ which is not necessarily the same as that for the bulk transport. A typical DST measurement has $U \sim 10^{-5}$ cm/s, $R_0 \sim 10^{-1}$ cm, $\delta \sim 10^{-2}$ cm, $h \sim 10^{-1}$ cm and $D \sim 10^{-5}$ cm²/s. These lead the above ratio to be $O(10^{-2})$, suggesting that the influence of convection is again less important than diffusion in the surface transport.

3. Discussion

In light of the dimensional analysis above, we can establish criteria for validating the three assumptions in terms of parameters used in DST measurement. The parameters include the initial bubble size R_0 , the clean-interface surface tension γ_0 and the equilibrium surface tension γ_∞ , the adsorption depth h , and the diffusivity of surfactant D . These parameters provide scales of the bubble displacement δ , the relaxation time of surface tension τ , and the induced fluid velocity U . Defining $\Delta\gamma \equiv \gamma_0 - \gamma_\infty$, according to (6) and (7), these scales are summarized below:

$$\delta \sim \frac{R_0 \Delta\gamma}{\gamma_0}, \quad \tau \sim \frac{h^2}{D}, \quad U \sim R_0 \left(\frac{\Delta\gamma}{\gamma_0} \right) \left(\frac{D}{h^2} \right) \quad (13)$$

Using these scales, we recast the results of the preceding dimensional analysis and summarize them below. For the first assumption both $Ca \ll 1$ and $ReCa \ll 1$ are necessary for rendering a bubble to be nearly hydrostatic; they require, respectively,

$$\frac{\mu R_0 \Delta\gamma D}{\gamma_0^2 h^2} \ll 1, \quad (14)$$

$$\frac{\rho R_0^3}{\gamma_0} \left(\frac{\Delta\gamma}{\gamma_0} \right)^2 \left(\frac{D}{h^2} \right)^2 \ll 1. \quad (15)$$

Condition (14) demands that surface tensions dominate over viscous forces. Condition (15) necessitates inertial effects to be much smaller than surface tension effects. Also note that (15) does not involve the liquid viscosity.

The second assumption entails $Ca/E \ll 1$ for ensuring the uniformity of the surface concentration. That is,

$$\frac{\mu R_0}{\Gamma_\infty R_g T} \left(\frac{\Delta\gamma}{\gamma_0} \right) \left(\frac{D}{h^2} \right) \ll 1. \quad (16)$$

This condition suggests that surfactant molecules are sufficiently crowded so that the interface can be hardly stretched. In this case, the interface tends to be *tangentially* immobile while it

still can move in its *normal* direction. The rigidified interface does not affect the features of DST as long as convection can be negligible compared to diffusion in the surfactant transport, which is discussed below.

Finally, convective transports of surfactant in both the bulk and the bubble surface can be negligible if both the convection-diffusion ratios $U\delta^2/(R_0D) \ll 1$ (for the bulk) and $(h/\delta)U\delta^2/(R_0D) \ll 1$ (for the surface) can be satisfied. These two conditions are equivalent to, respectively,

$$\left(\frac{R_0}{h}\right)^2 \left(\frac{\Delta\gamma}{\gamma_0}\right)^3 \ll 1, \quad (17)$$

$$\left(\frac{R_0}{h}\right) \left(\frac{\Delta\gamma}{\gamma_0}\right)^2 \ll 1. \quad (18)$$

It is interesting to notice that neither (17) nor (18) depend on D albeit the transports are diffusion-controlled. This is because U is proportional to D according to (13), the ratio of convection to diffusion makes D cancelled out. Also, since $\gamma_0/\Delta\gamma > 1$, (17) is sufficient to (18).

Conditions (14)–(17) constitute the constraints for fulfilling the requirements based on the assumptions commonly made in DST measurement. These conditions are derived by assuming that the kinetics for transporting surfactant is diffusion-controlled, as occurring in a typical DST measurement. Nevertheless, they are still applicable to the scenario even when the transport is mixed diffusive-kinetics controlled, viz., the adsorption/desorption rate is as low as the diffusion rate. In this case, either the diffusion or the kinetics time scale is appropriate for characterizing the relaxation behavior of DST; there is no fundamental difference from the present ansatz.

In practice, (14)–(16) are usually satisfied so that the use of the Young–Laplace equation for DST is warranted. (17) demands $R_0/h \ll (\gamma_0/\Delta\gamma)^{3/2}$. This suggests that if the size of a bubble (which can be controlled by the needle size) is too large compared to the adsorption depth, then the bulk convection could be susceptible to influencing the transport of surfactant,

and hence to the corresponding DST. That is, the smaller the adsorption depth, the smaller bubble size needed for eliminating the importance of convection. Moreover, if a surfactant has a very strong surface activity of lowering surface tension, the required bubble size for neglecting convective effects also has to be much smaller than the adsorption depth. This is because the larger $\Delta\gamma$, the greater the bubble displacement in response to DST. The resulting induced velocity becomes faster, thereby requiring a smaller bubble to expedite diffusion for diminishing the influence of convection.

In summary, we have examined the validity of the three common assumptions made for DST measurement using the pendant bubble method. Utilizing the dimensional analysis, we are able to identify the importance of convection in transport processes during a DST experiment. We also derive the criteria under which the influence of convection can be negligible. The criteria further furnish a guidance of how to choose appropriate conditions for conducting DST experiments.

Acknowledgement

This work was supported by the National Science Council of Taiwan under the grants NSC 89-2214-E-011-021 of SYL, and NSC 93-2214-E-006-021 of HHW.

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