NOTE

Diffusion-Controlled Adsorption at the Liquid–Air Interface: The Long-Time Limit

The applicability of the Hansen and Joos long-time limits for the dynamic surface tension of solutions is investigated by regressing diffusion coefficients from numerical solutions to the Ward and Tordai equation. The Hansen limit is found to correctly describe the dynamic surface tension evolutions at long times. However, both the surfactant concentration and the adsorption time affect the accuracy of the long-time limit. The study also indicates that, because the reduction in surface tension (at long times) may be smaller than can be measured by current tensiometry methods, the application of the Hansen limit to long-time data may not always be feasible. © 2001 Academic Press

Key Words: diffusion-controlled adsorption; dynamic surface tension; adsorption kinetics; diffusion coefficient.

INTRODUCTION

Adsorption of surfactant molecules to liquid–air interfaces is often studied via dynamic surface tension measurements. The simplest model considers diffusion of the surfactant through the bulk liquid to control the process, such that the interface is in local equilibrium with the layer of fluid directly below the surface (termed the subsurface). The most common expression for time-dependent adsorption is that of Ward and Tordai (1),

$$\Gamma(t) = \sqrt{\frac{4D}{\pi}} \left[C_o t^{1/2} + \int_0^t C_s(\tau) d\sqrt{t-\tau} \right],$$ [1]

where t is time, $\Gamma(t)$ is the surface concentration, D is the diffusion coefficient, C_o is the bulk concentration, $C_s(t)$ is the concentration at the subsurface, and τ is a dummy time-delay varible. Equation [1] must be solved numerically for all but the Henry (linear) adsorption isotherm (2). In an attempt to bypass the need for complicated numerical solutions when analyzing experimental data, equations for both short- and long-term adsorption behavior have been derived. Short-time behavior is obtained by considering only the first term (i.e., the $C_o t^{1/2}$ term) of Eq. [1]. Equations for long-time behavior have been derived by Hansen (3) and Joos (4). Hansen's equation is derived by examining expansions of the integral term at long times. The Joos analysis considers $C_s(t)$ to be constant at long times, such that it can be factored outside the convolution integral. The Hansen and Joos treatments of the Ward and Tordai equation yield the following different results, respectively,

$$\sigma(t)_{t\to\infty} = \sigma_{eq} + \frac{RT\Gamma_{eq}^2}{C_o}\sqrt{\frac{1}{\pi Dt}} \quad \text{(Hansen limit)}$$ [2]

$$\sigma(t)_{t\to\infty} = \sigma_{eq} + \frac{RT\Gamma_{eq}^2}{C_o}\sqrt{\frac{\pi}{4Dt}} \quad \text{(Joos limit),}$$ [3]

where σ_{eq} and Γ_{eq} are the equilibrium surface tension and concentration, respectively, and RT is the gas constant multiplied by the absolute temperature. The current literature contains many instances of the use of both of these long-time surface tension equations for estimating surfactant diffusion coefficients and measuring the equilibrium surface tension of slowly adsorbing surfactants. The Joos limit is the equation most commonly employed to interpret experimental data (5–8). Although the Hansen limit has also been used to analyze surface tension measurements (9), it most often appears in theoretical studies (10–12).

While both results exhibit the same $t^{-1/2}$ dependence, the slope of the Joos limit is 0.5π times larger than the slope of the Hansen limit. The discrepancy arises from differences in the treatment of Eq. [1]. The problem was addressed in Ref. (13), which determined that both limits showed "good agreement" if applied to different ranges of adsorption time. However, this finding suggests that any mathematical treatment of the Ward and Tordai equation should yield two equations equivalent to Eqs. [2] and [3] for specific ranges of t. A study by Hansen (14), which examined series expansions of the linear solutions derived by Sutherland, did not yield such a set of equations. In addition, the derivation of either Eq. [2] or Eq. [3] does not specify unique conditions on the interpretation of long-time results, such that a bounded range of applicability for each limit is not expected.

With regard to the referenced literature, the question of which limit is correct and what time range qualifies as "long-time" appears to be unresolved. This note seeks to determine which, if either, long-time equation approximates the Ward and Tordai equation correctly. This is done by generating numerical solutions to the Ward and Tordai equation and comparing the results to the long-time behavior predicted by the Hansen and Joos limits.

ANALYSIS

To test the applicability of the limits, a series of dynamic surface tension calculations for five different bulk concentrations is generated using a numerical solution to the Ward and Tordai equation. The solution to Eq. [1] is facilitated by a trapezoidal approximation of the convolution integral as described by Miller (15). For purposes of illustration, it is assumed that the Langmuir adsorption isotherm [4] describes the interfacial equilibrium,

$$\Gamma(t) = \frac{\Gamma_\infty C_s(t)}{C_s(t) + a_L},$$ [4]

where a_L characterizes the surface activity of the surfactant and Γ_∞ is the limiting surface concentration. All parameters, including Langmuir parameters and the diffusion coefficient, are specified. Next, the Ward and Tordai solutions are numerically differentiated and treated using long-time limit analysis. Specifically, diffusion coefficients are regressed from long-time calculations using the

Hansen and Joos slope limits,

$$D = \frac{1}{\pi} \left(\frac{RT\Gamma_{eq}^2}{S_{t\to\infty}C_o} \right)^2 \quad \text{(Hansen slope limit)} \qquad [5]$$

$$D = \frac{\pi}{4} \left(\frac{RT\Gamma_{eq}^2}{S_{t\to\infty}C_o} \right)^2 \quad \text{(Joos slope limit)}, \qquad [6]$$

where $S_{t\to\infty}$ represents the slope of the surface tension differentiated with respect to $t^{-1/2}$. In addition, a point-by-point estimate of the diffusion coefficient is obtained using a rearrangement of the approximated Ward and Tordai equation:

$$D = \frac{1}{\pi t} \left(\frac{\Gamma(t)}{C_o - C(0, t)} \right)^2 \quad \text{(Hansen point-by-point limit)} \qquad [7]$$

$$D = \frac{\pi}{4t} \left(\frac{\Gamma(t)}{C_o - C(0, t)} \right)^2 \quad \text{(Joos point-by-point limit)}. \qquad [8]$$

All results are scaled in accord with the nondimensional arguments presented in Ref. (16) such that the only parameter is the scaled concentration k:

$$k = \frac{C_o}{a_L}. \qquad [9]$$

Adsorption time is expressed on a dimensionless scale τ given by

$$\tau = \frac{DC_o^2 t}{\Gamma_{eq}^2}. \qquad [10]$$

Finally, a scaled apparent diffusion coefficient (represented by Δ) is calculated using

$$\Delta_{Slope} = \frac{1}{\pi D} \left(\frac{RT\Gamma_{eq}^2}{S_{t\to\infty}C_o} \right)^2 \quad \text{(Hansen slope limit)} \qquad [11]$$

$$\Delta_{Slope} = \frac{\pi}{4D} \left(\frac{RT\Gamma_{eq}^2}{S_{t\to\infty}C_o} \right)^2 \quad \text{(Joos slope limit)} \qquad [12]$$

$$\Delta_{Point} = \frac{1}{\pi Dt} \left(\frac{\Gamma(t)}{C_o - C(0, t)} \right)^2 \quad \text{(Hansen point-by-point limit)} \qquad [13]$$

$$\Delta_{Point} = \frac{\pi}{4Dt} \left(\frac{\Gamma(t)}{C_o - C(0, t)} \right)^2 \quad \text{(Joos point-by-point limit)}. \qquad [14]$$

It should be noted that Δ is simply the calculated diffusion coefficient divided by the specified diffusion coefficient. When $\Delta \approx 1$, the method for approximating the diffusion coefficient and its corresponding limit are valid.

Figure 1 presents the results of the Hansen and Joos Δ_{Slope} analysis. These results indicate that only the Hansen limit correctly predicts the adsorption behavior at long times. More specifically, all Hansen-derived Δ_{Slope} values approach unity as τ approaches infinity. This observation appears to hold for all k values included in this study and is supported by the independent point-by-point studies, presented in Fig. 2.

Figure 1 also indicates some general problems that may be encountered when analyzing dynamic surface tension data. First, the accuracy of the long-time approximation is strongly dependent on the time of observation. Regressions at $\tau = 100$ yield diffusion coefficients that are roughly within 15% of the specified value, while regressions below this time limit yield estimates that can be orders of magnitude above or below the set diffusion coefficient. In addition, the relative
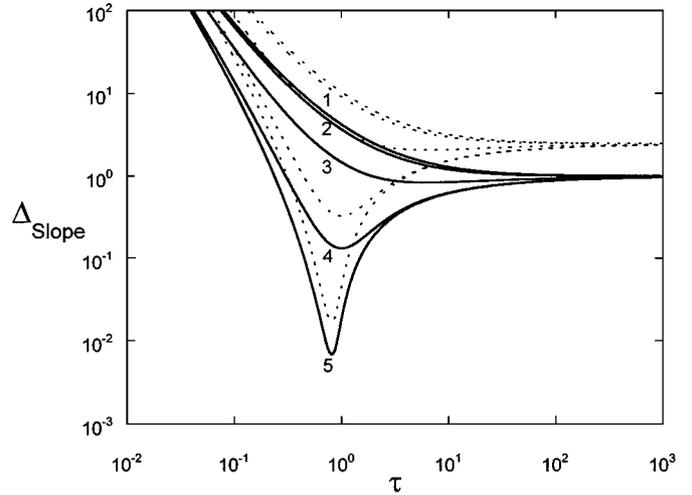
FIG. 1. Scaled apparent diffusion coefficients derived from the Hansen (solid lines) and the Joos (dashed lines) slope limits. Calculations are based on $\Gamma_{\infty} = 5.0 \times 10^{-10}$ mol/cm^2, $a_L = 1.0 \times 10^{-8}$ mol/cm^3, $D = 5.0 \times 10^{-6}$ cm^2/s, and $T = 22.0°$C. Concentrations studied were (1) $k = 0.01$, (2) $k = 0.1$, (3) $k = 1$, (4) $k = 10$, and (5) $k = 100$. The order of concentration is the same for both solid and dashed curves.

concentration of the solution is observed to strongly affect the estimated diffusion coefficient. At $\tau = 100$, the calculations yield $\Delta_{Slope} = 1.05$ for $k = 0.01$, but $\Delta_{Slope} = 0.87$ for $k = 100$. In short, the effect of both the observation time and the solution concentration should be considered when treating long-time data.

Surface tension measurements above $\tau = 100$ may be difficult to obtain in the laboratory because of slow surfactant adsorption. This is illustrated in Table 1, which shows regressed diffusion coefficients for $\tau > 100$ and specifies the time at which $\tau = 100$ is achieved. For most dilute solutions examined in this study, $\tau = 100$ represents times in excess of ten hours, and the measurement of surface tension in this regime would be tedious. As the
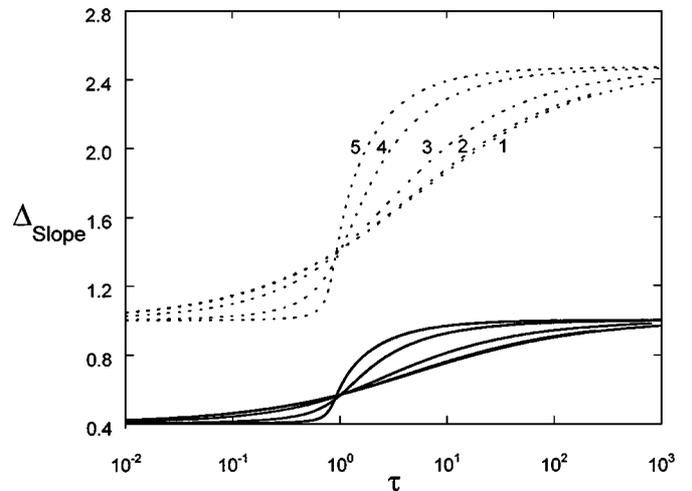
FIG. 2. Scaled apparent diffusion coefficients derived from the Hansen (solid) and Joos (dashed) point-by-point limits. Calculations are based on $\Gamma_{\infty} = 5.0 \times 10^{-10}$ mol/cm^2, $a_L = 1.0 \times 10^{-8}$ mol/cm^3, $D = 5.0 \times 10^{-6}$ cm^2/s, and $T = 22.0°$C. Concentrations studied were (1) $k = 0.01$, (2) $k = 0.1$, (3) $k = 1$, (4) $k = 10$, and (5) $k = 100$. The order of concentration is the same for both solid and dashed curves.

TABLE 1
Diffusion Coefficients Estimated by Linear Regression Above $\tau = 100$

K	Δ_{Slope} (Hansen)	Δ_{Slope} (Joos)	$t_{applicable}$[a]
0.01	1.01	2.49	13.6 h
0.1	1.01	2.49	11.4 h
1	0.96	2.37	3.6 h
10	0.98	2.42	6.8 min
100	0.95	2.35	5.1 s

Note. Indicates the time at $\tau = 100$ for the surfactant system described by $\Gamma_\infty = 5.0 \times 10^{-10}$ mol/cm^2, $a_L = 1.0 \times 10^{-8}$ mol/cm^3, $D = 5.0 \times 10^{-6}$ cm^2/s.

concentration increases, the time needed to achieve $\tau = 100$ becomes shorter and, at the highest concentration, is achieved in seconds.

Another problem associated with analyzing data beyond $\tau = 100$ is that, in this time regime, approximately 95% of the total reduction in surface tension has taken place. In dilute solutions showing low overall surface tension reductions, it may not be possible to measure long-time surface tension evolutions within experimental accuracy. For example, the $k = 0.1$ study involves a total reduction in surface tension of 1.2 dyne/cm. At $\tau = 100$, the measured surface tension would be within 0.1 dyne/cm of its equilibrium value. This is close to or beyond the limit of accuracy of most tensiometry methods, and changes in surface tension that are less than 0.1 dyne/cm would be difficult to track. On the other hand, more concentrated solutions are not as susceptible to this problem. At $\tau = 100$, the $k = 10$ solution is within 0.7 dyne/cm of its equilibrium, and changes in surface tension beyond this limit could be tracked with less difficulty.

CONCLUSIONS

Examination of the diffusion coefficients regressed from solutions to the Ward and Tordai equation imply that only the Hansen limit correctly describes surface tension behavior in the limit of long times. The present study shows that the Hansen limit may be applied up to $k = 100$ with only a 15% error in diffusion coefficients regressed beyond $\tau = 100$. Coefficients regressed below this limit yield estimates that are orders of magnitude above or below the true diffusion coefficient. In terms of experimental measurements, $\tau = 100$ may be difficult to achieve for weakly concentrated solutions or slowly adsorbing surfactants. In addition, 95% of the surface tension reduction takes place before $\tau = 100$,

and subsequent reductions in surface tension may not be measurable within the limit of experimental accuracy. In conclusion, while the Hansen limit correctly describes the Ward and Tordai equation in the limit of long times, it may not be possible to obtain experimental data in the regime of this limit's applicability.

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