

NOTE

Determination of Bulk and Surface Diffusion Coefficients from Experimental Data for Thin Liquid Film Drainage

This note presents a method for the determination of the surface diffusion coefficient and surface diffusion flux. The theoretical considerations are based on the Onsager linear theory for the definition of the surface diffusion flux and on the Einstein theorem for the definition of the surface diffusion parameter. In this interpretation the surface diffusion coefficient differs from the one commonly defined in the literature. It does not depend on the surfactant concentration and it is a function only of the type of surfactant and the liquid/liquid interface. The theoretical calculations indicate that the effect of the surface diffusion on the film drainage is stronger than that predicted by previous theoretical studies. The experimental data for thin liquid film drainage in the case of low surfactant concentration in the continuous phase could be used for the calculation of the bulk and surface diffusion coefficients. In the present study we utilized the experimental data for the drainage of nitrobenzene films stabilized by different concentrations of dodecanol. © 2000 Academic Press

Key Words: diffusion coefficients; thin film drainage.

INTRODUCTION

The rheological and dynamic properties of surfactant adsorption monolayers are major factors affecting the stability of foams and emulsions under dynamic conditions. A criterion for emulsion stability accounting for the interplay of thermodynamic and hydrodynamic factors was obtained in Refs. 1–3. In this interpretation and generalization of the Bancroft rule (1–3) the velocity of thin liquid film drainage is a main parameter. When the surfactant is soluble in the continuous phase, the Marangoni effect becomes operative and the rate of film thinning (of both foam and emulsion type) depends on the surface (Gibbs) elasticity (4). The bulk and surface diffusion fluxes, which arise to restore the uniform adsorption monolayers, dampen the surface tension gradients (which oppose the film drainage) and thus accelerate the film thinning.

Different experimental techniques are widely used for the determination of the bulk and surface diffusion coefficients (5–8). An original simple idea for the simultaneous measurement of both diffusion coefficients is discussed in Ref. 9. The authors used the experimental data for drainage of thin liquid plane-parallel films stabilized by different concentrations of surfactant. At low surfactant concentrations the ratio of the velocity of thinning and the Reynolds velocity (corresponding to tangentially immobile interfaces) depends linearly on $1/h$, where h is the film thickness. Knowing the parameters of the adsorption isotherm, from the intercept the bulk diffusion coefficient can be calculated and from the slope the surface diffusion coefficient is estimated. Reference 9 reported a gradient surface diffusion coefficient for nitrobenzene film stabilized by dodecanol that depends on the surfactant concentrations. To elucidate the concentration dependence of the diffusion coefficient in the present study, we apply the Onsager linear theory to determine the surface diffusion flux. The Einstein theorem for the surface diffusion phenomenological coefficient, $D_{s,0}$, is used. We calculated

$D_{s,0}$ utilizing the experimental data for the drainage velocity of the thin liquid film and interfacial tension isotherm from Ref. 9.

SURFACE DIFFUSION FLUX AND SURFACE DIFFUSION COEFFICIENT

We consider two homogeneous bulk liquid phases divided by an interfacial adsorption layer built from a nonionic surfactant. Following the Onsager linear theory from the nonequilibrium thermodynamics, the thermodynamic flux (in our case the surface diffusion flux, \mathbf{J}_s) is proportional to the thermodynamic force (in our case the surface gradient of the surface chemical potential, μ_s). To simplify our conclusions, we assume that the processes take place at constant temperature, T , and therefore

$$\mathbf{J}_s = -L \nabla_s \left(\frac{\mu_s}{T} \right) = -\frac{L}{T} \frac{\partial \mu_s}{\partial \Gamma} \nabla_s \Gamma, \quad [1]$$

where ∇_s is the surface gradient operator, Γ is the adsorption, and L is the Onsager coefficient. According to the Einstein theorem, the surface diffusion coefficient, $D_{s,0}$, defined as $D_{s,0} = kL/\Gamma$, where k is the Boltzmann constant, does not depend on the adsorption. Hence, from Eq. [1] we can introduce the gradient surface diffusion coefficient, D_s , which depends on adsorption. D_s is the coefficient of proportionality of the surface diffusion flux and the surface gradient of adsorption:

$$\mathbf{J}_s = -D_s \nabla_s \Gamma, \quad D_s \equiv \frac{D_{s,0}}{kT} \frac{\partial \mu_s}{\partial \ln \Gamma}, \quad [2]$$

For that reason in the literature it is called a “gradient diffusion coefficient” (see the definition on p. 430 in Ref. 5). In the case of a Langmuir adsorption isotherm the surface chemical potential reads (10)

$$\mu_s = \mu_{s,0} + kT \ln \frac{\theta}{(1-\theta)}, \quad [3]$$

where $\mu_{s,0}$ is the standard surface chemical potential, Γ_∞ is the maximum possible adsorption, and $\theta \equiv \Gamma/\Gamma_\infty$ is the degree of coverage. Therefore, from Eqs. [2] and [3] we can derive the following relationship for the gradient surface diffusion coefficient, D_s ,

$$D_s = \frac{D_{s,0}}{1-\theta}. \quad [4]$$

Following an analogous procedure, the dimensionless surface diffusion parameter, $D_s/D_{s,0}$, is derived for the most frequently used surfactant adsorption isotherms. The results are listed in Table 1, where c is the surfactant concentration, K is an adsorption parameter, m is the parameter of the Freundlich isotherm, and β is the interaction parameter (see Refs. 10–12). In all cases the gradient surface diffusion coefficient, D_s , increases when the density of the adsorption layer increases (see Eq. [4]). Then, at one and the same adsorption gradient the

TABLE 1
Dimensionless Surface Diffusion Parameter, $D_s/D_{s,0}$, for Most Frequently Used Surfactant Adsorption Isotherms

	Adsorption isotherm	Parameter $D_s/D_{s,0}$
Henry	$Kc = \theta$	1
Langmuir	$Kc = \frac{\Gamma_\infty \theta}{1-\theta}$	$\frac{1}{1-\theta}$
Freundlich	$(Kc)^m = \theta$	$\frac{1}{m}$
Volmer	$Kc = \frac{\Gamma_\infty \theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta}\right)$	$\frac{1}{(1-\theta)^2}$
Frumkin	$Kc = \frac{\Gamma_\infty \theta}{1-\theta} \exp\left(-\frac{2\beta\Gamma_\infty \theta}{kT}\right)$	$\frac{1}{1-\theta} - \frac{2\beta\Gamma_\infty \theta}{kT}$
van der Waals	$Kc = \frac{\Gamma_\infty \theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \frac{2\beta\Gamma_\infty \theta}{kT}\right)$	$\frac{1}{(1-\theta)^2} - \frac{2\beta\Gamma_\infty \theta}{kT}$

surface diffusion flux becomes more pronounced at higher surfactant concentrations (see Eqs. [2] and [4]).

The surface diffusion flux affects the interfacial dynamics and plays an important role in the thin liquid film stability and drainage. The problem for determining the drainage velocity, $V = -dh/dt$, of a plane-parallel thin liquid foam film in the presence of surfactant dissolved only in the continuous phase was solved by Radoev *et al.* (13). The final result reads

$$\frac{V}{V_{Re}} = 1 + b + \frac{h_s}{h}, \quad b \equiv \frac{3\eta D}{h_a E_G}, \quad h_s \equiv \frac{6\eta D_s}{E_G}, \quad [5]$$

where $h_a \equiv \partial\Gamma/\partial c$ is the slope of the isotherm, σ is the surface tension, $E_G \equiv -\partial\sigma/\partial \ln \Gamma$ is the Gibbs elasticity, η is the dynamic viscosity of the liquid, and D is the bulk surfactant diffusion coefficient. The coefficients b and h_s are the bulk diffusivity number and the characteristic surface diffusion length, respectively, which account for the influence of the bulk and surface diffusivity as compared to the Gibbs elasticity. In Eq. [5] the Reynolds velocity of thinning, V_{Re} , of a plane-parallel film between tangentially immobile interfaces has the form

$$V_{Re} = \frac{2h^3(P_c - \Pi)}{3\eta R^2}, \quad [6]$$

where R is the film radius, P_c is the capillary pressure, and Π is the disjoining pressure. The solution in Ref. 13 is derived under the assumption for small deviations from equilibrium in surfactant adsorption and concentration. Hence, to a leading order in the surface diffusion flux the gradient surface diffusion coefficient is a constant. Its value corresponds to the equilibrium one calculated from Eq. [4], $D_s(\Gamma) = D_s(\Gamma_{eq})$. On the contrary, the dependence of D_s on adsorption has to be taken into account when the deviations from equilibrium are large enough, or the processes of surfactant diffusion and film thinning are simultaneous, or the film drains in a non-quasi-steady-state regime. These processes appear in the initial stage of emulsion and foam preparation.

DETERMINATION OF BULK AND SURFACE DIFFUSION COEFFICIENTS FROM EXPERIMENTAL DATA

To illustrate the discussed above question about the definition of the surface diffusion coefficients, we used experimental data for nitrobenzene films stabilized by different concentrations of dodecanol (9). The first step in the experimental data interpretation is to calculate the equilibrium interfacial parameters from equilibrium surface pressure dependence on dodecanol concentration (see Fig. 1). The Langmuir-Szyszkowski adsorption isotherm is employed:

$$\frac{\Gamma}{\Gamma_\infty} = \frac{Kc}{1 + Kc}, \quad \sigma = \sigma_0 - kT\Gamma_\infty \ln(1 + Kc), \quad [7]$$

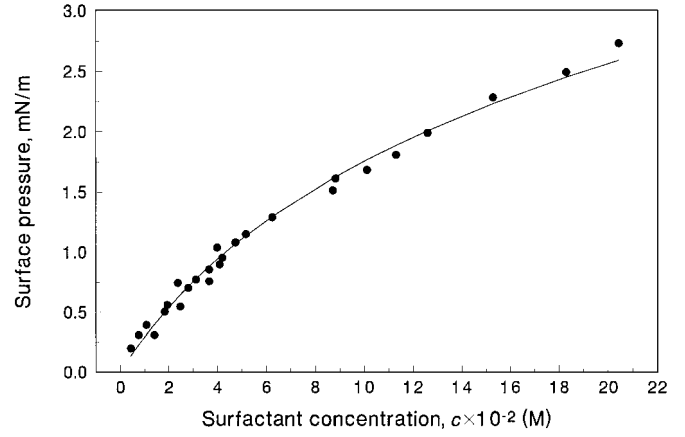


FIG. 1. Plot of the surface pressure isotherm at the air-nitrobenzene interface versus the dodecanol concentration. The symbols are experimental data from Ref. 9; the continuous line represents the best fit.

where σ_0 is the surface tension of pure nitrobenzene. From the fit the saturation adsorption, Γ_∞ , and the constant K are calculated to be $\Gamma_\infty = 6.47 \times 10^{-7}$ mol/m² and $K = 2.05 \times 10^{-2}$ m³/mol. The experimental data and the corresponding theoretical curve (solid line) are plotted in Fig. 1. The agreement between them is very good.

The second step is to plot the experimental data for the relative velocity of plane-parallel film thinning, V/V_{Re} , as a function of $1/h$. These plots are shown in Fig. 2 for three different concentrations of dodecanol: 11, 44, and 178 mM (9). A linear dependence is observed in accordance with Eq. [5]. From the intercepts and slopes of lines in Fig. 2, the parameters b and h_s are calculated and the results are given in Table 2. The Gibbs elasticity, $E_G = kT\Gamma_\infty Kc$, and the slope of the isotherm, $h_a = K\Gamma_\infty/(1 + Kc)^2$, corresponding to Eq. [7], are also listed in Table 2. Knowing the values of the parameters b , E_G , and h_a , from Eq. [5] we computed the bulk diffusion coefficient, D (see Table 2). The dynamic viscosity of nitrobenzene is $\eta = 2 \times 10^{-3}$ Ns/m. The value of D for concentrations 11 and 178 mM is $D = 7.3 \times 10^{-10}$ m²/s (the difference between them is within the experimental error). In the case of 44 mM the calculated bulk diffusion coefficient is too large (see Table 2). We believe that it can be due to some artifacts in this case (see also the discussion below).

Knowing the values of the parameters b , E_G , and h_a , from Eq. [5] we computed the gradient surface diffusion coefficient, D_s (see Table 2). From Table 2 it is seen that D_s increases from 3.55×10^{-9} to 13.4×10^{-9} m²/s with the increase of dodecanol concentration. In contrast, the calculated surface diffusion coefficient,

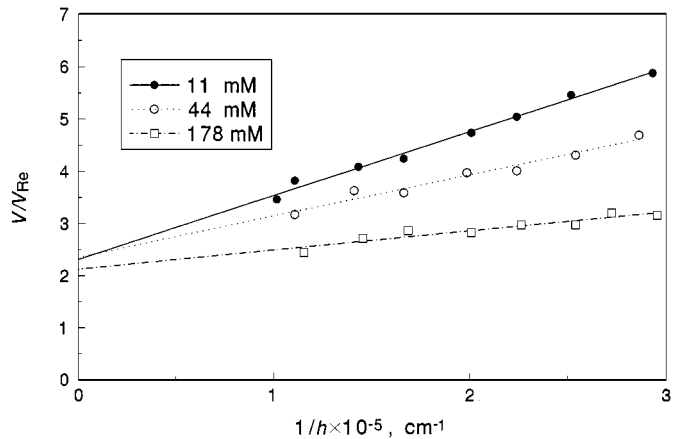


FIG. 2. A typical plot of V/V_{Re} versus $1/h$ for nitrobenzene foam films stabilized by various concentrations of dodecanol: 11, 44, and 178 mM.

TABLE 2
Experimental Data and Calculated Theoretical Parameters for Nitrobenzene Film Stabilized by Dodecanol (9)

c (mM)	b	h_s (nm)	E_G (mN/m)	h_a (nm)	D (m ² /s)	D_s (m ² /s)	$D_{s,0}$ (m ² /s)
11	1.40	120	0.355	8.82	7.30×10^{-10}	3.55×10^{-9}	2.90×10^{-9}
44	1.45	75	1.42	3.67	12.6×10^{-10}	8.87×10^{-9}	4.67×10^{-9}
178	1.25	28	5.74	0.615	7.35×10^{-10}	13.4×10^{-9}	2.89×10^{-9}

$D_{s,0}$, remains constant, 2.9×10^{-9} m²/s, at concentrations 11 and 178 mM. In the case of 44 mM $D_{s,0}$ differs from other calculated values. It is interesting to note that the values of the bulk and surface diffusion coefficients calculated at 44 mM have the same coefficient of proportionality to the corresponding values at other concentrations.

CONCLUSION

In this work the physical meaning of the gradient surface diffusivity and its dependence on the surfactant concentration is clarified (see Eq. [4]). The surface diffusion flux is defined according to the Onsager linear theory and on the Einstein theorem. Our theoretical considerations indicate that the effect of the surface diffusion on the film drainage is more pronounced than predicted by previous theoretical studies (see Eq. [5]). We demonstrated how to calculate the bulk and surface diffusion coefficients using experimental data for thin liquid film drainage in the case of low surfactant concentration in the continuous phase.

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