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.

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. 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) chemical potential reads (10)

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

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

\[ D_s = \frac{D_{s,0}}{1-\theta} \]  

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 \( \beta \) 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
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

\[
\frac{V}{V_{Re}} = 1 + \frac{h_s}{R} b \equiv \frac{3\Omega_{0} D_s}{h_s E_G}, \quad h_s \equiv \frac{6\Omega_{0} D_s}{E_G},
\]

where \( h_s \equiv \partial \Gamma / \partial \sigma \) is the slope of the isotherm, \( \sigma \) is the surface tension, \( E_G \equiv -\partial \sigma / \partial \Gamma \) is the Gibbs elasticity, \( \eta \) 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

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

where \( R \) is the film radius, \( P_c \) is the capillary pressure, and \( \Pi \) 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], \( D_s(\Gamma) = D_s(\Gamma_{\text{eq}}) \). 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 dodecane concentration (see Fig. 1). The Langmuir–Szyszkowski adsorption isotherm is employed:

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

where \( \sigma_0 \) is the surface tension of pure nitrobenzene. From the fit the saturation adsorption, \( \Gamma_{\infty}, \) and the constant \( K \) are calculated to be \( \Gamma_{\infty} = 6.47 \times 10^{-2} \text{ mol/m}^2 \) and \( K = 2.05 \times 10^{-2} \text{ m}^3/\text{mol} \). 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, \( E_G = kT \Gamma_{\infty} K_c \), and the slope of the isotherm, \( h_s = K \Gamma_{\infty} / (1 + K_c)^2 \), corresponding to Eq. [7], are also listed in Table 2. Knowing the values of the parameters \( b, E_G, \) and \( h_s \), from Eq. [5] we computed the bulk diffusion coefficient, \( D \) (see Table 2). The dynamic viscosity of nitrobenzene is \( \eta = 2 \times 10^{-3} \text{ Ns/m} \). The value of \( D \) for concentrations 11 and 178 mM is \( D = 7.3 \times 10^{-10} \text{ m}^2/\text{s} \) (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 \( h_s \), 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 \( 3.55 \times 10^{-9} \) to \( 13.4 \times 10^{-9} \text{ m}^2/\text{s} \) with the increase of dodecanol concentration. In contrast, the calculated surface diffusion coefficient,
TABLE 2
Experimental Data and Calculated Theoretical Parameters for Nitrobenzene Film Stabilized by Dodecanol (9)

<table>
<thead>
<tr>
<th>c (mM)</th>
<th>b</th>
<th>h₀ (nm)</th>
<th>E₀ (mN/m)</th>
<th>hₐ (nm)</th>
<th>D (m²/s)</th>
<th>Dₛ (m²/s)</th>
<th>Dₛₐ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>1.40</td>
<td>120</td>
<td>0.355</td>
<td>8.82</td>
<td>7.30 × 10⁻¹⁰</td>
<td>3.55 × 10⁻⁹</td>
<td>2.90 × 10⁻⁹</td>
</tr>
<tr>
<td>44</td>
<td>1.45</td>
<td>75</td>
<td>1.42</td>
<td>3.67</td>
<td>12.6 × 10⁻¹⁰</td>
<td>8.87 × 10⁻⁹</td>
<td>4.67 × 10⁻⁹</td>
</tr>
<tr>
<td>178</td>
<td>1.25</td>
<td>28</td>
<td>5.74</td>
<td>0.615</td>
<td>7.35 × 10⁻¹⁰</td>
<td>13.4 × 10⁻⁹</td>
<td>2.89 × 10⁻⁹</td>
</tr>
</tbody>
</table>

Dₛ₀ remains constant, 2.9 × 10⁻⁹ m²/s, at concentrations 11 and 178 mM. In the case of 44 mM Dₛ₀ 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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REFERENCES


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