Evaluation of adsorption of surfactant at a moving interface of a single spherical drop

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ABSTRACT

Numerical simulations of contaminated bubbles or drops adopt a model of adsorption-desorption kinetics developed for quiescent systems. However, the model has rarely been validated due to the lack of experimental data of surfactant concentration at a moving interface. Hence, we experimentally investigated surfactant concentration at the moving interface of a spherical drop falling in a stagnant liquid containing surfactant using the velocity distributions measured by spatiotemporal filter velocimetry (SFV). The molar flux of surfactant to the interface was also evaluated by substituting the measured velocity and surfactant concentration into the conservation equation of surface concentration of surfactant to examine the applicability of the Frumkin–Levich model to a drop falling in a contaminated system. We confirmed that the evaluation of surfactant concentration using SFV is of great use in understanding adsorption-desorption kinetics at an interface in a contaminated system and for validation of adsorption and desorption models. The measured results showed that the Frumkin–Levich model is not applicable to a moving interface, whereas it is applicable to an immobile interface, that the dependence of the molar flux on the molecular weight of surfactant is not so strong, and that the ratio of the surface concentration of surfactant to the maximum concentration, i.e. the surface coverage, is an appropriate index for judging an applicable range of the Frumkin–Levich model.

1. Introduction

Adsorption of surfactants at an interface changes the interfacial tension and induces the Marangoni stress which affects the boundary condition at the interface and alters interfacial mass and momentum transfer rates. Thus, knowledge on adsorption-desorption kinetics at an interface is of fundamental importance to understand motion and mass transfer of drops and bubbles. Many studies [1–3] have been carried out for understanding and modeling adsorption-desorption kinetics. Most of them have dealt with a static interface in a quiescent system. Several numerical simulations [4–8] have been conducted by using an adsorption-desorption model to predict distributions of surface concentration Γ of surfactant and the Marangoni stress at the moving interface of a bubble or a drop. However, the applicability of the model to the moving interface has rarely been examined due to the difficulty in measuring Γ and the Marangoni stress at the moving interface.

Although there are several methods [9–11] for measuring Γ at an interface, few methods [12–14] are available for a moving interface. Evaluation of adsorption-desorption model requires measurements of molar fluxes of adsorption and desorption to a moving interface.

Evaluation of the molar flux based on the conservation equation of Γ by measuring Γ and interfacial velocity is one of the possible methods. Although Vogel et al. [15] measured interfacial velocity and Γ using second-harmonic generation (SHG) and boundary fitted DPIV, they did not carry out evaluation of the molar flux of surfactant and validation of available adsorption-desorption models. Hosokawa et al. [16] proposed an evaluation method of Γ based on accurate velocity measurement using spatiotemporal filter velocimetry (SFV), and demonstrated its validity. Since the method provides interfacial velocity and Γ distributions, it can be used for evaluation of the molar flux.

In this study, we applied the method to the moving interface of a spherical drop falling in a stagnant liquid containing surfactant to measure the molar flux of surfactant to the interface, which was evaluated by substituting the measured velocity and surfactant concentration into the conservation equation of Γ. The applicability of the Frumkin–Levich model to a drop falling in a contaminated system was discussed based on the experimental results.

Nomenclature

a	ratio of rate constants for adsorption and desorption [mol/m³]
C	concentration of surfactant [mol/m³]
D	diffusion coefficient [m²/s]
d	drop diameter [m]
R	drop radius [m]
R_G	gas constant [J/K/mol]
r	coordinate in radial direction [m]
$\dot{S}$	molar flux of surfactant to an interface [mol/m²/s]
T	temperature [K]
t	time [s]
V_D	drop velocity [m/s]
v	velocity [m/s]
x	coordinate in horizontal direction [m]
Y	distance from nozzle tip [m]
y	coordinate in vertical direction [m]
$\Delta\tau_{r\theta}$	Marangoni stress [Pa]
Γ	surface concentration of surfactant [mol/m²]

μ	viscosity [Pa s]
θ	coordinate in tangential direction [°]
ρ	density [kg/m³]
σ	interfacial tension [N/m]
τ	interfacial shear stress [Pa]

Subscripts

0	clean system
C	continuous phase
D	drop
eq	equilibrium
in	inside of drop
max	maximum
out	outside of drop
S	surface
θ	θ component
θint	θ component at interface

2. Experimental apparatus

Fig. 1 shows a schematic of the experimental setup. Silicone oil (Shinetsu, KF-96-300cs, density ρ_C: 967 kg/m³, viscosity μ_C: 299 mPa·s) was filled in the rectangular container of 170 (D) × 170 (W) × 500 mm (H). A drop of glycerol-water solution (53.5 wt%, diameter d: 8.3 mm, density ρ_D: 1132 kg/m³, viscosity μ_D: 6.13 mPa·s) was released from the nozzle (inner diameter: 5.0 mm) located 450 mm above the bottom of the container at the center of the cross-section. Water purified by using a Millipore system (Elix 3) and pure glycerol (Kishida-Kagaku) were used for the glycerol-water solutions. The concentration of the glycerol-water solution was determined so as to make its refractive index the same as that of the silicone oil to eliminate optical distortion of tracer-particle images in the drop [17]. The drop diameter and fluid properties
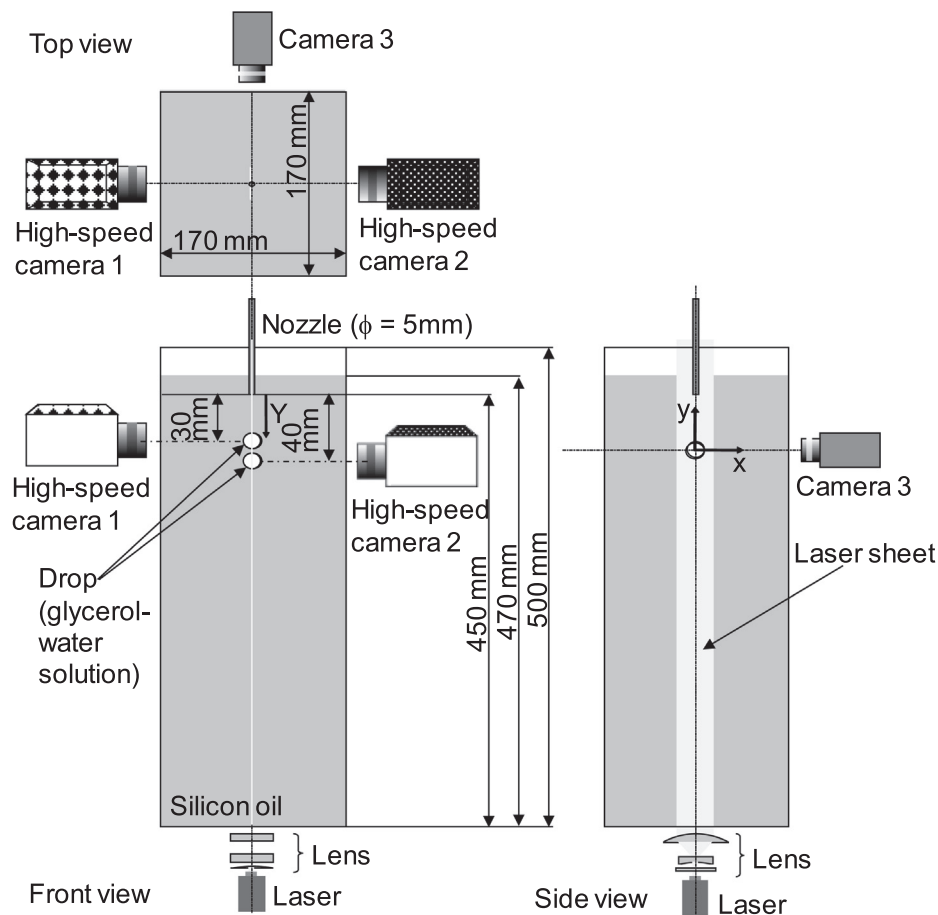

Fig. 1. Experimental setup.