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Marangoni flow around a camphor disk regenerated by the interaction between camphor and sodium dodecyl sulfate molecules

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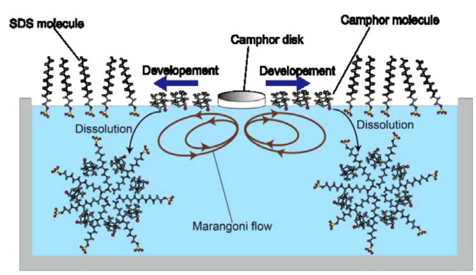
HIGHLIGHTS

- Marangoni flow around a camphor disk placed on an anionic surfactant aqueous phase was regenerated.
- Regeneration was investigated by ^{13}C NMR, NOE experiments, and mass spectrometry.
- We found that the complex formation between camphor and the surfactant causes regeneration.

GRAPHICAL ABSTRACT



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ABSTRACT

The interaction between camphor and sodium dodecyl sulfate (SDS) was experimentally investigated to understand restoration of Marangoni flow around a camphor disk on water under the addition of SDS. With an increase in the concentration of SDS, the flow velocity decreased to almost zero up to the critical micelle concentration (cmc), but increased above the cmc. Speed of Marangoni flow around the camphor disk increased with an increase in the scale of the aqueous channel. ^{13}C NMR, NOE experiments, and mass spectrometry were used to evaluate the interaction between camphor and SDS molecules, which increased the dissolution rate of camphor into the SDS aqueous solution. The experimental results suggest that an increase in the dissolution of camphor into SDS micelles induces the restoration of Marangoni flow.

1. Introduction

Marangoni flow is driven by a gradient of interfacial tension, which is induced by the heterogeneous distribution of temperature or the heterogeneous concentration of a substance at an immiscible interface [1–3], as seen in the "tears of wine" phenomenon [4–6]. It has been reported that a surfactant generally suppresses Marangoni flow since the spatial gradient of the interfacial tension is reduced by the adsorption of the surfactant molecules at the interface [7,8].

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"Camphor dancing" has been well known for several centuries [9,10], and Marangoni flow is also observed around solid camphor on water due to the gradient of the surface tension [11,12]. Marangoni flow in a camphor–water system should also be suppressed by the addition of a surfactant [12].

Recently, we found that the flow velocity around a camphor disk decreased to almost zero, and then increased with an increase in the concentration of sodium dodecyl sulfate (SDS) [13]. Although the surface tension of SDS-camphor aqueous solution and the dissolution rate of camphor in the SDS aqueous solution have been shown to play an important role in these different dependencies of the Marangoni effect, the interaction between camphor and SDS molecules to dissolve camphor into SDS micelles in the bulk phase has not yet been clarified. In this study, the molecular interaction between camphor and SDS was evaluated by ^{13}C nuclear magnetic resonance (NMR), one-dimensional NOE, and mass spectrometry (MS). Our experimental results suggest that SDS micelles enhance the dissolution of camphor into the SDS aqueous solution and as a result restore Marangoni flow.

2. Experimental

Sodium dodecyl sulfate (SDS), D-(+)-glucose, and (+)-camphor were purchased from Sigma–Aldrich (St. Louis, MO, USA). Visualization particles (DIAION, HP20S, Mitsubishi Chemical Co., Tokyo, Japan; particle size 100–200 μm) were dispersed in the aqueous phase to observe the convective flow in the aqueous phase, and glucose was added into the aqueous phase to maintain the density of the aqueous phase at 1.1 g/mL. Deuterated reagents and solvents, *i.e.*, 3-(trimethylsilyl)propionic-(2,2,3,3-d_4) acid sodium salt (TSP-d_4), D_2O, dimethyl sulfoxide-d_6, tetrahydrofuran-d_6, and acetonitrile-d_3 were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Other deuterated solvents, *i.e.*, cyclohexane-d_{10}, toluene-d_8, benzene-d_6, chloroform-d, pyridine-d_5, dichloromethane-d_2, acetone-d_6, ethanol-d_6, and methanol-d_4 were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). Preparation of a camphor disk (diameter, 3 mm; thickness, 1 mm; mass, 5 mg) was the same as those in the previous works [11–13]. Movie shooting of Marangoni flow with visualization particles and the image analysis were performed based on the previous paper [13]. The surface tension was measured with a surface tensiometer (CBVP-A3, Kyowa Interface Science Co. Ltd., Saitama, Japan). ^{1}H and ^{13}C NMR spectra were measured with a JEOL Lambda 500 and ECP 500 spectrometers (Japan) at room temperature, and chemical shifts (δ) were recorded with reference to TSP-d_4 as an external standard in aqueous solutions. Mass spectrometric detection was performed using a QqTOF/MS spectrometer (QSTAR-XL, Applied Biosystems, Foster City, CA, USA). The spray voltage for nano-ESI ionization was around 1000 V for the positive mode and 1000 V for the negative mode. Since small molecules in the range of m/z 50–500 were detected reproducibly, we focused only on small-molecule analyses in this report.

3. Results

Marangoni flow was observed around a camphor disk which was fixed on water. Fig. 1 shows the trajectories of small particles for 1 s to visualize the features of Marangoni flow depending on the concentration of SDS (C_{SDS}) in the aqueous phase. With an increase in C_{SDS}, the magnitude of Marangoni flow decreased (Fig. 1a and b), not clearly observed at C_{SDS} = 7 mM (Fig. 1c), but restored at C_{SDS} = 300 mM (Fig. 1d).

To clarify the driving force of Marangoni flow, the surface tension was measured for various SDS and camphor concentrations [13]. We reported that the surface tension γ decreased with an increase in C_{SDS} or the camphor concentration (C_{cam}). Fig. 2 shows (a) the gradient of the surface tension *versus* logarithm of the concentration of camphor $\partial\gamma/\partial \ln C_{cam}$ and (b) $k_{dis} \times \partial\gamma/\partial \ln C_{cam}$ depending on C_{SDS}. $\partial\gamma/\partial \ln C_{cam}$ decreased with an increase in C_{SDS}. With an increase in C_{SDS}, $k_{dis} \times \partial\gamma/\partial \ln C_{cam}$ decreased below

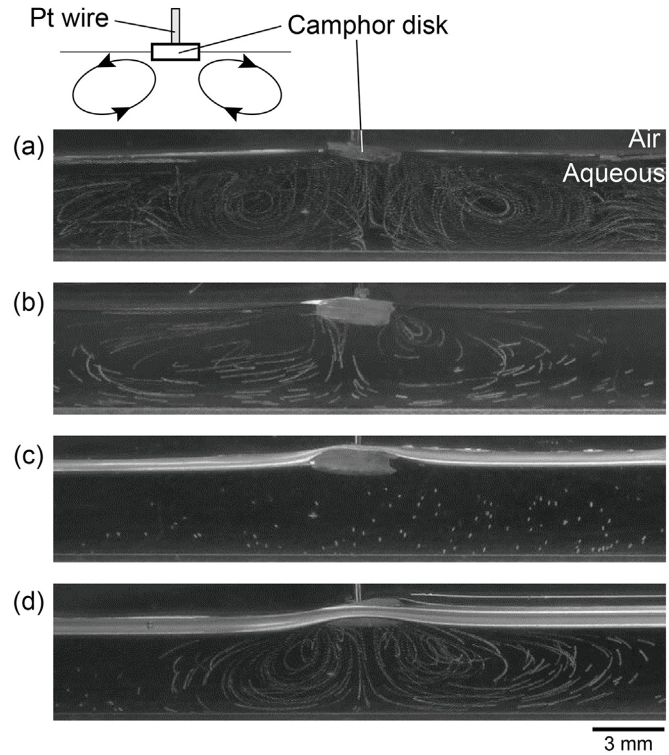

Fig. 1. Experimental results for typical profiles of convective flow obtained by extracting the locations of visualization particles from a movie for different concentrations of SDS ((a) 0, (b) 1.0, (c) 7.0, and (d) 300 mM). The exposure time of the superimposed image sequence was 1 s. The features of convective flow are shown in the supplementary content. For the aqueous phase, 2.3 mL of water with or without SDS (0–300 mM) was poured into a rectangular channel (width 5 mm, length 90 mm, water level 5 mm, surface area: 450 mm^2). Movies were shown in the Supplementary Material (SM).

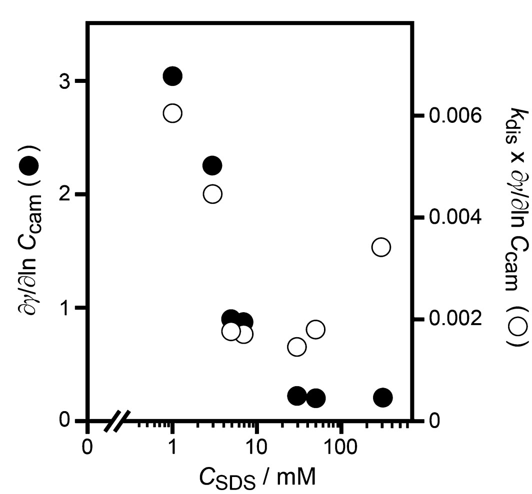

Fig. 2. Experimental results for (left vertical axis: filled circle) gradient of surface tension (γ) to the gradient of logarithm of camphor concentration (C_{cam}), $\partial\gamma/\partial \ln C_{cam}$, depending on the concentration of SDS (C_{SDS}) mixed in the aqueous solutions with different C_{cam}, and $k_{dis} \times \partial\gamma/\partial \ln C_{cam}$ (right vertical axis: empty circle) depending on C_{SDS}, where k_{dis} is the dissolution rate of camphor in the aqueous solution. The data of γ and k_{dis} were partly used in Ref. [13] but the other data of different concentrations were added to clarify the dependence of C_{SDS}.