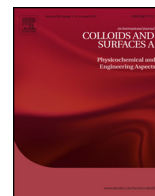Contents lists available at ScienceDirect

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Spontaneous motion of various oil droplets in aqueous solution of trimethyl alkyl ammonium with different carbon chain lengths

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HIGHLIGHTS

- Why nitrobenzene droplet has a high spontaneous motility?
- Micelle formation is unrelated to the spontaneous droplet motion.
- Contribution ratio among iodic ions to ion associate reaction with cationic surfactant.
- Temporal change of droplet contact angle during running motion.

GRAPHICAL ABSTRACT
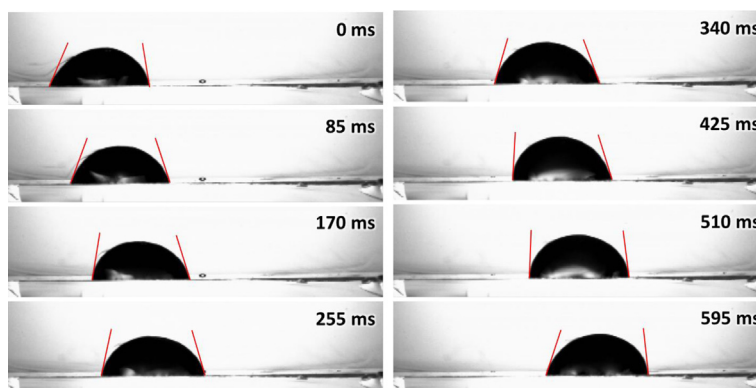
ARTICLE INFO

ABSTRACT

Spontaneous oil droplet motion in an aqueous bulk solution of cation surfactant with different carbon chain lengths was investigated using various organic solvent species such as nitrobenzene, benzyl alcohol, phenethyl alcohol, chlorobenzene, and quinoline, containing only iodine. The running velocities of nitrobenzene and benzyl alcohol droplet increased with increasing chain length of the surfactant. The effects of organic solvent species and surfactant chain length on the droplet running velocity were elucidated in terms of the balance of interfacial tension around the droplet. The relation between surfactant concentration and the droplet motility was also investigated, revealing that the micelle formation was unrelated to the droplet motion. We also observed temporal variation of the contact angle with high time resolution to confirm the motion mechanism. The reaction order and the rate constant of the reaction between the cation surfactant and iodic anion were estimated from the kinetic study, which showed that the reaction mechanism did not depend on the surfactant chain length, although the reaction rate increased with increasing chain length.

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1. Introduction

Several studies have been conducted to investigate the self-running motion of droplet on a solid surface. These motilities
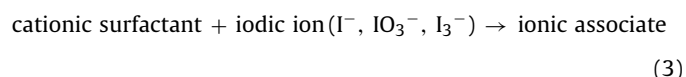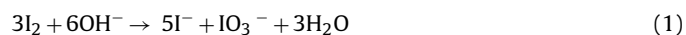
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are reportedly generated by the wettability gradient [1–5], thermal gradient [6,7], and chemical gradient on the substrate [8–11]. These gradients disrupt the balance of interfacial tension around the droplet. Studies of the spontaneous movement induced by the non-equilibrium of interfacial tension attributable to the chemical gradient have been conducted actively from the viewpoint of direct energy conversion from chemical energy to kinetic energy. A spontaneous interfacial oscillation system consisting of aqueous phase with cationic surfactant and nitrobenzene phase containing potassium iodide with saturated concentration and iodine was first reported by Dupeyrat and Nakache [12]. They reported that the fundamental mechanism of this spontaneous movement is based on the Marangoni effect as a result of the association between cationic surfactant and iodide ion. The Marangoni effect is a spontaneous convection flow induced by the interfacial tension gradient [13]. Subsequently, many systems based on that report have been investigated. Magome and Yoshikawa applied this oil–water system to spontaneous amoeba-like droplet motion [14]. Sumino et al. regulated the droplet motions under some designed boundary conditions and adopted a mathematical model to simulate the observed droplet motion [15,16]. Song et al. controlled the motion direction of droplet by local laser heating, which induces the contact angle variation [17]. Nevertheless, few reports describe use of the droplet phase other than nitrobenzene in this spontaneous motion system. Matsushita et al. adopted a mixture of nitrobenzene and chlorobenzene as the droplet phase [18]. They reported that the droplet solvent needed an appropriate electron withdrawing property for the spontaneous motion. However, other physical properties affecting the droplet motion have not been reported in previous studies. Therefore, the reason why nitrobenzene is appropriate for the spontaneous droplet running system needs to be clarified for further development.

We investigated the spontaneous motion of nitrobenzene droplet including only iodine. Then we confirmed the importance of the existence of iodic ions and inferred the following reaction around the droplet and the droplet motion mechanism [19].

$$3I_2 + 6OH^- \rightarrow 5I^- + IO_3{}^- + 3H_2O \tag{1}$$

$$I_2 + I^- \rightarrow I_3{}^- \tag{2}$$

$$\text{cationic surfactant} + \text{iodic ion}\,(I^-,\ IO_3{}^-,\ I_3{}^-) \rightarrow \text{ionic associate} \tag{3}$$

Iodic ions such as I^-, $IO_3{}^-$, and $I_3{}^-$ are produced from the disproportionate reaction of I_2 under alkaline conditions (Eqs. (1) and (2)) [20]. Cationic surfactant adsorbed on the glass substrate because the glass surface has a negative charge in the aqueous solution. In the adsorbed state, the oil-glass interfacial tension is low. These iodic ions react with the cationic surfactant at the oil–water interface on the glass substrate i.e. contact line of the droplet (Eq. (3)). Then, the aggregate of these ions desorbed from the glass surface owing to the loss of electrical charge. Accordingly, the oil–glass interfacial tension increased and the oil droplet contact angle increased. Therefore, the balance of the interfacial tension around the droplet was disrupted; the droplet moved spontaneously. This study inferred that the droplet contact angle was the most important factor for the droplet motion. The contact angle variation was expected to be induced by the interfacial tension change on the glass substrate attributable to the reactions between iodic ions and cationic surfactant. Nevertheless, the effects of interfacial tension components other than the contact angle have remained unclear.

Furthermore, we introduced a unique intermittent droplet motion with drastic contact angle variation using *o*-toluidine with iodine and saturated potassium iodide as a droplet phase [21]. The droplet repeated a running motion and a squashing motion on the glass surface. This repetition was interpreted by the mechanism of contact angle variation, as described above. However, a nitrobenzene droplet apparently runs with spherical shape, as shown in our early article [19] although it also ought to exhibit a nonlinear variation of the contact angle. Thus the details and relations associated with the reaction between surfactant and iodic ions, the contact angle variation, and the droplet motility remain as matters to be resolved through investigation.

In this study, the effects of the chain length of surfactants and the solvent species of the droplet phase on the running velocity of the spontaneous droplet motion are reported. These components have an effect on the interfacial tension around the droplet. We used trimethyl alkyl ammonium chloride (C_nH_{2n+1} (CH_3)$_3$ N^+ Cl^-: n = 12, 14, 16, 18) as the surfactant in aqueous phase, and used nitrobenzene, chlorobenzene, benzyl alcohol, phenethyl alcohol, and quinoline as droplet solvents. We investigated the respective effects of interfacial tension components around the droplet on the droplet motion. In addition, to confirm the droplet motion mechanism, we examined the surfactant chain length effects on the time variation of the contact angle associated with running motion. Furthermore, based on kinetics study, we elucidated the details of the reaction mechanism such as a contribution ratio among I^-, $IO_3{}^-$, and $I_3{}^-$ to the ion associate reaction with cationic surfactant.

2. Experimental methods

2.1. Materials

Cation surfactants, trimethyl lauryl ammonium chloride ($C_{12}TAC$), trimethyl myristyl ammonium chloride ($C_{14}TAC$), trimethyl cetyl ammonium chloride ($C_{16}TAC$), and trimethyl stearyl ammonium chloride ($C_{18}TAC$) were supplied by Tokyo Chemical Industry Co., Ltd. Nitrobenzene and quinoline were supplied by Kanto Chemical Co. Inc. Chlorobenzene, benzyl alcohol, phenethyl alcohol, iodine (I_2) and sodium hydroxide (NaOH) were supplied by Wako Pure Chemical Industries Ltd. Aqueous phase was prepared using Milli-Q pure water (resistivity of 18.2 MΩ cm at 25 °C). Surfactant ($C_{18}TAC$, $C_{16}TAC$, $C_{14}TAC$, or $C_{12}TAC$) and NaOH were dissolved, respectively, in this aqueous solution with concentrations of 0–5 mmol L^{-1} and 10 mmol L^{-1}. Organic solutions containing 3–10 mmol L^{-1} I_2 were prepared using nitrobenzene, chlorobenzene, benzyl alcohol, phenethyl alcohol, and quinoline as an oil droplet solution.

2.2. Measurement of droplet motion

Surfactant aqueous solution under alkaline condition (10 mL) was placed in a glass Petri dish (φ45 mm) as an aqueous bulk phase. Subsequently, 10 μL of organic solution was dropped on the toroidal glass substrate (ID, 26 mm; OD, 33 mm; thickness, 2 mm) immersed in the aqueous solution. The top of the droplet was separated from the aqueous surface by at least 1 mm. The droplet motion was evaluated quantitatively using this doughnut-shaped system depicted in Fig. S1. The motion was observed until the disappearance of motion, which is defined as a moment with no motion for more than 30 s. The droplet motion was recorded using a digital camera (CMS-V27SET; Sanwa Supply Inc.), and was analyzed using video editing software (Windows Live Movie Maker; Microsoft Corp.). During this operation, the video footage of droplet motion was checked using a frame-by-frame advance every 0.03 s.

2.3. Measurement of contact angle and interfacial tension

The contact angle and the interfacial tension were measured using a contact angle meter (Drop Master DM-501; Kyowa