学術論文

界面活性剤の濃度および分子長さを変更した時のマイクロ波照射中の

界面張力減少

Interfacial tension reduction during microwave irradiation with changing concentration and molecular length of surfactant

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Abstract

Previous studies revealed that microwaves have particular effects on the interfacial tension of the decane/water interface in the presence of Triton X-100. This study investigated the reasons for the hysteresis during and after microwave irradiation by varying the concentration and type of Triton surfactants: X-100 and X-405. As before, physiochemical changes were found to persist after the irradiation of Triton X-100. Interestingly, no hysteresis was observed for Triton X-405. The difference of temperature dependency was caused by different hydrophilicity of Triton X-100 and X-405. Desorption at the interface during the irradiation is easier for the shorter surfactant (Triton X-100) than its longer surfactant (Triton X-405), due to the length of the hydrophilic group. Moreover, the shorter surfactant has a stronger hysteresis during the heating/cooling cycles due to higher adsorption. The dynamic surfactant behaviour between two phases during the irradiation might be promisingly applicable to industrial processes such as de-emulsification.

1. Introduction

Microwave heating has been emerging as a more effective heating method than conventional (thermal) alternatives,

offering advantages such as higher heat efficiency, quick thermal response, homogenous heating, selective heating and non-contact heating [1–3]. Nevertheless, further application of microwaves in industry would be facilitated by a greater understanding of the behaviour of local heating around the fluid-fluid interface [4]. As an example, microwaves can pass through a phase with a low dielectric constant (such as oil or air), and selectively heat a more polarising phase (i.e. water) directly. As a result, the water layer around the interface is selectively heated by microwave irradiation, while heating of low and non-polar phases occurs as this heat is transferred by conduction and convection to the remainder of the solution.

Microwaves have a strong effect on ions or molecules containing dipoles. The rapid switching direction of the electromagnetic field exerts a force on the polarised bonds, causing them to shift to align with the applied field. In rotating, the dipoles upset the network of intermolecular bonds within the solution. The energy released by the disruption of these bonds translates to heating of the solution.

Microwaves decay exponentially while penetrating the solvent as energy is quickly absorbed by the solution. In water, studies have shown that microwaves penetrate roughly 1.3 cm from the interface [5]. In the event of rapid localised heating at the interface carried out by high-powered microwaves, sufficient energy can be absorbed in a small area to cause boiling and phase change at the interface before the energy can be dissipated by conduction or convection. In contrast, consider the case of low power irradiation. Heat dissipates from the interface to both bulk phases through conduction and convection [6,7], preventing the interfacial layer from heating quickly enough to boil while the bulk fluids remain cool.

While localised heating will always occur, the extent to which heat will "concentrate" in the interfacial layer is directly related to the microwave power and the physical properties of the phases in question: the irradiation power and dielectric properties of the solutions will influence the rate of energy absorption in the interfacial layer, whereas the speed of heating and heat transfer to the bulk solution are affected by heat capacity, viscosity and thermal conductivity. The competition between these two extreme cases, which never occurs during conventional heating, offers promising alternatives for controlling interfacial properties. Previous studies have measured the surface tension of the liquid-air interface during microwave irradiation through pendant drop method [6,7] and found reductions to the interfacial tension incurred during irradiation to persist after irradiation had stopped.

Recently, microwave irradiation has been employed for emulsification [8–10] and de-emulsification processes [5,11,12]. In these studies, the interfacial behaviour was mainly discussed based on thermal effects through emulsion coalescence on a microscopic scale. In contrast, this study aims to investigate microwave effects at the liquid-liquid interface on a macroscopic scale while distinguishing thermal and non-thermal effects.

Our previous study [4] on the oil-water interface in the presence of Triton surfactants indicated that microwave irradiation affected the liquid-liquid interface differently from conventional (thermal) heating. Evidence of fine bubbles and emulsions around the interface raised the possibility of metastable, localised emulsions affecting the interfacial tension for an extended period of time [4], and significant thermal gradients may alter the surfactant solubility in the fluid layers near to the interface. However, the study was unable to definitively determine the cause of the long-term reduction in interfacial tension, and the mechanism for the interfacial tension reduction has not been clarified. To further our understanding of this phenomenon, the present study investigates the non-thermal effect of microwave heating by altering surfactant concentration and tail length during cyclic microwave irradiations.

2. Experimental

2-1. Procedure

A small quartz cell (3×3×3 cm) was partially filled with an aqueous surfactant solution (Triton X-100 or X-405 at various concentrations) and covered with a layer of n-decane (2 mL). Decane (99%) and Triton surfactants were supplied

by Kanto and Kishida Chemical Companies, respectively, and used without further purification. A small Teflon ball (6.35 mm diameter) was suspended by a thin Teflon pipe (2 mm outer diameter, 1 mm inner diameter) and submerged until the decane-water interface showed considerable deformation while retaining contact with the ball. A temperature probe (FS-100, Anristu meter CO., LTD.) was inserted through the tube and through to the bottom of the ball to measure the temperature of the bulk aqueous solution. The cell and probe were placed inside of a microwave reactor equipped with a video camera and LED light as shown in Fig. 1a. The interface was captured on video during and after irradiation (Fig. 1b) and the interfacial tension was measured from the interfacial profile using the holm method [13]. In this experiment, reflector, which is placed on the other side of the microwave reactor, was moved so that the temperature probe showed maximum heating rate.

In order to investigate the lasting effects of microwaves, heat-cool irradiation cycles were performed on the liquid-liquid interfaces. The cell was subjected to microwave irradiation at 80 W for 60 s with a 30 minute interval between irradiation incidents, during which time the cell cools almost to room temperature. An example of the temperature profiles is given in Fig. 2.

As shown in Fig. 2, the bulk fluid temperature remains below the boiling point and the microwave power and duration is sufficiently moderate to avoid boiling at the liquid-liquid interface. The decane layer at the top of the cell also serves to prevent evaporation of the aqueous layer. Loss of decane to evaporation is minimal and does not affect the shape of the interface. The experiment conditions are listed in Table 1. It should be noted that X-405 is approximately four times longer than Triton X-100 (as shown in Fig. 1c). Concentrations below CMC were chosen as concentrations of each Triton X.
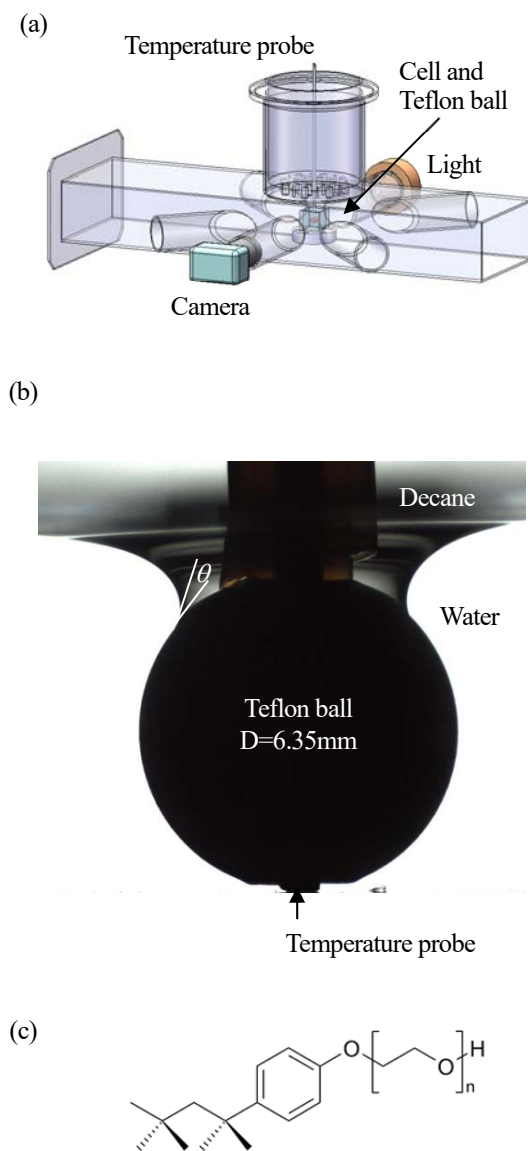
(a)

(b)

(c)

Fig. 1: Interfacial tension measurement: (a) Schematic diagram of microwave reactor; (b) image of the interface as used for fitting; (c) Triton X (100: n=10; 405: n=45) n represents the number of the periodic structure and tail length of Triton.
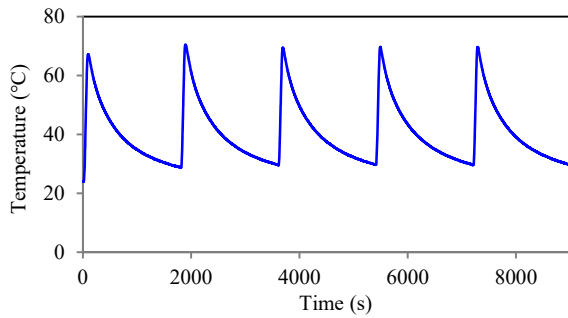
Fig. 2: Temperature profile during cyclic irradiation

Table 1: Experimental conditions for interfacial tension measurement

No.	Surfactant	CMC (Critical micelle concentration) [mM]	Concentration [mM]
1	Triton X-100	0.22 [14]	0.05, 0.1, 0.22, 0.66
2	Triton X-405	0.66 [15]	0.2, 0.66, 0.86

2-2. Analytical method of interfacial tension

Movies of the oil/aqueous interface were recorded during the experiment and analysed using a Matlab-based program with numerical optimization to find the best-fitting parameters for the Young-Laplace equation describing the shape of the holm meridian and contact angle (θ) between Teflon ball and two-liquids, from which the interfacial tension was determined [13]. Detailed theory and fitting procedure have been described elsewhere [4,13].

3. Results

Fig. 3 shows the interfacial tension profiles of 0.2 mM aqueous solutions of Triton X-100, with decane as the light phase, during (filled) and after (unfilled) the first and fifth irradiations (80 W for 60 s). As previously shown [4], the interfacial tension increased during heating. Furthermore, while the interfacial tension decreases as the sample cools, it in fact decreases further that the original equilibrium measurement, leaving a clear hysteresis between heating and cooling. By the fifth irradiation, the interfacial tension was substantially depressed.

Possible mechanisms for the persistent reduction in surface tension were postulated in Hyde et al. (2017) [4]. A promising explanation suggested that the reduced interfacial

tension was caused by the formation of fine decane-in-water and water-in-decane emulsions as their solubilities change with temperature [4,16]. As the solubility decreases while the irradiated sample cools [17], emulsions of water and decane extract into both the aqueous and organic phases and slowly coalescing. Surfactant adsorbs at the liquid-liquid interface of emulsions, stabilising the droplets. Furthermore, as the drops effectively increase the effective interfacial area, the number of surfactant molecules that can be held in the interfacial area increases substantially, contributing to the depression of the interfacial tension.
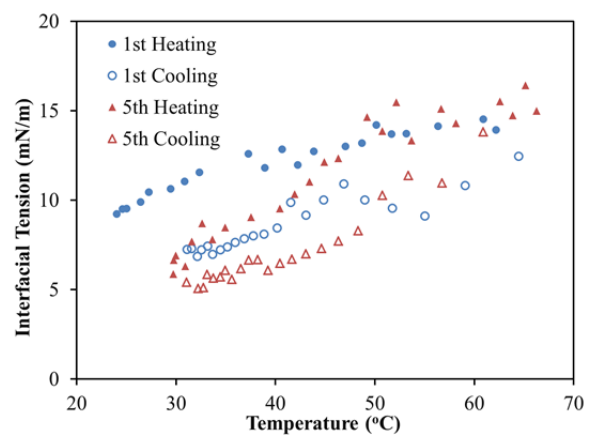

Fig. 3: Interfacial tension profiles during and after the first and fifth irradiation (Triton X-100, 0.22 mM).

Fig. 4 shows interfacial tension profiles for different concentrations of Triton X-100 during and after microwave irradiation. Hysteresis was observed in the interfacial tension profiles at each concentration. The interfacial tension reduction occurred after each irradiation instance, although the magnitude of the reduction decreased with successive irradiation instances, as can be seen in Fig. 5. For example, the reduction becomes negligible after the fourth or fifth irradiation. The interfacial tension reduction, which is defined as difference between initial value and value at room temperature after first or fifth cycle, is shown in Fig. 6 at different surfactant concentration.

Fig. 7 shows interfacial tension profiles during and after the first and the fifth irradiation of 0.86 mM solutions of Triton X-405. In contrast to Triton X-100, the interfacial tension of decane/Triton X-405 decreased during microwave irradiation.

Furthermore, no significant hysteresis was observed between the heating and cooling curves, nor did successive irradiation by microwaves alter the interfacial tension (examples in Fig. 8). In the case of Triton X-405, temperature dependency of interfacial tension is negative. Accordingly, interfacial tension during the irradiation becomes lower than that of cooling because temperature at interface is higher than measurement point due to the microwave absorption.
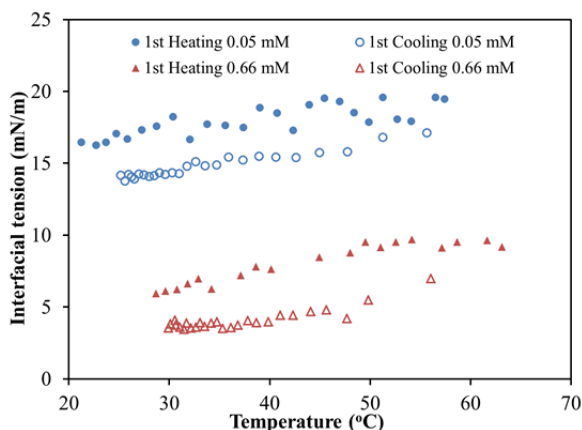

Fig. 4: Interfacial tension profiles for different concentrations of Triton X-100 during and after first irradiation.
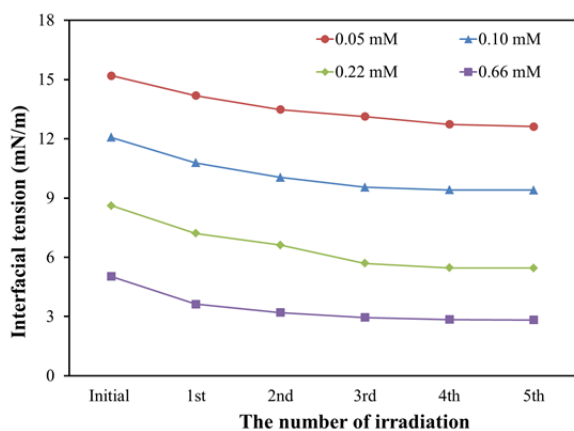

Fig. 5: Interfacial tension after each irradiation for different concentration of Triton X-100
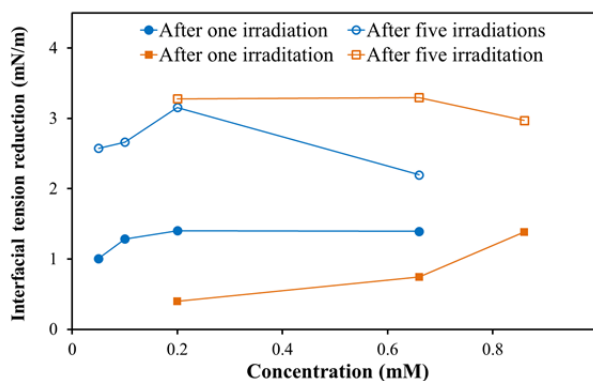

Fig. 6: Surface tension reduction after heating/cooling cycles: TX-100 (blue) and TX-405 (orange) after one (filled) and five (unfilled) irradiations
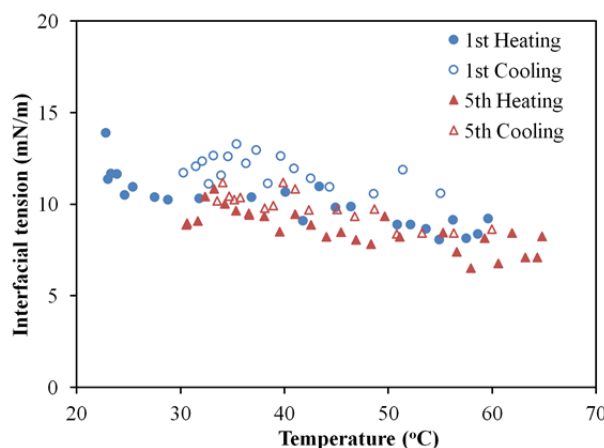

Fig. 7: Interfacial tension profiles during and after the first and the fifth irradiation (Triton X-405 0.86 mM)

Desorption of Triton X-405 molecules from the interface is more difficult than Triton X-100 as its hydrophilic group is four times longer. The longer, unwieldy molecule is less influenced by microwave irradiation.

Unlike conventional heating, microwaves exert a force on the on water molecules, causing them to rotate and disrupting the hydrogen bonding network. As the high interfacial tension of water is directly related to the unusual strength of its hydrogen bonding network, the disruption of these bonds around the interface leads to a lower interfacial tension [18,19]. Microwaves are reported to slightly decrease the surface tension of pure water [20]. In the case of Triton X-100, the thermal effect on the surfactant adsorption/desorption dominates the slight reduction in the
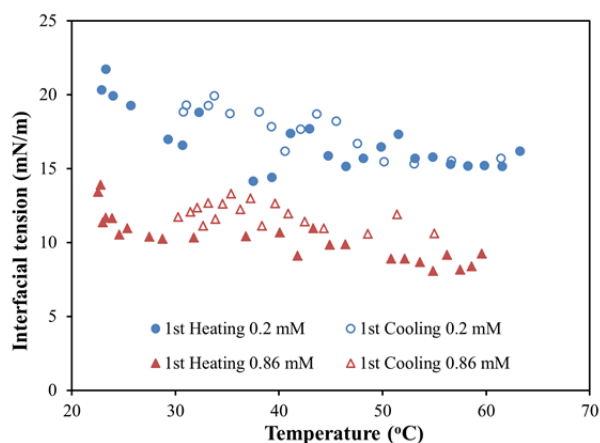
water-decane interfacial tension [21].

Fig. 8: Interfacial tension profiles for different concentration of Triton X-405 during and after first irradiation

According to data in Fig. 6, both surfactants produced similar reduction after cooling. However, Triton X-100 (Fig. 4) had stronger hysteresis than X-405 (Figs. 7 and 8) during cooling. The difference can be explained by its molecular size, which leads to higher adsorption.

To summarize the behaviours, hysteresis is mainly caused by non-thermal effect of the irradiation because quick desorption of Triton X-100 is almost impossible with thermal effect only [4]. Higher interfacial tension during the irradiation is unique phenomenon, caused by difference of rotations of water and decane molecules, which never happens in conventional heating. However, in the case of Triton X 405, desorption of the longer surfactant was not observed clearly as non-thermal effect. Therefore, a distinction between thermal effect and non-thermal effect still remains difficult to observe although non-thermal effect of interface is useful for the demulsification process [22–25].

4. Conclusions

This study investigated the effect of microwave irradiation on the interfacial tension of aqueous solutions of Triton X-100 and Triton X-405 with decane, with a particular emphasis on the effect of repeated irradiation. A substantial difference was found between the behaviour of the two surfactants. The interfacial tension of decane-Triton X-100

increased. However, the interfacial tension decreased as the solutions cooled, leading to hysteresis between the heating and cooling curves and overall depression of the interfacial tension that increased with successive irradiation. In contrast, the interfacial tension of decane-Triton X-405 decreased as temperature increased without hysteresis. Desorption of longer surfactant might be difficult and manly thermal effect by temperature difference between interface and cell bottom was observed. To utilize microwave effectively for two liquids system, microwave power, heating/cooling pattern and surfactant adsorption capability must be considered. Moreover, in-situ data of interfacial tension during the irradiation is needed for quantification of the hysteresis.

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