

수정진동자를 이용한 핵생성 속도의 측정

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Measurement of Nucleation Rate Using a Quartz Crystal Oscillator

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1. INTRODUCTION

Though the nucleation rate in crystallization processes is an important information for the process operation, the rate measurement requires special analytical equipments making it difficult. The nucleation rate in cooling crystallization relates to the shape and size of crystal products, key factors determining the product quality.

The nucleation of cadmium sulfide crystal was observed with a transmission electron microscope (TEM), and the identification of crystal forms during crystallization was conducted by Raman spectroscopy. Two ultrasonic velocity measurements were made on crystallization rate of n-hexadecane and palm kernel oil dispersed in oil-in-water emulsion. A quartz crystal sensor is so sensitive that it can detect mass variation on the surface in nano-gram scale. The crystal formation and growth in a cooling crystallization has been monitored with the quartz crystal oscillator to find the onset moment of crystallization [1], to determine a metastable zone width, and to measure the hysteresis between the processes of crystallization and dissolution [2].

Fatty acids have been widely used as functional materials in plastic, fiber, food, surfactant and biochemical industries. The hydrophobic fatty acids are miscible in organic solvents, but they are partially miscible in aqueous solutions. As a result, the fatty acid crystallization in an aqueous solution for purification has a quite different characteristic compared with common homogeneous phase crystallization. When the crystallization process of lauric acid from a mixed aqueous ethanol solution of lauric acid and myristic acid was combined with an extraction process, the lauric acid purity was significantly raised [3].

In this study, a simple measuring device using a quartz crystal sensor was utilized to monitor nucleation and crystal growth in a cooling crystallization process of dilute lauric acid solutions. The measurement was compared with the microscopic observation of the oscillator surface to explain the beginning moment of nucleation and crystal growth in different concentrations of the solution.

2. EXPERIMENTAL

2.1 Experimental Setup

The experimental setup of this study consists of a sensor module, a signal processing interface, two sets of temperature control system and a PC as shown in Figure 1. The sensor module locates in the middle of the setup, and the saturated lauric acid solution is circulated through the left room of the sensor module. The solution temperature was adjusted by placing a 500 mL glass bottle containing the solution in a water thermostat. An immersion-type magnetic stirrer was utilized to agitate the solution, and a peristaltic pump was used for the solution circulation.

Ethanol was circulated to the right hand side room in the sensor module using a peristaltic pump. A 500 mL glass bottle having ethanol was placed in a thermostat. Unlike the solution temperature maintained constant, the coolant temperature was slowly lowered to induce crystallization on the oscillator surface. While the coolant temperature lowers, the heater of the thermostat is turned off and an immersion cooler steadily reduces its water temperature.

The quartz crystal sensor placed in the sensor module was directly connected to an oscillation circuit contained in the box beneath the module to prevent a possible weakening of electric signal from the oscillator. Temperatures of the lauric acid solution and the coolant were measured with a thin thermocouple thermometer of 0.5 mm in diameter (Okazaki Manufacturing Co., Japan, Model NCF600) installed in the silicone tubes of liquid flows. The resonant frequency of the oscillator was counted using a home-made frequency counter, and its pulse signal was rectified to determine resonant resistance and an A/D converter was employed for signal processing. The digital signals of resonant frequency and resonant resistance were provided to a PC.

2.3 Experimental Procedure

A 0.02 g of lauric acid (Kishida Chemical Co., Japan, Code No. 010-43785) was dissolved into a 40 g of ethanol (Kanto Chemical Co., Japan, Code No. 14033-80) and a 360 g of distilled water in a 500 mL glass bottle. In the second run of experiment, a 0.06 g lauric acid was dissolved into a 60 g of ethanol and 340 g of water. In the third, an 80 g of ethanol and 320 g of water dissolved a 0.1 g of lauric acid. The bottle was placed in a thermostat maintained at a temperature of 45 °C. Another 500 mL glass bottle holding the ethanol coolant (Kanto Chemical Co., Japan, Code No. 14033-80) was put in the other thermostat of which the temperature was adjusted at 45 °C in the beginning of experiment and slowly lowered during the crystallization.

The sensor module was placed on top of the oscillation circuit box, and the two conductors of a quartz crystal oscillator were directly connected to the oscillation circuit. When temperatures of the lauric acid solution and the coolant had settled, the coolant was supplied first at a rate of 7.5 mL/min for the first run. The rates were 5.3 mL/min and 5.4 mL/min for the second and third, respectively. After about 5 minutes when the oscillator frequency had stabilized, the lauric acid solution was introduced at a rate of 5.1 mL/min for all three runs. The frequency had been stable after another 5 minutes, and the immersion cooler installed at the coolant thermostat was activated to lower the coolant temperature at a rate of 1 °C/min whereas the solution temperature was kept constant. The resonant frequency and resistance of the oscillator and the temperatures of the solution and coolant were continuously measured from the beginning and stored in a PC.

3. RESULTS AND DISCUSSION

In the first run of the experiment with 0.05 g/L lauric acid solution, the variations of resonant frequency and resistance, and solution and coolant temperatures are demonstrated. While the solution temperature remains constant except a bump caused from the initiation of solution supply, the coolant temperature steadily diminishes from 10 minutes after the supply began. While the coolant temperature was lowered, a small decrease of resonant frequency was yielded though it is not observed in the figure due to large frequency scale. The decrease will be discussed in detail below. Because a mass variation on the oscillator surface during the crystallization is more apparent leading to the frequency change than the surface roughness alteration resulting in the resonant resistance variation, the frequency reduction was analyzed here.

The steady decrease of the frequency expressed with a fitted line represents the effect of temperature decrease on the sensor frequency. When the crystallization of lauric acid initiates, the frequency reduction is discerned from the steady decrease of temperature effect and the beginning is denoted as nucleation in the figure. The concentration of lauric acid was so low that crystal growth was not observed as in the previous studies. The small reduction of the frequency also indicates that there is no crystal growth in this experiment. The crystal growth leads to much larger change of the

frequency. The continuous reduction of the frequency explains increased mass loading on the sensor surface due to the formation of more nuclei. This is examined through microscopic observation explained below.

The phase diagram of lauric acid solution indicates emulsification occurs before crystallization during the cooling process. As the concentration of lauric acid is raised in the figure, the temperatures of emulsification and crystallization are raised. Yet the increase of crystallization temperature is only observed in this experiment. Though the emulsification occurs near the sensor surface, it takes time to become larger oil drop to cling to the sensor surface and therefore an accurate determination of the beginning moment of emulsification was not possible. A large drop of the frequency from the emulsification was observed in Figure 2, which indicates the coalescence of small oil drops. The delayed detection of emulsification in the 0.05 g/L solution of lauric acid led to high emulsification temperature. This explains the relation between the solution concentration and the measured emulsification temperature.

In order to examine the results of frequency measurement, a microscopic observation using a scanning electron microscope (Hitachi Kyowa Engineering Co., Japan, Model S-9100) was conducted. When a low concentration of 0.05 g/L lauric acid solution was utilized, tiny crystals—nuclei—were obtained at a temperature of 7 °C as demonstrated with circles in Figure 3(b). A comparison with the SEM photograph of a bare sensor (Figure 3(a)) clearly indicates the nuclei on the surface. When the solution concentration increases to 0.15 g/L and 0.25 g/L, the number of nuclei is raised as shown in Figures 3(c) and 3(d).

The total amount of nuclei was monitored with the resonant frequency of sensor. Though sensor sensitivity was not determined in the lauric acid solution, the frequency reduction with mass loading on the surface in air was examined and it was found that the sensor sensitivity is 1.01 ng/Hz. In the measurement a dilute sodium chloride solution of a known amount was applied to the sensor surface, and the frequency variation was measured after dried the solution.

The amount of yielded nuclei on the sensor surface was calculated from the frequency reduction, and the outcome is shown in Figure 4. The nuclei amount per unit area of sensor is linearly increased with time, and the higher solution concentration is the more nuclei are obtained. In addition, the size of nuclei was measured from the SEM photographs to be shown. All the nuclei formed on a sensor surface were sized and counted by the size. As the solution concentration increases, the number and size of the nuclei are raised. Conversely the average size of crystals increases with the raised concentration. These results indicate that the monitoring device developed in this study is useful to examine the beginning moment of nuclei formation and crystal growth. Though previous studies utilized analytical instruments, such as spectrophotometer and laser particle analyzer, in the crystallization monitoring, relatively simple and in-line available device of this study has many advantages in the application.

4. CONCLUSION

An emulsification and nucleation in a dilute solution of lauric acid were monitored using a quartz crystal sensor. While cooling the sensor surface in contact with the solution, the emulsification and nucleation were detected to measure their temperatures. From the reduction of resonant frequency of the sensor the amount of nuclei was determined and the nucleus size was measured by microscopic observation.

As predicted from the phase diagram of lauric acid and ethanol solution, the emulsification was detected prior to the nucleation. With higher concentration of lauric acid solution more nuclei were obtained, but the nucleation rate was less than with lower concentration solution. Instead their size was larger than those of lower concentration. In high concentration solution, the crystal growth is faster than the nucleus formation.

ACKNOWLEDGMENT

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REFERENCES

- [1] B.C. Kim, Y.H. Kim, K. Fukui, Crystallization monitoring in supersaturated solution with a quartz crystal sensor, *Anal. Chim. Acta*, 491 (2003) 71-80.
 [2] O.J. Joung, Y.H. Kim, K. Maeda, K. Fukui, Measurement of hysteresis in crystallization with a quartz crystal sensor, *Korean J. Chem. Eng.*, 22 (2005) 99-102.
 [3] K. Maeda, Y. Nomura, M. Tai, Y. Ueno, K. Fukui, S. Hirota, New crystallization of fatty acids from aqueous ethanol solution combined with liquid-liquid extraction, *Ind. Eng. Chem. Res.*, 38 (1999) 2428-2433.

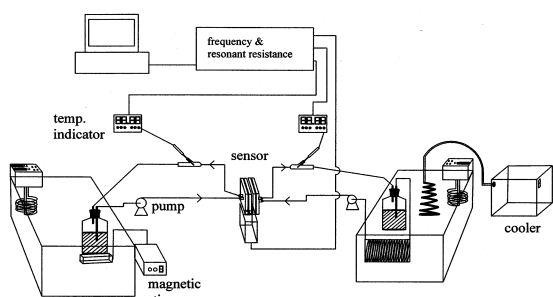


Figure 1. A schematic diagram of the experimental setup with liquid flows and electrical wiring.

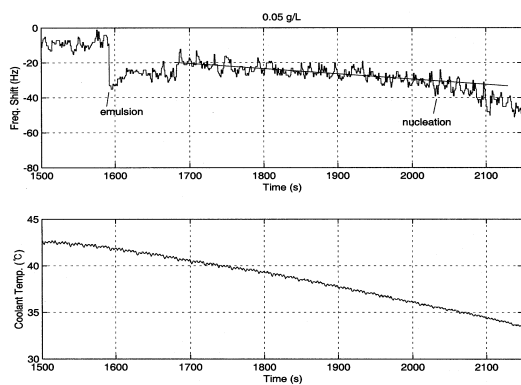


Figure 2. Magnified plots of frequency variation while sensor temperature decreases with a lauric acid concentration of 0.05 g/L.

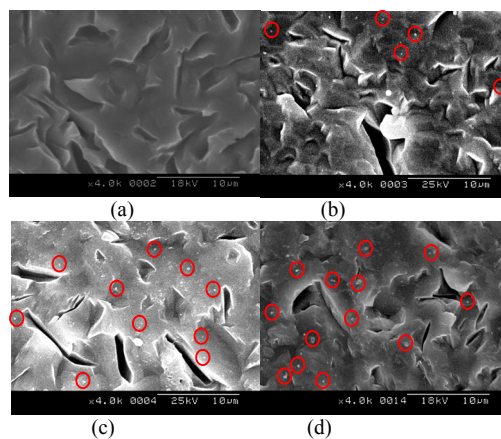


Figure 3. SEM photographs of bare sensor (a) and sensors taken at the coolant temperature of 7 °C from 0.05 g/L solution (b), 0.15 g/L (c) and 0.25 g/L (d).

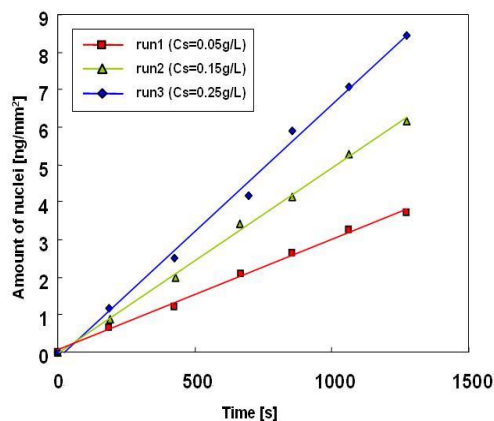


Figure 4. The amount of nuclei per unit area of sensor surface with increased time for different concentrations of lauric acid solution.