지방산의 승화압과 수정진동자 표면증착 측정

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Relationship of sublimation pressure of fatty acids and surface deposition on a quartz crystal resonator

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1. Introduction

Solar thermal energy is one of the most promising alternatives of fossil fuel energy causing the global warming. A significant shortcoming of the solar energy is its non-availability during night time and cloudy daytime. Thermal energy storage is the solution of the non-availability, and fatty acids and their derivatives are good candidates of the storage material utilizing the latent heat from phase change. Fatty acids have been widely used as functional materials in various fields, such as plastic, fiber, food, surfactant and biochemical industries. The long term use of the storage material is determined by thermal stability. The sublimation pressure of fatty acids is a measure of the thermal stability, but the low value of the pressure makes its measurement difficult.

A quartz crystal resonator comprised a thin quartz crystal sandwiched between two metal electrodes that establishes an alternating electric field across the crystal, causing vibrational motion of the crystal at its resonant frequency. This frequency is sensitive to mass changes at the interface of the crystal and its electrode. For example, a 9 MHz resonator detects a mass variation in the sensitivity of 1.4 ng/Hz [1]. The change of mass loading due to crystal formation has been used to detect the moment of crystal nucleation and growth. The change was also applied to detect the dew point of organic vapor from the condensation on the electrode surface[2]. When the small amount of vapor sublimated from the fatty acids deposited on the surface of the resonator, its amount can be determined from the measurement of resonant frequency variation.

In this study the sublimation of fatty acids was measured using the quartz crystal microbalance, and the measurements were compared with the sublimation pressure determined by Knudsen’s effusion method to show the relation between the variations of the resonant frequency and the sublimation pressure.

2. Experimental

2.1 materials

Capric acid (Code No. 24060-1201), lauric acid (Code No. 81070-0401) and myristic acid (Code No. 71030-0401) were purchased from Junsei Chemical Co., Japan, and palmitic acid (Code No. 160-00215) was from Hayashi Pure Chemical Co., Japan.

2.2 Analytical Instrument

Thermal analysis was conducted with a differential scanning calorimeter (TA Instruments Inc., U.S.A., Model Q-10). A microscope (Sometech, Korea, Model SV-55) was used for the observation of electrode surface.

2.3. Equipment

AT-cut quartz crystal resonators having a base frequency of 8 MHz was utilized in this experiment. The electrodes of the resonator were silver finished. The thicknesses of two plates were 1.2 mm. The front plate has a hole to make one electrode of the resonator open, and the other is sealed from the vapor. To prevent leakage two o-rings are placed between the two plates and the resonator. The size of the two plates was the same with a dimension of 19 mm by 10 mm. Four screws are tighten the two polypropylene plates.

2.4. Procedures

The quartz crystal resonator was mounted in the cell module, and placed horizontally in the sample tube. A glass tube of 25 mm in diameter and 190 mm long with one neck in Fig. 1 was used as the sample tube. The open hole of the cell module was facing down to the fatty acid sample in the distance of 35 mm. The sample amount was 0.1 g. When the connection to the PC was ready, vacuum pump has been activated until the vacuum gauge indicated zero pressure. After air had been evacuated from the sample tube, the valve to the vacuum pump was closed and the heater installed outside of the sample tube began to raise the temperature of the fatty acid sample. While the temperature was elevated, the resonant frequency of the resonator and temperature were collected to the PC for the later analysis of the experimental results.

3. Results and discussion

The experimental procedure of the blank test was the same to the sample test. The variation of frequency with different temperature was less than 20 Hz. Three runs of experiment were conducted with capric acid, and the frequency variation was demonstrated in Fig. 2. The frequency shift means the decrease of frequency due to the vapor deposition of capric acid on the electrode surface of the resonator. As the vapor pressure rises with increased temperature, more deposition occurs to elevate the shift. The frequency variation was less than capric acid due to the higher carbon number of 12 than 10 of capric acid. In the test the sample temperature was higher than others.

The correlation between the sublimation pressure of fatty acids and temperature was summarized using the following linear equation by Davies and Malpass[3].

$$\log_{10} p = a - b/T \quad (1)$$

where p is pressure in Pa and t is the absolute temperature in Kelvin. The coefficients a and b are listed in Table 1. When the calculated pressure and frequency drop for the fatty acids are shown in Fig. 3. Though there is some deviation, the relationship between the logarithm of pressure and frequency shift becomes linear. In other words, the sublimation pressure is estimated from the measured variation of resonant frequency of quartz crystal microbalance using the following equation.

$$\log_{10} p = 1.874 \times 10^{-3} \Delta f - 4.379 \tag{2}$$

where Δf is the frequency shift. The linear relation, Eq. (2) indicates that a simple measuring device for the determination of sublimation pressure is available. When temperature is relatively high, the pressure is high enough to be measured using a conventional pressure gauge. Many substances with low boiling point have very low vapor pressure at low temperature like ambient temperature. The quartz crystal microbalance is useful to determine the low pressure by measuring the variation of resonant frequency.

For the comparison of the thermal property of melting and solidification characteristic, the differential scanning calorimetry (DSC) was utilized. The temperature difference varies in the two acids, but no significance is observed in the measurement of sublimation pressure of this study.

The deposition of fatty acid on the electrode surface was examined with the microscopic observation of electrode surface. The frequency variation indicates the amount of vapor deposition on the electrode surface. When the vapor pressure of the fatty acids is very low at the low temperature like this experiment, the measurement of vapor either in pressure or mass amount is difficult. The quartz crystal microbalance utilized in this experiment is useful to determine such a small amount of mass variation as used in various applications, such as organic vapor deposition, crystalline deposition and solid deposition. The performance of vapor pressure measurement from the sublimation of fatty acids demonstrates that the quartz crystal microbalance can be utilized in the determination of low vapor pressure of organic compounds having high carbon number at low temperature.

References

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2. B. C. Kim, Y. H. Kim, and K. Fukui, "Crystallization monitoring in supersaturated solution with a quartz crystal sensor", *Anal. Chim. Acta.*, **491**,71-80 (2003).
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Table 1. List of coefficients for sublimation pressure estimation.

Name	a	b
Capric acid	19.25	-6119
Lauric acid	22.02	-7322
Myristic acid	20.86	-7291
Palmitic acid	22.34	-8069

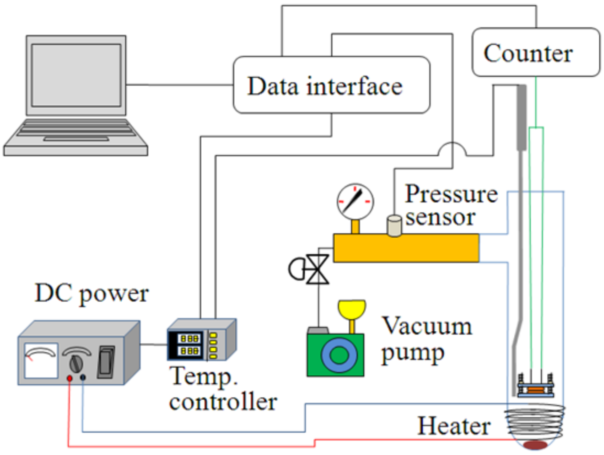

Fig. 1. A schematic diagram of experimental setup.

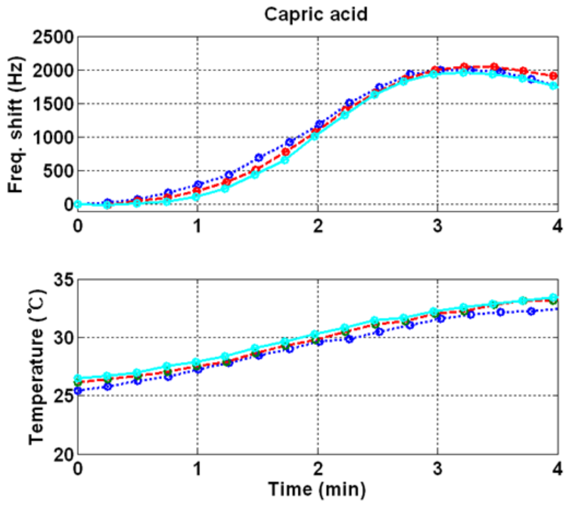

Fig. 2. The variation of resonant frequency of a resonator with increased temperature (Capric acid).

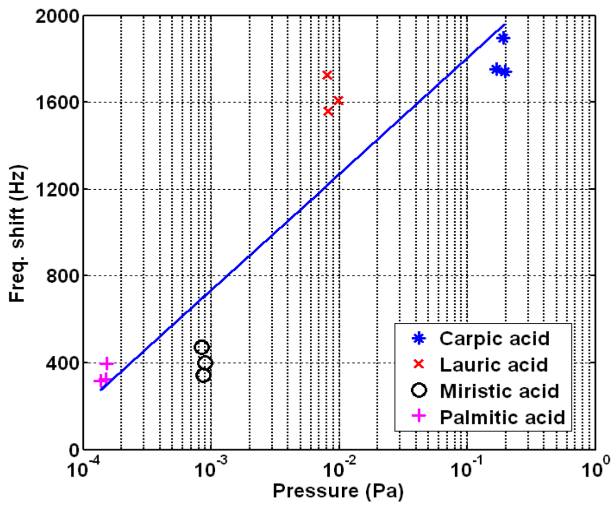

Fig. 3. The predicted pressure and frequency drop of the fatty acids.