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Effect of Immersion Angle of a One-Face Sealed Quartz Crystal Microbalance in Liquid

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The effect of the immersion angle θ of the QCM in a liquid was investigated using the impedance analyzer. In the QCM, with the two faces in contact with a liquid, the resonant frequency shift ΔF was independent of θ and was dependent on only the number of faces in contact with a liquid. On the other hand, in the QCM, with the one face in contact with a liquid, it became clear that ΔF depended on θ and had the largest value at $\theta = 90°$ and the smallest value at $\theta = 0°$. We also presented the simple model of ΔF in the QCM with the one face in contact with a liquid on the basis of experimental results.

The quartz crystal microbalance (QCM) has for a long time been used in a vacuum and gaseous environments as a mass sensor, but its oscillation in a liquid environment was later successful, and there have been many requirements for sensors in a liquid.[1−5] The ease of use, low detection limit, and continuous operation have attracted increasing interest for its utilization in this manner.[6−8]

When the QCM is dipped into a liquid, the oscillating frequency depends on a liquid viscosity. Several pioneering articles[9−11] to theoretically describe this phenomenon appeared. In those articles, the study of Kanazawa and Gordon[10] is most supported in a Newtonian liquid. They derived the following equation in the one-face immersion of the QCM from the behavior of the quartz crystal/fluid system by examining the coupling of the elastic shear waves in the quartz crystal to the viscous shear waves in a liquid.

$$\Delta F_{\eta} = -\frac{f_0^{3/2}}{\sqrt{\pi\rho\mu}}\sqrt{\rho_L \eta_L} \tag{1}$$

where ΔF_{η} is the frequency shift due to a liquid viscosity, f_0 the resonant fundamental frequency of a quartz crystal, μ the shear modulus of a quartz crystal, and η_L the absolute viscosity of a liquid and ρ and ρ_L are the densities of a quartz crystal and a liquid, respectively. Nevertheless, many attempts[12−19] profile only that eq 1 holds qualitatively: when ΔF_{η} is plotted against $(\rho_L \eta_L)^{1/2}$, a linear relationship is observed with the slope being different from that of the theoretical eq 1. On the other hand, one can recognize that, in those attempts, the angular mounting of the QCM in a liquid was varied by the arrangement of the apparatus. This fact leads us to the importance of the effect of the immersion angle of the QCM in a liquid. Hence, in this paper, our aim is to investigate the effect of the angular mounting of the QCM in a Newtonian liquid. Especially, we focus on the resonant frequency shift ΔF on the one-face immersion of the QCM.

EXPERIMENTAL SECTION

In our experiments, two types of AT-cut QCMs were investigated at the fundamental frequencies of 9 and 30 MHz: one is the one-face sealed QCM (Figure 1a), the other is the nonsealed QCM. The immersion angle θ between the horizon and the quartz crystal was varied (Figure 1b). The AT-cut quartz crystals (8 × 8 mm in 9 MHz and 5 × 5 mm in 30 MHz) with a pair of gold electrodes (5 × 5 mm in 9 MHz and 3 × 3 mm in 30 MHz) were used, where the configuration of the electrode was round. The crystals were obtained from Nihon Dempa Kogyo (Tokyo, Japan).

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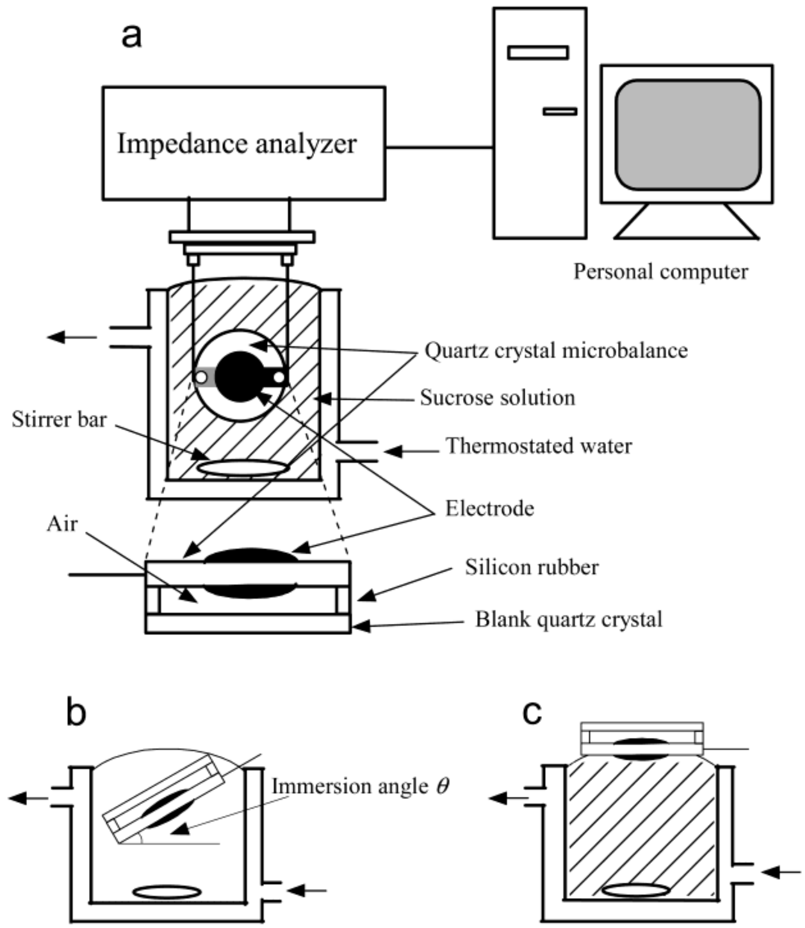

Figure 1. (a) Schematic illustration of an experimental apparatus. (b) Schematic illustration of the angular mounting of the QCM in the experiments. The illustration shows the case of the one-face sealed QCM, but the method in the nonsealed QCM is also the same. (c) Schematic illustration of the one-face sealed QCM at $\theta = 0°$ in the experiments. The illustration shows the method of the one-face sealed QCM, but the method in the nonsealed QCM is also the same.

In the one-face sealed QCM, the one face of the QCM was sealed with a blank quartz crystal casing, maintaining it in an air environment. This method enabled the one-face immersion of the QCM in a liquid. In the nonsealed QCM, the QCM did not have a blank quartz crystal casing. Newtonian solution was prepared using sucrose (analytical-reagent grade, Wako). The water with a specific resistance of 18.3 MΩ·cm was prepared with a Milli-Q apparatus (Millipore, Tokyo, Japan). The volume of the cell was 3 mL. The cell had the water jacket to keep the temperature constant at 20 ± 0.1 °C. The frequency shift of the QCM was measured by the impedance analyzer (Hewlett-Packard model 4396B) and was recorded onto a personal computer.

RESULTS AND DISCUSSION

Usually, in the experiments, the one-face sealed QCM are carried out at $\theta = 90°$ in a liquid. Figure 2 shows ΔF versus $(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}$ on the one-face sealed QCM of 9 MHz in a sucrose solution, where ρ_W and η_W denote the density and the viscosity of water, respectively. At $\theta = 90°$, eq 1 is not in quantitative agreement with ΔF in the experiments. On the other hand, at $\theta = 0°$ (Figure 1c), ΔF is in good quantitative agreement with eq 1. At both $\theta = 90°$ and $\theta = 0°$, only the one face of the QCM with an electrode is in contact with the liquid. However, these results are not the same. This important problem of

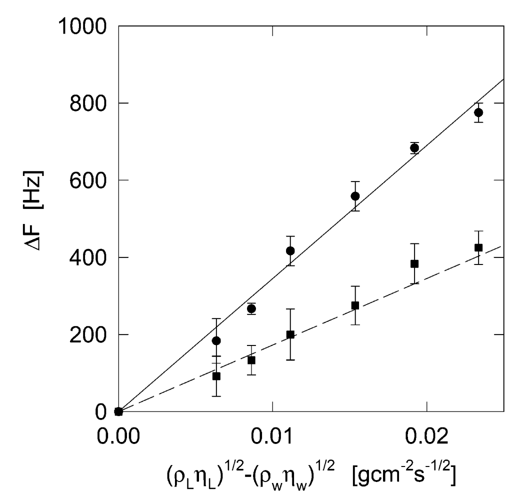

Figure 2. Resonant frequency shift versus $(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}$ on the 9-MHz QCM, whose one face is sealed with a blank quartz crystal casing. ● and ■ denote the experimental data at $\theta = 90°$ and $\theta = 0°$, respectively. The dashed line was calculated using eq 1. The solid line was calculated using eq 4. In comparison of the results of the one-face sealed QCM (■ in Figure 2) and the nonsealed QCM (■ in Figure 3b) at $\theta = 0°$, it is clear that the blank quartz crystal casing of the one-face sealed QCM does not prevent the free oscillation of a quartz crystal. The error bar represents the standard deviation. The measurements were repeated three times.

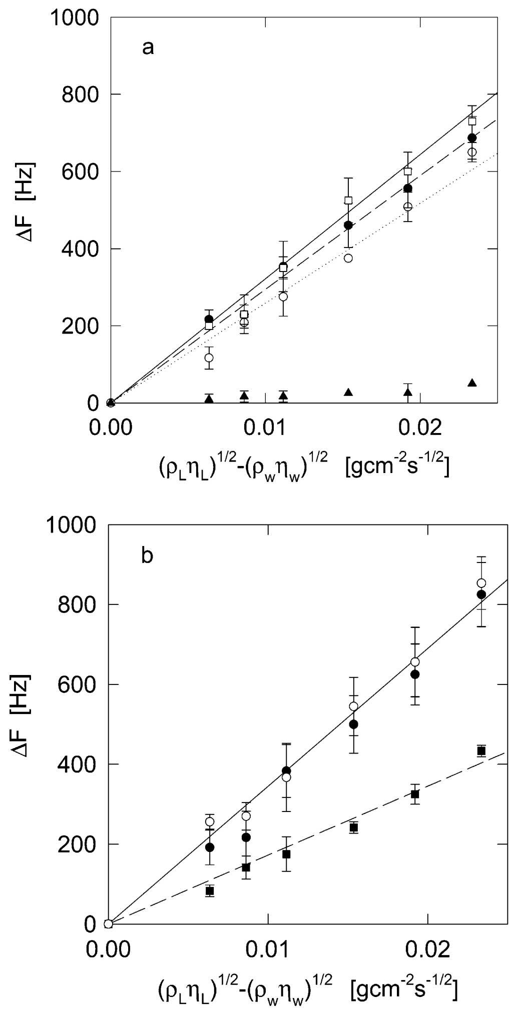

Figure 3. (a) Resonant frequency shift versus $(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}$ on the one-face sealed QCM of 9 MHz. The immersion angle of the QCM was varied in the experiments: □, $\theta = 60°$; ●, $\theta = 45°$; ○, $\theta = 30°$. The solid line, the dashed line, and the dotted line were calculated using eq 4 with $\theta = 60°$, 45°, and 30°, respectively. The resonant frequency shift of the face of a blank quartz crystal at $\theta = 0°$ is also indicated as ▲. The error bar represents the standard deviation. The measurements were repeated three times. (b) Resonant frequency shift versus $(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}$ on the nonsealed QCM of 9 MHz. The immersion angle of the QCM was varied in experiments: ●, $\theta = 90°$; ○, $\theta = 30°$; ■, $\theta = 0°$. The dashed line and the solid line are calculated using eq 1 and eq 5, respectively. The error bar represents the standard deviation. The measurements were repeated three times.

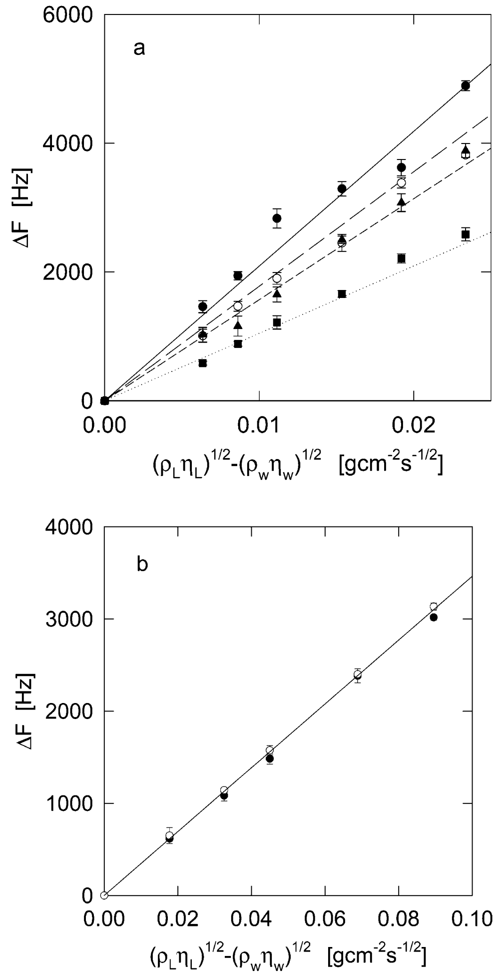

Figure 4. (a) Resonant frequency shift versus $(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}$ on the one-face sealed QCM of 30 MHz. The immersion angle of the QCM was varied in experiments: ●, $\theta = 90°$; ○, $\theta = 45°$; ▲, $\theta = 30°$; ■, $\theta = 0°$. The solid line, the long dashed line, the dashed line, and the dotted line were calculated using eq 4 with $\theta = 90°$, 45°, 30°, and 0°, respectively. The error bar represents the standard deviation. The measurements were repeated three times. (b) Resonant frequency shift versus $(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}$ with the immersion depth. We used the one-face sealed QCM of 9 MHz. The immersion angle was set at 90°. The immersion depths from the water surface to the center of the QCM were set at 0.5 (●) and 2.5 cm (○), where the difference of the frequency was ~800 Hz in pure water. The solid line is calculated from eq 4 with $\theta = 90°$. The relationship between ΔF and $(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}$ was linear up to more than 0.0895 g cm^{-2} s$^{-1/2}$ (30 wt %). The error bar represents the standard deviation. The measurements were repeated three times.

utilization of the QCM in the liquid is not yet reveled. Therefore, in this paper, we focus our interest on this behavior of the one-face sealed QCM in the liquid.

We consider the two effects as the cause of the deviation between eq 1 and the experimental result of the one-face sealed QCM at $\theta = 90°$: (1) effect of the face of a blank quartz crystal and (2) effect of the immersion angle θ. To investigate effect 1, ΔF due to the immersion of the face of a blank quartz crystal was measured at $\theta = 0°$, where the face with an electrode was not in contact with the liquid. As shown in Figure 3a, ΔF did not occur. Next, we measured ΔF at $\theta = 60°$, $\theta = 45°$, amd $\theta = 30°$ for effect 2. The values of ΔF varied with $(\rho_L\eta_L)^{1/2} - (\rho_W\eta_W)^{1/2}$ and were smaller than that of $\theta = 90°$ (Figure 3a). These results profile that ΔF depends only on θ of the QCM immersed into the liquid.

To obtain the further insight into the results of the one-face sealed QCM, we investigated the behavior of the nonsealed QCM in the liquid (Figure 3b). At $\theta = 0°$, eq 1 quantitatively accorded with ΔF in the experiments, where only the one face with an electrode was in contact with the liquid. On the other hand, at $\theta = 90°$ and $\theta = 30°$, the two faces of the QCM with electrodes were in contact with a liquid. At $\theta = 90°$, eq 1 was not able to describe ΔF in the experiments. The tendency of ΔF at $\theta = 30°$ was also equal to that at $\theta = 90°$. These results indicate that ΔF in the nonsealed QCM depends on the number of faces of the QCM in contact with the liquid.

The above experimental results allow us to discuss the behavior of the one-face sealed QCM in a Newtonian liquid. In a comparison between the results of the one-face sealed QCM and the nonsealed QCM, we can recognize that the asymmetry between the liquid side and the air side (blank quartz crystal side) of the one-face sealed QCM plays an important role. The first candidate for cause of the asymmetry is the hydrostatic pressure. However, in the one-face sealed QCM, the hydrostatic pressure of the pure water is canceled in the difference of the frequency shift and the effect of the hydrostatic pressure due to the increase of the liquid density is very small between $\theta = 90°$ and other angles. Therefore, we need to introduce the new physical view to explain the behavior of the one-face sealed QCM immersed in a Newtonian liquid.

The oscillating quartz crystal has the rigid layer of the liquid bound to the surface. The thickness r is called viscous penetration depth.[20] We may introduce the stress due to this layer Δs as the cause of the asymmetry. As a result, the entire resonant frequency shift ΔF in the one-face sealed QCM is given by

$$\Delta F = \Delta F_\eta + \Delta F_s \tag{2}$$

where ΔF_s denotes the resonant frequency shift by Δs. Here, supposing that Δs is caused by the mass loading per area $\Delta m = \rho_L r$ and that the effect of Δm is dependent on θ, we obtain using $r = (\eta_L/\pi\rho_L f_0)^{1/2}$ and eq 1

$$\Delta F_s = -\frac{f_0^{3/2}}{\sqrt{\pi\rho\mu}}\sqrt{\rho_L\eta_L}\,\sin\theta \tag{3}$$

Finally, the expression that describes ΔF induced by immersing the one face of the QCM in the liquid is derived from eq 1 and eq 3:

$$\Delta F = \Delta F_\eta + \Delta F_s = -\frac{f_0^{3/2}}{\sqrt{\pi\rho\mu}}\sqrt{\rho_L\eta_L}(1 + \sin\theta) \tag{4}$$

Equation 4 with $\theta = 0°$ is equal to eq 1 (Figure 2). The theoretical values calculated using eq 4 with $\theta = 90°$ and $\theta = 30°$ are shown in Figure 2 and Figure 3a, respectively. These results suggest that eq 4 is in good quantitative agreement with the results of the experiments.

We inquired into the dependence on f_0 in ΔF and the independence from the immersion depth of the QCM. First, we investigated the dependence on f_0 using the 30-MHz QCM. The result is shown in Figure 4a. ΔF is obviously dependent on f_0. Next, we determined whether ΔF was independent of the immersion depth of the QCM in the liquid. It is clear from Figure 4b that ΔF is independent of the immersion depth. These results also suggest that eq 4 is adequate for the one-face immersion of the QCM.

We also discuss the behavior of the nonsealed QCM in a Newtonian liquid. In this case, ΔF depends on the number of the faces in contact with the liquid. At $\theta = 30°$ and $\theta = 90°$, the number of the faces in contact with the liquid is two. As twice the area gives twice the mass loading on the QCM, the following equation is obtained.

$$\Delta F_\eta = -2\frac{f_0^{3/2}}{\sqrt{\pi\rho\mu}}\sqrt{\rho_L\eta_L} \tag{5}$$

The theoretical value calculated from eq 5 is indicated in Figure 3b. This theory is in good quantitative agreement with the results of the experiments at $\theta = 90°$ and $\theta = 30°$. At $\theta = 0°$, the number of faces is one. Equation 1 quantitatively accords with the results of the experiments (Figure 3b).

In this paper, we assumed that the stress by the rigid layer of the liquid bound to the surface of the QCM was dependent on the immersion angle. This assumption may be speculative. However, it is clear that eq 4 quantitatively describes the experimental data. On the other hand, it was reported that the resonant frequency shift in a liquid was caused by the several effects, e.g., surface roughness,[15] interfacial slip,[2,18] relative permittivity of a liquid,[17] longitudinal waves,[21] and so on. These factors may be important. We are now studying the physical meaning of the rigid layer in this paper.

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