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Detection of Interactions between Lipid/Polymer Membranes and Taste Substances by Quartz Resonator

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The response of a quartz resonator coated with a lipid/polymer membrane to basic taste substances was investigated. The quartz resonator was coated with the same lipid/polymer membrane as that possessed by a potentiometric multichannel taste sensor. The oscillation frequency of the coated quartz resonator showed different responses depending on the taste substances and the lipid in the membrane. The responses of the membrane potential and the quartz resonator to taste substances were compared to study the interaction between the membrane and the taste substance. Information different from the response of the membrane potential was obtained from the quartz resonator with the lipid/polymer membrane.

1. Introduction

A taste sensor that monitors the electric potential in a lipid/polymer membrane has been developed taking advantage of the lipid, an important element in biological membranes.[(1)] This taste sensor uses a lipid/polymer membrane as a transducer and determines the taste from changes in electric potential. The taste sensor is very sensitive to the basic taste substances and to many foods such as beer,[(2)] coffee,[(3)] sake,[(4)] tomatoes[(5)] and milk.[(6)]

However, this potentiometric taste sensor has lower sensitivity to hydrophobic and non-electrolytic taste substances compared to electrolytes. It is, therefore, important to investigate other measurements by which physical quantities other than the electric potential can be obtained. Unclear points concerning the interaction between the taste substances and the lipid/polymer membrane must also be clarified.

Many chemical sensors have been developed to determine tastes. They include methods of measurement that use the impedance of the lipid and the metal electrode,[7] surface plasmon resonance (SPR),[8] surface photovoltage (SPV)[9] and quartz resonators[10] with thin organic membranes.

Quartz resonators have been widely applied to various sensors.[11–13] These sensors determine a very small amount of adsorbed substance on the surface of the resonator as a function of the oscillation frequency. For the purpose of detection of chemical substances, the surface of a quartz resonator is coated with a sensitive membrane that adsorbs the target substance. The quartz resonator sensor is used not only for vapors but also for liquids to detect odor and taste substances.[10-12]

In this study, we investigated the responses of taste substances using a quartz resonator coated with a lipid/polymer membrane. To compare the responses of the electric potential, the quartz resonator was coated with the same type of lipid/polymer membrane applied to the potentiometric taste sensor. The quartz resonator sensor with a thin lipid/polymer membrane responded to five taste substances. The response varied depending on the taste substance and the lipid.

2. Materials and Methods

Figure 1 shows the devices used to make the measurements. The liquid measurement of the odor sensor (Sogo Pharmaceutical Co., SF–105W) was used as the sensor system. The devices used were a sensor element composed of a quartz resonator coated with a lipid/polymer membrane, a sensor probe to immerse the sensor element into the aqueous solution and an electronic circuit consisting of a driving circuit and a frequency counter. The frequency data was collected and imported into a personal computer.

A quartz resonator, an AT cut type with a resonant frequency of approximately 9MHz, was used. It was coated with the lipid/polymer membrane by the spin-coat method and was used as the sensitive device. A spinner (Kyowa Riken, K-359S-1) was used for coating. The artificial lipid that was the basic ingredient of the lipid/polymer membrane, dioctyl phenyl phosphonate (a plasticizer) and polyvinyl chloride (the base polymer) were dissolved in tetrahydrofuran (THF). Then the liquid was dropped onto the spinning quartz resonator. The quantity of THF was 10 times greater than that needed to make the lipid/polymer membrane of the potentiometric taste sensor.[1] The lipid/polymer membrane was coated so that the oscillation frequency changed in the range of 4 kHz and 5 kHz.

Eight lipid/polymer membranes composed of different lipids were used for the taste sensor,[2] which measured the membrane potential. Dioctyl phosphate (DOP), trioctyl methyl ammonium chloride (TOMA), oleyl amine (OAm), n-decyl alcohol (DA), oleic acid (OA) and mixed membranes of DOP and TOMA at molar concentration ratios of 3:7,

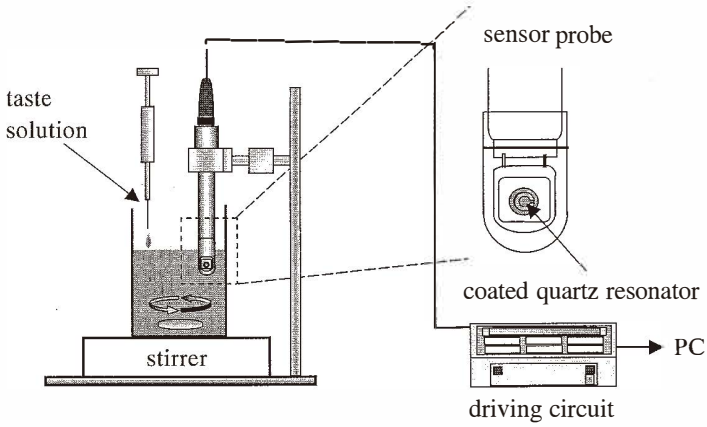

Fig. 1. Experimental apparatus using quartz resonator coated with lipid/polymer membrane.

5:5 and 9:1 were used. For the measurements in this study, DOP, the mixed membrane of DOP and TOMA 5:5, TOMA and OAm were selected.

When pure water was stirred in the beaker, the sensor probe was inserted (Fig. 1). The coated quartz resonator was assembled into a watertight tube housing, which exposed only the coated side of the resonator. Then the oscillation frequency was measured. After confirming that the oscillation frequency was stable, the taste substance was added to the pure water and the change in the frequency was examined. Sodium chloride for salty, hydrochloric acid for sour, sucrose for sweet, monosodium glutamate (MSG) for umami and quinine hydrochloride for bitter were used as the taste substances.

The sensor device was left in the pure water for one night after each measurement to prevent the response characteristics from changing due to the adsorption of the taste substance. Then it was reused after the taste substance was desorbed.

3. Results

Figure 2 shows an example of the transient response of the quartz resonator sensor device caused by an added substance. When sucrose was added in concentrations of 1 mM to 1 M every 6 min, a decrease in the oscillation frequency was indicated. The response of the sensor device that was coated with the lipid/polymer membrane 5:5 and the response of the non-coated quartz resonator that had the exposed gold electrode were compared under the same conditions.

Regarding the quartz resonator that was not coated with the lipid/polymer membrane, when the taste substance was added, the frequency of the non-coated quartz resonator decreased even at high concentrations. (Fig. 2) Regardless of the taste substance, the transient response did not last over 1 min and the frequency after the decrease was stable.

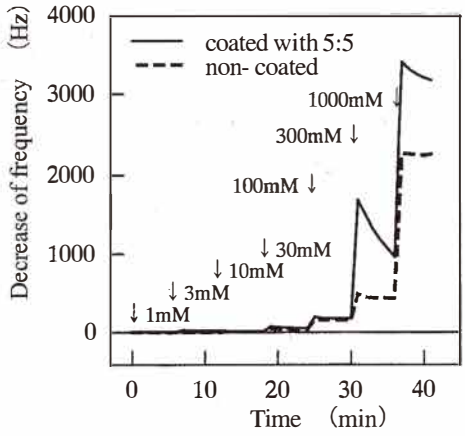

Fig. 2. Transient responses of a non-coated quartz resonator and a quartz resonator with 5:5 membrane when sucrose was added.

With the sensor device that was coated with the lipid/polymer membrane, the frequency changed significantly. Depending on the taste substance and the lipid, the transient response lasted over 6 min. For example, in the response of sucrose to the 5:5 membrane, both the decreased frequency and the transient response differed very little between the coated and the non-coated sensor up to a concentration of 100 mM. However, at concentrations of 300 mM and 1 M, the 5:5 membrane coated sensor device indicated a larger frequency decrease and a subsequent transient response. (Fig. 2)

The decreased frequency of the non-coated quartz resonator was subtracted from the decreased frequency of the lipid/polymer membrane coated sensor device. The resultant value was considered as the response of the lipid/polymer membrane. The frequency after 5 min was considered the response, and the cases where the transient state remained were also included.

Figure 3 shows the dependence of the response value of DOP, 5:5, TOMA and OAm membranes on the concentration of the taste substance to the 5 basic taste substances. To compare these responses with the characteristics of the potentiometric measurements, the response of the DOP-membrane potential is also included in Fig. 3.[1] The values were the average of measurements repeated four times. The standard deviation of the non-coated quartz resonator was approximately 10 Hz. The standard deviation of the lipid/polymer membrane coated device was significantly larger through repeated measurements. Depending on the combination of the lipid and the taste substance, the maximum standard deviation of the coated device reached approximately 100 Hz.

The responses of any lipid/polymer membrane to NaCl were not significant until around 10 mM. This was because there was no difference between the non-coated quartz resonator and the membrane-coated sensor device, and not because the frequency did not change. The frequencies of the 5 basic taste substances at the non-coated quartz resonator decreased identically to that of the sucrose in Fig. 2. The thresholds of the non-coated

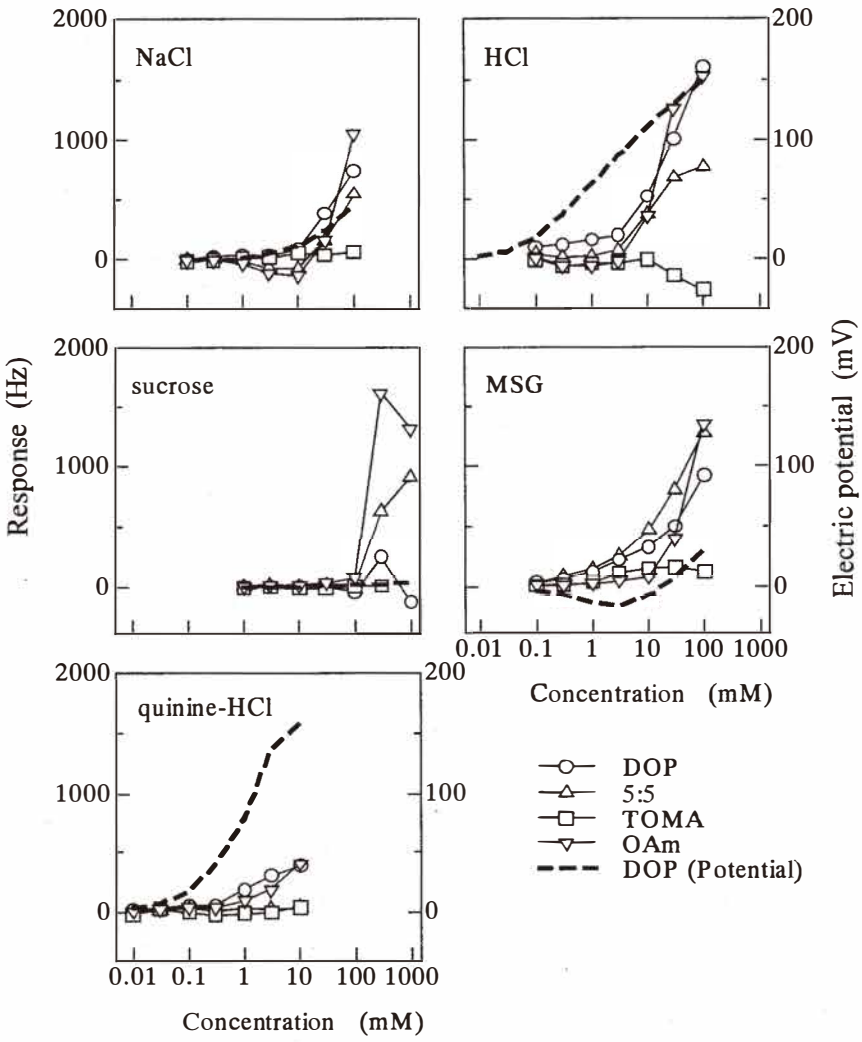

Fig. 3. The concentration dependence of the response frequency of four lipid/polymer membranes to five basic taste substances. Dotted lines are the electric potentials of the DOP membrane using a potentiometric taste sensor.[1]

quartz resonator were 0.1 mM (HCl), 0.3 mM (NaCl and quinine hydrochloride), 1 mM (MSG) and 30 mM (sucrose) (data not shown).

The thresholds of the lipid/polymer-membrane responses were 0.3 mM (MSG and quinine hydrochloride), 3 mM (NaCl and HCl) and 300 mM (sucrose) among the sensitive

membranes. This sequence was different from that of the non-coated quartz resonator. These thresholds, with the exception of MSG, were higher than those of the non-coated quartz resonator. This fact indicated that the effect of the coated membrane appeared at a higher concentration after the oscillation frequency decreased because of the added taste substance.

Regarding the different responses shown by the different lipid membranes, in the case of NaCl by way of example, the response of the DOP membrane simply increased, while the responses of the 5:5 membrane and the OAm membrane decreased once, then started increasing at the concentration of 10mM. The TOMA membrane had no significant response. This fact indicated that the responses of NaCl changed depending on the type of lipid/polymer membranes.

As for the specific lipid/polymer membrane, the response of the TOMA membrane to HCl decreased slightly when the concentration exceeded 30 mM, although it did not indicate any significant response to any of the basic taste substances. The OAm membrane showed responses to all of the taste substances. Especially at the maximum concentrations (NaCl 100 mM, HCl 100 mM, sucrose 1 M, MSG 100 mM, quinine hydrochloride 10 mM), the OAm membrane showed the largest response among the 4 membranes.

Figure 4 shows typical response patterns of the lipid/polymer membrane against the basic taste substances. The responses varied depending on the types of taste substance and their concentrations. Therefore, to see the difference in the patterns, the values were normalized to make the sum of the squares of the responses equal 1. The indicated patterns are the responses at 100 mM NaCl, 100 mM HCl, 300 mM sucrose, 100 mM MSG and 10

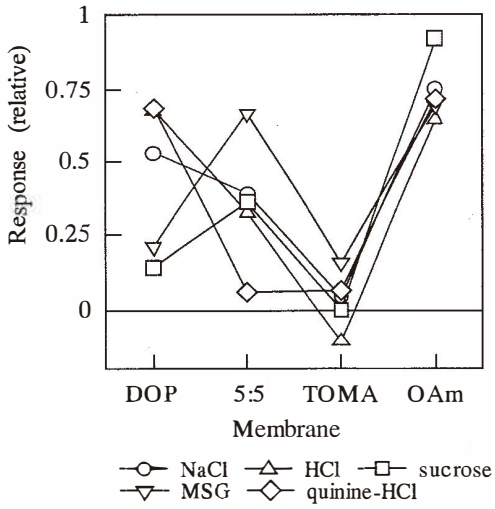

Fig. 4. Response patterns of four lipid/polymer membranes against five basic taste substances.

mM quinine hydrochloride; these are all in the high concentration range where maximum responses appeared.

From the results of the dependence on concentration of the taste substances (Fig. 3), the TOMA membrane responded slightly to each taste substance, but the OAm membrane responded significantly to each taste substance. The response patterns to basic taste substances were similar.

However, compared to the right half where the TOMA membrane and the OAm membrane were placed, the left half where the DOP membrane and the 5:5 membrane were placed responded differently depending on the taste substance. The DOP membrane showed small responses to sucrose and MSG, while the 5:5 membrane showed a large response to MSG. The response of the DOP membrane to quinine hydrochloride was very slight.

4. Discussion

In this paper, the oscillation frequency of a quartz resonator coated with each lipid/polymer membrane responded to the taste substances as shown in Fig. 3. There seem to be many factors that caused this frequency change during exposure to taste substances. When the quartz resonator is coated with the lipid/polymer membrane, the oscillation frequency depends on the density, the thickness and the elasticity of the membrane. It also depends on the density and the viscosity of the aqueous solution and on the driving circuit through the decreasing Q of the quartz resonator, when the quartz resonator is dipped into the solution.[13,14]

The interaction between the membrane and the taste substance is considered to affect the properties of the lipid/polymer membrane, because the membrane is pliable and has affinity for taste substances and water. The response, therefore, is considered to have occurred primarily because of several effects of the taste substance on the membrane properties including adsorption.

The quartz resonator with the lipid/polymer membrane responded to both hydrophobic and hydrophilic taste substances. The quartz resonator sensor showed different responses depending on the taste substance and the lipid in the sensitive membrane as shown in Fig. 4. In addition, the responses of the same lipid/polymer membrane compared to the quartz-resonator measurement and the potentiometric measurement had different characteristics as shown in Fig. 3. In other words, the lipid/polymer membrane, which is a mixture of PVC, lipid and plasticizer, has extensive ability to determine taste information using the quartz-resonator measurement.

The quartz-resonator measurement is fundamentally useful for the hydrophobic and nonelectrolytic taste substances compared to the potentiometric measurement. However, the sensitivity is not currently sufficient. The threshold of the DOP membrane to quinine hydrochloride, the hydrophobic substance, remains around 0.3 mM. This is, in contrast, 1 digit higher than the response of the membrane potential. (Fig. 3) Still, this result does not

mean that quinine hydrochloride is not adsorbed on the lipid/polymer membrane. Figure 5 shows the frequency change of the DOP membrane in pure water when measurements in the high-concentration taste solution and pure water were repeated. Zero indicates a return to the first oscillation frequency in pure water. Once the sensor was immersed in quinine hydrochloride, the frequency decreased irreversibly and remained low when the sensor was subsequently returned to the pure water. This behavior was caused by significant adsorption during which only quinine hydrochloride was not desorbed.

The required improvement in the sensitivity for hydrophobic and nonelectrolytic substances will become possible through the adjustment of the amount of PVC, the lipid and the plasticizer. To compare the quartz-resonator measurements with the potentiometric measurements, the sensitive membrane used in this study had the same composition as the potentiometric taste sensor. This composition is not necessarily optimum for the quartz resonator. It is also expected that there might be an optimum thickness based on the working depth of each taste substance, whereas the membrane potentials do not depend on the thickness.

In conclusion, the application of a lipid/polymer membrane to the quartz resonator for a taste sensor is possible because of the different responses depending on the taste substance and the lipid. The potentiometric and quartz-resonator measurements with lipid/polymer membranes are expected to make up for the structural defects of each. The selection of a lipid/polymer membrane suitable to the quartz resonator is a matter to be settled.

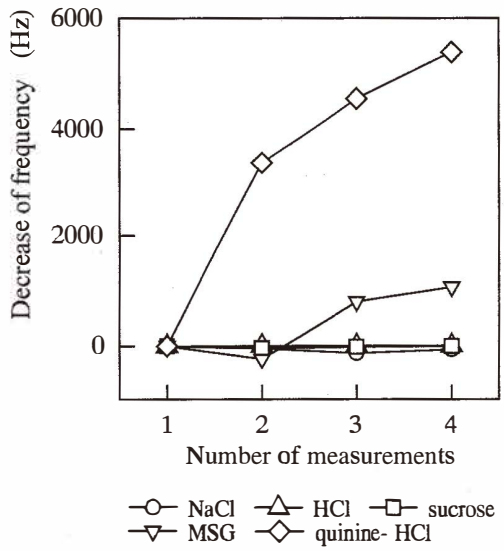

Fig. 5. Irreversible frequency change of the quartz resonator with a DOP membrane after repeated measurements in taste solution.

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