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The Characteristics of Quartz Crystal Microbalance Coated with Lipid Langmuir-Blodgett Films as an Olfactory Sensing System

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The characteristic patterns of adsorption-desorption of alcohols on lipids were investigated using quartz crystal microbalances (QCM) coated with different lipid Langmuir-Blodgett (LB) films. The lipid LB films were coated onto quartz crystal by transferring mixed monolayers of lipids and octadecylamin (ODA). The response curves of lipids to alcohols were obtained by blowing gas mixtures onto the QCM. The characteristic parameters were deduced from the retardation of adsorption and the frequency change. Based on the analysis of the response curves using a 6-channel sensor system, chemical identification was performed using a neural network pattern recognition system.

1. Introduction

Recently, olfactory sensors have been studied extensively and intensively by many researchers around the world. Human olfaction, the final sensor system that mankind desires to mimic, is very complex and the mechanism is not yet fully understood. Many kinds of hypothesis and sensor systems have been proposed.[1,2]

Lipids, major components of biological membranes[3] from bacteria level to human, are often used as sensing materials in artificial olfactory sensors. For this purpose, lipids are coated onto quartz resonator by various methods including the Langmuir-Blodgett (LB)

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technique.[4,5] The resonance frequency of quartz resonator decreases due to the mass-loading effect[6] as odorant molecules adsorb onto the sensing film. Applying such properties, quartz resonator has been used in many other fields related to mass sensitive devices.[7] In this study we used lipid LB films as a sensing membrane and quartz resonator as a transducer. The LB technique provides a unique layer structure of the artificial biological membrane when lipids are transferred by this method.

Although artificial odor sensing systems have been required in the fields of food, drink, cosmetics and environmental monitoring in the past, the difficulty in achieving good selectivity and sensitivity to many odorants has prevented such systems from being realized. Therefore, a practical method for odor sensing is to use multiple sensing membranes with different selectivities, analyze the output patterns and then identify the odor.[8,9]

In this paper, we examine some parameters from the response curve to characterize the sensing property of sensing membranes. Within those parameters, three different methanol-butanol mixtures of intermediate compositions were identified using a neural network pattern recognition system. The neural network system used in this study for identifying different alcohols was the 2-dimensional self-organizing feature maps neural network (SOFMNN).[10]

2. Materials and Methods

Dipalmitoylphosphatidylamine (DPPA), dipalmitoylphosphatidylcholime (DPPC), dipalmitoylphosphatidylethanolamine (DPPE), dipalmitoylphosphatidylserine (DPPS), sphingomyelin and cholesterol were used as the sensing materials. All the lipids which were of analytic grade were purchased from Sigma Co. and used without further purification.

A monolayer of lipids mixed with a surface active material, such as octadecylamine (ODA) (Aldrich Co.), was spread at an air-water interface. At a high subphase pH, the monolayer was transferred to form a multilayer of mixed LB film. The mixture of lipid and ODA was spread from chloroform/methanol (4/1, v/v) solution on an aqueous subphase containing 10^{-4}N NaOH. For DPPA which has an ionizable head group, the multilayer LB film could be transferred when the subphase contained divalent metal salt ($CaCl_2$ or $BaCl_2$) at pH 9. A constant-perimeter barrier langmuir film device was used as the film deposition device.

After being coated with LB films, the quartz crystal (AT-cut, 9 MHz) was connected to a modified normal-TTL oscillator circuit. The QCM was driven at 5 V dc, and the frequency signal output was measured by a frequency counter connected to a personal computer. In the gas generator, the sample gas was obtained by bubbling the liquid phase chemical (in this study, alcohols) with inert gas (N_2) and then mixing with excess N_2 gas in order to adjust the concentration of the ppm range. The target alcohols were methanol, ethanol, propanol and a methanol-butanol mixture. The sensor cell was designed to give a good contact with the inlet gas stream. The apparatus for the sensor experiments is illustrated in Fig. 1.

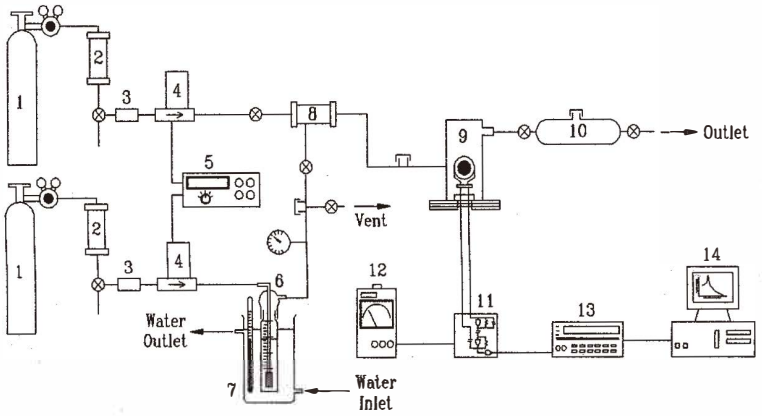

Fig. 1. Schematic diagram of sensor experimental apparatus.

3. Results and Discussion

3.1 *The characteristics of adsorption and desorption*

A typical adsorption-desorption response curve of odorant on the sensor, $f(t)$, is shown in Fig. 2. The interaction of adsorbate with the LB films can be characterized in terms of the equilibrium adsorption and the rate of adsorption. However, it is difficult to determine the amount of equilibrium adsorption in a short time and it is also impractical especially for sensor applications. Therefore, the frequency shift at 300 s (arbitrary time) was determined to distinguish between adsorption characteristics of the alcohols.

In general, the frequency shift at a certain time is considered as the sensitivity of a sensor. But, although the frequency shift of one chemical vapor for different sensing membranes is the same, the paths to the final frequency shift are very different. Therefore, the frequency change tendency which includes both the speed of response and the amount of adsorption must be considered when we discuss the sensitivity of a sensor.

We modeled the step response curve for the ideal case and we defined A_1 and A_2 as the relative vacancies for adsorption and desorption, respectively.

To characterize the response curve, the three parameters mentioned above were defined as follows.

$\Delta f(t_a)$; frequency change t_a s after the onset of response, defined as

$$\Delta f(t_a) = f(t_a) - f(0)$$

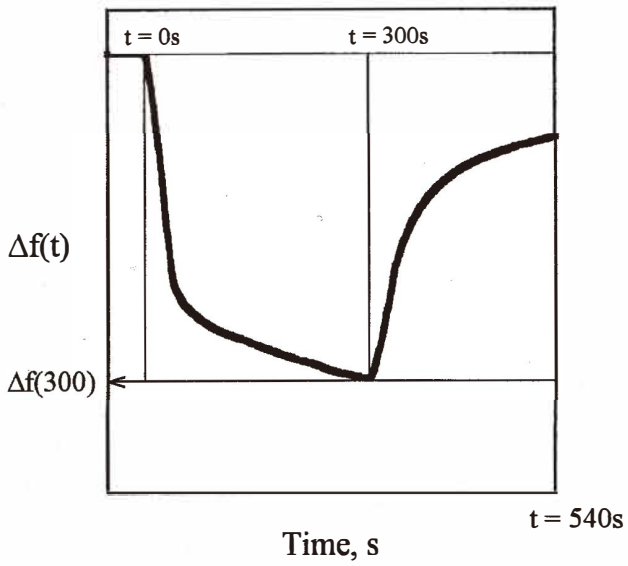

Fig. 2. Typical response curve of the sensor.

A_1 ; the fraction of adsorbed sites after t_a s, given by

$$-\int_0^{t_a} \Delta f(t)dt/[\Delta f(t_a) \times t_a]$$

A_2 ; the fraction of vacant sites t_b *s* after the onset of desorption, given by

$$-\int_{t_a}^{t_b} \Delta f(t)dt/[\Delta f(t_a) \times t_b]$$

In this study, t_a was 300 s and t_b was 240 s.

We can observe that A_1 is related to adsorption characteristics and A_2, desorption. The parameter $\Delta f(300)$ is related to the amount of adsorption. A_1 and A_2 can be affected by the affinity of chemical vapor to the sensing membrane and diffusion property of chemical vapor through the sensing membrane. The $\Delta f(300)$ must be large in order to clearly distinguish between odorants. Therefore, film materials which have large A_1, $\Delta f(300)$ and small A_2 are desirable for the sensor system. The parameters $\Delta f(300)$ and A_1 were selected for identification of the adsorbing materials because of the time limitation in application experiments.

The reproducibility and reversibility of the response to odorants of the sensing materials were repeatedly examined. When the exposure to odorants is terminated and the adsorbed odorants are blown with inert gas, the initial frequency should be recovered if the

films are reversible. Figure 3 shows an adsorption and desorption curve resulting from repeated measurement. In spite of the rapid adsorption, the recovery (desorption) was significantly delayed. When we checked the long term reproducibility of the membranes, the sensing membranes were durable and the sensor system reproduced almost the same signals for several months.

Figure 4 shows the three parameters for each lipid LB film upon exposure to the same odorant (methanol). Usually it is difficult to deposit a pure lipid multilayer and so the responses were tested using one layer of lipid LB film. In view of the optimum criteria of large $\Delta f(300)$ and A_1, and small A_2, the DPPE film was the best of the lipid films tested. The DPPC film showed fast adsorption and the DPPE film showed fast recovery.

Figure 5 shows the response characteristics of DPPA to three different alcohols of the same concentration. Methanol adsorbed more rapidly onto the lipid LB film, but the desorption rates for the three alcohols were almost the same.

As mentioned above, $\Delta f(300)$ should be large to improve the sensitivity. Therefore, it is important to find materials with large $\Delta f(300)$. However, it is a rather time-consuming process. Figure 6 shows the possibility of controlling $\Delta f(300)$ by changing the number of film layers. As the number of layers increases, $\Delta f(300)$ increases linearly. Therefore, it is possible to control the sensor output signal by controlling the number of layers in the film.

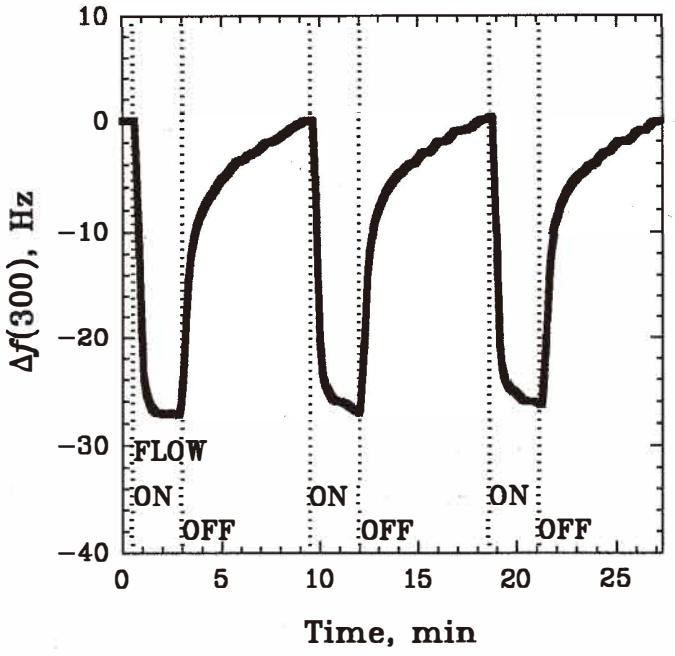

Fig. 3. Reproducibility of the frequency change pattern.

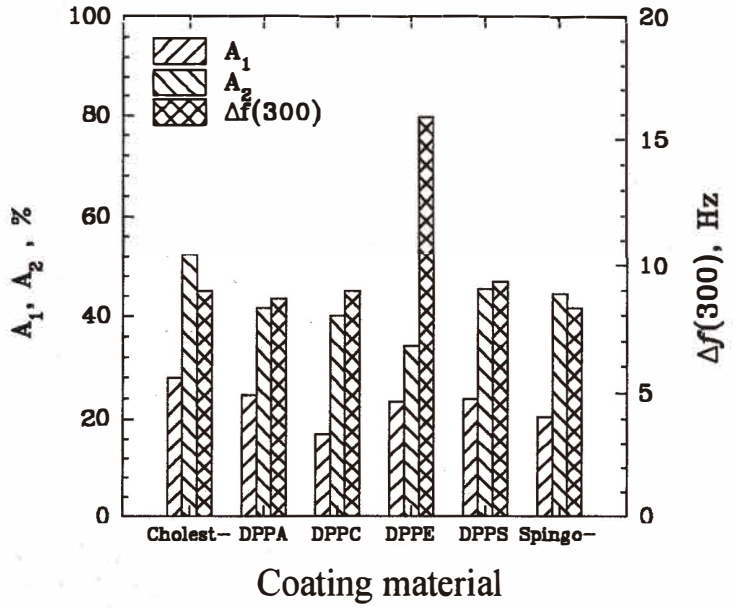

Fig. 4. Response characteristics of various lipid LB films to methanol (1.3×10^3 ppm).

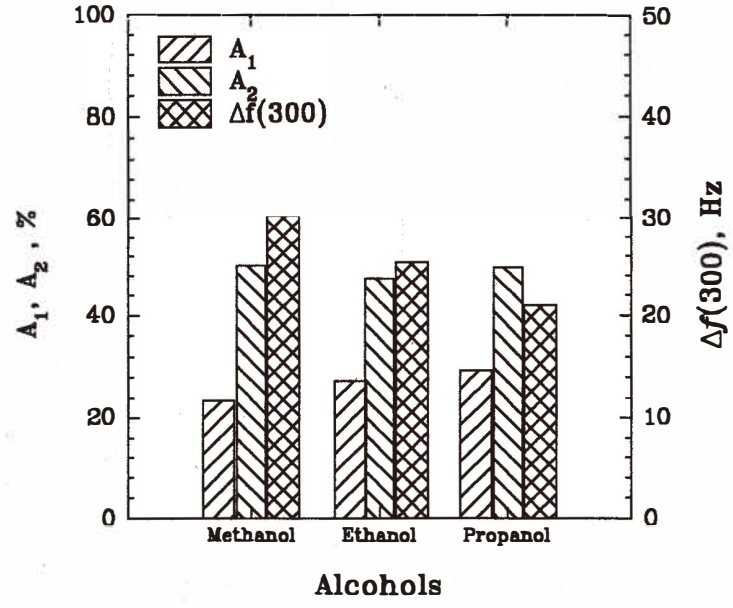

Fig. 5. Response characteristics to alcohols of 20 layers of DPPA LB film (conc.: 8.3×10^3 ppm).

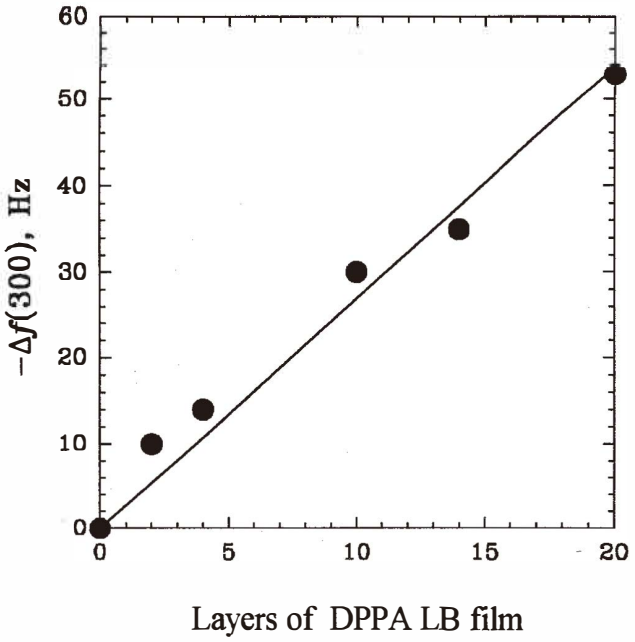

Fig. 6. The dependence of the signal output on the number of layers of LB film (conc.: 8.5×10^3 ppm).

3.2 *Pattern recognition*

We performed experiments with six different lipid LB films in order to obtain characteristic patterns for each odorant. The conditions for film deposition are listed in Table 1. The surface pressure when the films were deposited was 30 mN/m.

ODA was used as a film deposition promoter. As seen in Table 1, ODA enhanced the formation of a multilayer, but the signal from ODA-coated QCM was very weak, because the concentration of lipid in each channel was very low due to dilution by ODA. Multilayer films of pure lipid must be deposited to enhance the signal output.

Figure 7 shows different characteristic patterns for three alcohols from the six LB films. Each of the six lines corresponds to the signal intensity from the film specified on it. Thus, it was possible to construct an olfactory sensing system which could identify the alcohols tested using the pattern recognition mechanism.

From the measured values of $\Delta f(300)$, methanol was found to be most easily adsorbed on the lipid films, and films 2, 3 and 4 were better for distinguishing alcohols. In the case of A_1, the tendency is similar to that for $\Delta f(300)$ and films 5 and 6 provided good criteria for distinguishing alcohols.

To confirm the ability of the system to identify materials, A_1 and $\Delta f(300)$ for five different mixtures of methanol and butanol (mixed in solution) were input to the neural

Table 1
Coating membranes and deposition conditions.

Channel	Coating membrane	Salt, subphase pH	No. of depositions	Transfer ratio
1	ODA	None, 9.0	19	0.92
2	DPPS/ODA, 0.3/0.7	$BaCl_2$, 9.0	19	0.90
3	DPPA/DPPS/ODA 0.35/0.15/0.5	$BaCl_2$, 9.0	19	0.91
4	DPPE/ODA, 0.3/0.7	None, 9.0	19	0.64
5	DPPA/ODA, 0.3/0.7	$BaCl_2$, 9.0	19	0.94
6	Sphingomyelin/ODA, 0.2/0.8	$BaCl_2$, 9.0	19	0.84

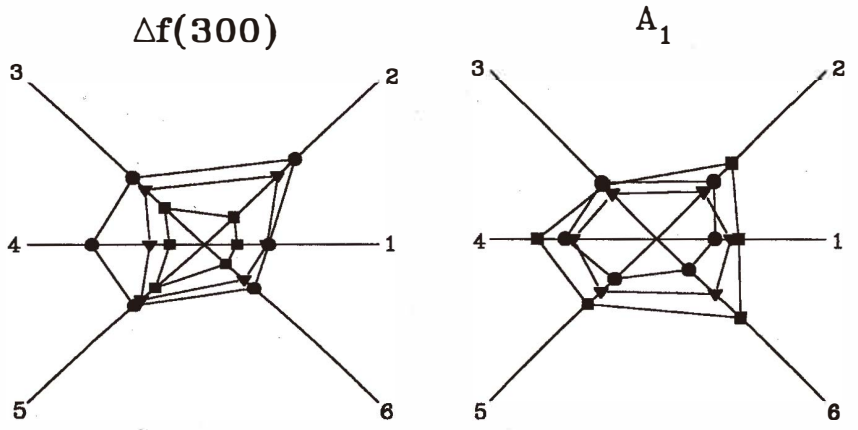

Fig. 7. The response patterns to three alcohols of the six different lipid LB films (●: Methanol, ▼: Ethanol, ■: Propanol).

network for training. The neural network system used in this study was a 2-dimensional self-organizing feature maps neural network (SOFMNN) with 400 (20 × 20) output nodes. A detailed description of the neural network evaluation has been reported in another paper.[11]

After 3000 training cycles with experimental data for 5 different compositions of binary mixtures, three different methanol-butanol mixtures of intermediate compositions were tested. The identification results are shown in Table 2. From this, we can say that A_1, as well as $\Delta f(300)$, can be used as an input to the neural network to identify materials. In this particular case, $\Delta f(300)$ was slightly better in distinguishing methanol-butanol mixtures.

Table 2
Identification results for the methanol/butanol mixture.

Sample (methanol/butanol, volume ratio)	Identification	
	$\Delta f(300)$	A_1
10/90	10/90	7/93
25/75	28/72	17/82
50/50	42.3/57.7	48/52

4. Conclusions

Three parameters $\Delta f(300)$, A_1 and A_2 of output response curves were used to represent adsorption-desorption characteristics of alcohols for various lipid LB films coated on QCM. A six-channel sensor system with six different kinds of LB films was used. Each channel gave different values of the three parameters for different alcohols or mixtures making it possible to identify them by analyzing sensor signal patterns.

In application, specific response patterns of $\Delta f(300)$ and A_1 were analyzed for the identifcation of three binary alcohol mixtures. A_1 gave identification results comparable to those given by $\Delta f(300)$.

Acknowledgments

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References

1 J. W. Gardner and P. N. Bartlett: Sensors and Actuators B **18–19** (1994) 211.
2 T. Nomura and K. Kurihara: Biochemistry **26** (1987) 6135.
3 W. M. Reicher, C. J. Bruckner and J. Joseh: Thin Solid Films **152** (1987) 345.
4 S.-M. Chang, E. Tamiya, I. Karube, M. Sato and Y. Masuda: Sensors and Actuators B **5** (1991) 53.
5 S.-R. Kim, S.-A. Choi, J.-D. Kim, K. H. Choi, S. K. Park and Y. H. Chang: Synthetic Metals **71** (1995) 2293.
6 W. H. King: Anal. Chem. **36** (1964) 1735.
7 J. F. Alder and J. J. McCallum: Analyst **108** (1983) 1169.
8 J. R. Stetter, P. C. Jurs and S. L. Rose: Anal. Chem. **58** (1986) 860.
9 K. Ema, M. Yokoyama, T. Nakamoto and T. Moriizumi: Sensors and Actuators **18** (1989) 291.
10 T. Kohonen: Self-Organization and Associative Memory (Springer-Verlag Press, New York, 1989).
11 M. S. Park, J. H. Chang, Y. K. Chang and B. H. Chung: Biotechnol. Tech. **8** (1994) 779.