Comparisons between Calixarene Langmuir-Blodgett and Cast Films in Odor Sensing Systems

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Calixarene (calix[6]arene) was deposited on a quartz crystal microbalance (QCM) by Langmuir-Blodgett (LB) and cast methods. The steady state and transient sensor responses to different organic vapors were measured and compared. The gas vapors measured were aromatic compounds having different side chains, such as benzene, toluene, ethylbenzene, xylene and propylbenzene. The results showed that cast films were more sensitive than LB films. However, the difference in time constants among gas samples for LB films is larger than that for cast films. The pH of the subphase during the deposition of the film, in the case of LB films, has an important influence on the time constant of the transient response because of the complexation of calixarenes with alkali ions, which modify the packing density of the films. Furthermore, the differences among the time constants for different samples increased with the amount of ions in the subphase during the deposition, enhancing the sensors' ability to classify or separate odor/gas samples.

1. Introduction

An odor sensing system is expected to contribute to quality control, to the inspection of food, beverages, cosmetics and other products, and to environmental testing. We have studied an odor sensing system using a quartz crystal microbalance (QCM) gas sensor array and neural-network pattern recognition.[1] Although the QCM gas sensor with a resonant frequency shift due to the mass loading effect was useful as a component in the odor sensing system, the dependence of the properties of the sensing film on its structure has not been studied thus far. There are several methods for enhancing the sensitivity and

selectivity of the sensor, e.g., the use of mixed sensing films[2] or a special kind of molecule, such as a calixarene with a peculiar molecular shape and large size. These characteristics can be used to obtain porous films suitable for application in gas sensors.

Many studies have been carried out on calixarenes films. Lamartine *et al.*[3] studied the complexation of calixarenes with toluene, benzene and chloroform. Furthermore, the complexation of calixarenes with alkali ions has been studied by Dei *et al.*[4] and by Ishikawa *et al.*[5] However, the structure and mechanism of adsorption of calixarene Langmuir-Blodgett (LB) sensing films are still not well understood. The analysis of transient sensor response gives us important information on the adsorption mechanisms based on the film structure.[6] In this work, the effects of the complexation of alkali ions with calixarenes on the transient responses of QCM sensors coated with LB films were studied. The results were compared with those obtained from sensors coated with cast films to determine the relationship between the structure of the sensing film and the characteristics of the sensor.

2.   Experimental

The solutions for deposition were prepared by dissolving calixarene powder (hexa-tert-butyl-hexa-hydroxy-calix[6]arene, Fig. 1) purchased from Tokyo Kasei Co., Ltd. into chloroform at a concentration of 0.5 mM for LB films and 0.1 mM for cast films. A 20 MHz AT-Cut QCM with gold electrodes was used for LB films, and silver electrodes were used for cast films.

The LB films (Y type, 10 strokes, 20 monolayers) were deposited at a speed of 5 mm/ min in the same manner as in previous work.[2,6] Two kinds of subphase, pure water (deionized water at pH = 6.5) and water with alkali ions (Na^+, Ca^{2+}) were used. The cast films were obtained by depositing a drop of a calixarene solution and allowing the solvent to evaporate.

Measurements of the sensor responses were performed at a temperature of 20°C in the system shown in Fig. 2.[6] It is a flow-type measurement system where a step change in the vapor concentration is generated. A diffusion method is used to obtain the specified
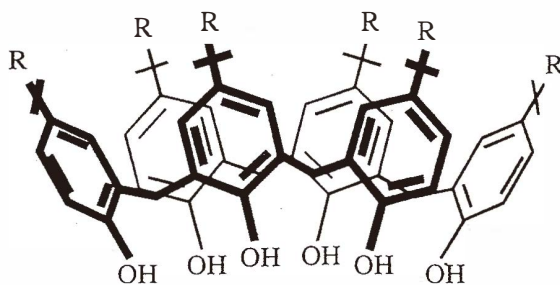

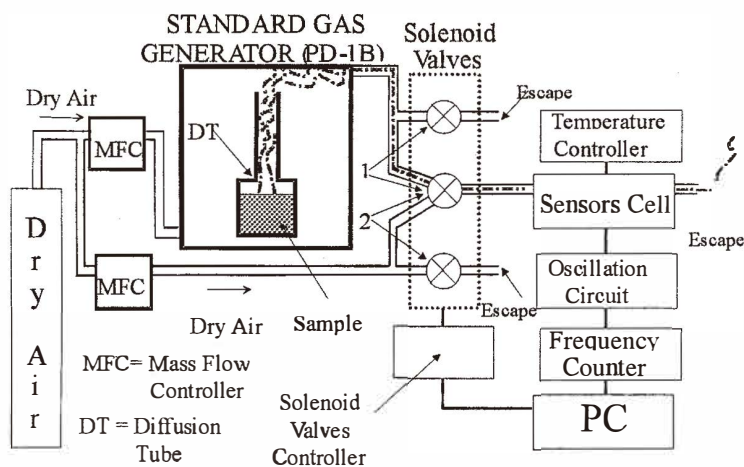Fig. 1.   Molecular structure of calixarene. R= tert-butyl

Fig. 2.   Sensor response measurement system.

concentration. The steady state response was obtained after the equilibrium was achieved, and the time constant was calculated using the whole waveform for 4 min in the rise region. The model used to analyze the transient response was the sum of two exponential decays with different time constants, as has been described in previous report.[6]   The parameters of the models were calculated using curve fitting so that the error between the values obtained from the model and the actual data could be minimized.

3.   Results and Discussion

3.1 *Sensors with LB sensing films*
3.1.1 *Pressure area isotherms*
Calix[6]arene does not form a stable monolayer at the water-air interface when pure water is used as a subphase. The stability of the monolayer depends strongly on the pH of the subphase. One of the characteristics of calixarenes is that they form complexes with ions in the subphase by interaction with their phenolic groups, which lie on the water surface after spreading. That characteristic is reflected in the pressure-area isotherms. The pressure-area isotherms for calixarene on subphases with different pH values are shown in Fig. 3. As can be observed from the figure, the solid-like region becomes clearer and the monolayer collapse pressure becomes higher as the pH increases. The formation of the calixarene-alkali ion complex enhances the stability of the calixarene molecules at the water-air interface. Furthermore, the generation of repulsive forces at the bottom of the molecules prevents them from losing parallel orientation. Therefore, the rigidity of the film increases. The same behavior is observed if the pH of the subphase is adjusted with NaOH or $Ca(OH)_2$.
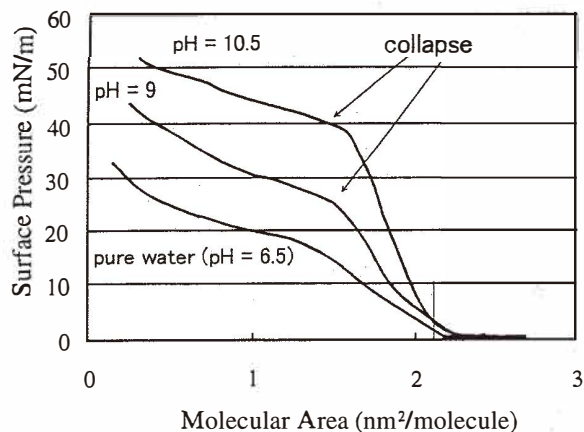
Fig. 3.   Pressure isotherms of calixarene for different pH values of the subphase.

3.1.2 *Deposition of the sensing LB films*

To investigate the effects of the subphase pH change on the deposition of LB films, 20 monolayers were deposited on QCMs at different surface pressures (10–40 mN/m). The effect of the increase in the subphase pH is shown in Fig. 4. The increment in the amount of the mass deposited at a high pH of the subphase indicates the increment in the deposition ratio. This result is created by the enhancement of the stability and rigidity of the monolayer as the subphase pH increases, as observed from the pressure area isotherms. The increment in deposited mass is not only due to the molecular weight of calixarene (973.39) but is also due to the addition of sodium or calcium ions since the atomic mass of sodium and calcium is 22.98 and 40.08, respectively. If we take the calixarene-alkali complex as 1:1,[4] the mass of the alkali ion for the case of calcium (the heavier ion of the two) is about 5% of the weight of the calixarene. That value is less than the experimental error in the mass deposition measurements. The calculated deposition ratio, using the molecular areas as obtained from the pressure isotherms, was 1.2 on average for pH = 10.5. In the other cases (pH= 6.5 and 9) where the film was not stable, the average deposition ratios were 0.12 and 0.6, respectively.

3.1.3 *Steady state response*

The sensor responses of the deposited films to benzene, toluene, ethylbenzene, xylene and propylbenzene were measured. These molecules are based on benzene with different side chains, listed in ascending order of size, and they have a high response for calixarene films. In Fig. 5, the steady state sensor responses as a function of the subphase pH for LB films deposited at 30 mN/m are shown. This value of deposition pressure was selected because of the large amount of calixarene deposition (see Fig. 4). The sensor response is
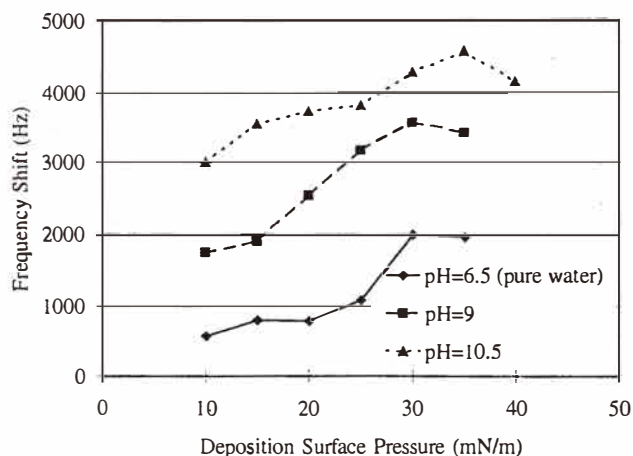
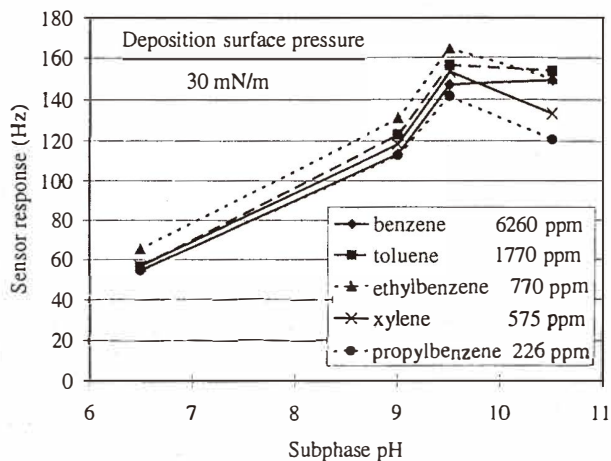Fig. 4. Deposition of calixarene at different values of subphase pH.

Fig. 5. Steady state sensor response as a function of the subphase pH for a film deposited at 30 mN/m.

enhanced as the pH increases because of the increment of the deposition ratio. However, at high pH (10.5), even though there was an increment of the deposition ratio (as can be observed from Fig. 4), the response decreased because of a higher packing density that does not permit the total diffusion of the odor/gas molecules inside the rigid film. A maximum in the steady-state response was obtained when the subphase pH was 9.5.

3.1.4 *Analysis of the transient sensor response*

To study the difference in transient responses and their relation to the film structure, the transient responses of all the sensors constructed were analyzed. Although the transient sensor response to a step change in the concentration can be expressed as the sum of two exponential decays, a smaller time constant was used since it was measured with negligible fluctuation, as was discussed in a previous report.[6] The time constant is a measure of the diffusion time of the odor/gas molecules inside the film.

The time constants as a function of the subphase pH for LB films deposited at 30 mN/m are shown in Fig. 6. For low pH values (6.5–9), the monolayers at the water-air interface were collapsed at the surface pressure values shown in Fig. 3. Therefore, under such conditions, the parallel orientation of the calixarene molecules is completely lost in the case of pure water and partially lost at pH = 9. The low deposition ratio and packing density of the film indicates its porous structure. This enables odor/gas molecules to penetrate into the film very quickly, independent of their sizes and side chains. However, as the pH value increased, the differences among the time constants for the different samples increased due to the increment in the deposition ratio and the rigidity of the film, whose structure may become more crystal-like. As can be observed in Figs. 5 and 6, at pH = 10.5, in spite of the decrement in the steady state sensor response, there is an increment in the difference among the time constants for the different samples.

In Fig. 7, the time constants of the calixarene LB films deposited at different surface pressures at high pH (10.5) are shown; the results are the same for both NaOH and Ca(OH)$_2$. All the plots are the average of three measurements. We focused on the case of pH = 10.5 since the variance in the time constants among the samples was largest at that value. It can be seen from Fig. 7 that for low deposition pressures (15–20 mN/m), the time constants are small as are the differences among them. They increase and saturate when
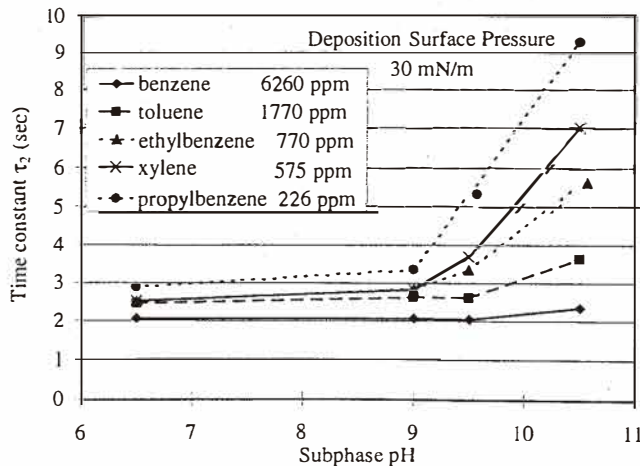

Fig. 6. Time constants for the LB film sensors in the rising region as a function of the pH of the subphase.
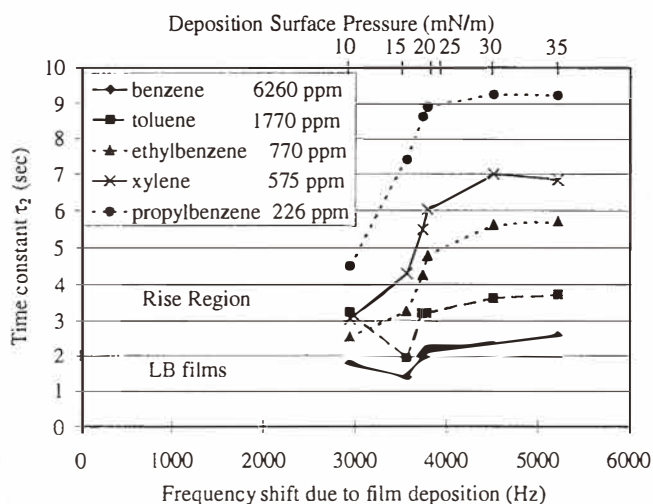
Fig. 7.   Time constants for the LB films as a function of deposited mass; in the rising region, at the top of the figure, are marked the corresponding deposition surface pressure values.

the deposition pressure is increased. The saturation was due to an insignificant change in the molecular area between 20 and 35 mN/m (see Fig. 3). This indicated that the packing density was unchanged at those pressures. The different samples were well separated according to the molecular sizes independent of the surface deposition pressure in that range. Therefore, a high value of the subphase pH and a deposition between 20 and 35 mN/m give the best conditions for depositing calixarene films for their use as odor/gas sensors.

3.2   *Sensors with cast sensing films in comparison to those with LB films*
3.2.1   *Steady state response*

The influence of the film structure can be investigated by comparing the characteristics of sensors with different film structures to those of LB films. The most typical among the different film structures is that from a casting film. The comparison of the steady state responses as a function of the amount of calixarene mass deposited is shown in Fig. 8. In this figure, the responses of LB films used were the same as the LB films deposited in the solid-like region (Fig. 3), i.e., before the collapse of the calixarene monolayer. The samples measured were benzene, toluene, ethylbenzene, xylene and propylbenzene. The steady state responses of cast films were about two times larger than the corresponding values of LB films. Cast films have a more porous structure due to the random arrangement of calixarene molecules. The well ordered structure and the high packing density of the LB film prevents vapor penetration into the film, whereas penetration into the cast films is easy due to their porous structure and low packing density. Such characteristics appeared in the steady state response.
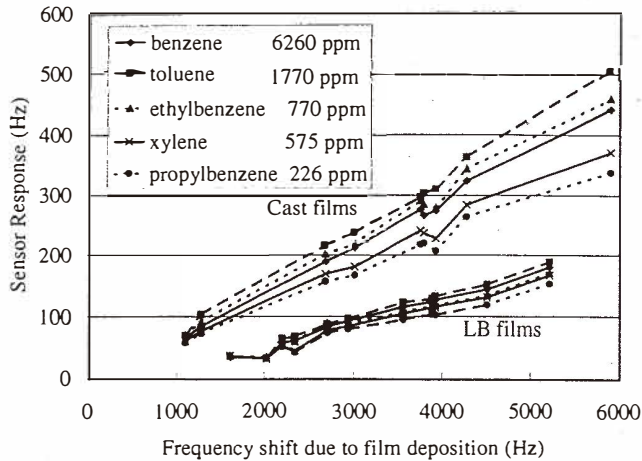
Fig. 8. Comparison between the sensor responses of calixarene LB and cast sensing films.
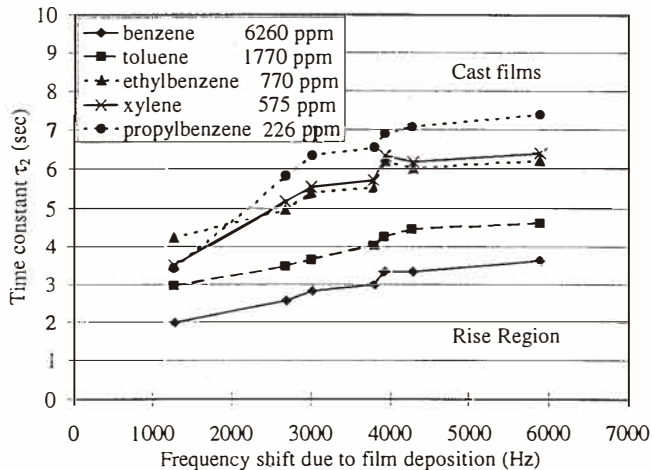

Fig. 9. Time constants for the cast films as a function of the deposited mass (rising region).

3.2.2 *Analysis of the transient response*

In Fig. 9 the time constants of sensor responses are shown after analysis of the transient responses of the cast films to the samples as a function of the amount of deposited mass. The cast films did not show well-separated time constants for three of the samples: ethylbenzene, xylene and propylbenzene, although LB films did. Therefore, this is more evidence of the porous structure of cast films compared with LB films. In

addition, LB film structure is crystal-like with well-ordered molecules and can be controlled by adjusting the deposition pressure, while cast film structure is amorphous and is difficult to control.

4.   Conclusions

The responses of sensors based on calixarene LB and cast films were studied. From the results obtained in the case at high pH it can be said that the use of complexation of calixarenes with alkali ions improves the stability of the monolayers at the water-air interface. This also prevents the early collapse of the monolayers, enhancing their rigidity and packing density, and permits stable deposition on the substrate. The effect of preventing monolayer collapse during deposition is an improvement in the monolayer quality, which offers an increase in the deposition ratio between 20 and 35mN/m of surface pressure. The effect of pH and deposition optimization on the transient response is an increase in the difference in time constants among the different samples, improving the separation and recognition properties of the sensors. The separation of the time constants was large for the LB films compared with cast films. The comparison of the sensor properties between LB and cast films gives us another basis for a better under-standing of film structure.

The sensor responses of LB films are lower than usual and that is why it is necessary to use higher concentrations than usual. However, the advantage of LB film is that the structure of the sensing film can be controlled. Furthermore, it is expected that the fundamental frequency of an LB film sensor can easily be raised to increase sensitivity since the influence of viscoelastic damping might be small because of the thinness of the film.

References

1 T. Nakamoto and T Moriizumi: Artificial Olfactory System Using Neural Network, Intelligent Sensors, ed. H. Yamasaki (Elsevier Science, 1996) p. 263.
2 S. Muñoz, A. Saitoh and T. Moriizumi: Odor Sensor Based on Mixed LB Films and Quartz Crystal Microbalance, T. IEE Jpn. 119-E (1999) p. 346.
3 R. Lamartine, R. Perrin, M. Perrin, S. Lecocq and C. Duchamp: Solid State Chemistry of Calixarenes and Supramolecular Systems with Calixarenes, Mol. Cryst. Liq. Cryst. **248** (1994) p. 61.
4 L. Dei, A. Casnati, P. Lo Nostro and P. Baglioni: Selective Complexation by P-Tert-Butylcalix[6]arene in Monolayers at the Water-Air Interface, Langmuir **11** (1995) 1268.
5 Y. Ishikawa, T. Kunitake, T. Matsuda, T. Otsuka and S. Shinkai: Formation of Calixarene Monolayers which Selectively Respond to Metal Ions, J. Chem. Soc., Chem. Commun. (1989) p. 736.
6 S. Muñoz, T. Nakamoto and T. Moriizumi: Study of Transient Response of QCM Odor/Gas Sensors Coated with Calixarene LB Films, T. IEE Jpn. 119-E (1999) p. 430.