

Electrical Characteristics of Lipid/PVC/DOPP Membrane and PVC/DOPP Membrane Used as Transducers in Chemical Sensors

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Electrical response characteristics of two kinds of membrane were studied; one membrane is composed of polyvinyl chloride (PVC) with dioctyl phenylphosphonate (DOPP) as a plasticizer, and the other is a membrane used as the transducer part of a multichannel taste sensor, which contains PVC, DOPP and a negatively charged lipid. These two membranes exhibited unusual behavior, namely, that the membrane electric potentials did not become saturated with increasing NaCl concentration. The electric potential tends to saturate in conventional polymer membranes. The PVC/DOPP membrane was found to respond to NaCl more sensitively than the lipid/PVC/DOPP membrane. Good quantitative agreement with the observed data was obtained using a theory in which the surface electric potential and the diffusion potential within the membrane are both taken into account. It was shown that the lipid/PVC/DOPP membrane changes from the weakly charged state to the fully charged state by dissociation of H^+ from the lipid with increasing NaCl concentration.

1. Introduction

A recently developed multichannel taste sensor utilizes artificial polymer lipid membranes to transduce taste characteristics to electric signals.⁽¹⁻³⁾ This sensor can be used to detect tastes in a manner similar to human gustatory sensation so that similar patterns are

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obtained for similar taste qualities. Therefore, it can detect differences in the tastes of various foods, such as beer,⁽⁴⁾ mineral water⁽⁵⁾ and sake.⁽⁶⁾ The sensitivity, reproducibility and durability are superior to those of humans.

The membrane of the taste sensor was prepared by mixing a lipid with polyvinyl chloride (PVC) and dioctyl phenylphosphonate (DOPP) in tetrahydrofuran (THF). DOPP, which is used as a plasticizer, is a popular material often incorporated in PVC membranes used as ion-selective electrodes.^(7,8) This kind of lipid/polymer membrane is so stable that it can be used as the receptor membrane in sensor devices used to detect chemical or taste substances. Lipid/polymer membranes have different electrical characteristics depending on the kind of lipid added to the membrane. Thus, the taste of foodstuffs can be discriminated and quantified using the output pattern composed of electric signals from several kinds of lipid/polymer membranes in the multichannel taste sensor, which responds to five kinds of taste qualities (i.e., sour, sweet, bitter, salty and *umami*) in different ways. A lipid/PVC/DOPP membrane containing a negatively charged lipid responds sensitively to cations.⁽¹⁻³⁾ In most conventional polymer membranes such as collodion membranes⁽⁹⁾ and lipid-adsorbed membrane filters,⁽¹⁰⁾ the electric potential tends to saturate at high NaCl concentrations, which is known as a simple screening effect.^(11,12) However, the electric potential of lipid/PVC/DOPP membranes does not become saturated, but the rate of change of the electric potential increases at high NaCl concentrations.^(1,2) The origin of the difference in electrical characteristics between lipid/PVC/DOPP membranes and conventional polymer membranes has not yet been clarified. Furthermore, it is known that membranes composed of PVC (and DOPP) show cationic permeability.⁽¹³⁻¹⁵⁾ In order to fabricate chemical or taste sensors, it is very important to clarify the electrical characteristics of these membranes.

We report a study of the electrical characteristics of lipid/PVC/DOPP membranes and PVC/DOPP membranes, and aim to explain the generation mechanism of the electric potentials in these membranes. It was found that addition of a negatively charged lipid to PVC and DOPP during membrane preparation decreases the change in the membrane electric potential with NaCl concentration; i.e., the PVC/DOPP membrane without lipid responds more sensitively to NaCl than the lipid/PVC/DOPP membrane. It may be natural to assume that membranes containing negatively charged lipids would respond more sensitively to cations than membranes without lipid, but the reverse was found to be true.

A theory was presented to explain quantitatively the observed experimental data. As a result, the generation mechanism of the electric potential of the PVC/DOPP membrane was shown to be different from that of the lipid/PVC/DOPP membrane. The surface electric potential is the main contributor to the response potential of the lipid/PVC/DOPP membrane, whereas both the surface potential and the diffusion potential within the membrane contribute to that of the PVC/DOPP membrane. It was also pointed out that the characteristic upward response of the lipid/PVC/DOPP membrane to NaCl is not caused by the usual screening effect but by an increase in the dissociation of protons from the membrane with increasing NaCl concentration.

2. Experimental Methods

We used dioctyl phosphate ($(C_8H_{17})_2POOH$) as the lipid in the artificial lipid membrane. In aqueous solution at neutral pH, $(C_8H_{17})_2POOH$ is negatively charged due to dissociation of the phosphoric acid group. $(C_8H_{17})_2POOH$ was mixed with 800 mg of polyvinyl chloride (PVC) as the polymer and 1.0 ml of dioctyl phenylphosphonate (DOPP) as a plasticizer in 18 ml of tetrahydrofuran (THF). Commercial DOPP usually contains a small amount of impurity, e.g., phenylphosphonic acid mono-octyl ester which is negatively charged as one candidate, although pure DOPP is uncharged. The mixture was dried on a glass plate 8.5 cm in diameter, which was placed on a hot plate at a temperature of about 30°C. The lipid/PVC/DOPP membrane thus prepared was a transparent, colorless, soft film about 200 μm thick. The PVC/DOPP membrane with no lipid was prepared in the same way.

The multichannel electrode was similar to that reported previously.⁽¹⁻³⁾ The main body consisted of an acrylic board with a conical hole. The hole was filled with 100 mM KCl solution, and the lipid/PVC/DOPP membrane or the PVC/DOPP membrane was fitted on the board to cover the hole. The external aqueous solution was 1 mM KCl, to which a small amount of taste substance solution was added to adjust the taste substance concentration. The electric potential across the membrane was detected using an Ag/AgCl electrode in the 100 mM KCl solution and a reference electrode (Ag/AgCl with saturated KCl) in the taste substance solution. The electric signal from the membrane was converted to a digital code using a digital voltmeter and was recorded in a computer.

Using this measuring system, we studied the electric potential responses of the lipid/PVC/DOPP membrane and the PVC/DOPP membrane to NaCl. The measurements were carried out at room temperature.

3. Theory

In charged membrane systems, the membrane potential usually consists of the surface potential formed in the aqueous phase touching the membrane and the diffusion potential within the membrane, as shown in Fig. 1. In this theoretical model, therefore, the membrane potential is obtained from the surface potential and the diffusion potential, which are calculated individually.

First, we describe the change in the surface potential with the concentration of NaCl. The change in the surface charge density due to the hydrophilic group of the lipid in the membrane which is in contact with the aqueous phase must also be taken into account. Therefore, the theory treats the situation in which the surface electric potential is changed by H^+ dissociation from lipid molecules, which causes a change in the electric charge density, as performed in some colloidal systems.⁽²⁾

The change in Gibbs free energy per lipid molecule in the above charging process in a system consisting of a lipid and an aqueous phase is given by^(11,16)

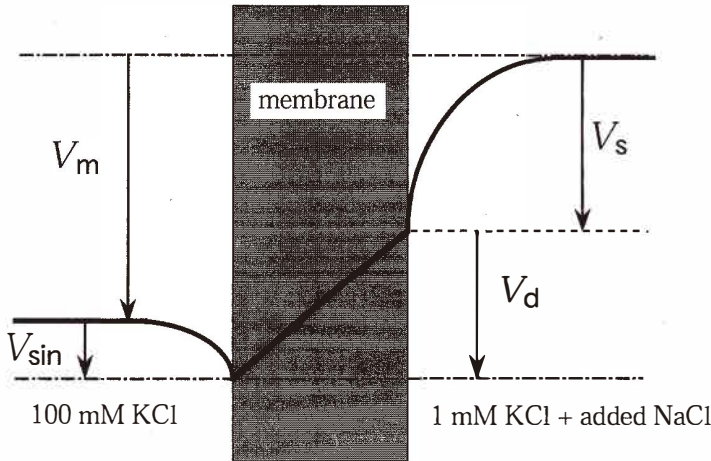


Fig. 1. The membrane electric potential in a charged membrane system. The left and right sides are the inner and outer phases, respectively. NaCl was added to the outer phase, from which the membrane potential was measured as the origin.

$$dG = k_B T \ln \frac{K}{[H^+]} \frac{\theta}{1 - \theta} d\theta, \quad (1)$$

where θ is the degree of H^+ binding to the hydrophilic groups of lipid molecules, K is the dissociation constant, $[H^+]$ is the proton concentration in the bulk solution, k_B is Boltzmann's constant and T is the absolute temperature. We obtain an expression for the free energy in the membrane system as

$$G = \int_0^\theta k_B T \ln \frac{K}{[H^+]} \frac{\theta}{1 - \theta} d\theta + A \int_0^\sigma V_s d\sigma, \quad (2)$$

where σ is the surface charge density, A is the occupied molecular surface area and V_s is the surface electric potential of the membrane. For simplicity, we assume that the membrane surface is a plane surface with uniform charge density σ .

The charge density σ at the membrane surface is determined using the Gouy-Chapman theory for an electrical double layer; i.e., the ion distribution near the membrane surface and the surface charge density are calculated by solving the Poisson-Boltzmann equation.^(11,16) For a 1:1 electrolyte the Gouy-Chapman theory leads to the expression

$$\sigma = \kappa' \sinh\left(\frac{eV_s}{2k_B T}\right); \quad (3)$$

$$\kappa' = \frac{\varepsilon}{2\pi} \frac{k_B T}{e} \kappa, \quad \kappa = \sqrt{\frac{8\pi C e^2}{\varepsilon k_B T}}. \quad (4)$$

Here ε is the dielectric constant, e is the elementary charge and C denotes the ion concentration in the bulk solution. The parameter, κ , is a characteristic value expressing the degree of spread of the diffuse electrical double layer, and hence $1/\kappa$ can be regarded as the thickness of the diffuse double layer.

Using the degree of H^+ binding θ , the surface charge density σ can be expressed as

$$\sigma = -\frac{e}{A}(1 - \theta). \quad (5)$$

If we eliminate σ from eqs. (3) and (5), we obtain

$$\kappa' \sinh\left(\frac{eV_s}{2k_B T}\right) = -\frac{e}{A}(1 - \theta). \quad (6)$$

Minimizing eq. (2) with respect to θ by taking account of eq. (5), we obtain

$$\frac{\theta}{1 - \theta} = \frac{[H^+]}{K} \exp\left(-\frac{eV_s}{k_B T}\right). \quad (7)$$

In eqs. (6) and (7), the two variables θ and V_s are unknown. Therefore, the surface potential V_s of the membrane can be calculated as a function of the ion concentration C in a similar way to that in a previous paper on polymer membranes of two lipid species.⁽¹⁷⁾

The diffusion potential within the membrane V_d is calculated as^(18,19)

$$V_d = \frac{k_B T}{e} U \ln \frac{XU + \sqrt{4C^2 + X^2}}{XU + \sqrt{4C_{in}^2 + X^2}}, \quad (8)$$

where X is the effective charge density, C_{in} is the ion concentration in another solution across the membrane, and U is the ion mobility ratio within the membrane.

$$U = \frac{u_+ - u_-}{u_+ + u_-}, \quad (9)$$

where u_+ and u_- denote the mobilities of cations and anions, respectively, within the membrane. The diffusion potential V_d is expressed as a function of the ion concentration in the bulk solution C with numerical parameters, U and X .

The membrane potential defined in Fig. 1 is given by

$$V_m = V_s + V_d - V_{\text{sin}}, \quad (10)$$

where V_{sin} is the surface electric potential formed in the aqueous phase of the opposite side across the membrane.

4. Results and Discussion

Figure 2 shows the electric potential responses of the lipid/PVC/DOPP membrane and PVC/DOPP membrane to NaCl. The electric potential was measured relative to the standard potential, which was that in 1 mM KCl solution without taste substance. The

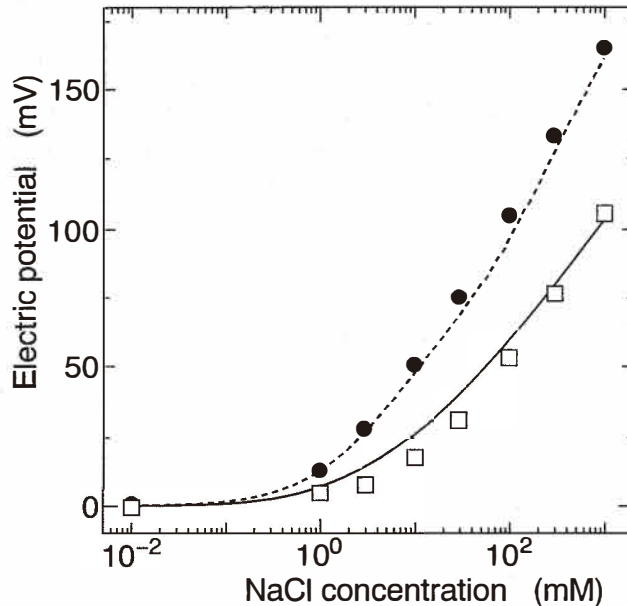


Fig. 2. Responses of the lipid/PVC/DOPP membrane (□) and the PVC/DOPP membrane (●) to NaCl. The solid and dashed lines represent the theoretical values for the lipid/PVC/DOPP membrane and the PVC/DOPP membrane, respectively. The observed absolute values of the membrane potentials without added NaCl were about -50 mV and -110 mV for the lipid/PVC/DOPP and PVC/DOPP membranes, respectively.

responses of the lipid/PVC/DOPP and PVC/DOPP membranes were positive for NaCl. Both membranes were negatively charged and responded to cations in agreement with the results of previous reports.^(1,14) The electric potential tends to saturate at high NaCl concentrations in most conventional polymer membranes;^(9,10) however, the rate of change of the potential response of the lipid/PVC/DOPP membrane increased with increasing NaCl concentration. Responses to other taste substances such as quinine and HCl are already reported elsewhere;^(1,17,20) hence, we focus here on the NaCl response. The PVC/DOPP membrane also responded sensitively to cations. The only difference between the two membranes is that one contains a negatively charged lipid.

The solid and dashed lines in Fig. 2 represent theoretical results calculated using the above theoretical model for lipid/PVC/DOPP and PVC/DOPP membranes, respectively. The theoretical electric potential is that relative to a standard potential, which is calculated at pH = 5.8, $T = 300$, $C = 1$ mM for 1 mM KCl solution and $C_m = 100$ mM for 100 mM KCl. The parameter values were chosen within reasonable ranges so as to obtain the best fit with the experimental results: $K = 10^{-4}$ M, $A = 120 \text{ \AA}^2$, $U = 0.1$ and $X = 50$ mM for the lipid/PVC/DOPP membrane, and $K = 10^{-3.5}$ M, $A = 1000 \text{ \AA}^2$, $U = 1$ and $X = 75$ mM for the PVC/DOPP membrane. The occupied molecular surface area A was estimated from the volume of the membrane and the quantity of lipid or an impurity such as phenylphosphonic acid mono-octyl ester.

As seen from Fig. 2, we can obtain fairly good quantitative agreement with the experimental results using the theory in which the surface potential and diffusion potential within the membrane are both taken into account. Theoretical curves of the surface and diffusion potentials are shown in Fig. 3. In the case of the lipid/PVC/DOPP membrane, the surface potential is the main constituent of the electric potential response; the effect of the diffusion potential is small even at high NaCl concentrations. On the other hand, the main constituent of the electric potential response of the PVC/DOPP membrane changes considerably with increasing NaCl concentration. The electric potential response is due to a change in the surface potential at low NaCl concentrations, whereas the diffusion potential plays an important role at high concentrations. This result suggests that the mechanism of generation of the membrane potential in the PVC/DOPP membrane is different from that in the lipid/PVC/DOPP membrane. The membrane potential in the lipid/PVC/DOPP membrane is considered to consist mainly of the surface potential, whereas both surface potential and diffusion potential are generated within the PVC/DOPP membrane. Cations permeate selectively through the PVC/DOPP membrane, because DOPP and PVC may have impurities with weak negative electric charges, as suggested previously,⁽¹³⁻¹⁵⁾ and partly confirmed later. The addition of a negatively charged lipid species to PVC and DOPP causes a decrease in the degree of ion permeation through the membrane.

We now consider the response characteristics in Fig. 2, where the electric potentials of the lipid/PVC/DOPP and PVC/DOPP membranes are not saturated at high NaCl concentrations. Figure 4 shows calculated results for the degree of H^+ binding to the lipid in lipid/PVC/DOPP membrane and to phenylphosphonic acid mono-octyl ester in PVC/DOPP membrane. In the case of the lipid/PVC/DOPP membrane, there is little dissociation of H^+ ions from the lipid at low NaCl concentrations, as indicated by the high degree of H^+ binding of 0.8. This is because the molecular surface area occupied by an individual lipid

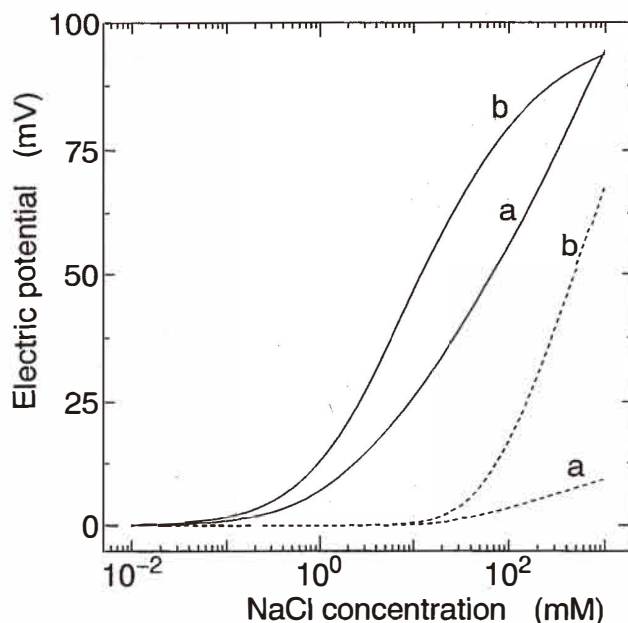


Fig. 3. Theoretical curves for the changes in surface and diffusion potentials of (a) lipid/PVC/DOPP membrane and (b) PVC/DOPP membrane. The solid and dashed lines represent the theoretical values of surface potential and diffusion potential, respectively.

is small due to the membrane preparation method, in which the amount of incorporated lipids is large. The lipid is packed densely in the membrane. This dense packing inhibits the charging process (i.e., dissociation of H^+ from the hydrophilic group of the lipid), which causes strong electric repulsion between charged molecules. The dissociation of H^+ ions is accelerated by the addition of NaCl. This implies an increase in the magnitude of the surface charge density; i.e., the membrane becomes more negatively charged. Increasing the NaCl concentration weakens the electric repulsion between lipids, and hence the H^+ ions dissociate more easily.

Therefore, it is reasonable that the lipid/PVC/DOPP membrane is not electrically charged to a great extent at low NaCl concentrations, and becomes more negatively charged due to the accelerating dissociation of H^+ ions with increasing NaCl concentration. As a result, the rate of change of the electric potential increases with increasing NaCl concentration, since the membrane becomes more negatively charged and the sensitivity to cations such as Na^+ is increased. In conventional fully charged membranes, Na^+ ions hardly affect the net electric charge density of a negatively charged membrane but affect the surface potential (i.e., the electric screening effect), and the electric potential tends to saturate at high NaCl concentrations.^(9,10) In the present case, however, the electric charge density changes considerably, and the potential response is not saturated even at high NaCl

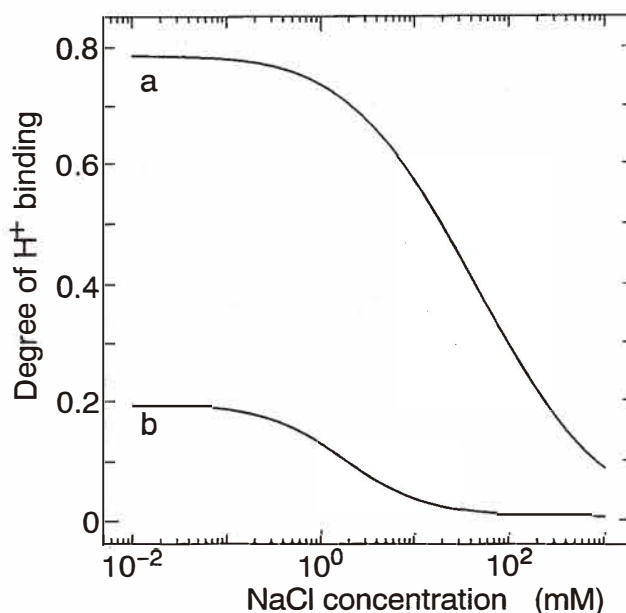


Fig. 4. The calculated degree of H⁺ binding to (a) lipid/PVC/DOPP membrane and (b) PVC/DOPP membrane.

concentrations.

On the other hand, the real molecular surface area occupied by monoester-type impurities in the PVC/DOPP membrane is large, because the impurity content is as low as 1% (data not shown; provided elsewhere). In the theoretical results for the PVC/DOPP membrane, H⁺ ions are almost completely dissociated even at low NaCl concentrations, as shown in Fig. 4. Therefore, the PVC/DOPP membrane can have a high net negative charge density, and respond sensitively to cations. The diffusion potential of the PVC/DOPP membrane becomes the main constituent of the membrane potential with increasing NaCl concentration.

These theoretical results suggest that the addition of a negatively charged species to PVC and DOPP does not always lead to an increase in the magnitude of the net surface charge density. To confirm this suggestion, we studied the electric potential responses of a series of PVC/DOPP membranes, which contained different amounts of DOPP, namely 5 times, 3 times, 1/3, and 1/10 that in the original PVC/DOPP membrane. The results obtained are shown in Fig. 5. The original PVC/DOPP membrane responded most sensitively to NaCl. The response of the PVC/DOPP membrane became smaller not only with increasing DOPP content in the membrane but also with decreasing DOPP content. This implies that an excessive amount of DOPP, which may contain negatively charged impurities, in the membrane is equivalent to adding a negatively charged lipid. Therefore,

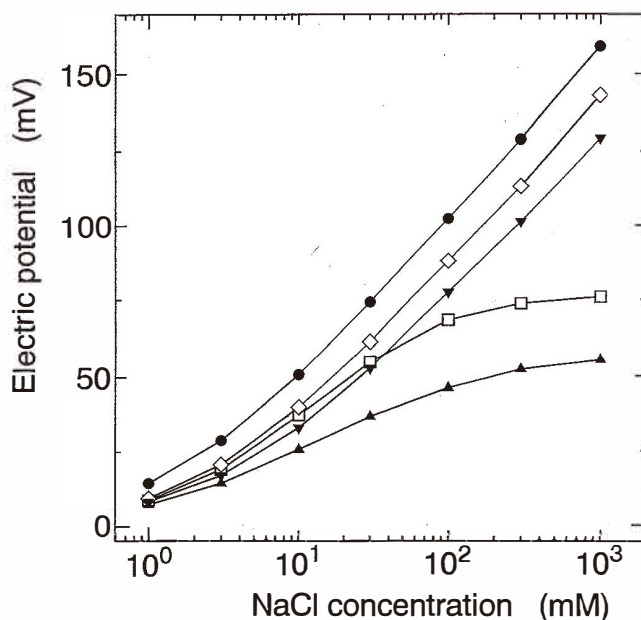


Fig. 5. Responses of PVC/DOPP membranes containing different amounts of DOPP, namely 5 times (▼), 3 times (◇), equal (●), 1/3 (□) and 1/10 (▲) that in the original PVC/DOPP membrane.

the effect of increasing the amount of DOPP in the membrane may be similar to that of adding a negatively charged lipid; the degree of H^+ ion dissociation on the membrane surface decreases with increasing DOPP content. On the other hand, decreasing the amount of DOPP in the membrane leads to a decrease in the net surface charge density. These results show that a suitable choice of the amount of DOPP is necessary to obtain good response characteristics for membranes used as transducers in taste sensors.

Finally, we provide further evidence of the cationic permeability of PVC membranes and DOPP-adsorbed membranes originating from their own negative electric charge. Figure 6 shows the electric potentials of a PVC membrane and a cellulose nitrate filter, the pores of which are filled with DOPP. The PVC membrane was prepared by dissolving 200 mg of PVC in 18 ml of THF. The DOPP-adsorbed membrane was prepared by impregnating DOPP into a membrane filter with a pore size of 5 μm . The responses of both membranes to NaCl were positive. This implies that the membranes are negatively charged so that they respond to cations. PVC may be charged due to the existence of sulfate or sulfonate groups, which are generated by a persulfate radical initiator.⁽⁷⁾ DOPP has negatively charged impurities, i.e., phenylphosphonic acid monoethyl ester.

In this work, the response characteristics of lipid/PVC/DOPP and PVC/DOPP membranes to NaCl were studied. It was shown that the lipid/PVC/DOPP membrane changes from a weakly charged state to the fully charged state by dissociation of H^+ from lipid

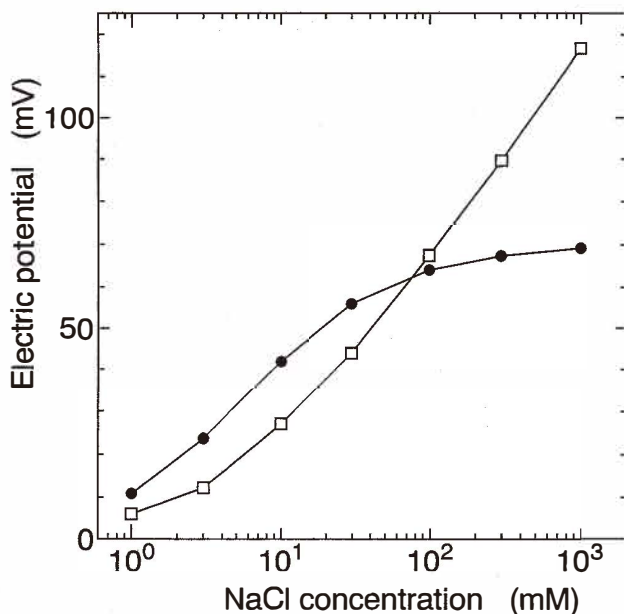


Fig. 6. Responses of the PVC membrane (●) and the DOPP-adsorbed membrane (□) to NaCl.

molecules with increasing NaCl concentration. The PVC/DOPP membrane was found to respond to NaCl more sensitively than the lipid/PVC/DOPP membrane. These results are applicable to the fabrication of chemical sensors, such as taste and ion-selective sensors; e.g., hybrid membranes composed of two lipid species were also used in the multichannel taste sensor.⁽¹⁷⁾ In this case, the choice of a suitable mixture ratio of lipids is required for obtaining desired responses to taste substances. The obtained results are very useful for preparation of the membranes, because the sign of the electric charge of the membrane seriously affects the response characteristics. In the ion-selective sensors, charged impurities contained in commercial plasticizers may affect the characteristics. This work is limited to the theoretical description and experimental observation of responses of membrane potentials. Identification of charged impurities using chemical analysis was not performed. This is a subject for a further report.

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