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Response of a Multichannel Electrode to Washing Detergents

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The response of a multichannel electrode to washing detergents was investigated. Sodium salts of several fatty acids greatly affected the membrane potential of the electrode by significantly lowering the potential of the positively charged membrane. Moreover, they changed the potential of the negatively charged membrane in an unexpected way. The results indicate the adsorption of fatty acids on the lipid membrane, even though they are easily removed from the membrane. Commercial washing detergents were also measured using the electrode. They were roughly classified into soaps, kitchen detergents and shampoos.

1. Introduction

Taste can be measured using a multichannel electrode sensor which responds to different taste qualities by producing a unique pattern of output signals.(1–11) A multichannel sensor utilizes lipid membranes as transducers of tastes and a computer as a data analyzer. The transducers transform taste information generated by chemical substances into electric potential changes. As a result, a sensor can easily distinguish among the five basic tastes and among some beverages such as beer, coffee, mineral water, milk and water-based drinks.

A multichannel electrode has the following characteristics. First, the development of the sensor was based on a concept very different from that of conventional chemical sensors, which selectively detect chemical substances. It responds to many ingredients in a solution simultaneously and displays eight output signals. Second, it does not require any sample pretreatment prior to measurement. Many beverages, including beer, coffee and milk, can be measured directly with the sensor. Third, the electrode detects not only the concentration of chemical substances but also their influence on living things. For example, the change in the electric potential of a negatively charged membrane caused by monovalent cations increases in order of their electronegativity, $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.(12) The order of electronegativity may be equivalent to the order of the ions' effect on living things.

At present, the chemical analysis of river water is primarily carried out by gas and liquid chromatographic methods. However, these methods have many problems such as the complexity of the procedures and the expense of the instruments. In contrast, the multichannel electrode seems to be suitable for on-the-spot measurements of river water. In addition, the electrode responds well to inorganic ions;(8,12) hence, we investigated candidates for water pollution, namely washing detergents.

2. Materials and Methods

2.1 *Detergents*

Salts of saturated fatty acids which differ in carbon number such as sodium laurate (12:0), sodium myristate (14:0), sodium palmitate (16:0) and sodium stearate (18:0), as well as salts of fatty acids differing in their degree of unsaturation such as sodium oleate (18:1) and sodium linolate (18:2) were obtained from Wako Pure Chem. and Tokyo Kasei Kogyo. Several washing detergents such as soaps (Nos.1~4), kitchen detergents (Nos. 5~7) and shampoos (Nos. 8~10) were purchased at a public market.

2.2 *Lipid membranes*

The multichannel electrode used in this study is similar to one previously reported.(1-12) The lipids are abbreviated as follows: dioctyl phosphate, C; trioctyl methylammonium chloride, T; oleyl amine, N; decyl alcohol, DA; oleic acid, OA. Lipid membranes designated C:T=9:1, C:T=3:7 and C:T=5:5 are a mixture of two lipids for which the ratio shows the molar concentration. The membranes C:T=3:7, T and N are positively charged, whereas C:T=9:1, C and OA are negatively charged. The membrane DA is somewhat negatively charged due to the presence of plasticizer.(13) The membrane C:T=5:5 is almost totally neutral.

2.3 *Measurements using a multichannel electrode*

The electric potential across the membrane was detected by means of an Ag_AgCl electrode in a well filled with 100 mM KCl and a reference electrode (TOA, HS205C). The construction of this measuring system is as follows: Ag_AgCl electrode in 100 mM KCl solution | membrane | reference electrode in detergent solution. The detergents changed the membrane potential, and the electric signal from each membrane was converted into a digital code using a digital voltmeter (ADVANTEST, R6551) through a high-input impedance amplifier and a laboratory-built eight-channel scanner and recorded in a computer (NEC, PC-9801).

3. Results

3.1 *Response of the electrode to salts of fatty acids*

Commercially available washing detergents usually contain components other than the main ingredient such as coloring agents and flavoring agents. Therefore, pure sodium salts of fatty acids were investigated first. The response of the multichannel electrode to each detergent was measured relative to a 1 mM KCl solution.

Prior to describing the study of the response of the electrode to detergents, we should first outline the fundamental properties of the electrode. Figure 1 shows the response of eight membranes of the electrode to NaCl. The sodium ions of NaCl affect the negatively charged membrane and reduce its negative charge by the shielding effect, thus increasing the membrane potential. The threshold concentration of Na$^+$ is 1 mM. On the other hand,

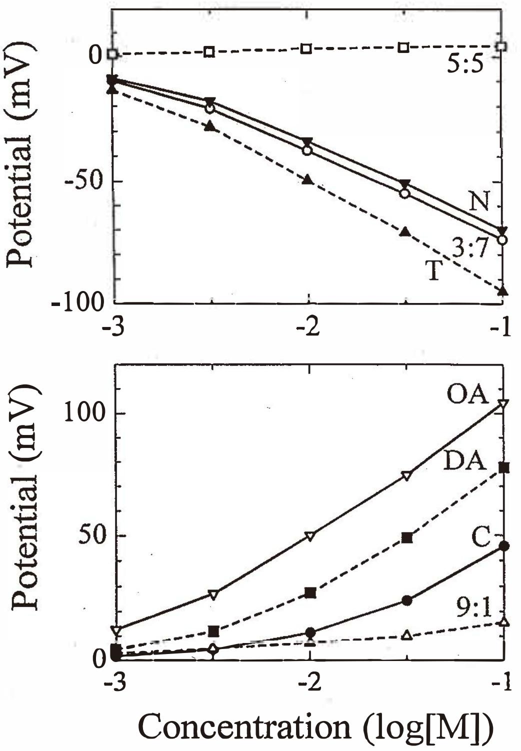

Fig. 1. Response of the multichannel electrode to NaCl.

chloride ions affect the positively charged membrane and reduce its positive charge by the shielding effect, thus decreasing the membrane potential. The threshold concentration of Cl^- is also approximately 1 mM.

The response of the electrode to sodium laurate is shown in Fig. 2. This fatty acid caused marked potential change in the positively charged membrane. At concentrations of 0.1 and 1.0 mM, the potential of N and T membranes changed by approximately 200 mV, which is significantly larger than the theoretical value of 60 mV. This suggests that adsorption rather than the shielding effect plays an important role. Typically, chemical substances raise the potential of negatively charged membranes such as 9:1, C, OA and DA, whereas sodium laurate lowered the potential. This also suggests the participation of adsorption. Other fatty acids induced similar potential changes. Figure 3 depicts the potential change caused by 1 mM sodium laurate as a function of membrane type. This graph represents the response of the electrode to chemical substances more effectively than Fig. 2.

The effects of carbon number in the hydrophobic chain and of the degree of unsaturation of a fatty acid on the response of a multichannel electrode are summarized in Table 1. The response of T and N membranes increased from carbon number 12 to 16 but decreased at 18. Therefore, the response is not proportional to the length of the hydrophobic chain.

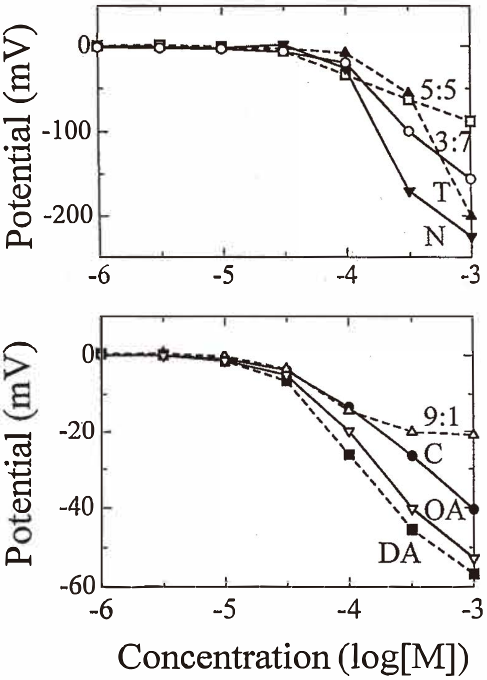

Fig. 2. Response of the multichannel electrode to sodium laurate.

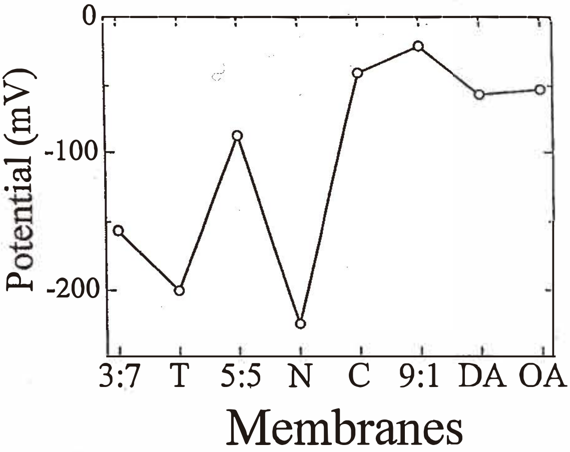

Fig. 3. Response of the multichannel electrode to 1 mM sodium laurate.

Table 1
Effect of (a) chain length and (b) degree of unsaturation of fatty acids on the response of a multichannel electrode. T and N are positively charged membranes. Responses are relative values.

(a)	Fatty acid	T	N
	12:0	100	100
	14:0	113	119
	16:0	128	126
	18:0	16	108

(b)	Fatty acid	T	N
	18 : 0	100	100
	18 : 1	641	125
	18 : 2	300	130

The response of the electrode is also independent of the degree of unsaturation, as shown by the T membrane.

The strength of adsorption of fatty acids to lipid membranes was estimated and compared with quinine, which is known to adsorb to lipid membranes.(14) First, the potential of each membrane was measured in 1 mM KCl solution to generate a reference potential pattern. Next, the electrode was soaked for 30 min in 1 mM sodium oleate or 1 mM quinine hydrochloride, and the potential was measured relative to the reference potential pattern. Then, the electrode was transferred into 1 mM KCl solution and the potential was measured again relative to the reference potential pattern. If nothing remains in the membrane, the response potentials for samples are expected to disappear in the 1 mM KCl solution. Table 2 lists the response potentials for samples and the remaining potentials in the 1 mM KCl solution. The aftereffect of quinine is quite large, because a considerable part of the potential change it causes is maintained in the 1 mM KCl solution. In contrast, the aftereffect of sodium oleate is small. Consequently, salts of fatty acids are easily removed from lipid membranes.

3.2 *Response of the electrode to commercial washing detergents*

Response patterns of the electrode to several commercial washing detergents diluted to 0.03% are shown in Fig. 4. Remarkable decreases in the potential of positively charged membranes and the opposite responses of negatively charged membranes are common for detergents, the same as the salts of fatty acids. The differences among soap, kitchen

Table 2
Adsorption of (a) quinine hydrochloride and (b) sodium oleate to lipid membranes. The unit of response is millivolts.

(a) Treatment	Membranes							
	3:7	T	5:5	N	C	9:1	DA	OA
1 mM quinine	–13.8	–9.6	16.2	–24.1	39.7	51.5	129.3	159.3
1 mM KCl	–10.5	3.9	–20.1	–21.7	7.3	–1.7	48.2	67.7

(b) Treatment	Membranes							
	3:7	T	5:5	N	C	9:1	DA	OA
1 mM Na oleate	–125.6	–205.0	–100.4	–254.7	–30.1	–36.85	–15.1	–12.5
1 mM KCl	–6.7	0.9	1.4	–12.5	–6.4	2.2	–14.8	–14.7

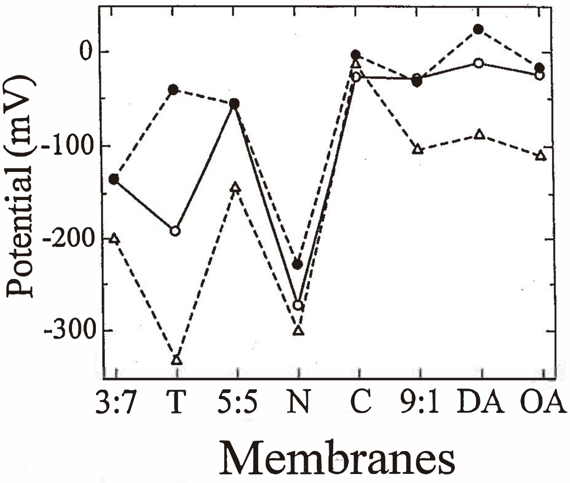

Fig. 4. Response of the multichannel electrode to commercial washing detergents. ○: soap No. 2, ●: kitchen detergent No. 7, △: shampoo No. 8.

detergent and shampoo can be observed in the responses of positively charged membranes. The response pattern of soap resembles that of a salt of a fatty acid (Fig. 3).

Data obtained using the multichannel electrode were further studied by principal component analysis (Fig. 5). In this case, the original data were expressed in eight-dimensional space composed of the outputs of the eight kinds of membranes. They were visualized on the two-dimensional plane using principal component analysis, which is very effective in reducing the dimensions with a minimum loss of information.(15) Soaps (Nos. 2~4), except No. 1, are concentrated at one point. Kitchen detergent No. 5 is located adjacent to No. 7, whereas No. 6 is separated from them. Shampoos (Nos. 8~10) are scattered widely; hence their ingredients may differ greatly.

4. Discussion

Multichannel electrodes are suitable for on-the-spot measurement of river water, because they do not require any sample pretreatment prior to measurement. Here, the response of the electrode to washing detergents, candidate water pollutants, was investigated. Salts of fatty acids were first used as samples, because commercial washing detergents usually contain ingredients other than the main one. Washing detergents markedly affected the membrane potential of the electrode. They greatly reduced the potential of positively charged membranes. Furthermore, they changed the potential of negatively charged membranes in an unexpected way (Fig. 3); the reason for this is obscure. This pattern may be typical of detergents, because it has not been reported in other samples.(1-12)

The potential change caused by fatty acids was proportional neither to the number of carbon atoms nor to the degree of unsaturation of the fatty acids. Salts of fatty acids are

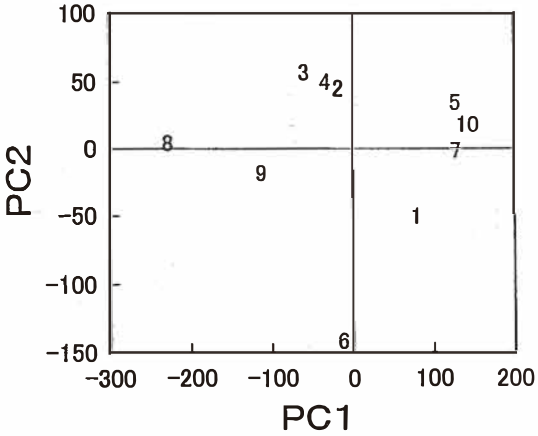

Fig. 5. Principal component analysis of commercial washing detergents. Nos. 1~4: soaps, Nos. 5~7: kitchen detergents, Nos. 8~10: shampoos.

alkaline. Moreover, the N membrane is sensitive to hydroxide ions, as shown in the following equation.

$$R\text{-}NH_3^+ + OH \rightarrow R\text{-}NH_2 + H_2O$$

The pH of the sodium salts of lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid and linolic acid are 7.0, 7.6, 9.3, 10.1, 9.7 and 8.8, respectively. The order does not coincide with that of the responses listed in Table 1; therefore, alkalinity is not the reason for the response.

The unusually large potential change (ca. 200 mV/decade) caused by fatty acids suggests the participation of adsorption. However, the potential change disappeared after the membranes were washed with 1 mM KCl solution (Table 2). Consequently, the adsorption of fatty acids on lipid membranes appears to be weak. Quinine is known to penetrate into the hydrophobic portion of membranes. The threshold concentrations to induce the potential changes are 10^{-6} M and 10^{-4} M for quinine hydrochloride and sodium laurate, respectively. Therefore, the strength of adsorption of fatty acids may be less than one hundredth that of quinine. The threshold concentration of sodium laurate is approximately 20 ppm. To investigate water pollution, improvement in the sensitivity of electrodes is essential, because the mean annual concentration of some detergents in rivers ranges from 0.01 to 0.4 ppm.(16)

Commercial washing detergents induced a potential change similar to the salts of fatty acids. This study demonstrates that a novel sensing device, the multichannel electrode, may be useful in the evaluation of water pollution.

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