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Behaviour of Red Tides in the System of Ion-Exchange Membrane Electrodialysis

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ABSTRACT

The sorption effects of red tides and their contents on the ion-exchange membranes have been investigated under various electrodialysis conditions. Aqueous NaCl solution suspended with the contents of *Chattonella antiqua*, which is a typical phytoplankton species of the red tide, was passed through the desalting chamber in an electrodialysis apparatus. The effects of current densities and the contents of *Chattonella antiqua* on electrodialysis were examined. The pH change of the effluent and limiting current density in the desalting chamber were measured, and sorped species on the ion-exchange membranes were analyzed. It was found that sorped species on the anion-exchange membrane were mainly chlorophyll *a*–protein complexes and pheophytin *a*–protein complexes and remarkably influenced the limiting current density; i.e., a pronounced decrease in the limiting current density occurred in the presence of the complexes. The contribution of *Chattonella antiqua* to the limiting current density of the cation-exchange membrane was found to be very small during the electrodialysis. The sorption of *Chattonella antiqua* contents on the cation-exchange membrane was almost undetectable.

INTRODUCTION

It is well known that red tides have often occurred in Seto Inland Sea due to the pollution and eutrophication of seawater (Iwasaki, 1979). The damage that they cause has been increasingly serious in salt production plants. The red tide is sorped on ion-exchange membranes and causes many problems such as the interruption of the flux of seawater in the electrodialysis apparatus. The pH change occurred due to water dissociation above the limiting current density. The electrodialysis plant operation has often had to be suspended and much work has been necessary to remove the red tide from the electrodialysis apparatus. There are as yet no effective plans to counteract these problems.

In order to achieve a solution, it is necessary to know the behaviour of red tides and their contents as well as their influence on ion-exchange membranes in the electrodialysis apparatus. *Chattonella antiqua* — the main species of the red tide — was selected as a representative species for this study and its various effects on the electrodialysis system were investigated.

MATERIALS AND METHODS

Red tide species

An axenic culture of a clonal strain of *Chattonella antiqua* (*C. antiqua*: NIES-1), which was offered by the National Institute for Environmental Studies, was used.

Culture conditions

The *C. antiqua* cells were grown in a Guillard f medium (Guillard and Ryther, 1962). After inoculation, the culture was subjected to two cycles of 12 h light and 12 h dark using 3000 lux daylight fluorescence lamps at 22.5°C. Cell concentration was measured by Coulter Counter model ZM.

Preparation of red tide suspension

The *C. antiqua* cells were collected by centrifugation at 3000 rpm for 10 min. A mass of the *C. antiqua*

cells was suspended in an aqueous 0.05 M NaCl solution. The *C. antiqua* suspension was treated with an ultrasonic wave (20 kHz, 200 W, 5 min) and the contents of the *C. antiqua* cells were leaked out from the cells.

Ion-exchange membranes

Commercially available ion-exchange membranes were used: the cation-exchange membrane was Selemion CMV and the anion-exchange membrane Selemion AMV (Asahi Glass Co., Ltd.). The ion-exchange characteristics of these membranes are shown in Table 1.

TABLE 1

Characteristics of ion-exchange membranes

Name and classification	Selemion CMV	Selemion AMV
Transport number[1]	>0.91	>0.93
Ion-exchange capacity (meq/g dry memb.)	1.5–1.8	2.0–2.3
Water content (g H_2O/g dry memb.)	0.20–0.30	0.24–0.25
Electric resistivity[2] ($\Omega \cdot cm^2$)	3.0	3.5
Thickness (mm)	0.11–0.15	0.11–0.15
Tensile strength (kg/cm^2)	3.0–5.0	3.0–5.0

[1]Calculated by membrane potential measured in 0.1–0.2 M NaCl solution.
[2]Equilibrated with 0.5 M NaCl solution at 25.0°C.

Electrodialysis apparatus

Electrodialysis was carried out using an apparatus consisting of 7 chambers, as shown in Fig. 1. Cation- and anion-exchange membranes were set alternately as the diaphragms of each chamber. Electrode chambers were separated by a cellophane membrane. The effective area of the membranes was 4 cm^2 and the distance between the membranes was 1 cm. Ag–AgCl electrodes (made of silver net) were located at each end of the chamber for electrodialysis. An aqueous 0.1 M (M = $mol \cdot dm^{-3}$ NaCl solution was passed through the electrode chambers and polar chambers (I, V) from the lower inlets to the upper outlets at a flow rate of 3 $cm^3 \cdot min^{-1}$. Concentrating chambers (II, IV) were filled with 6 cm^3 NaCl (0.01 M) solution. NaCl solution (0.05 M, 20 cm^3) suspended with the contents of *C. antiqua* was circulated in the desalting chamber (III) from lower to upper at a flow rate of 3 $cm^3 \cdot min^{-1}$. Electrodialysis was carried out by changing concentration of the contents of *C. antiqua* for 30 min at current densities of 2.5, 5.0 and 12.5 $mA \cdot cm^{-2}$. The pH value of the effluent from the desalting chamber was measured to discover the effects of the *C. antiqua* suspension on true current density during the electrodialysis with a combination pH-electrode (flow type GS-80, TOA Electronics Co., Ltd.). The pH of the concentrating chamber was also measured with a pH meter after the electrodialysis. Measurements of the electrodialysis were carried out at 25.0°C unless otherwise stated.

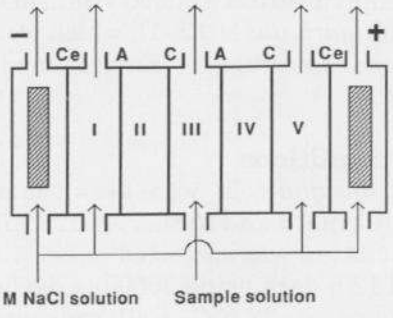

Fig. 1. Schematic diagram of electrodialysis apparatus. C: Cation-exchange membrane; A: anion-exchange membrane; I, V chamber: 0.1 M NaCl, flow rate of 3 $cm^3 \cdot min^{-1}$; III chamber: 0.05 M NaCl, or sample solution was circulated at flow rate of 3 $cm^3 \cdot min^{-1}$; II, IV: 0.01 M NaCl; +: anode; –: cathode; area of membranes: 4 cm^2.

Measurement of limiting current density

The limiting current densities of cation- and anion-exchange membranes in the desalting chamber were measured as soon as each electrodialysis was terminated. The cell apparatus for measuring the polarization characteristic and limiting current density is shown in Fig. 2. Polarization characteristics were examined in 0.05 M NaCl solution at 20.0°C. Ag-AgCl electrodes (made of 0.8 mm ∅ silver

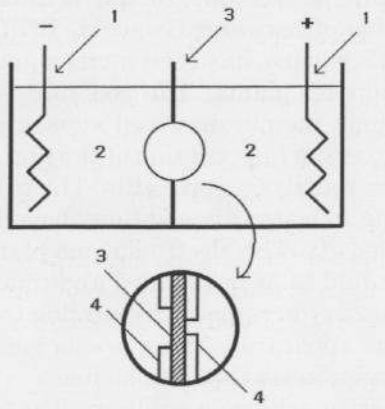

Fig. 2. Cell apparatus for measuring limiting current. 1: AgCl-coated Ag electrodes; 2: 0.05 M NaCl solution; 3: ion-exchange membranes; 4: membrane holder (vinyl chloride plate, 1 mm thick). Surface area of the membrane (CMV): right side 0.0314 cm^2, left side 0.1256 cm^2, in case of AMV, + and – were exchanged.

wire) were used for the polarization. The current density was measured by changing the applied voltage step-wise. The current value after keeping a desired voltage for 1 min was selected to avoid the capacitive current. The limiting current density was determined from the bend of the current against voltage curves as illustrated in Fig. 3.

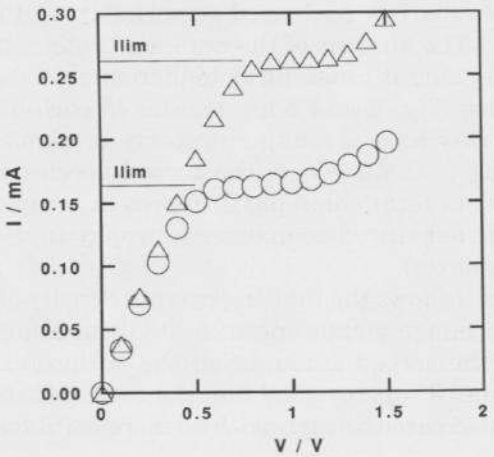

Fig. 3. Example of current voltage curves of cation- and anion-exchange membranes in 0.05 M NaCl solution. Area of membrane was 0.0314 cm^2. O: Selemion CMV; Δ: Selemion AMV.

Determination pigments and protein

(a) Extraction of pigments

C. antiqua includes many pigments such as chlorophyll *a*, c_1, c_2, fucoxanthin, vioraxanthin, β-carotene and pheophytin, where chlorophyll *a* is the main species of *C. antiqua* and pheophytin *a* is its acidic degradation product. Among them the sorption property of chlorophyll *a* and pheophytin *a* was examined. Either the original solution including the *C. antiqua* contents or the effluents passed through the desalting chamber of electrodialysis were filtered by suction filtration with 0.5 μm PTFE membrane filter (Advantec Toyo Co., Ltd.). Pigments were extracted by keeping the filtrates for 24 h in 90% acetone. The amount of the pigments extracted in the supernatant solution was determined by the method Jeffrey and Humphrey and Lorenzen method (Lorenzen, 1967; Jeffrey and Humphrey, 1975).

(b) Extraction of protein

The lipid was removed from the pigment-free residue with mixed solvent of ethanol and ether (1:1) at 40°C for 10 min. The lipid-free residue was rinsed with 1 M perchloric acid, ethanol and ether successively and dried at room temperature. After hydrolysis in 1 M NaOH solution at 37°C for 18 h, the amount of protein extracted in the supernatant solution was determined by the modified method of Bensadoun and Weinstein and Hartree (Hartree, 1972; Bensadoun and Weinstein, 1976).

(c) Amount of sorped species

The sorped amounts of chlorophyll *a*, pheophytin *a* and protein were calculated from the difference between the initial concentrations and those in the effluent after the electrodialysis.

RESULTS AND DISCUSSION

Figure 4 illustrates the salt concentration distribution around the membrane. When an electrical current is passed through an ion-exchange membrane placed in a solution containing monovalent cations and anions, a boundary layer is assumed to be formed on the desalting and concentrating surfaces of the membrane. As the current density increases, the current reaches a certain finite value where the ion concentration (Ci) goes to zero at the boundary of the desalting chamber and the ion-exchange membrane. The water molecule on the desalting surface of anion-exchange membrane is decomposed into H^+ and OH^- ions above the limiting current density (I_{lim}). The pH value of the solution changes due to the resultant H^+ ions (Rosenberg and Tirrell, 1957). Figure 5 shows the time dependencies of pH in the solution of 0.05 M NaCl proper and the solution containing the *C. antiqua* contents in the desalting chamber (III) under various current densi-

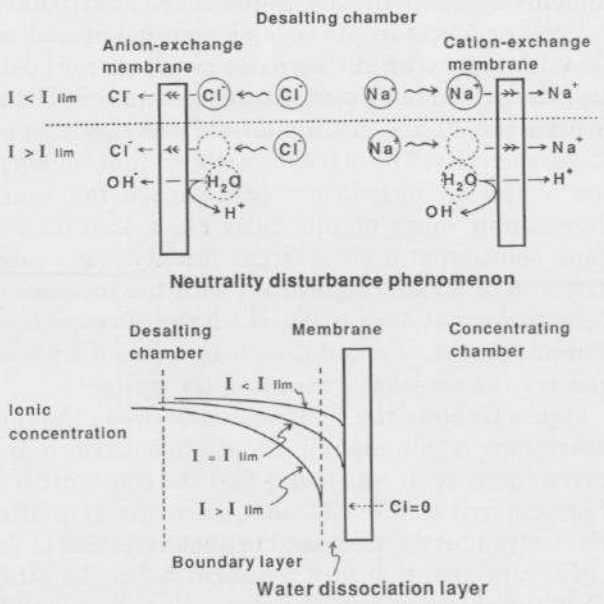

Fig. 4. Conceptual view of neutrality disturbance phenomenon and water dissociation layer.

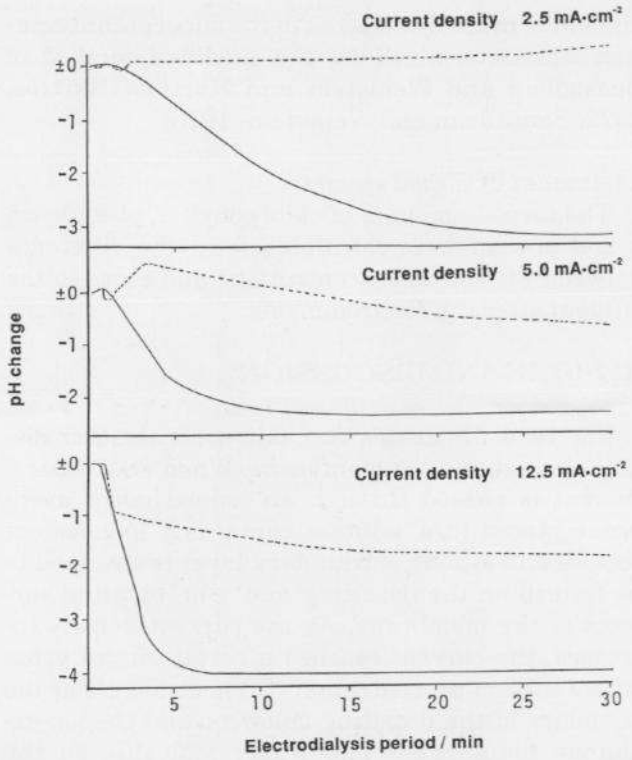

Fig. 5. pH Change of desalting chamber during electrodialysis at various current densities. Broken lines: blank solution (0.05 M NaCl solution); solid lines: sample solution (5.84×10^4 cells·cm^{-3} suspension).

ties. Blank solution (0.05 M NaCl) did not show any significant pH change at a low current density, 2.5 mA·cm^{-2}. On the other hand, the pH of the solution containing the *C. antiqua* contents began to decrease immediately after the beginning of the electrodialysis. The decrease in pH became significant and occurred rapidly with the increase in the current density. The pH values of concentrating chambers II and IV after the 30 min electrodialysis was about 2 and 12, respectively. These results suggest that the sorption of the *C. antiqua* contents caused the water dissociation more significantly than that in the blank solution at a low current density. The water dissociation became significant with the increase of the true current density, in which the effective area of anion-exchange membrane was reduced with increasing the sorption amounts of the contents.

Figure 6 shows the relationship between the concentrations of chlorophyll *a* and pheophytin *a* and current density. It was found that the concentration of chlorophyll *a* in the *C. antiqua* suspension after the electrodialysis decreased to about one half of the initial concentration at 2.5 mA·cm^{-2}. On the other hand, the amount of pheophytin *a* increased rapidly in spite of its low initial concentration. This result indicates that chlorophyll *a* changed into the acidic denatured pheophytin *a* during the electrodialysis, as shown in Fig. 7. It was therefore considered that the sorped amount of (chlorophyll *a* + pheophytin *a*) on the anion-exchange membrane was kept constant irrespective of current density.

Figure 8 shows the change of protein concentration at various current densities. Concentration of residual protein in the *C. antiqua* suspension after the electrodialysis decreased remarkably up to 2.5 mA·cm^{-2}. The amount of the residual protein, however, was almost constant at higher current densities. Since Figs. 6 and 8 are similar to each other, protein may have a similar property to pigments. According to the analogy, the sorped species were supposed to form chlorophyll *a*–protein complexes and their denatured complexes (pheophytin *a*–protein complexes).

Figure 9 shows the limiting current density of the anion-exchange membrane in a desalting chamber against the sorped amounts on the surface of the membrane. It was revealed that the limiting current density decreased linearly with an increase in sorped

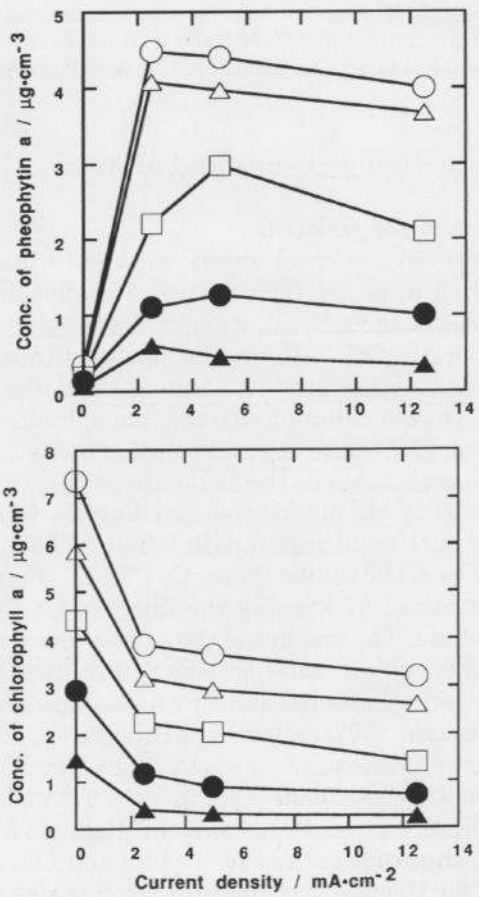

Fig. 6. Concentration change of pigments (chlorophyll *a*, pheophytin *a*) vs. current density curves after 30 min electrodialysis).

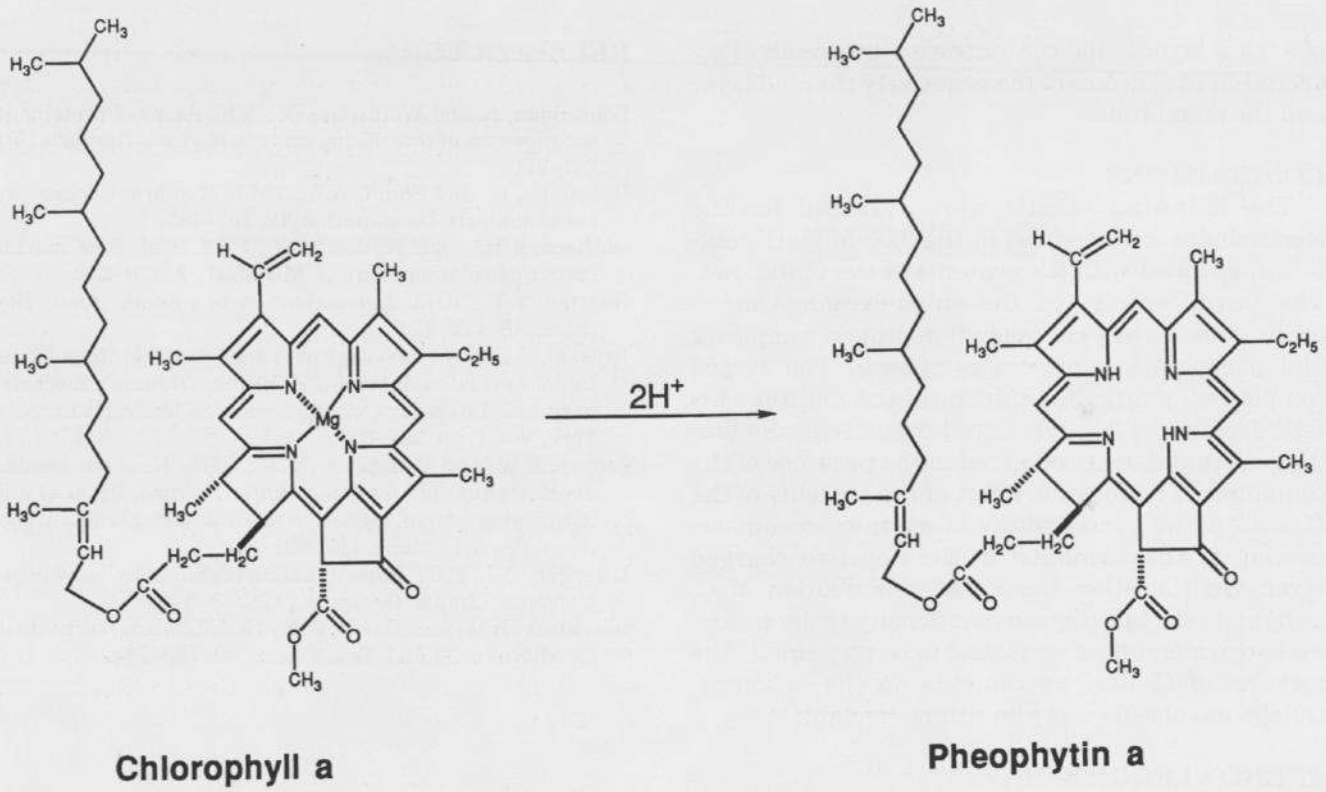

Fig. 7. Acidic degradation of chlorophyll *a*.

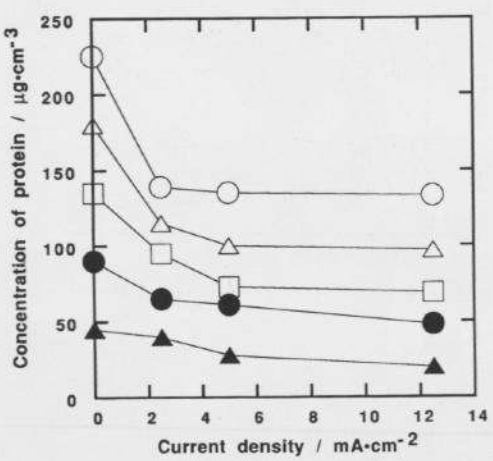

Fig. 8. Concentration of protein vs. current density after 30 min. electrodialysis.

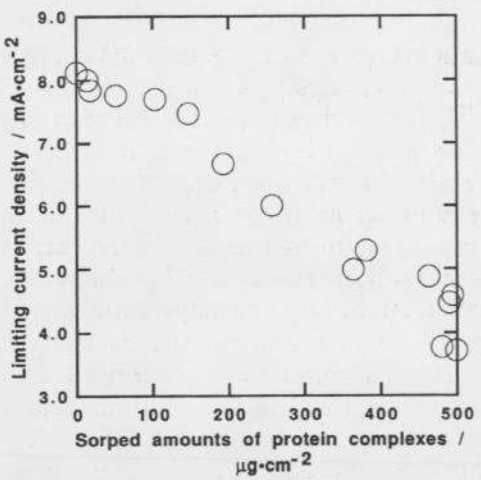

Fig. 9. Effect of sorption amounts of chlorophyll a on limiting current density.

amounts. On the other hand, the contents of the *C. antiqua* were no longer sorped on the cation-exchange membrane and have a negligible influence on the limiting current density.

The decrease in limiting current density of the anion-exchange membrane was ascribable to the following inference. The chlorophyll *a* and pheophytin *a*–protein complexes with negative charges were transferred toward the ammonium group ($-NH_4^+$) in an anion-exchange membrane and sorped on a desalting surface forming a negatively charged layer. Grossman and Sonin (1973) show that the negative charge decreases in the apparent anion transport number associated with the membrane. A significant reduction of the limiting current density due to the synergistic effect might be caused by the formation

of such a layer if the concentration polarization occurred on the surface of the negatively charged layer and the membrane.

CONCLUSIONS

The following results were obtained for the electrodialysis carried out in the 0.05 M NaCl solution suspended with the contents of the *C. antiqua*. The sorped species on the anion-exchange membrane were mainly chlorophyll *a*–protein complexes and pheophytin *a*–protein complexes. The sorped complexes remarkably influenced the limiting current density; i.e., a pronounced decrease in the limiting current density occurred in the presence of the complexes. The sorption effect of the contents of the *C. antiqua* was successfully taken into account according to the formation of the negative charged layer. On the other hand, the contribution of *C. antiqua* to the limiting current density of the cation-exchange membrane was found to be very small. The sorption of *C. antiqua* contents on the cation-exchange membrane was almost undetectable.

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