Taste Transduction Mechanism

Similar Effects of Various Modifications of Gustatory Receptors on Neural Responses to Chemical and Electrical Stimulation in The Frog

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ABSTRACT Responses in the frog glossopharyngeal nerve induced by electrical stimulation of the tongue were compared with those induced by chemical stimuli under various conditions. (a) Anodal stimulation induced much larger responses than cathodal stimulation, and anodal stimulation of the tongue adapted to 5 mM MgCl₂ produced much larger responses than stimulation with the tongue adapted to 10 mM NaCl at equal current intensities, as chemical stimulation with MgCl₂ produced much larger responses than stimulation with NaCl at equal concentration. (b) The enhansive and suppressive effects of 8-anilino-1-naphthalenesulfonate, NiCl₂, and uranyl acetate on the responses to anodal current were similar to those on the responses to chemical stimulation. (c) Anodal stimulation of the tongue adapted to 50 mM CaCl₂ resulted in a large response, whereas application of 1 M CaCl₂ to the tongue adapted to 50 mM CaCl₂ produced only a small response. This, together with theoretical considerations, suggested that the accumulation of salts on the tongue surface is not the cause of the generation of the response to anodal current. (d) Cathodal current suppressed the responses induced by 1 mM CaCl₂, 0.3 M ethanol, and distilled water. (e) The addition of EGTA or Ca-channel blockers (CdCl₂ and verapamil) to the perfusing solution for the lingual artery reversibly suppressed both the responses to chemical stimulus (NaCl) and to anodal current with 10 mM NaCl. (f) We assume from the results obtained that electrical current from the microvillus membrane of a taste cell to the synaptic area supplied by anodal stimulation or induced by chemical stimulation activates the voltage-dependent Ca channel at the synaptic area.

INTRODUCTION

It has been known since the time of Volta that electrical stimulation of the human tongue evokes taste sensation. Numerous studies on "electrical taste" performed psychophysically revealed the characteristics of electrical taste...
(Bujas, 1971 and 1977). To explain the psychophysical data, a number of hypotheses as described below have been advanced (Bujas, 1971 and 1977): (a) Electrical taste is the result of an adequate stimulation of taste receptors by some specific products of the electrolysis of the saliva. (b) Electrical taste is induced by direct stimulation of the gustatory nerve with electric current. (c) The current directly provokes taste receptors. Despite numerous studies, it is not yet known which hypothesis is correct. For further studies on a mechanism of electrical taste, an electrophysiological technique seems to be a useful tool. However, only a limited number of electrophysiological works (Pfaffman, 1941; Smith and Bealer, 1975; Pfaffmann and Pritchard, 1980) have been done and no systematic studies have been carried out as far as we know.

In a previous paper (Aiuchi et al., 1976), we proposed the following hypothesis for a taste transduction mechanism: adsorption of chemical stimuli on the microvillus membrane of a taste cell depolarizes the membrane potential at the microvillus membrane, which induces an electric current from the microvilli to the synaptic area of the taste cell to produce nerve impulses. If this hypothesis is correct, it would be expected that an electric current from the tongue surface to the back side of the tongue elicits gustatory responses similar to those induced by chemical stimulation. Thus, electrical stimulation seems to be a useful tool for elucidating the taste transduction mechanism.

In this study, the function of the frog gustatory receptors was modified by various reagents and the effects of the modifications on the glossopharyngeal nerve responses to chemical and electrical stimulation were compared. We found that various modifications of electrical and chemical stimulation produce responses that are quite similar to each other. In addition, electrical stimulation of the tongue was performed while the lingual artery was perfused with artificial solutions containing Ca-channel blockers to inhibit the release of a chemical transmitter from taste cells; and we found that responses to electrical stimulation, as well as those to chemical stimulation, are reversibly suppressed under this condition. Discussion is made on a taste transduction mechanism as well as a mechanism of electrical taste.

**MATERIALS AND METHODS**

**Animals**

Adult bullfrogs, *Rana catesbeiana*, weighing 260–300 g, were used in these experiments. For the perfusion of the lingual artery, frogs obtained in the winter were used, since they exhibited stable responses under perfusing conditions at this time.

**Recording of Gustatory Nerve Activities**

The responses to chemical stimuli and electric current were recorded from the glossopharyngeal nerves. The method of the preparation of the glossopharyngeal nerves and recording of the nerve activity were the same as those described in a previous paper (Kashiwagura et al., 1980). The nerve impulses were integrated with an electronic integrator with time constant of 0.3 s.
Chemical Stimulation

Chemical stimulation was carried out essentially as described in a previous paper (Kamo et al., 1978). Stimulating solutions were applied to the tongue with a flow rate of 2 ml/s after 20 mM NaCl had perfused the tongue with the same flow rate.

Electrical Stimulation

Electrical stimulation in most experiments was carried out by supplying a constant current (0.7 mA) to the frog tongue with an electronic stimulator (MSE-3R; Nihon Koden Kogyo, Tokyo) and an isolating unit (MSE-JM; Nihon Koden Kogyo). The frog tongue was placed in a chamber filled with an adapting solution. One platinum electrode (electrode 1) for electrical stimulation was immersed in an adapting solution and another platinum electrode (electrode 2) was placed on the back side of the root part of the tongue where the tongue was not immersed in a solution. Similar results were obtained when electrode 1 was placed in direct contact with the tongue surface instead of immersing it in an adapting solution. When an adapting solution of low conductance such as distilled water was used, electrode 1 was placed in direct contact with the tongue surface. Electric current that flowed from electrode 1 to electrode 2 and that from electrode 2 to electrode 1 are referred to as anodal and cathodal current, respectively.

8-Anilino-1-naphthalenesulfonate (ANS) Treatment

The treatment of the frog tongue with ANS was carried out as described in a previous paper (Kashiwagura et al., 1977): The tongue was incubated in 1 mM ANS solution at 5°C for 2 min and the ANS solution was washed away by flowing 20 mM NaCl solution at 20°C on the surface of the tongue for 2 min with a flow rate of 2 ml/s. For chemical stimulation, a stimulating solution (0.4 M NaCl solution) was applied to the tongue at the same flow rate. For electrical stimulation, anodal current was supplied to the tongue adapted to 10 mM NaCl solution after the ANS treatment.

Effect of Uranyl Acetate

For chemical stimulation, the tongue was adapted to 20-mM NaCl solution containing uranyl acetate of various concentrations for 2 min and stimulating solutions containing uranyl acetate of the same concentration as the adapting solution were supplied. For electrical stimulation, anodal current was supplied to the tongue adapted to 10-mM NaCl solution or 5-mM MgCl₂ solution containing uranyl acetate of various concentrations.

Perfusion of the Lingual Artery

Perfusion of the lingual artery was carried out essentially as described by Morimoto and Sato (1975): A polyethylene tube was cannulated into the lingual artery and Ringer's solution (112 mM NaCl, 3.4 mM KCl, 0.2 mM CaCl₂, 3.6 mM MgSO₄, 2.5 mM NaHCO₃, pH 7.2) containing 10 U of sodium heparin was perfused through the tube into the artery by using a peristaltic pump (SJ-1215; Mitsumi Scientific, Inc., Tokyo) at a rate of 0.1 ml/min. The perfused solution was drained through the vein at the bottom of the tongue. During perfusing, the response to 1 mM CaCl₂ was measured as a reference response. After blood was completely eliminated from the vein and stimulation by 1 mM CaCl₂ came to give a constant response, the control response was recorded. Addition of Ca-channel blockers was performed by switching the perfusing solution to the Ringer's solution containing the blockers.
Chemicals

ANS was purchased from Eastman Kodak Co., Rochester, N. Y. and ethylene glycol-bis-(β-aminoethyl ether)-N,N',-tetraacetic acid (EGTA) was purchased from Dojindo Laboratory, Kumamoto, Japan. Uranyl acetate and sodium heparin were purchased from Wako Pure Chemical Co., Osaka, Japan. Verapamil was kindly supplied by Eisai Co., Tokyo.

All the experiments were carried out at 20°C.

RESULTS

Anodal stimulation of frog tongue that was rinsed thoroughly with distilled water did not increase activities of the glossopharyngeal nerve, but stimulation of the tongue adapted to salt solutions greatly increased the activities. Fig. 1A shows the summated responses induced by anodal current when the tongue is adapted to various salt solutions. Solutions of 10 mM 1:1 type salts (NaCl, choline chloride, and tetraethylammonium chloride) and of 5 mM 2:1 type salt (MgCl2) were chosen as adapting solutions because these salts elicit only small responses in the glossopharyngeal nerve and, moreover, the responses were easily adapted to the spontaneous level. As seen from the figure, the magnitude of the responses varied with ion species in the adapting solution even though the tongue is adapted to solutions containing salts that are electrochemically equivalent. For example, the response of the tongue adapted to 5 mM MgCl2 is much larger than that of the tongue adapted to 10 mM salts of monovalent cations at equal current intensity. The average ratio of the magnitude of the response with 5 mM MgCl2 to that with 10 mM NaCl, which was observed with eight frogs, was 3.6 ± 0.8 for the peak response and 3.8 ± 0.5 for the response 20 s after onset of stimulation. This tendency coincides with that of the responses to chemical stimulation where the responses to NaCl and MgCl2 are compared at equal electrochemical equivalent: the magnitude of the response to 0.2 M MgCl2 is much larger than that to 0.4 M NaCl (Fig. 1 B) or that to 0.1 M MgCl2 is much larger than that to 0.2 M NaCl. The average ratio of the magnitude of the response to 0.2 M MgCl2 to that to 0.4 M NaCl, which was observed with seven frogs, was 3.0 ± 0.7 for the peak response and 4.2 ± 0.5 for the response 20 s after onset of stimulation. Fig. 1C shows the magnitude of the responses to anodal and cathodal current of various intensities when the tongue is adapted to 10 mM NaCl and 5 mM MgCl2. The responses to anodal current increase with increasing current intensity and the responses with 5 mM MgCl2 are much greater than with 10 mM NaCl at all intensities. The responses to cathodal current are much less than to anodal current. The current intensity required for induction of electric responses in the frog is much higher than that in the rat (Bujas, 1971; Pfaffmann and Pritchard, 1980). The frog tongue is much more tender and contains more water than the rat tongue and hence most current applied to the frog tongue may pass through tissues other than taste cells.

As shown in a previous paper (Kashiwagura et al., 1977), treatment of the frog tongue with ANS lead to great enhancement of the responses to salt
Figure 1. (A and B) Summated responses of the frog glossopharyngeal nerve to anodal current (A) and chemical stimuli (B). For electrical stimulation, the tongue was adapted to 10 mM NaCl, 10 mM choline chloride, 10 mM tetraethylammonium chloride, (TEA), and 5 mM MgCl₂. Bars at the bottom of each record represent duration of application of anodal current or chemical stimuli. (C) Relative magnitude of the peak responses to electric current as a function of current intensity. Each point in the figure is the average value of the data obtained with three frogs. , anodal stimulation of the tongue adapted to 10 mM NaCl; □, anodal stimulation of the tongue adapted to 5 mM MgCl₂; , cathodal stimulation of the tongue adapted to 10 mM NaCl; ■, cathodal stimulation of the tongue adapted to 5 mM MgCl₂; Responses (R) were calculated relative to the response to 1.1-mA anodal current with 5 mM MgCl₂.
stimuli. Fig. 2A shows that a chemical response to 0.4 M NaCl is greatly enhanced after ANS treatment. The ANS treatment also greatly increased the response to anodal current (Fig. 2B) when the responses before and after ANS treatment are compared at equal current intensity.

The response to 100 mM NaCl was greatly enhanced by the presence of 1 mM NiCl₂, whereas that to 100 mM LiCl was only slightly increased (Kashiwagura et al., 1978). The electrical response of the tongue adapted to 10 mM NaCl was also greatly enhanced by the presence of 1 mM NiCl₂, whereas the response of the tongue adapted to 10 mM LiCl was not pronounced. In Fig. 3, the magnitude of the response to 100 mM NaCl and that to anodal current with 10 mM NaCl are plotted against the NiCl₂ concentration where responses (Fig. 3, R) are calculated relative to respective responses at 10 mM NiCl₂. Here, current intensity is fixed at 0.7 mA. Both responses to the chemical stimulus and to anodal current are increased with an increase of NiCl₂ concentration. The response to anodal current is larger than that to the chemical stimulus in the low-concentration range of NiCl₂; because anodal current with 10 mM NaCl induces appreciable responses even in the absence of NiCl₂, but 100 mM NaCl induces only a very small response.

The addition of uranyl acetate to a stimulating solution greatly affected both responses to chemical stimuli and anodal current. Fig. 4 shows the magnitudes of the responses to the chemical stimuli (0.4 M NaCl and 0.2 M MgCl₂) and electric current of constant intensity (0.7 mA) as a function of uranyl acetate concentration where the magnitude of each response in the absence of uranyl acetate is taken as a unit in the ordinate. Both curves for chemical responses to 0.4 M NaCl and electrical responses with 10 mM NaCl show a peak at ~10⁻⁶ M uranyl acetate, whereas both curves for chemical responses to 0.2 M MgCl₂ and electrical responses with 5 mM MgCl₂ show no peak and the responses decrease monotonically with an increase of uranyl acetate concentration >3 × 10⁻⁶ M.
The above results indicate that the effects of various modifications of frog gustatory receptors on the responses to anodal current are quite similar to those on the chemical responses. There is a possibility that an electrical response is induced by salts accumulated on the tongue surface by iontophoresis. This possibility was checked by the experiments shown in Fig. 5. As shown in Fig. 5 A, the magnitude of the response to CaCl$_2$ shows a maximum response at ~2 mM and decreases with a further increase of CaCl$_2$ concentration. As expected from the above relation, application of 0.1 M and 0.5 M CaCl$_2$ to the tongue adapted to 50 mM CaCl$_2$ brought about no response. Fig. 5 B shows a typical record where 1 M CaCl$_2$ was applied, at the point indicated by an arrow, to the tongue that had been adapted to 50 mM CaCl$_2$,

indicating that 1 M CaCl$_2$ brought about only a small response. On the other hand, electrical stimulation of the tongue adapted to 50 mM CaCl$_2$ gave a large response as shown in Fig. 5 C. This suggests that accumulation of salts on the tongue surface is not the cause of generation of the response to anodal current. All results shown in Fig. 5 were confirmed with four frogs.

In the above experiments, the frog tongue was stimulated by anodal current. As shown in Fig. 1 C, cathodal stimulation induced only small responses. In Fig. 6, 1 mM CaCl$_2$, 0.3 M ethanol, and distilled water were first applied to the tongue and cathodal current was then applied after the responses induced by the chemical stimuli approached the steady-state level. The responses were suppressed by cathodal stimuli, and with cessation of the cathodal current, the responses were recovered. Similar results were obtained with four frogs.
There is a possibility that the responses to electric current were brought by direct stimulation of the gustatory nerve with electric current. To check this possibility, the frog lingual artery was perfused with artificial Ringer's solution and electrical stimulation of the tongue was carried out under the condition where release of a chemical transmitter from taste cells was blocked. In a separate study, we showed that elimination of Ca\(^{2+}\) from the perfusing solution or addition of Ca-channel blockers such as CdCl\(_2\), MnCl\(_2\), and

\[^1\] Nagahama et al., manuscript in preparation.
verapamil reversibly suppressed the gustatory nerve responses to salts, sugars, amino acids, and distilled water. Fig. 7A shows that a decrease of Ca\(^{2+}\) concentration by addition of 1 mM EGTA to a perfusing solution greatly
A)  
- a) Ringer
- b) +1 mM EGTA
- c) -EGTA

B)  
- a) Ringer
- b) +0.1 mM CdCl₂
- c) -CdCl₂

C)  
- a) Ringer
- b) +0.1 mM Verapamil
- c) -Verapamil
suppressed both responses to 0.4 M NaCl and to anodal current with 10 mM NaCl; when EGTA was removed from the perfusing solution, both responses recovered. Addition of Ca-channel blockers (0.1 mM CdCl₂ and 0.1 mM verapamil) to a perfusing solution also reversibly suppresses both the response to NaCl and the response to anodal current with 10 mM NaCl, as shown in Fig. 7B and C. Similar results to those shown in Fig. 7 were obtained with four frogs. The above results rule out the possibility that the responses to anodal current are induced by direct stimulation of the gustatory nerve with electric current.

**DISCUSSION**

Our results show that anodal stimulation of the frog tongue induces responses similar to responses to chemical stimuli, although the former appear slightly more transient than the latter. As shown by Fig. 1, the responses to anodal current depend on the ion species in an adapting solution of the tongue. For example, electrical stimulation with 5 mM MgCl₂ brings about a much larger response than with 10 mM NaCl at all current intensities. Because Mg²⁺ has a larger Stokes' radius than Na⁺, Mg²⁺ may be less permeable to the cell membrane than Na⁺. Furthermore, electrical stimulation with 10 mM choline chloride or 10 mM tetraethylammonium chloride (which may barely permeate the membrane) causes the responses. Therefore, the difference in the magnitude of the electrical responses cannot be explained in terms of the difference in permeability of cations to the membrane. In the frog, MgCl₂ always induces much larger responses than NaCl at equal electrochemical equivalents. This suggests that a common mechanism exists between electrical and chemical responses. The results described above are consistent with those reported by Pfaffmann and Pritchard (1980): with equal current intensity, the response of rat chorda tympani to anodal current with NaCl was greater than the response with KCl, whereas a chemical response to NaCl was greater than to KCl in the rat.

In a previous paper (Kashiwagura et al., 1977), we suggested that the treatment of the frog tongue with ANS removes Ca²⁺ from the receptor membrane and therefore a conformational change of the receptor domains for salts is easily induced by adsorption of salts to the domains. The present results indicate that the responses to anodal current with 10 mM NaCl are also enhanced after ANS treatment. This also suggests that electrical responses are induced by a mechanism similar to that for chemical responses.

After one treatment with ANS, frog tongue exhibits enhanced responses to salt stimuli unless Ca²⁺ is applied to the tongue. On the other hand, the tongue exhibits enhanced responses in the presence of NiCl₂, but with removal of NiCl₂ from the tongue surface, responses return to the original level (Kashiwagura et al., 1978). That is, the enhancement of the responses by...
NiCl₂ is not brought about by removal of Ca²⁺ from the receptor membrane. Probably NiCl₂ acts on the receptor domains so that a conformational change is easily induced by adsorption of salts. As similar to the case of ANS treatment, electrical responses with NaCl are also enhanced by the presence of NiCl₂.

The mechanism of action of uranyl acetate is unknown. The enhanced or suppressed responses to salt stimuli in the presence of uranyl acetate recover to the original level immediately after elimination of uranyl acetate from the tongue surface. Thus, uranyl acetate does not appear to penetrate taste cells but acts on the taste cell membrane. The enhance and suppressive effects of uranyl acetate on the electrical responses with NaCl are similar to those on chemical responses to NaCl and the effects on the electrical responses with MgCl₂ are similar to those on chemical responses to MgCl₂. Thus, responses to electrical stimuli under various modifications are quite similar to chemical stimuli in all cases examined in this study.

As described in the Introduction, a number of hypotheses on a mechanism of "electrical taste" have been advanced. The possibility that electrical taste is the result of stimulation of taste receptors by specific products of the electrolysis of the saliva can be ruled out by the present results which indicate that the magnitude of the responses to anodal current is highly dependent on the species of ions in an adapting solution.

Our results have shown that a decrease of Ca²⁺ concentration in a perfusing solution or addition of Ca channel blockers to the perfusing solution reversibly suppresses both responses to the chemical stimulus and to anodal current. This suggests that Ca²⁺ is involved in the transduction process of electrical responses as well as chemical responses, although we notice that some of the blockers may act on the Na channel under certain conditions (Baker et al., 1973; Kostyuk and Krishtal, 1977; Nachshen and Blaustein, 1979; Pellmar and Carpenter, 1979). Thus, the present results rule out the possibility that electrical responses are brought about by direct stimulation of the gustatory nerves with electric current.

There is a possibility that salts accumulated on the tongue surface by iontophoresis stimulate the receptors. The results shown in Fig. 5, however, suggest that accumulation of salts by iontophoresis is not a main cause of electrical responses. Whether or not salts are accumulated on the tongue surface by iontophoresis can be subjected to theoretical consideration; the actual system of electrical stimulation is rather complex for theoretical treatment. It is not known which ions carry the electric current through the cell membrane. Ions contained in the mucus on the surface of the tongue as well as ions in an adapting solution must be taken into consideration as current carriers across the membranes, especially when the tongue is adapted to a solution of salts having impermeable ions. For theoretical analysis, a simplified model system is presented in the Appendix where concentration polarization occurring at the membrane-solution interface as electric current flows through the membrane is analyzed theoretically in a system where the two aqueous solutions of 1:1-type electrolyte are separated by a negatively charged mem-
brane. The theoretical analysis indicates that the concentration at the membrane-solution interface at the anode side is lower than the concentration in the bulk solution. If the theoretical treatment described in the Appendix is applicable to the electrical stimulation of the tongue, the concentration of salts at the tongue surface-solution interface becomes lower than that in an adapting solution during anodal stimulation and becomes higher during cathodal stimulation. Therefore, it is unlikely that responses to anodal current are produced by salts accumulated on the tongue surface. On the other hand, the small responses produced by cathodal stimulation (see Fig. 1 C) may have been induced by salts accumulation on the tongue surface.

In a previous paper (Aiuchi et al., 1976), we proposed a hypothetical mechanism for taste transduction. The responses to electric current might be explained similarly. Fig. 8 shows a schematic diagram illustrating the mechanism of generation of gustatory nerve responses to chemical stimuli and electric current. Notations in the figure are described in the text.

**Figure 8.** A hypothetical model and equivalent circuit illustrating a mechanism of generation of gustatory nerve responses to chemical stimuli and electric current. Notations in the figure are described in the text.
and induces Ca influx from intercellular medium into the taste cell. This Ca influx will lead to a release of a chemical transmitter. If, instead of chemical stimulation, the electric current, \( i_{b} \), is supplied to the taste cell by anodal stimulation of the tongue, response similar to that induced by chemical stimulation will be induced. Cathodal current cancels the electric current produced by chemical stimuli to the tongue surface and thereby suppresses the responses induced by chemical stimuli.

Chemical stimulation of the frog tongue by 0.2 M MgCl\(_2\) elicited a much larger response than that by 0.4 M NaCl. This suggests that the number of the receptor domains whose conformation is changed by adsorptin of Mg\(^{2+}\) is larger than that by adsorption of Na\(^{+}\) under the condition employed and/or the extent of the conformational change induced by adsorption of Mg\(^{2+}\) is larger than that by Na\(^{+}\). A similar relation may hold in the condition of electrical stimulation where the tongue is adapted to 5 mM MgCl\(_2\) and 10 mM NaCl, although concentrations of both salts are one-fortieth of those for chemical stimulation. The conformational changes of the receptor domains may lead to easier flow of the electric current across the taste cell membrane and then anodal stimulation of the tongue adapted to 5 mM MgCl\(_2\) will elicit a larger response than that to 10 mM NaCl. This explanation suggests that anodal stimulation to 5 mM MgCl\(_2\) induces a larger current across the taste cell membranes than with 10 mM NaCl at equal voltage. One may consider that the above explanation is not consistent with the experimental results which show that an imposed identical current (0.7 mA) has different effects with different salts perfusing the tongue. However, it should be noted that the ratio of area occupied by taste cells to the total surface area of the tongue is extremely small, thus, most of the current applied to the tongue flows through other areas than the taste cells. The experimental results, therefore, do not rule out the possibility that more current may flow through the taste cells with 5 mM MgCl\(_2\) than with 10 mM NaCl, even when the identical currents are applied to the tongue. However, the above mechanism is still highly speculative and further study will be needed to confirm the mechanism.

The mechanism by which ANS, NiCl\(_2\), and uranyl acetate enhance the responses to certain species of salt stimuli and to anodal current is unknown. One possible explanation is as follows: The treatment of the tongue with ANS or the presence of NiCl\(_2\) and uranyl acetate leads conformational changes of the receptor domains for certain species of salt stimuli and then electric current will flow more easily across the microvillus membrane, leading to enhancement of the responses.

**APPENDIX**

The concentration polarization that occurs at the membrane-solution interface as electric current flows has been analyzed theoretically and experimentally (Gregor and Peterson, 1964; Kobatake and Kamo, 1973). Here, we deal with a simple system where the two aqueous solutions of 1:1-type electrolyte are separated by a membrane bound between \( x = 0 \) and \( x = L \) when electric current is passed through the membrane (see Fig. 9). The membrane is assumed to be negatively charged like most biological membranes. The stagnant layer of thickness, \( \delta \), is adjacent to the membrane surface.
and the solution phases in the cathode and anode compartments placed in \( x < -\delta \) and \( x > L + \delta \), respectively, have a uniform concentration, \( C \). The salt concentrations at \( x = 0 \) and \( x = L \) are denoted by \( C' \) and \( C'' \), respectively. If the value of \( \delta \) is assumed to be small compared with \( L \) and then \( C' \) and \( C'' \) may be expanded in powers of the relative thickness of the stagnant layer (\( \nu = \delta/2L \)):

\[
C' = C + f(C)\nu \\
C'' = C - f(C)\nu,
\]

where \( f(C) \) represents the magnitude of the concentration polarization.

\[\text{Figure 9. A schematic diagram illustrating concentration polarization of electrolytes when electric current flows through a negatively charged membrane. The membrane is bound between } x = 0 \text{ and } x = L, \text{ and stagnant layers are placed between } x < -\delta \text{ and } x > L + \delta. C, C', \text{ and } C'' \text{ represent electrolyte concentrations in a bulk solution: at the membrane-solution interface, at the anode side, and at the membrane-solution interface at the cathode side, respectively.}\]

The activity \( a_i \) and the mobility \( u_i \) of ion species (\( i = \pm \)) in the membrane are represented as follows:

\[
a_+ = a_- + \phi X, \quad a_- = C_- \\
u_+C_+ = u^0_+(C_- + \phi X), \quad u_-C_- = u^0_-C_+.
\]

Here, \( u^0_i \) stands for the mobility of \( i \)-th ion in the bulk solution, \( \phi X \) is the effective fixed charge density. Setting up the flux equation of movable ions in the membrane phase and assuming the condition of steady state, we obtain the following expression for \( f(C) \) (Kobatake and Kamo, 1973):

\[
f(C) = -\frac{L}{RT} \frac{u^0_+ + u^0_-}{u^+_+u_-^-} (\tau^+ - \alpha)I,
\]

where \( \tau^+ \) and \( \alpha \) stand for the transference number of cations relative to the local center of mass in the membrane and that in the bulk solution. \( \tau^+ \) is defined by \( u_+C_+/ (u_+C_+ + u_-C_-) \) and \( \alpha \) is given by \( u^0_+/ (u^0_+ + u^0_-) \). \( I \) is the electric current intensity.
Eq. 4A can be rewritten as

\[
f(C) = \frac{L}{RT} \left( \frac{u_{+}^{0} + u_{-}^{0}}{u_{+}^{0} u_{-}^{0}} \right) \left[ \frac{u_{+}}{u_{+} + (u_{-} C_{-}/C_{+}) u_{-}} - \frac{u_{+}^{0}}{u_{+}^{0} + u_{-}^{0}} \right].
\]  

(5A)

The relation in Eq. 4A indicates that \( C_{-}/C_{+} \) is \(<1 \) in a negatively charged membrane, and hence \( f(C) \) is always negative. Therefore

\[
C' < C, \quad C'' > C.
\]  

(6A)

The above relation implies that concentration at the membrane-solution interface at the anode side is lower than concentration in the bulk solution, and the concentration at the cathode side is higher than concentration in the bulk solution.

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