a three-dimensional fringing effect and cannot be obtained with a two-dimensional theoretical formulation.

We might also note the following points in Ref. 1: (i) the turbulent flow correlation Eq.(46) is inconsistent with Eqs.(42) and (44); (ii) the results plotted on Fig. 7 do not agree numerically with either the given correlation equations [Eqs.(42) to (46)] or with the same results plotted on Figs. 5 and 6; (iii) the curve purporting to represent Eq.(46) on Fig. 7 must be mislabelled. Eq.(46) would be a straight line on a log-log plot.

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LIMITING CURRENT IN ELECTRODIALYSIS CONTROLLED BY DIFFUSION AND MIGRATION*

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Making a further study with respect to some comments from Profs. Sonin and Probstein, we found few minor mistakes in our previous conclusions in laminar region, which are corrected in this paper. However, we confirmed that the outline and the main conclusions should leave as they are, although there still exists question on the physical meaning of the term $\hat{C}_i \nabla \hat{\phi}$, which is related to the ionic mass transport in turbulent flow.

I) Regarding the definition of limiting current and limiting potential

In this study, the empirical limiting point (L.C. and L.P.) was defined as the first point where the I - V curve** touches the tangent of its lower plateau^{5,6}. According to our numerical calculations of laminar flow ($W/D \gg 1$), this definition seems to correspond to a condition under which the boundary concentration becomes zero halfway down the test section (see Fig. 2).

II) Replies to three comments

- (a) The analytical result by Sonin et al.¹² agreed with our experimental results, though they introduced such assumptions as $\mathcal{D}_+ = \mathcal{D}_- = \mathcal{D}$, $z_+ = z_- = z$.
- (b) The authors believe that the instantaneous concentration of the transferring ionic species C_i and the local electric potential ϕ etc. can be expressed as

$$\begin{aligned} C_i &= \bar{C}_i + \hat{C}_i \\ \phi &= \bar{\phi} + \hat{\phi} \end{aligned} \quad (1)$$

* Received on May 22, 1971.

** The I - V curve of electrodialysis of NaCl solution has two convexes for the L. C. and the corresponding L.P. The lower convex corresponds to the L.C. of Na^+ ion on the surface of a C.E.M., and the higher one to the L.C. of Cl^- ion on the surface of an A.E.M.. According to Eqs.(34), (35) of Ref. 4, the ratio of these two L.C.s is

$$\frac{I_L(\text{Cl}^-)}{I_L(\text{Na}^+)} = \left(\frac{1 - \frac{z_- \mathcal{D}_-}{z_+ \mathcal{D}_+}}{1 - \frac{z_+ \mathcal{D}_+}{z_- \mathcal{D}_-}} \right) = - \frac{z_- \mathcal{D}_-}{z_+ \mathcal{D}_+} \approx 1.5$$

which quite agreed with the experimental results.

All the fluctuations of these intensive variables, of course, are brought about directly by the velocity fluctuation. Therefore, there seems no doubt about the appearance of the term $\hat{C}_i \nabla \hat{\phi}$ in Eq.(12) of Ref. 4. We assumed that

$$\hat{C}_i \nabla \hat{\phi} = K C_i' \nabla \phi', \quad (2)$$

where C_i' and ϕ' are the root mean square of their fluctuations, respectively, that is $C_i' = \sqrt{\overline{\hat{C}_i^2}}$, $\phi' = \sqrt{\overline{\hat{\phi}^2}}$. K is a constant.

Referring to some reports on electric conductivity, we considered that the scales of fluctuation, C_i' , $\nabla \phi'$, could be proportional to their time-smoothed values, and introduced intuitively

$$\overline{\hat{C}_i \nabla \hat{\phi}} = \varepsilon_\phi(y^+) \bar{C}_i \nabla \bar{\phi} \quad (3)$$

ε_ϕ could be determined as an empirical function of position against the time-smoothed value of transferring component $\bar{C}_i$. ε_ϕ means the superficial increase rate of the time-smoothed conductivity.

We also considered another expression based on Prandtl's mixing length theory¹⁴), and found that it contained the product of two terms, $d\bar{C}_i/dy$ and $d^2\bar{\phi}/dy^2$. However, it was so complicated that the physical meanings were not understandable.

We are aware of a more advanced consideration to deal with the term $\hat{C}_i \nabla \hat{\phi}$, and now consider that the limiting position, X_0/L , is another important factor

Fig. 1 Signal flow chart for computing the laminar mass transfer rate at the limiting current density

in describing the I - V characteristics of the turbulent region^{4a)} (compare Fig. 3 with Fig. 2).

Furthermore, we want to point out that the theory of nonisotropic "wall" turbulence described only by the time-smoothed values should not be applied to the region near the inlet of mass transfer, where $\bar{C}_i=0$. Because the time-smoothed values are defined in a time T , where $T_1 \ll T \ll T_2$ ⁴⁾, their variation much less than a microscopic scale s should not be discussed, where $T_1 \bar{u}(y) \ll s \ll T_2 U_o$ or $\lambda \ll s \ll A$. Here, λ and A mean the microscale of eddy and the integral scale of eddy, respectively³⁾.

However, the region of transient state of mass transfer at the inlet is very short, i.e. $x/D \ll 1$, in the case of turbulent flow with high Schmidt number ($> 5 \times 10^2$)¹³⁾.

It might be possible to describe turbulent ionic mass transfer without use of $\epsilon\phi$, if ϵ_D in $0 \leq y^+ \leq 2$ is corrected to such a function as was introduced by Lin et al.⁸⁾ with the assumption of either $\epsilon_D = \epsilon_M$ ⁸⁾ or $\epsilon_D \neq \epsilon_M$ ⁹⁾.

Judging from the experimental studies of the turbulent velocity profile,^{1,3,7,11)} it was not possible to measure $\bar{u}(y)$ so accurately in $0 \leq y^+ \leq 3$ that the value of ϵ_M can be decided as a function of y^+ definitely.

It is reported that an adiabatic compression by ultrasonic waves at about 10^2 KHz raised the conductivity of an aqueous salt solution because of direct pressure influence and of temperature increase, etc., and that the increment was in proportion to the applied wave intensity but was independent of wave frequency²⁾. This effect seems to be somewhat similar to that by turbulent fluctuation.

(c) All the equations from Eq.(42) to Eq.(46) in Ref. 4 are empirical ones.

In our computation, the numerical integration of Eq.(37) or Eq.(33) was carried out by trapezoid approximation. The value of the "limiting potential" was not diverged.

We assumed that the surface concentration at one side of the channel $\bar{C}_w$ became zero at the limiting current. If the weak degree of ionization of neutral water, H^+ and OH^- , is taken into account, that boundary condition might have to be replaced by

$$\bar{C}_w = 10^{-10} \text{ (g} \cdot \text{ion/cc)} \simeq [H^+] \div [OH^-]$$

According to our finite difference method, almost no difference occurred between the results obtained from $\bar{C}_w = 0$ and from $\bar{C}_w = 10^{-10}$.

The numerical analyses of ionic mass transfer for laminar flow were only done for $W/D \gg 1$. The velocity profile was assumed to be parabolic and finite difference equations based on Laaonen's 4-points implicit form were solved by Thomas' method.

The signal flow chart for computing the laminar mass transfer rate at the limiting current density is shown in Fig. 1. The calculated examples of the current-voltage characteristics for $(W/D) \gg 1$ are shown in Figs. 2 and 3. The effects of the mean flow velocity, the length of the test section and the channel thickness agree well enough with the experimental results.

As the three-dimensional fringing effect of current was observed experimentally in the laminar region, many measurements were carried out for the various aspect ratios, and the asymptotic value of current for $W/D \gg 1$ was accurately obtained from their extrapolation.

As stated above, our empirical method to determine the limiting point seems to correspond to the case of $X_o = 0.5 \cdot L$, where L is the length of the test section and X_o is the distance from the inlet to a position where the boundary concentration becomes zero.

If the current is controlled only by electromigration (electric conduction), this effect is evaluated by the potential theory using the Schwarz-Christoffel transformation¹⁰⁾ and is given by

$$\frac{R_\infty}{R} = \left(\frac{\pi}{2\epsilon} \right) \frac{K(\tanh^2 \epsilon)}{K(1/\cosh^2 \epsilon)} \quad (4)$$

where $R_\infty = (D/\kappa WL)$, $\epsilon = (\pi W/2Df_e)$ and $K(m)$ is the complete elliptic integral of the first kind. f_e is an adjustable constant which indicates an amount of the fringing effect caused by diffusion. If we put $f_e = 1.0$, Eq.(4) indicates the effect of fringing of the electric conduction¹⁰⁾. However, the effect of the aspect

Fig. 2 Three examples of current-voltage characteristics and their limiting points computed by the laminar theoretical model

Fig. 3 Two examples of current-voltage characteristics and their limiting points computed by the turbulent theoretical model. The results are very different from those for laminar flow

$\frac{R_{\infty}}{R} = \left(\frac{\pi}{2\epsilon} \right) \frac{K(\tanh^2 \epsilon)}{K(1/\cosh^2 \epsilon)}$, where $R_{\infty} = (D/\kappa WL)$, $\epsilon = (\pi W/2Df_c)$ and $K(m)$ is the complete elliptic integral of the first kind. f_c is an adjustable constat.

Fig. 4 The effect of aspect ratio on the current density in laminar flow

ratio on the current density in laminar flow agreed quite well with Eq.(4) by putting $f_c=5.0$, as shown in Fig. 4. This result suggests that the effect of aspect ratio may be greater in a system controlled by electromigration and diffusion than in a system controlled only by electromigration.

More advanced details on these subjects will be reported in the near future^(4a).

All our corrections to the previous report⁽⁴⁾ are shown as follows;

* all the subscripts of $z_i \mathcal{D}_i$ ($i=+$ or $-$) in Eqs.(34) and (35) should be interchanged with each other.

* Eq.(42) of Ref. 4 should be corrected as

$$St_i = 5.0 \left(1 + 0.8 \frac{D}{W} \right) \left(\frac{L}{D} \right)^{-0.33} \xi_i \quad 10 \leq Re \leq 10^3 \quad (42)$$

* Eq.(43) of Ref. 4 should be corrected as

$$Sh_{Al} = 4.0 \left(1 + 2.0 \frac{D}{W} \right) \left(\xi_i \frac{L}{D} \right)^{-0.42} \quad 10 \leq Re \leq 10^3 \quad (43)$$

* Eqs.(45) and (46) of Ref. 4 should be corrected as

$$\Phi_i = \left(\frac{L}{D} \right)^{0.22} \left(\frac{1}{Pe_A} \frac{L}{D} \right)^{-0.32} \quad 10 \leq Re \leq 10^3 \quad (45)$$

$$\Phi_i = 0.075 Pe_A^{0.72} Sc_A^{-0.47} \quad 10^3 \leq Re \quad (46)$$

* Fig. 7 of Ref. 4 should be corrected to Fig. 5 in this paper.

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Fig. 5 Characteristics of the limiting voltage for two-dimensional channel flow
(Fig. 7 of Ref. 4 should be corrected to this Figure.)

Nomenclature

Unless otherwise noted in this paper, all quantities are defined in Reference 4.

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