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New Interpretation of the Transfer Coefficient in Electrochemistry

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A new theory and interpretation of the transfer coefficient based on electrostatic screening of the electrode potential is proposed. A new theory constructed based on the Debye–Hückel theory could quantitatively explain the dependence of transfer coefficient on the ionic strength of the electrolyte solution. The experimental results of the transfer coefficient for hydrogen evolution and Fe^{3+} / Fe^{2+} redox reactions were analyzed by this theory. It demonstrates that the transfer coefficient represents the electrostatic screening of the electrode potential by ions in the electrolyte solution near to the electrode. It is also shown theoretically that the information on the "electron transfer distance" is contained in the transfer coefficient.

In electrode kinetics, the Butler–Volmer equation relates the electrochemical rate, i.e. the current density (i), to the overpotential (η).[1,2] It is

$$i = i_0\left[\exp -\frac{e\alpha}{kT}\eta - \exp -\frac{e(1-\alpha)}{kT}\eta\right]. \tag{1}$$

Equation 1 applies to simple one-step electron transfer reactions. Since this equation can well explain the current-overpotential behaviors in many systems, it is widely accepted and presently used a by a number of electrochemists. However, the Butler–Volmer equation is a phenomenological one based on the transition state theory.[1] The parameter α in Eq. 1 is called the transfer coefficient or symmetry factor. It is fair to regard transfer coefficient (α) as the heart of electrode kinetics.[3] In the electrochemical theory based on the transition state theory, the transfer coefficient α is considered to indicate the symmetry of the potential barrier of the transition state of electron transfer at the electrode.[1,2,3] Figure 1 shows the relation between the transfer coefficient and the symmetry of the potential curve at the transition state in electrochemistry based on the transition state theory.[1]

Recently, one of the present authors (T.S.) proposed a theory of quantum mechanical electron transfer at metal electrodes.[5] In this theory a quantum mechanical Butler–Volmer equation is derived in the weak coupling case where the overlapping between the distribution function of electrons in the electron donor (metal electrode in the case of cathodic electron transfer reaction) and the distribution function of electron acceptor is weak. Interestingly, the quantum mechanical Butler–Volmer equation is of the same form as Eq. 1. In the quantum mechanical Butler–Volmer equation, a parameter α, corresponding to the transfer coefficient, appears. However, the parameter α in the quantum mechanical Butler–Volmer equation represents the electrostatic screening of the electrode potential by ions in the electrolyte solution layer between the metal electrode and the electron acceptor. Therefore, it has a quite different physical meaning compared with that of the transfer coefficient in Eq. 1 based on transition state theory.

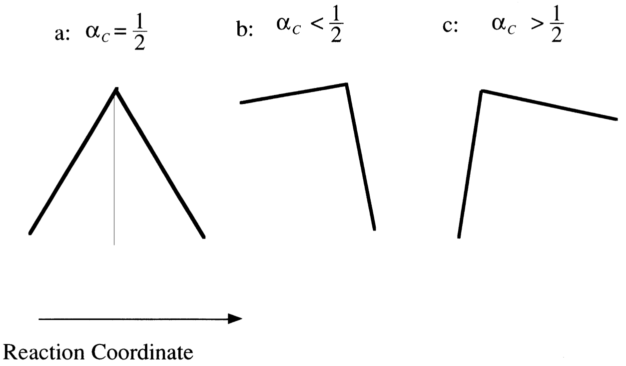

Fig. 1. In the classical electrochemistry based on the transition state theory transfer coefficient α_C is a measure of the symmetry of the energy barrier at the transition state. In this figure the shape of the potential barrier is drawn by straight lines for simplicity.

$$\text{a: for } \alpha_C = \frac{1}{2},\ \text{b: for } \alpha_C < \frac{1}{2},\ \text{c: for } \alpha_C > \frac{1}{2}.$$

In the present manuscript, we propose a new theory of the transfer coefficient based on the Debye–Hückel theory. We also show that the magnitude of the transfer coefficient depends on the ionic strength of the electrolyte, and can be evaluated quantitatively by this new theory.

Experimental

The electrochemical reactions of hydrogen evolution and redox reactions of $Fe^{3+} + e \longleftrightarrow Fe^{2+}$ were studied at a Pt plate electrode (purity, 99.98%; surface area, 0.332 cm^2) as a working electrode. Before electrochemical reactions, Ar gas was bubbled through the aqueous electrolyte solutions to remove oxygen. A <Ag|AgCl| saturated KCl> electrode was used as a reference electrode and a Pt plate electrode was used as an anode. Current -voltage curve measurements were carried out at 25 °C by using a potentiostat/

[#] Emeritus Professor of Tokyo Institute of Technology galvanostat (Hokuto, HA-501) connected with a function generator (Hokuto, HB-105) at a sweep rate of 50 mV/s.

Aqueous electrolyte solutions of various concentrations of HCl, H_2SO_4, HNO_3, Fe^{2+}, and Fe^{3+} were prepared from reagent grade chemicals (Kanto Chemicals, Ltd.) and distilled water (Wako Pure Chemicals, Ltd.). Solutions of Fe^{2+} and Fe^{3+} were prepared from reagent grade $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ (Kanto Chemicals, Ltd.), respectively. Various amount s of KCl or NaCl were added to the aqueous electrolyte solutions to change their ionic strength.

Theoretical Consideration

Let us consider the following cathodic one electron transfer reaction at a metal electrode:

$$A + e \longrightarrow A^{-\bullet}, \tag{2}$$

where A represents an electron acceptor molecule or ion near to the electrode surface in the electrolyte and e represents an electron from the metal electrode. The cathodic current flows accompanying this cathodic reaction.

In electrochemistry based on the transition state theory the cathodic current (i_c) is expressed by the following equation: [1]

$$i_c = i_0 \exp -\frac{e\alpha_c}{kT}\eta, \tag{3}$$

where i_c and i_0 represent the cathodic current and the exchange current, respectively. η represents the overpotential; k is the Boltzmann constant and T is the absolute temperature; and e is the electronic charge. The parameter α_c is called the transfer coefficient. Suffix c of the transfer coefficient (α_c) reprents the transfer coefficient in classical electrochemistry based on the transition state theory. Here we call it here classical electrochemistry in order to distinguish it from the quantum mechanical electron transfer theory proposed by one of the present authors (T.S). Suffix c of α_c is used to distinguish the transfer coefficient from the screening factor (α) which is introduced in the quantum mechanical electrode theory.[5,6]

In the quantum mechanical electrode theory, the cathodic current i_c is expressed in the weak coupling case by the following equation: [5]

$$i_{cv} = i_0 \exp -\frac{e(1-\alpha_{fi})}{kT}\eta. \tag{4}$$

Here the weak coupling case occurs when the overlapping between the state density of electron accepting state and the distribution function of free electrons in the metal electrode is weak.[5] We assume the weak coupling case throughout this manuscript. In Eq. 4 i_0 is the exchange current and α_{fi} represents the shielding factor of the electrode potential imposed on the electrode. Parameter α_{fi} is defined as

$$\alpha_{fi} \equiv \alpha_f - \alpha_i \tag{5}$$

Where α_f and α_i represent the shielding factor of the electrode potential at the final state and the initial state of the electron transfer, respectively. At the initial state of electron transfer in cathodic electron transfer a transferred electron exists in the metal electrode and is absent at the electron acceptor A. At the final state of electron transfer, an electron is transferred from the metal electrode to electron acceptor A.

At the final state of the electron transfer, the electron energy level of the electron acceptor is influenced by $-e\alpha\eta$ $(0 < \alpha < 1)$ due to the electrostatic shielding at the electron acceptor near to the electrode surface.[5,6] Consequently, in the cathodic electron transfer reaction of Eq. 2, it is satisfactory to take into consideration the electrostatic screening at the final state of the electron transfer, because the electron energy level of the electron acceptor is influenced by the electrostatic screening at the final state of the electron transfer.[6]

Therefore, we may assume in Eq. 5

$$\alpha_{fi} = \alpha_f = \alpha,\ \alpha_i = 0. \tag{6}$$

In the quantum mechanical electrode theory the exchange current (i_0) can be expressed analytically by the following equation: [6]

$$i_0 = \frac{2\pi e}{\hbar} v^2 C_A \rho(E_f) \exp -\frac{\Delta E}{kT}, \tag{7}$$

where v represent the electron exchange integral of an elecron acceptor with free electrons of the metal electrode; $\rho(E_f)$ represents the state density of electrons in the metal electrode at the Fermi level (E_f); [5] C_A represents the concentration of the electron acceptor A near to the electrode surface; and ΔE represents the activation energy of the exchange current.[6] As is given in Eq. 7, the exchange current i_0 can be expressed in an analytical form in the quantum mechanical electrode theory, whereas it can not be described in an analytical form in classical electrode theory based on transition state theory.[1–4]
It is noted that Eq. 4 is of the same form as Eq. 3.
When Eq. 6 is used in Eq. 4,

$$i = i_0 \exp -\frac{e(1-\alpha)}{kT}\eta \tag{8}$$

is obtained.[6] A comparison of Eq. 8 with Eq. 3 gives

$$\alpha_c = 1 - \alpha. \tag{9}$$

Difference in the Physical Meaning between α_c and α. Interestingly the physical meanings of α_c and α are quite different. In classical electrochemistry the transfer coefficient (α_c) indicates the symmetry of the potential curve of the transition state,[1,2] as shown in Fig. 1. On the other hand, α represents the screening factor of the electrode potential imposed on the electrode in the quantum mechanical theory of electrode reaction.[5,6] When the overpotential η is imposed on the electrode, η is not imposed on the electron acceptor A but $\alpha\eta$ $(0 < \alpha < 1)$ is imposed on the electron acceptor A, due to screening of the potential. Consequently, the energy level of the electron acceptor shifts by $-\alpha e\eta$ $(0 < \alpha < 1)$, whereas the energy level of electrons in the metal electrode shifts by $-e\eta$. The energy level of the electron acceptor A (E_a) can be written as

$$E_a = E_a^0 - e\alpha\eta, \tag{10}$$

where E_a^0 represents the energy level of the electron acceptor in the absence of an overpotential (η).[6] Thus, the energy gap

(ΔE) between E_a and the Fermi level of the metal electrode is

$$\begin{aligned}\Delta E \equiv E_a - E_f &= E_a^0 - e\alpha\eta - (-eV) \\ &= E_a^0 + eV_{eq} + e(1-\alpha)\eta. \end{aligned} \tag{11}$$

In Eq. 11 we used the following relations for the electrode potential (V) and the overpotential (η):

$$E_f = -eV, \tag{12}$$

$$\eta = V - V_{eq}. \tag{13}$$

Here, V_{eq} represents the equilibrium potential. When a negative overpotential is imposed on the electrode, Eq. 11 can be written as

$$\Delta E = E_a^0 + eV_{eq} - e(1-\alpha)|\eta|. \tag{14}$$

Since $0 < 1 - \alpha < 1$ holds, the energy gap ΔE decreases with increasing $|\eta|$, as is seen in Eq. 14. This means that the increased $|\eta|$ makes the cathodic electron transfer take place more easily at the electrode.

Now let us consider the case of complete potential screening, i.e. $\alpha = 0$. In this case, the energy level of the electron acceptor (E_a) does not shift even under an imposed overpotential, as is seen from Eq. 10, whereas the Fermi level of the metal electrode moves by $-e\eta$. Therefore, in the case of complete potential screening, the decreasing rate of the energy gap (ΔE) shows the largest value, as can be seen in Eq. 14. In this case, cathodic electron transfer proceeds most efficiently. This situation is illustrated in Fig. 2a. On the contrary, in the absence of electrostatic screening, α is equal to 1. In this case Eq. 14 gives

$$\Delta E = E_a^0 + eV_{eq}. \tag{15}$$

Eq. 15 shows that the energy gap (ΔE) is constant and does not decrease even when the overpotential is imposed on the electrode. In this case cathodic electron transfer is not accelerated even by increasing the overpotential imposed on the electrode, because the energy gap (ΔE) is kept always constant. This unusual situation can be explained by the fact that the energy level shift of E_a is equal to the shift of the Fermi level of the metal electrode, as can be seen in Eq. 10.

In the case of the usual potential screening, $0 < \alpha < 1$ and $0 < 1 - \alpha < 1$ hold. In this usual case, the magnitude of the energy level shift of electrons in the metal electrode is larger than that of the electron acceptor. In this case, the energy gap (ΔE) decreases with increasing the overpotential, as can be seen in Eq. 14. Consequently, the increased overpotential makes the cathodic electron transfer proceed efficiently.

Figure 2b illustrates this situation. According to this model, the difference in the energy level shift is considered to be the reason for the electron transfer reaction at the metal electrode. In this model the transfer coefficient (α_c) represents the fraction of the electrostatic screening: complete screening corresponds to $\alpha_c = 1.0$, because of $\alpha = 0$ (see Eq. 9). $\alpha_c = 0$ represents the absence of electrostatic screening, because of $\alpha = 1.0$, (see Eq. 9). The above consideration indicates that the physical meaning of α is quite different from that of the transfer coefficient α_c, as an indicator of the symmetry of the energy barrier at the transition state of the electrode reaction, which has been explained based on the transition state theory.[1–4]

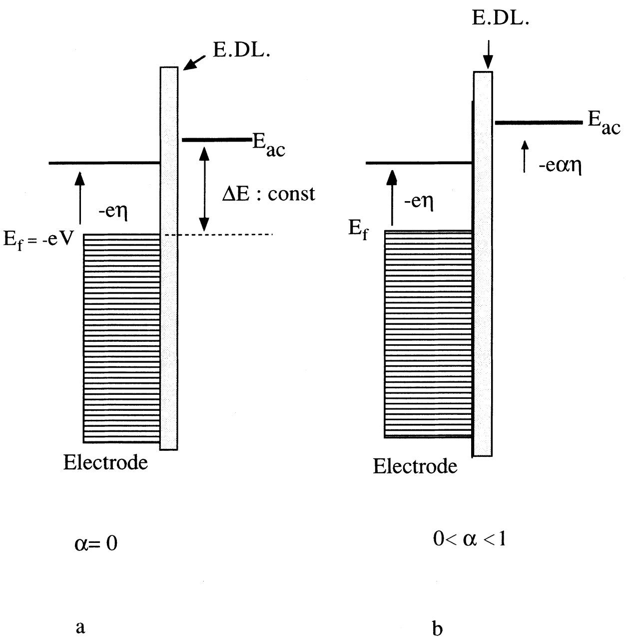

Fig. 2. In the quantum mechanical theory of electrode reaction, the over potential η is screened by ions in the electrolyte near to the electrode.
a: the case of the complete screening ($\alpha = 0$). Only the Fermi level of the metal electrode shifts to the negative direction under imposed overpotential, whereas the energy level of the electron acceptor E_a does not shift.
b: usual cases: $0 < \alpha < 1$. The Fermi level of the metal electrode shifts by $-e\eta$, whereas the energy level of the electron acceptor E_a moves by $-e\alpha\eta$.

Theory of the Screening Factor (α). Let's consider the screening of electrostatic potential at an electrolyte/electrode(metal) interface. In order to consider this problem, we assume that the electrolyte/electrode interface is composed of metal electrode/electric double layer/electrolyte. This model of the electrolyte/electrode interface is illustrated in Fig. 3.

The electrostatic screening of the electrode potential occurs at the electric double layer and the electrolyte outside the electrode. The electrode potential imposed on the electrode is screened by ions in the electrolyte layer between the electrode and electron acceptor A.[5,6] This situation resembles the electrostatic screening by free electrons in metal, i.e. the Thomas Fermi screening effect in solid state physics.[7]

In the model of the electrolyte/electrode interface illustrated in Fig. 3, the electrostatic screening of the electrode potential (α) is expressed by the product of the electrostatic screening factor by the electric double layer α_D and the electrostatic screening factor by the electrolyte outside of it (α_{EL}), as follows:

$$\alpha = \alpha_D \cdot \alpha_{EL}. \tag{16}$$

Here, α_D represents the electrostatic screening factor by the

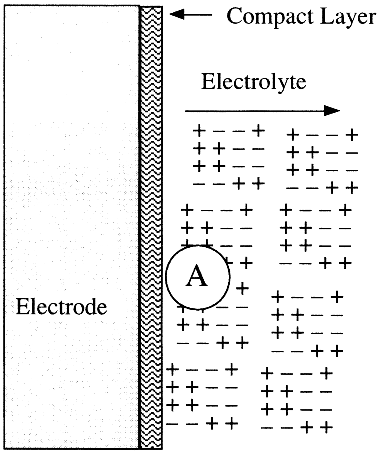

Fig. 3. The model of the electrolyte/ electrode interface for the electrostatic potential shielding near to the metal electrode.

electric double layer and α_{EL} represents the electrostatic screening factor by the electrolyte outside of it. The electrostatic screening in the electrolyte has already been studied in the Debye–Hückel theory for electrolyte solutions.[2]

According to the Debye–Hückel theory,[2] the electrostatic potential of an electric charge with Ze is screened in the electrolyte as

$$\varphi(r_0) = -\frac{Ze}{\varepsilon r_0}\exp -\chi r_0, \tag{17}$$

where φ (r_0) represents the potential by the charge Ze at r_0. The parameter r_0 represents the distance from the central electric charge Ze, ε is the dielectric constant of the electrolyte solution; χ^{-1} represents the Debye length ; and Debye length χ^{-1} corresponds to the Thomas Fermi's screening length in the electrostatic screening of the Coulombic potential in the metal.[7]

Eq. 17 indicates that the Coulomb potential of the central charge (*Ze*) is screened in the electrolyte and becomes zero at $r_0 \gg \chi^{-1}$.

From Eq. 17, α_{EL} can be given by the following equation.[2]

$$\alpha_{\mathrm{EL}} = \exp -\chi r_0. \tag{18}$$

According to the Debye–Hückel theory, the Debye length (χ^{-1}) can be expressed at room temperature (25 °C) as

$$\chi^{-1} = \frac{3.04\times 10^{-8}}{\sqrt{I}}\,\mathrm{cm}. \tag{19}$$

In the calculation of Eq. 19, $\varepsilon = 78.56$ was used for the dielectric constant of water. Here *I* represents the ionic strength of the electrolyte. The ionic strength of the electrolyte (*I*) is defined as[2]

$$I \equiv \frac{1}{2}\sum_i c_i z_i^2. \tag{20}$$

Here c_i represents the molar concentration of the *i*-th ion in the electrolyte and z_i the charge number of the *i*-th ion.

Eqs. 16, 18 and 19 yield

$$\alpha = \alpha_{\mathrm{D}}\cdot\exp -\frac{r_0}{3.04}\sqrt{I}. \tag{21}$$

In Eq. 21 the unit of r_0 is in Angstroms.

Taking the logarithm of Eq. 21, we obtain a useful equation for α,

$$\ln\alpha = \ln\alpha_{\mathrm{D}} - \frac{r_0}{3.04}\sqrt{I}. \tag{22}$$

Analysis of the Experimental Results

If the above new idea of electrostatic screening for α is correct, ln α should be proportional to $\sqrt{I}$ with a negative slope of $-\frac{r_0}{3.04}$, as can be seen in Eq. 22. We carried out experiments to measure the I dependence of α. Eq. 8 yields

$$\alpha = 1 + \frac{kT}{e}\cdot\frac{\partial \ln i_{\mathrm{C}}}{\partial\eta} = 1 + \frac{2.3kT}{e}\cdot\frac{\partial \log i_{\mathrm{C}}}{\partial\eta}, \tag{23}$$

which indicates that the screening factor α can be determined from the slope of the log i_{C} vs η curve. The screening factor (α) was determined experimentally by this method from the current-overpotential measurements. Once α is obtained, α_{c} is calculated from Eq. 9.

Figure 4 shows a ln α vs $\sqrt{I}$ plot for hydrogen evolution from an aqueous HCl solution. As shown in Fig. 4, experimental points of ln α are almost on a straight line. This result clearly supports our present model for the screening factor (α). If the present model is correct, ln α should change proportionally to $\sqrt{I}$.

The ionic strength (*I*) of the electrolyte solution can be changed by adding to the solution an electrolyte that is indifferent to the electrochemical reaction. When *I* is changed by this method, the screening factor α is expected to change according to Eq. 22. From this point of view, we changed the

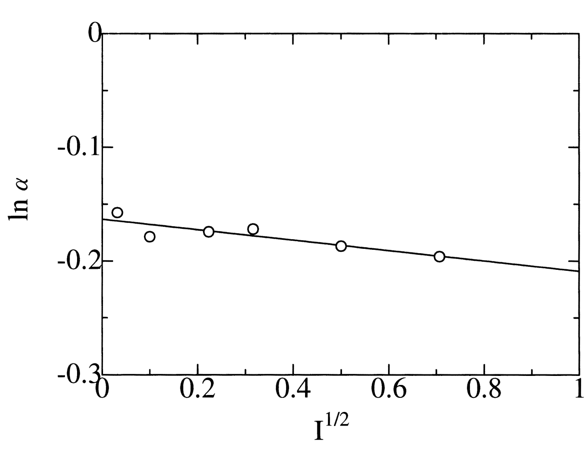

Fig. 4. ln α vs $I^{1/2}$ plot for hydrogen evolution at a Pt electrode from HCl aqueous solutions. The ionic strength *I* was changed by variing concentration of HCl. The solid line was determined by the method of least squares.

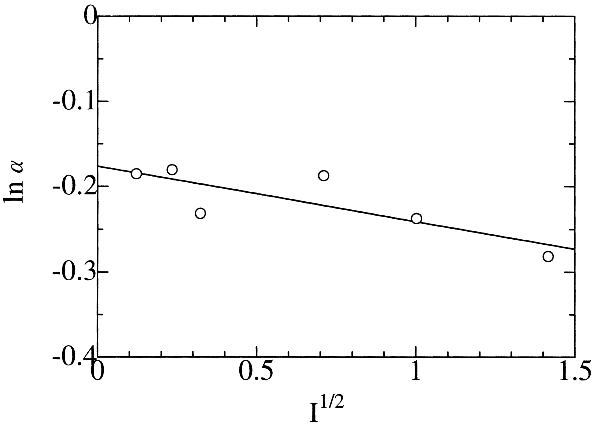

Fig. 5. ln α vs $I^{1/2}$ plot for hydrogen evolution at a Pt electrode from 0.005 M HCl aqueous solution + various amount of KCl. The ionic strength I of the electrolyte was changed by variing the amount of KCl added to 0.005 M HCl aqueous solution. The solid line was determined by the method of least squares.

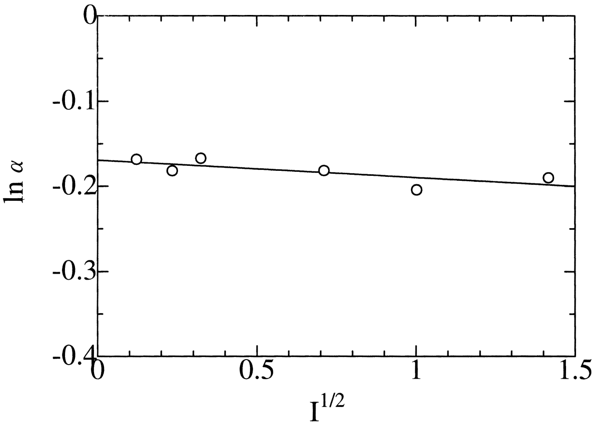

Fig. 6. ln α vs $I^{1/2}$ plot for hydrogen evolution at a Pt electrode from 0.005 M HNO_3 aqueous solution to which various amount of NaCl was added to change the ionic strength I of the electrolyte. The solid line was determined by the method of least squares.

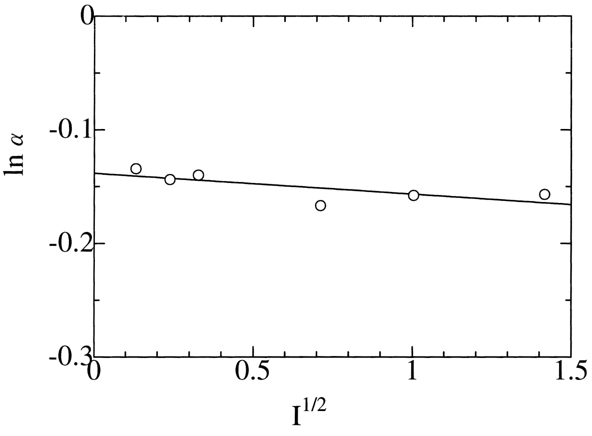

Fig. 7. ln α vs $I^{1/2}$ plot for hydrogen evolution at a Pt electrode from 0.0025 M H_2SO_4 aqueous solution to which various amount of NaCl was added to change the ionic strength I of the electrolyte. The solid line was determined by the method of least squares.

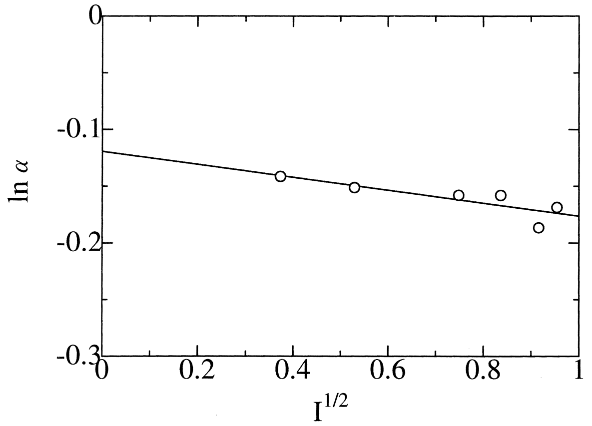

Fig. 8. ln α vs $\sqrt{I}$ plot for the one electron reduction of Fe^{3+} to Fe^{2+} at Pt electrode. The concentration of $FeNH_4(SO_4)_2$ was changed to vary the ionic strength of the Fe(III) solution.

ionic strength of the electrolyte solution by adding various amounts of KCl and NaCl to 0.005 M HCl aqueous solution. The result of adding KCl to a 0.005 M HCl aqueous solution is shown in Fig. 5. Similarly, various amounts of NaCl was added to 0.005 M HNO_3 aqueous solutions. The results are shown in Fig. 6. When various amounts of NaCl were added to 0.0025 M H_2SO_4 aqueous solutions in order to change I, α changed depending on I. The dependence of ln α on I is shown in Fig. 7.

As shown in Figs. 4, 5, 6, and 7, all the experimental points of ln α are almost on a straight line. These results indicates that ln α is proportional to $\sqrt{I}$, as predicted by the present theory, i.e. by Eq. 22. If the transfer coefficient is a measure of the symmetry of the potential barrier at the transition state, as explained in classical electrochemistry based on transition state theory,[1,2] the transfer coefficient would not change depending on the ionic strength, because the shape and the symmetry of the potential barrier is considered not to change depending on the ionic strength of the electrolyte solution. However, it changes depending on the ionic strength of the electrolyte solutions, as shown in Figs. 4, 5, 6, and 7.

Analysis of the experimental results for the Fe^{3+}/Fe^{2+} redox system. If the present theory is correct, the same method could be applied not only for hydrogen evolution, but also for other one electron transfer reactions. We carried out experiments on a typical one electron transfer reaction of the Fe^{3+}/Fe^{2+} redox system at Pt electrode to analyze the I dependence of the screening factor α. Figure 8 shows a ln α vs $\sqrt{I}$ plot for the one electron reduction of Fe^{3+} to Fe^{2+},

$$Fe^{3+} + e \longrightarrow Fe^{2+}. \qquad (24)$$

As shown in Fig. 8, the experimental points of ln α are almost on a straight line. The solid line in Fig. 8 shows a line ex-

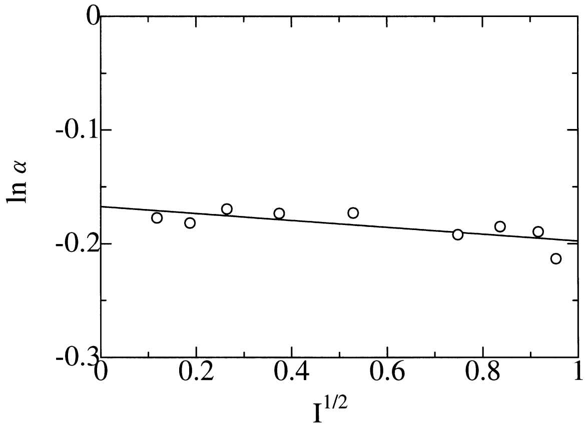

Fig. 9. ln α vs $\sqrt{I}$ plot for the one electron oxidation of Fe^{2+} to Fe^{3+} at Pt electrode. The concentration of $Fe(NH_4)_2\,(SO_4)_2$ was changed to vary the ionic strength of the Fe(II) solution.

pressed by Eq. 22 with $\alpha_D = 0.888$ and $r_0 = 0.174$ Å:

$$\ln \alpha = -\,0.0571\sqrt{I}\, -\, 0.119. \tag{25}$$

We also carried out experiments on the typical one electron oxidation of Fe^{2+} to Fe^{3+} at a Pt electrode to analyze the I dependence of the screening factor (α). As can be seen in Eq. 18, the screening factor α_{EL} does not depend on the sign of the central charge Ze. It means that α_{EL} does not depend on the direction of the electron transfer. Therefore , Eq. 18 holds independently of cathodic or anodic electron transfer. Consequently, Eq. 22 can also be applied for the one electron oxidation of Fe^{2+} to Fe^{3+}:

$$Fe^{2+} \longrightarrow Fe^{3+} + e \tag{26}$$

Fig. 9 shows the ln α vs $\sqrt{I}$ plot for the one electron oxidation of Eq. 26 at a Pt electrode. As is shown in Fig. 9, the experimental points of ln α are almost on a straight line. The solid line in Fig. 9 shows the line of Eq. 22 with $\alpha_D = 0.846$ and $r_0 = 0.092$ Å:

$$\ln \alpha = -\,0.03\sqrt{I}\, -\, 0.1675. \tag{27}$$

The results of Figs. 8 and 9 support clearly our present theory, i.e, the electrostatic screening theory for α.

Table 1. Comparison between Theoretical and Experimental Values of α_C for Hydrogen Evolution at Hg Electrode in Acidic Aqueous Solutions

Electrolyte solution	I	α_C(Expt.)	α_C(Theo.)
0.1 M HCl	0.1	0.48	0.48
0.25 M H_2SO_4	0.75	0.50	0.49
1.0 M HCl	1.0	0.49	0.50
3.0 M HCl	3.0	0.41	0.50
5.0 M HCl	5.0	0.51	0.52
7.0 M HCl	7.0	0.54	0.53
10.0 M HCl	10.0	0.61	0.54
5.0 M H_2SO_4	5.0	0.5	0.56

α_C(Theo.): Theoretical value calculated from Eq. 22.
α_C(Expt.): Experimental values from Ref. 9.

Table 2. Comparison between Theoretical and Experimental Values of α_C for Hydrogen Evolution at Hg Electrode in Alkaline Aqueous Solutions

I	α_C(Expt.)	α_C(Theo.)
0.002	0.59	0.56
0.02	0.64	0.56
0.1	0.59*	0.58
0.2	0.59*	0.59

α_C(Theo.): Theoretical value calculated from Eq. 22.
α_C(Expt.): Experimental values from Ref. 9.
*: Average value of the experimental α_C's from Ref. 9.

Table 3. Comparison between Theoretical and Experimental values of α_C for Hydrogen Evolution at Ni Electrode in HCl Aqueous Solutions at 30 °C.

I	α_C(Expt.)	α_C(Theo.)
0.001	0.39	0.40
0.01	0.33	0.41
0.1	0.42	0.42
1.0	0.47	0.47

α_C(Theo.): Theoretical value calculated from Eq. 22.
α_C(Expt.): Experimental values from Ref. 9.

Analysis of Past Data on the Transfer Coefficient. There are also a number of experimental results that suggest that the transfer coefficient changes depending on the concentration of the electrolyte, i.e. the ionic strength.[9,10] We analysed the I dependence of the transfer coefficient (α_C) for hydrogen evolution at a Hg electrode in aqueous acidic solutions[9] by applying the same method as used for Figs. 4–9. The I dependence was found to be explained well by Eq. 22 with $\alpha_D = 0.5247$ and $r_0 = 0.146$ Å. When $\alpha_D = 0.5247$ and $r_0 = 0.146$ Å are used in Eq. 22, we can theoretically calculate the transfer coefficient (α_C) for hydrogen evolution at a Hg electrode for various I. Table 1 shows the theoretical values compared with the experimental values.[9] As shown in this table, the theoretical values calculated from Eq. 22 with $\alpha_D = 0.5247$ and $r_0 = 0.146$ Å agree well with the experimental values reported for the Hg electrode.[9] This result indicates that the present model is valid not only for a Pt electrode, but also for a Hg electrode.

In Ref. 9, the I dependence of the transfer coefficient (α_C) for hydrogen evolution at the Hg electrode in aqueous alkaline solutions is reported. We analysed those data by the same method. The I dependence was found to be well explained by Eq. 22 with $\alpha_D = 0.449$ and $r_0 = 0.67$ Å. We calculated the theoretical α_C values from Eq. 22 with $\alpha_D = 0.449$ and $r_0 = 0.67$ Å. Table 2 gives the theoretical values calculated by this method and the experimental values for a comparison. As shown in Table 3, the theoretical values agree well with the experimental α_C values. The mechanism of hydrogen evolution in alkaline solution is considered to be different from that in acidic solution, because of the large difference in the proton concentration. From this point of view the results given in Table 2 shows the generality of the present theory. Bockris and Potter have reported on the I dependence of the transfer coefficients at various temperatures for hydrogen evolution at a Ni electrode in HCl solutions.[10] We analysed their data at 30 °C by applying the same method as that used for Figs. 4–9. The I dependence was found to be explained well by Eq. 22 with $\alpha_D = 0.60$ and $r_0 = 0.38$ Å. When $\alpha_D = 0.60$ and $r_0 = 0.38$ Å are used in Eq. 22, we can calculate theoretically the transfer coefficient (α_C) for hydrogen evolution at a Ni electrode for various I. Table 3 gives the theoretical values compared with the experimental values at 30 °C.[10] As is shown in this Table, the theoretical values agree well with the reported values at a Ni electrode. These results indicate that the present model is valid not only for Pt and Hg electrodes, but also for a Ni electrode, indicating the generality of the present theory.

All of the above results support our present theory that the transfer coefficient in classical electrochemistry represents the electrostatic screening of the electrode potential by the ions electrolyte near to the electrode. Since the theory is closely related with the quantum mechanical theory of electron transfer at metal electrodes, it also supports the quantum mechanical electrode theory proposed by us.[5,6] It is noted that all of the ln α vs $\sqrt{I}$ plots of Figs. 4–9 are almost on a straight line even in the large $\sqrt{I}$ region, i.e. even in the high electrolyte concentration. In the case of activity coefficients, Debye–Hückel theory cannnot be applied in the high electrolyte concentration.[2] However, the ln α vs $\sqrt{I}$ plots of Figs. 4–9 indicate that the Debye–Hückel theory can be applied at high electrolyte concentration, in the case of the transfer coefficient. The reason for this interesting result should be studied further.

Electron Transfer Distance. Table 4 gives the values of α_D and r_0 evaluated by analyzing the I dependence of α for hydrogen evolution at a Pt electrode in various acidic solutions. In this table the theoretical values of the transfer coefficient α_C (Theo.) are given. At first α was calculated from Eq. 22 using α_D and r_0 determined from the analysis of the I dependence of α. The transfer coefficient α_C was calculated theoretically by using Eq. 9. It is noted that theoretically calculated α_C agrees well with the experimental α_C. As shown in Table 4, α_D is 0.84–0.87. This means that 84–87% of the overvoltage is imposed at the electric double layer as a result of electrostatic screening. It indicates that the electrostatic screening by the electric double layer is 13–16%, because $1-\alpha_D = 0.13$–0.16. It means that the electrostatic screening by the electric double layer is small in these systems.

Now let us consider the physical meaning of the parameter

Table 4. Ionic Strength (I) Dependence of the Transfer Coefficients for Hydrogen Evolution at Pt Electrode in Various Electrolyte Solutions Together with the Values of α_D and r_0.

Electrolyte solution	I(Exp.)	α_C(Exp.)	α_C(Calc.)	α_D	r_0/Å
HCl	0.5	0.18	0.18	0.849	0.139
	0.25	0.17	0.17		
	0.1	0.16	0.16		
	0.05	0.16	0.16		
	0.01	0.16	0.15		
	0.001	0.15	0.15		
0.005 M HCl + KCl (varied)	2.005	0.25	0.24	0.839	0.197
	1.005	0.21	0.21		
	0.505	0.17	0.20		
	0.105	0.21	0.18		
	0.055	0.17	0.17		
	0.015	0.17	0.17		
0.005 M HCl + NaCl (varied)	0.505	0.27	0.26	0.837	0.535
	0.105	0.19	0.21		
	0.055	0.18	0.20		
	0.015	0.20	0.18		
	0.01	0.19	0.18		
0.025 M H_2SO_4 + NaCl (varied)	2.0075	0.15	0.15	0.871	0.056
	1.0075	0.15	0.15		
	0.5075	0.15	0.14		
	0.1075	0.13	0.13		
	0.0575	0.13	0.13		
	0.0175	0.13	0.13		
0.005 M HNO_3 + NaCl (varied)	2.005	0.17	0.18	0.844	0.063
	1.005	0.18	0.17		
	0.505	0.17	0.17		
	0.105	0.15	0.16		
	0.055	0.17	0.16		
	0.015	0.15	0.16		

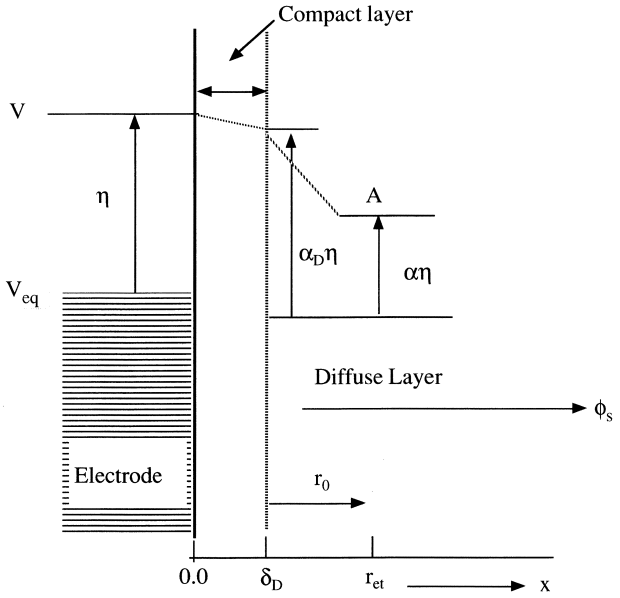

Fig. 10. The potential profile at the electrode/electrolyte interface. x represents the distance from the electrode surface at $x = 0.0$. ϕ_S represents the potential of the bulk electrolyte solution. δ_D represents the thickness of the compact layer of ~2 Å. r_{et} represents the distance from the electrode surface to the electron acceptor A. It represents the electron transfer distance.

r_0 which appears in Eqs. 17 and 18. Table 1 gives the values of r_0 determined by Eq. 22. As can be seen in Eq. 17, the parameter r_0 represents the distance from the potential source to the place where the potential is imposed. In the present model, the interface near to the electrode is composed of a metal electrode/electric double layer/electrolyte, as shown in Fig. 3. The electrostatic screening expressed by Eq. 18 represents the screening by ions in an electrolyte solution that extends outside the electric double layer. Therefore, in the present model, the potential source, i.e. $r_0 = 0.0$ Å, is not at the electrode surface but just at the outside of the electric double layer, as can be seen in Fig 3 and Eq. 18. It is also illustrated in Fig. 10.

We now define r_{et} as

$$r_{et} = \delta_D + r_0, \tag{28}$$

where δ_D represents the thickness of the electric double layer. Because r_{et} of Eq. 28 represents the distance from the electrode surface to the place where electron transfer reaction takes place, we may call r_{et} the "electron transfer distance". The electrode reaction described in Table 1 is hydrogen evolution reaction. Figure 10 illustrates the relation between δ_D, r_0 and r_{et} at the electrode/electrolyte interface. The rate determining step of the hydrogen evolution reaction at Pt electrode is the following electron transfer reaction.[5,6]

$$H^+ + e \longrightarrow \cdot H_{ad}. \tag{29}$$

Here, $\cdot H_{ad}$ represents the atomic hydrogen adsorbed on the electrode surface.

r_0 obtained in Table 4 is 0.1–0.5 Å. The magnitude of r_0 is very small. As can be seen from Eq. 28, it indicates that the electron transfer of Eq. 29 takes place just outside of the electric double layer.

Now let's assume that δ_D represents the thickness of the inner Helmholtz layer (IHL) because it is considered to have a rigid structure of ions adsorbed on the electrode surface. This layer is also called "compact layer".[1]
If $\delta_D \approx 2$ Å is assumed tentatively,[8]

$$r_{et} = \delta_D + r_0 \approx 2.1\text{–}2.5\ \text{Å} \tag{30}$$

is obtained. This means that that the electron transfer distance for the reaction of Eq. 29 is 2.1–2.5 Å. As was demonstrated in the above discussion, the information about the electron transfer distance is contained in the screening factor (α) as well as the electrostatic screening. The magnitude of the electron transfer distance $r_{et} \approx 2.1$–2.5 Å in Eq. 30 looks reasonable. This seems to be an interesting new aspect of the present theory.

Electrostatic Screening and Double Layer Effect. In classical electrochemistry based on transition state theory the overpotential imposed on a metal electrode is considered to be applied directly on the redox species involved in the electrode reaction and to shift the height of the potential barrier by $-e\eta$.[1] However, this original idea is modified in the double layer effect, i.e. the *Frumkin effect*. In the double layer effect the potential drop in the double layer is taken into consideration. Because of the potential drop in the double layer, the overpotential imposed on the the redox species is modified from η to $\eta - \phi_2$.[1] Here, ϕ_2 represents the potential at the plane of the closest aproach. This modified potential affects the electrode reaction kinetics.

On the other hand, in the present theory, only a part of the overpotential, i.e. $\alpha\eta$, is imposed on the redox species because of the electrostatic screening.

Figure 10 also shows a potential profile at the electrode/electrolyte interface in the present model. At the outside of the inner Helmholtz plane, i.e. $x = \delta_D$, the imposed overpotential is $\alpha_D\eta$. At $x = r_{et}$ where electron acceptor A is located, the imposed overpotential is $\alpha\eta$. Although the interface model in the present theory is slightly different from the ordinary double layer model, the present theory resembles the potential profile in classical electrochemistry. Interestingly, it takes into consideration naturally the potential drop near to the electrode surface. In this sence it may be said that the double layer effect is taken into consideration in a different form in the present theory. Further study would be needed in this respect to develop the present theory.

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