Resistance of solution without supporting electrolyte under the reduction of HCl

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Abstract

The resistance of HCl solution without supporting electrolyte at a microelectrode was evaluated by the ac impedance technique of which the dc-potential was in the diffusion-controlled domain for the reduction of the hydrogen ion. The hydrogen ion is reduced to hydrogen gas. The Cl\(^-\) takes the same concentration profile as the hydrogen ion in order to keep electric neutrality. Then, no ion is present near the electrode. Consequently, the resistance between the working and the counter electrode should be extremely large, from the theoretical viewpoint. However, well-defined voltammograms can be obtained without adding supporting electrolyte. This contradiction is discussed on the basis of the experimental results of the solution resistance during the reduction. The evaluated conductance was linear with the concentration of HCl. The linearity indicates that Cl\(^-\) is responsible for the conductivity, by collapsing the electric neutrality in the diffuse layer. A model of the concentration distributions is proposed, in which the concentration of the hydrogen ion is proportional to the distance from the electrode, whereas that of Cl\(^-\) is invariant to the distance in the diffuse layer. The conductivity evaluated from the model is twice the experimental value. Both the conductance and the current are proportional to the concentration, of which the ratio gives the ohmic potential drop, 0.52 V, independent of values of the current. This is a reason why voltammograms at microelectrodes are not so deformed even at high concentrations of electroactive species. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

An interesting feature of microelectrode techniques is a possibility of obtaining a well-defined sigmoidal voltammogram even when supporting electrolyte is not deliberately added to solution [1]. A system without supporting electrolyte has been applied for the study on ionic interactions between an electroactive species and its counterion, as exemplified by polyelectrolytes [2–11], colloidal particles [12–15], and labile metal complexes [16–19]. Although a shape of voltammograms without supporting electrolyte is drawn out owing to large solution resistance [20,21], values of the limiting current can be obtained so accurately that they agree with theoretical values [22] for completely dissociated acids [23]. The limiting current for the insufficiently dissociated acids was not predicted well without the ion–ion interaction [24,25]. It agrees with the theoretical value if it is corrected by ion–ion interaction and change of viscosity [26].
Conductance of solution without supporting electrolyte is provided mostly by the ions dissociated from electroactive species and solvent. We consider, at first, the contribution of pure water (resistivity $\rho$) to the ionic resistance at a hemispherical working electrode $a = 5$ μm in radius when no electrode reaction occurs. If the ionic medium with concentration $c$ and the molar conductivity $A$ occupies a gap between this electrode and an extremely large concentric shell of a counter electrode, the resistance between the two electrodes is expressed by

$$R = \int_{a}^{\infty} \frac{\rho}{2\pi r^2} \, dr = \frac{1}{2\pi Ac}$$

(1)

where $r$ is the radial distance from the center of the electrodes. For values of $A = 54.87 \times 10^{-3}$ S m$^2$ mol$^{-1}$ [27] and $c = 10^{-7}$ M (pH 7), Eq. (1) gives $R = 5.8 \times 10^9 \Omega$. This is much larger than the value (18 MΩ) of the resistance between confronted sides of a 1 cm$^3$ cube. The value is ascribed to the small size and the geometry of the working electrode. Since the migrationally diffusion-controlled current of $c^* = 1$ mM electroactive species gives 3.0 nA ($= 2\pi c^* D Fa$) for the diffusion coefficient of $D = 10^{-5}$ cm$^2$ s$^{-1}$, the ohmic potential drop is predicted to be 3 nA $\times$ 5.8 GΩ = 17 V. This is far from the usual experimental results. It is not until pH 4 that the ohmic potential drop becomes actually negligible (17 mV).

Next, we consider the contribution of the dissociated electroactive species, for instance HCl, to the resistance without supporting electrolyte when the hydrogen ion is reduced at the electrode. Letting $c_H$ be the concentration of the hydrogen ion at a distance $r$, the steady state current at the hemispherical electrode is governed by the spherical diffusion, $d(r^2 c_H) / dr = 0$. A solution under the limiting current condition ($c_H = 0$ at $r = a$) is simply given by

$$c_H = c^* (1 - a/r)$$

(2)

where $c^*$ is the bulk concentration. The concentration of Cl$^-$ takes the same profile as $c_H$ because of keeping the electric neutrality. Replacing $\rho$ in Eq. (1) by $1/Ac_H$ and inserting Eq. (2) into this $1/Ac_H$, we obtain

$$R = \int_{a}^{\infty} \frac{dr}{2\pi Ac^* r (r - a)} = \frac{1}{2\pi Ac^* a} \left[ \ln \frac{r - a}{r} \right]_{a}^{\infty}$$

(3)

The integral is divergent at $r = a$, suggesting infinity of the resistance. Then, this resistance might block voltammetric currents. The infinity is caused by a depletion of the ions near the electrode owing to the electrode reaction. Since the hydrogen ion serves, not only as an electroactive species, but also a supporting electrolyte, the increase in the extent of the electrode reaction increases the resistance. The Cl$^-$ cannot improve the conductance either, if the electric neutrality is maintained. Since the infinity in Eq. (3) results mathematically in a logarithmic singularity, a slight deviation of the concentration profile from $(1 - a/r)$ may alter the infinity to a finite value of the resistance. For instance, $(1 - a/r)^{1 - \Delta}$ for a small positive value of $\Delta$ gives zero resistance. Since the profile $1 - a/r$ can be regarded as a thermodynamic average of fluctuated profiles like $(1 - a/r)^{1 - \Delta}$, the ions closer to the electrode than the average profile may offer a finite value of the resistance.

The aim of the present work is to evaluate the resistance by the ac-impedance when the electrode reaction occurs without supporting electrolyte. The resistance value may predict an actual concentration profile.

2. Experimental

The electrochemical cell was a one-compartment cell. The working electrode was a platinum disk 5 μm in radius. The electrode surface was polished with alumina powder before each potential scan. A saturated calomel electrode (SCE) was routinely used for the reference electrode. A platinum wire was also used for the reference electrode in case KCl leaks to and contaminates the solution. It was confirmed that both reference electrodes gave identical values of dc- or ac-current.

Hydrochloric acid of analytical grade was used without further purification. Water was deionized, of which conductance was 1.3 μS at 25°C. The hydrochloric acid solution was purged with nitrogen gas before each run of the potential scan.

The alternating voltage, $E_{ac}$, was superimposed to the computer-controlled dc-voltage by a home-made adder circuit. The potentiostat was HECS 972 (Fuso, Kawasaki) for the microelectrode use. The output from the potentiostat, which included the ac component, was averaged with a home-made software to obtain the dc component. The lock-in amplifier was Model 5110 (EG & G, Princeton, NJ). The sensitivity of the potentiostat for detection of the ac-current was 200 times lower than that for the dc-current in order to get a rapid response at the potentiostat. Thus, the ac-current data could not be detected simultaneously together with the dc-current.

3. Results

The dc-voltammogram of the hydrochloric solution showed a sigmoidal steady-state current of the reduction of H$^+$ with good reproducibility in both cases with and without KCl when the potential scan rate, $v$, ranged from 10 to 50 mV s$^{-1}$. With a decrease in $v$ (< 10 mV s$^{-1}$), the limiting current decreased. This decrease may be ascribed to the accumulation of hydrogen gas on the electrode surface by the long electrode reduction. Every voltammetric run was made at 20 mV s$^{-1}$.
at the freshly polished electrode. The limiting dc-current was confirmed to be independent of the superimposed alternating voltage.

With a decrease in the concentration of the supporting electrolyte (KCl), the limiting current increased, and then reached the value 1.9 times larger than the current with an excess amount of KCl (0.1 M), as shown in Fig. 1. The increase has been explained by the participation of the electric migration. This ratio is in consistent with the theoretical value, 2, for 1:1 strong acid [22,23]. The half-wave potential of the voltammogram without KCl shifted negatively from that with KCl by ca. 20 mV.

Thus, the solution resistance without KCl is 0.85 MΩ (= 17 nA/20 mV) from the viewpoint of the dc-current. This value is similar to the value (1.4 MΩ) calculated from Eq. (1) for \( c = 0.5 \text{ mM} \) which the surface concentration (1 mM) takes at the halfwave potential.

Figs. 2 and 3 show potential-dependence of the amplitude, \( |I_{ac}| \), and the phase angle, \( \phi \), respectively, of the ac-current in 1 mM HCl solutions with (0.1 M) and without KCl. The amplitude versus potential curve shows two peaks at \(-0.32\) and \(-0.45\) V. The peak at \(-0.32\) V may be related with adsorption, partly because there is no dc-response near \(-0.32\) V and partly because the ac-current is mostly capacitive (Fig. 3). The peak at \(-0.45\) V corresponds to the half-wave potential of the dc-voltammogram. Thus, it is attributed to the reduction of H\(^+\). The amplitude in the solution with KCl is larger than that for a solution without KCl except for the domain around \(-0.45\) V, because KCl increases the conductance. The opposite variation near \(-0.45\) V can be explained in terms of the smaller slope of the dc-voltammogram without KCl than the slope with KCl. The phase shift (Fig. 3) in the solution without KCl is smaller in the domain \( E < -0.45 \) V than that in the solution with KCl. This can be interpreted by the lesser amount of ions to form the double layer capacitor.

As the sensitivity (a current/voltage converter) of the potentiostat is selected to be higher, the response time gets slower, generally. Consequently, a response to high frequency may contain a delay. The delay of the potentiostat was examined by use of a dummy cell which was a series connection of a resistance (300 kΩ) and a capacitance (0.5 nF). Frequencies less than 40 Hz did not vary the amplitude and the phase. The frequency providing reliable data ranged from 5 to 40 Hz, in the light of the time constant of the lock-in amplifier and the potential sweep rate (20 mV s\(^{-1}\)).

4. Discussion

The impedance measurement was made at the potential of the limiting current (\(-1.0\) V vs. SCE) without supporting electrolyte. This potential corresponds to neglecting both, the Warburg impedance for the mi-
croe electrode diffusion and the charge transfer resistance. The equivalent circuit of evaluating the resistance was a series combination of a resistance \((R)\) for the solution resistance and capacitance \((C)\) for the double layer. Since the impedance is expressed by \(R + 1/\omega C\), we have

\[
|E_{ac}/I_{ac}|^2 = R^2 + (1/\omega^2 C^2)
\]

(4)

Fig. 4 shows plots of \(|E_{ac}/I_{ac}|^2 (= Z^2)|\) against \(f^{-2} (= (\omega/2\pi)^{-2})\). A linear relation is found for various concentrations of HCl, although larger scattering occurred at lower concentrations. From the intercept, the resistance was evaluated and its inverse (conductance, \(G\)) was plotted against the concentration of HCl in Fig. 5. The plot shows a linear relationship, indicating the conductance should be provided by HCl. Therefore, the concentration profile supported by the electric neutrality (Eq. (2)) is not valid. The electric neutrality is not fulfilled in the vicinity of the electrode. The line in Fig. 5 crosses the abscissa at a positive intercept. The positive value was reproducible. Since it corresponds to the conductivity obtained when \(c^*\) is extrapolated to zero, it may be ascribed to the impurity of ions in the solution. Actually, addition of small amounts of electrolytes increased the intercept.

The boundary condition for the concentration of Cl\(^-\), denoted by \(c_{A}\), at the electrode is given by \(d c_{A}/dr = 0\) because Cl\(^-\) does not react at the electrode. Thus, \(c_{A}\) should not vary with \(r\) in the vicinity of the electrode. In contrast, \(c_H\) is an increasing function of \(r\). Consequently, the electric neutrality, \(c_{A} = c_{H}\), has to collapse near the electrode \((a < r < a + \delta)\), whereas it holds far from the electrode. Here, a value of \(\delta\) is of the order of the Debye–Hückel length, e.g. 10 nm for 1 mM HCl, and is only 0.2% of \(a\). The concentration profile possibly realized is shown in Fig. 6. A value of \(c_{A}\) at \(r = a\) can be estimated as follows: The flux of the hydrogen ion at the electrode, \(I = F c_{H}^* d c_{H}/dr\), is approximated as \(D_{H}(c_{H})_{a + \delta}/\delta\). When replacing \(c_{H}\) by \(c_{A}\) by use of the electric neutrality at \(r = a + \delta\), we obtain

\[
D_{H}(c_{A})_{a + \delta}/\delta = I/\pi a^2 F
\]

(5)

Assuming \((c_{A})_{a + \delta} = (c_{A})_{a}\) and inserting the diffusion-controlled current, \(I = F c_{H}^* D_{H}/a\), into Eq. (5), we obtain the approximate expression

\[
(c_{A})_{a} = 4c^* \delta/\pi a
\]

(6)

The conductance of the solution in \(a < r < a + \delta\) near the disk electrode is similar to the conductance of the cylindrical block \(a\) in radius and \(\delta\) high with the uniform concentration \((c_{A})_{a}\). This conductance is expressed by

\[
G = \pi a^2 \kappa/\delta
\]

(7)

where \(\kappa\) is the conductivity in the cylinder. Neglecting the contribution of H\(^+\) to the conductivity in the cylinder, we can approximate \(\kappa\) as \((c_{A})_{a} A_{-}\), where \(A_{-}\) is the molar conductivity of Cl\(^-\). By use of Eq. (6), \(\kappa\) is rewritten as \(\kappa = 4c^* A_{-} \delta/\pi a\). Eliminating \(\kappa\) from Eq. (7), we have the expression

Fig. 4. Plots of the square of the impedance against the square of the frequency for 0.3 (○) and 0.5 (•) mM HCl. The intercept gives the resistance, according to Eq. (4).

Fig. 5. Dependence of the conductance obtained in Fig. 4 on the concentration of HCl.

Fig. 6. A model of concentration profiles of H\(^+\) and Cl\(^-\) without supporting electrolyte. The value of \(\delta\) is so large that variations are exaggerated to be seen well.
\[ G = 4aeA \]  \tag{8} \]

The value of \( G/ae \), which corresponds to the equivalent molar conductivity, is \( 4A = 30.5 \times 10^{-3} \) S m² mol⁻¹ when the known value for Cl⁻ (7.64 \times 10^{-3} \) S m² mol⁻¹) is used.

In contrast, the value determined from the slope in Fig. 5 is \( 13.5 \times 10^{-3} \) S m² mol⁻¹. Although the value calculated from Eq. (8) is 2.3 times larger than the experimental one, the conductance can be ascribed mainly to the presence of Cl⁻ in the double layer.

One may doubt whether the electric neutrality may really collapse in the diffusion layer. In order to demonstrate a possibility of the collapse, we take into account semiquantitatively the Nernst–Planck equation, which expresses the ion transport by both diffusion and electro migration. The electric coordinate \( r \), the Nernst–Planck equation for H⁺ under the steady state is expressed [28] by

\[ \frac{d\phi}{dr} = \frac{c_{f}F}{RRT} \frac{d\phi}{dr} = 0 \]  \tag{9} \]

where \( \phi \) is the inner potential of the solution. The value of \( c_{f} \) in the second term is similar to \( (c_{A})_{o} \) at \( r = a \), and \( dc_{f}/dr \) can be represented by the steady-state flux of \( H^{+} \), i.e., \( I/FF_{D}(a/r)^{2}4e^{*}/\pi a \). Consequently, the electric field, \( f \), at the electrode is rewritten as

\[ f = \frac{d\phi}{dr} \bigg|_{r=a} = -\frac{4e*RT}{\pi a (c_{A})_{o}F} \]  \tag{10} \]

Eliminating \( (c_{A})_{o} \) with the use of Eq. (6), we obtain

\[ f = \frac{RT}{F\delta} \]  \tag{11} \]

The values of \( f \) is \( 2.6 \times 10^6 \) V m⁻¹ for the Debye–Hückel length (10 nm) of \( \delta \) at 25°C. Although the potential difference for the charge separation is only \( RT/F = 26 \) mV, the electric field is very large owing to the small value of \( \delta \).

Not only the current but also the conductance were proportional to the concentration of HCl. Thus, the ratio, \( I/G \), or the IR drop is expected to be independent of \( e^{*} \). The value of the IR drop obtained from the limiting current in Fig. 1 and the slope in Fig. 4 is 0.52 V. It is much larger than the IR drop at the halfwave potential (0.02 V in Fig. 1). This large value indicates the depletion of both concentrations in the limiting current domain. On the other hand, the theoretical expression for IR obtained from Eq. (8) is

\[ I/G = 2FD_{H}/A \]  \tag{12} \]

of which value is 0.22 V. Half of the experimental value is due to the overestimation of \( (c_{A})_{o} \). Of interest is the absence of concentration-depending terms in Eq. (12). Thus, the voltammograms are not deformed even at very high concentrations of electroactive species, as demonstrated for detection of highly concentrated metal ions [29].

5. Conclusions

The solution resistance at the potential for the limiting current looks infinite because of the depletion of the electroactive species by the electrode reaction. However, the conductance is retained at some extent with the counterion by collapsing the electric neutrality near the electrode. The reason for the failure of the electric neutrality is the difference in the boundary conditions at the electrode; \( dc_{A}/dr = 0 \) and \( dc_{H}/dr = I/FF_{D}H \), as illustrated by concentration profiles in Fig. 6. Although the model of the profiles is quite simple, it can explain the finite value of the resistance rather than the infinity. The conductance and the current are proportional to the concentration of the electroactive species, and hence the IR drop is independent of the concentration. This conclusion is valid for 1:1 dissociated electrolytes.

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