Application of Electrochemical Impedance Spectroscopy to Analysis of Solvent Extraction Mechanism of Mn(II)-8-Hydroxyquinoline System

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An electrochemical impedance spectroscopy (EIS) was used for the investigation of the solvent extraction of Mn(II) across water/1,2-dichloroethane interface. The electrochemical measurement allows one to obtain direct information concerning the charge transfer rate across the interface. The electrochemical impedance showed a capacitive semicircle and Warburg impedance on the Nyquist plane. The capacitive semicircle originates from the charge transfer resistance and the interfacial capacitance. The appearance of the Warburg impedance indicates the contribution of the diffusion process to the total charge transfer rate. A theoretical expression which presents the electrochemical impedance for Mn(II) solvent extraction was derived. The solvent extraction mechanism was discussed including some results in a simulation.

Keywords Electrochemical impedance spectroscopy, solvent extraction, Mn(II), 8-hydroxyquinoline

Solvent extraction is one significant method to separate chemicals in analytical chemistry. The application of the solvent extraction has been extended to many fields, *i.e.*, radioisotope analysis, nuclear technology, and metal refining. The solvent extraction of metallic ions is a complex reaction involving a diffusion process, dissociation of chelating reagent, complex formation, ion-pair formation, and mass transfer across the liquid-liquid interface. The kinetic analysis on the solvent extraction is meaningful because this produces the information regarding the rate determining step (rds) and the intermediate species. Honaker and Freiser reported some results of kinetic analysis of solvent extraction in 1962.¹ They showed that the solvent extraction rate of a metal by the dithizone-derivations was controlled by complex formation rate in the aqueous phase. The electrochemical study can be expected to characterize the mass transfer across the liquid-liquid interface during solvent extraction. The charge transfer across the liquid-liquid interface is the fundamental process of ion permeation through a biomembrane, an ion selective electrode, and a solvent extraction. The electrochemical measurement has the helpful features that the transfer rate can be monitored strictly under the suitable potential difference at the interface and that the total reaction can be separated into diffusion and charge transfer processes. Therefore, the electrochemical study of liquid-liquid interfaces is important for theoretical and experimental approaches. In 1979, Koryta² applied the electrochemical method for the investiga-

tion of liquid-liquid interface of the ion selective electrode. Later, Koryta and a co-worker developed its fundamental theory.^{3,4} Yoshida and Freiser⁵ studied the ion transfer of Co²⁺- and Zn²⁺-1,10-phenanthroline complex ions, employing current scan polarography and chronopotentiometry at the ascending water electrode (AWE). Freiser and co-workers⁶⁻⁸ investigated the liquid-liquid interface in solvent extraction system by voltammetry. Afterward, Liu and co-workers⁹ reported the solvent extraction mechanism and obtained the reaction order from the limiting current in the polarogram for metallic ions transfer at aqueous/1,2-dichloroethane (DCE) interface. Senda *et al.*¹⁰⁻¹⁵ discussed kinetic parameters of various cations transfer at water/nitrobenzene by electrochemical measurements. Itagaki *et al.*¹⁶ presented a preliminary application of the electrochemical impedance spectroscopy (EIS) to the analysis of solvent extraction. In the present research, the detailed solvent extraction mechanism of Mn(II) by 8-hydroxyquinoline (HQ) was studied by using EIS, and the contribution of the diffusion process in solvent extraction of metallic ions and the extraction rate were investigated.

Experimental

The scheme of the experimental cell is depicted in Fig. 1. A cylindrical glass tube whose inner diameter was 18 mm was filled with 1,2-dichloroethane (DCE). The capillary tube was set in the cylindrical glass tube, and water/DCE interface was made at the top of the

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Fig. 1 Scheme of electrochemical cell for ion transfer at water/DCE interface. (a) Ag/AgCl (WE1), (b) Pt (WE2), (c) Ag/AgCl (RE), (d) micro syringe, (e) aqueous solution injector, (f) glass frit, (g) capillary.

capillary tube. The interfacial area between the two liquid-liquid phases was controlled by a microsyringe and was stationary (0.36 cm^2). The interface was always monitored by a digital camera set in front of the cell during the measurement. MgSO_4 was chosen as a supporting electrolyte because the electrolyte containing MgSO_4 has a wide potential window.¹⁷ The aqueous phase involved $0.5 \text{ mol/dm}^3 \text{ MgSO}_4$ and an arbitrary concentration of MnSO_4 . The aqueous phase was prepared by doubly distilled water. The organic phase (DCE) involved 0.1 mol/dm^3 tetrabutylammonium (TBA^+)-tetraphenylborate (TPB^-) as a supporting electrolyte and an arbitrary concentration of HQ. All chemicals used in this measurement were of analytical grade. Two working electrodes (WE1 and WE2) and one reference electrode (RE) were used in the present electrochemical measurements. WE1 and WE2 were Ag/AgCl and Pt, respectively. RE was

The current, i , was measured between WE1 and WE2. The potential difference, E , was represented by the potential of WE1 against RE. The current and potential were controlled by a potentiostat-galvanostat (Hokuto, HA501G). Current-potential curves were measured by a current scan method in which the sweep rate was $0.5 \mu\text{A/s}$, and the potential was recorded on the recorder. Measurements of electrochemical impedance were performed by a frequency response analyzer (FRA, NF5020) in the frequency range from 10 mHz to 10 kHz . The amplitude of applied current modulation was $1 \mu\text{A}$.

Fig. 2 Current-potential curves for the transfer of Mn(II)-HQ complex ions across water/DCE interface. The concentration of HQ in DCE phase was 0.1 mol/dm^3 . (1) the current-potential curve when aqueous solution involves no metallic ions and DCE solution involves no HQ (background curve). The concentration of Mn(II) in the aqueous solution was 0.01 mol/dm^3 . The pH values of the aqueous solution were (2) 3, (3) 5, (4) 7, and (5) 8.

Results and Discussion

Current-potential curves

Figure 2 shows the i - E curves corresponding to the charge transfer across the water/DCE interface. In the present analysis, the positive current is related to the transfer of cations from aqueous phase to DCE phase or of anions from DCE phase to aqueous phase. The positive current in i - E curves in Fig. 2 was mainly due to the transfer of Mn(II) from the aqueous solution to DCE. The solution resistance was approximately $7.5 \text{ k}\Omega$ and the ohmic drops in the i - E curves presented in Figs. 2 - 4 were compensated. The i - E curve (1) in Fig. 2 is the background current when aqueous phase (pH 8) and DCE involve only supporting electrolytes. When the aqueous phase (pH 8) and DCE involve $0.01 \text{ mol/dm}^3 \text{ MnSO}_4$ and $0.1 \text{ mol/dm}^3 \text{ HQ}$, respectively, the i - E curve shows an apparent limiting current region between 0.05 V and 0.15 V . When the pH of the aqueous phase decreases, the difference of the limiting current and the background current decreases. At pH 3, the limiting current region is not clearly observed. This phenomenon was due to the formation of the complexes of proton and HQ in the aqueous phase. Namely, HQ was distributed into aqueous phase and formed $1:1 \text{ H}^+$ -HQ complex at low pH, because H^+ caused electrophilic addition to HQ which has an electron-releasing group. Eventually, $1:1 \text{ H}^+$ -HQ complex transferred into organic phase (DCE). As above-mentioned, the metallic ion, Mn(II), could not form a $1:1 \text{ Mn-HQ}$ complex at pH 3 because this complex formation is a competitive reaction between Mn(II) and H^+ . The limiting current region was not observed when proton complexes were extracted at pH 3, indicating that the charge trans-

Fig. 3 Current-potential curves for the transfer of Mn(II)-HQ complex ions across the water/DCE interface. The concentration of HQ in DCE phase was 0.1 mol/dm³. (1) background curve. The concentrations of Mn(II) in the aqueous solution were (2) 0.01, (3) 0.03, (4) 0.06, and (5) 0.1 mol/dm³. The pH of the aqueous solution was 8.

Fig. 4 Current-potential curves for the transfer of Mn(II)-HQ complex ions across water/DCE interface. The concentration of Mn(II) in the aqueous solution was 0.01 mol/dm³. (1) background curve. The concentrations of HQ in DCE were (2) 0.1, (3) 0.3, and (4) 1.0 mol/dm³. The pH of the aqueous solution was 8.

fer rate was not influenced by diffusion process of HQ in DCE in this experimental condition. Namely, if the charge transfer rate was influenced by the diffusion process of HQ in DCE, the limiting current region should be observed when proton complexes were extracted at low pH. In the following measurements, the pH of aqueous phase is set at 8 because the influence of proton complex formation can be neglected and Mn(II) in aqueous phase is deposited as Mn(OH)₂ at pH values higher than 9. Figure 3 shows the *i*-*E* curves when DCE involved 0.1 mol/dm³ HQ and the concentration of MnSO₄ in aqueous phase was varied. The limiting current increases with increasing the concentration of MnSO₄. The limiting current, from which is subtracted the background current, is in proportion to the concentration of MnSO₄. Figure 4 shows the *i*-*E* curves when the aqueous phase involved 0.01 mol/dm³ MnSO₄ and the concentration of HQ in DCE phase was varied. The limiting current increases with increasing the concentration of HQ. The limiting current, which is subtracted by the background current, is in proportion to the concentration of HQ.

Electrochemical solvent extraction model and its Faradaic impedance

The electrochemical solvent extraction mechanism is proposed as depicted in Fig. 5. HQ involved in DCE phase is distributed into the aqueous phase, and dissociated in the boundary layer at the interface. Mn(II) is diffused to the interface in the aqueous phase and forms the complex MnQ⁺ with the dissociated reagent. The complex MnQ⁺ is extracted into the DCE phase by the electrochemical driving force. On the basis of the proposed model, Faradaic impedance for Mn(II) solvent extraction is derived by the following procedure.

The transfer rate of MnQ⁺ complex from aqueous phase to DCE phase, *v*, is:

Fig. 5 Reaction model of the transfer of metal-HQ complex ion across water/DCE interface. *h* is the thickness of boundary layer and HQ means chelating agent, 8-hydroxyquinoline. *k'* is rate constant.

$$v = k' c_{\text{MnQ},s} \quad (1)$$

where *k'* is the transfer rate constant and *c*_{MnQ,s} is the concentration of MnQ⁺ in the boundary layer at the aqueous phase side of the interface. The subscript "s" means the chemical in the boundary layer. Since the charge transfer of MnQ⁺ is an electrochemical process, *k'* is a potential-dependent parameter:

$$k' = k_0 \exp(bE), \quad (2)$$

where *E* is a potential against an arbitrary potential scale which involves a potential difference across a water/DCE interface, *k*₀ is a rate constant, and *b* is the Tafel constant. Assuming that the chemical steps in the boundary layer are rapid and attain the equilibrium, the *c*_{MnQ,s} is related to the concentrations of HQ, H⁺, Mn²⁺ in the boundary layer, *c*_{HQ,s}, *c*_{H,s}, *c*_{M,s}, with the equilibrium

constant K :

$$c_{\text{MnQ},s} = K c_{\text{HQ},s} c_{\text{M},s} / c_{\text{H},s} \quad (3)$$

From Eqs.(1) and (3), the v can be rewritten as:

$$v = k c_{\text{M},s}, \quad (4)$$

where $k = k' K c_{\text{HQ},s} / c_{\text{H},s}$. The diffusion of Mn^{2+} from the bulk of the aqueous phase to the interface is governed by Fick's second law:

$$\partial^2 c_{\text{M}} / \partial t^2 = D \partial^2 c_{\text{M}} / \partial x^2, \quad (5)$$

where c_{M} is the concentration of Mn^{2+} in aqueous phase, D is the diffusion coefficient of Mn^{2+} and t is time. When a sinusoidal alternating electrochemical signal is imposed on the interface, the concentration of Mn^{2+} , c_{M} , in the diffusion layer is modulated by the applied perturbing signal:

$$c_{\text{M}} = c_{\text{M}}^* + \Delta c_{\text{M}}, \quad (6-1)$$

$$\Delta c_{\text{M}} = |\Delta c_{\text{M}}| \exp(j\omega t), \quad (6-2)$$

where j is an imaginary number, ω is an angular frequency and c_{M}^* is the steady state concentration of Mn^{2+} . Because the concentration of Mn^{2+} is constant in the bulk of the aqueous phase:

$$\Delta c_{\text{M}} = 0 \quad (x = \infty). \quad (7)$$

From Eqs. (5) and (6), the following equation is derived by the same calculation as in reference 16:

$$\Delta c_{\text{M}} = B \exp\{-x(j\omega/D)^{1/2}\}, \quad (8)$$

where B is a constant. From Fick's first law,

$$\Delta J = -D(\partial \Delta c_{\text{M}} / \partial x) = -(j\omega/D)^{1/2} \Delta c_{\text{M},s}, \quad (9)$$

is derived, where J is a flux of Mn^{2+} from the bulk to the interface in aqueous phase. Therefore,

$$\Delta c_{\text{M},s} / \Delta J = -(j\omega/D)^{-1/2}. \quad (10)$$

The current is:

$$i = nFAv = nFAk c_{\text{M},s}, \quad (11)$$

where F and A are the Faraday constant and the interfacial area, respectively, and n is the valence of the complexes which across the interface ($n=1$ in the present analysis). The mass balance of Mn^{2+} in the boundary layer is related to the charge transfer rate and the flux of Mn^{2+} as follows:

$$h(\partial c_{\text{M},s} / \partial t) = -v - J, \quad (12)$$

Fig. 6 Experimental results of electrochemical impedance for the ion transfer across water/DCE interface. The concentration of HQ in DCE was 1.0 mol/dm³. The concentration of Mn(II) in the aqueous solution (pH 8) was 0.01 mol/dm³. The pH of the aqueous solution was 8. The imposed direct current (DC) was (A) 20, (B) 30, (C) 40, (D) 50 and (E) 60 μA .

where h is the thickness of the boundary layer at the interface. Equation (13) can be transformed by substituting Eq. (6) and using a Taylor series expansion:

$$j\omega h \Delta c_{\text{M},s} = -\Delta v - \Delta J. \quad (13)$$

From Eqs. (10) and (13),

$$\Delta c_{\text{M},s} / \Delta v = \{-j\omega h + (j\omega/D)^{1/2}\}^{-1}. \quad (14)$$

Furthermore,

$$\Delta c_{\text{M},s} / \Delta i = \{-nFA\{j\omega h + (j\omega/D)^{1/2}\}\}^{-1}. \quad (15)$$

Because the value of h was reported as 10^{-7} cm in reference 18 and $j\omega h \ll (j\omega/D)^{1/2}$, h can be neglected in Eq. (15):

$$\Delta c_{\text{M},s} / \Delta i = \{-nFA(j\omega/D)^{1/2}\}^{-1}. \quad (16)$$

Equation (11) is transformed by a Taylor series expansion:

$$\Delta i = nFAk(bc_{\text{M},s}\Delta E + \Delta c_{\text{M},s}). \quad (17)$$

The Faradaic impedance, Z_F , is represented as follows:

$$Z_F = \Delta E / \Delta i = 1 / (nFAk c_{\text{M},s}) - \Delta c_{\text{M},s} / (bc_{\text{M},s} \Delta i). \quad (18)$$

Fig. 7 (a) Scheme of electrochemical impedance of water/DCE interface on Nyquist plane. (b) Equivalent circuit of charge transfer across water/DCE interface. R_{sol} , Z_F and C_{dl} are solution resistance, Faradaic impedance and capacitance of electric double layer, respectively.

Substituting Eq. (17) into Eq. (18), we get,

$$Z_F = \{1 + k/(j\omega/D)^{1/2}\} / (nFAkbc_{MnQ,s}) \\ = R_{ct} \{1 + k/(j\omega/D)^{1/2}\}, \quad (19)$$

where

$$R_{ct} = 1/bi. \quad (20)$$

The Z_F was derived under the assumption of finite diffusion layer in reference 16. However, the Z_F for infinite diffusion layer was derived in this analysis, because the experimental results of electrochemical impedance, as shown in Fig. 6 later, describe an apparent infinite Warburg impedance, which showed a straight line at 45 degrees on the complex plane.¹⁹

Experimental results of electrochemical impedance

Figure 6 shows the i - E curve and the Nyquist plot of electrochemical impedance, Z , for charge transfer across the water/DCE interface when the aqueous phase (pH 8) involved $0.01 \text{ mol/dm}^3 \text{ MnSO}_4$ and the DCE phase involved $1.0 \text{ mol/dm}^3 \text{ HQ}$. At the low current (points A and B), the Z shows the capacitive semi-circle which originates from the charge transfer resistance and the interfacial capacitance. In the limiting current region (plots C and D), the Z shows an apparent Warburg impedance, indicating that the diffusion process contributes to the total charge transfer rate. The Warburg impedance disappears at point (E) in Fig. 6, because the charge transfer is mainly caused by the supporting electrolyte. The diameter of the capacitive semicircle corresponds to the charge transfer resistance at the interface in the general analysis of EIS, and decreases with increasing potential difference. The solution resistance originating from the high resistivity of the organic phase can be separated clearly in the EIS measurement.

Fig. 8 Simulated results of electrochemical impedance for the transfer of Mn(II)-HQ complex ion across water/DCE interface. Aqueous phase involved $0.01 \text{ mol/dm}^3 \text{ Mn(II)}$. DCE involved $1.0 \text{ mol/dm}^3 \text{ HQ}$. The direct current was (A) 20, (B) 30, (C) 40, (D) 50 and (E) 60 μA . The parameters for the simulation are as follows: $D(\text{ref.20}) = 1.424 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, (A) $R_{sol} = 7660 \text{ }\Omega$, $R_{ct} = 600 \text{ }\Omega$, $C_{dl} = 6.6 \times 10^{-4} \text{ F cm}^{-2}$, $b = 83 \text{ V}^{-1}$, $k \ll 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; (B) $R_{sol} = 7600 \text{ }\Omega$, $R_{ct} = 550 \text{ }\Omega$, $C_{dl} = 1.2 \times 10^{-3} \text{ F cm}^{-2}$, $b = 61 \text{ V}^{-1}$, $k \ll 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; (C) $R_{sol} = 7550 \text{ }\Omega$, $R_{ct} = 200 \text{ }\Omega$, $C_{dl} = 1.3 \times 10^{-4} \text{ F cm}^{-2}$, $b = 125 \text{ V}^{-1}$, $k = 1.0 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; (D) $R_{sol} = 7600 \text{ }\Omega$, $R_{ct} = 100 \text{ }\Omega$, $C_{dl} = 8.8 \times 10^{-6} \text{ F cm}^{-2}$, $b = 200 \text{ V}^{-1}$, $k = 1.4 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; (E) $R_{sol} = 7580 \text{ }\Omega$, $R_{ct} = 93 \text{ }\Omega$, $C_{dl} = 6.9 \times 10^{-3} \text{ F cm}^{-2}$, $b = 179 \text{ V}^{-1}$, $k \ll 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Simulated results of electrochemical impedance

Figure 7 shows the scheme of the Nyquist plot and the equivalent circuit for the Z in Fig. 6. In Fig. 7, R_{sol} , R_{ct} and C_{dl} represent a solution resistance, a charge transfer resistance and an interfacial capacitance, respectively. From Eq. (19) and the equivalent circuit in Fig. 7 (b), the Z can be represented as follows:

$$Z = R_{sol} + \frac{1}{j\omega C_{dl} + \frac{1}{R_{ct}(1 + \frac{k}{\sqrt{j\omega D}})}} \quad (21)$$

The simulated results of the Z are shown in Fig. 8, and are in good agreement with the experimental results in Fig. 6. These agreements lead to the conclusion that the electrochemical solvent extraction of metallic ions can be explained by the present model. On the basis of the kinetic parameters, R_{ct} , C_{dl} , k , b , obtained in the course of simulation, the solvent extraction mechanism will be discussed. Figure 9 shows the potential dependence of the reciprocal of R_{ct} at various concentrations of MnSO_4 in the aqueous solution of pH 8.0. The R_{ct}^{-1} corresponds to the interfacial charge transfer rate except for

Fig. 9 Plots of the reciprocal of charge transfer resistance, R_{ct}^{-1} , and potential difference, E . The concentration of HQ in DCE phase was 1.0 mol/dm³. The concentrations of Mn(II) in the aqueous solution (pH=8) were (1) 0.01, (2) 0.03, (3) 0.06 and (4) 0.1 mol/dm³.

Fig. 10 Plots of the interfacial capacitances obtained by the simulation on the basis of electrochemical impedance against the potential difference. The concentration of HQ in DCE was 1.0 mol/dm³. The concentrations of Mn(II) in the aqueous solution (pH=8) were (1) 0.01, (2) 0.03, (3) 0.06 and (4) 0.1 mol/dm³.

the contribution of the diffusion process. The charge transfer rate increases with increasing the potential difference. The plots in Fig. 9 show a plateau from 1.0 V to 1.8 V. The value of R_{ct}^{-1} increases with increasing the $MnSO_4$ concentration at the plateau, indicating that the reaction order of $MnSO_4$ is unity. The effect of HQ concentration on R_{ct}^{-1} was investigated as same as Fig. 9, and it was found that the reaction order of HQ was also unity. From Eq. (11), the $c_{M,s}$ is calculated by following equation:

$$c_{M,s} = i / (nFAk). \quad (22)$$

In the present analysis, the $c_{MQ,s}$ could not be determined because the thermodynamic equilibrium con-

Fig. 11 Plots of the concentrations of Mn(II), c_M^s , determined from the simulation against the potential difference, E . The concentration of HQ in DCE was 1.0 mol/dm³. The concentrations of Mn(II) in the aqueous solution (pH=8) were (1) 0.01, (2) 0.03, (3) 0.06 and (4) 0.1 mol/dm³.

stant K has not been obtained. Since the $c_{MQ,s}$ is in proportion to the $c_{M,s}$ in Eq. (3), the behavior of $c_{MQ,s}$ can be discussed by that of $c_{M,s}$. Figures 10 and 11 show the potential dependences of the interfacial capacitance C_{dl} and the interfacial Mn^{2+} concentration $c_{MQ,s}$, respectively.

As shown in Fig. 10, the C_{dl} decreases with increasing the potential difference. In Fig. 11, the $c_{M,s}$ shows similar potential dependence to that of C_{dl} . The above-mentioned result indicates that the interfacial capacitance is a function of the amount of the intermediate in the boundary layer. The steep increases of C_{dl} and $c_{M,s}$ above 0.2 V originate from the transfer of supporting electrolyte across the liquid-liquid interface.

Summary

The i - E curves shows the positive current corresponding to the transfer of the MnQ^+ complex across the water/DCE interface. The apparent diffusion limiting current was observed when the pH of aqueous phase was 8. In the case of low pH, the formation of MnQ^+ complex is interfered by the formation of H^+ -HQ complex. The extraction rate is in proportion to the Mn(II) concentration in aqueous phase and the HQ concentration in DCE phase, indicating that the Mn(II) formed a 1:1 complex with HQ.

In the present paper, the electrochemical impedances were measured in order to investigate the solvent extraction mechanism of Mn(II)-8-hydroxyquinoline system. The capacitive semicircle which originates from the charge transfer resistance and the interfacial capacitance was described on the Nyquist plane. In the limiting current region, the Nyquist plots showed an apparent Warburg impedance, indicating that the diffusion process contributes to the total charge transfer rate. Furthermore, the kinetic parameters were obtained by the simulation. The interfacial capacitance is a func-

tion of the amount of the intermediate in the boundary layer. Above the limiting current region, the charge transfer was mainly done by the supporting electrolyte and the charge transfer resistance decreased abruptly.

A kinetic model of MnQ^+ transfer at water/DCE interface was proposed by the electrochemical investigations.

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