VOLTAMMETRIC ANALYSIS OF CHEMICAL REACTIONS AT LIQUID/LIQUID OR LIQUID/MEMBRANE INTERFACES

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Abstract The voltammetry for the charge transfer at the liquid/liquid interface, VICTLLI, is demonstrated to be very useful for the analysis of reactions at liquid/liquid or liquid/membrane interfaces, choosing distribution processes of ions at the aqueous/organic interface as examples among many interfacial reactions. (1) The extraction constant in the ion-pair extraction, K_{ex} , is related quantitatively to the half-wave potential in the voltammogram for the reversible ion transfer, and the effect of characteristics of the objective ions on K_{ex} is considered on the basis of the results given by VICTLLI. (2) The distribution of ions in the presence of interfacial redox reactions is discussed referring to the voltammograms for the ion and the electron transfer at an aqueous/organic interface. The distribution depends on the ratio of redox agents available for the electron transfer in the aqueous and/or in the organic as well as on standard transfer energies for both transfers. The interaction between the ion and the electron transfers is also discussed from the viewpoint of the separation of ions.

Key words charge transfer voltammogram, ion transfer, electron transfer, distribution of ion, liquid/liquid interface

The voltammetry for the charge (ion or electron) transfer at the liquid/liquid interface, VICTLLI, is a most promising method of elucidating the electrochemical features of the charge transfers across the interface because of the advantage that the transferring charge can be specified from the potentials where the voltammogram appears and the number of charges transferred can be determined from the current simultaneously[1,2].

The VICTLLI has been employed so far for the investigations of the potential generating process in an ion-selective electrode[3,4], relation between the ion transfer at the aqueous(W)/organic(O) interface and the characteristic of the ion [5,6], the solvent extraction mechanisms[7-9], the effect of temperature[10] or coexisting salts[11] on the ion transfer, the electron transfer at the W/O interface[12], the interaction between the ion transfer and the electron transfer[13], the potential oscillation at W/O or W/membrane interface[14,15], etc.

In the present paper, we focus our attention on the distribution of ions in the ion-pair extraction and that coupled with the electron transfer among many interfacial reactions as mentioned above, and elucidate the distribution processes with the aid of VICTLLI.

EXPERIMENTAL

The charge transfer voltammograms in the present work were recorded by the current-scan polarography at the electrolyte solution dropping electrode[16]. Hence, the voltammogram will be called as the polarogram hereafter. The procedure, apparatuses and chemicals used for the measurement of polarograms were identical with those described in previous works[5,6,16].

The potential in the present work are referred to an imaginary potential denoted as TPhE, where the transfer Gibbs energy, ΔG_{tr} , corresponds to zero and is determined on the basis of the extrathermodynamic assumption that the standard transfer Gibbs energies, ΔG_{tr}^0 , of TPhAs⁺ and TPhB⁻ across a liquid/liquid interface are equal[16].

All data given in this paper were obtained at 25 ± 0.5 °C.

RESULTS AND DISCUSSION

Ion transfer polarograms Previous voltammetric and polarographic works on the ion transfers of various ions at the W/O interface have demonstrated that the ion transfer processes of most of ions studied in the following are fast and controlled by the diffusion of the ions in W and/or O[5,6,16].

The polarogram for a reversible transfer reaction (1) of an ion, i^z , at the W/O interface and its half-wave potential, $\Delta V_{1/2}$, are expressed as eqns. (2) and (3), respectively, when the ion-pair formation with counter ion X^{z-} (eqn. 5) or the complex formation of i^z with p of complexing agents such as ionophores, Y, (eqn. 8) takes place in O[3,6].

$$\Delta V = P(i^z) + (RT/zF) \ln(D_{i^z,w}/D_{i^z,o})^{1/2} + (RT/zF) \ln[(I_{lc}-I)/(I-I_{la})] \quad (2)$$

$$\Delta V_{1/2} = P(i^z) + (RT/zF) \ln(D_{i^z,w}/D_{i^z,o})^{1/2} \quad (3)$$

Fig. 1 Relation between half-wave potentials ($\Delta V_{1/2}$) at W/NB interface and the reciprocal of thermochemical chemical radii (r) of transferring ions.

Fig. 2 Relation between extraction constants (K_{ex}) and $\Delta V_{1/2}$. Counter ion: cetyltrimethylammonium ion; organic solvent: chloroform.

where, in the presence of ion-pair formation with association constant K_a in O,

$$P(i^z) = \Delta\phi_{iz}^0 - (RT/zF) \ln(\gamma_{iz,w}/\gamma_{iz,o}) - (RT/zF) \ln(1 + K_a c_{X^{z-},o} \gamma_o^2) \quad (4)$$

$$K_a = c_{i^z_o X^{z-}_o} / c_{i^z_o} c_{X^{z-}_o} \gamma_o^2 \quad (6)$$

or, in the presence of complex formation with sufficiently large stability constant K_{st} in O,

$$P(i^z) = \Delta\phi_{iz}^0 - (RT/zF) \ln(\gamma_{iz,w}/\gamma_{iz,o}) - (RT/zF) \ln(K_{st} c_{Y,o}^p) \quad (7)$$

$$K_{st} = c_{iY_p,o} / c_{i^z_o} c_{Y,o}^p \quad (9)$$

In eqns. (2) to (9), subscripts w and o mean in W and O, and ΔV , $\Delta\phi_{iz}^0$, z , D , γ , I and c are the electrical potential difference which we measure, the standard Galvani potential difference, the charge, the diffusion coefficient, the mean activity coefficient, the current which we measure and the concentration, respectively. The γ of $i^z_o X^{z-}_o$ or Y is assumed to be unity. I_{la} and I_{lc} are the anodic and the cathodic diffusion controlled limiting currents.

The relation between $\Delta V_{1/2}$ and characteristics of ions The $\Delta V_{1/2}$ can be connected to the standard transfer free energy of an ion from W to O, ΔG_{tr}^0 , taking into account the relation as eqn. (10).

$$\Delta\phi_{iz}^0 = -\Delta G_{tr}^0 / zF \quad (10)$$

For example, from eqn. (3)

$$-\Delta G_{tr}^0 / zF = \Delta\phi_{iz}^0 = \Delta V_{1/2} - (RT/zF) \ln(D_{iz,w}/D_{iz,o})^{1/2} + (RT/zF) \ln(\gamma_{iz,w}/\gamma_{iz,o}) - (RT/zF) \ln(1 + K_a c_{X^{z-},o} \gamma_o^2) \quad (11)$$

The ΔG_{tr}^0 of a chemical species from W to O is attributable to the difference between its chemical potentials in each solution which is characterized by the solvation and ion-pair formation or complex formation of the solute.

The standard solvation energies, ΔG_{solv}^0 , of an ion of small volume such as alkaline metal ions or halides and their oxo-acid are determined by Born type and/or ion-dipole electrostatic interactions[5] in which there exists linear relation between ΔG_{solv}^0 and the inverse of the ionic radii as expected from Born or modified Born equations[10].

The $\Delta V_{1/2}$ for the transfer of halides, their oxo-acid anions or other polyatomic anions from W to nitrobenzene (NB) are plotted against the thermochemical radii of the anions in Fig. 1. The linear relation is clearly demonstrated in the figure. In this connection, the ion-pair formation in NB is negligible because of the high dielectric constant of NB.

Considering a voluminous ion, such a non-electrostatic contribution as the formation of a cavity to immerse the ion in the solvent makes a substantial contribution to solvation energy in addition to the electrostatic contribution[6].

Polarograms for the transfer of $\text{CH}_3(\text{CH}_2)_n\text{COO}^-$ or $\text{CH}_3(\text{CH}_2)_n\text{SO}_3^-$ ($n = 5 - 8$) from W to NB were investigated.

Since the negative charge is localized on the COO^- or SO_3^- group in these anions, the solvation of these ions may be divided here into the non-electrostatic solvation of the uncharged moiety, the $\text{CH}_3(\text{CH}_2)_n$ group, and both electrostatic and non-electrostatic solvation of the charged moiety, the COO^- or SO_3^- group. The $\Delta V_{1/2}$ shifted linearly with the increase of n (i.e., about 37 mV more positive with the increment of one methylene group), which suggests that the transfer of the carboxylate or sulphonate ions become easier linearly with the increase of the volume of the uncharged moiety reflecting the increase of the cavity formation energy (especially in the highly structured solvent, water).

Relation between K_{ex} and $\Delta V_{1/2}$ The ion-pair extraction of univalent anion, X^- , with univalent cation, i^+ , from W to O of equal volume to W will be discussed in this paragraph. The initial concentration of X^- or i^+ in W is assumed to be c_{X}^0 or c_{i}^0 , respectively.

When W and O are made in contact, the Galvani potential difference established with X^- , $\Delta\phi_{\text{X}}$, at the interface is

$$\Delta\phi_{\text{X}} = \Delta\phi_{\text{X}}^0 + (RT/F) \ln \{ \gamma_{\text{w}} c_{\text{X,w}} / \gamma_{\text{o}} (c_{\text{X}}^0 - c_{\text{X,w}}) \} \quad (12)$$

If X^- forms ion-pair with i^+ in O, eqn. (12) is substituted by eqn. (13) consulting with eqns. (5) and (6).

$$\Delta\phi_{\text{X}} = \Delta\phi_{\text{X}}^0 + (RT/F) \ln \{ \gamma_{\text{w}} c_{\text{X,w}} / \gamma_{\text{o}} (c_{\text{X}}^0 - c_{\text{X,w}}) \} - (RT/F) \ln (1 + K_{\text{a}} c_{\text{i,o}} \gamma_{\text{o}}^2) \quad (13)$$

Similarly to eqn. (13), the Galvani potential difference established by i^+ , $\Delta\phi_{\text{i}}$, in the presence of ion-pair formation with X^- in O is expressed by

$$\Delta\phi_{\text{i}} = \Delta\phi_{\text{i}}^0 - (RT/F) \ln \{ \gamma_{\text{w}} c_{\text{i,w}} / \gamma_{\text{o}} (c_{\text{i}}^0 - c_{\text{i,w}}) \} + (RT/F) \ln (1 + K_{\text{a}} c_{\text{X,o}} \gamma_{\text{o}}^2) \quad (14)$$

Since $\Delta\phi_{\text{X}}$ should be equal to $\Delta\phi_{\text{i}}$ at the extraction equilibrium and the extraction constants for X^- and i^+ , $K_{\text{ex,X}}$ and $K_{\text{ex,i}}$, are given as eqns. (15) and (16), we obtain eqn. (17).

$$K_{\text{ex,X}} = (c_{\text{X}}^0 - c_{\text{X,w}}) / c_{\text{X,w}} \quad (15)$$

$$K_{\text{ex,i}} = (c_{\text{i}}^0 - c_{\text{i,w}}) / c_{\text{i,w}} \quad (16)$$

$$\begin{aligned} \Delta\phi_{\text{X}}^0 + (RT/F) \ln (\gamma_{\text{w}} / \gamma_{\text{o}}) - (RT/F) \ln K_{\text{ex,X}} - (RT/F) \ln (1 + K_{\text{a}} c_{\text{i,o}} \gamma_{\text{o}}^2) \\ = \Delta\phi_{\text{i}}^0 - (RT/F) \ln (\gamma_{\text{w}} / \gamma_{\text{o}}) + (RT/F) \ln K_{\text{ex,i}} - (RT/F) \ln (1 + K_{\text{a}} c_{\text{X,o}} \gamma_{\text{o}}^2) \end{aligned} \quad (17)$$

Taking into account eqns. (3) and (4), eqn. (17) can be rewritten as

$$\Delta V_{1/2,\text{X}} - (RT/F) \ln (D_{\text{X,w}} / D_{\text{X,o}})^{1/2} - (RT/F) \ln K_{\text{ex,X}} = \Delta V_{1/2,\text{i}} + (RT/F) \ln (D_{\text{i,w}} / D_{\text{i,o}})^{1/2} + (RT/F) \ln K_{\text{ex,i}} \quad (18)$$

Hence,

$$\ln K_{\text{ex,X}} = (F/RT) \Delta V_{1/2,\text{X}} - (F/RT) \Delta V_{1/2,\text{i}} - \ln (D_{\text{X,w}} / D_{\text{X,o}})^{1/2} - \ln (D_{\text{i,w}} / D_{\text{i,o}})^{1/2} - \ln K_{\text{ex,i}} \quad (19)$$

In the extraction of various kinds of X^- with a definite i^+ , terms in the right hand side other than the first in eqn. (19) can be regarded as constant.

$$\ln K_{\text{ex,X}} = (F/RT) \Delta V_{1/2,\text{X}} + \text{const.} \quad (20)$$

Equation (20) suggests that there exists a linear relation between $K_{\text{ex,X}}$ and $\Delta V_{1/2,\text{X}}$, and $K_{\text{ex,X}}$ is larger when $\Delta V_{1/2,\text{X}}$ is more positive.

In Fig. 2, $\log K_{\text{ex}}$ for univalent anions obtained by the ion-pair extraction from W to chloroform using cetyltrimethylammonium ion as the counter cation[17] are plotted against $\Delta V_{1/2}$ observed in polarograms for the transfer of the ions from W to chloroform.

It is clear from eqn. (19) that $\ln K_{\text{ex}}$ depends strongly on the nature of the counter ion. Counter ions of large ionic radii and low charge or those which have voluminous uncharged moiety may enhance $\ln K_{\text{ex}}$.

Electron transfer polarograms At the W/O interface not only ion but also electron transfers through the interfacial redox reaction.

The polarogram and its $\Delta V_{1/2}$ for electron transfer reaction (21) between the redox couples $\text{O1(W)}/\text{R1(W)}$ in W and $\text{O2(O)}/\text{R2(O)}$ in O at the W/O interface were proposed as eqns. (22) and (23), respectively[12].

$$\begin{aligned} \Delta V = P(\text{el}) + (RT/n_1 n_2 F) \ln [(D_{\text{O1}}^{n_2} D_{\text{R2}}^{n_1}) / (D_{\text{R1}}^{n_2} D_{\text{O2}}^{n_1})]^{1/2} \\ + (RT/n_1 n_2 F) \ln [(I_{\text{dR1}} - I)^{n_2} (I_{\text{dO2}} - I)^{n_1} / (I_{\text{dO1}} - I)^{n_2} (I_{\text{dR2}} - I)^{n_1}] \end{aligned} \quad (22)$$

$$\begin{aligned} \Delta V_{1/2} = P(\text{el}) + (RT/n_1 n_2 F) \ln [(D_{\text{O1}}^{n_2} D_{\text{R2}}^{n_1}) / (D_{\text{R1}}^{n_2} D_{\text{O2}}^{n_1})]^{1/2} \\ + (RT/n_1 n_2 F) \ln [2(I_{\text{dR1}} - I_{\text{la}} - I_{\text{lc}})^{n_2} (2I_{\text{dO2}} - I_{\text{la}} - I_{\text{lc}})^{n_1} / (2I_{\text{dO1}} - I_{\text{la}} - I_{\text{lc}})^{n_2} (2I_{\text{dR2}} - I_{\text{la}} - I_{\text{lc}})^{n_1}] \end{aligned} \quad (23)$$

where,

$$P(\text{el}) = \Delta\phi_{\text{el}}^0 + (RT/n_1 n_2 F) \ln [(\gamma_{\text{R1}}^{n_2} \gamma_{\text{O2}}^{n_1}) / (\gamma_{\text{O1}}^{n_2} \gamma_{\text{R2}}^{n_1})] \quad (24)$$

Fig. 3 Polarograms for the transfer of K^+ or Na^+ from W to NB facilitated by Val or DB18C6 and for the transfer of electrons from W to NB. (1) Residual current in the polarograms. (2) 10^{-4} M K_2SO_4 in W / 10^{-3} M Val in NB. (3) 10^{-4} M Na_2SO_4 in W / 10^{-3} M Val in NB. (4) 10^{-4} M K_2SO_4 in W / 10^{-2} M DB18C6 in NB. (5) 10^{-4} M Na_2SO_4 in W / 10^{-2} M DB18C6 in NB. (6) - (10) 5×10^{-4} M $H_4[Fe(CN)_6]$ in W / 5×10^{-3} M TCNQ in NB in the presence of (6) 10^{-3} , (7) 2×10^{-3} , (8) 5×10^{-3} , (9) 10^{-2} or (10) 1.5×10^{-2} M TCNQ $^-$. Supporting electrolytes: 1 M $MgSO_4$ in W, 0.05 M $CV^+ \cdot TPhB^-$ in NB.

In these equations, n_1 and n_2 are related to the redox reactions in the individual phases

E_i^0 is the standard potential for the reaction (25) or (26), I_{la} and I_{lc} are the anodic and cathodic limiting currents and I_{di} is the potential diffusion current of species i which is proportional to the bulk concentration of i , c_i .

The standard Galvani potential difference for the electron transfer reaction, $\Delta\phi_{el}^0$, was demonstrated to be the difference between $E_{O2/R2}^0$ and $E_{O1/R1}^0$ [12].

$$\Delta\phi_{el}^0 = E_{O2/R2}^0 - E_{O1/R1}^0 \quad (27)$$

Equations (22), (23) and (27) are valid for the reversible electron transfer reactions including the system investigated in the present work which is composed of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ in W and 7,7,8,8-tetracyanoquinodimethane (TCNQ)/TCNQ anion radical (TCNQ $^-$) in NB.

Comparing eqns. (3) with (23), it is impressive that though $\Delta V_{1/2}$ for the ion transfer is independent of the concentration of i^z , $\Delta V_{1/2}$ for the electron transfer includes I_{di} s and hence depends on the concentrations of redox agents in W and NB, which means that the potentials where the electron transfer occurs can be varied by changing concentrations of redox agents. In this connection, Stewart et al. [18] pointed out that midpeak potentials in voltammograms for an electron transfer at a liquid/liquid interface vary with ratios of reactants and products in both phases.

In the following, we will discuss the interaction between the ion transfer and the electron transfer.

Polarograms for the ion or electron transfer The typical example of the residual polarogram is shown as curve 1 in Fig. 3 which was recorded at the interface of W containing 1 M $MgSO_4$ and NB containing 0.05 M $CV^+ \cdot TPhB^-$. Curves 2 and 3 realize polarograms for the ion transfer of K^+ and Na^+ , respectively, facilitated by valinomycin, Val. The polarograms were recorded at the interface of W containing 10^{-4} M K_2SO_4 or Na_2SO_4 and NB containing 10^{-3} M Val. Curves 4 and 5 are polarograms for the transfer of K^+ and Na^+ facilitated by 10^{-2} M dibenzo-18-crown-6, DB18C6, recorded under the same condition as curves 2 and 3 but using DB18C6 instead of Val. The transfer processes of K^+ and Na^+ facilitated by 10^{-3} M Val or 10^{-2} M DB18C6 were confirmed to be controlled by the diffusion of K^+ and Na^+ , when the concentration of K^+ or Na^+ is less than 2.5×10^{-4} M.

Curves 6 to 10 in Fig. 3 are the electron transfer polarograms observed with W containing 5×10^{-4} M $H_4[Fe(CN)_6]$ and NB containing 5×10^{-3} M TCNQ and 10^{-3} to 1.5×10^{-2} M TCNQ $^-$. The reaction involved in these polarograms is attributable to eqn. (28) and is controlled by the diffusion of $Fe(CN)_6^{4-}$ in W referring to the previous work [12].

$\Delta V_{1/2}$ in the polarograms shifted positively with the increase of the ratio of c_{TCNQ}/c_{TCNQ^-} , as expected from eqn. (23).

Estimation of the interaction between the ion and electron transfers based on charge transfer polarograms Let us consider the spontaneous interaction between the ion transfer and the electron transfer at the W/NB interface, when W containing 2×10^{-4} M K^+ and 5×10^{-4} M $Fe(CN)_6^{4-}$ and NB containing 5×10^{-3} M TCNQ, 10^{-2} M TCNQ $^-$ and 10^{-3} M Val are made in contact without applying potential or current. The rate of the transfer of electrons, which carry minus charges, from W to NB due to the redox reaction between $Fe(CN)_6^{4-}$ and TCNQ should be equal to that of the transfer of cations from W to NB or that of anions from NB to W in order to hold the electroneutrality in both phases. Here, as it is obvious from polarograms in Fig. 3, the transfer of K^+ from W to NB occurs in the present case since the transfer of K^+ is much easier than the transfer of $TPhB^-$, the supporting electrolyte anion, from NB to W. The

potential difference at the W/NB interface established by the interaction between two charge transfers can be estimated from the charge transfer polarograms, taking into account that the current corresponds to the rate of the charge transfer. That is, under the present experimental condition, the potential difference is determined to be *a* in Fig. 3, where the current (indicated as *A*) in polarogram 2 is equal to that in polarogram 9. When c_{TCNQ^-} in NB is 10^{-3} M instead of 10^{-2} M, since the electron transfer polarogram is as curve 6, the rates of the ion and electron transfers increase to be those which correspond to current *B* and the potential difference (*b* in Fig. 3) is more positive than *a*. When 2×10^{-4} M Na^+ is added to W instead of K^+ , the rates of the transfers of Na^+ and electron are nearly zero regardless of c_{TCNQ^-} , because the polarogram for the transfer of Na^+ lies at much more positive potentials than that for the transfer of K^+ .

Estimation of the concentration of i^z transferred with the electron transfer after the equilibrium When W containing 2×10^{-4} M K^+ and 5×10^{-4} M $\text{Fe}(\text{CN})_6^{4-}$ is made in contact with equal volume of NB containing 5×10^{-3} M TCNQ, 10^{-2} M TCNQ^- and 10^{-3} M Val, the initial rate of ion transfer and that of electron transfer correspond to *A* in curves 2 and 9 in Fig. 3 (which are reproduced as curves 1 and 1' in Fig. 4) as mentioned previously. The transfer of K^+ from W to NB and that of the equivalent amount of electrons from W to NB proceed with standing the system. Consequently, the concentrations of K^+ and $\text{Fe}(\text{CN})_6^{4-}$ in W and TCNQ in NB decrease and those of $\text{Fe}(\text{CN})_6^{3-}$ in W and K^+ and TCNQ^- in NB increase instead. Hence, the ion and electron transfer polarograms should be transformed as curves 1 to 4 and curves 1' to 4' in Fig. 4, respectively, with the increase of the standing time, if we could measure the ion and electron transfer polarograms individually. Curves 1', 2', 3' and 4' in Fig. 4 are the electron transfer polarograms after standing for the same times as those for the ion transfer polarograms 1, 2, 3 and 4, respectively. Here, the polarograms are illustrated based on eqn. (2).

As can be understood intuitively with the assistance of Fig. 4, the rates of the ion and electron transfers decrease and the potential difference at zero current in the ion transfer polarogram, $\Delta V_{i^z, I=0}$, and that in the electron transfer polarogram, $\Delta V_{e^-, I=0}$, come close each other with the increase of the standing time. Finally, when the distribution equilibrium is attained, the apparent rates of the charge transfers become zero and $\Delta V_{i^z, I=0}$ coincides with $\Delta V_{e^-, I=0}$.

The above consideration is verified by the following experiments; After equilibrating 100 ml of W containing 2×10^{-4} M K^+ and 5×10^{-4} M $\text{Fe}(\text{CN})_6^{4-}$ with 100 ml of NB containing 5×10^{-3} M TCNQ, 10^{-2} M TCNQ^- and 10^{-3} M Val, each phase was separated by the centrifugation. Here, W and NB after the equilibrium are denoted as W_{eq} and NB_{eq} , respectively. Curves 1 and 2 in Fig. 5 are the polarogram recorded at the interface of W_{eq} and a fresh NB containing 10^{-3} M Val and that at the interface of a fresh W containing supporting electrolyte only and NB_{eq} , respectively. Polarograms 1 and 2 correspond to the transfer of K^+ remained in W_{eq} to NB and that of K^+ moved to NB_{eq} to W, respectively. The electron transfer reaction does not occur in these polarographic conditions, because $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ or TCNQ and TCNQ^- are not added to the fresh W or NB. Curve 3 is the polarogram composed of curves 1 and 2 which corresponds to the ion transfer polarogram for K^+ at the $W_{\text{eq}}/NB_{\text{eq}}$ interface. Curve 4 is the electron transfer voltammogram measured at the interface of W_{eq} and a fresh NB containing 5×10^{-3} M TCNQ and 10^{-2} M TCNQ^- . In curve 4 the transfer of K^+ from W_{eq} to NB is not observed as NB does not contain Val. Here, c_{TCNQ} and c_{TCNQ^-} in NB_{eq} is considered to be substantially equal to those in the initial NB before the equilibrating procedure, since c_{TCNQ} and c_{TCNQ^-} are much larger than c_{K^+} . Therefore, curve 4 corresponds to the electron transfer at the interface of W_{eq} and NB_{eq} . Not only $\Delta V_{i^z, I=0}$ in curve 3 and $\Delta V_{e^-, I=0}$ in curve 4 in Fig. 5 coincide with each other but also these $\Delta V_{I=0}$ s agree with $\Delta V_{I=0}$ s in curves 4 and 4' in Fig. 4.

The $V_{i^z, I=0}$ for ion transfer reaction (1) facilitated by reaction (8) is given as eqn. (29) substituting 0 to 1 in eqn. (2).

$$\Delta V_{i^z, I=0} = P(i^z) - (RT/zF) \ln(c_{i^z, w}/c_{i^z, o}) \quad (29)$$

Fig. 4 Time courses of ion transfer and electron transfer polarograms after W containing 2×10^{-4} M K^+ and 5×10^{-4} M $\text{Fe}(\text{CN})_6^{4-}$ is brought into contact with an equal volume of NB containing 5×10^{-3} M TCNQ, 10^{-2} M TCNQ^- and 10^{-3} M Val. Curve 1(1'): at initial condition. Curves 2(2'), 3(3') and 4(4'): $c_{\text{K}^+, w}$ is decreased to be 1.5×10^{-4} , 1.2×10^{-4} and 7.1×10^{-5} M, respectively, incorporated with the electron transfer.

Fig. 5 Ion transfer and electron transfer polarograms recorded at the W/NB interface using W_{eq} or NB_{eq} (W and NB after equilibration; W containing 2×10^{-4} M K^+ and 5×10^{-4} M $\text{Fe}(\text{CN})_6^{4-}$ and NB containing 5×10^{-3} M TCNQ, 10^{-2} M TCNQ^- and 10^{-3} M Val). (1) The transfer of K^+ from W_{eq} to fresh NB containing 10^{-3} M Val. (2) The transfer of K^+ from NB_{eq} to fresh W containing supporting electrolyte only. (3) Polarogram composed of curves 1 and 2. (4) The electron transfer at the interface of W_{eq} and fresh NB containing 5×10^{-3} M TCNQ and 10^{-2} M TCNQ^- . Supporting electrolytes: 1 M MgSO_4 in fresh W or W_{eq} , 0.05 M CV^+TPhB^- in fresh NB or NB_{eq} .

TABLE 1. The concentration of K⁺ or Na⁺ transferred with the electron transfer after the equilibrium

In initial NB c _{TCNQ} /M	c _{TCNQ} /M	ionophore	10 ⁴ c _{K⁺} /M			10 ⁴ c _{Na⁺} /M		
			in W	found in NB	calc. in NB	in W	found in NB	calc. in NB
5x10 ⁻³	10 ⁻³	Val	0.23	1.77	1.81	1.99	<0.01	0.03
5x10 ⁻³	2x10 ⁻³	Val	0.34	1.66	1.70	2.00	<0.01	0.02
5x10 ⁻³	5x10 ⁻³	Val	0.48	1.52	1.49	2.00	<0.01	0.01
5x10 ⁻³	10 ⁻²	Val	0.79	1.21	1.29	2.00	<0.01	0.01
5x10 ⁻³	1.5x10 ⁻²	Val	0.86	1.14	1.17	2.00	<0.01	0.01
5x10 ⁻³	10 ⁻³	DB18C6	1.68	0.32	0.22	1.98	0.02	0.05
5x10 ⁻³	2x10 ⁻³	DB18C6	1.86	0.14	0.16	1.99	<0.01	0.04
5x10 ⁻³	5x10 ⁻³	DB18C6	1.94	0.06	0.10	2.00	<0.01	0.02
5x10 ⁻³	10 ⁻²	DB18C6	1.98	0.02	0.07	2.00	<0.01	0.02
5x10 ⁻³	1.5x10 ⁻²	DB18C6	2.00	<0.01	0.06	2.00	<0.01	0.01

Initial concentration of K⁺ or Na⁺: 2x10⁻⁴ M.

The $\Delta V_{el,I=0}$ for the electron transfer reaction (21) is given as eqn. (30) substituting 0 to I in eqn. (22).

$$\Delta V_{el,I=0} = P(el) + (RT/n_1 n_2 F) \ln[(c_{R1}^{n_2} c_{O2}^{n_1}) / (c_{O1}^{n_2} c_{R2}^{n_1})] \quad (30)$$

Since the equilibrium condition for the ion transfer reaction (1) facilitated by the chemical reaction (8) coupled with the electron transfer reaction (22) at an interface is given in eqn. (31), eqn. (32) is derived from eqns. (29) and (30).

$$\Delta V_{iz,I=0} = \Delta V_{el,I=0} \quad (31)$$

$$P(iz) - (RT/zF) \ln(c_{iz,w}/c_{iz,o}) = P(el) + (RT/n_1 n_2 F) \ln[(c_{R1}^{n_2} c_{O2}^{n_1}) / (c_{O1}^{n_2} c_{R2}^{n_1})] \quad (32)$$

Considering that W containing $c_{iz,w}^0$ of iz , c_{O1}^0 of O1 and c_{R1}^0 of R1 is made in contact with NB containing $c_{iz,o}^0$ of iz , c_{O2}^0 of O2 and c_{R2}^0 of R2 and that $c_{iz,w}$ decreases from $c_{iz,w}^0$ to $c_{iz,w}^0 - x$ after the equilibrium, eqn. (32) for $n_1 = n_2 = 1$ is transformed to eqn. (33) when $z = 1$.

$$P(iz) - (RT/F) \ln[(c_{iz,w}^0 - x) / (c_{iz,o}^0 + x)] = P(el) + (RT/F) \ln[(c_{R1}^0 - x)(c_{O2}^0 + x) / (c_{O1}^0 - x)(c_{R2}^0 + x)] \quad (33)$$

Separation of ions with the aid of an electron transfer reaction The above discussion suggests that, if we choose an appropriate electron transfer reaction taking into account both $\Delta\phi_{el}^0$ and concentrations of R1(W), O1(W), R2(NB) and O2(NB), we may not only control the instantaneous rate of the ion transfer but also realize the separation of an ion in W from various coexisting ions of different $\Delta\phi_{iz}^0$ s transferring the ion to NB by the electron transfer reaction.

Table 1 summarizes results on the following experiments; 10 ml of W containing 2 x 10⁻⁴ M K⁺ or Na⁺ and 5 x 10⁻⁴ M H₄[Fe(CN)₆] was equilibrated shaking for 1 h with 10 ml of NB containing TCNQ and TCNQ⁻ in various concentration ratio (c_{TCNQ} = 5 x 10⁻³ M) and 10⁻³ M Val or 10⁻² M DB18C6, and then concentrations of K⁺ or Na⁺ in W and NB were determined by the flame spectrometry.

The results experimentally found agree fairly well with those calculated based on eqn (33) which are added to Table 1 demonstrating that the separation of an ion from coexisting ions can be attained with the aid of an electron transfer reaction chosen appropriately.

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