Volatammetry with an Ion-Selective Microelectrode Based on Polarizable Oil/Water Interface

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Theoretical expressions are presented for the potential step chronoamperometry, normal pulse voltammetry and cyclic voltammetry of the ion-transfer at an ion-selective microelectrode in which a polarizable nitrobenzene/water interface is formed at the tip of a micropipet of µm-order diameter with the nitrobenzene phase inside the micropipet. Experiment includes the ion transfer voltammetry of acetylcholine at the microelectrode. The experimental results are well explained by the theoretical predictions. Stripping voltammetry with the microelectrode is also studied; this proved to be promising for determination of acetylcholine at micromolar concentration levels.

Keywords Acetylcholine, ion-selective electrode, microvoltammetry, stripping voltammetry, theoretical prediction

Recent electrochemical studies on the transfer of ions across the interface between two immiscible electrolyte solutions (or, in short, the oil/water (O/W) interface) have shown that the polarizable oil/water interface can function as an ion-selective electrode (ISE) interface. Such an electrode interface responds in both amperometric (or voltammetric) and potentiometric modes to the specified ion(s) that is (are) transferable across the interface in the polarizable potential range. One can design not only an oil or organic ISE for monitoring analyte ion(s) in aqueous solvent but also a water or aqueous ISE for monitoring analyte ion(s) in organic solvent.

There are dramatic changes of “conventional” electrochemical responses when very small electrodes are substituted for the working electrodes in voltammetry and the voltammetric studies on micro- or ultramicroelectrodes have been the subject of keen interest in recent years. In this study we examined an ion-selective microelectrode (ISME) based on the polarizable nitrobenzene/water interface formed at the tip, usually of about 10 µm diameter, of a micropipet with the organic phase inside. We wanted to apply the ISME for trace determination of analyte ion(s) in aqueous sample solutions. This paper describes theoretical aspects and some experimental results of the potential step chronamperometry, normal pulse voltammetry and cyclic linear potential sweep voltammetry of ions (acetylcholine and choline ions) in aqueous solution with the ISME based on the polarizable nitrobenzene/water interface.

Part of the experimental results has been reported in a preliminary form and in a book. Independently of this study Taylor and Girault have reported ion-selective micropipet electrodes with the aqueous phase located inside the micropipet and some cyclic voltammetric results of the ion transfer at the 1,2-dichloroethane/water interface obtained with their microelectrodes.

Experimental

The ISMEs were fabricated from glass micropipet of a tip diameter of a=10 to 20 µm. The micropipet was filled with a nitrobenzene solution of 0.1 mol/dm³ tetrabutylammonium tetraphenylborate (0.1 M TBATPB(NB)) to the depth of a few hundreds to a few thousands of micrometers from the tip. Then, an aqueous solution of 0.1 mol/dm³ tetrabutylammonium chloride (0.1 M TBACI(W)) was placed over the nitrobenzene in the micropipet and an Ag/AgCl electrode was immersed in the 0.1 M TBACI(W). The glass micropipets were prepared from glass capillary tubes using a microelectrode puller Type PP-83 and a stone grinder type EG-5 (Narishige Scientific Instrument Lab., Tokyo).

Electrochemical measurements

The electrochemical cell for voltammetric measurements is represented by

\[ \text{an ion-selective microelectrode} \quad \begin{array}{c}
\text{Ag} | \text{AgCl} | 0.1 \text{ M TBACI(W)} | 0.1 \text{ M TBATPB(NB)} | \\
\text{test soln.(W)} | \text{AgCl} | \text{Ag}
\end{array} \]
The applied potential, \( E (= \text{the potential of the right-hand side terminal of the cell referred to the potential of the left-hand}) \), was imposed on the cell. The resulting current, \( I \), associated with the transfer of ion(s) across the polarized NB/W interface (marked by * in the cell) was recorded. The flow of positive charge from the W to NB phase across the interface was taken as the positive current.

A two-electrode system was used to record the voltammetric curves with the ISME. All measurements were done at room temperature (20 to 25°C). Instruments and chemicals have been described elsewhere.

Theoretical

Let us consider the transfer of ions from the aqueous (W) to the organic (O) phase across the disk NB/W interface at the tip of the glass micropipet electrode. We assume that initially (at the time \( t=0 \)) the ion is present homogeneously in the W phase at the concentration of \( c_w \). Then the surface concentrations of the ion in the W and O phase, \( [c_w]_{x=0} \) and \( [c_o]_{x=0} \), respectively, where \( x=0 \) means the interface between the W and O phases, are given by:

\[
L[(c_w)_{x=0}] = \frac{c_w}{s} - L[h_1(t)]L[I/zF],
\]
\[
L[(c_o)_{x=0}] = L[h_2(t)]L[I/zF].
\]

Here \( L \) is the operator for the Laplace transformation, \( s \) the variable of the Laplace transformation, \( I \) the total current, \( z \) the number of charge of the ion and \( F \) the Faraday constant; \( h_1(t) \) and \( h_2(t) \) are certain functions of \( t \) that are characteristic to the mode of diffusion of the ion in the W and O phases, respectively. For the three-dimensional diffusion in the W phase (see Fig. 1), Aoki and Osteryoung have introduced the function \( L[h(t)] = \frac{1}{4\pi a^2} \left( \frac{1}{D_w s} \right)^{1/2} \). This can be expressed by a power series of \( \xi = (a/2)(s/Dw)^{1/2} \), where \( a \) is the radius of the disk and \( D_w \) the diffusion coefficient of ion in a phase \((a=W, O)\). Thus, it can be shown that on taking the first term of the series for a small value of \( \xi \), that is, for \( 0.36a/(Dw t)^{1/2} \ll 1 \) (see Eq. (7) in ref. 15), the function \( h_1(t) \) is reduced to the approximate equation given by Eq. (2a) below. On the other hand the diffusion in the O phase inside the micropipet can be regarded as linear diffusion (see Fig. 1) and hence \( h_2(t) \) is given by Eq. (2b):

\[
L[h_1(t)] = 1/4Dw a \quad \text{(for } 0.36a/(Dw t)^{1/2} \ll 1 \text{)}
\]
\[
L[h_2(t)] = (1/\pi a^2)(1/D_o s)^{1/2}. 
\]

Chronoamperometry and normal pulse voltammetry

When a step potential \( E \) is applied to the interface at \( t=0 \), we have for the reversible ion transfer at the interface

\[
[c_o]_{x=0}/[c_w]_{x=0} = \zeta \exp\left(\frac{zF}{RT}(E-E^0)\right),
\]

where \( E^0 \) is the standard potential of the ion transfer, \( R \) the gas constant and \( T \) the thermodynamic temperature. Combining Eqs. (1a), (1b), (2a) and (2b) with Eq. (3), we get the expression of \( I/zF \) in the form of Laplace transformation, which gives by the reverse transformation the \( I/zF \) for chronoamperometry at the very small disk electrode:

\[
I/zF = 4Dw a c_w \exp\left(\xi^2\right) \text{erfc}(\xi),
\]

where \( \xi = (a/2)(s/Dw)^{1/2} \). Accordingly, we get the equation of the reversible current-potential curve in a more familiar form:

\[
\zeta = \exp\left(\frac{zF}{RT}(E-E^0)\right),
\]

where \( E^0 \) is the standard potential of the ion transfer, \( R \) the gas constant and \( T \) the thermodynamic temperature. Combining Eqs. (1a), (1b), (2a) and (2b) with Eq. (3), we obtain the current-potential curve, equivalent to the normal pulse polarogram, at the disk micropipet electrode. It can be shown that the function \( \exp(x^2)\text{erfc}(x) \) is approximated well by \( 1/(1+(1.301x)^{1.079}) \). Accordingly, we get the equation of the reversible current-potential curve in a more familiar form:

\[
I = I_0 \left[ 1 + \exp\left( -1.08zF/RT(E-E_{1/2}) \right) \right]
\]

with

\[
I_0/zF = 4Dw a c_w \zeta,
\]

\[
E_{1/2} = E^0 + (RT/1.08zF)\ln((D_w/D_o)^{1/2} \times 1.30[4(D_w t)^{1/2}/\pi a])
\]

Linear potential sweep voltammetry

For the reversible ion transfer at the interface we have

\[
[c_o]_{x=0}/[c_w]_{x=0} = \bar{\zeta}(t), \quad \bar{\zeta}(t) = \exp\left(\frac{zF}{RT}(vt+E_t-E^0)\right),
\]
where \( v \) is the rate of the potential sweep, \( E_i \) the initial potential, here assumed to be largely negative than \( E^0 \). For the small values of \( v \) and \( a \), that is, for \( p = \frac{(zF^2a^3v}{RTD^w})^{1/2} < 0.1 \) (see Eqs. (6)-(8) and Figs. 1 and 2 in ref. 16), we have a formal solution for the current \( I(t) \), as given by

\[
\frac{I(t)}{zF} = \Phi(t) = 4D^wac_w/[1+e^{\phi}B(t)] \tag{9}
\]

with

\[
\Phi(t) = \Phi(t) = h_1(t) * \Phi(t) = h_1(t) * \Phi(t), \tag{10}
\]

where \( h_1(t) \) and \( h_2(t) \) are given by Eqs. (2a) and (2b) and \( f_1 * f_2 \) denotes the convolution of two functions \( f_1 \) and \( f_2 \). Equation (9) may be solved by the method of successive substitution. Thus, in the first place by substituting \( \Phi(t) = 4D^wac_w[1+e^{\phi}B(t)]^{-1} \) for \( \Phi(t) \) in Eq. (10) the function \( B(t) \) was numerically calculated; the result can be approximated by \( B(t) = 1.2(t/\tau_D)^{1/2}(D^w/a)^2 \).

Hence we have for the first approximation

\[
\frac{I}{zF} = I_{11,a} / [1+e^{\phi}(zF/RT)(vt+E_{11/2})] \tag{11}
\]

with

\[
I_{11,a} = 4D^wac_w, \tag{12}
\]

\[
E_{11/2} = E^0 + (RT/2F)\ln(D^w/D^a)^{1/2} \times 0.68[4(D^w)^{1/2}/n_a]. \tag{13}
\]

Cyclic linear potential sweep voltammetry

For the first scan of the potential sweep to the anodic (that is, positive) direc tion, the anodic (that is, positive) current associated with the transfer of ion from the aqueous to the organic phase should be predicted by Eq. (10) or Eq. (11) with Eq. (12). Then, upon scanning back the potential to the cathodic (that is, negative) direction, the current associated with the transfer back of the ion from the organic to the aqueous phase is observed. Exact mathematical analysis of the cathodic back transfer process of ions from the NB to W phase has not been done. However, it can be stated that this cathodic current—potential (or time) curve should be of the peak-height shape, since the transfer back process is controlled by the linear diffusion of ions in the O phase near the tip inside the micropipet. The peak height should be proportional to the bulk concentration of analyte ion in the W phase. Further important features of the cathodic peak-shaped current are discussed below.

Results and Discussion

Figure 2 shows anodic current—potential (\( I-E \)) curves (corrected for the base current) of potential step chronoaamperometry (normal pulse voltammetry) for the transfer of \( 5\times10^{-4} \) mol dm\(^{-3} \) acetylcholine (Ach\(^+ \)) ion from the aqueous to nitrobenzene phase, measured at \( t_s = 5 \) s (plot A) and 20 s (B) with a microelectrode of \( a = 7.5\times10^{-4} \) cm. Figure 3 shows the logarithmic analysis of the \( I-E \) curves in Fig. 2. The slope of the logarithmic plots is 59 mV for both (A) and (B) with the observed half-wave potentials of 0.365 and 0.381 V for (A) and (B), respectively. The results are well explained by the theoretical prediction of Eqs. (5)–(7); Table 1 shows the diffusion coefficient of Ach\(^+ \) ion in aqueous solution as calculated by Eq. (6) and the observed and calculated half-wave potentials of Ach\(^+ \) ion at the NB/W interface. The calculated half-wave potentials were obtained by taking \( E_{1/2} = E^0 + (RT/2F)\ln(D^w/D^a)^{1/2} \) at the NB/W interface of conventional size = 0.289 V, \( D^w = 0.9\times10^{-5} \) cm\(^2\) s\(^{-1} \) and \( a = 7.5\times10^{-4} \) cm by Eq. (7).
Figure 4 shows a cyclic voltammogram of $5 \times 10^4$ mol dm$^{-3}$ Ach$^+$ ion in the aqueous phase with a microelectrode of $a=5.5 \times 10^{-4}$ cm at $v=10$ mV s$^{-1}$. The anodic current is of sigmoid form while the cathodic current is a peak-shaped wave, as predicted from theoretical considerations. The anodic limiting current was proportional to the bulk concentration of Ach$^+$ ion in the range of $5 \times 10^5$ to $2 \times 10^3$ mol dm$^{-3}$. Dependences of the limiting current and the half-wave potential on the sweep rate are summarized in Table 2. The anodic limiting current was independent of $v$ between 2 and 20 mV/s, which is in agreement with the theoretical prediction as given by Eq. (12). The slightly increasing tendency of the limiting current with increasing $v$ for $v>50$ mV/s may become understandable by considering that the current height increases with increasing $p$ value and that $p=0.002v$ mV s$^{-1}$ for this particular microelectrode (see discussion on Eq. (9) above). The observed half-wave potentials shifted to more negative potential values with increasing $v$. The agreement between the experimental half-wave potentials and the ones calculated by Eq. (11) with Eq. (13) (that is, $E_{a,1/2}=E_{a,1/2}(t=t')$ where $v'=E_{a,1/2}(t=t')-E_0$) is fairly good, especially for the smaller values of $v$.

The peak height of the cathodic current was proportional to the bulk concentration of Ach$^+$ ion in the aqueous phase (Fig. 5, curve A). The peak potentials were always more negative than the half-wave potential of the anodic current, which appears not unusual for the peak-shaped current. On the other hand, the peak heights depend only slightly on $v$. This is in contrast to the ordinary behavior of the peak height in linear potential sweep voltammetry with an electrode of conventional size where the peak height increases linearly with the square root of $v$ (but can be explained reasonably as described below). Another interesting fact, especially from an analytical point of view, is that the cathodic peak current is rather high compared with the limiting current of the anodic current. This can be explained by the following process: during the anodic ion transfer process...
in the first potential scan the ion concentration in the organic phase at the tip inside the micropipet is elevated by the diffusion influx of ions from the large volume of the outside aqueous phase into the small volume of the organic phase adjacent the tip inside the micropipet. This elevated-concentration effect, similar to the stripping voltammetry effect in the ordinary analytical voltammetry, can more clearly be demonstrated by the following experiment. The electrode potential was stepped from the initial potential $E_0$, e.g. 0.24 V, up to the potential where the limiting anodic current is obtained, e.g. 0.48 V, and was kept for the period of $T_e$, the pre-electrolysis (or pre-electroextraction) time. This was followed by the potential sweep linearly in the cathodic direction back to the $E_0$ value (see the insert in Fig. 6). A large cathodic peak current was obtained; the peak height was proportional to the bulk concentration of $\text{Ach}^+$ ion in the aqueous phase (Fig. 5, curve B). Also, the peak height increased with increasing $T_e$, proportional to the square root of $T_e$ as seen in Fig. 6. During the period of the pre-electrolysis time the influx of the ion from the aqueous to the organic phase can be expressed by $\frac{1}{zFA} = \frac{4Dwacw}{\pi a^2}$, where the surface area $A = \pi a^2$. This influx is balanced by the linear diffusion flux of the ion from the interface to the bulk of the organic phase, which is given by $\frac{1}{zFA} = \frac{D^0[\text{Ach}]_{\text{eq}}}{(\pi D^0 T_e)^{1/2}}$. Consequently, we have $4Dwacw/\pi a^2 = D^0[\text{Ach}]_{\text{eq}}/(\pi D^0 T_e)^{1/2}$; hence the elevation of the surface concentration as expressed by the ratio $[\text{Ach}]_{\text{eq}}/c^w$ can be evaluated by $\frac{(Dw/(D^0)^{1/2} \times 4(\pi D^0 T_e)^{1/2})/\pi a^2}$. This predicts that the peak height should increase proportionally to the square root of $T_e$, which agrees with the experimental result (Fig. 6). This consideration predicts also that, in the cyclic linear potential sweep voltammetry of ions with a micropipet NB/W interface electrode, the cathodic peak height should remain nearly constant, independent of the potential sweep rate because the first anodic potential scan is equivalent to the pre-electrolysis for the following cathodic potential scan. Hence the "pre-electrolysis time" in cyclic voltammetry may be regarded as nearly inversely proportional to the sweep rate, while the peak height itself should increase proportionally to the sweep rate, as stated above. The combined effect should be the independency or little dependency of the peak height on the sweep rate, which is in line with the experimental results (Table 3). The (small) dependence of the peak height as well as that of the peak potential on the sweep rate would be explained by the exact theoretical equations of the cathodic peak current of the cyclic voltammetry with the micropipet electrode; these are left for further study. Due to the preconcentration effect, the stripping microvoltammetric technique appears promising for determination of ions at very low concentration levels.

Choline (Ch) ion also gave a voltammetric wave at the half-wave potential of 0.37 V at the polarizable NB/W electrode interface of conventional size, whereas $\text{Ach}^+$ ion at the half-wave potential of 0.29 V under the same condition. Stripping voltammetric determination of $\text{Ach}^+$ ion in the presence of both $\text{Ach}^+$ and $\text{Ch}^+$ ions at $10^{-3}$ mol dm$^{-3}$ levels in solution was already examined with success.$^{17}$ The differential pulse voltammetric technique has also been examined for the simultaneous determination of $\text{Ach}^+$ and $\text{Ch}^+$ ion at $10^{-3}$ mol dm$^{-3}$ levels with the NB/W interface microelectrodes.$^{18}$

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**References**


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**Table 3** Dependence of the cathodic peak current, $I_{pc}$, and the peak potential, $E_{pca}$, on the voltage scan rate, $v$ of the cyclic voltammograms of acetylcholine

<table>
<thead>
<tr>
<th>$v$/mV s$^{-1}$</th>
<th>$I_{pc}$/nA</th>
<th>$E_{pca}$/V</th>
<th>$-(E_{pca}-E_{1/2a})$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.43</td>
<td>0.31</td>
<td>0.06</td>
</tr>
<tr>
<td>5</td>
<td>1.52</td>
<td>0.30</td>
<td>0.07</td>
</tr>
<tr>
<td>10</td>
<td>1.58</td>
<td>0.29</td>
<td>0.07</td>
</tr>
<tr>
<td>20</td>
<td>1.62</td>
<td>0.28</td>
<td>0.07</td>
</tr>
<tr>
<td>50</td>
<td>1.72</td>
<td>0.26</td>
<td>0.08</td>
</tr>
<tr>
<td>100</td>
<td>1.78</td>
<td>0.25</td>
<td>0.08</td>
</tr>
<tr>
<td>200</td>
<td>1.83</td>
<td>0.25</td>
<td>0.08</td>
</tr>
</tbody>
</table>

a. The peak height was measured from the anodic limiting current.

$C_w^a = 5 \times 10^{-4}$ mol dm$^{-1}$, $a = 6.5 \times 10^{-4}$ cm.


17. T. Ohkouchi and M. Senda, Unpublished results.

18. H. Miyazaki, private communication.

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