Faradaic Rectification Polarographic Studies of Reduction of Zinc Ions in Indifferent Electrolytes

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The faradaic rectification polarography and ac polarography at audio-frequencies have been used to obtain kinetic parameters at the half-wave potential for the reduction of zinc ions at the dropping mercury electrode. The values of transfer coefficient and rate constants obtained in several indifferent electrolytes, are comparable to those corresponding to the second electron charge transfer step of the reaction. The rate constants in the different supporting electrolytes follow the order: \( \text{NO}_3^->\text{Br}^->\text{Cl}^->\text{CIO}_4^->\text{SO}_4^{2-} \).

In kinetic studies of fast electrode reactions, the faradaic rectification method, discovered by Doss and Agarwal\(^2\), appears to be full of promise\(^3-8\). Barker\(^9\), and Delahay and coworkers\(^4-5\) recognized the advantages of using very high frequencies in the determination of kinetic parameters of fast reactions. The merits of the method, when the sinusoidal voltage was superimposed on a varying d.c. polarizing potential, were investigated by Barker\(^9\), which he termed as low level faradaic rectification (LLFR) method or radio frequency polarography. Using this technique the kinetic parameters of some fast reactions were obtained and it was used for estimation of metal ion concentration as low as \( 10^{-8} \) to \( 10^{-10} \) of a gram in 0·01 ml of the solution.

Recently Sluyters et al.\(^10\) have extended the method and have carried out a more systematic and theoretical study and renamed it as faradaic rectification polarography. In the recent paper by Reimuther\(^11\) the importance of second order methods in the study of the kinetics of more complex electrode reactions has been emphasized.

Faradaic rectification polarography has now been applied for the study of reduction of zinc ions in different supporting electrolytes at d.m.e. using an alternating current at audio-frequency. The ac polarograms and faradaic rectification polarograms (which will be called FR polarograms) in the audio-frequency range have been used for determining the kinetic parameters in a few indifferent electrolytes.

Materials and Methods

All the solutions were prepared in doubly distilled water using AR (BDH/E. Merck) reagents. In the first instance solution of the supporting electrolyte alone was taken into the cell and deaerated by passing pure \( \text{N}_2 \).

The circuit diagram used for ac polarography and FR polarography is shown in Fig. 1. The output from an audio-oscillator (Philips model No. GM-2030/90) capable of giving frequencies from 10 Hz to 15 kHz was superimposed on a variable d.c. potential obtained from a precision potentiometer (accuracy 2\( \mu \)V per division). The negative end of potentiometer was connected to d.m.e. The pool was connected to the ground through a precision resistance of 100 ohms. The alternating current and the rectified current at varying d.c. potentials were measured at C, the junction of the pool and the resistance. For ac measurements key \( K_a \) was disconnected and key \( K_1 \) was pressed so as to connect C to the transistorized mixer preamplifier (Ahuja, type ASE/7MTR). The magnitude of the ac output voltage from the amplifier was measured on a solartron double beam oscilloscope (type CD 1014-3, sensitivity 1 mV/cm). For the measurement of rectified direct current the key \( K_2 \) was disconnected and \( K_a \) was pressed so as to connect C to the input of low pass filter F. The output from the filter was connected to the d.c. microvoltmeter (Philips model GM 6020/90, sensitivity 1 \( \mu \)V per division), so as to measure the rectified voltage. The residual d.c. potential if any, was also measured by putting off ac. This was subtracted from the rectified potential obtained at any frequency for a fixed value of interfacial potential which was always less than 10 mV.

The characteristics of the d.m.e. were: \( m = 0.64 \) mg/sec; and \( t = 8.0 \) sec in distilled water in an open circuit.
The use of fine capillary with longer drop time helped in accurate measurement of voltages on the oscilloscope screen. The FR-polarograms were obtained by plotting rectified current at varying dc potentials. The ionic strength of the supporting electrolyte (1·0N and 0·5N) was kept much higher than that of the electro-active species (1-2 mM), so as to minimize the effect of post separation and of frequency dispersion of the double layer.

Results and Discussion

The general nature of the FR-polarograms obtained in KCl supporting electrolyte in presence of the depolarizer is shown in Fig. 2. For brevity sake the FR-polarograms in other supporting electrolytes are not incorporated. It is interesting to note from the plots in Fig. 2 that in absence of the depolarizer (i.e. in supporting electrolyte alone) the faradaic rectified current is zero. In the presence of depolarizer the FR-summit peak currents are obtained and the respective summit peak potential corresponds to the half-wave potential of the depolarizer.

A comparison of the results of ac-polarography (Fig. 3) with that obtained by FR-polarography reveals the following salient features:

(i) The width of ac-polarograms spread over almost in a range three times more as compared to FR-polarograms in the proximity of half-wave potential of the Zn2+. (ii) The FR-polarographic method appears to be more versatile as compared to that of ac polarography in qualitative and quantitative analysis of even such mixtures which contain electro-active species whose half-wave potential may differ even by less than 40 mV. This fact is particularly confirmed on analysing mixture of nickel and zinc ions in 1·0N KCl.

It is interesting to note that the FR-summit peak current varies linearly with [depolarizer], unlike in ac-polarograms (Fig. 4). Thus the concentration order of 10^-4M can easily be carried out. Under determination of the unknown species even up to similar conditions the FR-summit peak current is obtained even at much higher frequencies as compared to the ac-summit peak current.

It has generally been observed that for quasi-reversible and irreversible reactions the FR-summit peaks are obtained in the audio-frequency range whereas for fast reactions the FR-summit peaks are obtained even up to 100 kHz or above. The faradaic rectification theory has been applied for determining the kinetic parameters using the summit peak current values at varying frequencies at the half-wave potential (when C0D = C0D). The faradaic rectification equation under these conditions simplifies to

\[ \Delta E_\alpha = \frac{nF}{RT} \cdot V^2 \cdot \frac{1}{4} \cdot \frac{1}{k_\alpha} \times \sqrt{\frac{\omega D}{2}} \cdot \frac{1}{2} + \frac{1}{k_\alpha} \sqrt{\frac{\omega D}{2}} + \frac{1}{2} + \frac{1}{k_\alpha} \cdot \frac{\omega D}{2} \]

... (1)
and when \( \frac{1}{k_a} \sqrt{\frac{\omega D}{2}} \ll 1 \), Eq. (1) reduces to

\[
\Delta E_a = \frac{nF}{RT} \cdot V_A^2 \frac{(2\alpha - 1)}{4} \quad \ldots \quad (2)
\]

when \( \frac{1}{k_a} \sqrt{\frac{\omega D}{2}} \gg 1 \) then Eq. (1) can be written as

\[
\Delta E_a = \frac{nF}{RT} \cdot V_A^2 \frac{(2\alpha - 1)}{4} \frac{1}{2} \sqrt{\frac{\omega D}{2}} \quad \ldots \quad (3)
\]

In Eqs (1-3) \( \Delta E_a \) is the rectified potential at the half-wave potential of the depolarizer at varying frequencies of ac; \( V_A \) is the ac potential at the electrode solution interface, \( \alpha \) is the transfer coefficient, \( \omega = 2\pi f \) (\( f \) being the frequency of ac); \( D \) is the diffusion coefficient; \( k_a \) is the rate constant; \( n \) is the number of electrons involved in the charge transfer reaction; and \( F, R \) and \( T \) have their usual significance.

For applying the above formulation for determining the kinetic parameters, it is necessary to obtain the values of interfacial ac potential at the corresponding frequency, so as to obtain the total impedance in the d.m.e. circuit. From the total impedance thus obtained, the resistance due to potentiometer, resistance in the output of the audio-oscillator, and the resistance (100 ohms) in the external circuit of d.m.e. were subtracted and the remainder corresponded to the impedance of the d.m.e. interface. This impedance on being multiplied with sum peak current enables the determination of \( V_A \), the ac potential (20 mV) initially superimposed by the magnitude of ac summit peak current of the cell. The method however has a limited application. It is not applicable in those cases where ac polarograms are not obtained (in very slow reactions i.e. \( k_a < 10^{-4} \) cm/sec). In such cases the impedance measurements have got to be made using low frequency impedance bridge. The rectified potential was obtained by multiplying the rectified summit peak current with the impedance across the electrode solution interface.

The plot between \( \Delta E_a / V_A^2 \) vs \( \sqrt{\omega} \) was obtained for the frequency range from 25 Hz to 600 Hz. At high frequencies (>200 Hz) the \( \Delta E_a / V_A^2 \) tends to constant and using Eq. (2), the value of \( \alpha \) can be calculated. From the slope of the curve at frequencies <200 Hz, the value of \( k_a \) can be determined using Eq. (3) provided the value of diffusion coefficient \( D \) is known. The values of \( D \) in different supporting electrolytes were experimentally determined using McBain-Dowson porous diaphragm cell and applying King-Cathard equation.

The values of kinetic parameters obtained in measuring the impedance at the solution interface, \( X_I \) is the transfer coefficient, \( f \) the number of electrons involved in the charge transfer reaction; and \( R \), \( T \) and \( A \) have their usual significance.

References


Table 1 — Kinetic Parameters of Zn^2+ in Different Electrolytes at d.m.e. at 25°C

<table>
<thead>
<tr>
<th>Supporting electrolyte</th>
<th>( D (\text{cm}^2/\text{sec} \times 10^4) )</th>
<th>( \alpha ) (cathodic)</th>
<th>( k_a^2 ) (cm/sec \times 10^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-0 N KCl</td>
<td>8-4</td>
<td>0-52</td>
<td>2-5</td>
</tr>
<tr>
<td>1-0 N KNO₃</td>
<td>7-8</td>
<td>0-52</td>
<td>2-8</td>
</tr>
<tr>
<td>1-0 N KBr</td>
<td>6-7</td>
<td>0-52</td>
<td>2-6</td>
</tr>
<tr>
<td>0-5 N K₂SO₄</td>
<td>4-8</td>
<td>0-53</td>
<td>2-2</td>
</tr>
<tr>
<td>1-0 N NaClO₄</td>
<td>4-6</td>
<td>0-53</td>
<td>2-4</td>
</tr>
</tbody>
</table>

(Concentration of the zinc ion in KNO₃ was 1-0 mM and in the rest of the electrolytes it was 2-0 mM)

The values of kinetic parameters as given in Table 1 are found to be of the order of 10^{-2}, similar to those reported by Van Der Pol et al., for the second electron charge transfer step. This shows the second electron charge transfer process in control of the overall reaction.

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