Polarographic Study of the Electrode Reaction of Zn(II) in Formamide and Dimethylformamide

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Zinc(II), Formamide, Dimethylformamide, Polarographic Study

The reduction of Zn(II) at the d.m.e. has been studied in aqueous mixtures of formamide and dimethylformamide. The general polarographic characteristics have been determined, using 0.1 M NaNO₃ as the supporting electrolyte. The reduction of Zn(II) in these organic solvents is irreversible and diffusion controlled. The kinetic parameters, \( \alpha_m \) and \( k_f, h \), have been calculated separately by Koutecky and Delahay treatments. The change of polarographic characteristics and kinetic parameters is explained in terms of solvation of the metal ion in these solvents. The electrocapillary curves in the presence of these solvents have also been studied.

Introduction

Hale and Parsons¹ have studied the polarography of Cd(II), Pb(II) and Tl(I) in both purely non-aqueous formamide and other substituted amides as well as in their aqueous mixtures. Brown and Hsiung² have reported E₁/₂ of various cations in purely non-aqueous formamide solutions. Gaur and Goswami³ have studied the polarography of Mn(II), Ni(II) and Co(II) in formamide, dimethylformamide and acetonitrile and have calculated the kinetic parameters of these cations.

Though the polarographic behaviour of Zn(II) in formamide has been studied qualitatively by Brown and Hsiung (1.c.) and Jha and Srivastava⁴ yet a detailed quantitative study of the electrode reaction of this cation in formamide and dimethylformamide is lacking.

This study deals with the reduction of Zn(II) at the d.m.e. in 0.1 M NaNO₃ as the supporting electrolyte, in the presence of varying percentages of formamide and dimethylformamide in aqueous medium. The reduction of Zn(II) has been found irreversible in the presence of these solvents. The kinetic parameters \( \alpha_m \) and \( k_f, h \) of the electrode reaction have been calculated separately by Koutecky⁵ and Delahay treatments.

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Experimental

A manual polarograph (Toshniwal, CLO-2) in conjunction with Toshniwal polyflex galvanometer (PL 50) was used. The d.m.e. had the following characteristics:

\[
m = 3.144 \text{ mg/sec (in open circuit), } t = 3.26 \text{ sec, } \]
\[
m^{2/3}t^{1/6} = 2.610 \text{ mg}^{2/3}\text{sec}^{-1/2}, h_{corr} = 64.5 \text{ cms.}
\]

The diffusion currents were corrected for the residual currents, the IR-drop correction was made. All the experiments were carried out at 25 ± 0.1 °C.

Purified hydrogen was used for removing dissolved oxygen. The gas presaturated with water vapour was passed through a solution having the same composition as that of the experimental mixture.

Reagent grade chemicals and conductivity water were used to prepare all solutions. Solutions containing different percentage of solvent and 1 mM Zn(II) in 0.1 M NaNO₃ were prepared. Triton X-100 was used as maximum suppressor. Saturated Calomel electrode (S.C.E.) was used as a reference electrode.

Results and Discussion

Zn(II) gives a single well defined wave in aqueous as well as in the presence of aqueous mixtures of formamide and dimethylformamide. The reduction is diffusion controlled in each case as shown by idVs/h and idVsC plots (Figs. 1 and 2). The plot of log \( \frac{i}{i_d} \) vs. Eₜ is linear in all cases. The values of the slopes indicate that the reduction is irreversible.
in all cases. Fig. 3 gives typical polarograms of Zn\(^{2+}\) in the presence of 50% formamide at different heights.

**Table I.** Polarographic characteristics and kinetic parameters for 1 mM Zn\(^{2+}\) in 0.1 M NaN\(_3\) and different percentages of formamide.

<table>
<thead>
<tr>
<th>Percentage solvent by Vol.</th>
<th>(i_d) ((\mu A))</th>
<th>(-E_{1/2}) (V vs S.C.E.)</th>
<th>Slope (V)</th>
<th>(D \times 10^6) (cm(^2)/s)</th>
<th>(\eta) (centipoise)</th>
<th>(i_d) (\eta^{1/2})</th>
<th>(a_m)</th>
<th>(k_{t,h}) (\eta^{1/2})</th>
<th>(k_{t,h}) (a_m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.33</td>
<td>1.060</td>
<td>0.062</td>
<td>7.614</td>
<td>0.8931</td>
<td>8.810 0.97</td>
<td>0.94</td>
<td>4.23 (\times 10^{-10})</td>
<td>3.70 (\times 10^{-10})</td>
</tr>
<tr>
<td>10</td>
<td>9.15</td>
<td>1.088</td>
<td>0.200</td>
<td>7.355</td>
<td>0.9160</td>
<td>8.892 0.91</td>
<td>0.92</td>
<td>2.47 (\times 10^{-10})</td>
<td>2.17 (\times 10^{-10})</td>
</tr>
<tr>
<td>20</td>
<td>8.97</td>
<td>1.090</td>
<td>0.167</td>
<td>7.073</td>
<td>0.9886</td>
<td>8.954 0.97</td>
<td>0.94</td>
<td>1.69 (\times 10^{-10})</td>
<td>1.65 (\times 10^{-10})</td>
</tr>
<tr>
<td>30</td>
<td>7.74</td>
<td>1.168</td>
<td>0.143</td>
<td>5.267</td>
<td>1.0690</td>
<td>8.008 1.03</td>
<td>1.03</td>
<td>1.34 (\times 10^{-11})</td>
<td>1.34 (\times 10^{-11})</td>
</tr>
<tr>
<td>40</td>
<td>7.57</td>
<td>1.170</td>
<td>0.125</td>
<td>5.030</td>
<td>1.1890</td>
<td>8.241 1.17</td>
<td>1.18</td>
<td>6.08 (\times 10^{-13})</td>
<td>6.37 (\times 10^{-13})</td>
</tr>
<tr>
<td>50</td>
<td>7.21</td>
<td>1.170</td>
<td>0.118</td>
<td>5.566</td>
<td>1.3200</td>
<td>8.279 1.09</td>
<td>1.04</td>
<td>4.03 (\times 10^{-13})</td>
<td>3.80 (\times 10^{-13})</td>
</tr>
<tr>
<td>60</td>
<td>6.95</td>
<td>1.238</td>
<td>0.105</td>
<td>4.242</td>
<td>1.4700</td>
<td>8.420 0.94</td>
<td>0.97</td>
<td>4.15 (\times 10^{-12})</td>
<td>3.80 (\times 10^{-12})</td>
</tr>
<tr>
<td>70</td>
<td>6.50</td>
<td>1.100</td>
<td>0.100</td>
<td>3.796</td>
<td>1.7250</td>
<td>8.523 1.36</td>
<td>1.30</td>
<td>5.17 (\times 10^{-13})</td>
<td>4.85 (\times 10^{-13})</td>
</tr>
<tr>
<td>80</td>
<td>6.68</td>
<td>1.105</td>
<td>0.100</td>
<td>3.922</td>
<td>2.1110</td>
<td>9.705 1.33</td>
<td>1.27</td>
<td>1.15 (\times 10^{-13})</td>
<td>1.60 (\times 10^{-13})</td>
</tr>
</tbody>
</table>

The rate constant \(k_{t,h}\) for a cathodic irreversible process varies with the electrode potential according to the equation:

\[
k_{t,h} = k_{t,h} \exp \left(\frac{-a_m F (E + O \cdot 2412)}{RT}\right)\]  

where the potential \(E\) is referred to the S.C.E. According to equation (1) a plot of \(
log k_{t,h}\) vs potential yields a straight line whose slope is \(-0.434\). The parameters \(k_{t,h}\) and \(a_m\) can thus be determined experimentally for various values of \(E\).

Tables I and II give the polarographic characteristics and kinetic parameters of Zn(II) in the presence of aqueous mixtures of formamide and dimethylformamide.

From Table I it is clear that with the gradual increase in the percentage of formamide, the diffusion coefficient of the ion is decreased and hence the diffusion current \('i_d'\) shows a regular decrease. Viscosity however increases with the increasing content of formamide. But \(i_d\) \(\eta^{1/2}\) is not constant so that the change in diffusion coefficient \('D'\) which
ultimately affects $i_d$, is not solely due to viscosity changes. The varying values of $i_d \eta^{1/2}$ suggest that the size of the ion must have suffered a change by solvation. The $z_{1/2}$ is shifted to more negative values. This is indicative of complexation.

From Table II it follows that from aqueous to 60% dimethylformamide $i_d$ decreases. However, it increases at higher percentage of dimethylformamide. This is due to the decrease in viscosity at higher percentages of dimethylformamide.

Table II. Polarographic characteristics and kinetic parameters 1 mM Zn$^{2+}$ in 0.1 M NaN$\textsubscript{3}$ and different percentages of dimethylformamide.

<table>
<thead>
<tr>
<th>Percentage solvent by Vol.</th>
<th>$i_d$ ($\mu$A)</th>
<th>$E_{1/2}$ (V vs. S.C.E.)</th>
<th>Slope (V)</th>
<th>$D \times 10^6$ (cm$^2$/s)</th>
<th>$\eta$ (centipoise)</th>
<th>$i_d \eta^{1/2}$</th>
<th>$\alpha_n$</th>
<th>$k_{t,h}$ (Koutecky Delahay)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.33</td>
<td>1.06</td>
<td>0.0625</td>
<td>7.614</td>
<td>0.8931</td>
<td>8.810</td>
<td>0.97</td>
<td>0.94 $4.23 \times 10^{-10}$</td>
</tr>
<tr>
<td>10</td>
<td>7.92</td>
<td>1.06</td>
<td>0.1340</td>
<td>4.624</td>
<td>1.146</td>
<td>8.478</td>
<td>1.00</td>
<td>0.998 $1.80 \times 10^{-10}$</td>
</tr>
<tr>
<td>20</td>
<td>7.48</td>
<td>1.06</td>
<td>0.0883</td>
<td>4.154</td>
<td>1.255</td>
<td>8.380</td>
<td>1.292</td>
<td>1.292 $1.55 \times 10^{-12}$</td>
</tr>
<tr>
<td>30</td>
<td>6.68</td>
<td>1.04</td>
<td>0.077</td>
<td>3.300</td>
<td>1.524</td>
<td>8.250</td>
<td>1.603</td>
<td>1.603 $4.40 \times 10^{-14}$</td>
</tr>
<tr>
<td>40</td>
<td>6.27</td>
<td>1.05</td>
<td>0.050</td>
<td>2.890</td>
<td>1.700</td>
<td>8.166</td>
<td>1.390</td>
<td>1.390 $1.10 \times 10^{-12}$</td>
</tr>
<tr>
<td>50</td>
<td>5.37</td>
<td>1.05</td>
<td>0.0454</td>
<td>2.122</td>
<td>2.223</td>
<td>8.011</td>
<td>1.742</td>
<td>1.742 $8.18 \times 10^{-15}$</td>
</tr>
<tr>
<td>60</td>
<td>5.10</td>
<td>1.05</td>
<td>0.0431</td>
<td>1.835</td>
<td>2.427</td>
<td>7.952</td>
<td>1.758</td>
<td>1.758 $2.08 \times 10^{-15}$</td>
</tr>
<tr>
<td>70</td>
<td>5.28</td>
<td>1.105</td>
<td>0.0444</td>
<td>2.042</td>
<td>2.223</td>
<td>7.870</td>
<td>1.816</td>
<td>1.816 $1.33 \times 10^{-15}$</td>
</tr>
<tr>
<td>80</td>
<td>5.46</td>
<td>1.105</td>
<td>0.0416</td>
<td>2.080</td>
<td>2.031</td>
<td>7.715</td>
<td>1.138</td>
<td>1.138 $4.58 \times 10^{-18}$</td>
</tr>
</tbody>
</table>

Fig. 4. log $k_{t,h}$ Vs $E$ for 1 mM Zn$^{2+}$ in 0.1 M NaN$\textsubscript{3}$ at various percentages of formamide at 25°C.
observation is supported by Stokes-Einstein equation:
\[ \text{id}^2 a D = kT/6\pi\eta. \]

From aqueous to 20% dimethylformamide, the \( E_{1/2} \) remains constant but from 30% to 60% it is shifted to more positive values. At still higher percentages however it shifts to more negative values. This may be due to complex formation at higher percentages. The positive shift in \( E_{1/2} \) is explicable on the basis of treatment due to Schaar®. In absence of complexation, the equation of Schaar predicts the shift of \( E_{1/2} \) to positive values. Further, \( E_{1/2} \) is affected by ion-pair formation in low dielectric constant which is 36.7 for dimethylformamide as compared to 78 for water. The shift takes place as the supporting electrolyte will be less dissociated and a few anions will be available for the ion-pair formation. As the dielectric constant of formamide (109) is higher than water, the shift in \( E_{1/2} \) does not take place to more positive values. These conclusions are borne out by the relationship between half-wave potential and dielectric constant of the solvent as given by Born®.

The value of \( \alpha_n \) and \( k_{t,h} \) have been calculated separately by applying Koutecky and Delahay treatments. These values are tabulated in Table I and II. The plots of \( \log k_{t,h} \) and \( E \) (Vs S.C.E.) are straight lines in all cases (Figs. 4, 5). There is an excellent agreement in the values of kinetic parameters, \( \alpha_n \) and \( k_{t,h} \) derived from two different approaches that of Delahay and Koutecky.

![Graph](image-url)  
Fig. 5. \( \log k_{t,h} \) Vs \( E \) for 1 mM Zn\(^{2+}\) in 0.1 M NaNO\(_3\) at various percentages of dimethylformamide at 25 °C.
Fig. 6. Electrocapillary curves in the presence of 1 mM Zn$^{2+}$ and 0.1 M NaN$_3$ at different percentages of formamide. 

Fig. 7. Electrocapillary curves in the presence of 1 mM Zn$^{2+}$ and 0.1 M NaN$_3$ at different percentages of dimethylformamide.

The decrease in the values of $k_{th}$ from aqueous to 80% formamide and dimethylformamide shows that irreversibility increases in the presence of these organic solvents.

A simple qualitative study of electrocapillary curves (Figs. 6, 7) has been made where drop time (taken as a measure of interfacial tension between mercury and solution) is varied with applied potential. The shape of these electrocapillary curves depends on the nature of the solution, and provides information on the equilibrium structure of the double layer and on the capillary activity of dissolved substances. A truncation of the electrocapillary curve takes place at higher percentages of dimethylformamide (from 50% to 80%). This shows that dimethylformamide acts as a surface active substance at higher percentages.

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8. I. M. Kolthoff and J. J. Lingane, ibid, p. 211.