NOTES

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References

Polarographic Behaviour of L-Glutamic Acid at d.m.e.

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The polarographic behaviour of L-glutamic acid 
\[\text{HOOCCH}_2\text{CH}_2\text{CH(NH}_3\text{)}\text{COOH}\] in 1% DMSO and in the presence of 0·1M NaClO₄ and 0·001% Triton-x-100 has been studied. The electrode process is irreversible, two-electron transfer and diffusion-controlled under the experimental conditions. Kinetic parameters, viz., transfer coefficient (α) and formal rate constant (K_{f,h}) for the electrode reaction have been determined by Koutecky's method. The enthalpy of activation for the electrode reaction is 8·50 kcal/mole. The results have been interpreted on the basis of the existence of L-glutamic acid in 1% DMSO as a zwitterion.

A SURVEY of literature reveals that not much work has been reported on the direct polarographic behaviour of L-glutamic acid\(^1\). Hence a detailed polarographic study of L-glutamic acid has been carried out in 1% DMSO and in the presence of 0·1M NaClO₄ and 0·001% Triton-x-100. The polarograms of L-glutamic acid in the presence of different base-electrolytes produce a well-defined irreversible cathodic wave. The nature of the wave remains unchanged and the diffusion current constant (I) has the following order: 
\[\text{NaClO}_4 > \text{LiNO}_3 > \text{(CH}_3\text{)}_4\text{NBr} > \text{KCl} > \text{KNO}_3 \] 

This may be due to the change in the composition and viscosity of solution (I \(\propto \text{1/viscosity})

The values of I, E₁ and the slopes are summarized in Table 1.

The polarograms of 8×10⁻⁴M glutamic acid in 0·1M NaClO₄ using 50% (by volume) different organo-aqueous media, were recorded which showed an irreversible cathodic reduction wave. The values of diffusion current constant in different solvents such as acetonitrile, methanol, ethanol, isopropanol, DMSO, DMF are 1·674, 1·644, 1·552, 1·309, 1·216 and 0·973 at pH 3·70, 3·72, 3·75, 3·79, 4·50 and 4·52 respectively.

The I values in different solvents follows the decreasing order acetonitrile > methanol > ethanol > isopropanol > DMSO > DMF. This may be due to decrease in dielectric constant of the solution which leads to an increase in the size of diffusing species or may be due to increase in ionic interactions.

Distortion in waves in DMSO and DMF was due to depletion of [H⁺] at the dropping electrode surface.

Mechanism of electrode reaction — It is observed that increase in the [DMSO] brings about a corres-

<table>
<thead>
<tr>
<th>Supporting Electrolyte</th>
<th>I (mA)</th>
<th>(-E₁(V))</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₃)₄NBr</td>
<td>4·067</td>
<td>1·3765</td>
<td>0·1125</td>
</tr>
<tr>
<td>KCl</td>
<td>3·989</td>
<td>1·3400</td>
<td>0·1143</td>
</tr>
<tr>
<td>KNO₃</td>
<td>3·941</td>
<td>1·3445</td>
<td>0·1167</td>
</tr>
<tr>
<td>(CH₃)₄NBr</td>
<td>3·756</td>
<td>1·4420</td>
<td>0·1071</td>
</tr>
<tr>
<td>NaClO₄</td>
<td>3·599</td>
<td>1·3465</td>
<td>0·1000</td>
</tr>
<tr>
<td>Li₂SO₄</td>
<td>2·919</td>
<td>1·3510</td>
<td>0·1000</td>
</tr>
</tbody>
</table>
The above mechanism suggests that L-glutamic acid being a bifunctional acid, two electrons are involved in the reduction process. The values of diffusion current constant given in Table 2 in various supporting electrolytes also support that glutamic acid reduction proceeds by a two-electron process.

In 100% DMSO, Purdy et al. have reported two waves of equal length each representing one electron process. It appears that these waves might coalesce and a single wave may be formed in aqueous solution probably due to the rapid conversion of (A) to (B), i.e., formation of zwitterions in aqueous solution. The carboxyl group adjacent to the α-amino group is reduced first very rapidly due to the proximity of charged (N+H3) and before reaching its limiting current potential value, the reduction of another carboxyl group starts resulting in the coalescence of the two waves into one.

Solution (5 ml) of 8×10^{-4} M glutamic acid in 0.1 M NaClO₄, 0.002% Triton-X-100 at a limiting current potential (1.54 V) was electrolysed under nitrogen atmosphere. A cathodic wave was obtained before, after 2 hr and after 6 hr electrolysis of the above solution. The changes in $E_{1/2}$ and $i_d$ are summarized below:

<table>
<thead>
<tr>
<th>Temp.</th>
<th>$K_{f,h}$</th>
<th>$\alpha n$</th>
<th>$-E_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>10.36×10^{12}</td>
<td>0.452</td>
<td>1.370</td>
</tr>
<tr>
<td>40</td>
<td>16.69×10^{13}</td>
<td>0.502</td>
<td>1.351</td>
</tr>
<tr>
<td>50</td>
<td>43.81×10^{14}</td>
<td>0.542</td>
<td>1.333</td>
</tr>
</tbody>
</table>

The sign and meaning of the terms are same as described earlier. The values of the kinetic parameters at different temperatures are given in Table 3.

It was observed that with increase in temperature, the value of $E_{1/2}$ shifts towards more positive values, showing the slower reduction which supports the irreversible nature of the electrode reaction. The enthalpy of activation ($\Delta H$) for the electrode reaction has been calculated by equating the slope of log $K_{f,h}$ vs 1/T plot to $(-\Delta H/2.303)R$ and was found to be 8.50 kcal/mole.

References

Polarographic Behaviour of Cu²⁺, Cd²⁺, Ni²⁺, Zn²⁺ & Mn²⁺ Ions in Tris(hydroxymethyl)-methylamine & Their Simultaneous Determination in Ternary Mixtures

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A polarographic method has been developed for the simultaneous quantitative determination of metal ions in their ternary mixtures: (i) Cu²⁺, Zn²⁺, Mn²⁺; (ii) Cu²⁺,