DMSO should be in 'zwitterion' form (B) and it results in a corresponding decrease in diffusion current constant and half-wave potential (Table 2). From these results it is concluded that glutamic acid in 1% DMSO should be in 'zwitterion' form (B) and its reduction in acidic aqueous media proceeds by a two-electron process.

In 100% DMSO, Purdy et al.3 have reported two waves of equal length each representing one electron process. It appears that these waves might coalesce 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 E1/2 and i_d are summarized below:

<table>
<thead>
<tr>
<th></th>
<th>E1/2 (V)</th>
<th>i_d (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before electrolysis</td>
<td>1.3385</td>
<td>5.60</td>
</tr>
<tr>
<td>After 2 hr electrolysis</td>
<td>1.3415</td>
<td>4.70</td>
</tr>
<tr>
<td>After 6 hr electrolysis</td>
<td>1.3570</td>
<td>3.00</td>
</tr>
</tbody>
</table>

Increase in −E1/2 after electrolysis supports the irreversible nature of the electrode reaction. The decrease in i_d is due to decrease in the rate, at which the electroactive species diffuse into the electrode surface as electrolysis is prolonged.

Since the reduction of L-glutamic acid (8 × 10−4 M) in 1% DMSO is irreversible, it is considered expedient to determine the values of transfer coefficient (α) and formal rate constant \((K_{f,h})\) for the electrode reaction by applying Koutecky's theoretical treatment as extended by Meites and Israel and tabulated below. The value of α was obtained by equating the slope of \(E_{1/2}\) vs log \([-i_d−1−0.546 \log \delta]\) plot to −0.546/α and the intercept of the same plot giving \(E_{1/2}\). The value of \(K_{f,h}\) was used to calculate \(K_{f,h}\) from Eq. (I).

\[
E_{1/2} = -0.2412 + \frac{0.05915}{\alpha} \log \left( \frac{1.349 \times K_{f,h}}{D_{1/2}} \right)
\]

**Table 2 — Effect of Varying DMSO Concentration on Diffusion Current Constant**

<table>
<thead>
<tr>
<th>% DMSO in water</th>
<th>Diff. current constant (I)</th>
<th>(E_{1/2}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01-0</td>
<td>4.087</td>
<td>1.3765</td>
</tr>
<tr>
<td>11-0</td>
<td>3.065</td>
<td>1.2570</td>
</tr>
<tr>
<td>21-0</td>
<td>2.378</td>
<td>1.2270</td>
</tr>
<tr>
<td>31-0</td>
<td>1.946</td>
<td>1.2145</td>
</tr>
<tr>
<td>41-0</td>
<td>1.411</td>
<td>1.2060</td>
</tr>
<tr>
<td>51-0</td>
<td>0.925</td>
<td>1.2050</td>
</tr>
</tbody>
</table>

**Table 3 — Values of the Various Kinetic Parameters**

<table>
<thead>
<tr>
<th>Temp. ((°C))</th>
<th>(K_{f,h})</th>
<th>(\alpha)</th>
<th>(-E_{1/2}) (V)</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^{-12}</td>
<td>0.502</td>
<td>1·351</td>
</tr>
<tr>
<td>50</td>
<td>43·81 × 10^{-12}</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 irreversibility of the nature of the electrode reaction.

The enthalpy of activation \((\Delta H)\) for the electrode reaction has been calculated by equating the slope of \(K_{f,h}\) 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) methyamine & Their Simultaneous Determination in Ternary Mixtures**

K. Saraswathi & R. Sreenivasulu
Department of Chemistry, S.V. University, Tirupati 517502
Received 16 August 1976; accepted 29 December 1976

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

Cd\textsuperscript{2+}, Zn\textsuperscript{2+} and (iii) Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, Zn\textsuperscript{2+}. Tris(hydroxymethyl)methylamine (0.5M) is used as a complexing agent in the determination of individual and mixtures of metal ions at pH 10.5 and \( \mu = 0.1 \). 

Only a few methods are described in literature for the simultaneous polarographic determinations of copper, cadmium, nickel, zinc and manganese ions. Zuliani and Pozzo\textsuperscript{1} determined Cu\textsuperscript{2+}, Zn\textsuperscript{2+} and Mn\textsuperscript{2+} ions in the presence of iron and nickel. Jezdinsky\textsuperscript{2} estimated Cu\textsuperscript{2+}, Ni\textsuperscript{2+} and Zn\textsuperscript{2+} ions using a base solution containing Tiron and KCN. Skobets and Povkh\textsuperscript{3} determined Cu\textsuperscript{2+}, Cd\textsuperscript{2+} and Zn\textsuperscript{2+} ions in ammonium acetate medium by oscillographic polarography. Nitric acid (1M) and molten ammonium formate\textsuperscript{4} have been used for determination of Cu\textsuperscript{2+}, Cd\textsuperscript{2+}, Pb\textsuperscript{2+} and Zn\textsuperscript{2+}. Wolf and Nuernberg\textsuperscript{5} used a radiofrequency method for analysis of several mixtures. The polarographic behaviour of Cu\textsuperscript{2+}, Cd\textsuperscript{2+}, Ni\textsuperscript{2+}, Zn\textsuperscript{2+} and Mn\textsuperscript{2+} ions individually and of their mixtures, viz. Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, Mn\textsuperscript{2+}; Cu\textsuperscript{2+}, Cd\textsuperscript{2+}, Zn\textsuperscript{2+}; and Cu\textsuperscript{2+}, Ni\textsuperscript{2+}, Zn\textsuperscript{2+} in tris(hydroxymethyl)methylamine has been investigated and methods developed for their simultaneous quantitative determination in mixtures.

All the chemicals used were of reagent grade. Conductivity water was used in the preparation of all solutions. Metal ion solutions were prepared from AR samples. The ionic strength was kept at 0.1 by adding the requisite amount of potassium nitrate (AR grade). Tris(hydroxymethyl)methylamine was a BDH sample. The polarograms of the deaerated solutions were recorded at 25\degree C and pH 10.5 with conductive polarograph system, Heyrovsky LP55. The potentials were measured against the saturated calomel electrode using agar-KNO\textsubscript{3} bridge. pH measurements were made using Elico pH model LI-10. Doubly distilled mercury was used for drop. The half-wave potentials of the ions shifted to more negative values with increasing [Tris] (0.5 to 2.0M) and increasing pH values. The reduction waves remained well-defined at all [Tris] and pH studied. The half-wave potentials in 0.5M Tris in the pH range 9 to 12.0 are reported in Table 1.

A series of polarograms were recorded with different aliquots of metal ions in 0.5M 'tris' at pH 10.5. When the diffusion current was plotted against concentration, linear plots were obtained indicating the feasibility of this

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Cu\textsuperscript{2+} (mg)} & \textbf{Zn\textsuperscript{2+} (mg)} & \textbf{Mn\textsuperscript{2+} (mg)} \\
\hline
0.5228 & 0.5242 & 0.5500 \\
0.7842 & 0.7768 & 0.5500 \\
0.9802 & 0.9802 & 0.6600 \\
\hline
\end{tabular}
\caption{Effect of pH on Half-Wave Potentials \([\text{KNO}_3]=0.1 \text{M} \text{[Tris]}=0.5 \text{M}; \text{[metal ion]}=1 \text{mM}]\)}
\end{table}

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Cu\textsuperscript{2+} (mg)} & \textbf{Zn\textsuperscript{2+} (mg)} & \textbf{Mn\textsuperscript{2+} (mg)} \\
\hline
1.5252 & 1.5268 & 1.5270 \\
1.5252 & 1.5268 & 1.5270 \\
1.5885 & 1.5552 & 1.5270 \\
2.2242 & 2.2107 & 1.5270 \\
\hline
\end{tabular}
\caption{Analysis of Ternary Mixture Containing Cu\textsuperscript{2+}, Zn\textsuperscript{2+} and Mn\textsuperscript{2+} \([\text{Tris]}=0.5 \text{M}; \text{pH} \sim 10.5]\)}
\end{table}

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Cu\textsuperscript{2+} (mg)} & \textbf{Cd\textsuperscript{2+} (mg)} & \textbf{Zn\textsuperscript{2+} (mg)} \\
\hline
1.2708 & 1.3500 & 1.3240 \\
1.2708 & 1.3500 & 1.3240 \\
1.5885 & 1.5552 & 1.5552 \\
2.2242 & 2.2107 & 2.2107 \\
\hline
\end{tabular}
\caption{Analysis of Ternary Mixture Containing Cu\textsuperscript{2+}, Cd\textsuperscript{2+} and Zn\textsuperscript{2+} \([\text{Tris]}=0.5 \text{M}; \text{pH} \sim 10.5]\)}
\end{table}

\begin{table}[h!]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{Cu\textsuperscript{2+} (mg)} & \textbf{Ni\textsuperscript{2+} (mg)} & \textbf{Zn\textsuperscript{2+} (mg)} \\
\hline
1.2708 & 1.2708 & 1.2708 \\
1.5252 & 1.5252 & 1.5252 \\
1.2708 & 1.2708 & 1.2708 \\
\hline
\end{tabular}
\caption{Analysis of Ternary Mixture Containing Cu\textsuperscript{2+}, Ni\textsuperscript{2+} and Zn\textsuperscript{2+} \([\text{Tris]}=0.5 \text{M}; \text{pH} \sim 10.5]\)}
\end{table}
method for the quantitative determination of the metal ion.

The effect of height of mercury column on \( i_d \) has been studied and the plot between \( i_d \) vs \( \sqrt{R} \) is linear indicating diffusion-controlled limiting current of all these reductions. However, the log plots obtained gave values for slope different from those required for reversible reduction except in the case of cadmium. Hence these metals, except cadmium, are reduced irreversibly.

The \( E_1 \) values were well separated and in view of the analytical applications of different metal ions in mixtures, different synthetic mixtures were prepared. The analysis of the following mixtures were carried out in \( pH \sim 10:5 \) using 0.5 M tris and 0.1 M KNO\(_3\): (i) Cu\(^{2+}\), Zn\(^{2+}\) and Mn\(^{2+}\) (Table 2); (ii) Cu\(^{2+}\), Cd\(^{2+}\) and Zn\(^{2+}\) (Table 3); and (iii) Cu\(^{2+}\), Ni\(^{2+}\), and Zn\(^{2+}\) (Table 4). The results obtained are satisfactory.

References

Reduction of Cd(II)-Itaconate & Cd(II)-Oxalate-Itaconate Complexes at d.m.e.

Pratap D. Jadhav & Ramesh A. Bhole*
Department of Chemistry, Marathawada University
Aurangabad

Received 29 January 1977; accepted 7 April 1977

Electrode reactions of Cd(II) with itaconate and with oxalate-itaconate as mixed ligand ions have been studied polarographically. Cadmium(II) forms three complexes with itaconate ions (ITA) with their respective stability constants, in two different electrolytes (KNO\(_3\) and NaNO\(_3\)) at ionic strength 2.5M, as follows: \( \log \beta_1 = 1.73, 1.78; \log \beta_2 = 2.36 \pm 0.09, 2.30 \pm 0.04; \) and \( \log \beta_3 = 3.20 \pm 0.05, 3.39 \pm 0.07. \) Schaar and McMasters treatment points to the existence of three mixed ligand chelates having 1:1:1, 1:1:2 and 1:2:1 ratio of Cd(II)-Ox-ITA. The observed enhancement of the complexation constant of the mixed ligand chelates has been explained on statistical considerations and on the possibility of simultaneous \( n \)-bonding of Cd(II) with itaconate and mixed ligand complex with oxalate.

The formation of mixed ligand chelates of Nd\(^{3+}\) and V\(^{3+}\) with itaconate and phenolic acids were investigated potentiometrically in this laboratory.\(^1\)\(^2\) In continuation of our earlier studies,\(^3\) we report here the polarographic determination of the formation constants of Cd(II) with itaconate and mixed ligand complex with oxalate.

Reagents used were of AR grade. Potassium oxalate and potassium itaconate, at \( pH \) 7-0, were used as complexing agents. KNO\(_3\) and NaN\(_3\) were used as supporting electrolytes and to maintain the ionic strength at 2.5M. The experimental technique was the same as described earlier.\(^3\)\(^4\)

DeFord and Hume's method was applied to evaluate stability constants for the two-electron, reversible and diffusion-controlled reduction of Cd(II)-oxalate system at \( pH \) 7.0 and at ionic strength of 2.5M (KNO\(_3\)). The values came out to be \( \log \beta_{10} = 2.70 \pm 0.04, \log \beta_{20} = 4.07 \pm 0.15 \) and \( \log \beta_{30} = 5.14 \pm 0.06 \) and agreed well with those obtained by earlier workers.\(^3\)\(^5\)\(^1\)

In each solution of the system Cd(II)-itaconate, Cd\(^{2+}\) was 1 mM. The [ligand] was varied from 0-05 to 0-70M, and the ionic strength was adjusted to 2.5M by adding appropriate quantity of KNO\(_3\). In a second set instead of KNO\(_3\), the supporting electrolyte used was NaNO\(_3\). A single well-defined reduction wave appeared in both the sets and the plots of \( i_d \) vs \( \sqrt{R} \) (\( h \) = effective height of mercury column) were linear, passing through the origin. Again, as expected, the plot of \( i_d \) vs [metal ion] was linear. The results obtained showed that the reduction was diffusion-controlled.

The plots of \( log \mathcal{L} \) vs \( E \) were linear with slopes \( = 32 \pm 1 \) mV, corresponding to reversible reduction with \( n = 2 \). The half-wave potential shifted continuously towards more negative values as the diffusion current decreased with increasing [ligand], indicating positively a complex formation of metal ion with the ligand.

Plots of \(-E_{1/2} \) vs \(-log \mathcal{L} \) (\( \mathcal{L} \) = ligand concentration) were smooth curves pointing to the formation of two or more complex ions, in equilibrium. The DeFord and Hume's method, as modified by Irving,\(^8\) was used for calculating successive stability constants of various species. The values of overall log stability constants, as obtained from \( F_{d(X)} \) vs \( C \) curves for the complex species [Cd(ITA)], [Cd(ITA)\(^{2+}\)] and [Cd(ITA)\(^{3+}\)] are: 1.78, 2.36 \pm 0.04, 3.39 \pm 0.07 and 1.73, 2.36 \pm 0.09, 3.20 \pm 0.05 respectively at \( \mu = 2.5 \text{M} \) (NaNO\(_3\)) and KNO\(_3\). The stability constants of Cd(II)-itaconate at \( \mu = 2.5 \text{M} \) (KNO\(_3\)) were used in the calculation of stabilities of mixed ligand systems, since the experimental conditions were identical in the both.

For the mixed ligand study the two concentrations of itaconate chosen were 0.05 and 0.24M at which 1:1 and 1:2 species predominated. Each solution contained 1 mM Cd\(^{2+}\), 0.08M itaconate and only the oxalate concentration was varied from 0-02 to 0.50M. The ionic strength was adjusted to 2.5M by adding appropriate amount of KNO\(_3\) at \( pH \) 7.0. The exact procedure was repeated for (itaconate) = 0.24M.

The plots of \(-E_{1/2} \) vs \( log \mathcal{L}/(i_d-i) \) in the two sets studied were linear with the slope values lying in the range 30-32 mV, which clearly showed that the reduction of Cd(II) ion in the absence and presence of the ligands is reversible involving two electrons. That the reduction was diffusion-controlled was evidenced by the direct proportionality of diffusion current to the square root of the effective height of the mercury head.

*To whom all correspondence should be addressed.