STEPWISE STABILITY CONSTANTS OF Ce (III) COMPLEXES WITH GLYCINE, IMINODIACETIC ACID AND NITRILOTRIACETIC ACID : A POLAROGRAPHIC STUDY

V. K. CHITALE AND K. S. PITRE

Department of Chemistry, University of Sagar, Sagar (M. P.).

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In continuation of our previous works on the complex formation of Pr (III) with glycine, IDA & NTA by polarographic technique. We, now investigate the composition and stability constants of the binary complexes of Ce (III) with these legands.

EXPERIMENTAL

The stock solutions (0.1 M) of each of glycine (E. Merck, Germany), iminodiacetic acid (BDH) and nitritriacetic acid (Reanal Hungary) were prepared in carbon-dioxide free double distilled water. Cerium (III) solution (0.1M) was prepared by dissolving a calculated quantity of CeCl₃·6H₂O (Fluka AG, Switzerland) in double distilled water, and was standardised with EDTA method. To prepare potassium chloride (2M) and gelatin solutions (0.1%) the requisite amount of the chemical was dissolved in distilled water in the former case and hot distilled water in the latter case.

The following preliminary experimental set was prepared:

2mM Ce (III) + 1.0M KCl + 0.01% gelatin, the ionic strength of the test solution was kept constant at 1.0 by adjusting with potassium chloride. While in other sets, in addition to the above metal ion, supporting electrolyte and maximum suppressor, the ligand concentration was varied from 0.25 mM to 16.0 mM. The pH of the test solution was fixed at 3.0±0.02 by hydrochloric acid.

Polarograms were recorded on a C I C (Baroda, India) automatic pen recording polarograph. The capillary used had a m value 8.4 mg/sec. and drop time 3.0 sec/drop at a 35 cm effective height of mercury \( \frac{m^{2/3}}{t^{1/6}} = 4.963 \text{ mg}^{2/3} \text{ sec}^{-1/2} \). Dissolved oxygen was removed by bubbling purified nitrogen gas before recording the polarograms. For adjusting pH at 3.0 ± 0.02 on Elico digital pH meter (Model L1 - 120) was used. All the measurements were made at room temperature, 27 ± 1°C.

RESULTS AND DISCUSSION

Ce (III) gives a well defined reversible three electron reduction wave in 1.0 M potassium chloride + 0.01% gelatin at pH 3.0 ± 0.02, \( E_{1/2} = 1.85 \text{ V vs SCE} \). The reduction of
TABLE—1

<table>
<thead>
<tr>
<th>Complex</th>
<th>Stability constants of Ce (III) complexes</th>
<th>Stability constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ce (III)-Glycine]⁺⁺</td>
<td>Ratio 1:1</td>
<td>log β₁ 3.6980</td>
</tr>
<tr>
<td>[Ce (III)-(Glycine)₂]⁺</td>
<td>Ratio 1:2</td>
<td>log β₂ 6.0000</td>
</tr>
<tr>
<td>[Ce (III)-IDA]⁺</td>
<td>Ratio 1:1</td>
<td>log β₁ 3.9956</td>
</tr>
<tr>
<td>[Ce (III)-(IDA)₃]⁻</td>
<td>Ratio 1:2</td>
<td>log β₃ 6.2742</td>
</tr>
<tr>
<td>[Ce (III)-NTA]</td>
<td>Ratio 1:1</td>
<td>log β₁ 5.90</td>
</tr>
</tbody>
</table>

Ce (III) and Ce (III) complexes with all the three ligands under study were found to be of diffusion controlled nature, as the plots of \( i/Vs \sqrt{h} \) yielded straight lines passing through the origin. The plots of \( \log \frac{i}{i_d - i} \) Vs \( E_{d_e} \) for each of the polarogram was found to be linear with a slope of \( 20\pm1 \) mv, indicating a reversible nature of the reduction wave of Ce (III) as well as Ce (III) complexes under study.

**Effect of ligand concentration:**

On gradual increase of the ligand concentration to the Ce (III) test solution, here also the half wave potential is shifted to more electronegative values.

A Deford-Hume treatment of the data revealed the formation of 1 : 1 and 1 : 2 Ce (III) with glycine, 1 : 1 and 1 : 2 Ce (III) with IDA and 1 : 1 Ce (III) — NTA complexes respectively. The values of stability constants are tabulated in table 1:—

It could be concluded from the data obtained in the case of Ce (III) that the metal ligand stability constants (for 1 : 1 complexes) follow the same order as in the case of Pr (III) — glycine < IDA < NTA.

The increased values of the metal ligand stability constants in the said order may be explained on the basis of the presence of two acetic acid groups in IDA and three acetic acid groups in NTA, which render these ligands a good deal more reactive towards the generality of the cations, than glycine, as a result of which increased liganding ability is observed from glycine to NTA.

One of the authors (K. S. P.) thanks U. G. C., New Delhi, for providing financial assistance. The other author (V. K. C.) thanks U. G. C., New Delhi and Government of M. P. for the award of Teacher Fellowship. Authors also thank the Head, Department of Chemistry, University of Sagar, for laboratory facilities.

**SUMMARY**

The polarographic study of Ce (III) complexes with glycine, iminodiacetic acid and nitrilotriacetic acid has been carried out at a pH 3.0±0.02. It is observed that Ce (III) and its complexes are reversibly reduced at the dme surface having diffusion controlled nature. The stepwise stability constants have been calculated by Deford-Hume method and is noted
that Ce (III) form 1 : 1 and 1 : 2 complexes with glycine and iminodiacetic acid, while only 1 : 1 complex is formed with nitrilotriacetic acid. The order of stability constant is for 1 : 1 complexes, glycine < IDA < NTA, and for 1 : 2 complexes the order is glycine < IDA.

REFERENCES

COMPLEXES OF PRASEODYMIUM (III) WITH GLYCINE, IMINODIACETIC ACID AND NITRILOLRIACETIC ACID: A POLAROGRAPHIC STUDY.

By

K. S. Pitre and V. K. Chitale

Department of Chemistry, University of Sagar
Sagar (M. P.) 470 003

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The use of amino acids for the complex formation with various metals have been studied by various workers. Among the amino acids the complexing tendency of the derivatives of acetic acid is of worth importance. In recent years rare earth complexes with various complexing agents have studied using pH titration, potentiometric and spectrophotometric techniques etc. However, the use of polarography for the study of complex formation of rare earths has not been done extensively. In the present communication the authors have reported the polarographic study of Pr (III) complexes with glycine, iminodiacetic acid and nitrilotriacetic acid.

EXPERIMENTAL

Stock solution of Pr (III) was prepared by dissolving a requisite amount of the metal oxide in minimum quantity of hydrochloric acid (Analar). The metal solution was standardised by E.D.T.A. method. The glycine (E. Merck, Germany), iminodiacetic acid (BDH) and nitrilotriacetic acid (Reanal, Hungary) solutions were prepared in carbondioxide free double distilled water. Potassium chloride 0.2 M (BDH) and gelatin (Analar) solutions were prepared in double distilled water.

A preliminary experimental set was prepared by keeping overall concentrations of potassium chloride, gelatin and Pr (III) fixed at 0.1 M, 0.01% and 4 m M respectively, while in other sets in addition to the above supporting electrolyte, maximum-suppressor and metal ion, the ligand concentration was varied from 0.25m M to 6.0m M. The ionic strength was fixed at 0.1 M by adjusting with potassium chloride. The pH value of the test solutions was fixed at 2.75±0.02 with hydrochloric acid. For pH adjustments an Elico digital pH meter was used.

The polarograms were recorded on CIC (Baroda, India) Polarograph, the capillary used had a m value of 2.15 mg/sec. drop time 3.0 sec./drop at -1.778v vs SCE, when measured in air free 0.1 M KCl solution at 45 cm of effective height of mercury (m²/s ² =2.15mg²/m sec⁻¹/m). Dissolved oxygen was removed by passing purified nitrogen gas through the solutions and current voltage curves were obtained.

RESULTS AND DISCUSSIONS

Pr (III) gives a well defined reversible reduction wave in 0.1 M potassium chloride and 0.01% gelatin at pH 2.75. Three electrons are involved in the reduction. The reduction of Pr (III) and Pr (III) complexes with all three ligands were found to be of diffusion controlled nature, as the plots of i Vs h (effective height of the mercury column) yielded straight lines.
passing through the origin. An analysis of the plots of $\text{Edme Vs Log}^{1/\text{ld-I}}$ and $\text{E}^{3/4} - \text{E}^{1/4}$ values for the simple Pr (III) and for its complexes with all the three ligands, i.e. (substituted amino group derivatives of acetic acid) revealed a reversible nature of the reduction waves.

**Effect of Ligand Concentration**

At pH 2.75 the half wave potential of Pr (III) shifted to more negative values on increasing the concentrations of ligands.

A Lingane treatment of the data revealed 1:1 complexes of Pr (III) with all the three ligands, i.e. glycine, IDA and NTA. The metal/ligand ratio and the values of stability constants have been tabulated below:

**Table—I**

<table>
<thead>
<tr>
<th>Stability constants of Pr (III) complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pr (III)—Glycine</td>
</tr>
<tr>
<td>2. Pr (III)—IDA</td>
</tr>
<tr>
<td>3. Pr (III)—NTA</td>
</tr>
</tbody>
</table>

It is clear from the above data that the metal ligand stability constants for the three ligands under study follow the order of glycine < IDA < NTA. This is in agreement with the stability sequence obtained by Marsh and others\textsuperscript{14,15,16} for the rare earth chelates. The literature, however, records higher values for the stability constants of the three chelates under study\textsuperscript{7,14}. The difference in the stability constants may be attributed to the pH value of the experimental sets\textsuperscript{17}. The increased values of the metal ligand stability constants in the said order may be explained on the basis of the presence of 2 acetic acid groups in IDA and 3 acetic acid groups in NTA, which renders these ligands a good deal more reactive towards the generality of the cations than glycine. As a result, increased liganding ability is observed from glycine to NTA.

One of the authors K.S.P. is thankful to the U.G.C. New Delhi for providing financial assistance under the scheme of Financial Assistance to the teachers. The other author V.K.C. is thankful to U.G.C, and Government of M.P., for providing him teacher fellowship. Thanks are also due to Head, Chemistry Department, University of Saugar, Sagar, M.P. for providing laboratory facilities.

**Summary**

Complexes of Pr (III) with glycine, iminodiacetic acid and nitrilotriacetic acid at pH 2.75±0.02 have been studied polarographically. It is observed that each of the three ligands form 1:1 complex with stability constants following the order glycine < IDA < NTA. It was also observed that Pr (III) and its complexes under study are reversibly reduced at the dme surface having diffusion controlled nature.
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1. Foad and Lorces; Tids, Kjems, Berqsvsen Met 6, 83 (1943).
Complexes of Neodymium(III) with Glycine, Iminodiacetic Acid and Nitrilotriacetic Acid: A Polarographic Study

K. S. PITRE and V. K. CHITALE
Department of Chemistry, University of Saugar, Sagar-470 003 (M. P.)
Manuscript received 14 February 1980, accepted 5 November 1980

AMINO acids have been extensively used for the complex formation with various metals. Among the amino acids the chelating ability of the derivatives of acetic acid is particularly noteworthy. In recent years, rare earth complexes with various complexing agents have been studied employing pH titration, potentiometric and spectrophotometric techniques etc. However, little attention has been given on the polarographic study of the rare earth complexes. In the present communication the authors have reported the polarographic study of Nd(III) complexes with glycine, iminodiacetic acid and nitrilotriacetic acids.

Experimental

Stock solutions of 0.01 M glycine (E. merck, Germany), iminodiacetic and (BDH) and nitrilotriacetic acid (Reanal, Hungary) were prepared in carbon dioxide free double distilled water. The Nd(III) solution was prepared by dissolving a calculated quantity of the metal oxide in minimum amount of dil. hydrochloric acid (AnalaR). The metal solution was standardised by EDTA method.

Potassium chloride 2.0 M and gelatin (AnalaR), solution were prepared in double distilled water.

A preliminary experimental set was prepared by keeping overall concentration of potassium chloride, gelatin and Nd(III) fixed at 1.0 M, 0.01% and 2 M M respectively. In the other sets, in addition to the above metal ion, supporting electrolyte and gelatin concentrations, the ligand concentration was varied from 0.25 M to 3.0 M. The ionic strength was fixed at 1.0 by adjusting with potassium chloride. Hydrochloric acid was used to fix the pH value of the solution at 2.75 ± 0.02.

Current-Voltage curves were obtained by using a C.I.C (Baroda, India) polarograph, the capillary used had m value of 2.15 mg/sec, and drop time of 3.1 sec/drop at -1.765 V vs SCE, when measured in an air free 1.0 M KCl solution at 45 cm of effective height of mercury (m²τ¹/₄ = 2.15 mg²/sec⁻¹/₄). Dissolved oxygen was removed by passing purified nitrogen gas through the solutions and the polarograms were recorded. For adjusting pH at 2.75 ± 0.02 an Elico digital pH meter was used. All the measurements were carried out at room temperature 32 ± 0.1°C.

Results and Discussion

Nd(III) gives a well defined reversible reduction wave in 1.0 M potassium chloride plus 0.01% gelatin at pH 2.75 ‑ 2.8. The reduction of Nd(III) and Nd(III) complexes with all the three ligands were found to be of diffusion controlled nature as the plots of i vs √h (effective height of mercury column) yield straight lines passing through the origin. An analysis of the plots of Echrono vs log I/ld-I and E_n/4 – E_1/4 values for the simple Nd(III) and for its complexes with all the three ligands i.e., (substituted amino gr. derivatives of acetic acid) revealed a reversible nature of the reduction waves.

Effect of Ligand Concentration:

At pH 2.75 the half wave potential of Nd(III) shifted to more negative values on increasing the concentration of ligands.

A Lingane treatment of the data revealed 1:1 complexes of Nd(III) with all the three ligands e.g., glycine, iminodiacetic acid and nitrilotriacetic acid. The metal ligand ratio and the values of the stability constants have been tabulated below.

<table>
<thead>
<tr>
<th>Stability Constants of Nd(III) Complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Nd(III) - Glycine</td>
</tr>
<tr>
<td>log β</td>
</tr>
<tr>
<td>4.00</td>
</tr>
<tr>
<td>2. Nd(III) - Iminodiacetic acid</td>
</tr>
<tr>
<td>log β</td>
</tr>
<tr>
<td>4.36</td>
</tr>
<tr>
<td>3. Nd(III) - Nitrilotriacetic acid</td>
</tr>
<tr>
<td>log β</td>
</tr>
<tr>
<td>4.78</td>
</tr>
</tbody>
</table>

It is clear from the data that the metal ligand stability constants for the three amino acids under examination follow the order of glycine < iminodiacetic acid and < nitrilotriacetic acid, which is in excellent agreement with the results reported by Schwarzenbach and Biedermann. The increased values of the metal ligand stability constants in the said order may be explained on the basis of the presence of 2 acetic acid groups in IDA and 3 acetic acid groups in NTA, which render these ligands a good deal more reactive towards the generality of the cations, than glycine, as a result of which increased liganding ability is observed from glycine to NTA.
NOTES

Acknowledgement

One of the authors (K.S.P.) is thankful to the U.G.C., New Delhi for providing financial assistance under the scheme of Financial Assistance to teachers. The other author (V.K.C.) is thankful to U.G.C. and Government of M.P., for providing him teacher fellowship. Thanks are also due to the Head, Chemistry Department, University of Saugar, Sagar (M.P.) for providing laboratory facilities.

References

1. Flood and Lorcks, Tids, Kjens, Bergsuen Met., 1945, 6, 83.

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Complexes of Cerium(III) with Benzoic Acid, 
Protocatechuic Acid and Salicylic Acid : 
A Polarographic Study 
V. K. CHITALE and K. S. PITRE

Department of Chemistry, University of Sagar, Sagar-470 001
Manuscript received 4 December 1980, revised 8 September 1981, accepted 30 October 1981

In previous communications the complexes of Pr(III) and Nd(III)1-8 with benzoic acid, protocatechuic acid and salicylic acid by polarographic technique were reported1-8. However, the literature is silent about the study of complexes of Ce(III) with these ligands at a DME. The present paper deals with the composition and stability constants of Ce(III) with benzoic acid, protocatechuic acid and salicylic acid respectively by Lingane and Deford-Hume treatment of the observed polarographic data.

Experimental

All the chemicals used were of Analar/BDH grade. Ce(III) (0.01 M) solution was prepared by dissolving a calculated quantity of CeCl₃·6H₂O (Fluka AG, Switzerland) in conductivity water and was standardized by EDTA method9. Potassium chloride and gelatin solutions were prepared in double distilled water. The stock solutions (0.1 M) of sodium benzoate, protocatechuic acid and potassium salicylate were prepared in carbon-dioxide-free double distilled water.

A preliminary experimental set was prepared by keeping overall concentrations of metal ion, potassium chloride and gelatin at 1 mM, 1.0 M and 0.01 % respectively. While in other sets in addition to the above metal ion, supporting electrolyte and maximum suppressor, the concentration of ligand in each case was varied from 0.25 mM to 30.0 mM. The ionic strength was fixed at I = 1.0 by adding requisite amount of potassium chloride. The pH of the test solutions was kept at 3.0 ± 0.02 by necessary addition of hydrochloric acid and was measured with an Elico digital pH meter (Model LI-120).

An automatic pen recording polarograph CIC (Baroda, India) was used for recording polarograms. Potentials were measured against saturated calomel electrode. The capillary had the following characteristics: m = 2.13 mg/sec, t = 3.0 sec/drop (m²/s t¹/₂ = 2.323 mg²/s sec⁻¹/₂) in 1.0 M potassium chloride at 35 cm effective height of the mercury column. Pure nitrogen gas was passed through the test solutions before recording the polarograms. All the measurements were made at room temperature, 26 ± 1\°C.

Results and Discussion

Ce(III) gives a well defined, reversible three electron reduction wave in 1.0 M potassium chloride in presence of 0.01% gelatin at pH 3.0 ± 0.02. The reduction of Ce(III) and of its complexes with all the three ligands under study were found to be diffusion controlled as the plots of iₚ vs √ν yielded straight lines passing through the origin. For each polarogram the average value of log iₚ plot slope was found to be 20 ± 1 mV indicating reversibility of the electrode process involving three-electron reduction.

Effect of ligand concentration: The half wave potential of Ce(III) shifted to more negative values on gradual increase of the concentration of the ligands under study. The plots of -Eₚ against log Cₐ (logarithm of the concentration of the ligands) gave straight lines and segmented lines, indicating the formation of single complex in Ce(III)-benzoate and Ce(III)-protocatechuic systems and plural complex formation in Ce(III)-salicylate system (Fig. 1). The stoichiometry of complexes was found to be [Ce(III)-benzoate]⁺, [Ce(III)-protocatechuic]⁺, [Ce(III)-salicylate]⁺ and [Ce(III)-salicylate]⁺. The values of stability constants were calculated by Lingane method8 in case of single species complex, while Deford-Hume* method was used to calculate the formation constants of step wise complex formation of Ce(III)-salicylate system as tabulated in Table 1.

The stability constants are in agreement with the previously published results of Pr(III) and Nd(III) complexes with benzoic acid, protocatechuic acid and salicylic acid respectively10,8.
Table 1—Stability Constants of Ce(II) Complexes

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Complex</th>
<th>Ratios</th>
<th>Stability constant</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ce(III)-benzoate</td>
<td>1:1</td>
<td>log β = 4.1</td>
<td>Lingane DeFord-Hume method</td>
</tr>
<tr>
<td>2</td>
<td>Ce(III)-protocatechuate</td>
<td>1:2</td>
<td>log β = 6.28</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>Ce(III)-salicylate</td>
<td>1:1</td>
<td>log β = 3.6</td>
<td>3.47</td>
</tr>
<tr>
<td>4</td>
<td>Ce(III)-salicylate</td>
<td>1:2</td>
<td>log β = 7.2</td>
<td>6.98</td>
</tr>
</tbody>
</table>

Acknowledgement

One of the authors (V.K.C.) is thankful to the University Grants Commission, New Delhi and the Government of Madhya Pradesh for a Teachers Fellowship. Thanks are also due to the Head, Department of Chemistry, University of Saugar for laboratory facilities.

References

STUDY ON COMPLEXES OF PRASEODYMIUM (III) WITH BENZOIC ACID, PROTOCATEUCHIC ACID AND SALICYLIC ACID ON A D M E

V. K. Chitale and K. S. Pitre

Department of Chemistry, University of Sāugar, Sagar (M. P.).

(Received 29 November 1980)

Benzoic acid and its substituted hydroxy derivatives have been extensively used for complex formation with various metals, involving pH titration, spectrophotometric, potentiometric and polarographic methods. However, in literature no mention is made about the polarographic study of complex formation between lanthanons and these ligands. The present communication deals with the polarographic study of binary complexes of Pr(III) with benzoic acid, protocatechuic acid and salicylic acid respectively.

EXPERIMENTAL

All chemicals used were of AnalAR/BDH grade. Pr(III) solution was prepared by dissolving a calculated quantity of the metal oxide in minimum quantity of hydrochloric acid and was standardised by EDTA method.² Potassium chloride (2M) and gelatin (0.1%) were prepared in double distilled water in the former case and in hot double distilled water in the latter case. Stock solutions (0.1 M) each of sodium benzoate, potassium salicylate and protocatechuic acid were also prepared in carbon dioxide free double distilled water.

A preliminary experimental set was prepared by keeping over all metal ion, potassium chloride and gelatin concentration at 2 mM, 1.0 M and 0.01% respectively. While in other sets in addition to the above metal ion, supporting electrolyte and maximum suppressor concentrations, the ligand concentration in each case was varied 0.25 mM to 12 mM. Potassium chloride was used to keep constant ionic strength (κ=1.0). Hydrochloric acid was used to adjust the pH of the test solution to 2.75 ± 0.02. An Elico digital pH meter (Model LI-120) was used to measure the pH of the test solutions.

Dissolved oxygen was removed by bubbling purified nitrogen gas through the test solutions for five minutes before recording the polarograms. The polarograms were recorded on a C I C (Baroda, India) polarograph. Saturated calomel electrode was used as reference electrode connected to the cell through saturated KCl agar bridge. The capillary characteristics were \( m = 2.31 \text{ mg/sec, } t = 3.0 \text{ sec/drop (m}^{2/3} \text{t}^{1/6} = 2.136 \text{ mg}^{2/3} \text{sec}^{-1/2}) \) in 1.0 potassium chloride at 35 cm effective height of the mercury column. All observations were made at room temperature 26 ± 1°C.

RESULTS AND DISCUSSION

Pr(III) gives a well-defined three electron reduction reversible wave²². The linear plots of \( i_d V \sqrt{h} \) for Pr(III) and its complexes under study, indicated the diffusion controlled
nature of the reduction. The plots of log $i/id$ vs $E_{d}$ for each polarogram were found to be linear with a slope of $20 \pm 2$ mv, indicating reversibility of the electrode process involving three electron reduction.

**Effect of ligand concentration:**

At pH 2.75, with each of three ligands, the half wave potential for Pr(III) shifted to more negative value on increasing the concentration of ligand.

A Lingane treatment of the observed polarographic data revealed $1 : 1$, $1 : 2$ and $1 : 2$ complexes of Pr(III) with benzoic acid, protocatechuic acid and salicylic acid respectively. The values of the stability constants are tabulated below:

<table>
<thead>
<tr>
<th>Complex</th>
<th>Ratio M:L</th>
<th>Stability constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr(III)-benzoate</td>
<td>1:1</td>
<td>Log $\beta = 3.4$</td>
</tr>
<tr>
<td>Pr(III) (Protocatechu)</td>
<td>1:2</td>
<td>Log $\beta = 7.14$</td>
</tr>
<tr>
<td>Pr(III) (Salicylate)</td>
<td>1:2</td>
<td>Log $\beta = 7.48$</td>
</tr>
</tbody>
</table>

The sequence of the stability constants of the complexes is benzoate $<$ protocatechuic $<$ salicylate, which may be explained on a simple argument that benzoic acid forms a simple co-ordination compound with Pr(III), while other two ligands form chelates. The difference in stability constants of Pr(III)-(Protocatechu) and Pr(III)-(salicylate) may be explained on the presumption that the chelating groups (hydroxy and carboxylate groups) are at $-O$ position in salicylic acid, while dihydroxy groups are at $-m$ and $-p$ positions in protocatechuic acid ($3 : 4$ dihydroxy benzoic acid). This renders salicylate ion to behave as a stronger chelating agent than protocatechuic ion, as also reported by Bhattacharya and co-workers.

One of the authors V. K. C. is thankful to U. G. C. New Delhi and Govt. of M. P. for the award of Teacher Fellowship. Thanks are also due to Head, Department of Chemistry, University of Saugar for providing laboratory facilities.

**Summary**

The polarographic behaviours of Pr(III) with benzoic acid, protocatechuic acid and salicylic acid have been studied using a dropping mercury electrode at a pH $2.75 \pm 0.02$. Single well defined, three electron reversible reduction waves were obtained for Pr(III) and complexes under study. The reduction was found to be diffusion controlled. The stability constants were calculated by Lingane method. The order of stability constants of Pr(III) with these ligands was benzoate $<$ protocatechuete $<$ salicylate respectively.

**References**

A POLAROGRAPHIC STUDY OF THE COMPOSITION AND STABILITY CONSTANTS
OF BENZOATE, PROTOCATECHUATE AND SALICYLATE COMPLEXES OF
NEODYMIUM (III)

V.K. CHITALE AND K.S. PITRE
Department of Chemistry,
University of Sagar, Sagar
A POLAROGRAPHIC STUDY OF THE COMPOSITION AND STABILITY CONSTANTS OF BENZOATE, PROTocatechuATE AND SALICYLATE COMPLEXES OF NEODYMIUM (III)

V.K. CHITALE and K.S. PITRE

Department of Chemistry,
University of Sagar, Sagar

A polarographic study of Nd (III)—complexes with benzoic acid, protocatechuic acid and salicylic acid has been carried out at a pH 2.75±0.02. It is observed that Nd (III) and its complexes with these ligands are reversibly reduced at the dme surface. The composition and stability constants of the complexes have been calculated by Lingane treatment of the observed polarographic data. It has been observed that Nd (III) forms 1 : 1, 1 : 2 and 1 : 2 complexes with benzoic acid, protocatechuic acid and salicylic acid respectively.

The authors earlier reported the complex formation of Pr (III) and Ce (III) with benzoic acid, protocatechuic acid and salicylic acid by polarographic technique\(^1\). A survey of literature reveals that the polarographic study of complexes of Nd(III) with these ligands has not been made. The present study was undertaken to investigate the composition and stability constants of binary complexes of Nd(III) with benzoic acid, protocatechuic acid and salicylic acid respectively, by Lingane treatment of the observed polarographic data.

All the chemicals used were of AnalAr/BDH grade. The stock solutions (0.1M each) of sodium benzoate, protocatechuic acid and potassium salicylate were prepared in double distilled water. Nd(III) solution was prepared by dissolving a calculated quantity of the metal oxide in minimum quantity of hydrochloric acid and was standardised by EDTA method\(^2\). Potassium chloride and gelatin solutions were also prepared in double distilled water.

A preliminary experimental set was prepared by keeping overall concentrations of metal ion, supporting electrolyte and maximum suppressors at 1mM 1.0M and 0.01% respectively. The ionic strength of the test solutions was kept constant at \(\mu=1.0\) by potassium chloride. While in other sets in addition to the above metal ion, supporting electrolyte and maximum suppressor, the ligand concentration was varied from 0.25 mM to 30mM. Hydrochloric acid was used to keep the pH of the test solutions at 2.75±0.02.

Current voltage curves were obtained on a CIC (Baroda, India) automatic pen recording polarograph. Purified nitrogen gas was passed through the test solutions before recording the polarograms. The capillary had \(m=8.4\) mg/sec and \(t=3.0\) sec/drop at a 35 cm effective height of the mercury, when measured in air free 1.0 M potassium chloride \((m^{2/3} t^{1/6}=4.963\text{mg}^{2/3} \text{t}^{1/6})\). An Elico digital pH meter (Model L1—120) was used to measure the pH of the test solutions. All the observations were recorded at 26±1°C.

Nd(III) gives a well defined reversible three electron reduction wave in 1.0 M potassium chloride +0.01% gelatin at pH 2.75±0.02\(^5\). The reduction of Nd(III) and its complexes with all the three
ligands, under study, was found to be diffusion controlled as the plots of \( i_d V_{\sqrt{h}} \) gave straight lines passing through the origin. The plots of \( i / i_d \) vs \( E_{e} \) for each polarograms were found to be linear with a slope of \( 20 \pm 2 \text{ mV} \), indicating the reversibility of the electrode process involving three electron reduction.

On gradual increase of the ligand concentration, the half wave potential of Nd(III) shifted to more negative values in all the cases under study. The plots of \(-E_{1/2} V_{x} \log C_{x}\) were straight lines, indicating the formation of a single complex with all the three ligands under study. A Lingane\(^{6}\) treatment of the data revealed the formation of 1:1, 1:2 and 1:2 complexes of Nd(III) with benzoic acid, protocatechuic acid and salicylic acid respectively. The values of the stability constants are given below:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complexes</th>
<th>Ratio M : L</th>
<th>Stability constant log ( \beta_{n} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Nd(III)—benzoate</td>
<td>1 : 1</td>
<td>3.45</td>
</tr>
<tr>
<td>2.</td>
<td>Nd(III)—(Protocatechuace)(n)</td>
<td>1 : 2</td>
<td>7.54</td>
</tr>
<tr>
<td>3.</td>
<td>Nd(III)—(salicylate)(n)</td>
<td>1 : 2</td>
<td>7.70</td>
</tr>
</tbody>
</table>

The observed values of the metal-ligand stability constants of the complexes may be explained on a simple argument that benzoic acid forms a simple coordination compound with Nd(III), while the other two ligands form chelates. Further although the difference in stability constants of Nd(III)—(protocatechuace)\(n\) and Nd(III)—(salicylate)\(n\) is very small but may be explained on the presumption that the chelating groups in salicylic acid are present at ortho-position, while in protocatechuic acid the hydroxy groups are in meta-and para-positions with respect to carboxylate group as a result of which salicylate ion behaves as a stronger chelating agent than protocatechuic ion.\(^{1,8,7}\)

One of the authors V.K.C. is thankful to the University Grants Commission, New-Delhi and Government of Madhya Pradesh for the award of Teacher Fellowship. Thanks are also due to Head Department of Chemistry, University of Saugar Sagar (M.P.) for providing laboratory facilities.

REFERENCES

Separation of Polarographic Waves of Zn(II), Ni(II) and Co(II) in Potassium Chloride by Differential Complexation with Potassium Salicylate and Iminodiacetic Acid

K. S. PITRE and V. K. CHITALE

Department of Chemistry, University of Sagar, Sagar, M.P.

Manuscript received 18 June 1980, revised 5 March 1981, accepted 15 July 1981

Polarographic waves of (a) Zn(II)+Ni(II) and (b) Zn(II)+Co(II) in a mixture have been separated with IDA. The waves are $0.3 \pm 0.02V$ apart in the former case and $0.35 \pm 0.02V$ apart in the latter. The separation of Ni(II)+Co(II) in a mixture with IDA is not reproducible. The polarographic waves of (a) Zn(II)+Co(II) and (b) Ni(II)+Co(II) in a mixture have been separated with potassium salicylate. The waves are $0.32 \pm 0.03V$ and $0.3 \pm 0.03V$ apart from each other respectively. The separation of polarographic waves of Zn(II) and Ni(II) with potassium salicylate is poor as the waves are only $0.1 \pm 0.01V$ apart from each other.

The polarographic waves of Zn(II), Ni(II) and Co(II) in a mixture have been separated by potassium salicylate. The waves of Zn(II) and Co(II) are $0.2 \pm 0.02V$ apart and that of Ni(II) and Co(II) are $0.3 \pm 0.02V$ apart from each other. A poor polarographic separation is observed with IDA.

ZINC(II), Nickel(II) and Cobalt(II) in 1.0 M potassium chloride separately give well defined polarographic waves. But when present in a mixture of two or three, the waves of these metal ions are so close that they are almost superimposed, and a measurement of individual wave height and half-wave potential becomes impossible. An inorganic analyst can usually deal with the problem of wave separation by differential complexation. Use of a suitable complexing agent may improve the shape of the wave or bring it to a more readily accessible region of applied potential. Keeping this in mind an attempt has been made to separate the polarographic waves of Zn(II), Ni(II) and Co(II) in 1.0 M KCl using their complexation with potassium salicylate and iminodiacetic acid (Sodium salt).

Experimental

All chemicals used were of Analar/BDH grade. The solutions (0.1 M) of Zn(II), Ni(II) and Co(II) were prepared by dissolving calculated quantities of salts of these metals [ZnSO$_4$·7H$_2$O, NiSO$_4$·6H$_2$O and Co(NO$_3$)$_2$·6H$_2$O] in double distilled water. Potassium chloride solution was also prepared in double distilled water.

Test solutions containing varying amounts of single metal ion, a mixture of two metal ions and all the three metal ions in 1.0 M KCl were prepared. All measurements were made at pH $6.5 \pm 0.2$. For the purpose of wave separation, test solutions with varying concentration of two and three metal ions in 1.0 M KCl plus complexing agents i.e., potassium salicylate and IDA (30 mM) separately were also prepared. The ionic strength ($\mu$) was fixed at 1.0 by adjusting with potassium chloride.

Current voltage curves were obtained on a CIC (Baroda) automatic pen-recording polarograph.

The capillary used had a m value 8.4 mg/second and drop time 3.0 second at 35 cm effective height of mercury ($\text{m}^{2/3}, \text{t}^{1/3} = 4.963 \text{ mg}^{2/3} \text{ sec}^{-1/3}$). The pH of the test solution was measured on an Elico digital pH meter (Model L1-120). Purified nitrogen gas was passed through the test solution before recording the polarograms. All observations were made at room temperature $25 \pm 1^\circ$.

Results and Discussion

Each of the three metal ions i.e., Zn(II), Ni(II) and Co(II) gives a single reduction wave in 1.0 M KCl. The $E_1$ values for these ions are Zn(II) $-0.995 \text{ V vs SCE}$, Ni(II) $-1.10 \text{ V vs SCE}$ and Co(II) $-1.20 \text{ V vs SCE}$ respectively.

(i) Separation of Zn(II) and Ni(II) waves: The wave of Zn(II) precedes that of Ni(II) on polarography a sample containing 2.0 mM Zn(II) and 1.0 mM Ni(II) in 1.0 M KCl. The plateau of the Zn(II) wave is reasonably long and remarkably parallel to the residual current. The wave height can, therefore, be measured without difficulty. As the concentration of Ni(II) or Zn(II) increases the separation becomes poorer and the waves are almost superimposed. The problem of wave separation has been tackled by utilizing the differential complexation of Zn(II) and Ni(II) with potassium salicylate and IDA respectively.

On adding IDA the waves are very well separated. The waves are $0.3 \pm 0.02V$ apart from each other. Under the experimental condition the half-wave potential for Zn(II) is $-1.05 \pm 0.02 \text{ V vs SCE}$ and that for Ni(II) is $-1.37 \text{ V vs SCE}$. This separation of waves is possible only when almost equimolar solution of Zn(II) and Ni(II) are polarographed (Fig. A). A poor separation is observed
TABLE 1—Separation of Polarographic Waves of Zn(II) and Ni(II) in 1.0 M KCl using Complexones (i) Potassium Salicylate and (ii) IDA. Sensitivity 0.2 μA/mm.

<table>
<thead>
<tr>
<th>Concentration of Zn(II) and Ni(II) used</th>
<th>Polaro graphic data for Zn(II)</th>
<th>Polaro graphic data for Ni(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>id[μA] f/C</td>
<td>f(C_m²/m²) Eₐ/ₐ - Eₐ/ₐₐ</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(II) Ni(II)</td>
<td>5.0 5.0 1.00745 65 - 0.97e</td>
<td>7.8 7.8 1.5716 69 - 1.05e</td>
</tr>
<tr>
<td>1:1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:10</td>
<td>7.2 4.8 0.9671 68 - 0.95e</td>
<td>7.4 7.4 1.4910 68 - 1.05e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(II) Ni(II)</td>
<td>7.0 7.0 1.4104 60 - 1.05e</td>
<td>7.6 7.6 1.5313 90mv - 1.37e</td>
</tr>
<tr>
<td>1:10</td>
<td>10.2 6.8 1.3701 60 - 1.03e</td>
<td>7.8 7.8 1.5716 90mv - 1.37e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wave are not separated</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poor Separation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Separation is not possible</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Separation is not possible</td>
<td></td>
</tr>
</tbody>
</table>

Note: Without complexones the separation is not possible.
Both the waves get superimposed on each other.

When potassium salicylate is used as a complexing agent, the separation becomes more prominent if the concentration of Ni(II) is increased 10 to 20 folds to that of Zn(II) concentration. Other polarographic data for Zn(II) and Ni(II) with these complexones have been enlisted in Table 1.

(ii) Separation of Zn(II) and Co(II) waves: The polarographic wave of Zn(II) precedes that of Co(II) when a mixture of 2 mM Zn(II) and 1 mM Co(II) in 1.0 M KCl is polarographed. The waves were separated by 0.2 V ± 0.01 V but on increasing the concentration of either of the two ions the waves are superimposed. On using IDA and potassium salicylate as complexing agents separately the waves get separated. The Eₐ values and other polarographic data have been tabulated in Table 2. Both the complexing agents are equally effective in bringing out the separation. The waves are 0.32 ± 0.03 V apart from each other with potassium salicylate as the complexing agent. The half wave potential value for Zn(II) is -0.99 ± 0.01 V vs SCE and that for Co(II) is -1.32 ± 0.03 V vs SCE. With IDA the waves are 0.35 ± 0.03 V apart from each other. The Eₐ for Zn(II) is -1.0 V ± 0.04 V vs SCE and that for Co(II) is -1.35 ± 0.03 V vs SCE (Figs. B, C). The separation is possible even if the concentration of Co(II) is ten to twenty folds to that of Zn(II).

(iii) Separation of Ni(II) and Co(II) waves: In this system the polarographic wave of 1 mM Ni(II) precedes that of 1 mM Co(II) in 1.0 M KCl when a mixture of these two ions are polarographed. The waves are 0.25 ± 0.02 V apart from each other. On increasing the concentration of either of the ions the two waves get superimposed. The use of potassium salicylate and IDA as complexing agents facilitates the separation of these two waves. Though the separation with IDA is not perfect, potassium salicylate helped in the separation of Ni(II) and Co(II) even when the concentration of either of the two ions is ten to twenty folds to that of the other. The half wave potential for Ni(II) is -0.92 ± 0.1 V vs SCE and that for Co(II) is -1.22 ± 0.05 V vs SCE. The waves are 0.3 ± 0.03 V apart from each other (Fig. D). The other polarographic data have been given in Table 3.

(iv) Separation of Zn(II), Ni(II) and Co(II) waves: On polarographing a mixture containing 1 mM Zn(II), 1 mM Ni(II) and 1 mM Co(II) in 1.0 M KCl only two waves are observed. It has been already observed that Zn(II) and Ni(II) waves are superimposed on each other and the other wave is that of Co(II). By using potassium salicylate
**TABLE 3—SEPARATION OF POLAROGRAPHIC WAVES OF Zn(II) AND Co(II) IN 1.0 M KCl; WITHOUT COMPLEXONES AND USING POTASSIUM SALICYLATE AND IMINODIACETIC ACID. SENSITIVITY 0.3µA/mm.**

<table>
<thead>
<tr>
<th>Concentration of Zn(II) and Co(II) in mM</th>
<th>Polarographic data for Zn(II)</th>
<th>Polarographic data for Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>id(µA)</td>
<td>Id/C</td>
</tr>
<tr>
<td>Zn(II) Co(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>4.4</td>
<td>4.4</td>
</tr>
<tr>
<td>1.2</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>1.3</td>
<td>4.2</td>
<td>4.2</td>
</tr>
<tr>
<td>1.4</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 1.0 Pot. Salicylate 30 mM</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>1.0 1.0</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>1.5 1.0</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>2.0 1.0</td>
<td>10.4</td>
<td>10.4</td>
</tr>
<tr>
<td>2.0 1.5</td>
<td>9.4</td>
<td>9.4</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
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<tr>
<td>Poor separation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separation is not possible</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE 4—SEPARATION OF POLAROGRAPHIC WAVES OF Ni(II) AND Co(II) IN 1.0 M KCl; WITHOUT COMPLEXONES AND USING POTASSIUM SALICYLATE. SENSITIVITY 0.3µA/mm.**

<table>
<thead>
<tr>
<th>Concentration of Ni(II) and Co(II) in mM</th>
<th>Polarographic data for Ni(II)</th>
<th>Polarographic data for Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Id(µA)</td>
<td>Id/C</td>
</tr>
<tr>
<td>Ni(II) Co(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>5.2</td>
<td>5.2</td>
</tr>
<tr>
<td>1.2</td>
<td>10.2</td>
<td>10.2</td>
</tr>
<tr>
<td>1.3</td>
<td>12.6</td>
<td>12.6</td>
</tr>
<tr>
<td>1.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Potassium Salicylate 30 mM</td>
<td>9.4</td>
<td>9.4</td>
</tr>
<tr>
<td>1.1</td>
<td>12.0</td>
<td>12.0</td>
</tr>
<tr>
<td>1.1</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>1.1</td>
<td>15.8</td>
<td>15.8</td>
</tr>
<tr>
<td>1.1</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td>1.1</td>
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<td></td>
</tr>
<tr>
<td>Poor separation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Separation is not possible</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: With iminodiacetic acid separation is not possible.

**TABLE 4—SEPARATION OF POLAROGRAPHIC WAVES OF Zn(II), Ni(II) AND Co(II) IN 1.0 M KCl USING COMPLEXONES POTASSIUM SALICYLATE, IMINODIACETIC ACID AND WITHOUT COMPLEXONES. SENSITIVITY 0.3µA/mm.**

<table>
<thead>
<tr>
<th>Concentration of Zn(II), Ni(II) and Co(II) in mM</th>
<th>Polarographic data for Zn(II)</th>
<th>Polarographic data for Ni(II)</th>
<th>Polarographic data for Co(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Id(µA)</td>
<td>Id/C</td>
<td>Id/Cm²/s</td>
</tr>
<tr>
<td>Zn(II) Ni(II) Co(II)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 1.1 Potassium salicylate 30 mM</td>
<td>6.2</td>
<td>6.2</td>
<td>1.2492</td>
</tr>
<tr>
<td>1.1 1.1</td>
<td>5.8</td>
<td>5.8</td>
<td>0.7798</td>
</tr>
<tr>
<td>1.1 1.1</td>
<td>6.6</td>
<td>6.6</td>
<td>0.5319</td>
</tr>
<tr>
<td>1.1 1.1</td>
<td>9.0</td>
<td>9.0</td>
<td>1.8184</td>
</tr>
<tr>
<td>1.1 1.1</td>
<td>9.0</td>
<td>9.0</td>
<td>1.2089</td>
</tr>
</tbody>
</table>

Note: Without ligand only two waves are observed.
(30 mM) the three waves are well separated from each other. Though the wave of Zn(II) is a bit suppressed [diffusion current constant for Zn(II) is 0.779 ± 0.4], it allows the measurements of half wave potential and wave height. On increasing the concentration of Zn(II), the wave becomes prominent and meaningful (Fig. E). The waves are 0.2 ± 0.02 V apart in case of Zn(II) and Ni(II) and for Ni(II) and Co(II), 0.3 ± 0.02 V apart from each other. The half wave potential values for Zn(II) −0.86 ± 0.02 V vs SCE, Ni(II) −1.03 ± 0.01 V vs SCE and that for Co(II) −1.31 V vs SCE have been observed. With IDA, poor separation is observed. If equimolar solution of Zn(II), Ni(II) and Co(II) are polarographed, the separation is effective. The value for half wave potential for Zn(II) is −1.0 ± 0.05 V vs SCE, Ni(II) is −1.28 ± 0.06 V vs SCE and that for Co(II) is 1.32 ± 0.08 V vs SCE. The other polarographic data are given in Table 4.

The separation of polarographic waves in all these cases may be presumed to be due to the differences in the stability constants of the complexes of the metal ions under study. The more the stability of the complex the more negative is its half wave potential values.

Acknowledgement

One of the authors (K.S.P.) is thankful to the UGC, New Delhi for financial assistance under the scheme of financial assistance to teachers. The other author (V.K.C.) is thankful to the UGC and Govt. of M. P. for a teacher fellowship. Thanks are also due to Head, Chemistry Department, University of Saugar, Sagar, M. P. for laboratory facilities.

References

ANALYTICAL POLAROGRAPHIC SEPARATION OF Cu(II)-Cd
AND Cu(II)-Ni BY DIFFERENTIAL COMPLEXATION WITH
SALICYLIC ACID OR IMINODIACETIC ACID

Y.K. Chitale and K.S. Pitre

Department of Chemistry, University of Sagar,
Sagar (M.P.)-470 003 India

Received 24.8.81; accepted 28.2.82
ABSTRACT

The polarographic waves of mixtures of Cu(II)-Cd and Cu(II)-Ni have been separated by differential complexation. The separation with salicylic acid (SA) and iminodiacetic acid (IDA) is fruitful in the Cu(II)-Cd system, where the waves are 0.15±0.02 V apart. For the Cu(II)-Ni system, SA is effective for separation and the waves are separated by 0.20±0.02 V. The separation of this system with IDA is not reproducible.

INTRODUCTION

The separation of the polarographic waves of two or three metals (having $E_{1/2}$ values close to each other), is a very difficult problem, when the waves of the metal ions are so close together as to be almost superimposed. An inorganic analyst usually deals with the problem of wave separation by differential complexation. A suitable complexing agent may improve the shape of one or more of the waves, or bring them to a more readily accessible region of the applied potential /1/. In a previous communication, the authors have already reported the separation of Zn(II), Ni(II) and Cu(II) in potassium chloride by using their complexation with salicylic acid (SA) and iminodiacetic acid (IDA) /2/.

Copper (II), cadmium and nickel separately give well defined polarographic waves in potassium thiocyanate with gelatin, as a supporting electrolyte and maxima suppressor respectively /3/. The waves are also observed in ammonium thiocyanate. When present in a mixture, however, the waves as such are not perfectly separated, but by using a suitable complexing agent, the separation of these waves is possible. The present paper reports the separation of these polarographic waves using differential complexation with SA and IDA.

EXPERIMENTAL

Analar (BDH grade) chemicals were used. Metal solutions (0.1 M) were prepared by dissolving the requisite amount of the corresponding salts (viz. CuSO$_4$.5H$_2$O, Cd(NO$_3$)$_2$.2H$_2$O and NiSO$_4$.6H$_2$O) in double distilled water. Ammonium thiocyanate (2.0 M), gelatin 0.1% and ligand solutions were also prepared in double distilled water.

Test solutions containing varying amounts (1-10 mM) of single metal ion or a mixture of two metal ions in 1.0 M ammonium thiocyanate as
supporting electrolyte is 0.01% gelatin were prepared separately. For the purpose of wave separation, salicylic acid and iminodiacetic acid were separately used. The ionic strength was kept at µ = 1.0 by ammonium thiocyanate. The pH of the test solutions was fixed at 6.0±0.2 by the addition of hydrochloric acid or sodium hydroxide and was measured on an Elico digital pH meter (Model L1-120).

Polarograms were recorded on a CIC (Baroda, India) automatic pen recording polarograph. The capillary characteristics were m = 2.3733 mg/sec, t = 3.0 sec. in 1.0 M ammonium thiocyanate (open circuit) at 35 cm effective height of the mercury column (m^2 t^1 = 2.136 m^2 s^2 cm^-1). Pure nitrogen gas was passed through the test solutions before recording the polarograms. All the observations were recorded at room temperature 27±1°C.

RESULTS AND DISCUSSION

It was observed that each of the three metal ions separately gave a well defined single reduction wave in 1.0M ammonium thiocyanate + 0.01% gelatin at pH 6.0±0.2. The half wave potential values for these ions are Cu(II) = -0.50 V Vs SCE, Cd = -0.598 V Vs SCE and Ni = -0.63 V Vs SCE respectively. When two of the three metal ions are present in a mixture (without SA and IDA) the waves are almost superimposed.

(I) Separation of Cu(II) and Cd System:

On polarographing a sample containing 2.0 mM Cu(II) and 1.0 mM Cd, the wave of Cu(II) precedes that of Cd. The plateau of Cu(II) wave is well defined and the measurement of polarographic data is possible. But as the concentration of either of the two ions is increased, the separation becomes poorer and waves are finally superimposed. The separation of the waves is possible by complexation with SA or IDA. Both the complexing agents are equally effective in bringing out the separation (Fig. 1 A,B). The waves are 0.15±0.02 V apart from each other. The \( E_{1/2} \) value for Cu(II) = -0.52 ±0.02 V Vs SCE and that of Cd = -0.67 ± 0.02 V Vs SCE with both the ligands under study. Other polarographic data are summarized in Table 1.

The log plot slope values are in agreement with irreversible nature of Cu(II) wave and reversible nature of Cd, even in presence of each other. The separation is possible even if the concentration of either of the ions
Fig. 1. Polarograms of (A) 1 mM Cu(II) + 1 mM Cd(II) in 1 M HCl + 0.1 M NaOH, (B) 1 mM Cu(II) + 1 mM Cd(II) in 0.05 M HCl, (C) 1 mM Cu(II) + 1 mM Pb(II) in 0.1 M NaOH, and (D) 1 mM Cu(II) + 2 mM Ni(II) in 1 M NH₄CN, using SA.
<table>
<thead>
<tr>
<th>Concentration (Cu(II) and Cd(II)) in mM</th>
<th>Polarographic data for Cu (II)</th>
<th>Polarographic data for Cd (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_1/2 (V vs SCE)</td>
<td>i_d (mA)</td>
</tr>
<tr>
<td>1  S.A.</td>
<td>0.50</td>
<td>4.0</td>
</tr>
<tr>
<td>2  1</td>
<td>0.503</td>
<td>7.2</td>
</tr>
<tr>
<td>3  1</td>
<td>0.50</td>
<td>12.8</td>
</tr>
<tr>
<td>4  1</td>
<td>0.504</td>
<td>15.2</td>
</tr>
<tr>
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<td>IDA  Poor Separation</td>
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<td>1  10</td>
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</tr>
<tr>
<td>Concentration</td>
<td>Ligand</td>
<td>Polarographic Data for Cu(II)</td>
</tr>
<tr>
<td>---------------</td>
<td>--------</td>
<td>-------------------------------</td>
</tr>
<tr>
<td>Cu(II) Ni(II) in mM</td>
<td></td>
<td>-$E_{1/2}$ (V)</td>
</tr>
<tr>
<td>2  1</td>
<td>Without</td>
<td>0.50</td>
</tr>
<tr>
<td>3  1</td>
<td>ligand</td>
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</tr>
<tr>
<td>4  1</td>
<td></td>
<td>0.518</td>
</tr>
<tr>
<td>4  2</td>
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<td>4  3</td>
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<tr>
<td>4  4</td>
<td></td>
<td>0.50</td>
</tr>
</tbody>
</table>

1. 1 S.A. | | 0.51 | 5.6 | 5.6 | 2.621 | 85 | 0.67 | 6.8 | 6.8 | 3.183 | 80 |
2  1       | | 0.50 | 7.8 | 3.9 | 1.825 | 78 | 0.67 | 6.5 | 6.5 | 3.089 | 82 |
3  1       | | 0.50 | 12.0 | 6.3 | 3.043 | 78 | 0.69 | 8.4 | 8.4 | 3.932 | 90 |
4  1       | | 0.50 | 15.6 | 3.9 | 1.825 | 65 | 0.682 | 9.8 | 9.8 | 4.588 | 81 |
4  2       | | 0.51 | 6.2 | 6.2 | 2.90 | 80 | 0.685 | 11.6 | 5.8 | 2.715 | 85 |
4  3       | | 0.50 | 4.0 | 4.0 | 2.247 | 80 | 0.68 | 19.6 | 6.6 | 3.089 | 80 |
4  4       | | 0.51 | 3.0 | 3.0 | 2.34 | 85 | 0.68 | 24.4 | 6.1 | 2.855 | 80 |
4  5       | Poor Separation | 0.906 | 28.0 | 2.80 | 1.348 | 80 | 0.71 | 9.6 | 9.6 | 4.494 | 80 |

Note: With TDA Separation is possible in only equimolar amount of the metal ions, on further increase of either of the ions causes super-

is ten to thirty fold with SA. With IDA, the separation is possible up to 20 fold concentration of Cu(II) to that of Cd.

(ii) Separation of Cu(II)-Ni System:

Korshunov and Kirillova [4] worked on the polarographic analysis of Cu(II) and Ni(II) in fats in 0.2M ammonium chloride without any added ligand. In the present study, separation of Cu(II) and Ni waves has been observed (the waves are 0.1 ± 0.02 V apart), but on increasing the concentration of either of the ions, the two waves become superimposed. The use of SA or IDA as complexing agent facilitates the separation of these two waves. Though the separation with IDA is not perfect, SA is quite effective, even if the concentration of either of the two ions is ten to twenty-five fold that of the other ion. The waves are 0.20 ± 0.02 V apart from each other with IDA. The half wave potential of Cu(II) = -0.52 ± 0.05 V vs SCE and that of Ni = -0.69 ± 0.01 V vs SCE in this system (Fig. 1C).

The other polarographic data are listed in Table 2. The preparation of the polarographic waves of Cd(II) and Ni(II) in the presence of both ligands is not effective.

The separation of polarographic waves in the cases discussed above may be presumed to be due to the differences in the stability constants of the complexes of the metal ions under study. Severally the greater the stability constant of the complex the more negative is its half wave potential value /5/.

ACKNOWLEDGEMENTS:

The authors thank Prof. A.V. Mahajani, Head, Department of Chemistry, University of Sagar, Sagar for facilities. Thanks are also due to U.G.C., New-Delhi and the Government of M.P. for the award of a Teacher-Fellowship to one of us (VEC).
REFERENCES

Canadian Journal of Chemistry

21 January 1983

Dr. V.K. Chitale
Teachn. Fellow
Department of Chemistry
University of Sagar
Sagar (M.P.) India
470 003

Dear Dr. Chitale:

Thank you for the revised version of your manuscript "ININARY COMPLEXES OF Pb (II) WITH ITAONIC ACID AND NICOTINIC ACID: A POLAROGRAPHIC STUDY" which was received 20 January 1983.

Your figure 1 in this manuscript is not acceptable as it was submitted. Please resubmit this drawing, following the instructions as set out in the enclosed pamphlet, and return it, with two photocopies, as soon as possible so that we may submit it for publication.

I apologize for not noticing this error earlier.

Yours sincerely,

W.R. Fawcett,
Editor

W. R. / Fawcett

P.S. The same applies to the diagram on our control No. C83-5-F submitted to us for review.

Dr. W.R. Fawcett
Editor
Department of Chemistry
University of Guelph
Guelph, Ontario, Canada
N1G 2W1
Ref: ECSI /82/E-

Date: 24.8.1982

Dr. V.K. Chitale
Department of Chemistry
University of Sagar
SAGAR (M.P.) - 470 003.

Dear Sir,

Sub: paper entitled "Electrochemical behaviour of the mixed complexes of Pb(II) with citraconic acid and nicotinic acid: A polarographic study" by V.K. Chitale and C.S. Patre.

********

You had sent the above paper to us to be presented in the ATM-1982, which went off last week of ultimo. But the same was not presented by anyone of the authors at that occasion. We intend to publish it in our Journal in normal course. Kindly intimate your willingness or otherwise. If so, kindly send us one more copy of the paper and also intimate your requirement of reprints at an early date.

Thanking you,

Yours faithfully,

EDITOR.
Dear Sir/Madam,

I am to inform you that your Paper(s) No. __________________________ has/have been finally accepted for publication in the Journal of the Indian Chemical Society as an Article/Note.

Yours truly,

Executive Editor.