

## Electrochemical Studies of Bismuth(III) Complexes by Polarographic Technique

SANTOSH KUMAR and O.D. GUPTA\*

Department of Chemistry, University of Rajasthan, Jaipur-320 055, India

\*Corresponding author: E-mail: gupta\_od@yahoo.com; skv\_06@yahoo.com

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Polarographic studies of Bi(III) complexes with L-tyrosine, citrulline, citraconic acid and hippuric acid have been studied at two different temperatures using potassium nitrate as supporting electrolyte in aqueous medium. In all the systems, Bi(III) reduced quasireversibly with the involvement of three electrons. The overall formation constants were determined by DeFord and Hume's method. There was no change in the numbers of species formed by increasing the temperature from 300-308 K but the stability constants of complex species decreased with the rise in temperature. It was found that stability constants of Bi(III)-L-tyrosinate system was highest in comparison to other systems.

**Key Words:** Bismuth(III)-L-tyrosine, Citrulline, Citraconic acid, Hippuric acid, Supporting electrolyte.

### INTRODUCTION

In polarography, many workers have reported the electrochemical studies of the metal complexes with some biocarbocyclic acids<sup>1-7</sup>.

Spirevska and Rekalic<sup>8</sup> have studied the polarographic behaviour of some unsaturated bicarboxylic acids. Polarographic behaviour of divalent metal ions, with many ligands have also been studied polarographically<sup>9-16</sup> in aqueous medium. Bi(III) reduced quasireversibly and hence for each solution  $E_{r1/2}$  values were obtained by Gelling method. The present paper deals with the polarographic studies of complexes of Bi(III) with L-tyrosine, citrulline, hippuric acid and citraconic acid at 300 and 308 K in aqueous medium.

### EXPERIMENTAL

The reagents used were of A.R. grade purity and all the solutions, were prepared in double distilled water. The temperature was kept constant by using Haake-Type ultrathermostat. Potassium nitrate was used as supporting electrolyte in all the investigations, to maintain ionic strength constant. Triton X-100 was used as maxima suppressor. The capillary had the following characteristic  $m = 2.38$  mg/s and  $t = 4.55$  s (in open circuit). The polarograms were recorded manually by plotting current reading of galvanometer against potential applied by the potentiometer in connection with 2 V capacity lead accumulator. All polarograms were recorded after deaeration of the test solution by passing nitrogen gas for 10-15 min.

### RESULTS AND DISCUSSION

The complexation between metal ion Bi(III) and ligands was evidenced by the increasing cathodic shift in half-wave potential and decreasing diffusion current, observed as the increasing amount of ligand was added to the solution containing Bi(III) and sufficient amount of  $KNO_3$  to keep the constant ionic strength of the solution.

Gellings method was applied to evaluate the reversible half-wave potential ( $E'_{1/2}$ ) because the slope of 'log plots' indicated the quasireversible nature of reduction. DeFord and Hume's method was used to determine the stability constants. The  $F_0[(X)]$  function values when plotted against  $C_x$ , a smooth curve passing almost through the origin was observed. However  $F_2[(X)]$  values plotting against  $C_x$  gave a straight line but having slope which indicated the formation of penultimate complex. The plot between  $F_3[(X)]$  and  $C_x$  gave a straight line parallel to  $C_x$  axis. This suggests the formation of highest stoichiometric complex species. The various stability constants values at two different temperature have been recorded in Table-1 and represented graphically in Figs. 1-4. The mathematical method of Mihailov was also applied to verify the formation constants of complexes. Thermodynamic function have also been evaluated to study the effect of temperature on complexation reaction. The change in free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and change in entropy ( $\Delta S^\circ$ ) are summarized in Table-2.

It is shown that the Bi(III) forms three complexes each with L-tyrosine, citrulline, hippuric acid and citraconic acid.

**TABLE-1**  
**STABILITY CONSTANTS OF Bi(III) AT 300 AND 308 K**

|                 |                    | DeFord and Hume's |       | Mihailov's |       |
|-----------------|--------------------|-------------------|-------|------------|-------|
|                 |                    | 300 K             | 308 K | 300 K      | 308 K |
| Tyrosine        | log β <sub>1</sub> | 2.25              | 2.17  | 2.22       | 2.14  |
|                 | log β <sub>2</sub> | 3.89              | 3.64  | 4.18       | 4.01  |
|                 | log β <sub>3</sub> | 6.24              | 6.10  | 5.96       | 5.71  |
| Citrulline      | log β <sub>1</sub> | 2.00              | 1.96  | 1.96       | 1.93  |
|                 | log β <sub>2</sub> | 3.47              | 3.36  | 3.94       | 4.13  |
|                 | log β <sub>3</sub> | 6.12              | 5.97  | 5.75       | 6.33  |
| Citraconic acid | log β <sub>1</sub> | 1.97              | 1.92  | 1.95       | 1.90  |
|                 | log β <sub>2</sub> | 3.39              | 3.30  | 3.74       | 3.71  |
|                 | log β <sub>3</sub> | 5.83              | 5.80  | 5.36       | 5.34  |
| Hippuric acid   | log β <sub>1</sub> | 1.74              | 1.70  | 1.72       | 1.69  |
|                 | log β <sub>2</sub> | 3.11              | 3.05  | 3.37       | 3.29  |
|                 | log β <sub>3</sub> | 5.32              | 5.20  | 4.84       | 4.72  |

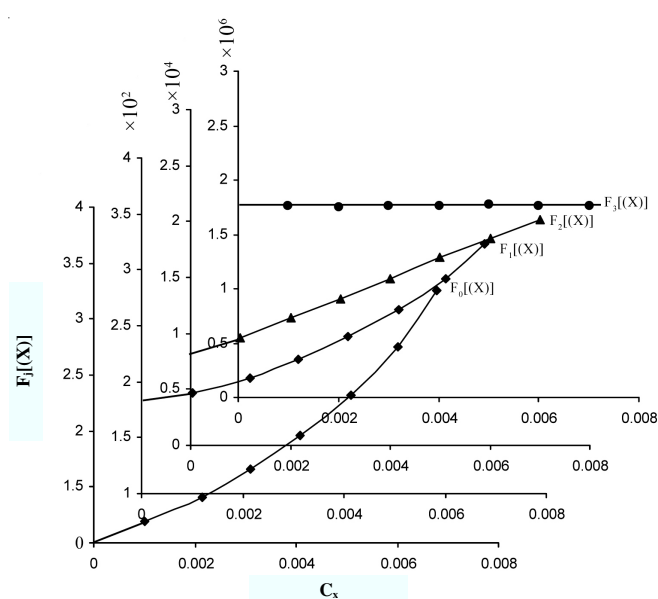


Fig. 1. Plots of  $F_j(X)$  versus  $C_x$  for bismuth(III)-tyrosinate system at 300 K in aqueous medium

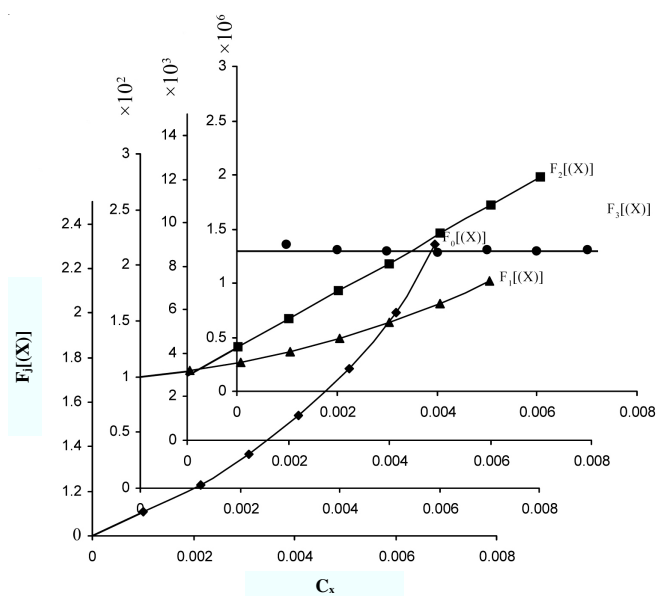


Fig. 2. Plots of  $F_j(X)$  versus  $C_x$  for bismuth(III)-citrulline system at 300 K in aqueous medium

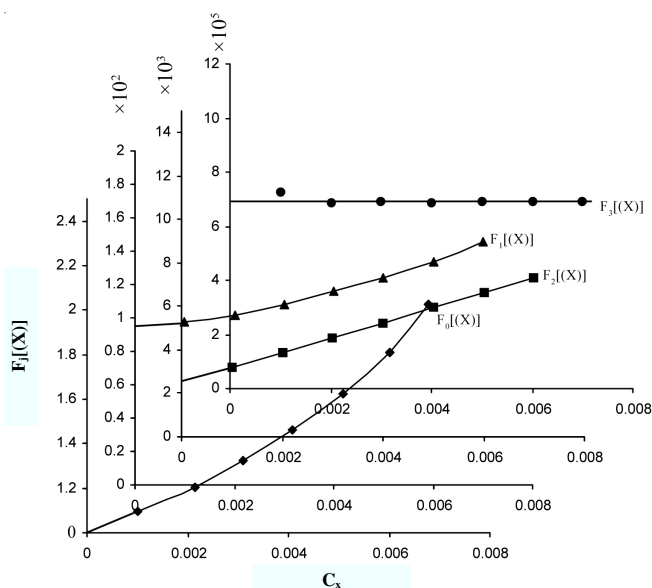


Fig. 3. Plots of  $F_j(X)$  versus  $C_x$  for bismuth(III)-citraconate system at 300 K in aqueous medium

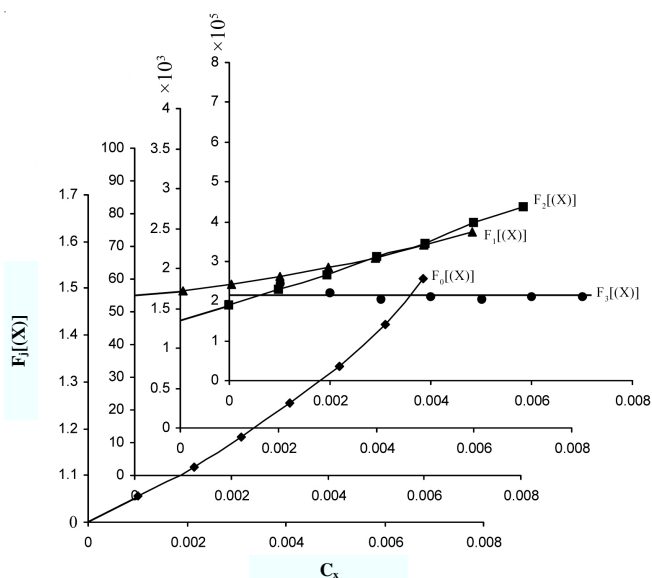


Fig. 4. Plot of  $F_j(X)$  versus  $C_x$  for bismuth(III)-hippurate system at 300 K in aqueous medium

**TABLE-2**

| Ligand          | Metal complex species | $\Delta G^\circ$ (-) (Kcal mol <sup>-1</sup> ) | $\Delta H^\circ$ (-) (Kcal mol <sup>-1</sup> ) | $\Delta S^\circ$ (-) (Cal mol <sup>-1</sup> deg <sup>-1</sup> ) |
|-----------------|-----------------------|--|--|---|
| Tyrosine        | 1:1                   | 12.968   | 18.042   | -0.0169   |
|                 | 1:2                   | 22.388   | 56.210   | -0.1127   |
|                 | 1:3                   | 35.889   | 32.642   | 0.0108  |
| Citrulline      | 1:1                   | 11.537   | 8.871  | 0.0088  |
|                 | 1:2                   | 19.931   | 24.355   | -0.0147   |
|                 | 1:3                   | 35.154   | 33.172   | 0.0066  |
| Citraconic acid | 1:1                   | 11.360   | 10.682   | 0.0022  |
|                 | 1:2                   | 19.518   | 21.431   | -0.0063   |
|                 | 1:3                   | 33.539   | 64.770   | 0.0902  |
| Hippuric acid   | 1:1                   | 9.996  | 9.153  | 0.0028  |
|                 | 1:2                   | 17.886   | 14.142   | 0.0124  |
|                 | 1:3                   | 30.571   | 27.325   | 0.0108  |

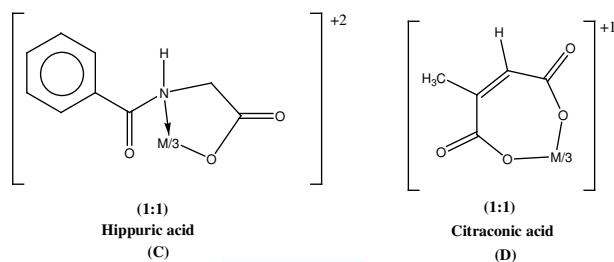
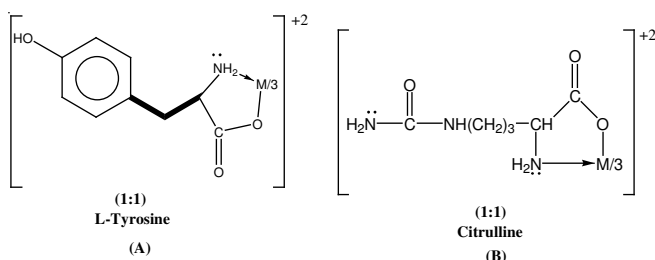
The highest complex species 1:3 of Bi(III) with all four ligands show six coordination number of Bi(III). The donation of electron pair will be from the oxygen atom of carboxylic group and nitrogen atom of amino group.

In case of L-tyrosine, there is nitrogen of amino group and oxygen of carboxylic group which take part in coordination with Bi(III) and form five membered chelate ring. In case of citrulline, chelation also occurs but the number of donor atoms are three nitrogen atoms and oxygen atom, due to which there is uncertainty of number of chelate rings and ring size. Due to this uncertainty, citrulline form weaker complex with metal in comparison to L-tyrosine. Hippuric acid also forms five membered chelate ring with metal as a bidentate ligand but the lone pair present on nitrogen atom are in resonance with oxygen atoms of carbonyl group. Due to this the availability of lone pair of nitrogen for coordination decreases.

In case of citraconic acid, there is the formation of seven-membered ring. For most stable complexes the chelated ring should be 5 or 6 membered. On decrease or increase of ring size of chelates, the stability decreases. So this ligand formed least stable complex with metal in comparison to other three ligands.

### Conclusion

It is concluded that the effect of chelation plays a great role in complexation and their stability. The probable structure of metal ligand complexes are shown below.



M = Bi(III)

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