*Oriental Journal of Chemistry* Vol. **25**(3), 523-528 (2009)

# Polarographic studies of As(III) and Sb(III) with Tyrosine

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(Received: April 27, 2009; Accepted: May 30, 2009)

## ABSTRACT

The reduction of As(III) and Sb(III) with tyrosine is investigated polarographically in aqueous medium. As(III) and Sb(III) both formed 1:1, 1:2 and 1:3 complex species. The stability constants of As(III) and Sb(III) with tyrosine were measured by the method of DeFord and Hume. The reduction of the system in each case is quasireversible and diffusion controlled, involving three electrons. The thermodynamic parameters have been determined. The stability constants of these species at 300K for As(III) are $\log\beta_1 = 2.96$, $\log\beta_2 = 5.14$, $\log\beta_3 = 7.82$ and at 310 K are $\log\beta_1 = 2.50$, $\log\beta_2 = 4.91$, $\log\beta_3 = 6.78$ and thermodynamic parameters free energy (Kcal $mol^{-1}$), enthalpy (Kcal $mol^{-1}$) and entropy (cal $mol^{-1}$ $deg^{-1}$) are -3.88, -35.94 and -0.10 ($MX_1$), -6.74, -40.65 and -0.11 ($MX_2$), -10.26, -36.89 and -0.08 ($MX_3$) respectively. The stability constants of these species at 300K for Sb(III) are $\log b_1 = 2.07$, $\log\beta_2 = 4.60$ $\log\beta_3 = 6.68$ and at 310 K are $\log\beta_1 = 2.20$, $\log\beta_2 = 4.32$, $\log\beta_3 = 6.63$ and thermodynamic parameters free energy (Kcal $mol^{-1}$), enthalpy (Kcal $mol^{-1}$) and entropy (cal $mol^{-1}$ $deg^{-1}$) are -2.71, -45.22 and -0.14 ($MX_1$), -6.04, -39.96 and -0.11 ($MX_2$), -8.77, -42.23 and -0.11 ($MX_3$), respectively. The Mathematical Mihailov's method has also been applied for the comparison of stability constants values obtained by graphical method.

**Key words:** Polarography, Dropping mercury electrode, Arsenic, Antimony, Tyrosine, Stability constant, DeFord and Hume's method, Mihailov's method, Thermodynamic parameters.

## INTRODUCTION

Polarography plays very important role in identification of metal ligand complexes. Many workers[1-3] have studied biologically active metal complexes of amino acids which are important in analytical, biochemical and pharmaceutical fields[4-6] and attract wide attention in different fields of research.

The recent work in our laboratory has opened many new areas in the study for biologically important ligands with different metals and their ability of complexation.

The complexation behaviour of ligand with different metals Cu(II),Zn(II),Ni(II) and Co(II) have been studied by many workers[7-14] but literature is quite silent about the studies of metal ligand complexes of As(III) and Sb(III) with tyrosine. Hence the present work has been undertaken for the study. The overall formation constants of the resulting complexes in aqueous medium which have been evaluated graphically by DeFord-Hume's method[15]. The overall formation constants of the complexes have also been calculated using mathematical method of Mihailov[16]. Thermodynamics of the complexes has been discussed.

## EXPERIMENTAL

A manual polarograph is used to record polarograms, using a saturated calomel electrode as the reference electrode. All the chemicals used were of analytical reagent grade. Tyrosine were used as complexing agents. Potassium nitrate was used as a supporting electrolyte to maintain the ionic strength at 0.1 M. The temperature was maintained constant at 300 ± 1 K and 310 ± 1 K. The capillary with the following characteristics m = 1.96 mg/s, t = 4.10 sec. per drop (in open circuit) and h = 40 cm, was used. Solution of As(III) and Sb(III) contains concentration of $5 \times 10^{-4}$ M. The experimental techniques were the same as described earlier. The various polarographic measurements and Fj[(X)] functions for As(III) and Sb(III) with tyrosine have been recorded at 300K and 310 K. The temperature was kept constant with the help of Haak type ultra thermostat. Purified nitrogen was used for deaeration.

## RESULTS AND DISCUSSION

In each case, a simple well defined reduction wave appeared. The diffusion current were found to decrease with increase of ligand concentration as a result of the complex formation. The complex ions formed are of much bulky size as compared to the aquo-metal ion, hence there is the low value of diffusion current with increase of ligand concentration.

The various polarographic measurments and Fj[(X)] function for As(III) and Sb(III) with tyrosine have been recorded at 300K and 310K in Table 1,3 and 5,7 respectively. Mihailov constants 'a' and 'A' were also evaluated for various combinations of different concentration respectively to determine the stability constants mathematically. The constants 'a' and 'A' values have recorded at 300K and 310K in Table 2, 4 and 6, 8 respectively together with their average values.

**Table 1: Polarographic characteristics and Fj[(X)] functions values for the As(III)-Tyrosine system**
**As(III) = 0.5mM, μ = 1.0 , $E^r_{1/2}$ of As(III) = - 0.2650 V vs SCE, Id = 52 div., Temp. = 300K**

| [tyr] | $\Lambda E^r_{1/2}$ | log $I_m/I_c$ | $F_0[(X)]$ | $F_1[(X)] \times 10^3$ | $F_2[(X)] \times 10^5$ | $F_3[(X)] \times 10^7$ |
|---|---|---|---|---|---|---|
| 0.001 | 0.0062 | 0.0017 | 2.1355 | 1.1355 | 2.0554 | 6.5542 |
| 0.002 | 0.0113 | 0.0258 | 3.9383 | 1.4691 | 2.6959 | 6.4797 |
| 0.003 | 0.0161 | 0.0258 | 6.8743 | 1.9581 | 3.4270 | 6.7569 |
| 0.004 | 0.0202 | 0.0347 | 11.2934 | 2.5733 | 4.1038 | 6.7709 |
| 0.005 | 0.0238 | 0.0439 | 17.5181 | 3.3029 | 4.7456 | 6.6918 |
| 0.006 | 0.0271 | 0.0532 | 26.2457 | 4.2076 | 5.6277 | 6.7712 |
| 0.007 | 0.0300 | 0.0627 | 37.5634 | 5.2233 | 6.1333 | 6.7619 |

log $\beta_1$ = 2.96 log $\beta_2$ = 5.14 log $\beta_3$ = 7.82; [tyr] = L-Tyrosine concentration in moles litre$^{-1}$

**Table 2: Mihailov Constant 'a' for various combinations of Tyrosine concentrations and 'A' at various Tyrosine concentrations at 300K for As(III)-Tyrosinate system in aqueous medium**

| Combinations of Tyrosine Concentrations (moles litre$^{-1}$) | 'a' | Concentrations of Tyrosine (moles litre$^{-1}$) | 'A' |
|---|---|---|---|
| 0.001<br>0.002 | 505.6249 | 0.001 | 1.2345 |
| 0.002<br>0.003 | 613.6079 | 0.002 | 1.1503 |
| 0.003<br>0.004 | 651.8979 | 0.003 | 1.1325 |
| 0.004<br>0.005 | 665.0311 | 0.004 | 1.1310 |
| 0.005<br>0.006 | 775.0331 | 0.005 | 1.1329 |
| 0.006<br>0.007 | 756.3782 | 0.006 | 1.1524 |
| 0.007<br>0.001 | 621.1060 | 0.007 | 1.1654 |

Average 'a' = 656.8113; Average 'A' = 1.1570

The values of overall formation constants log $b_j$ were calculated by graphical extraplotation method. The experimentally determined values calculated for As(III) and Sb(III) with tyrosine systems at 300 K and 310 K are given Table 9 and 10 respectively.

The results show that the As(III) form more stable complexes with tyrosine than Sb(III) with tyrosine at both temperatures.

The system have been investigated at two temperature *viz.* 300 K and 310 K, the Thermodynamic functions (DG°, DH° and DS°) have been calculated (given in Table 11) to understand. The temperature effect on the stability of the complexes.

The thermodynamic datas are obtained like b values i.e. b values increases, the DG° becomes more negative. The values of DG° become more negative when that of DS° becomes more positive. The more values of DS° will leads to a more negative value of DG° and hence a more stable complex is formed. The greater the amount of heat released in a reaction, the more stable are the

**Table 3: Polarographic characteristics and $F_j$[(X)] functions values for the As(III)-Tyrosine system**
**As(III) = 0.5mM, μ = 1.0, $E^r_{½}$ of As(III) = - 0.2622 V vs SCE, $I_d$ = 59 div., Temp. = 310K.**

| [tyr] | $\Lambda E^r_{½}$ | log Im/Ic | $F_0$[(X)] | $F_1[(X)] \times 10^2$ | $F_2[(X)] \times 10^4$ | $F_3[(X)] \times 10^6$ |
|---|---|---|---|---|---|---|
| 0.001 | 0.2651 | 0.0074 | 1.4088 | 4.0885 | 8.8856 | 5.8567 |
| 0.002 | 0.2680 | 0.0226 | 2.0209 | 5.1046 | 9.5230 | 6.1152 |
| 0.003 | 0.2703 | 0.0632 | 2.8730 | 6.2435 | 10.1452 | 6.1507 |
| 0.004 | 0.2731 | 0.0718 | 4.0133 | 7.5334 | 10.8337 | 6.3342 |
| 0.005 | 0.2755 | 0.0896 | 5.4738 | 8.9477 | 11.4955 | 6.3911 |
| 0.006 | 0.2778 | 0.0987 | 7.2380 | 10.3966 | 11.9944 | 6.1574 |
| 0.007 | 0.2797 | 0.1176 | 9.3578 | 11.9397 | 12.4853 | 5.9790 |

log $\beta_1$ = 2.50 log $\beta_2$ = 4.91 Log $\beta_3$ = 6.78; [tyr] = L-Tyrosine concentration in moles litre$^{-1}$

**Table 4: Mihailov constant 'a' for various combinations of Tyrosine concentrations and 'A' at various Tyrosine concentrations at 310K for As(III)-Tyrosinate system in aqueous medium**

| Combinations of Tyrosine Concentrations (moles litre$^{-1}$) | 'a' | Concentrations of Tyrosine (moles litre$^{-1}$) | 'A' |
|---|---|---|---|
| 0.001<br>0.002 | 433.0179 | 0.001 | 0.8922 |
| 0.002<br>0.003 | 403.3979 | 0.002 | 0.9172 |
| 0.003<br>0.004 | 392.5096 | 0.003 | 0.9279 |
| 0.004<br>0.005 | 375.6017 | 0.004 | 0.9333 |
| 0.005<br>0.006 | 335.0763 | 0.005 | 0.9326 |
| 0.006<br>0.007 | 320.2517 | 0.006 | 0.9203 |
| 0.007<br>0.001 | 384.884 | 0.007 | 0.9059 |

Average 'a' = 377.8198; Average 'A' = 0.9185

**Table 5: Polarographic characteristics and $F_j[(X)]$ functions values for the Sb(III)-Tyrosine system Sb(III) = 0.5mM, μ = 1.0 , $E^r_{1/2}$ of Sb(III) = - 0.3901 V vs SCE, Id = 74 div., Temp. = 300K.**

| [tyr] | $\Lambda E^r_{1/2}$ | log Im/Ic | $F_0[(X)]$ | $F_1[(X)] \times 10^2$ | $F_2[(X)] \times 10^4$ | $F_3[(X)] \times 10^6$ |
|---|---|---|---|---|---|---|
| 0.001 | 0.0012 | 0.0059 | 1.1651 | 1.6516 | 4.5163 | 5.1638 |
| 0.002 | 0.0029 | 0.0118 | 1.4389 | 2.1949 | 4.9746 | 4.8733 |
| 0.003 | 0.0047 | 0.0303 | 1.8503 | 2.8345 | 5.4485 | 4.8285 |
| 0.004 | 0.0070 | 0.0303 | 2.4164 | 3.5411 | 5.8527 | 4.6319 |
| 0.005 | 0.0091 | 0.0367 | 3.1286 | 4.2572 | 6.1145 | 4.2290 |
| 0.006 | 0.0114 | 0.0431 | 4.1476 | 5.2456 | 6.7409 | 4.5682 |
| 0.007 | 0.0134 | 0.0496 | 5.3092 | 6.1561 | 7.0801 | 4.4002 |

$\log \beta_1 = 2.07$ $\log \beta_2 = 4.60$ $\log \beta_3 = 6.68$; [tyr] = L-Tyrosine concentration in moles litre$^{-1}$

**Table 6: Mihailov constant 'a' for various combinations of Tyrosine concentrations and 'A' at various Tyrosine concentrations at 300K for Sb(III)-Tyrosinate system in aqueous medium**

| Combinations of Tyrosine Concentrations (moles litre$^{-1}$) | 'a' | Concentrations of Tyrosine (moles litre$^{-1}$) | 'A' |
|---|---|---|---|
| 0.001<br>0.002 | 562.1257 | 0.001 | 0.2590 |
| 0.002<br>0.003 | 531.8117 | 0.002 | 0.2675 |
| 0.003<br>0.004 | 486.9504 | 0.003 | 0.2715 |
| 0.004<br>0.005 | 411.8395 | 0.004 | 0.2708 |
| 0.005<br>0.006 | 565.2363 | 0.005 | 0.2641 |
| 0.006<br>0.007 | 402.8889 | 0.006 | 0.2681 |
| 0.007<br>0.001 | 502.6633 | 0.007 | 0.2629 |

Average 'a' = 494.7879; Average 'A' = 0.2663

**Table 7: Polarographic characteristics and $F_j[(X)]$ functions values for the Sb(III)-Tyrosine system. Sb(III) = 0.5mM, μ = 1.0 , $E^r_{1/2}$ of Sb(III) = - 0.3897 V vs SCE, $I_d$ = 85 div., Temp. = 310K.**

| [tyr] | $\Lambda E^r_{1/2}$ | log Im/Ic | $F_0[(X)]$ | $F_1[(X)] \times 10^2$ | $F_2[(X)] \times 10^4$ | $F_3[(X)] \times 10^6$ |
|---|---|---|---|---|---|---|
| 0.001 | 0.0013 | 0.0103 | 1.1850 | 1.8507 | 2.5073 | 4.0738 |
| 0.002 | 0.0028 | 0.0209 | 1.4371 | 2.1857 | 2.9285 | 4.1426 |
| 0.003 | 0.0047 | 0.0209 | 1.7789 | 2.5965 | 3.3218 | 4.0729 |
| 0.004 | 0.0066 | 0.0317 | 2.2578 | 3.1446 | 3.8615 | 4.4039 |
| 0.005 | 0.0086 | 0.0317 | 2.8264 | 3.6529 | 4.1058 | 4.0116 |
| 0.006 | 0.0106 | 0.0429 | 3.6301 | 4.3836 | 4.6393 | 4.2322 |
| 0.007 | 0.0127 | 0.0486 | 4.6561 | 5.2230 | 5.1758 | 4.3940 |

$\log \beta_1 = 2.20$ $\log \beta_2 = 4.32$ $\log \beta_3 = 6.63$; [tyr] = L-Tyrosine concentration in moles litre$^{-1}$

**Table 8: Mihailov constant 'a' for various combinations of Tyrosine concentrations and 'A' at various Tyrosine concentrations at 310K for Sb(III)- Tyrosinate system in aqueous medium**

| Combinations of Tyrosine Concentrations (moles litre$^{-1}$) | 'a' | Concentrations of Tyrosine (moles litre$^{-1}$) | 'A' |
|---|---|---|---|
| 0.001<br>0.002 | 323.1802 | 0.001 | 0.3993 |
| 0.002<br>0.003 | 340.0615 | 0.002 | 0.3877 |
| 0.003<br>0.004 | 402.0976 | 0.003 | 0.3803 |
| 0.004<br>0.005 | 314.9053 | 0.004 | 0.3834 |
| 0.005<br>0.006 | 447.3401 | 0.005 | 0.3743 |
| 0.006<br>0.007 | 471.9947 | 0.006 | 0.3811 |
| 0.007<br>0.001 | 369.6071 | 0.007 | 0.3888 |

Average 'a' = 381.3123; Average 'A' = 0.3850

**Table 9: Stability Constants of As(III)-tyrosine complex**

| Metal ion | Temp. | Log $\beta_j$ | DeFord and Hume | Mihailov |
|---|---|---|---|---|
| As(III) | 300K | Log $\beta_1$ | 2.96 | 2.88 |
| | | Log $\beta_2$ | 5.14 | 5.39 |
| | | Log $\beta_3$ | 7.82 | 7.73 |
| | 310K | Log $\beta_1$ | 2.50 | 2.54 |
| | | Log $\beta_2$ | 4.91 | 4.81 |
| | | Log $\beta_3$ | 6.78 | 6.91 |

**Table 10: Stability Constants of Sb(III)-tyrosine complex**

| Metal ion | Temp. | Log $\beta_j$ | DeFord and Hume | Mihailov |
|---|---|---|---|---|
| Sb(III) | 300K | Log $\beta_1$ | 2.07 | 2.11 |
| | | Log $\beta_2$ | 4.60 | 4.51 |
| | | Log $\beta_3$ | 6.68 | 6.73 |
| | 310K | Log $\beta_1$ | 2.20 | 2.16 |
| | | Log $\beta_2$ | 4.32 | 4.44 |
| | | Log $\beta_3$ | 6.63 | 6.55 |

**Table 11: Thermodynamic function of As(III) and Sb(III)–Tyrosine Complex system**

| Metal | Ligand | Complex species | ΔG° (–) (Kcal $mol^{-1}$) | ΔH° (–) (Kcal $mol^{-1}$) | ΔS° (–) (Cal $mol^{-1}deg^{-1}$) |
|---|---|---|---|---|---|
| As(III) | Tyrosine | $MX_1$ | 3.88 | 35.94 | 0.10 |
| | | $MX_2$ | 6.74 | 40.65 | 0.11 |
| | | $MX_3$ | 10.26 | 36.89 | 0.08 |
| Sb(III) | Tyrosine | $MX_1$ | 2.71 | 45.22 | 0.14 |
| | | $MX_2$ | 6.04 | 39.96 | 0.11 |
| | | $MX_3$ | 8.77 | 42.23 | 0.11 |

reaction products. The greater amount of disorder produced in the product during the reaction relative to the reactants, the greater the increase in entropy during the reaction and hence the greater the stability of products

## ACKNOWLEDGEMENTS

The authors are thankful to the Head, Department of Chemistry University of Rajasthan, Jaipur for providing necessary facilities and steady cooperation to carrying out the research work.

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