# ELECTROKINETIC STUDY OF $Sb^{3+}$ AND $Bi^{3+}$ IN DISODIUM TARTRATE-SODIUM HYDROXIDE MEDIUM USING POLAROGRAPHIC TECHNIQUE

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$Sb^{3+}$ and $Bi^{3+}$ in 0.25 M disodium tartrate + 0.1M Na OH (pH = 11.5) gave diffusion-controlled irreversible wave and the formal rate constants ($k^0_f$) were determined using Delahay, Koutecky-Weber, Koutecky Cizek and Oldham-Parry treatments. Appropriateness of Oldham Parry treatment over Koutecky-Cizek treatment is shown. Some parameters viz. $\eta$, D, $\alpha$, $E_{0.5}$, $\Delta H_p^*$, $\Delta H_r^*$, $\Delta G^*$, $\Delta S^*$ and r were determined and explained in view of $Sb^{3+}$ and $Bi^{3+}$ reduction. The solvation of reduced species is reported on the basis of effect of temperature on the value of r.

It is found [1-12] that most of the work done on either antimony or bismuth ions was concentrated in determining nature of the wave, diffusion current constant and half wave poteatial of both the ions in various supporting electrolytes, except those dealing with kinetic study [13-21] of the electrode process viz. heterogeneous rate constant of the electrode process and stability constant of the complex using various methods of determination, transfer coefficient ($\alpha$) and energy of activation.

In the present investigation an attempt is made to determine (i) the nature of the wave (ii) formal rate constants at SCE, and (iii) other thermodynamic functions of $Sb^{3+}$ and $Bi^{3+}$ reduction in presence of 0.25M sodium tartrate + 0.1M NaOH (pH = 11.5) as supporting electrolyte at different temperatures using various treatments viz. Delahay [22], Koutecky-Weber [23], Koutecky-Cizek [24] and Oldham-Parry [25], employed for average current, in order to decide appropriateness of any one method over the other and to show the validity of the derived formal rate constant for the system in study. Thermodynamic parameters viz. enthalpy of activation ($\Delta Hp^*$), free energy of activation ($\Delta G^*$), transfer coefficients ($\alpha$), diffusion coefficients (D) formal rate constants ($k^0_f$) and viscosity coefficients ($\eta$) are determined in order to throw some light on the size of the reduced species of $Sb^{3+}$ and $Bi^{3+}$.

## EXPERIMENTAL

Antimony trichloride, bismuth trichloride, disodium tartrate, sodium hydroxide and gelatin used in the work were of A. R. grade. All the polarographic solutions were prepared in doubly distilled air-free water. Temperature was maintained with an accuracy $\pm 0.2°C$, and the mercury required for the polarographic work was obtained by distilling the same in a slow current of air.

Polarographic solutions viz. (i) 1.44 mM $S^{3+}$ + $Na_2$ tartrate + 0.1M NaOH + 0.01% gelatin at PH = 11.5 and (ii) 1.52 mM of $Bi^{3+}$ + 0.25 M $Na_2$ tartrate + 0.1 M NaOH + 0.01% gelatin at PH = 11.5 kept, one after the other, in H-type cell was deaerated with oxygen-free nitrogen and the current-voltage measurements of each solution were made vs S.C.E. using Toshniwal polarograph type CLO 2A and Beltronix microammeter.

Average current ($\bar{i}$) vs applied voltage (E) of the solution were noted for different heights of mercury head (h) in order to decide the nature of the current. The measurements of the solution were also noted at the interval of 10°C in the temperature range of 30° to 50°C, keeping constant value of h, when capillary constant $m^{2/3} t_1^{1/6}$, had the value of 2.02 $mg.^{2/3} sec^{-1/2}$ for $Sb^{3+}$ and 2.0° for $Bi^{3+}$. Here $t_1$ is the average drop time.

The number of electrons involved in the electrode process of trivalent antimony was determined as three by comparing $\bar{i}_d$ under identical conditions with $Pb^{2+}$, for which the number of electrons involved in the electrode process is known. This is also verified with information available in the literature [26,27]. The number of electrons involved in the electrode process of trivalent bismuth was calculated by comparing $\bar{i}_d$ of the system consisting of $Bi^{3+}$ with the system consisting of $Sb^{3+}$ under identical conditions. The value of n was found as three. Viscosity coefficient of the solution was measured for each temperature. The rate constant ($k_f$) of each type of ion was calculated using Koutecky-Weber [23], Koutecky-Cizek [24], Delahay [22] and Oldham-Parry [25] treatments. The value of $k_f^\circ$ was found out in each treatment for each temperature from the plots of log $k_f$ vs E extrapolated to potential of S.C.E. The enthalpy of activation were calculated from the slope of the plots of log $k^\circ_f$ vs $T^{-1}$ and log D vs $T^{-1}$ respectively. The heat of activation at constant volume was determined using relation $\Delta Hp^* =$

$\Delta H_v^* + RT$. The activation free energy change $\Delta G^*$ was calculated using relation $k^\circ_f = \frac{kT}{h}(r_o) \exp\frac{\Delta G^*}{RT}$ where $r_o$ represents mean distance between two depolariser ions in the bulk solution and its value generally considered as $2 \times 10^{-8}$ cm. The activation entropy was calculated using relation $\Delta S^* = \frac{\Delta H_v^* - \Delta G^*}{T}$.

Transfer coefficients ($\alpha$) of $Sb^{3+}$ and $Bi^{3+}$ present in the system were also determined from traditional log plot, Oldham-Parry log plot and from slope values of log $k_f$ vs E for each temperature. The approximate radius of the reduced species was also calculated assuming Stokes-Einstein law is obeyed in this system.

## Results and Discussion

Plot of $\bar{i}_d$ vs $h^{1/2}$ is linear for both the ions. Further temperature coefficient of $\bar{i}_d$ expressed in per cent degree$^{-1}$ varied from 1.34 (40°C) to 1.22 (50°C) in case of $Sb^{3+}$ and from 1.09 (40°C) to 1.08 (50°C) in case of $Bi^{3+}$. The results suggest diffusion-controlled nature of the current[28,29]. The diffusion coefficients and their temperature coefficients expressed in $cm^2$/sec and per cent degree$^{-1}$ vary from $4.20 \times 10^{-6}$ to $7.78 \times 10^{-6}$ and 2.86 to 2.56 respectively in case of $Sb^{3+}$; and $2.77 \times 10^{-6}$ to $4.17 \times 10^{-6}$ and 2.30 to 2.26 respectively in case of $Bi^{3+}$.

For both the ions, polarograms were of drawn-out nature, having slope value of the linear log plot, larger than the value expected for reversible wave of three electron system. Further, the stepwise temperature coefficients of $E_{0.5}$ were found nearly 2 mV degree$^{-1}$. The values of $\alpha$ determined from traditional log plot vary from 0.207 (30°) to 0.233 (50°) in case of $Sb^{3+}$ and from 0.158 (30°) to 0.162 (50°) in case of $Bi^{3+}$ while from Oldham-Parry log plot the values of $\alpha$ are varying from 0.26 (30°) to 0.217 (50°) for $Sb^{3+}$ and 0.149 (30°) to 0.159 (50°C) for $Bi^{3+}$. All these results show the irreversible nature of the wave. Further, the results suggest that irreversibility decreases with temperature and comparatviely there is more irreversible nature in case of $Bi^{3+}$ than the $Sb^{3+}$. The values of $\alpha$ determined from log $k_f$ vs E, where $k_f$ is the forward rate constant determined in different treatments, are also in agreement with the conclusion made. The values of $k_f^\circ$ and the thermodynamic functions $\Delta H_p^*$, $\Delta H_v^*$, $\Delta G^*$, $\Delta S^*$, determined in different treatments for $Sb^{3+}$ and $Bi^{3+}$ are shown in Tables 1 and 2 respectively. The values of $\Delta HD^*$ are found 4.70 and 4.14 k cal./mole respectively for $Sb^{3+}$ and $Bi^{3+}$. The viscosity coefficients (c p) are 0.925 (30°) to 0.650 (50°) for $Sb^{3+}$ and 1.940 (30°) to 0.669 (50°) for $Bi^{3+}$. The values of r, calculated by assuming Stokes-Einstein law are 5.74Å (30°) to 5.36Å (50°) for $Sb^{3+}$ and 8.52Å (30°) to 8.47Å (50°C) for $Bi^{3+}$.

Table 1 Thermodynamic parameters of $Sb^{3+}$ reduction in various treatments : $[Sb^{3+}]$ : 1.44 mM : Supporting electrolyte : 0.25M $Na_2$ tartrate + 0.1M Na OH (pH = 11.5) ($k_f$ in cm/sec ; $\Delta H$ & $\Delta G$ in k cal/mole)

| Parameters | 30°C | 40°C | 50°C |
|---|---|---|---|
| **Koutecky-Weber** | | | |
| $k_f^\circ \times 10^{14}$ | 2.00 | 4.37 | 9.33 |
| $\Delta H_p^*$ | | 14.72 | |
| $\Delta H_v^*$ | 14.11 | 14.72 | 14.07 |
| $\Delta G^*$ | 26.24 | 26.64 | 27.02 |
| $\Delta S^*$ | -40.01 | -40.07 | -40.07 |
| **Koutecky - Cizek** | | | |
| $k_f^\circ \times 10^{14}$ | 1.74 | 3.75 | 7.94 |
| $\Delta H_p^*$ | ... | 15.10 | ... |
| $\Delta H_v^*$ | 14.49 | 14.47 | 14.45 |
| $\Delta G^*$ | 26.32 | 26.73 | 27.12 |
| $\Delta S^*$ | -39.04 | -39.16 | -39.21 |
| **P Delahay** | | | |
| $k_f^\circ \times 10^{14}$ | 1.59 | 3.39 | 7.24 |
| $\Delta H_p^*$ | ... | 14.90 | ... |
| $\Delta H_v^*$ | 14.29 | 14.27 | 14.25 |
| $\Delta G^*$ | 26.38 | 26.79 | 27.18 |
| $\Delta S^*$ | -39.88 | -40.00 | -40.02 |
| **Oldham-Parry** | | | |
| $k_f^\circ \times 10^{14}$ | 1.82 | 3.98 | 8.71 |
| $\Delta H_p^*$ | ... | 15.27 | ... |
| $\Delta H_v^*$ | 14.66 | 14.64 | 14.62 |
| $\Delta G^*$ | 26.10 | 26.69 | 27.06 |
| $\Delta S^*$ | -38.39 | -38.50 | -38.54 |

Table 2 Thermodynamic parameters of $Bi^{3+}$ reduction in various treatments : [$Bi^{3+}$] : 1.52 mM : Supporting electrolyte : 0.25M $Na_2$ tartrate + 0.1M Na OH (pH = 11.5) ($k_f$ in cm/sec ; $\Delta H$ & $\Delta G$ in k cal/mole)

| Parameters | 30°C | 40°C | 50°C |
|---|---|---|---|
| **Koutecky-Weber** | | | |
| $k_f^0 \times 10^{10}$ | 5.37 | 10.00 | 17.78 |
| $\Delta H_p^*$ | | 11.69 | ... |
| $\Delta H_v^*$ | 11.08 | 11.06 | 11.04 |
| $\Delta G^*$ | 20.06 | 20.35 | 20.65 |
| $\Delta S^*$ | -29.64 | -29.68 | -29.75 |
| **Koutecky-Cizek** | | | |
| $k_f^0 \times 10^{10}$ | 5.01 | 9.12 | 16.98 |
| $\Delta H_p^*$ | ... | 11.96 | ... |
| $\Delta H_v^*$ | 11.35 | 11.33 | 11.31 |
| $\Delta G^*$ | 20.10 | 20.41 | 20.68 |
| $\Delta S^*$ | -28.88 | -29.01 | -29.01 |
| **P-Delahay** | | | |
| $k_f^0 \times 10^{10}$ | 4.37 | 7.94 | 14.40 |
| $\Delta H_p^*$ | ... | 11.50 | ... |
| $\Delta H_v^*$ | 10.89 | 10.87 | 10.85 |
| $\Delta G^*$ | 20.18 | 20.50 | 20.79 |
| $\Delta S^*$ | -30.66 | -30.77 | -30.77 |
| **Oldham-Parry** | | | |
| $k_f^0 \times 10^{10}$ | 5.13 | 9.55 | 16.98 |
| $\Delta H_p^*$ | ... | 11.87 | ... |
| $\Delta H_v^*$ | 11.26 | 11.24 | 11.22 |
| $\Delta G^*$ | 20.09 | 20.38 | 20.68 |
| $\Delta S^*$ | -29.14 | -29.20 | -29.29 |

From tables 1 and 2 it is marked that the values of $k_f^0$ in each treatment increase with temperature suggesting thereby decrease in irreversibility. The values of $k_f^0$ determined by different treatments have shown the same order showing thereby validity of the results derived. Further, the values of $k_f^0$ determined by Koutecky-Cizek treatment are in good agreement with Oldham-Parry treatment, probably because of the reason that while placing suitable criteria for reversibility and total irreversibility Oldham and Parry might have considered curvature effect resulting from electrode spheric ty, as considered by Koutecky and Cizek in introducing correction factor and influence of double layer structure on electrode kinetics. However, the Oldham-Parry treatment is more preferable over Koutecky-Cizek treatment. Such observations are also marked with other supporting electrolytes employed in the electrokinetic study of $Sb^{3+}$ and $Bi^{3+}$[30]. The values of $k_f^0$ determined for $Sb^{3+}$ and $Bi^{3+}$ for the system studied at various temperatures have shown that $Bi^{3+}$ reduces easily than the $Sb^{3+}$. The values of thermodynamic functions, $\Delta H^*$ ($= \Delta H_p^*$ or $\Delta H_v^*$), $\Delta G^*$ and $\Delta S^*$, follow the same trend as that of $k_f^0$ in reference to easier reduction of $Bi^{3+}$ than that of $Sb^{3+}$. The positive value of $\Delta G^*$ for both the ions suggests difficult reduction of the species. The negative sign of $\Delta S^*$ obtained for both the ions suggests that the activated state has more rigid structure than the initial state. The values of r of $Sb^{3+}$ and $Bi^{3+}$ suggest that probable size of the reduced species of $Bi^{3+}$ is more compared with $Sb^{3+}$ which may be because of the difference in the nature and extent of solvation of the reduced species. The decrease in the value of r of each ion with temperature clearly suggests that the reduced species are solvated.

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