# Role of PtO on the Oxidation of Arsenic (III) at Pt RDE in 1M H$_2$SO$_4$ and 1M Na$_2$SO$_4$ through Linear Sweep Voltammetry Technique

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Linear Sweep Voltammetry (LSV) has been conducted using platinum (Pt) disc electrode to investigate the effect of PtO on the Arsenic (III) oxidation. The changes of As(III) oxidation peak currents and peak potential in 1M H$_2$SO$_4$ and 1M Na$_2$SO$_4$ solutions have been evaluated. Effects of As(III) concentration, scan rate, rotation speed of the electrode on the oxidation of As(III) have been studied extensively. Oxidation peak current values increases linearly with the concentration, scan rate and electrode rotation speed in both of the media and the dependence plot goes through the origin, except in the case of square root of angular velocity and ip$_a$ in the Na$_2$SO$_4$ solution. A sharp increase in the As(III) peak current values are found in 1M H$_2$SO$_4$ but not in 1M Na$_2$SO$_4$ medium because of the formation of PtO is higher than in sulphuric acid medium with in the potential range of interest. The PtO layer blocks the available surface area for the As (III) oxidation. Presence of the PtO layer, shifts the As(III) oxidation potential to less positive, suggesting the PtO layer some how facilitates the oxidation of As(III) reaction.

## 1. INTRODUCTION

Arsenic is one of the worst toxic element present in the water. It is the 20th most abundant element in the earth's crust, 14th in the sea water and 12th in the human body [1]. Arsenic has been identified as a public health hazardous because of its highly toxic in nature, even at low exposure

levels [2]. The arsenic contamination in natural water has been reported from several part of the world like Bangladesh, USA, Inida, Taiwan, China, Japan, Canada, Mexico, Hungary and Poland [3,4]. Exposure to arsenic can cause variety of health problems, including dermal changes and respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and carcinogenic effects (1). Bangladesh, in particular, has upto 50 million people at risk in what the WHO call the worlds worst mass human poisoning disaster [5-7].

The arsenic occurs in the environment in different oxidation states such as As(v), As(III), As(0) and As(-III) [8]. Among the different forms, As(III) is reported to be 25-60 times more toxic than As(v), and several hundred times as toxic as organic arsenicals [9, 10]. These fact impetuses the researchers to intensive and deep study on the arsenic properties and removal.

Various types of analytical methods are employed for the determination of arsenic including electroanalytical methods [11-14], atomic absorption spectroscopy [15], Inductively coupled plasma atomic emission spectroscopy [16, 17] and spectrophotometry techniques [18]. In the recent reviews and research papers a variety of electrochemical methods used for the detection of As(III) at different electrode such as gold, platinum, mercury and at modified electrodes [19-24].

As As(III) is the most dangerous elemental form of Arsenic, lot of studies mainly focused on the As(III) oxidation and reduction at different electrode surfaces. The electrochemical oxidation of arsenious acid ($As^{3+}$) has been reported to be electrochemically irreversible at Pt and Au electrodes in acidic or basic solutions[25-27]. However, there are controversy among the authors (researchers) regarding the role of the surface oxides on the Pt surface, whether it facilitate or inhibit the oxidation of As (III). Hence, the present study aims to bringing out the role of Pt electrode surface oxide on the arsenic oxidation, concentration, scan rate and the influence of the rotation speed of the working electrode on the As(III) oxidation. Linear Sweep Voltammetry technique have been used as a effective tool for the oxidation of As(III) at the Pt electrode in 1M $Na_2SO_4$ and 1M $H_2SO_4$ acid media.

## 2. EXPERIMENTAL

All the chemicals used in this study were analytical Reagent grade, unless otherwise mentioned. As(III) stock solution was prepared by dissolving appropriate amount of sodium arsenite in de-ionized water and neutralized by the addition of concentrated $H_2SO_4$. EG & G PAR Instrument, model 398 Electrochemical Impedance analyzer was used to carryout the LSV studies. A three cell electrode assembly: a coiled Pt wire was served as the counter and Teflon embedded Pt disc with an working area of $0.071cm^2$ and saturated calomel electrodes were used as the working and reference electrode respectively. 1M sulphuric acid and sodium sulphate solutions were prepared by using de-ionized water and 100 ml capacity electrochemical cell was used to conduct the LSV experiments.

The working electrode was cleaned before running the experiment with Alumina powder and washed thoroughly with water and consequently with de-ionized water. To study the effect of rotation of the Pt electrode on the oxidation of As (III), the rotation speed of the electrode was controlled by MSR rotator with a speed controller (Pine). Arsenic containing 100ml of 1M $H_2SO_4$ / $Na_2SO_4$ solution was taken in to a clean electrochemical cell and nitrogen gas was purged over a period of 15 minutes to

eliminate the dissolved oxygen present in the solution. After the purging time, the $N_2$ gas was allowed to flow over the electrolytic solution to prevent the re-entry of atmospheric oxygen.

## 3. RESULTS AND DISCUSSION

The electrochemical behaviour of As(III) in 1M $H_2SO_4$ and $Na_2SO_4$ solution was investigated at the Pt electrode through LSV technique. The effect of concentration of As(III) on the oxidation of $As^{3+}$ at the Pt electrode surface in both of the electrolyte was studied. The As(III) concentration range was varied from 200ppm to 500ppm with a step value of 100ppm for the sulphuric acid medium and for the sodium sulphate medium the range was 100ppm – 4,000ppm of As(III) levels. The effect of scan rate was varied from 50 to 500mV/Sec. and the rotation speed of the working electrode was varied from 200rpm to 1000rpm for both the sulphuric acid and sodium sulphate medium. The role of the PtO on the oxidation of As(III) was also investigated extensively.
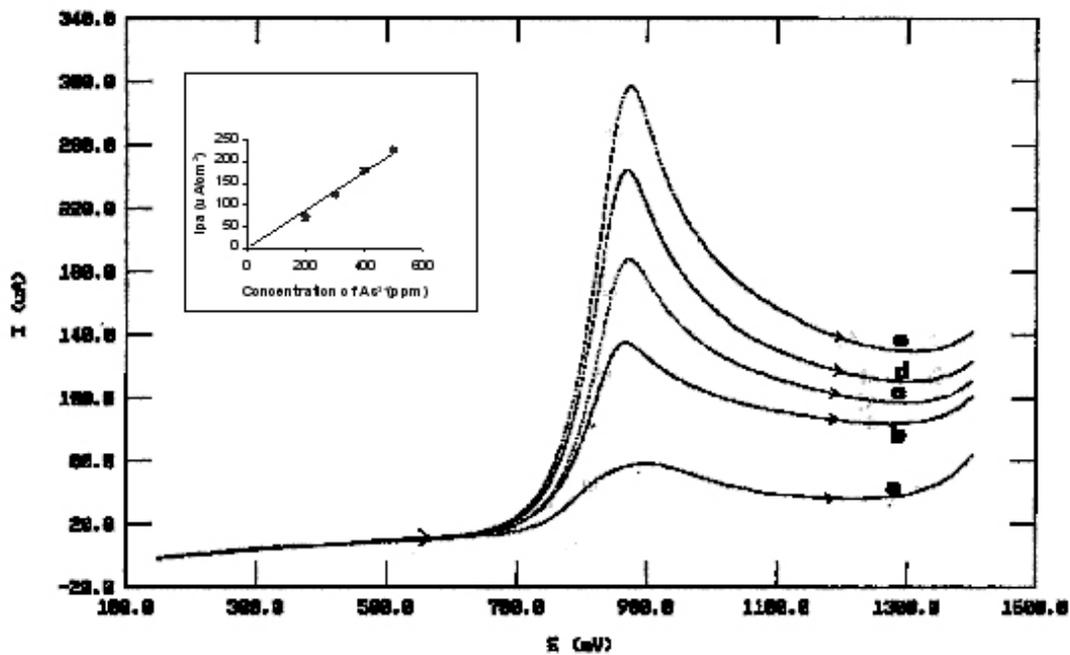


**Figure 1**: LSV spectra of $As^{3+}$ oxidation (Different concentration) in 1M $H_2SO_4$ at Pt electrode with a scan rate of 100mV/Sec. a)Blank, b) 200, c) 300, d) 400 and e) 500ppm of $[As^{3+}]$. Inset: Dependence plot between $ip_a$ and $[As^{3+}]$

Linear Sweep Voltammetry for the blank (without $As^{3+}$) in 1M $H_2SO_4$ was recorded to fix the usefull range of potential window and it was 150mV - 1400mV. One predominant peak was found at 893±7mV, this is due to the formation of PtO. There is a gradual increase in current with increasing potential, beyond 0.5V as a result of anodic discharge of $H_2O$ to form PtOH and PtO. The positive scan was terminated at 1.4V, because Ea >1.4V, tremendous increase in current was observed as a result of

evolution of $O_2$ [28]. The effect of concentration of $As^{3+}$ on the $As^{3+}$ oxidation peak current and potential was studied at different concentration levels (200-500ppm of $As^{3+}$) with 100mV/Sec.scan rate at Pt disc electrode. All the experiments were duplicated. The LSV spectra were taken for different concentration of As(III) and presented in Figure 1. The anodic peak current values are increasing with increase in concentration of As(III). The peak current (ipa) for 200ppm concentration is 137±2 micro Amps. but for the highest level of As(III) concentration 500ppm, the peak current is increased to 292±5 uA/cm$^2$. This tremendous increase in the current values are due to the oxidation of As(III) to As(v) but in the blank solution only 59 uA/cm$^2$. The $As^{3+}$ oxidation peak occurs at slightly less positive potential at lower potential 867±9mV when compared to the PtO formation at 893±7mV in the absence of arsenic. Oxidation potential of As(III) is independent of As(III) concentration. In the presence of As(III), some of the As(III) (As(OH)$_3$ is adsorbed at the oxide free Pt electrode surface with the result that the onset of oxide formation is suppressed at ~600mV [29]. And thus the onset of As(III) oxidation and oxide formation occur concurrently to produce a peak response at 867±9mV. Beyond the oxidation potential of As(III), there is a decline in anodic signal is undoubtedly on the consequence of the potential dependence of the kinetics for the formation of inert oxide (PtO). A plot of As(III) oxidation current Vs As(III) concentration was drawn and presented in inset Figure 1. The dependence plot gives straight line and goes through the origin. This indicates that the oxidation of As(III) to As(V) is takes place under diffusion control.
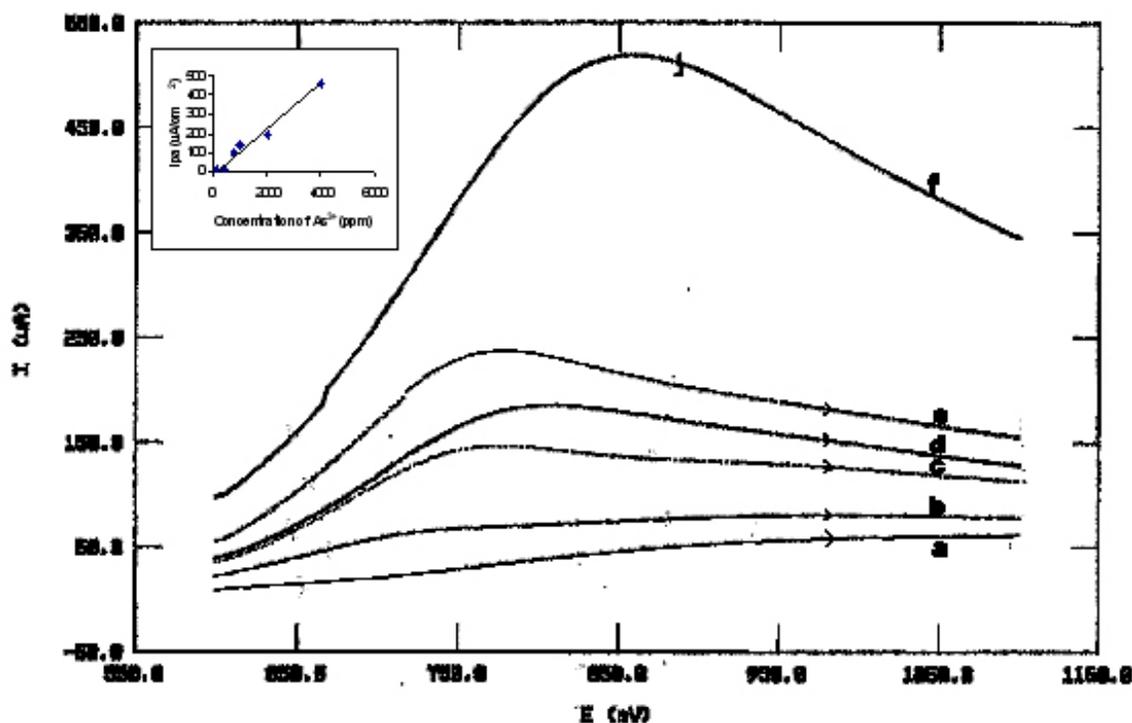


**Figure 2**: LSV spectra of As$^{3+}$ oxidation (Different concentration) in 1M Na$_2$SO$_4$ at Pt electrode with a scan rate of 100mV/Sec. a)100, b) 400, c) 800, d) 1000, e) 2000 and f) 4000ppm of [As$^{3+}$]. Inset: Dependence plot between ip$_a$ and [As$^{3+}$]

The oxidation of As(III) at the platinum electrode in 1M $Na_2SO_4$ medium at pH 7 with various concentration of As(III) was studied with 100mV/Sec. scan rate. Recorded LSV spectra are given in Figure 2. All the experiments were duplicated four times. The useful potential range for the Pt in 1M $Na_2SO_4$ solution at pH 7 is fixed as 600mV - 1000mV. Only one broad peak is appeared at around 990±5mV is due to the formation of PtO (not shown). In Figure 2, 2a is for the lower concentration of As(III) 100ppm, there is no new peaks appeared at 990±5mV except for PtO formation, and the peak current also in the same range (for blank 51±5), 55±5. At 400ppm As(III) concentration, a new peak is appeared at potential 730±38 and the current increased to 62±10uA/cm². Beyond 800ppm, the peak for PtO is diminished and only the broad peak for As(III) oxidation appeared at potential 828± 40mV. And the peak current values increased linearly with concentration to 518±7uA/cm² for the 4000ppm of $As^{3+}$. At the lower concentration of As(III), in $Na_2SO_4$ medium, the formation of PtO is dominant, hence the availability of active surface for the As(III) oxidation is lower. In 400ppm As(III), two peaks are appeared, clearly for As(III) oxidation at 730±38mV and 990±mV for the PtO formation. At lower concentrations of As(III), the formation of PtOH and PtO is higher at lower potential. These layer bringdown the As(III) oxidation to less potential when compared with the oxidation of As(III) at higher concentration. Here also, the arsenic oxidation takes place at less positive potential than the formation of PtO. Inset Figure 2 is for the dependence plot between the concentration of As(III) and peak current, shows that it is straight line and goes through the origin. It can be infer the oxidation of As(III) is under diffusion limit.
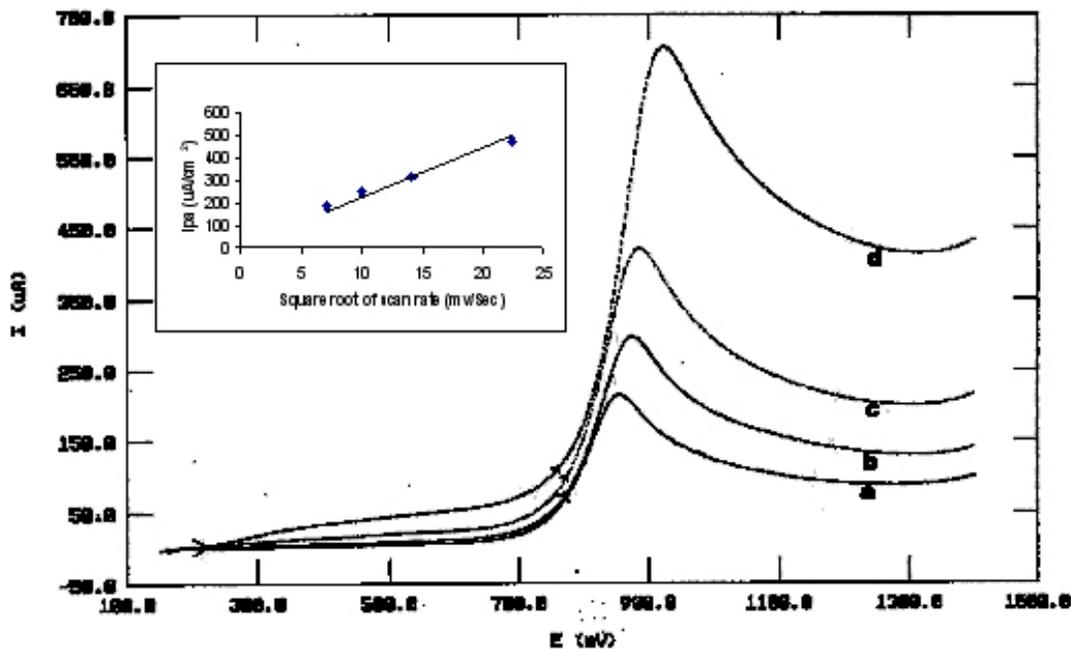


**Figure 3**: LSV spectra of $As^{3+}$ oxidation (500ppm) in 1M $H_2SO_4$ on Pt electrode at
        different scan rate. a) 50, b) 100, c) 200 and d) 500 mV/Sec. scan rates
        Inset: $ip_a$ Vs Square root of scan rates

The effect of scan rate on the oxidation of As(III) in 1M $H_2SO_4$ was investigated. The anodic LSV were recorded between 150mV and 1400mV at different scan rate (50 – 500mV) with

500ppm of As(III) at Pt disc electrode and presented in Figure 3. For all the scan rates, voltammogramms were taken in the blank acid for the correction purpose (not shown). The anodic peak values for the As$^{3+}$ oxidation, are corrected by the subtracting the corresponding blank current values. The current values for the As(III) oxidation increases linearly from 185±5uA/cm$^2$ to 473 ±27uA/cm$^2$ for 50mV/Sec. and 500mV/Sec. scan rates respectively. There is no typical change in the As(III) oxidation potential. But in the case of blank solution, the PtO formation potential shifts towards more positive potential to 1250±5mV/cm$^2$ for 500mV/Sec, scan rate. As can be seen from the Figure 3 inset, dependence plot between square root of the scan rate Vs peak current is straight line and goes through the origin, confirming this the oxidation of As(III) is diffusion limit.
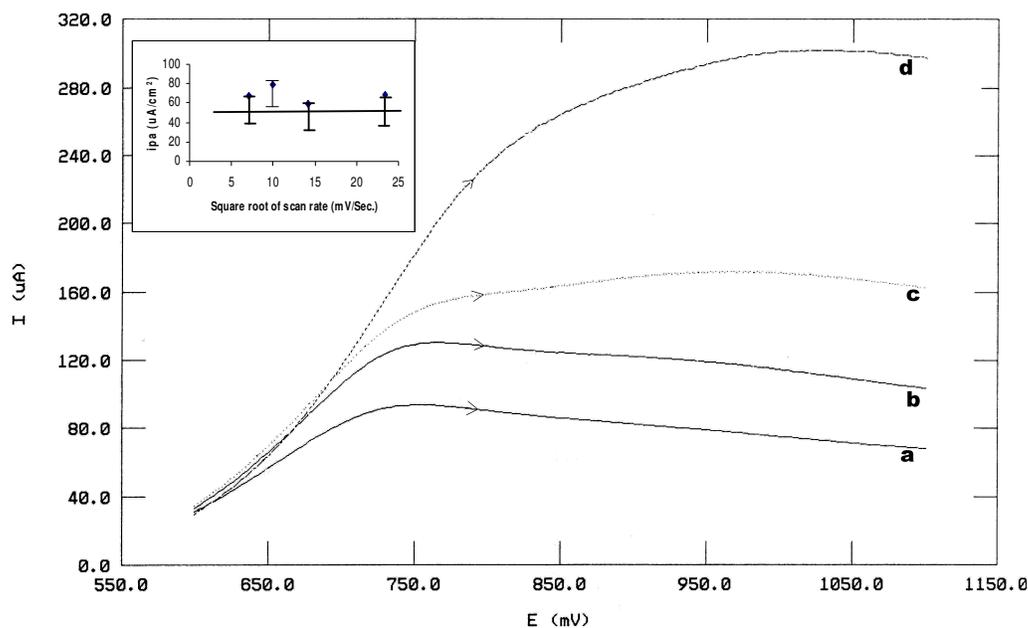


**Figure 4:** LSV spectra of As$^{3+}$ oxidation (800ppm) in 1M Na$_2$SO$_4$ on Pt electrode at
different scan rate. a) 50, b) 100, c) 200 and d) 500 mV/Sec. scan rates
Inset: ip$_a$ Vs Square root of scan rates

In 1M Na$_2$SO$_4$ medium, the As(III) concentration was maintained at 800ppm, oxidation was carried out on the Pt electrode at pH 7. The LSV spectra taken at different scan rate are presented in Figure 4. After correction, the peak current values of As$^{3+}$ oxidation with the respective scan rate of blank peak current, there is no increase in current values. The dependence plot between square root scan rate and peak current values was drawn and presented in figure 4 inset. Plot is not goes through the zero and it is horizontal line. This may be due to the unavailability of more adsorbed As(III) on Pt electrode or with the rapid positive potential scan formation of PtO on the electrode. The formed PtO surface is insulative in nature and thus the As(III) oxidation is prevented/ inhibited.

The effect of rotation speed of the working Pt electrode on the oxidation of As(III) was studied in 500ppm As(III) concentrated 1M H$_2$SO$_4$ at different rotation speed (200-1000rpm) with 100mV/Sec. scan rate. The potential window was maintained constantly as mentioned earlier. Figure 5

portray the result of effect of rotation speed, it show, the As(III) oxidation peak current increases with increasing the rotation speed of the working electrode. The anodic peak current values for the oxidation of As(III) were corrected for the background (recorded for blank) as noted before. The dependence plot between square root of the Angular velocity and peak current is straight line and goes through the origin (shown in Figure 5 inset). It confirms that the oxidation of As(III) reaction is under diffusion control. Further more, the As(III) oxidation potential independent of the rotation speed of the electrode. As observed before, the oxidation of As(III) take place at less positive potential than the PtO formation potential. The diffusion co-efficient values are calculated using Levich equation for 200rpm and 1000rpm is $22 \times 10^{-8}$ and $14 \times 10^{-8}$ respectively. And for the other rotation speed of the electrode, the diffusion co-efficient falls with in this range.
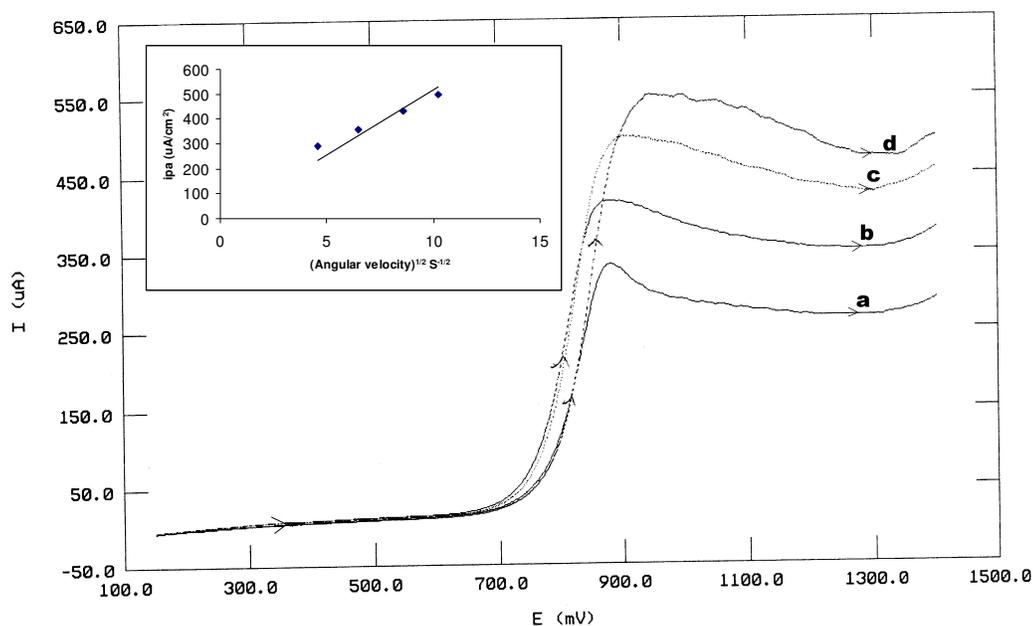


**Figure 5:** LSV spectra of $As^{3+}$ oxidation (500ppm of $As^{+}$) at Pt electrode with different rotation speed in 1M $H_2SO_4$ at 100mV/Sec. scan rate. a) 200, b) 400, c) 700 and d) 1000rpm of electrode. Inset: Relationship between $ip_a$ and (Angular velocity)$^{1/2}$S$^{-1/2}$

Effect of rotation speed of the Pt electrode on the As(III) oxidation was studied in 1M $Na_2SO_4$ solution with 800ppm of As(III) concentration at pH 7. LSV spectra were recorded both for the blank (for correction purpose) and for the presence of As(III). In both of these cases, there is not much changes in their electrochemical characteristics compared with the results of oxidation of As(III) in 1M $H_2SO_4$. Here also, the peak current values are increased linearly with increasing the rotation speed as shown in Table 1 and the plot between the square root of angular velocity and peak current values shows straight line and goes through the origin, given in Figure 6. The current values are increased linearly from $171 \pm 10uA/cm^2$ to $376 \pm 10uA/cm^2$ for 200rpm and 1000 rpm respectively. This reiterate the oxidation of As(III) at Pt electrode is under diffusion control. Diffusion co-efficient of As(III) is in the range of $5-4 \times 10^{-9}$ for all the rotation speeds of the interest.

**Table 1**.Effect of rotation speed of the working electrode (Pt) on the oxidation of the $As^{3+}$ in 1M $Na_2SO_4$ at 800ppm of $As^{3+}$ concentration

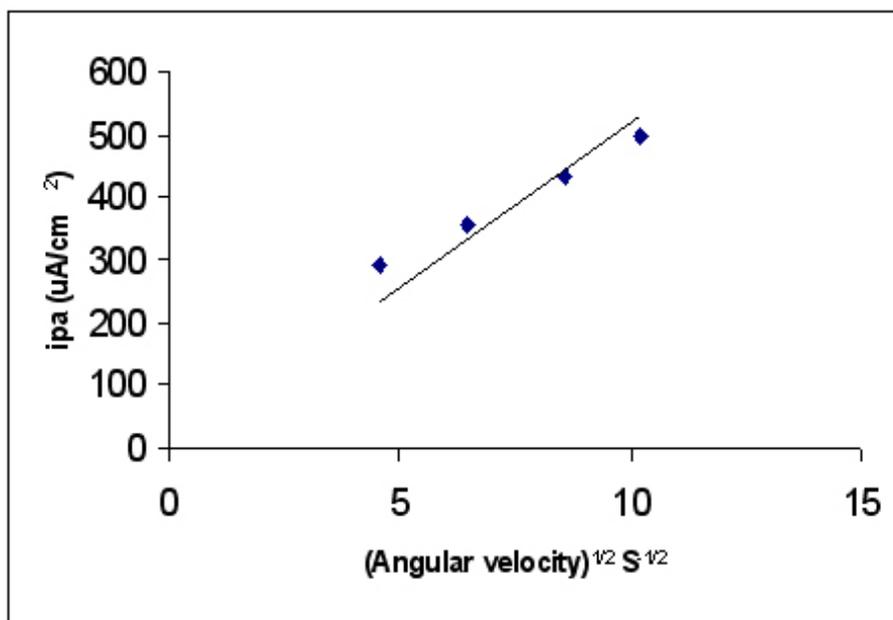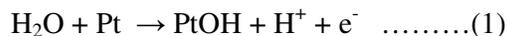| Sl.No. | Rotation speed | | (Blank) | Ipa | Corrected ipa | Epa |
|---|---|---|---|---|---|---|
| | (rpm) | ($\omega^{1/2}$) | Ipa ($\mu$A) | ($\mu$A) | for background ($\mu$A) * | (mV)* |
| 1 | 200 | 4.576 | 44 | 215 | 171± 10 | 758± 38 |
| 2 | 400 | 6.472 | 48 | 252 | 204± 10 | 906± 38 |
| 3 | 600 | 7.927 | 49 | 298 | 249± 10 | 904± 38 |
| 4 | 1000 | 10.233 | 54 | 430 | 376± 10 | 910± 38 |

* The presented error is estimated



**Figure 6:** Relationship between (Angular velocity) $^{1/2}$ S$^{-1/2}$ and ip$_a$ ( Values calculated for As$^{3+}$ (800ppm) in 1M Na$_2$SO$_4$ at Pt electrode with different rotation speed at 100mV/Sec. scan rate).

### 3.1 Effect of PtO formation on the Oxidation of As(III)

The effect of PtO on the oxidation of As(III) was investigated by the LSV technique in 1M $H_2SO_4$. As(III) concentration was maintained at 500ppm and LSV was recorded between the potential of 650mV and 1400mV. The electrode was kept at 1400mV for different period of time (0-15 minutes) before each experiment, the potential at which PtO formation takes place rapidly.  The onset of the O-

transfer at the Pt occurs at substantial over potential and concomitantly with the anodic discharge of water ($H_2O$) to generate hydroxide radical at the Pt electrode. The adsorbed hydroxide radical is the intermediate state of Oxygen in the process of PtO inactive oxide formation as follows:

$H_2O + Pt \rightarrow PtOH + H^+ + e^-$ ………(1)

$PtOH \rightarrow PtO + H^+ + e^-$ ……….(2)

Oxidation of As(III) is takes place through the transfer of Hydroxyl radical formed on the Pt surface as equation 3:

$As(OH)_3 + \rightarrow PtOH \rightarrow Pt + OAs(OH)_3 + H^+ + e^-$ ……… (3)
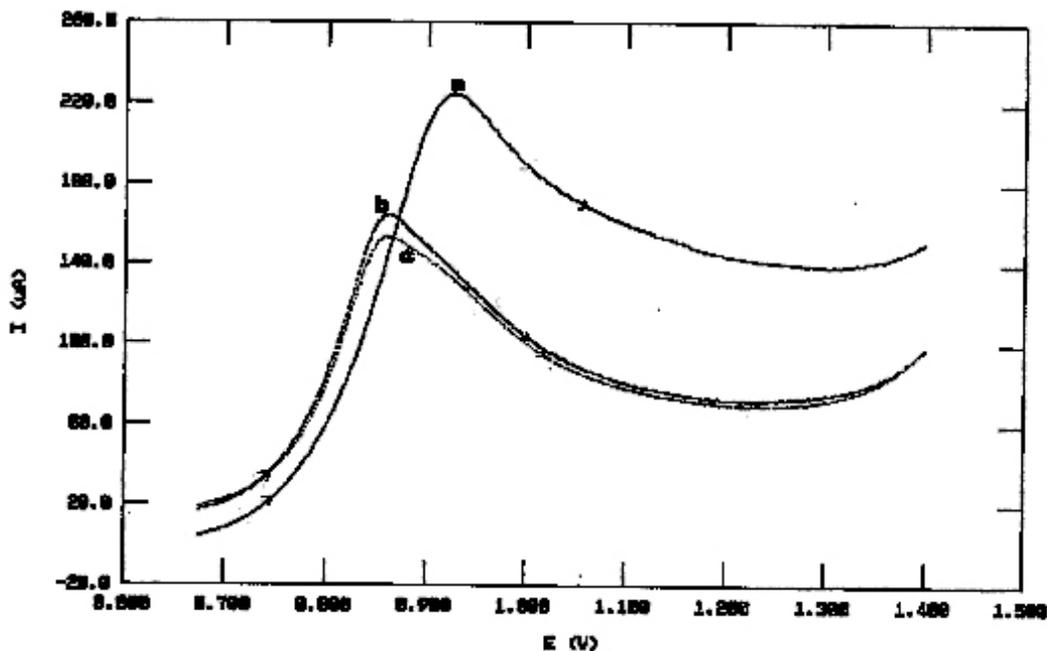


**Figure 7:** Effect of PtO formation on the oxidation of $As^{3+}$ (500ppm) in 1M $H_2SO_4$ for various length of holding time at 1.4V. a) 0, b) 5, and c) 15 Minutes

Figure 7 is for the LSV spectra taken for the effect of PtO on the oxidation of As(III), where the ipa values are decreased with increasing holding time at 1400mV potential. The As(III) oxidation peaks are decreased after the PtO film had been formed and the oxidation peak potential for As(III) is shifted towards the less positive potential. Most of the above changes occurred at the higher holding time, but at the lower shows less effect.

## 4. CONCLUSION

The electrochemical oxidation of As(III) at platinum electrode in 1M $H_2SO_4$ and 1M $Na_2SO_4$ is under diffusion control. Oxidation of As(III) in 1M $Na_2SO_4$ takes place less positive potential compared with in 1M $H_2SO_4$ medium. During the study of effect of scan rate, in Sulphuric acid medium, dependence plot goes through the origin but not in the case of $Na_2SO_4$ medium. This may be due to the formation of PtO on the electrode active surface is faster in 1M $Na_2SO_4$ medium at a

fraction of seconds before the diffusion of As(III) to the electrode surface. Presence of the oxide layer at the working electrode, shifts the oxidation potential of As(III) to less positive values, suggesting the PtO layer some how facilitates the oxidation of As(III). In the presence of oxide layer at the platinum electrode, the oxidation peak current values are decreased, which is probably due to the no-availability of enough active surface area of the electrode for the As(III) oxidation and the insulating nature of PtO do not have the Hydorxyl radical to participate in Arsenic oxidation much.

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