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Electrochemical Investigation of Pb-Se Interaction by Cyclic Voltammetry

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In this study, electrochemical behaviour of selenite was investigated in the presence of Pb(II) in acidic media, using cyclic voltammetry. In selenite solution, there are two cathodic peaks at - 0.54 and - 0.59 V and one anodic peak at - 0.52 V. When both selenite and Pb(II) are present in the same solution, three new peaks appeared at - 0.25, - 0.30 and - 0.82 V in cathodic scan and two new peak at - 0.12 and - 0.21 V in the anodic scan beside peaks of selenite and Pb(II). These anodic peaks were attributed to the oxidation of lead in Hg(SePb) and $SePb_{(on\ HgSe)}$ to Pb(II) and elemental mercury to Hg(II). The peaks at - 0.25 and - 0.30 V were attributed to the reduction of Pb(II) on the HgSe and the reduction of Pb(II) on the $Se_{(on\ HgSe)}$, respectively. The peak which appeared after the reduction peak of selenite at - 0.82 V was taken as the decomposition of Hg(SePb) and $SePb_{(on\ HgSe)}$ films to H_2Se.

Key Words: Electrochemical behaviour, Selenite, Lead(II), Cyclic voltammetry, Mercury electrode.

INTRODUCTION

The trace amount of selenium is an essential nutrient of fundamental importance to human biology. This has become increasingly obvious, as new research has shown a hitherto unsuspected role for this element in areas import to human health[1]. US Recommended daily allowance of selenium is 55-70 μg. Selenium is a rare element both in metabolism and the earth's crust with a natural abundance of 7×10^{-5} by mass[2]. The important properties of selenium are widely studied and in every study a new unique property is discovered. Naturally the determination of such an important element organic or inorganic media has become increasingly important.

Selenium analysis can be performed wide range of analytical methods, such as atomic absorption spectroscopy, normal polarography, differential pulse polarography and differential pulse stripping voltammetry depending upon the chemical and physical properties of the sample[3-9].

In real life samples there are number of other ions present with Se such as trace earth elements (*i.e.*, Cd, Sn, Pb, Zn, Te, Ni, Sb and as). The cationic forms of these elements interact with Se in electrochemical procedures[8-14]. In some studies, it was reported that, Pb^{2+}, Cd^{2+}, Sn^{2+}, Cu^{2+} were reduced either early or latter potentials than expected depending on the ions present at the surface of selenium[12-20]. However there were no mention of the formation mechanisms of these pre and post peaks and their possible role for the determination of selenite and Pb(II).

In this study, electrochemical behaviour of selenite was investigated in the presence of Pb(II) in acidic media, using cyclic voltammetry.

EXPERIMENTAL

Cyclic voltammetric experiments were carried out with CHI 660B electrochemical workstation (CH instrument from USA) equipped with a BAS CGME electrode system. The working electrode employed was a hanging mercury electrode. The reference and counter electrodes were Ag/AgCl/$KCl_{sat.}$, (BAS MF-2052) and a platinum wire (BAS MW-1032). All the voltammograms were recorded at a scan rate of 250 mV/s. The potential range was between 0.0 to -1.0 V. An ORION 720A pH meter was used for pH measurements.

All reagents used were of analytical reagent-grade. Human power I^+ Scholar water purification system with water quality of 18.3 mΩ cm was used throughout the experiments. 0.1 M stock standard solutions of the related ions were prepared from SeO_2 (BDH) and $Pb(NO_3)_2$ (Merck). All the solutions used were prepared daily at 10^{-3}-10^{-5} M concentrations. Dissolved oxygen in the solution was purged with high purity argon (99.999 %) for at least 5 min prior to the experiments.

The cyclic voltammograms of SeO_3^{2-} and Pb^{2+} solutions were acquired in 0.01 M HNO_3 medium. Then Pb^{2+} was added on SeO_3^{2-} and the changes in SeO_3^{2-} peaks were investigated. This was followed by the addition SeO_3^{2-} into Pb^{2+} and the changes on Pb^{2+} peaks were examined. The cyclic voltammetric peaks were characterized with changing the reversal potential at different scan rates.

Determination of experimental conditions: All the cyclic voltammetric (CV) studies were repeated for different concentrations of Pb^{2+} and SeO_3^{2-}, at different pH values and scan rates. In order to elucidate the effect of the acidity of the medium, cyclic voltammetric experiments were carried out at different pH values. The pre and post peaks observed in the acidic media were disapp-eared in the alkaline media. However in the solutions of pH less than 1, the deterioration of the CV peaks were observed, probably due to the dissolution of mercury and other surface effects. Therefore the pH value of the medium was taken as 2 throughout the study. Since, the scan rate is an important parameter in CV experiments and the peaks are much more interpretable, it was kept between 150 and 500 mV/s and used mostly as 250 mV/s. In the studies with different Pb^{2+} and SeO_3^{2-} concentrations pre and post peak were observed. Therefore the Pb^{2+} and SeO_3^{2-} concentrations were selected at random.

RESULTS AND DISCUSSION

Electrochemistry of selenite in acidic media: The cyclic voltammograms of SeO_3^{2-} in acidic media between 0.0 and - 0.2 V at the mercury electrode revealed that selenite is irreversibly reduced to elementary selenium with a broad peak giving a HgSe amalgam film and some free selenium at the HgSe film surface, as can be given with the following surface equation[14,21-24,26] (Fig. 1):

$$SeO_3^{2-} + 6H^+ + 4e^- + Hg \longrightarrow HgSe + 3H_2O \qquad (1a)$$

$$SeO_3^{2-} + 6H^+ + 4e^- \longrightarrow Se^0_{(on\ HgSe)} + 3H_2O \qquad (1b)$$

The formation of HgSe on the surface mercury drop has been verified with chemical analysis using macro electrodes as reported in the literature[21-25].

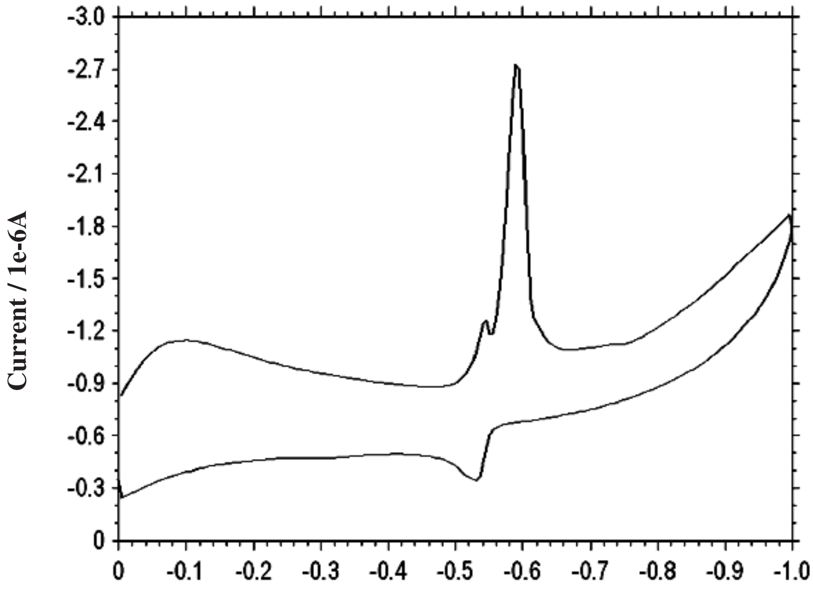

Fig. 1. Cyclic voltammogram 2.50×10^{-7} mol SeO_3^{2-} in 10 mL pH = 2.0 HNO_3 on Hg electrode *vs.* $Ag/AgCl/KCl_{sat}$ scan rate was 250 mV/s

When the potential scan is continued in the negative direction, Se in the HgSe amalgam on the mercury drop is stripped from the surface at - 0.59 V giving H_2Se[14,23,27] as shown in Fig. 1, according to the following reaction:

$$HgSe + 2H^+ + 2e^- \rightleftharpoons H_2Se + Hg \qquad (2)$$

H_2Se thus formed is reoxidized at - 0.52 V to give HgSe again in the reverse scan in accordance with the following reaction[14,28].

$$H_2Se + Hg \rightleftharpoons HgSe + 2H^+ + 2e^- \qquad (3)$$

A small peak at - 0.54 V is assigned to the reduction of elemental selenium deposited at the HgSe film in accordance with eqn. 1b[25-27]. Reduction of elemental selenium on HgSe, that is $Se^0_{(on\ HgSe)}$, to H_2Se can be written as follows:

$$Se^0_{(on\ HgSe)} + 2H^+ + 2e^- \rightleftharpoons H_2Se \qquad (4)$$

The cumulative results of the above mentioned processes at the mercury electrode is the formation of partial coverage of Hg with the HgSe and $Se^0_{(on\ HgSe)}$, films alongside the uncovered Hg surface.

Electrochemical behavior with the addition of lead(II) into selenite solution: When 1.0×10^{-7} mol Pb(II) was added to 2.5×10^{-7} mol selenite at pH = 2.0 (HNO_3) there appeared three cathodic peaks at - 0.25, - 0.30 and - 0.82 V and two anodic peaks at - 0.12 and - 0.21 V in addition to the peaks of Pb(II) and selenite. The addition of Pb(II) resulted in the disappearance of the small cathodic peak of selenite at - 0.54 V and the anodic peak at - 0.52 V, while the cathodic peak at - 0.59 V decreased substantially. When the additions of Pb(II) were continued, the cathodic peak of the selenite at - 0.59 V was observed to decrease and disappeared completely with the further addition of Pb(II). On the other hand the cathodic and anodic peaks of Pb(II) became apparent and increased with the addition of Pb(II). The new peaks which appeared at - 0.25 and - 0.30 V in cathodic and - 0.12 and - 0.21 V in anodic directions were not observed to change to a significant extent. The peak at - 0.82 V increased at first but remained constant latter on (Fig. 2). The phenomena mentioned above were observed for the ion mixtures prepared at various amounts.

The addition of Pb(II) into the selenite solution results the reduction of Pb^{2+} ions at the partially coated Hg surface[19,20]. This reduction may take place at three different sites of the above mentioned surface:

$$Pb^{2+} + HgSe + 2e^- \rightleftharpoons Hg(SePb) \qquad (-\ 0.25\ V) \qquad (5)$$

$$Pb^{2+} + Se^0_{(on\ HgSe)} + 2e^- \rightleftharpoons SePb_{(on\ HgSe)} \qquad (-\ 0.30\ V) \qquad (6)$$

$$Pb^{2+} + Hg + 2e^- \rightleftharpoons PbHg \qquad (-\ 0.37\ V) \qquad (7)$$

The reduction peaks corresponding to the above electrode reactions of (eqns. 5-7) were depicted in Fig. 2. The conversion of HgSe layer to

Hg(SePb) form according to eqn. 5 was indicated by decreasing the reduction of the HgSe film at - 0.59 V which was assigned to the stripping of this layer forming H_2Se. The complete disappearing of the small peak at - 0.54 V was verified by the process in eqn. 6, exploiting the elemental Se to form PbSe compound. The newborn peak at - 0.82 V is probably due to the decomposition of Hg(SePb) and $SePb_{(on\ HgSe)}$ layers to the H_2Se and HgPb according to the electrode reaction given by eqn. 8. The asymmetric shape of this peak shows that it is the combination of two different electron transfer phenomena with different energies. One is the reduction of Hg(SePb) layer and the other is that of $SePb_{(on\ HgSe)}$ layer:

$$\text{Hg(SePb) (or SePb}_{(on\ HgSe)}) + 2H^+ + 2e^- \rightleftharpoons \text{HgPb} + H_2Se \quad -0.82\ V \qquad (8)$$

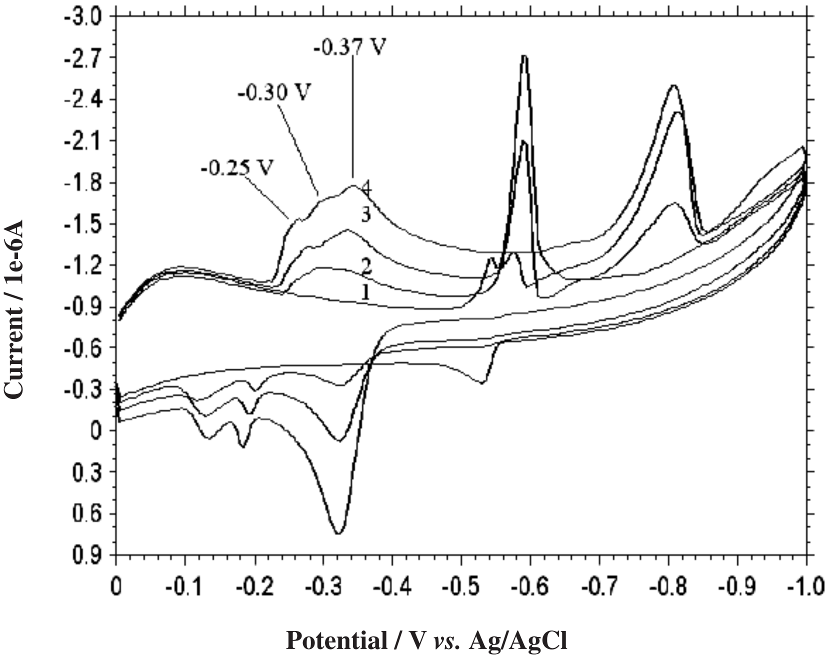

Fig. 2. Cyclic voltammograms for the addition of Pb^{2+} on SeO_3^{2-} solution in 10 mL 0.01 M HNO_3 on Hg electrode *vs.* Ag/AgCl/KCl_{sat}, scan rate was 250 mV/s (1) 2.50×10^{-7} mol SeO_3^{2-}, (2) 1 + 1.00×10^{-7} mol Pb^{2+}, (3) 2 + 1.00×10^{-7} mol Pb^{2+}, (4) 3 + 1.00×10^{-7} mol Pb^{2+}

Difference in energy of these two processes is not so high to cause separate the peaks. Actually, it is the decomposition of SePb compound but in different sites. In the anodic scan, two characteristic peaks were observed in addition to the anodic counterpart of the Pb^{2+} cathodic peak.

These anodic peaks are not observed in individual voltammograms of SeO_3^{2-} and Pb^{2+} and it only appears where these two ions are present in the same solution. First one at - 0.21 V which is attributed to the oxidation of Hg at the Hg(SePb) and $SePb_{(on\ HgSe)}$ surface (eqn. 10). Mercury is normally oxidized to Hg^{2+} at + 0.4 V at the pure mercury surface *vs.* $Ag/AgCl/KCl_{sat}$. However, this potential is shifted to - 0.21 V due to Hg(SePb) and $SePb_{(on\ HgSe)}$ films in which the oxidation of Hg is more favourable. The second one at - 0.12 V attributed to the oxidation of amalgamated lead in the Hg(SePb) and $SePb_{(on\ HgSe)}$) layers (eqn. 9). The confirmation of the peak at - 0.12 V can be achieved by changing the reversal potential before the decomposition of Hg(SePb) and $SePb_{(on\ HgSe)}$ layers at - 0.82 V. If the potential is reversed before - 0.82 V, Pb in Hg(SePb) and $SePb_{(on\ HgSe)}$, oxidation peak at - 0.12 V appeared to be much greater than the former scan which was reversed at - 1.0 V (Fig. 3).

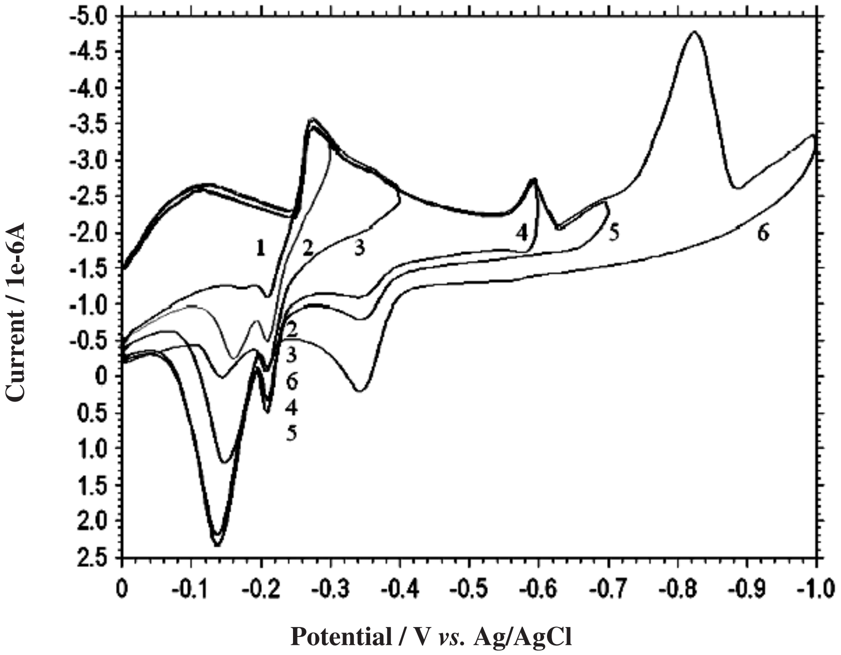

Fig. 3. The investigation of peaks with different reversal potentials scanning (5.00 × 10^{-7} mol Pb(II) + 2.50 × 10^{-7} mol SeO_3^{2-} in 10 mL pH = 2 HNO_3 support electrolyte on Hg electrode *vs.* $Ag/AgCl/KCl_{sat}$) (1) Reversed from - 0.25 V; (2) Reversed from - 0.30 V; (3) Reversed from - 0.40 V; (4) Reversed from - 0.60 V; (5) Reversed from - 0.70 V; (6) Reversed from - 1.00 V

$$\mathrm{Hg(SePb)\ (or\ SePb_{(on\ HgSe)})} \rightleftharpoons \mathrm{HgSe + Pb^{2+} + 2e^-} \quad (-0.12\ \mathrm{V}) \qquad (9)$$

$$\mathrm{Hg(SePb)\ (or\ SePb_{(on\ HgSe)}) + Hg} \longrightarrow \mathrm{SePb + Hg^{2+} + 2e^-} \quad (-0.21\ \mathrm{V}) \qquad (10)$$

When we look at the early reversals in Fig. 3, the height of the peak at - 0.21 V is not significantly dependent of the coverages of the various films on the pure mercury surface. This behavior can be explained by the effects of two opposite phenomena operating at the electrode surface. According to eqn. 10, the increase in the coverage of Hg(SePb) (or $SePb_{(on\ HgSe)}$) film decreases the Hg surface available. Because of these two opposing effects, no significant net changes can be observed on the oxidation peak current of Hg.

Keeping the amount of selenite constant and increasing the amount of Pb(II) increases the coverage of Hg(SePb) film and decreases the HgSe on mercury drop. That is why the cathodic peak corresponding to eqn. 2 at - 0.59 V will decrease at first and totally disappear upon the addition of enough Pb(II) (Voltammogram 3 in Fig. 2) resulting the complete coverage of the surface with Hg(SePb). Further additions of Pb(II) after the complete conversion of HgSe to Hg(SePb) will result no change in the Hg(SePb) film coverage and therefore the heights of the corresponding peaks at - 0.30 and - 0.82 V. Excessive increase in Pb(II) will reduce HgSe present on the surface into Hg(SePb) and HgSe on the surface will be exhausted. The excess amount of Pb(II) will then be reduced on Hg(SePb) at - 0.37 V. Further increase in the amount of Pb(II) present in the medium will increase this peak according to the reaction:

$$\mathrm{Hg(SePb) + Pb^{2+} + 2e^-} \longrightarrow \mathrm{Pb_{(on\ Hg(SePb))}} \qquad (11)$$

The reason why the anodic peak at - 0.34 V corresponding to the oxidation of lead is bigger than it is supposed to be, can be explained as follows (Fig. 2): This peak appears according to eqn. 7 in the presence of Pb(II) only. However in the presence of SeO_3^{2-} in addition to Pb(II) in the medium this process takes place *via* eqn. 9 as well as eqn. 7.

Electrochemical behavior with the addition of selenite on lead(II) solution: When 5.0×10^{-8} mol selenite was added to the 10 mL of 0.01 M HNO_3 solution containing 2.0×10^{-7} mol Pb(II), cathodic (at - 0.37 V) and anodic (at - 0.34 V) peaks of Pb(II) were suppressed and three cathodic peaks at - 0.25, - 0.30 and -0.82 V were appeared. The anodic peaks at - 0.12 and - 0.21 V were also appeared which were discussed above in detail. As the selenite additions were continued, it was observed that Pb(II) peaks decreased and other cathodic peaks increased. The further addition of selenite resulted in the emerging a new cathodic peak at - 0.59 V alongside the above mentioned peaks. This peak is the reduction of elemental selenium to H_2Se, as shown in Figs. 1 and 2. It is important to note that, the selenite peak at - 0.59 V were not observed, although selenite ions were added to the medium until the complete coverage of the surface with Hg(SePb) (Voltammograms 3, 4 and 5 in Fig. 4). This observation is one of the most striking finding of this work. When the amount of selenite added to the medium which gives HgSe amalgam totally converts it into Hg(SePb) intermetallic compound according to eqns. 8 and 9, the peak corresponding to the stripping of HgSe at - 0.59 V is not observed. The addition of selenite to the medium will increase its relative amount to Pb(II) which will increase the formation of HgSe upon the surface and the stripping peak at - 0.59 V will become apparent (Fig. 4).

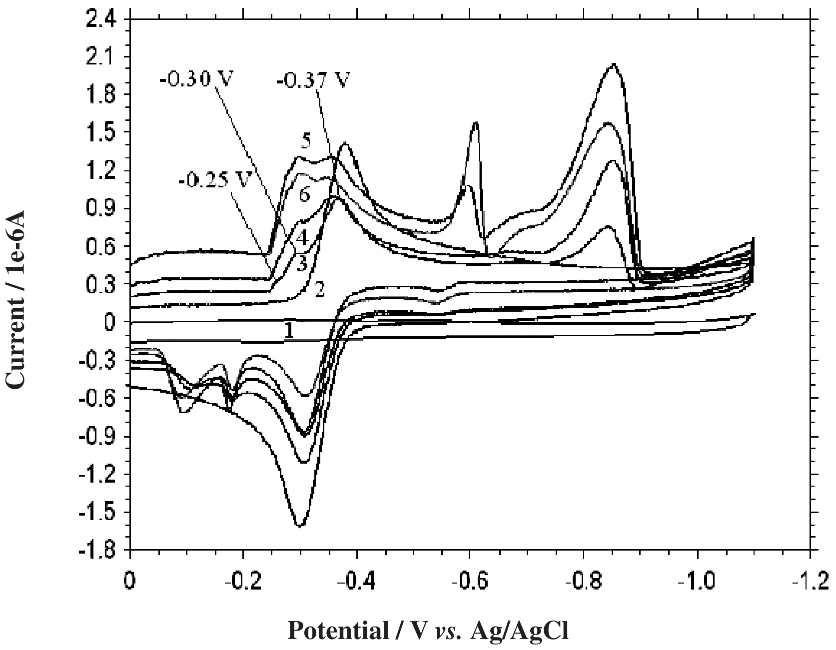

Fig. 4. Cyclic voltammograms for the addition of SeO_3^{2-} on Pb(II) solution in 10 mL 0.01 M HNO_3 on Hg electrode *vs.* Ag/AgCl/KCl_{sat}, scan rate was 250 mV/s (1) 2.00×10^{-7} mol Pb^{2+}, (2) 1 + 5.00×10^{-8} mol SeO_3^{2-}, (3) 2 + 5.00×10^{-8} mol SeO_3^{2-}, (4) 3 + 5.00×10^{-8} mol SeO_3^{2-}, (5) 4 + 5.00×10^{-8} mol SeO_3^{2-}, (6) 5 + 5.00×10^{-8} mol SeO_3^{2-}

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