Asian Journal of Chemistry Vol. 14. No. 1 (2002), 90–94

Polarography of Selenium and Tellurium: A New Arena of Electrochemistry†

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Investigations on polarographic behaviour and brief surveys of electrode kinetics of selenium and tellurium opened new arenas in electochemical problems of importance. The polarogram of 1 mM Se(IV) was recorded under distinct experimetal conditions. It produced single four-electron reduction wave in pH ranging trom 3 to 8 in NH_4Cl as base electrolyte. At pH 4.2, $E^r_{1/2}$ value was found to be –1.522 V *vs.* SCE. Te(IV) undergoes reduction to its elemental state at pH 8.4. It gives ill defined wave at pH ≤ 8.0 $E^r_{1/2}$ value was found to be-0.684 V *vs* SCE. $E^r_{1/2}$ values were computed by Koutecky's method. The stepwise reduction +4, +2, 0, –2 was also observed on the polarograpic wave. The reduction states of the various waves of Se(IV) and Te(IV) observed have been established conclusively by the Devries and Kroon's millicoulmetric method. The striking feature of the polarogram of Te(IV) is the large maximum which appears at limiting current plateau. This may be due to polytellurite ion Te_x^{2-} on the electrode surface. Calibration plots, polarograms, kinetic parameters and each of the voltammetric data will be fruitful for analytical, clinical, alloy production and for industrial purposes.

Key words: Polarography, selenium, tellurium, electrochemistry.

INTRODUCTION

Anomalies on the polarographic reduction of Se(IV) and Te(IV) have been sometimes published in the literature.[1, 2] However, correct voltammetric data are not reported so far.[3–5] The present work reports the various aspects of the voltammetric studies of selenium and tellurium from the viewpoints of analytical, clinical and alloy industrial aspects.

EXPERIMENTAL

The stock solutions 0.1 mol dm^{-3} of each, of Se(IV) and Te(IV) were prepared from sodium selenite and potassium tellurite (A.R. Loba reagent grade) in bidistilled water. NH_4Cl solution was used as supporting electrolyte. Experimental

†Paper presented at 69th session of National Acadamy of Sciences, Allahabad.

sets were prepared and pH of the test solution was adjusted with dil. NaOH/HCl. Gelatin was used as maxima suppressor in distinct composition range.

Polarographic studies were carried out on CLO-2B Toshniwal digital polarograph. In some cases polarograms of Se(IV) and Te(IV) were recorded on Elico-pen recording polarograph model Cl-25D with recorder LR-101P. Millicoulometric method was applied to determine the number of electrons (n) involved in the reduction process[6]. The capillary characteristics $m^{2/3}$, $t^{1/6}$ = 2.13 $mg^{2/3}t^{-1/2}$ at 40 cm effective height of mercury column were noted during polarographic studies. All observations were taken at room temperature, 25±1°C.

RESULTS AND DISCUSSION

Selenium(IV) undergoes single four-electron reduction in the entire range of pH 3.8 to 8.2, under the observed experimental conditions. However, the wave was not well defined in KCl. The polarogram of 1.00 mM Se(IV) in NH_4Cl is shown in Fig. 1. The influence of pH is reported in Table-1. Data report that increase in i_d is a function of pH, up to 4.4 and above this pH value i_d attains nearly constant value. Log plot slope indicated the irreversible behaviour. Koutecky's method[7] was applied. $E^r_{1/2}$ = −1.522 V *vs.* SCE at pH 4.2 and $E^r_{1/2}$ = −1.540 V *vs.* SCE at pH 7.4 were computed. Necessary data have been reported in Table-1.

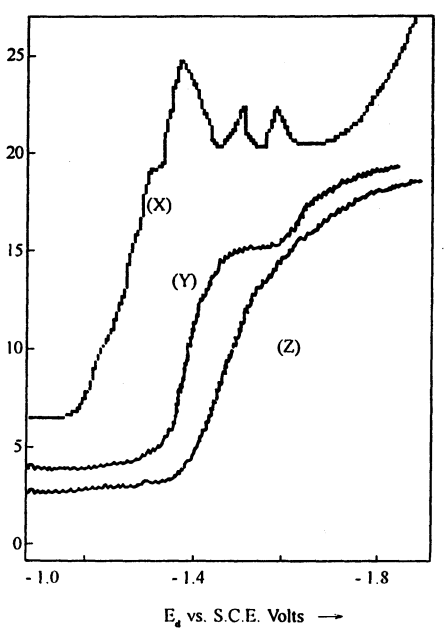


Fig. 1. Polarogram of 1 m mol Se(IV) in 0.1 mol dm^{-3} NH_4Cl at pH 8.0 in different maxima suppresser

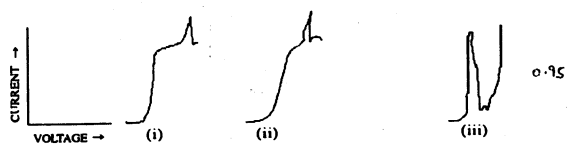
TABLE-1
POLAROGRAPHIC CHARACTERISTICS OF SELENIUM(IV) AT DISTINCT pH
Selenium = 1.0 mMol dm^{-3}, μ = 0.1 mol dm^{-3}, gelatin = 0.001%, temperature = 25 ± 1°C

S. No.	pH ± 0.02	– $E_{1/2}$ V *vs.* SCE	i_d (μA)	I	α_{na}	K^0_{fh}
1.	3.0	1.52	13	9.0	0.40	5.6×10^{-12}
2.	3.4	1.50	20	13.8	0.36	7.1×10^{-11}
3.	3.8	1.44	23	15.9	0.36	1.8×10^{-10}
4.	4.2	1.47	24	17.0	0.40	1.3×10^{-10}
5.	4.6	1.52	24	16.6	0.28	3.8×10^{-9}
6.	5.0	1.53	22	15.6	0.28	3.1×10^{-9}
7.	6.1	1.54	22	15.4	0.40	7.3×10^{-12}
8.	7.8	1.54	22	15.2	0.50	3.9×10^{-14}
9.	8.2	1.58	20	14.2	0.50	1.7×10^{-14}

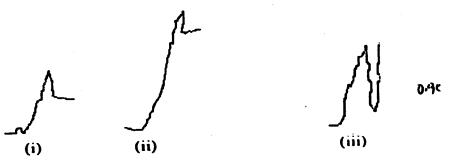
Tellurium is an important metal in alloy and steel industry. It is observed that its hexavalent state is not reducible on a DME. Its electrochemistry involves complexity because of presence of multivalent (+6, +4, +2, 0, –2) species. Te(IV) undergoes reduction to its elemental state in different suporting electrolytes. The polarogams are shown in Fig. 2. In 0.1 mol dm^{-3} NaOH containing 0.001% gelatin tellurium reduces on DME at pH 9.0. $E_{½}$ was found to be –0.86 V *vs.* SCE. Te(IV) produces ill defined wave at pH < 8.0. However, at pH > 8.4, the well defined reproducible waves have been recorded. The values of $E_{½}$, k^0_{fh}, α_{na} have been computed in Table-2. The striking feature of the polarogram of Te(IV) is the large maximum which apears at limiting current plateau. This attributes to the formation of polytellurite ion (Te_x^{2-}).

I. TAST II. NPP III. DPP

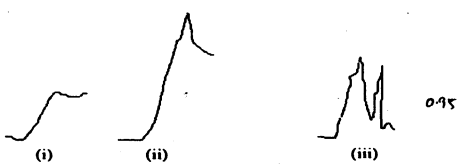
(a) In 0.1 mol dm^{-3} NH_4Cl, pH = 8.40



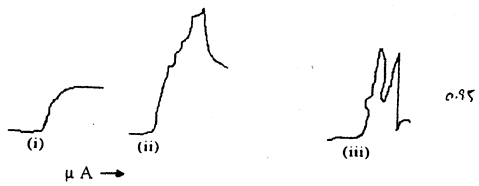
(b) In 0.2 mol dm^{-3} KCl, pH = 6.50



(c) In 0.1 mol dm^{-3} NaOH, pH = 9.00



(d) In 0.1 mol dm^{-3} KNO_3, pH = 8.20



Initial Applied Voltage = –0.2 V *vs.* SCE, S = 10 μA

Fig. 2. Voltammograms of 1.0 m mol dm^{-3}, Tellurium(IV) in Different Experimental set up

TABLE-2
POLAROGRAPHIC CHARACTERISTICS OF TELLURIUM(IV) AT DISTINCT pH
Tellurium = 1.0 mMol dm^{-3}, μ = 0.1 mol dm^{-3}, gelatin = 0.001%, temperature = 25 ± 1°C

S. No.	pH ±0.02	$-E_{1/2}$ V *vs.* SCE	i_d (μA)	I	α_{na}	K^0_{fh}
1.	6.0	0.61	6	4.3	0.57	2.7×10^{-7}
2.	6.1	0.63	7	5.0	0.50	7.4×10^{-7}
3.	7.4	0.65	11	7.6	0.28	0.0×10^{-7}
4.	8.0	0.67	12	8.3	0.50	5.4×10^{-7}
5.	8.4	0.68	11	7.9	0.50	1.1×10^{-8}
6.	8.9	0.74	10	6.9	0.55	3.5×10^{-5}
7.	9.5	0.77	9	0.2	0.20	2.5×10^{-5}

Calibration plots as recorded after the series of polarograms of Se(IV) and Te(IV) are of clinical and alloy industrial importance, as the concentration of these metalloids could be successfully determined form these graphs (Fig. 3).

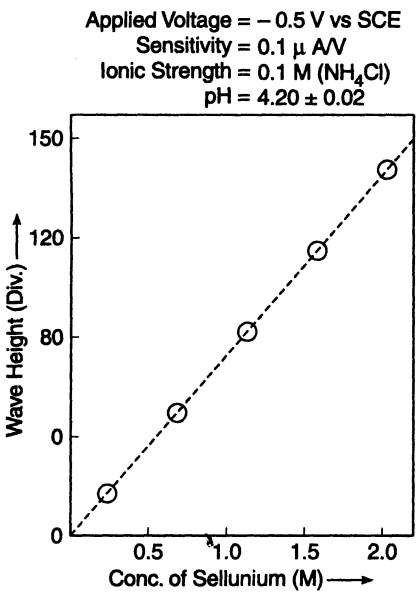


Fig. 3. (a) Calibration Plot Se(IV)

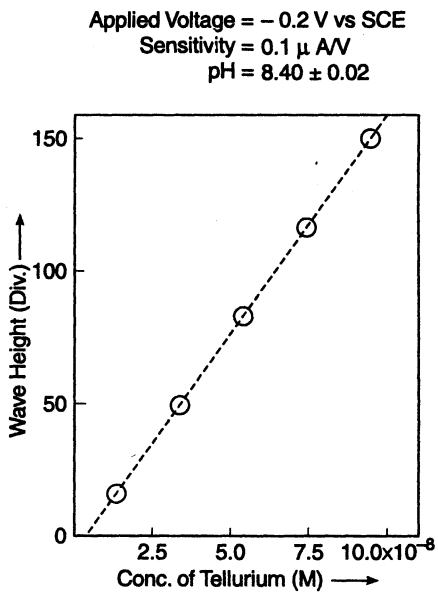


Fig. 3. (b) Calbration Plot Te(IV)

Computed polarographic data, kinetic parameters and the above experimentation have opened a new arena in the electrochemistry of selenium and tellurium.

ACKNOWLEDGEMENTS

We are grateful to UGC for providing minor research project; thanks are also due to Dr. S.S. Katare, Principal, for providing laboratary facilities.

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(*Received:* 5 July 2001; *Accepted:* 29 September 2001) AJC-2455