POLAROGRAPHIC STUDIES ON SELENITE IONS IN AQUEOUS HYPOPHOSPHOROUS ACID SOLUTIONS

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The polarographic behaviour and determination of Se(IV) in hypophosphorous acid solutions of concentrations varying from 0.05 mol l^{-1} to 4.0 mol l^{-1} at 25 ± 0.1 °C were investigated. It was shown that the reduction of $5 . 10^{-4}$ mol l^{-1} Se(IV) at the DME takes place in two waves independent on the acid concentration. The reduction waves correspond to the transfer of 6 electrons. A mechanism of the reduction at the DME has been suggested. A method for the analytical determination of Se(IV) species in 0.1 mol l^{-1} and 0.05 mol l^{-1} hypophosphorous acid in absence and in presence of $3 . 10^{-6}$ mol l^{-1} Cd(II) and Zn(II) was developed using a differential pulse technique.

Key words: Polarography; Selenite; Hypophosphorous acid.

Selenium is an important element because of its industrial and biological applications. Metallurgically, the addition of selenium to stainless steel is known to improve its mechanical properties. Numerous analytical methods using e.g. gravimetry[1,2], titrimetry[3–6], cyclic and stripping voltammetry[7,8], and oscillopolarography[9] were developed.

A number of authors have recommended solutions containing NH_4^+-ion as electrolytes suitable for determination of Se(IV) (refs[10–21]). Among them, however, a considerable diversity exists regarding the number and origin of the polarographic waves obtained, as well as the type of the electrode reaction. This encouraged me to study the electroreduction of selenite ions at the DME in hypophosphorous acid. The reduction states have been established conclusively by the coulometric analysis at controlled potential using a large mercury cathode. In the present paper the polarographic determination of Se(IV) species in absence and presence of both Cd(II) and Zn(II) ions has been investigated by DPP method.

EXPERIMENTAL

All chemicals used were of analytical grade. A stock 0.02 M sodium selenite was prepared by dissolving the required amount of its pentahydrate salt (99%) in double distilled water. The resulting solution was standardized according to Vogel[22]. A stock solution of 5 mol l^{-1} hypophosphorous acid

(49.5%) was prepared and standardized against a standard sodium hydroxide solution. All solutions of lower concentrations were prepared by accurate dilution.

DC polarographic measurements were carried out using a three electrode polarograph OH-105 with dropping mercury electrode (DME), auxiliary platinum electrode and a saturated calomel reference electrode (SCE). The dropping mercury electrode had the following characteristics: the rate of mercury flow m = 1.72 mg s^{-1}, drop time t = 3.6 s and the height of the mercury column was adjusted to 50 cm. Differential pulse polarographic (DPP) measurements were carried out with a polarographic analyzer EG & G Model 264A coupled with a recorder (RE0089). The working electrode was a PAR 303 A SMDE, medium size drop with an area of 0.017 cm^2 equipped with a platinum auxiliary electrode and an Ag/AgCl (saturated KCl) reference electrode.

Procedure

An aliquot of 10 ml of the supporting electrolyte (0.05 and 0.1 mol l^{-1} hypophosphorous acid solution) was deareated with purified nitrogen for 12 min. The selenite ions were then introduced into the cell solution and polarograms were recorded. The following parameters have been imposed for DPP: drop time 1 s, scan rate 5 mV s^{-1}, and the pulse amplitude 25 mV. For all measurements an equilibration time of 15 s was applied before recording the polarograms. The known concentration of Se(IV) in model samples was determined using a calibration curve.

RESULTS AND DISCUSSION

Current-Potential Curves

The DC polarographic behaviour of 0.5 mmol l^{-1} SeO$_3^{2-}$ in hypophosphorous acid solutions with the concentration of H$_3$PO$_2$ varying from 0.1 to 4.0 mol l^{-1} is illustrated in Fig. 1.

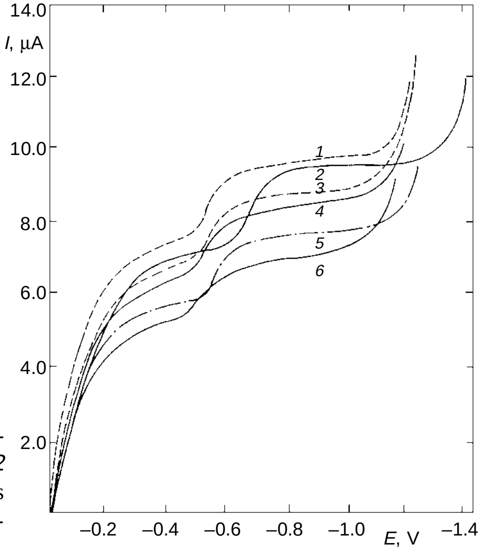

FIG. 1
Polarograms of 5 . 10^{-4} M Se(IV) in hypophosphorous acid at various concentrations: *1* 0.1, *2* 0.5, *3* 1.0, *4* 1.5, *5* 2.0, *6* 4.0 mol l^{-1}. Potentials vs SCE, sweep direction towards negative potentials

The results show that the reduction of Se(IV) species at the DME occurs in two waves within the investigated range of concentrations. The height of both the first and second waves decreases with the rise of acid concentration. This decrease results from the change of the viscosity for the concentration of acid varying from 0.1 to 4.0 mol l^{-1}. First, a coulometric reduction of 1.5 mmol l^{-1} Se(IV) in hypophosphorous acid solutions at concentrations of 0.1, 0.5 and 1 mol l^{-1} was performed using a large mercury cathode with the potential maintained at the plateau position of the 1st wave i.e. at –0.35 V vs SCE.

During the electrolysis, a red colloidal selenium was formed and a black precipitate HgSe appeared on the mercury cathode. When the electrolysis had been completed, the number of electrons exchanged was found to be $n = 4.04$.

Then the potential of the mercury cathode was set at the plateau position of the 2nd wave (–0.85 V vs SCE) and the solution was subjected to further electrolysis. During the electrolysis, hydrogen selenide was evolved and the number of electrons exchanged in this reaction was found to be $n = 2.01$.

The foregoing results obtained for the polarographic behaviour of Se(IV) in hypophosphorous acid solutions, reveal that it is reduced ultimately to H_2Se in two waves.

The 1st wave can be ascribed to the reaction (*A*),

$$\mathrm{Hg} + \mathrm{H_2SeO_3} + 4\,\mathrm{H^+} + 4\,\mathrm{e} \rightarrow \mathrm{HgSe} + 3\,\mathrm{H_2O} \tag{A}$$

while the 2nd wave corresponds to the Eq. (*B*).

$$\mathrm{HgSe} + 2\,\mathrm{H^+} + 2\,\mathrm{e} \rightarrow \mathrm{Hg} + \mathrm{H_2Se} \tag{B}$$

For the overall reaction:

$$\mathrm{H_2SeO_3} + 6\,\mathrm{H^+} + 6\,\mathrm{e} \rightarrow \mathrm{H_2Se} + 3\,\mathrm{H_2O}\ . \tag{C}$$

Thus, the first step described by Eq. (*A*) represents the uptake of four electrons whereas two electrons are involved in the second step according to Eq. (*B*).

The reduction of Se(IV) in hypophosphorous acid at varying concentrations (0.1–4.0 mol l^{-1}) was found to be irreversible as follows from $\log i/i_d - i$ vs E plots. These plots were utilized to evaluate the kinetic parameters[23] and wave characteristics including slope, αn, (α is charge transfer coefficient, n is number of electrons in the rate determining step), K^0_{fh}(standard rate constant), ΔG^* (energy of activation) and $K^0 D^{-1/2}$ (D is diffusion coefficient). Table I summarizes the kinetic parameters and micro-coulome-

TABLE I

Kinetic parameters and microcoulometric data for the reduction waves of 5 . 10^{-4} mol l^{-1} Na_2SeO_3 in hypophosphorous acid of various concentrations *c*

c mol l^{-1}	Wave	i_d μA	$E_{1/2}$ V (NHE)	Slope V^{-1}	αn	K^0_{fh} cm s^{-1}	ΔG KJ	$KD^{-1/2}$	S^a	D^b cm^2 s^{-1}	Microcoulometric data	
											E V (SCE)	*n*
0.1	1st	7.1	–0.075	0.56	3.36 . 10^{-2}	2.3 . 10^{-4}	214.5	0.38	0.47	1.95 . 10^{-7}	–0.35	4.00
	2nd	2.2	–0.580	0.78	4.7 . 10^{-2}	4.2 . 10^{-4}	210.6	0.54	0.50		–0.85	2.01
0.5	1st	7.1	–0.15	0.54	3.24 . 10^{-2}	2.25 . 10^{-4}	211.1	0.53	0.48	1.85 . 10^{-7}	–0.35	4.04
	2nd	1.95	–0.75	0.75	4.5 . 10^{-2}	4.1 . 10^{-4}	205.0	0.95	0.54		–0.85	2.01
1.0	1st	6.55	–0.10	0.52	3.12 . 10^{-2}	2.05 . 10^{-4}	214.6	0.41	0.44	1.63 . 10^{-7}	–0.35	4.04
	2nd	1.95	–0.60	0.73	4.38 . 10^{-2}	3.36 . 10^{-4}	208.6	0.72	0.48		–0.85	2.01
1.5	1st	6.20	–0.095	0.51	3.06 . 10^{-2}	1.95 . 10^{-4}	212.3	0.53	0.40	1.48 . 10^{-7}	–	–
	2nd	1.90	–0.475	0.96	5.76 . 10^{-2}	2.96 . 10^{-4}	207.1	0.87	0.47		–	–
2.0	1st	5.50	–0.08	0.50	3.00 . 10^{-2}	1.65 . 10^{-4}	211.3	0.65	0.54	1.20 . 10^{-7}	–	–
	2nd	1.80	–5.80	0.72	4.32 . 10^{-2}	2.90 . 10^{-4}	208.7	0.84	0.52		–	–
4.0	1st	5.20	–0.09	0.44	2.60 . 10^{-2}	8.00 . 10^{-5}	222.2	0.25	0.38	1.01 . 10^{-7}	–	–
	2nd	1.5	–0.55	0.71	4.26 . 10^{-2}	1.92 . 10^{-4}	313.0	0.60	0.42		–	–

[a] Slope of log *i* – log *h* plot. [b] Diffusion coefficient.

tric data for the reduction of selenite ions according to Eq. (*A*) and Eq. (*B*) in hypophosphorous acid. Coupled with the direct proportionality of diffusion current i_d to the square root of the effective height of the mercury column, these results indicate the reduction of Se(IV) in the 1st and 2nd waves to be an irreversible diffusion-controlled process.

TABLE II
Relation between the peak height i_p from Fig. 2 and concentration *c* (in mol l^{-1}) of Se(IV) in 0.05 M H_3PO_2 containing 3 . 10^{-6} M Cd(II) and Zn(II)

Parameter	1 . 10^{-6}	4 . 10^{-6}	7 . 10^{-6}	1 . 10^{-5}	1.3 . 10^{-5}	1.6 . 10^{-5}
i_p, nA	3.25	12.5	22.5	32.5	44.5	55.0
$i_p/c_{Se(IV)}$. 10^{-6}	3.25	3.13	3.21	3.25	3.32	3.43
Average			3.31			
Error, %	–1.8	–5.44	–3.02	–1.8	+0.3	+3.62

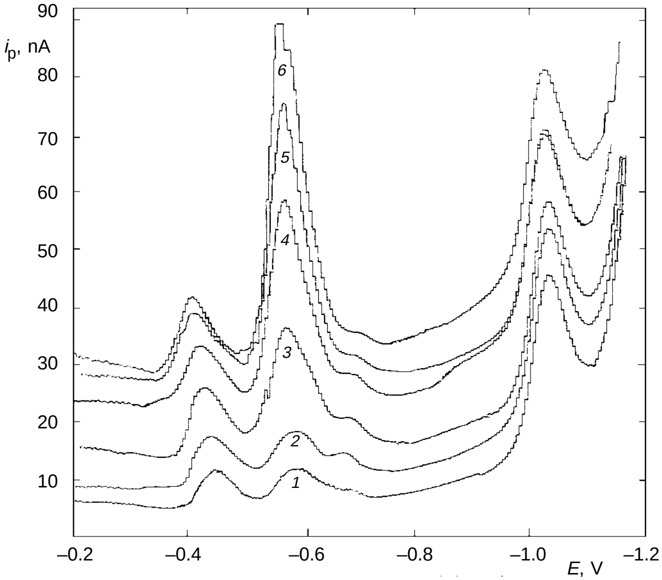

FIG. 2
Differential pulse polarography of Se(IV) at various concentrations in 0.05 mol l^{-1} H_3PO_2 in presence of 3 . 10^{-6} M Cd(II) and Zn(II). Starting potential –0.2 V vs Ag/AgCl, drop time 1 s, pulse amplitude 25 mV, scan rate 5 mV s^{-1}, Se(IV) concentration: *1* 1 . 10^{-6}, *2* 4 . 10^{-6}, *3* 7 . 10^{-6}, *4* 1 . 10^{-5}, *5* 1.3 . 10^{-5}, *6* 1.6 . 10^{-5} mol l^{-1}. Potentials vs Ag/AgCl (saturated KCl), sweep direction towards negative potentials

Differential Pulse Polarography

Differential pulse polarography in 0.05 mol l^{-1} hypophosphorous acid shows a good base line in the potential range –0.20 to –1.20 V vs Ag/AgCl. The reduction peak observed at –0.58 V for DPP at different concentrations of Se(IV) ions in 0.05 mol l^{-1} H_3PO_2 is suitable for the analytical determination of Se(IV) within the range of 0.8 µg l^{-1} (1 . 10^{-8} mol l^{-1}) to 20.5 µg l^{-1} (2.6 . 10^{-7} mol l^{-1}).

Figure 2 shows the differential pulse polarograms at various Se(IV) concentrations in the presence of 3 . 10^{-6} mol l^{-1} of both Cd(II) and Zn(II) in 0.05 mol l^{-1} hypophosphorous acid. Each of these polarograms consists of three peaks corresponding to the reduction of Cd(II), Se(IV) and Zn(II) at peak potential E_p –4.75, –5.60 and –1.03 V vs Ag/AgCl.

The optimum conditions for the analytical determination of SeO_3^{2-} ions in presence of 3 . 10^{-6} mol l^{-1} Cd(II) and Zn(II) were found to be 0.05 mol l^{-1} H_3PO_2, pulse amplitude 25 mV, drop time 1 s and scan rate 5 mV s^{-1}. Under these conditions the differential pulse polarograms of SeO_3^{2-} were recorded as a function of selenite ion concentration.

The DPP peak height i_p was found to be a linear function of selenite concentration. A linearity has been obtained in the range from 7.9 . 10^{-2} µg ml^{-1} (1 . 10^{-6} mol l^{-1}) to 1.263 µg ml^{-1} (1.6 . 10^{-6} mol l^{-1}). The validity of the method according to Ilkovic[24] is supported by the constant $i_p/C_{Se(IV)}$ ratio as shown in Table II.

Interferences

Since metal ions, such as W, Th, Se(VI), Pt, Sn(IV) and Ti do not undergo reduction at the DME, they do not interfere. Other metals, such as Ag, Au, Ce, Sn(III) and Bi precipitate. Only In(III) and Cr(III) can interfere. As Te(IV) does not produce any wave in buffer solutions of pH < 7 (ref.[25]), determination of Se(IV) in presence of Te(IV) can be made in 0.05 mol l^{-1} hypophosphorous acid solutions.

The polarographic method performed in 0.05 mol l^{-1} H_3PO_2 acid solution can therefore be used to determine Se(IV) in steels.

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