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Preliminary Polarographic Studies of Sulfur and Selenium Solutions in Hydrazine Hydrate

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The dropping mercury electrode polarographic behavior of sulfur and selenium solutions in hydrazine hydrate has been studied in highly alkaline aqueous solution containing supporting electrolyte of 0.1 M ammonium tartrate (1 M=1 mol dm^{-3}). Both the sulfur and selenium revealed a composite anodic–cathodic waves. The values of $E_{1/2}$ for sulfur and selenium solutions, taken from the cathodic wave of the polarograms corresponded to $E_{1/2}$=−0.78 and −1.03 V vs. SCE respectively. The effect of mercury pressure and concentration of depolarizer on the relative magnitude of the wave heights has also been studied on the basis of typical reactions involved at DME in this solvent medium. No maxima supressor was used in the present study for both cases.

Polarographic study of sulfur solution in pyridine and ethanol, using sodium acetate-acetic acid buffer, exhibits elemental behavior[1–4] while in strongly alkaline medium, sulfur dissolves as sulfide and polysulfide ions.[5–7] Elemental sulfur and selenium dissolve in alkaline solution of sulfides of alkali metals with the formation of selenosulfide (Se_2S^-),[11] and in concentrated alkaline solutions to give polysulfides and polyselenides.[12] This transformation of elemental sulfur and selenium into selenosulfide is a convenient method for determining these elements. Konapik and Werner[7–9] carried out the polarographic studies of polysulfide ions in 2 M (M=mol dm^{-3}) NaOH and suggested the following reaction mechanism. They proposed that the anodic wave of the polarogram is due to the oxidation of mercury by sulfide ions, and the reduction of polysulfide and elemental sulfur is responsible for the cathodic wave as:

$$Hg + S^{2-} \longrightarrow HgS + 2e$$
$$S_2^- + 2e \longrightarrow 2S^{2-}$$
$$S + 2e \longrightarrow S^{2-}$$

Lingane and Niedrach[10] reported the polarography of selenide ions in different media with pH ranging from 1 to 14. Toropova et al.[11,12] have shown that selenium dissolves in highly alkaline media, as polyselenide ions. They proposed similar reaction mechanism at DME as suggested by Konapik and Werner.[7–9] In highly alkaline solutions like hydrazine hydrate the elemental selenium and sulfur are transformed to selenosulfide and polysulfide for determination. In the case of hydrazine hydrate, it is reported that sulfur and selenium in any oxidation state is readily reduced to elemental sulfur/selenium and dissolved in hydrazine forming solvation complex. The polarographic behavior of sulfur and selenium in hydrazine hydrate solutions at DME is less studied. In the present study, hydrazine hydrate in 50–50% mole ratio with water was employed as solvent for the polarographic determination of S and Se in elemental form and in various oxidation states. In our preliminary studies it was observed that 50% hydrazine hydrate+50% water was the suitable solvent composition for analysis. The effect of mercury pressure and depolarizers on wave heights of the polarograms have also been studied and results have been discussed.

Experimental

The commercially available (BDH) analytical grade hydrazine hydrate ($N_2H_4 \cdot H_2O$) was further purified by standard distillation procedure before use. Various volume ratios of distilled hydrazine hydrate was mixed with deionized water. Since, 50 volume % $N_2H_4 \cdot H_2O$+50% H_2O was found to have high solubility for sulfur and selenium, the same ratio of the solvent was used as the solvent in the present investigation. The standard solutions of AR-grade sulfur and selenium were prepared by dissolving accurately weighed quantity of the elements in 25 ml of the solvent. Ammonium tartarate (0.1 M) was used as the supporting electrolyte. The total volume of the supporting electrolyte and the analyte was made upto 25 ml and transferred to the polarographic cell. The flow rate '*m*' and time '*t*' of the dropping mercury electrode (DME) assembly at a mercury height of 35 cm were 1.5 mg s^{-1} and 5.0 s, respectively. All the currents and potentials reported in this work were corrected for the residual current as well as the IR drop involved. The solutions were deaerated by bubbling nitrogen and the polarograms were recorded with the Leeds and Northup Electrochemograph type E at 25±1 °C.

Results and Discussion

As evident from Figs. 1 and 2, both the sulfur and selenium solutions in hydrazine hydrate, produce a composite anodic–cathodic waves.

Hydrazine hydrate dissociates according to the equilibrium in aqueous solution.

$$N_2H_4 \cdot H_2O \rightleftarrows N_2H_5^+ + OH^-$$

Hydrazinium ions reduce sulfur to sulfide (S^{2-}) and polysulfide (S_n^{2-}) ions with the evolution of nitrogen according to the following reactions.

$$4N_2H_5^+ + S_8 + 20OH^- \longrightarrow 4N_2 + 8S^{2-} + 20H_2O$$
$$S^{2-} + nS \rightleftarrows S_n^{2-}$$

Similarly, elemental selenium produces selenide (Se^{2-})

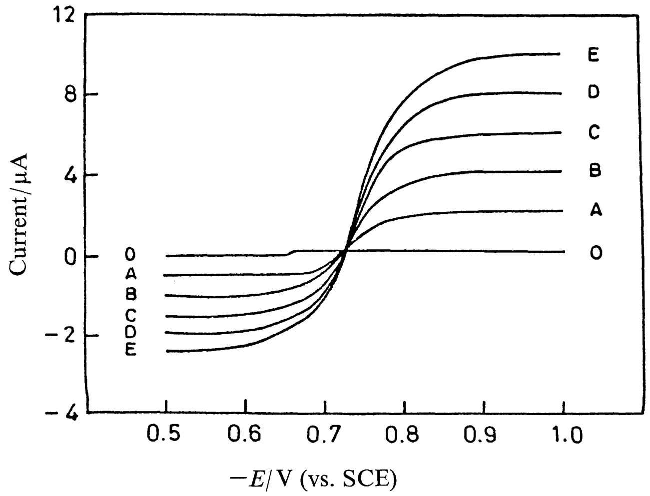

Fig. 1. Polarographic curves of sulfur solutions in hydrazine hydrate at various concentrations: A, 0.5079 mM; B, 1.0080 mM; C, 1.5000 mM; D, 1.9850 mM; E, 2.4610 mM (Line '0' is residual current, H_{Hg}=35 cm, pH=ca. 12).

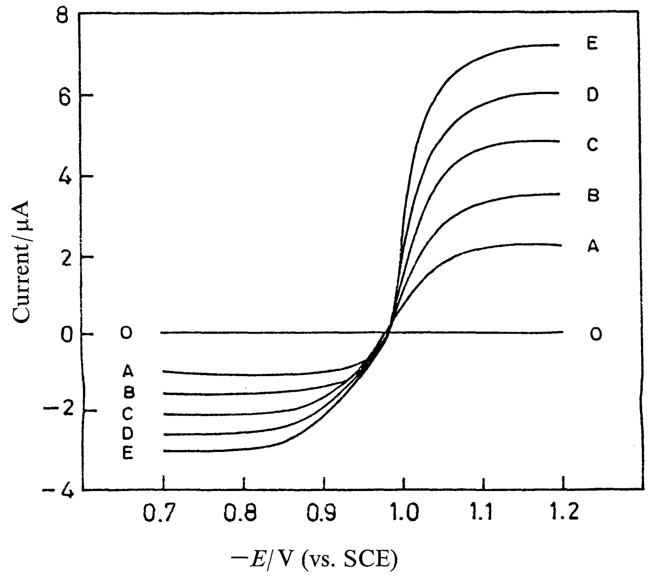

Fig. 2. Polarographic curves of selenium solutions in hydrazine hydrate at various concentrations: A, 0.6640 mM; B, 0.9911 mM; C, 1.3151 mM; D, 1.6358 mM; E, 1.9535 mM (Line '0' is residual current, H_{Hg}=35 cm, pH=ca. 12).

and polyselenide (Se_n^{2-}) ions, when dissolved in hydrazine hydrate.

The typical reaction mechanism proposed by Konopik and Werner,[7–9] and Totopova et al.[11,12] can be utilized in explaining the existence of composite anodic–cathodic waves in both cases. The sulfide (S^{2-}) and polysulphide (S_n^{2-}) ions produced in the solution react with mercury drop according to the following reactions.

$$S^{2-} + Hg \longrightarrow HgS + 2e \qquad (1)$$

$$\begin{array}{l} S_2^{2-} + Hg \longrightarrow HgS + S^{2-} \\ \underline{HgS + 2e \longrightarrow Hg + S^{2-}} \\ S_2^{2-} + 2e \longrightarrow 2S^{2-} \end{array} \qquad (2)$$

and

$$\begin{array}{l} Hg + S \longrightarrow HgS \\ \underline{HgS + 2e \longrightarrow Hg + S^{2-}} \\ S + 2e \longrightarrow S^{2-} \end{array} \qquad (3)$$

The anodic wave can be attributed to the oxidation of mercury by sulfide (S^{2-}) ions, whereas the reduction of polysulfide (S_n^{2-}) ions and elemental sulfur is responsible for the cathodic step. Selenium also revealed a composite anodic–cathodic wave based on the similar mode of reaction mechanism. The values of $E_{1/2}$ for sulfur and selenium solutions taken from the cathodic wave of the polarogram correspond to $E_{1/2}$=−0.78 and −1.03 V vs. SCE, respectively. Similarly, the values reported in Tables 1 and 2 corresponded to the cathodic wave of the respective polarograms. Although there is no other direct evidence to prove this assumption, there appears to have no other options. One of the important advantages of this procedure is that the sulfur and selenium in any oxidation state can be reduced to elemental state and slowly dissolved in the hydrazine hydrate+water solvent. Therefore, this may be utilized as a new and convenient method for the determination of sulfur and selenium present in various analytes.

A plot of concentration vs. diffusion current gave a straight line, and the values calculated for diffusion current constant (I) were fairly constant (Tables 1 and 2) indicating the utility of the data for analytical purposes.

Table 1. Relationship of Diffusion Current with Sulfur Concentration and Values of Diffusion Current Constant

Curve	Sulfur concentration C/mM	Diffusion current i_d/μA	Diffusion current constant, I	Half wave potential $E_{1/2}$/V (vs. SCE)
A	0.5079	1.95	2.2	
B	1.0080	3.90	2.2	
C	1.5000	5.85	2.2	
D	1.9850	7.80	2.3	
E	2.4610	9.75	2.3	−0.78

Table 2. Relationship of Diffusion Current with Selenium Concentration and Values of Diffusion Current Constant

Curve	Selenium concentration C/mM	Diffusion current i_d/μA	Diffusion current constant, I	Half wave potential $E_{1/2}$/V (vs. SCE)
A	0.0640	2.25	2.0	
B	0.9911	3.45	2.0	
C	1.3151	4.80	2.1	
D	1.6358	6.00	2.1	
E	1.9535	7.20	2.1	−1.03

Table 3. Relationship of Diffusion Current with Mercury Height for Sulfur Solution

Mercury height H_{Hg}/cm	Diffusion current i_d/μA	i_d/μA/ $\sqrt{H_{Hg}/cm}$
30	4.05	0.73
40	4.50	0.71
50	5.10	0.72
60	5.40	0.69

Table 4. Relationship of Diffusion Current with Mercury Height for Selenium Solution

Mercury height H_{Hg}/cm	Diffusion current i_d/μA	i_d/μA/ $\sqrt{H_{Hg}/cm}$
35	6.00	1.01
45	6.75	1.00
55	7.50	1.01
65	8.25	1.02

The plot of log i_d vs. log H_{Hg} was a straight line with the slope closer to 0.5 and the values calculated for $i_d/\sqrt{H_{Hg}}$ at different heights of mercury column were fairly constant (Tables 3 and 4) showing that the waves were diffusion controlled in both systems.

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