Polarographic Study of the Reaction between Ce(IV) and Thiocyanate II

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With 2 Figures

Summary

Reaction between Ce(IV) and SCN$^-$ has been studied polarographically. At low concentration of SCN$^-$, Ce(IV) is reduced to Ce(III) with resultant formation of SO_3^{--} or SO_4^{--}, involving the intermediate formation of thiocyanogen free radical. However, in presence of excess of SCN$^-$ it is likely that thiocyanogen or it's polymerised form is formed during the reaction, predominantly.

Alkali thiocyanate has been found susceptible to oxidation by certain reagents[1][2]. DESHMUKH and SANT[3] have claimed that Ce(IV) oxidizes thiocyanate according to the equation:

$$6\,Ce(IV) + SCN^- + 4\,H_2O = 6\,Ce(III) + HSO_4^- + HCN + 6\,H^+.$$
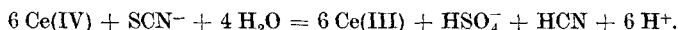
MEITES and coworkers[4] have studied the polarography of Ce(IV) in presence of one molar thiocyanate solution and have observed a cathodic wave with $E_{\frac{1}{2}}$ value of -0.526 volts vs. S. C. E. at $25°$. However they could not propose an electrode reaction.

Authors, in an earlier communication[5] have shown that the cathodic wave of Ce(IV) in sulphuric acid or lithium sulphate medium is suppressed by the addition of 1/4th to 1/6th amount of KCNS. In this paper, they have discussed the polarographic behavio ur of Ce(IV) in presence of excess of potassium thiocyanate and have proposed a mechanism for the reaction between Ce(IV) and thiocyanate.

[1]) I. R. WILSON and G. M. HARRIS, J. Amer. chem. Soc. **82**, 4515 (1960); ibid **83**, 286 (1961).

[2]) V. R. S. RAO and A. R. V. MURTHY, Current Science (India) **30**, No. 5, 176 (1961).

[3]) G. S. DESHMUKH and B. R. SANT, Proc. Ind. Acad. Sci. **37** A, 504 (1953).

[4]) L. MEITES, I. JOHN and W. GRANIER, Anal. Chim. Acta **14**, 482 (1956).

[5]) O. P. AGRAWAL and R. C. KAPOOR, Z. analyt. Ch. (in press).

Material and Apparatus

Ammonium hexanitratocerate, from which the solution of ceric sulphate was prepared[6]), was BDH AnalaR product and potassium thiocyanate was Merk's G. R. Product. All other reagents used were also of analytical grade. Mercury used in dropping mercury electrode (d. m. e.) was first purified chemically by treatment with nitric acid and then distilled twice.

Polarograms were recorded on a Leeds & Northrup Electro-Chemograph Type E. All potentials were measured against a HUME and HARRIS[7]) saturated calomel electrode. Characteristics of the d. m. e. capillary used were:

$m = 1.357$ mg. sec^{-1}; $t = 3.37$ secs. (open circuit); $h = 40$ cms. $m^{2/3} t^{1/6} = 1.501$ mg. $^{2/3} t^{-1/2}$.

pH measurements were done on a Leeds & Northrup pH meter. A general purposes glass electrode was used for all the measurements.

All experiments were done at 30°

Results and Discussion

Qualitative tests indicate that the Ce(IV) is reduced to Ce(III) in presence of KCNS. AGRAWAL and KAPOOR[5]) have shown amperometrcally that when thiocyanate solution is added to a Ce(IV) solution of 1×10^{-3} M or lower concentration, they react in the ratio of 1:6. At higher Ce(IV) concentrations, the ratio of Ce(IV):SCN$^-$ approaches a value of 4:1.
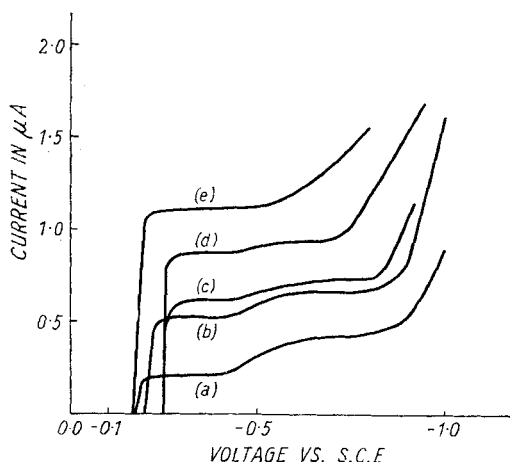

Fig. 1 c-v curwes of 5×10^{-4} M Ce(IV) in (a) 1 M KCNS, (b) 2 M KCNS, (c) 3 M KCNS, (d) 3-5 M KCNS, (e) 1 M KCNS (affer 22 howes exposwre to air)

[6]) A. I. VOGEL, A Text Book of Quantitative Inorganic Analysis, Longmans, London, 1951, p. 302.

[7]) D. N. HUME and W. E. HARRIS, Ind. Eng. Chem., Analyt. Ed. 15, 465 (1943).

Polarograms of ceric sulphate in 1 M KCNS, showed two waves of nearly equal heights. Diffusion region of the first wave started in the region of mercury dissolution and the second wave started in the region of -0.4 volts. The $E_{\frac{1}{2}}$ value of the second wave was found to be -0.49 ± 0.002 volts, which was very near to the $E_{\frac{1}{2}}$ value reported by Meites et al.[4]). On analysis of second wave, a slope of 0.07 volts was observed.

The height of the first wave increased, while that of the second wave decreased, on increasing SCN^- concentration, until in 4.5 M solution, the second wave almost disappeared. However, in 4.5 M KCNS solution, precipitation of cerous sulphate occured. Plot of limiting current of first wave against the concentration of thiocyanate gave a straight line. Observations have been summarised in Table 1.

Table 1

Concn. of thiocyanate (M)	Concn. of Ce(IV) $M \times 10^3$ (C)	i_1 in μA at -0.35 V. (First wave)	i_1/C (First wave)	i_1 in μA at -0.7 V. (Second wave)	i_1/C (Second wave)
0.1	1.9047	—	—	0.05	—
1.0	0.500	0.204	0.408	0.2130	0.426
	0.952	0.450	0.472	0.4425	0.464
	1.363	0.687	0.504	0.6090	0.446
2.0	0.500	0.520	1.040	0.1430	0.286
	0.952	0.990	1.040	0.2970	0.311
	1.363	1.736	1.270	—	—
3.0	0.500	0.620	1.240	0.1200	0.240
	0.952	1.420	1.491	0.2150	0.225
3.5	0.500	0.875	1.750	0.0650	0.130
	0.952	1.630	1.712	0.1320	0.137
4.5	0.475	0.335	0.705	No second wave	
	0.910	0.875	0.961	—	—

Second wave was found to decrease in height with time (Fig. 2). The pink colour of the reaction mixture, containing Ce(IV) and thiocyanate, increased with increasing concentration of thiocyanate. The coloured product seemed to be volatile, since it disappeared after bubbling nitrogen gas through the reaction mixture. A polarogram of a mixture of 5×10^{-4} M Ce(IV) and 1 M KCNS after intensive nitrogen bubbling (when pink colour had faded completely), showed only the first wave. A similar mixture, when kept for two days in inert atmosphere, showed only the first wave and had no pink colour in the solution phase.

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The effect of oxygen on this reaction was also studied. When the polarogram was taken after exposure to air for a considerable time, only one wave was observed with unusually high current, starting in the region of mercury dissolution. The current increased with increase in exposure time to air. Results are summarised in Table 2.
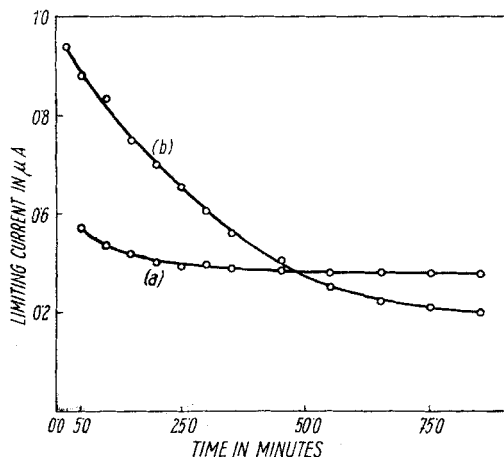

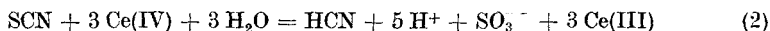Fig. 2. Current — time curwes of 1×10^{-3} M Ce(IV) in 1 M KCNS, (a) First wave, (b) Second wave

Table 2

Polarograms of 5×10^{-4} M Ce(IV) in 1 M KCNS

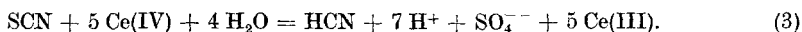| Exposure time in hours.	Limiting current in μA.	Remarks
0.0	0.253	Polarogram taken after keeping the solution for two days in nitrogen atmosphere, during which time, pink colour disappeared
4.0	0.216	Pink colour reappeared but faded on passing nitrogen
22.0	1.107	Pink colour reappeared, but faded on passing nitrogen
73.0	4.390	Pink colour reappeared, but faded on passing nitrogen

Since Ce(IV) is reduced to Ce(III) in presence of excess of exess KCNS, the waves observed, must be due to the reaction products. It is proposed that Ce(IV) and CNS⁻ react in a number of steps, the first step being the formation of thiocyanogen radical:

$$CNS^- + Ce(IV) = Ce(III) + SCN. \qquad (1)$$

The SCN in presence of excess of Ce(IV) may react in two ways:

$$SCN + 3\,Ce(IV) + 3\,H_2O = HCN + 5\,H^+ + SO_3^- + 3\,Ce(III) \tag{2}$$

or

$$SCN + 5\,Ce(IV) + 4\,H_2O = HCN + 7\,H^+ + SO_4^{--} + 5\,Ce(III). \tag{3}$$

It is likely that both SO_4 and SO_3 ions are formed. The presence of SO_3 has actually been detected in the reaction mixture.

If SO_3^{--} was the only product, $Ce(IV) - SCN^-$ ratio should have been $4:1$. In case SO_4^{--} was the only product, ratio should have been $6:1$. If both are produced togeather, an intermediate ratio will result. Results of amperometric titrations[5] indicate that at very dilute concentration of Ce(IV) $(1 \times 10^{-3}\,M$ and below) reaction (3) dominates, while at higher concentrations, reaction (2) dominates.

In presence of excess SCN^-, the stoichiometry of the reaction after (1), is likely to change. It is more likely that the thiocyanogen or it's polymer is formed predominantly:

$$X\,SCN = (SCN)_X. \tag{4}$$

The second wave is very likely due to the reduction of thiocyanogen or its polymer. Thiocyanogen or it's polymer is likely to be volatile. This explains the decrease in height of second wave with time or on prolonged gas bubbling. It is noteworthy that the reaction mixture of excess SCN^- and Ce(IV) assumes pink colour. The intensity of colour increases on increasing SCN^- concentration. It has been reported that polymerised form of thiocyanogen possesses a brick red colour[8].

The reaction mixture of Ce(IV) and excess SCN^- showed oxidizing properties. It liberated iodine from iodide solution, although no Ce(IV) was present in the solution. This is also characteristic reaction of thiocyanogen[8]. Polarograms taken after adding successive amounts of potassium iodide showed gradual decrease and ultimate disappearance of the second wave.

The volatile pink colour could be collected on a filter paper which was used to cover the vessel, containing the reaction mixture. The washing of the filter paper gave a white precipitate of CN^- or SCN^- with silver salt. These are the normal hydrolysis products of thiocyanogen[8].

Nature of the first wave is not clear, but it is certainly not due to the reduction of Ce(IV) to Ce(III).

[8] P. Walden and L. F. Audrieth, Chem. Rev. 5, 339 (1928).

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