Asian Journal of Chemistry Vol. 14, No. 1 (2002), 400–404

Polarographic Behaviour of Dy(III) on Mercury Drop Cathode†

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The nature and behaviour of reduction of Dy(III) on a mercury drop cathode has been extensively investigated. It was observed that Dy(III) gave a single step well defined reduction wave in KCl in the entire range of pH 2.1 to 3.4. Above this pH value aquo ions have a predominant role. The reduction has been found to be diffusion controlled and variation in wave height and concentration was linear. The effect of pH, supporting electrolyte concentration and Dy(III) concentration have been observed. The polarographic reduction of Dy(III) is abnormal. It produces reversible, quasireversible and irreversible reduction wave under distinct experimental conditions. The log plot analysis of each of the polarograms revealed that Dy(III) produces a reversible three electron wave at pH 2.6 to 0.5 mole dm^{-3} KCl and 0.01% gelatin $E_{1/2}$, i_d and $E_{3/4} - E_{1/4}$ values are −1.72 V, 3.9 and 19 mV respectively.

Key words: Polarography, Dy(III), mercury drop, cathode.

INTRODUCTION

Comparatively less is known about the polarographic behaviour of dysprosium(III)[1–4]. In continuation of our work on the investigation of rare earths[5, 6], the present paper deals with reduction of Dy(III) on a mercury drop cathode under the different experimental conditions.

EXPERIMENTAL

All the chemicals used were of analytical grade (AR). Dy(III) solution was prepared by dissolving a calculated quantity of Dy_2O_3 in hydrochloric acid and its subsequent evaporation to dryness and finally the residue was extracted in double distilled water. The metal solution was standardized by standard method[7]. Potassium chloride 2.0 M and gelatin 0.1% were prepared to be used as supporting electrolyte and maximum suppressor respectively. An automatic pen recording polarograph CL-25D with a recorder LR-101P was used to record the polarogram. The capillary characteristics $m^{2/3}t^{1/6} = 1.23$ $mg^{2/3}$ $S^{-1/2}$. The Systronics pH meter

†This work was presented at the 17th Annual Conference of Indian Council of Chemists, University of Madras, Chennai, India on 26 November 1998.

model was used for measuring the pH of test solution. All the measurements were carried out at 25 ± 1°C The test solution was cleared by bubbling hydrogen gas before recording the polarogram. Jones reductor was used for reducing the trivalent dysprosium ion.

RESULTS AND DISCUSSION

A series of polarograms were recorded to study the effect of pH on the polarographic reduction of Dy(III) and kinetics of electrode process. The reduction was found to be diffusion controlled as shown in Fig. 1. A typical polarogram

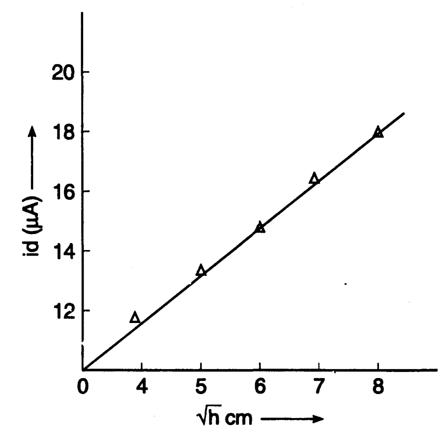

Fig. 1. Diffusion controlled wave of Dy(III) i_d *vs.* $\sqrt{h}$ plot

of 2 mM Dy(III) ion and 0.4 M KCl at pH 2.6 is shown in Fig. 2 (Table-1). At pH ≤ 2.0 the shape of the wave was distorted and at pH ≥ 3.5 no wave was obtained. The log plot slope suggests the reversible reduction of Dy(III) at pH

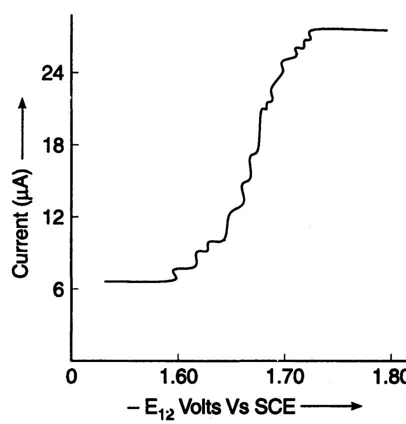

Fig. 2. A typical polarogram of Dy(III) at pH 2.6

TABLE-1
EFFECT OF pH ON POLAROGRAM OF Dy(III)

Dy(III) = 2.0 mM, μ = 0.4(KCl), Gelatin = 0.01%

S. No.	pH	$-E_{1/2}$ V *vs.* SCE	i_d (μA)	I	$E_{3/4} - E_{1/4}$	$-E_{1/2}$ V *vs.* SCE	$K_s \times 10^3$ cm s^{-1}
1.	≤ 2.0	Distorted wave					
2.	2.1	1.81	15.1	3.53	29	1.770	5.04
3.	2.4	1.76	15.4	3.60	27	1.738	7.78
4.	2.6	1.72	16.7	3.90	19	1.720	*
5.	2.9	1.68	16.0	3.74	23	1.660	4.58
6.	3.4	1.65	15.2	3.50	27	1.642	1.00
7.	≥ 3.5	No wave					

*D.C. polarography cannot be employed to calculate K_s for reversible process.

2.6. However, all other waves were found to be quasireversible. Gelling's treatment[8] has been used to evaluate $E^r_{1/2}$ and kinetic parameters. The values of K_s and α suggest quasireversible nature of the reduction wave at other pH value. The effect of supporting electrolyte concentration on the polarogram of Dy(III) are presented in Table-2. The optimum condition for the reversibility of wave at 0.4 M concentration and the effect of Dy(III) on the polarogram of Dy(III) are also presented in Table-3. Jones' reductor[9] was used to reduce Dy(III) and oxidation wave of the reduced form was recorded. The $E_{1/2}$ values of oxidation and reduction are evaluated from Fig. 3.

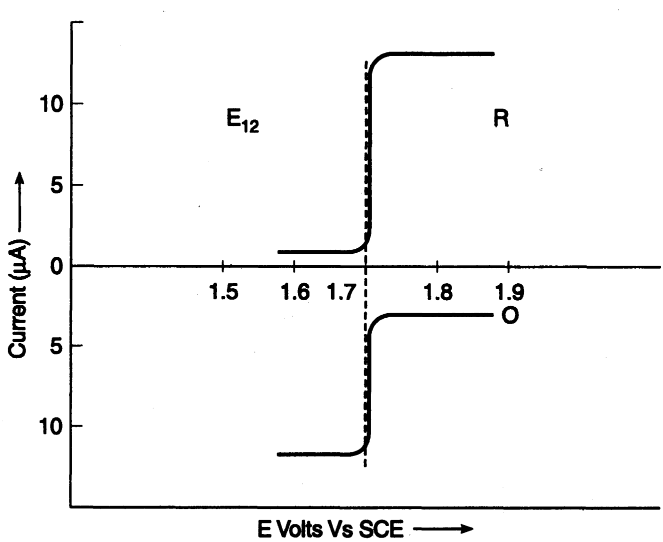

Fig. 3. Redox wave of 1 mM Dy(III) at pH 2.6 in 0.4 M KCl

The following electrode may follow in this reduction process:

$$Dy^{3+} + 3e^- \rightleftharpoons Dy(Hg) \qquad \text{[at pH 2.6]}$$

The number of electrons (n) in the above reduction process was determined by millicoulometric method of Deveries and Kroon[10] and was found to be n = 3.

TABLE-2
EFFECT OF KCl CONCENTRATION ON POLAROGRAM OF Dy(III)

Dy(III) = 2.0 mM, μ = 2.6 + 0.02, Gelatin = 0.002%

S. No.	Concentration of KCl (molar)	$-E_{1/2}$ V *vs.* SCE	i_d (μA)	I	$E_{3/4} - E_{1/4}$	α na	K^0_{th} cm s^{-1}
1.	0.1	1.725	14.3	3.36	47	1.590	2.38×10^{-42}
2.	0.2	1.710	14.7	3.45	40	1.310	5.80×10^{-38}
3.	0.3	1.680	15.3	3.59	32	1.175	3.85×10^{-19}
4.	0.4	1.720	16.6	3.89	20	0.985*	—
5.	0.6	1.705	16.2	3.78	25	1.113	3.50×10^{-24}
6.	0.8	1.715	15.2	3.55	30	1.295	7.69×10^{-23}
7.	1.0	1.730	14.5	3.40	35	1.426	2.54×10^{-38}

*Wave calculated from $E_{3/4} - E_{1/4}$ value.

TABLE-3
EFFECT OF Dy(III) CONCENTRATION ON POLAROGRAM OF Dy(III)

μ = 0.4, Gelatin = 0.002%, pH = 2.6 ± 0.02

S. No.	Concentration of Dy(III) (mM)	$-E_{1/2}$ V *vs.* SCE	i_d (μA)	I	log plot slope
1.	1	1.720	8.41	3.92	0.020
2.	2	1.718	16.70	3.90	0.020
3.	3	1.715	25.00	3.91	0.019
4.	4	1.717	33.90	3.94	0.019
5.	6	1.715	49.50	3.87	0.020
6.	8	1.717	66.10	3.89	0.020
7.	10	1.720	83.00	3.89	0.018
8.	15	1.715	125.60	3.91	0.019

ACKNOWLEDGEMENT

One of the authors (SCL) is thankful to Dr. Kamlakar Singh, Joint Secretary and Head, UGC-CRO, Bhopal for financial assistance.

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(*Received*: 24 September 2001; *Accepted*: 5 November 2001) AJC-2510