Asian Journal of Chemistry Vol. 12, No. 2 (2000), 561–564

Polarographic Studies on Interaction of 2-Aminoquinoxaline with Cd(II) in Aqueous Medium

P.L. PRATIHAR, R.K. LOHIYA, R.V. SINGH and S.K. MUKHERJI*
Department of Chemistry
University of Rajasthan, Jaipur-302 004, India

The effect of ionic concentration of the medium on the complexation has been studied with the help of two different ionic strengths ($\mu = 0.10$ and $\mu = 0.30$) which were maintained by adding requisite quantities of $NaClO_4$. All other conditions were kept the same at two different ionic strengths. The shift of half wave potentials towards a more negative value with increasing concentration of 2-amino quinoxaline (AQ) indicated complex formation. The diffusion current was found to decrease regularly with the increase of 2-amino quinoxaline concentration.

INTRODUCTION

Metal complexes of heterocyclic compounds with nitrogen as tne netero atom have been studied polarographically and through other methods by several workers. All the elements of the periodic table are amenable to polarography. Concentrations as small as 10^{-9} M can tell the presence of an element. The electrode kinetics and mechanism of the oxidation/reduction process can be determined from the current-voltage curves of the simple and complexes metal ion in aqueous media. Polarography has proved is immense importance in the study of coordination compounds in solutions. The traces of metals present in the alloys mark the physical properties of an alloy to a remarkable extent. Such traces of elements have been determined by polarographic methods Chromium in steel, alkali metals, aluminium, cadmium, zinc, lead and copper in zinc ores are a few such examples. Thus polarography plays an important role in metallurgy. Polarographic studies of organic compounds with conjugated system containing quinonoid structures, *e.g.*, quinone and hydroquinone have also been carried out. The reduction waves of the various aldehydes and heterocyclic compounds have also been investigated. In food industry polarographic determination of the origin and quality of the honey, lead in tinned food, aldehyde in spirit, ascorbic acid in fruits and vegetables and iodine in table-salts are a few examples which prove its superiority over other electroanalytical methods.

Actinides, the radioactive elements, have also been studied polarographically which are now-a-days a source of nuclear energy. Agricultural archaeology, polymer chemistry, explosives, colloids and surfactants are the other fields where polarographic technique has been well established. The present work comprises of electro-chemical behaviour of Cd(II) with 2-amino quinoxaline which has two nitrogen atoms in the ring, at dropping mercury electrode.

EXPERIMENTAL

The polarograms were obtained with a manual set up. The dropping mercury electrode has the following characteristics: m = 1.65 mg per sec, t = 2.98 sec (open circuit). Solution of 2-amino quinoxaline in doubly distilled weter served as the complexing agent. Solution of Cd(II) was prepared from nitrate and standardised by conventional method[3]. Sodium perchlorate solution was used to maintain constant ionic strength at 0.1%. Solution containing 0.5 mM of Cd(II) of various concentrations of 2-amino quinoxaline (AQ) were prepared from the stock solutions.

RESULTS AND DISCUSSION

The plots of log $i/i_d - i$ *vs.* $E_{d.e.}$ were linear with a slope of 31 ± 2 mv, indicating the reversibility of the reduction in both the cases. The plots of $E_{1/2}$ *vs.* – log Cx were linear in each ease (Fig. 1a). The value of 'p' obtained from Defort and Humes treatments[4] has been applied to determine the stability constants of the complexes formed. The plot of $F_0([X])$ *vs.* Cx is a smooth curve,

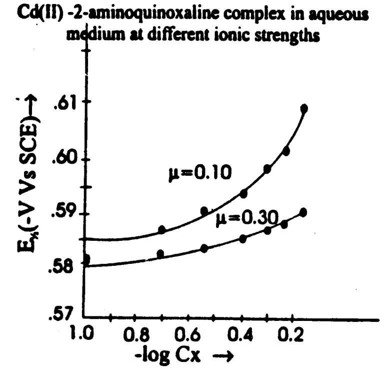

Fig. 1a Plots of $E_{1/2}$ *vs.* –log Cx

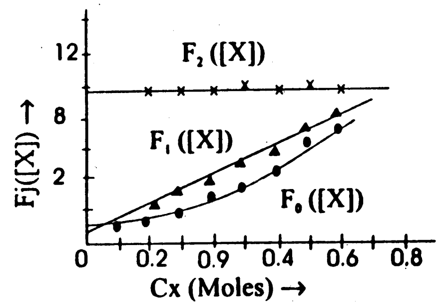

Fig. 1b Plots of $F_j(X)$ *vs.* Cx at μ = 0.10

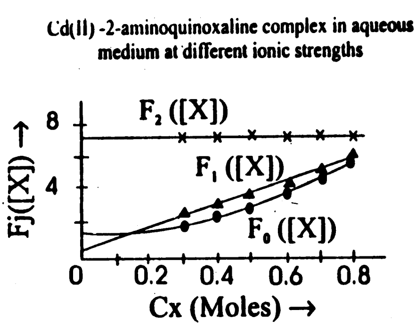

Fig. 1c Plots of $F_j([X])$ *vs.* Cx at μ = 0.30

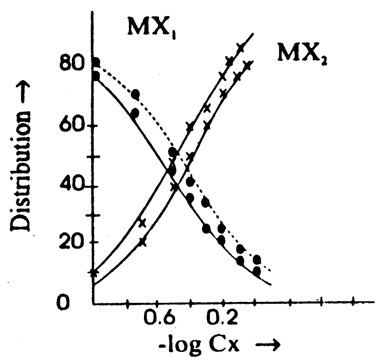

Fig. 1d Distribution of various complex species at μ = 0.10 (___) and μ = 0.30 (-----)

$F_1([X])$ *vs.* Cx a straight line with a slope and $F_2([X])$ *vs.* Cx a straight line parallel to x-axis (Fig. 1b and 1c) in both the cases. The polarographic characteristics and $F_j([X])$ values have been given in Tables 1 and 2. Two complex species $[Cd(2\text{-}AQ)]^{2+}$ and $[Cd(2\text{-}AQ)_2]^{2+}$, having the formation constants $\beta_1 = 0.40$, $\beta_2 = 9.60$ at $\mu = 0.10$ and $\beta_1 = 0.40$, $\beta_2 = 6.60$ at $\mu = 0.30$ were found to be present in each cases. This proves the validity of Deford and Hume method for very weak complexes.

The first 1 : 1 complex formed in both the cases is very weak with the same value of stability constant but the second 1 : 2 complex formed has higher value of stability constant at lower ionic strength. It is, therefore, obvious that the stability of the complexes decreases with increase in the ionic strength. The precentage compositions of the various complex species in both the cases are presented in Fig. 1d. The formation constants have also been evaluated by Mihailov's method[5]. This involves the calculation of the constant 'a' for various combinations of ligand concentrations and constant 'A' at different ligand concentrations. The values of 'a' and 'A' have been recorded in Table 3 and the values of the formation constants have been calculated using the relation $\beta_n = A \cdot a^n/n!$, where a and A are Mihailov constants

TABLE-1

POLAROGRAPHIC CHARACTERRISTICS AND F_j ([X]) FUNCTIONS FOR Cd(II)-2-AMINO QUINOXALINE SYSTEM AT 30°C

[M] = 0.5 mM, μ = 0.10 [$NaClO_4$]

Cx (moles)	i_d (divs.)	$E_{1/2}$ (–V *vs.* S.C.E.)	F_0([X])	F_1([X])	F_2([X])
0.00	71	0.5810	–	–	–
0.10	66	0.5850	1.136	–	–
0.20	63	0.5880	1.464	2.32	9.60
0.30	62	0.5910	1.993	3.31	9.73
0.40	59	0.5945	2.704	4.26	9.66
0.50	58	0.5985	3.675	5.35	9.90
0.60	57	0.6062	4.696	6.16	9.60
0.70	56	0.6100	6.187	7.41	10.02
0.80	54	0.6144	7.472	8.09	9.62

TABLE-2

POLAROGRAPHIC CHARACTERISTICS AND F_j ([X]) FUNCTION FOR Cd(II)-2-AMINO QUINOXALINE SYSTEM AT 30°C

[M] = 0.5 mM, μ = 0.30[$NaClO_4$]

Cx (moles)	i_d (divs.)	$E_{1/2}$ (–V *vs.* S.C.E.)	F_0([X])	F_1([X])	F_2([X])
0.00	70.0	0.5722	–	–	–
0.10	67.0	0.5799	–	–	–
0.20	65.0	0.5810	–	–	–
0.30	63.0	0.5830	1.744	2.48	6.96
0.40	62.0	0.5852	2.216	3.04	6.60
0.50	61.0	0.5871	2.810	3.62	6.44
0.60	60.5	0.5894	3.562	4.27	6.45
0.70	57.5	0.5917	4.472	4.96	6.52
0.80	55.5	0.5953	5.544	5.68	6.60

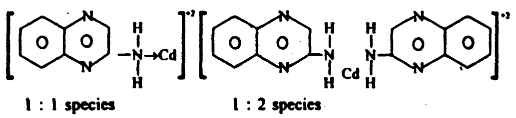

Fig. 2

TABLE-3
MEHAILOV CONSTANTS FOR Cd(II)-2-AMINO QUINOXALINE COMPLEXES AT 30*symbol*C

Combination of 2-Amino quinoxaline concentration (moles)	'a'	Concentration of 2-aminoquinoxaline (moles)	'A'
0.10	1.125*	0.10	0.076
0.20			
0.20	13.896	0.20	0.041
0.30			
0.30	64.418*	0.30	0.049
0.40			
0.40	17.292	0.40	0.052
0.50			
0.50	14.261	0.50	0.058
0.60			
0.20	21.884	0.70	0.060
0.40			
0.10	13.960	0.80	0.058
0.40	Average 'a' = 16.250		Average 'A' = 0.056

The values marked with asteriks being exceptionally deviated are excluded from average.

The data of formation constants as calculated by the two methods are given below:

	β_1	β_2
DeFord-Hume method	0.40	9.60
Mihailov method	0.90	8.05

The probable structures of the complexes with divalent cadmium metal may be proposed as shown in Fig. 2.

ACKNOWLEDGEMENT

One of the authors (P.L. Pratihar) is thankful to the Head of the Chemistry Department, Rajasthan University, Jaipur for providing necessary facilities for completing this piece of work.

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(*Received*: 19 November 1999; *Accepted*: 14 December 1999) AJC-1948