POLAROGRAPHIC STUDY OF COPPER WITH δ - VALEROLACTAM AND ITS ANALYTICAL APPLICATIONS

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The polarographic behaviour of copper(II) has been studied in various complexing agents. Less attention is paid towards the thermodynamics of complex formation which has the potentiality to provide good information about complex phenomenon. The present work deals with the determination of the thermodynamic parameters and the stability constants of the complexes formed by copper with δ-valerolactam at different temperatures i.e. 303, 313 and 323 K. It is found that in most of these cases mixed electrolytes have been used and in certain cases a maximum supressor is also required. Thus, the sensitivity and accuracy in the measurement of the diffusion-current tend to decrease. With the use of δ -valerolactam there is no need of an auxilary electrolyte and a maximum supressor.

EXPERIMENTAL

The stock solution of δ -valerolactam (Fluka, GR grade) was prepared in double distilled water. A solution of copper was prepared by dissolving copper sulphate (BDH, A.R.) in distilled water and standardized [1]. pH of the solutions were adjusted with aqueous solutions of ammonia and perchloric acid. pH was measured with Elico pH meter. Ionic strength was maintained constant with potassium nitrate.

A balancing type [2] manual polarograph was set up to obtain current - potential curves. All polarographic measurements were carried out in a water thermostat (accuracy ± 0.1 C). Pure nitrogen was used for deaeration. The dme had the following characteristics: m = 2.90 mg/s, t = 2.9 s at h_{corr} = 58.7 cm in 0.1 M potassium nitrate solution. SCE was the reference electrode. The number of electrons (n) involved in the reduction process was determined by the millicoulometric method of Devries and Kroon [3].

RESULTS AND DISCUSSION

A number of polarograms were recorded, keeping other factors constant. A well defined wave was obtained in the pH range 3.0-6.5. Below pH 3.0 the lower plateau was distorted and at higher pH a turbidity appeared, resulting in a decrease of the current. It was observed that the negative shift in $E_{1/2}$ was maximum at pH 6.0 and hence this pH was chosen for studying the complex formation between copper(II) and δ-valerolactam.

Polarograms over the concentration range of Cu(II), 1.0 - 3.5 mM were drawn at optimum conditions. The diffusion currents were measured by the extrapolation method. The value of diffusion current constant (I) was calculated using Ilkovic equation, $I = i_d / cm^{2/3} t^{1/6}$, and found to be 2.82 which is constant over the concentration range of 1.0-3.5 mM. Therefore, the polarographic results are used for the quantitative determination of copper. Ten replicate determinations of a sample solution containing 1 mM of Cu(II) gave a mean diffusion current of 6.85 μA with a standard deviation of 0.085 and a relative standard deviation of 0.96%.

The linear dependence of the i_d on $\sqrt{h}$ indicates that the rate of reduction of copper ion is diffusion-controlled. It is also supported by the fact that the temperature coefficient of the diffusion current is 1.1 percent per

TABLE 1

POLAROGRAPHIC CHARACTERISTICS AND F_j (X) VALUES FOR COPPER δ VALEROLACTAM SYSTEM

C_x [M]	$-E_{1/2}$ vs SCE (V)	i_d (μ A)	F_0 (x)	F_1 (x)	F_2 (x)
0.00	0.245	7.0	1.00	-	-
0.05	0.249	6.90	1.38	7.52	-
0.10	0.253	6.85	1.88	8.80	78.00
0.15	0.258	6.82	2.76	11.75	71.69
0.20	0.263	6.75	4.09	15.42	72.15
0.25	0.268	6.71	6.02	20.06	76.25
0.30	0.272	6.66	8.22	24.27	76.89
0.35	0.275	6.60	10.42	26.93	74.08
0.40	0.278	6.58	13.14	30.35	73.38
0.45	0.281	6.54	16.62	34.70	74.89
0.50	0.284	6.51	20.98	39.96	71.91
0.60	0.287	6.48	20.58	45.97	74.95

$\beta_1 = 7.5 \pm 1$ $\beta_2 = 70.0 \pm 2.$

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degree. The plots of log $[i/(i_d-i)]$ vs E were found to be linear with a slope of the order (32 ± 2) mV showing the reversibility of the reduction. The value of n was found to be 2 at pH 6.0. A negative shift in $E_{1/2}$ values with increasing concentration of δ -valerolactam indicates the formation of complexes.

A plot of $E_{1/2}$ vs log C_x (where C_x is the total ligand concentration) was found to be a smooth curve, showing the formation of more than one complex. Copper is found to form 1:1 and 1:2 complexes with the values of the constants β_1 = 7.5 ± 1 and β_2 = 70.0 ± 2 at 303°K. Owing to the weakly basic nature of δ-valerolactam, strong complexation is not expected. But it was sufficiently distinct to indicate complex formation and to allow quantitative assessment of stability constants. (Table 1). The stability constants obtained were used to calculate [4] various thermodynamic parameters (Table 2) The percentage distribution of various complex species present at different ligand concentrations has been presented in Fig 1.

The stability of complex changes with the change in temperature, depending upon the thermodynamics of complexation. The stability of complexes is found to be enhanced by an increase in temperature, showing the endothermic nature of the reduction. The values of thermodynamic parameters ΔG, ΔH, and ΔS have been obtained.

General Procedure for the Determination of Copper(II)

The polarograms of copper at various concentrations in 0.1 M δ-valerolactam at pH 6.0 gave a linear calibration curve. Polarogram of the solution containing the metal in unknown concentration was recorded under identical conditions. Concentration of the copper in the solution was determined from the calibration curve (Table 3).

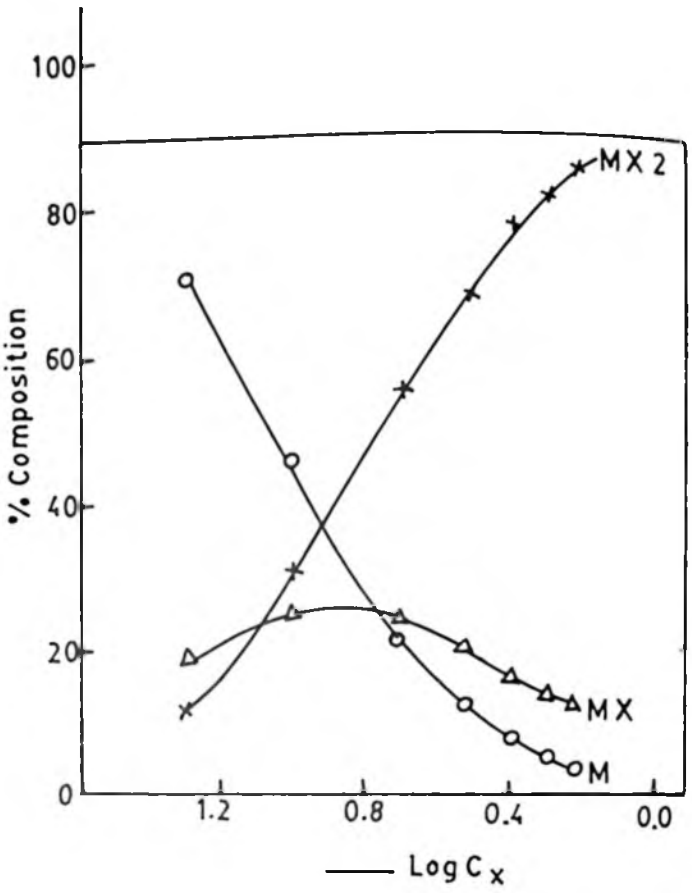


Fig. 1 Distribution diagram for Cu(II)- δ - valerolactam system

Determination of Copper in Alloys

A 0.1 g of the alloy was dissolved in concentrated hydrochloric acid in the presence of a few drops of nitric acid. The solution was heated to reduce the volume to about 5 ml. After cooling, 10 ml of hydrochloric acid were added and diluted to 100 ml in a standard flask with distilled water. An aliquot of this solution was taken and copper was determined as described above. The results are given in Table 4.

TABLE 2

STABILITY CONSTANT AT 303°, 313° AND 323° K AND THERMODYNAMIC FUNCTIONS Cu(II) - 1.0 mM, μ - 0.1 M KNO_3, pH = 6.0

Complex	log K			-Δf° Kcal mol^{-1}			ΔH°	ΔS°	
	303° K	313° K	323° K	303° K	313° K	323° K	Kcal mol^{-1}	Cal deg^{-1}	mol^{-1}
Cu(δ -valerolactam)	0.86	0.93	1.00	1.20	1.34	1.49	3.39	4.08	
Cu(δ -valerolactam)$_2$	1.85	2.05	2.29	2.58	2.96	3.41	9.16	11.22	

TABLE 3

POLAROGRAPHIC DETERMINATION OF COPPER WITH δ - VALEROLACTAM
SENSITIVITY = 1/50; [ligand] = 0.1M; pH 6.0

Amount taken (mg)	Amount found* (mg)	Error (%)
0.565	0.560	-0.85
0.980	0.972	-0.82
1.465	1.454	-0.75
2.084	2.105	+1.01
2.685	2.660	-0.93

* Average of ten replicate determinations.

Interferences.

The effect of acetate, oxalate, formate, nitrate, salicylate, citrate and sulphate was studied on the polarograms of copper (1 mM). In all the cases, the $E_{1/2}$ remained almost constant. Among the metal ions studied, Ti(IV), W(VI), Se(IV), Fe(III), Al(III), Sc(VI), Cr(III) and alkaline earth metals like Ca(II), Mg(II), Sr(II) and Ba(II) were not reduced under these conditions and can be tolerated upto 10 fold-excess. The metal ions such as Ni(II), Zn(II), Cd(II), Pb(II), As(III), V(V), Te(IV), Sn(IV), and Mn(II) were reduced at higher potentials and can be tolerated up to 3 fold-excess.

TABLE 4

DETERMINATION OF COPPER IN ALLOYS
δ-VALEROLACTAM - 0.1 M, pH = 6.0, SENSITIVITY = 1/50

Alloy	Certified composition (%)	Amount of copper		Error (%)
		Taken (mg)	Found* (mg)	
Monal wire	Ni:66.24, Cu:37.18 Fe: 1.18, Mn: 1.08 Mg:0.093, Al:0.093 Si:0.083, C :0.083 S :0.0033	2.755	2.735	-0.73
Brass No.42	Cu:58.18, Pb:2.86 Zn:38.95, Fe:0.09 Sn:0.12	3.060	3.085	+0.82
Mallory No.3	Cu:19.2, Cr:80.8	2.245	2.224	-0.94
Steel 33d (NBS)	Cu:1.54, Fe:90.3 Ni:2.38, Cr:0.32 C :2.3, Si:1.03 Mn:0.68	3.545	3.515	-0.85

* Average of ten replicate determinations

REFERENCES

1. A.I. Vogel, *Text Book of Quantitative Inorganic Analysis* Longmans, London (1969).
2. B.K. Puri and Ashok Kumar, *Analyst*, 108 (1983) 1345 I.M. Kolthoff and J.J. Lingane, *Polarography* Interscience New York (1946).
3. T. De Vries and J.L. Kroon, *J. Am. Chem. Soc.*, 75 (1953) 2484; B.K. Puri and Ashok Kumar, *Zh. Analit Khim*, 39 (1984) 360.
4. J.K. Gupta and C.M. Gupta, *Indian J. Chem.*, 6 (1968) 50; B.K. Puri, Ashok Kumar and A.L.J. Rao, *J. Electrochem. Soc., India*, 30 (1985) 49.

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