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Electrochemical Studies of Copper(II) Complexes with Oxoglutarate at Dropping Mercury Electrode in Aqueous Medium

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The composition and stability constants of complexes formed by copper(II) with oxoglutarate have been investigated in aqueous medium. The complexes with metal to ligand ratio as 1:1, 1:2, 1:3 have been reported at pH 6.8. The values of formation constants log β_1 = 2.66, log β_2 = 3.34, log β_3 = 4.37 at 303 K and log β_1 = 2.14, log β_2 = 3.32, log β_3 = 3.39 at 313 K were calculated by DeFord and Hume method. The mathematical Mihailov method was also used. Thermodynamic functions and kinetic parameters have been determined.

Key Words: Electrochemistry, Copper(II) complexes, Oxoglutarate, Dropping mercury electrode.

INTRODUCTION

Polarographic behaviour of divalent metal ion with acetate[1], glycinate[2], isovalerate[3], 1,3-diamonopropane[4] and oxalate[5] has been studied and determined stability constants in aqueous medium. Manhan[6] and others[7-13] studied some mixed ligand complexes in non-aqueous medium. Sarkar and Kruck[14,15] have reported the isolation of Cu(II) complexes with threonine and theonine from normal human serum. Mixed ligand complexes of Cu(II), Zn(II), Ni(II) and Co(II) with wide range of ligands have also been studied polarographically in aqueous media[16-23]. Electrokinetics of Zn(II) and Ni(II) with α-amino acids have been studied by Verma *et al.*[24,25]. The importance of such compounds has been recognized in biochemical and pharmaceutical field and attracting wide attention in different fields of research. However, less attention has been paid to determine the kinetic parameters (K_s and λ) of an electrochemical reaction, taking into account the slow rates of mass-transfer and charge-transfer phenomenon, the Gellings method[26] has been used to determine the kinetic parameters.

The present paper deals with the determination of kinetic parametrs, composition, the overall formation constants of the resulting complexes in aqueous medium graphically by DeFord-Hume method[27]. The overall formation constants of the complexes have also been calculated using mathematical method of Mihailov[28].

EXPERIMENTAL

Reagents grades chemicals were used. The solutions of copper(II) nitrate was prepared in double distilled water. The sodium salt of oxoglutaric acid was prepared, pH-controlled constant at 6.8-6.9. The ionic strength was kept contant by adding requisite amount of potassium nitrate. Triton-X-100 was used as maxima suppressor. A manual set up was used for taking polarograms. The dropping mercury electrode had the following characteristics: m = 1.247 mg/sec and t = 4.19 sec in open circuit and the height of the mercury column was 50 cm. A H-type cell saturated with potassium chloride agar-agar bridge was used. The temperature was kept constant at 303-313 K with the help of Haake type ultra thermostat. Purified nitrogen was used for deaeration.

RESULTS AND DISCUSSION

Solutions containing 5×10^{-4} M Cu(II) and 0.025, 0.05 and 0.25 M sodium oxoglutarate were prepared and the requisite amount of potassium nitate was added to maintain a constant ionic strength ($\mu = 0.5$). In each case a single well defined reduction wave appeared, whose half wave potential shifted towards more negative values and the diffusion current decreased with increasing concentration of oxoglutarate. The above observations indicate the occurrence of complex formation between Cu(II) and oxoglutarate. The plots of log i/i_d-i against $E_{d.e}$ were linear and the slope was about 33 + 0.05 mV. The plots of i_d against $h^{½}$ (h = effective height of the mercury column after applying back pressure correction) were straight lines which passed through the origin.

Furthermore, plots of i_d against concentration of Cu(II) were linear. This shows that although the reduction is diffusion controlled, it is not a reversible process. The reversible half wave potential $E^r_{½}$ was obtained from the observed $E_{½}$ by a method developed by Gellings.

We can determine $E^r_{½}$ (reversible half wave potential) by plotting against i and by extrapolating it to i = 0. The standard rate constant can be calculated by the following procedure:

$$\frac{i}{i_d} = \frac{1}{1+e} \cdot \frac{\wedge \sqrt{t_d}}{1.13 + \lambda t_d} \tag{1}$$

where

$$\wedge \frac{K_s f_o f_R}{(D_o D_R)^{1/2}} (e^{-\alpha\xi} - e^{-\alpha\xi}) \tag{2}$$

and f_o and f_R are the activity coefficients of oxidized and reduced forms, respectively.

$$\xi = \frac{nF}{RT}(E - E^r_{1/2}) \tag{3}$$

and $\alpha + \beta = 1$ can be represented as

$$\ln \frac{(i_d - i)}{i} = (\xi - \ln Z) \tag{4}$$

Eqn. 4 can be written as

$$Z = \text{antilog}\frac{nF}{2.303RT}(E^{r}_{1/2} - E) - \log\frac{i}{i_d - i} \qquad (5)$$

and
$$\ln(Z-1) = \ln\frac{1.13}{i_d}(1-\alpha)^{\xi} \qquad (6)$$

where Z can be considered as a measure of the degree of irreversibility. The values of Z at various potentials are calculated from the experimental data. Eqn. 6 can be written as:

$$\log(Z-1) = \log\frac{1.13}{i_d} - \frac{(1-\alpha)nF}{2.303RT}(E - E^{r}_{1/2}) \qquad (7)$$

Eqn. 7 shows that the plots of log (Z-1) against (E-$E^{r}_{½}$) should give a straight line. From the slope and intercept of this plot, the values of α, ∧ and K_s are calculated.

Having obtained $E^{r}_{½}$ by plotting $E - \left(\frac{(RT)}{nf}\ln\frac{(i_d - i)}{i}\right)$ against i and extrapolating it to i = o. The values of K_s and ∧ were determined from the intercept and slope of a plot of log (Z-1) against (E - $E^{r}_{½}$). Kinetic parameters, reversible half-wave potential and diffusion coefficients values of Cu(II) as function of ligand concentration are recorded in Tables 1 and 2.

TABLE-1
POLAROGRAPHIC MEASUREMETNS AND $F_j(X)$ FUNCTIONS OF Cu(II)-OXOGLUTARATE SYSTEM AT 303 K

Oxoglutarate conc. moles	$E^{r}_{½}$ (-V *vs.* S.C.E.)	i_d (division)	$F_o(X)$	$F_1(X)$	$F_2(X)$	$F_3(X) \times 10^2$
0.000	–0.0188	43	–	–	–	–
0.025	0.0125	40	11.80	435.20	1866.66	–
0.050	0.0250	40	31.00	600.00	4120.00	–
0.075	0.0330	39	58.72	769.60	4600.00	256
0.100	0.0390	39	93.07	920.70	5576.00	240
0.125	0.0445	38	145.70	1157.60	5693.33	270
0.150	0.0485	38	198.10	1314.00	6365.71	232
0.150	0.0480	38	198.10	1314.00	6365.71	232
0.175	0.0525	37	276.60	1574.85	6620.00	238
0.200	0.0555	36	357.80	1784.00	7740.00	221
0.225	0.0590	35	481.20	2134.22	–	232
0.250	0.0635	34	700.00	2796.00	9344.00	285

Complexation between copper(II) and oxoglutarate ions was confirmed by the more negative shift in $E^{r}_{½}$ and decrease in i_d of copper(II). $E^{r}_{½}$ values of Cu(II) at various ligand concentration in solutions were determined by the method discussed above. $E^{r}_{½}$ values for different ligand concentrations were put in the expression of $F_o(X)$ giving rise to corresponding $F_o(X)$ values. $F_o(X)$ values plotted against C_x have smooth curve indicating the presence of two or more than two complexes. Further analysis of plots of $F_3(X)$ values *versus* C_x showed the presence of three consecutive complexes in solution as the plot of $F_3(X)$ *versus* C_x was straight line parallel to the C_x axis at 303-313 K. The polarographic measurements are recorded in Tables 3 and 4 and the plots of F_j9x) *versus* C_x are shown in Figs. 1 and 2 at 303-313 K, respectively.

TABLE-2
POLAROGRAPHIC MEASUREMETNS AND $F_j(X)$ FUNCTIONS OF Cu(II)-OXOGLUTARATE SYSTEM AT 313 K

Oxoglutarate conc. moles	$E^r_{½}$ (-V Vs S.C.E.)	i_d (division)	$F_o(X)$	$F_1(X)$	$F_2(X)$	$F_3(X) \times 10^2$
0.000	-0.0170	48	–	–	–	–
0.025	0.0090	45	7.3520	252.800	4480.00	95200.00
0.050	0.0190	45	15.4500	289.000	2800.00	14000.00
0.075	0.0275	44	29.7000	382.666	3235.00	15133.00
0.100	0.0335	43	50.5800	495.800	3200.00	11000.00
0.125	0.0395	43	78.9800	600.000	3680.00	12640.00
0.150	0.0440	42	106.0000	700.000	3733.33	10886.66
0.175	0.0480	42	142.7000	809.714	3822.85	9840.00
0.200	0.0510	41	182.8000	909.000	3845.00	8725.00
0.225	0.0550	40	252.2000	1116.444	4337.77	9942.22
0.250	0.0580	39	322.9000	1287.600	4588.00	9952.00

TABLE-3
KINETIC PARAMETERS FOR Cu(II) OXOGLUTARATE SYSTEM AT 303 K

C_x (mol)	$D^{½} \times 10^3$ cm^2 s^{-1}	Λ	$K_s \times 10^2$ cm s^{-1}
0.000	2.37	1.06	2.52
0.025	2.20	1.06	2.34
0.500	2.13	1.65	3.51
0.075	2.07	3.91	8.10
1.100	2.05	2.22	4.56
0.175	1.99	3.24	6.45
0.200	1.96	3.03	5.94
0.225	1.90	5.38	1.02
0.250	1.81	11.02	2.03

TABLE-4
KINETIC PARAMETERS FOR Cu(II) OXOGLUTARATE SYSTEM AT 313 K

C_x (mol)	$D^{½} \times 10^3$ cm^2 s^{-1}	Λ	$K_s \times 10^2$ cm s^{-1}
0.000	2.6490	0.7970	2.1112
0.025	2.4820	0.7973	1.9790
0.050	2.3940	0.8784	2.1011
0.100	2.2910	1.5400	3.5291
0.175	2.1924	1.5870	3.4770
0.200	2.2106	1.4510	3.2060
0.225	2.1310	1.6900	3.1410

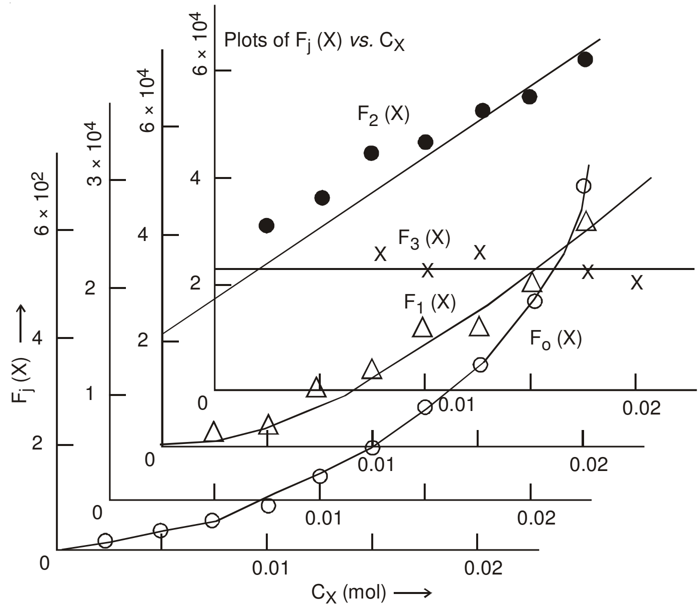

Fig. 1. Cu(II)-oxoglutarate system, at 303 K

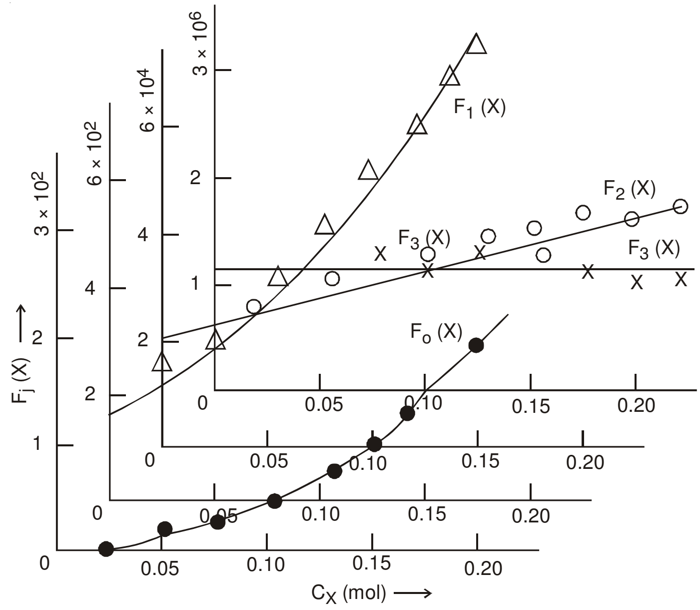

Fig. 2. Cu(II)-oxoglutarate system, at 303 K

The Mihailov constants are recorded in Tables 5 and 6 at 303-313 K, respectively. The two methods resulted the following values of overall formation constants. The results from two methods show that the values of overall formation constants at 303-313 K are in good agreement. The change in free energy (ΔF_o) enthalpy (ΔH_o) and change in entropy (ΔS_o) were calculated and the values are summarized below:

TABLE-5
MIHAILOV CONSTANT 'a' FOR VARIOUS COMBINATIONS OF OXOGLUTARATE CONCENTRATIONS AND 'A' AT VARIOUS OXOGLUTARATE CONCENTRATION AT 303 K

Combination of oxoglutarate concentrations (M)	'a'	Concentration of oxoglutarate	'A'
0.075 0.100	14.87	0.10	22.40
0.075 0.175	14.57	0.150	22.08
0.075 0.150	15.84	0.175	22.38
0.075 0.200	15.71	0.200	21.68
0.100 0.150	22.71	0.225	22.40
0.100 0.125	22.76	0.250	25.56
0.150 0.100	4.53	Average 'a' Average 'A'	17.34 22.75
0.100 0.225	17.37	–	–
0.150 0.200	15.67	–	–
0.250 0.150	22.01	–	–

TABLE-6
MIHAILOV CONSTANT 'a' FOR VARIOUS COMBINATIONS OF OXOGLUTARATE CONCENTRATIONS AND 'A' AT VARIOUS OXOGLUTARATE CONCENTRATIONS AT 313 K

Combination of oxoglutarate concentrations (M)	'a'	Concentration of oxoglutarate	'A'
0.100 0/125	22.78	0.100	2.43
0.100 0.150	15.65	0.125	3.14
0.100 0.175	17.69	0.150	2.49
0.150 0.175	11.72	0.20 0.225	1.89 1.84
0.175 0.250	19.29	0.250	1.74
		Average 'a' = Average 'A' =	17.55 2.47

Electrode kinetics: A persual of the Tables 3 and 4 shows that the values of standard rate consetant in oxoglutarate at 303 K are less than the corresponding values at 313 K. It reveals that the reduction of copper is facilitated by increasing the temperature *i.e.*, reduction reaction occurs relatively fast at higher temperature. At both the temperatures it is seen that as ligand concentration increases the values of K_s also increases in general upto a certain ligand concentration and then decreases. An abrupt irregularity is observed at 0.225 M ligand concentration. The irregularity may be attributed to steriochemical and stoichiometric and thermal changes taking place during reduction. In general, it is suggested that reduction goes fast as ligand concentration goes on increasing till 0.075 M and then continuously decreases upto 0.225 M ligand concentration.

Temperature	DeFrod and Hume method	Mihailov method
300 K	log β_1 2.66	log β_1 2.59
	log β_2 3.34	log β_2 3.53
	log β_3 4.57	log β_3 4.29
313 K	log β_1 2.14	log β_1 1.63
	log β_2 3.32	log β_2 2.57
	log β_3 3.99	log β_3 3.34

The values are summarized below:

ΔF^o (Kcal mol^{-1})	ΔH^o (Kcal mol^{-1})	ΔS^o (Cal mol^{-1} deg^{-1})
-207.50	-3.69	-672.60
-207.50	-3.69	-72.60

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