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Study of Simple and Mixed Ligand Complexes of Copper Ions with some Amino-Acids and Succinate Anions by Differential Pulse Polarography – II

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The formation of binary and ternary complexes of some amino-acids (aspartic acid, glutamic acid and lysine) and succinate with Cu(II) have been investigated using differential pulse (d.p.) polarography. The results reveal the formation of one ternary complex with 1:1:1 stoichiometry. The reduction processes of all the systems were reversible and diffusion controlled. The formation constants of binary and ternary systems have been calculated. The mixed ligand stability constants were calculated statistically and compared with the observed values. The mixing, stabilization and disproportionation constants of the mixed species are also given.

INTRODUCTION

Mixed complexes in which a metal ion is bonded to two or more complexing species are usually formed when the metal ion is present in a mixture of two or more ligands in solution.[1-4] The binary and ternary complexes of amino acids have been studied by several workers[5-8] using electrochemical techniques.

It has been established that mixed-ligand complexes play an important role in biological processes. Mixed chelation commonly occurs in biological fluids, and numerous potential ligands are likely to compete for metal ions *in vivo*.[9] Also, enzymes are known to be activated by metal ions.[10]

In the present work, the mixed ligand complexes of succinate ion as a primary ligand and amino-acids (aspartic acid, glutamic acid and lysine) as a secondary ligand with Cu(II) ions, were investigated using differential pulse (d.p.) polarography as a continuation of our earlier studies.[4,11,12]

EXPERIMENTAL

Polarograms were obtained using a Metrohm polarographic analysis instrument (626 polarecord), which was connected to a 663 VA stand. A three-electrode cell is incorporated in the VA stand. The Ag/AgCl/KCl = 3 M as a reference electrode and a Pt wire as a counter electrode were used throughout the measurements. A drop time of 1.0 s and a scan rate of 5 mV s^{-1} and 50 mV pulse amplitude were employed.

The concentration of Cu(II) ions was 1 x 10^{-4} M. The ionic strength was maintained constant at μ = 1 M, using $NaNO_3$ supporting electrolyte for all measurements.

Reagent grade chemicals, deionized water and triple distilled mercury were employed in all cases.

RESULTS AND DISCUSSION

Nature of Reduction

The polarographic reduction of binary systems of Cu(II) in the presence of succinate, aspartate, glutamate and lysinate was found to be reversible and diffusion controlled consuming two-electrons. The same was found in the case of the present ternary systems. In all cases, the wave had a slope of 31±1 mV for the plots of log $[i/(i_d-i)]$ *vs. E*. The reversibility of the binary and ternary complexes was confirmed using d.p. polarography in nitrate medium (μ = 1.0 M), the half-peak widths ($w^{1/2}$) were 62±1 mV with 50 mV pulse amplitude as represented in Tables II–IV, which is in good agreement with the values calculated by Dillard and Hanck using digital simulation.[13] On the other hand, the plots of i_d against $h^{1/2}$ (mercury height) in direct current polarography were linear and passed through the origin, indicating that the reduction of simple and mixed species of the present systems was essentially diffusion controlled. The values of exponent x in the relation ($i_L = k\, h^x$) amounts to 0.57–0.61, indicating a low contribution of adsorption.

Binary Systems

The formation constants of the binary systems have been calculated using the DeFord-Hume expression,[14] as modified by Health and Hefter,[15] in the case of d.p. polarography. This expression can be given as follows:

$$F_o(X) = \sum \beta_j C_x^j$$

$$= \text{antilog}\left[0.434\left(\frac{nF}{RT}\right)\Delta E_p + \log\frac{(I_p)_s}{(I_p)_c}\right] \qquad (1)$$

where $(I_p)_s$ and $(I_p)_c$ are the peak currents of simple and complex metal ions, respectively. ΔE_p is the shift in the peak potential due to complexation.

The formation of the complexes of copper(II) with succinate, aspartate, glutamate and lysinate were measured separately before the study of the ternary systems using eq. (1). The results are given in Table I. The stability constants of the present aminoacids systems follow the order:

Cu(asp) > Cu(glu) > Cu(lys)

which is due to the increasing size of the ligand and the expected behaviour of the amino acids. Also, the pK_a of the amino acids follow the above order.

TABLE I

Formation constants of binary systems. Ionic strength = 1.0 M ($NaNO_3$). T = 25 °C, pH = 8.0 and $[Cu]^{2+}$ = 1 × 10^{-4} M

Cooper complex		Formation constants			
		This work	Lit.		
$[Cu(succinate)]$	log β_{01}	3.10±0.16	3.30[a],	2.0[b],	3.33[c]
$[Cu(succinate)_2]^{2-}$	log β_{02}	4.65±0.24	4.03[b],	–	–
$[Cu(aspartate)]^+$	log β_{10}	8.40±0.21	8.57[c],	–	–
$[Cu(aspartate)_2]$	log β_{20}	15.65±0.39	15.35[c],	–	–
$[Cu(glutamate)]^+$	log β_{10}	7.90±0.14	7.85[c],	–	–
$[Cu(glutamate)_2]$	log β_{20}	15.20±0.27	15.14[c],	14.4[c],	14.8[c]
$[Cu(lysinate)]^+$	log β_{10}	7.45±0.22	–	–	–
$[Cu(lysinate)_2]$	log β_{20}	14.10±0.41	13.7[c],	13.6[c]	

[a] E. Gelles and R. M. Hay, *J. Chem. Soc.* (1958) 3673.

[b] R. M. Saxena, Rajanikumari, C. P. S. Chandel, and C. M. Gupta, *Transactions of the SAEST* **169** (1987) 2213.

[c] J. Bjerrum, G. Schwarzenbach, and L. Sillen, *Stability Constants, Part I: Organic Ligands*, The Chemical Society, London, Burlington House, 1957.

The observed formation constant values are in the range of the reported values, considering the difference in the experimental conditions and techniques.

Ternary Systems

For the mixed systems, the Schaap and McMasters expression[1] has been modified by Killa *et al.*[4] to determine the formation constants of ternary complexes, using d.p. polarography. This expression can be given as follows:

$$F_{00}\,(XY) = \text{antilog}\left[0.434\left(\frac{nF}{RT}\right)\Delta E_{\mathrm{p}}\right] \tag{2}$$

The $F_{00}(XY)$ function is defined later.

The Cu(asp-succ), Cu(glu-succ) and Cu(lys-succ) systems were studied by keeping the concentration of succinate constant (0.30 M) while varying the concentration of aspartate, glutamate and lysinate ions in each system. In all the systems, pH = 8 was chosen in order to avoid the formation of protonated complexes and to keep the concentration of succinate ions constant in solution. The aspartate, glutamate and lysinate concentrations were calculated from their pK_a values and the pH of the solution. The pK_a values (9.65, 9.52 and 8.90, respectively) were determined using the Albert and Serjent method,[16] which agrees well with the reported values.[17,18]

Solutions containing 1 x 10^{-4} M $[Cu]^{2+}$ ions together with a constant concentration of the weaker ligand (succinate 0.30 M) and the required amount of $NaNO_3$ (to maintain ionic strength 1.0 M) were measured using d.p. polarography at different concentrations from aspartate, glutamate and lysinate for each system.

Since Cu^{2+} forms individually four-coordinate complexes with dicarboxylic acid, and also with the amino acids of bidentate nature, there can be the possibility of the existence of only one mixed species of the type Cu(xy), and the total number of ligands is limited to two due to the bidentate nature of the ligands under investigation. Thus, the Schaap and McMasters treatment[1] for the present mixed complexes could be written as follows:

$$F_{00}(XY) = A + B[X] + C[X]^2 \tag{3}$$

where,

$A = \beta_{00} + \beta_{01}\,[Y] + \beta_{02}\,[Y]^2$
$B = \beta_{10} + \beta_{11}\,[Y]$
$C = \beta_{20}$

where X and Y refer to amino-acids and succinate ligands, respectively.

The original graphical method[14] may be applied to F_{oo} function if the activity of one ligand is held constant while that of the others is varied. The intercept on the F_{oo} axis in the plot of F_{oo} *vs.* [X] gives A, and

$$F_{10} = \frac{F_{00} - A}{[X]} = B + C[X] \tag{4}$$

and

$$F_{20} = \frac{F_{10} - B}{[X]} = C \tag{5}$$

By a similar plotting of F_{10} and F_{20} functions *vs.* [X], B and C were obtained for Cu(asp-succ), Cu(glu-succ) and Cu(lys-succ) systems, respectively. The polarographic data are given in Tables (II–IV).

It should be noted that the obtained E_p values from the d.p. polarograms were reproducible to ±1 mV. On the other hand, to show the reliability of the obtained results, the deviation average and the relative error of the ΔE_p measurements were calculated using the F_{20} (XY) function, which essentially depends on the ΔE_p values. The results show that the measurements were within the experimental error, as shown in Tables II–IV.

TABLE II

Derived (F_{10}) functions for the Cu(asp-succ) system.
$[Cu^{2+}] = 1 \times 10^{-4}$ M, Ionic strength = 1 M, [Succinate] = 0.3 M

$[asp]_{total}$	$[asp]_{free}$	$W^{1/2}$	ΔE_p	$F_{oo} \times 10^8$	$F_{10} \times 10^{12}$	$F_{20} \times 10^{14}$
M x 10^{-3}		mV	V			
0.02	0.44	63	0.259	5.75	1.31	–
0.04	0.88	63	0.277	23.34	2.65	–
0.06	1.32	62	0.285	43.52	3.29	–
0.08	1.72	62	0.292	75.10	4.26	23.81
0.10	2.20	63	0.296	102.50	4.66	20.84
0.125	2.75	62	0.301	151.29	5.50	19.73
0.15	3.30	61	0.306	223.32	6.77	20.30
0.20	4.40	62	0.313	385.18	8.75	19.72
0.25	5.50	62	0.318	568.54	10.34	18.66
0.30	6.60	62	0.324	907.15	13.74	20.71

Average of deviation of F_{20} function = 1.07×10^{14}.
Relative error = 5.35 %.

TABLE III

Derived (F_{10}) functions for the Cu(glu-succ) system.
$[Cu^{2+}]$ = 1 x 10^{-4} M, ionic strength = 1 M, [Succinate] = 0.3 M

$[glu]_{total}$	$[glu]_{free}$	$W^{1/2}$	ΔE_p	F_{oo} x 10^8	F_{10} x 10^{11}	F_{20} x 10^{13}
M x 10^{-3}		mV	V			
0.02	0.58	63	0.244	1.78	–	–
0.04	1.20	63	0.265	9.17	7.64	–
0.06	1.70	62	0.274	18.48	10.87	–
0.08	2.30	62	0.283	37.24	16.19	68.45
0.10	2.90	62	0.289	59.43	20.49	69.12
0.125	3.60	62	0.295	94.82	26.34	71.91
0.15	4.40	61	0.300	140.00	31.80	71.27
0.20	5.80	62	0.307	241.40	41.62	70.98
0.25	7.30	62	0.313	385.18	52.76	71.66
0.30	8.70	62	0.317	525.94	60.45	68.97

Average of deviation of F_{20} function = 1.28 x 10^{13}.
Relative error = 1.89 %.

TABLE IV

Derived (F_{10}) functions for the Cu(lys-succ) system.
$[Cu^{2+}]$ = 1 x 10^{-4} M, ionic strength = 1 M, [Succinate] = 0.3 M

$[lys]_{total}$	$[lys]_{free}$	$W^{1/2}$	ΔE_p	F_{oo} x 10^9	F_{10} x 10^{12}	F_{20} x 10^{13}
M x 10^{-2}		mV	V			
0.02	0.22	63	0.273	1.71	0.777	–
0.04	0.44	62	0.287	5.10	1.16	–
0.06	0.66	62	9.296	10.24	1.55	–
0.08	0.88	62	0.305	20.67	2.35	26.59
0.10	1.10	62	0.309	28.21	2.56	23.18
0.125	1.38	62	0.316	48.65	3.53	25.51
0.15	1.70	61	0.320	66.44	3.91	22.94
0.20	2.20	62	0.327	114.59	5.21	23.64
0.25	2.80	62	0.334	197.64	7.06	25.18
0.30	3.30	62	0.339	291.73	8.84	26.76

Average of deviation of F_{20} function = 1.34 x 10^{13}.
Relative error = 5.36 %.

From the B values, the formation constant (log B_{11}) of the mixed systems, Cu(asp-succ), Cu(glu-succ) and Cu(lys-succ) have been calculated and the values are 11.40, 11.15 and 10.52, respectively. It is interesting to note that the log C values of Cu(asp-succ), Cu(glu-succ) and Cu(lys-succ) systems are 15.30, 14.85 and 14.40, respectively, *i.e.* in the range of the experimental values of log B_{20} (15.65, 15.20 and 14.10) of the complexes, $Cu(asp)_2$, $Cu(glu)_2$ and $Cu(lys)_2$, respectively.

Comparison Between Mixed and Simple Complexes

The mixing constant (log K_M)[19] can be written as follows:

$$\log K_M = \log \beta_{11} - (\log \beta_{20} + \log \beta_{02})/2$$

the values obtained for the following reactions are 1.25, 1.22 and 1.13, respectively.

$$\frac{1}{2}\,[\mathrm{Cu(asp)_2}] + \frac{1}{2}\,[\mathrm{Cu(succ)_2}]^{2-} \;=\; [\mathrm{Cu(asp{-}succ)}]^{-} \qquad (6)$$

$$\frac{1}{2}\,[\mathrm{Cu(glu)_2}] + \frac{1}{2}\,[\mathrm{Cu(succ)_2}]^{2-} \;=\; [\mathrm{Cu(glu{-}succ)}]^{-} \qquad (7)$$

$$\frac{1}{2}\,[\mathrm{Cu(lys)_2}] + \frac{1}{2}\,[\mathrm{Cu(succ)_2}]^{2-} \;=\; [\mathrm{Cu(lys{-}succ)}]^{-} \qquad (8)$$

Also, the stabilization constants ($\log K_s = \log K_M - \log 2$)[20] for the same reactions are 0.95, 0.92 and 0.83, respectively. The positive values of the mixing and stabilization constants reveal the stability of ternary complexes in solution as compared to simple ones.

The greater stability of the mixed-ligand complexes relative to that of $[\mathrm{Cu(succ)_2}]^{2-}$ species is due to the entropy effect arising from the lower charge on ternary complexes.[7]

The equilibria between various species existing in the solution for each system with the log equilibrium constants (log *K*) values are given in Table V (a, b, and c) for the present mixed systems. It was found for the Cu(asp-succ) system that the addition of (succ) to Cu(asp) is easier than to Cu(succ) [equilibria (2) and (3)]. On the other hand, the addition of (asp) to Cu(succ) is easier than to Cu(asp) complex [equilibria

TABLE V

Equilibria involved between simple and mixed complexes and the equilibrium constant (log K) values

Equilibrium			log *K* values at 25 °C
	Cu(asp-succ) system		
Cu + asp + succ	=	Cu(asp-succ)	11.40
Cu(asp) + succ	=	Cu(asp-succ)	3.0
Cu(succ) + succ	=	$\mathrm{Cu(succ)_2}$	1.55
Cu(asp) + asp	=	$\mathrm{Cu(asp)_2}$	7.25
Cu(succ) + asp	=	Cu(asp-succ)	8.30
$\mathrm{Cu(succ)_2}$ + asp	=	Cu(asp-succ) + succ	6.75
$\mathrm{Cu(asp)_2}$ + succ	=	Cu(asp-succ) + asp	–4.25
	Cu(glu-succ) system		
Cu + glu + succ	=	Cu(glu-succ)	11.15
Cu(glu) + succ	=	Cu(glu-succ)	3.25
Cu(succ) + succ	=	$\mathrm{Cu(succ)_2}$	1.55
Cu(glu) + glu	=	$\mathrm{Cu(glu)_2}$	7.30
Cu(succ) + glu	=	Cu(glu-succ)	8.05
$\mathrm{Cu(succ)_2}$ + glu	=	Cu(glu-succ) + succ	6.50
$\mathrm{Cu(glu)_2}$ + succ	=	Cu(glu-succ) + glu	–4.05
	Cu(lys-succ) system		
Cu + lys + succ	=	Cu(lys-succ)	10.52
Cu(lys) + succ	=	Cu(lys-succ)	3.07
Cu(succ) + succ	=	$\mathrm{Cu(succ)_2}$	1.55
Cu(lys) + lys	=	$\mathrm{Cu(lys)_2}$	6.65
Cu(succ) + lys	=	Cu(lys-succ)	7.42
$\mathrm{Cu(succ)_2}$ + lys	=	Cu(lys-succ) + succ	5.87
$\mathrm{Cu(lys)_2}$ + succ	=	Cu(lys-succ) + lys	–3.62

(4) and (5)]. Thus, the formation of ternary complexes is more favoured than that of binary complexes. At the same time, the Cu(succ)$_2$ complex can accommodate (asp) in place of (succ) and the Cu(asp)$_2$ complex can not accommodate (succ) in place of (asp) [equilibria (6) and (7)], respectively. The results clearly indicate the weaker nature of the (succ) ligand, as compared to the (asp) ligand. Similarly, the same behaviour was found for the other two systems.

Waters-Dewitt Expression

The observed mixed ligand stability constants ($\log B_{11}$) for the present systems can be compared with the statistically calculated values according to the following expression.[21]

$$\beta_{11} = 2(4/9\ \beta_{02} \times \beta_{20})^{1/2}$$

The values of ($\log \beta_{11}$) are given below and compared with the observed values.

System	$\log \beta_{11}$ (observed)	$\log \beta_{11}$ (statistically calc.)
Cu(asp-succ)	11.40	10.27
Cu(glu-succ)	11.15	10.05
Cu(lys-succ)	10.52	9.50

The experimental values of the mixed complexes are higher than the statistically calculated ones. This behaviour has been explained by many authors[1,20] considering the cooperative effects of electrostatic forces between different kinds of ligands (*e.g.* succinate and amino-acids). This may also be attributed to steric effects and the lowering of the charge on ternary complexes.[19]

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SAŽETAK

Studij jednostavnih i miješanih kompleksa bakrovih iona s nekim aminokiselinama i sukcinat anionima metodom diferencijalne pulsne polarografije – II

H. M. Killa, E. M. Mabrouk, M. M. Moustafa i R. M. Issa

Nastajanje binarnih i ternarnih kompleksa bakar(II)-iona s nekim aminokiselinama (asparaginska, glutaminska kiselina i lizin) i sukcinatom istraživano je diferencijalnom pulsnom polarografijom. Rezultati upućuju na stvaranje jednog ternarnog kompleksa sa stehiometrijom 1:1:1. Redukcijski procesi svih sustava bili su reverzibilni i kontrolirani difuzijom. Izračunane su konstante stabilnosti binarnih i ternarnih sustava. Konstante stabilnosti miješanih liganada izračunane su statistički i uspoređene s izmjerenim vrijednostima. Također su navedene konstante izmjene, stabilizacije i disproporcije miješanih kompleksa.