Polarographic Study of Copper Arginine Complexes in Mixed Solvents

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Copper complexes of arginine have been studied, polarogaphically, in aqueous mixtures 20 and 40% methanol and ethanol media. The reduction was found to be reversible in all the cases. The stability constants have been evaluated in all the cases by DeFord and Hume's method The decrease in dielectric constant is found to favour greater association of ions resulting in higher values of stability constants.

The present paper deals with the polarographic study of copper-arginine complexes in aqueous and aqueous mixtures of methanol and ethanol with a view to study the effect of solvents on complexation and electrode kinetics.

EXPERIMENTAL

The experimental procedure was same as described earlier (1).

RESULTS AND DISCUSSION

Copper is reduced reversibly in most of the supporting electrolytes, both in presence and absence of complexing agents. A single well defined reversible wave was obtained for copper in 0.5 M KNO_3 and in presence of arginine and at different values of pH. Concentration of arginate ion in each case is calculated from the pH of the solution and the pK value.

Copper complexes with arginine ions are indicated by the shift in the half-wave potential to more negative values and the decrease in diffusion current. Plot of $E_{1/2}$ vs pA resulted in a smooth curve indicating more than one complex species with comparable stabilities. DeFord and Hume's (2) method was adopted for evaluation of stability constants. The values of F_j functions are given in table 1. Two complexes were identified with stabilities:

$\beta_1 = 2.0 \times 10^9$, $\beta_2 = 9.45 \times 10^{12}$

which is in good agreement with earlier reported values.

TABLE 1

COPPER-ARGININE SYSTEM IN AQUEOUS SOLUTION, ANALYSIS OF DATA BY DEFORD AND HUMES METHOD

$[Cu^{+2}] = 0.4$ mM, $\mu = 0.5 M KNO_3$. Temp. 30°C $m^{2/3} t^{1/6} = 1.80$ $mg^{2/3}$ $Sec^{1/2}$
pK = 9.05, $(E_{1/2})_s = +0.020$, $i_d = 2.66$

[HA] M	pH	pA	$E_{1/2}$ -V vs SCE	i_d µA	$Fo(A) \times 10^{-7}$	$F_1(A) \times 10^{-9}$	$F_2(A) \times 10^{-12}$
0.01	7.85	3.23	0.221	2.39	0.5015	7.952	9.432
0.01	8.12	2.98	0.232	2.38	1.126	11.26	9.263
0.01	8.31	2.81	0.241	2.36	2.741	17.29	9.648
0.01	8.58	2.60	0.253	2.33	6.448	25.67	9.423
0.01	8.90	2.38	0.266	2.32	15.63	39.26	9.359
0.02	8.71	2.20	0.276	2.30	38.04	60.29	9.238
0.02	9.11	1.97	0.290	2.29	95.80	95.81	9.381
0.04	8.87	1.80	0.300	2.26	243.4	153.5	9.563
0.04	9.33	1.58	0.314	2.22	598.0	238.1	9.398
0.08	8.99	1.43	0.322	2.21	1506.3	378.4	9.455
0.08	9.49	1.23	0.334	2.12	3789.6	600.6	9.486

$\beta_1 = 2.0 \times 10^9$, $\beta_2 = 9.45 \times 10^{12}$

MIXED SOLVENT MEDIA

The half-wave potentials of the simple metal ion was found to shift to more positive values with increase in percentage of solvent(3). The half-wave potential of copper 'simple ion' in case of 20 and 40% (V/V) methanol were + 0.025 V and +0.027 and in case of 20 and 40% (V/V) ethanol the values were + 0.027 V and + 0.029 V vs SCE. The diffusion currents were lower than that observed in aqueous solution and this is because of higher values of viscosity and dielectric constant of these media as compared to water. The reduction was reversible in all these cases and the $E_{1/2}$ vs pA was a smooth curve. The data was analysed using Deford and Hume's method. The half-wave potentials as a function of ligand concentration and values of F_j functions are listed in (table 2 to 5). Two complexes could be identified in all the four cases the values of stability constants are as

$\beta_1 = 3.0 \times 10^9$, $\beta_2 = 1.19 \times 10^{13}$ in 20% methanol
$\beta_1 = 2.0 \times 10^{10}$, $\beta_2 = 4.45 \times 10^{13}$ in 40% methanol
$\beta_1 = 5.0 \times 10^9$, $\beta_2 = 2.69 \times 10^{13}$ in 20% ethanol
$\beta_1 = 7.0 \times 10^{10}$, $\beta_2 = 8.0 \times 10^{13}$ in 40% ethanol

The values of copper complexes in different media were found to be greater than that in aqueous media. The decrease in dielectric constant results in increased attraction between oppositely charged ions, therefore the stability of these complexes increased with increase in percentage of solvent.

TABLE 2

COPPER-ARGININE SYSTEM (20% METHANOL) , ANALYSIS OF DATA BY DEFORD OF HUMES METHOD

$[Cu^{+2}]$ = 0.4 mM, = 0.5 $MKNO_3$, Temp. = 30°C , $m^{2/3} t^{1/6}$ = 1.80 $mg^{2/3} sec^{-1/2}$

pK = 9.20 , $(E_{1/2})$ = + 0.025 $(i_d)_s$ = 2.52

[HA] M	pH	pA	$E_{1/2}$ -V vs SCE	i_d μA	$Fo(A)\times10^{-7}$	$F_1(A)\times10^{-10}$	$F_2(A)\times10^{-13}$
0.01	8.01	3.22	0.227	2.22	0.6439	1.020	-
0.01	8.28	2.97	0.239	2.20	1.509	1.509	1.209
0.01	8.46	2.81	0.247	2.18	3.537	2.231	1.218
0.02	8.36	2.60	0.261	2.16	8.292	3.301	1.194
0.02	8.58	2.41	0.271	2.14	19.44	4.883	1.151
0.02	8.86	2.20	0.284	2.11	49.43	7.834	1.194
0.04	8.75	1.98	0.297	2.10	124.55	12.45	1.215
0.04	8.98	1.82	0.306	2.08	315.31	19.89	1.236
0.04	9.40	1.61	0.318	2.04	746.7	29.72	1.171
0.08	9.19	1.40	0.331	2.01	1900.3	47.73	1.191
0.08	9.37	1.32	0.336	2.00	3024.1	60.33	1.197
0.08	9.82	1.19	0.344	1.98	4837.2	76.66	1.210

$\beta_1 = 3.0 \times 10^9$, $\beta_2 = 1.19 \times 10^{13}$

TABLE 3

COPPER-ARGININE SYSTEM (40% METHANOL) , ANALYSIS OF DATA BY DEFORD OF HUMES METHOD

$[Cu^{+2}]$ = 0.4 mM, μ = 0.5 M KNO_3 , Temp. = 30°C, $m^{2/3}\ t^{1/6}$ = 1.80 $mg^{2/3}\ Sec^{1/2}$,
pK = 9.35, Simple ion $E_{1/2}$ = + 0.027, i_d = 2.48

[HA] M	pH	pA	$E_{1/2}$ -V vs SCE	i_d µA	Fo(A)x10^{-8}	F_1 (A)x10^{-10}	F_2 (A)x10^{-13}
0.01	8.16	3.22	0.248	2.14	0.304	4.821	4.472
0.02	8.10	2.97	0.259	2.14	0.657	6.576	4.576
0.02	8.27	2.81	0.268	2.10	1.435	9.053	4.450
0.02	8.51	2.60	0.281	2.09	3.348	13.33	4.510
0.02	8.72	2.42	0.290	2.08	7.815	19.63	4.429
0.02	9.06	2.17	0.305	2.04	18.50	29.33	4.321
0.04	8.87	2.00	0.315	2.02	46.86	46.86	4.487
0.04	9.12	1.83	0.325	2.00	114.23	72.07	4.421
0.04	9.63	1.58	0.340	1.97	279.8	111.4	4.356
0.08	9.34	1.40	0.350	1.93	716.14	179.9	4.469
0.08	9.52	1.32	0.355	1.92	1140.3	227.5	4.499
0.08	9.92	1.20	0.362	1.89	1834.2	290.7	4.574

$\beta_1 = 2.0 \times 10^{10}$ $\beta_2 = 4.45 \times 10^{13}$

TABLE 4

COPPER-ARGININE SYSTEM (20% ETHANOL), ANALYSIS OF DATA BY DEFORD AND HUMES METHOD

$[Cu^{+2}]$ =0.4mM, μ =0.5M KNO_3, Temp. =30°C, $m^{2/3}\ t^{1/6}$ =1.80 $mg^{2/3}$ $Sec^{1/2}$

pK =9.20, simple ion $E_{1/2}$ = +0.027, i_d =2.39

[HA] M	pH	pA	$E_{1/2}$ -V vs SCE	i_d µA	Fo (A) x 10^{-7}	F_1 (A) x10^{-10}	F_2 (A) x 10^{-13}
0.01	8.01	3.22	0.239	2.13	1.369	2.170	2.647
0.01	8.26	2.99	0.250	2.11	3.210	3.210	2.710
0.02	8.12	2.81	0.260	2.09	7.528	4.750	2.681
0.02	8.39	2.57	0.274	2.05	17.82	7.096	2.626
0.02	8.59	2.40	0.285	2.04	44.92	11.28	2.708
0.02	8.83	2.22	0.294	2.00	106.4	16.86	2.593
0.04	8.75	1.98	0.309	1.99	268.1	26.81	2.632
0.04	9.02	1.80	0.320	1.98	675.8	42.63	2.658
0.08	8.85	1.61	0.330	1.96	1711.9	68.15	2.693
0.08	9.19	1.40	0.344	1.94	4336.9	108.9	2.723
0.08	9.48	1.28	0.350	1.93	6903.2	137.7	2.738
0.08	9.77	1.20	0.355	1.89	10339.4	163.8	2.590

$\beta_1 = 5.0 \times 10^{9}$, $\beta_2 = 2.69 \times 10^{13}$

TABLE 5

COPPER-ANGININE SYSTEM (40% ETHANOL), ANALYSIS OF DATA BY DEFORD AND HUMES METHOD

[Cu^{+2}] = 0.4mM, μ = 0.5M KNO_3, Temp =30°C ; $m^{2/3}$ $t^{1/6}$ = 1.80 $mg^{2/3}$ $Sec^{1/2}$

pK = 9.65, simple ion $E_{1/2}$ =+0.029 i_d =2.25

[HA] M	pH	pA	$E_{1/2}$ -V vs SCE	i_d µA	Fo(A) x 10^{-8}	$F_1(A)$ x 10^{-11}	$F_2(A)$ x 10^{-14}
0.02	8.14	3.22	0.262	1.81	0.7580	1.201	0.7945
0.02	8.38	2.99	0.271	1.79	1.527	1.527	0.8273
0.02	8.58	2.80	0.281	1.77	3.078	1.942	0.7835
0.02	8.78	2.62	0.289	1.75	6.697	2.666	0.7826
0.04	8.73	2.37	0.303	1.75	15.55	3.907	0.8056
0.04	8.92	2.20	0.313	1.73	36.54	5.791	0.8069
0.04	9.16	2.01	0.323	1.71	85.87	8.587	0.7887
0.04	9.45	1.81	0.334	1.69	217.8	13.7[illegible]	0.8230
0.08	9.31	1.60	0.347	1.65	518.3	2[illegible].63	0.7934
0.08	9.61	1.42	0.357	1.63	1266.0	[illegible]1.80	0.7813
0.08	9.85	1.31	0.363	1.61	2029.7	40.49	0.7940
0.08	10.13	1.22	0.368	1.59	3254.5	51.58	0.8063

β_1= 7.0×10^{10} , β_2= 8.0×10^{13}

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