1 B. Sarkar, in 'Metal Ligand Interaction in Organic Chemistry and Biochemistry', Part 1; B. Pullman, N. Goldblum (eds.), Reidel, Dordrecht, Holland, 1977, pp. 193–228.

U9

Polarographic Investigations on Stereoselectivity of some Ternary Complexes of Aminoacids with Copper(II)

J. PRASAD, A. K. SINGH and H. L. NIGAM

Department of Chemistry, University of Allahabad, Allahabad-211002, India

and K. B. PANDEYA

Chemistry Department, Delhi University, Delhi-110007, India

The biological significance of histidine residue as a metal binding site in proteins has prompted many workers to investigate copper(II) histidine complexes. It has been found that elucidation of the complex formation between Cu(II) and histidine is not easy since histidine involves a bulky imidazole ring and has three or four coordination sites, and Cu(II) requires a tetragonal coordination [1–3]. The probable electrostatic interactions giving rise to stereoselective aspects of the problem have been mainly investigated using potentiometric, spectral and magnetic measurements [4]. No polarographic studies are reported in the literature. In the present communication the parent and ternary complexes of D- and L-histidinato copper(II) with some L-aminoacids, *viz.* phenylalanine, tryptophan, valine, proline, methionine, leucine, lysine, serine, threonine, alanine, glutamic acid and aspartic acid have been studied in aqueous 0.5 *M* KNO_3 at the dropping mercury electrode under varying experimental conditions with a view to calculate the kinetic parameters. Besides half wave potential ($E_{1/2}$), transfer coefficient (α), the formal rate constant (Kr), the activation energy of the rearrangement of the depolizer (Q_e) and the activation energy of diffusion (Q_D) have been evaluated for each system. Electronic spectra (in solution) of these complexes have also been recorded.

Experimental

Experimental details are described in several earlier communications from this laboratory [5]. The characteristics of dme for one set of measurements are given below:

$$h = 40 \text{ cm},\ m = 2.458 \text{ mg s}^{-1},\ t = 2.0 \text{ s},\ m^{2/3}\,t^{1/6} = 1.6234 \text{ mg}^{2/3}\text{ s}^{-1/2}$$

Results

Polarographic characteristics for some of these ternary complexes (1:1:1 ratio) are given in Table I. All these complexes are observed to undergo diffusion-controlled single-step two electron irreversible electro-reduction at dme. A perusal of the Table shows that Kr and also i_d increase with increase in temperature in the case of Cu–histidine–alanine/or serine, indicating an easier reduction, which is also supported by the shift of $E_{1/2}$ to comparatively more positive potentials with the rise of temperature. However, in the case of Cu–histidine–aspartic and/or threonine, such trend in $E_{1/2}$ is disturbed. The significance of results will be discussed in detail.

1 D. D. Perrin and V. S. Sharma, *J. Chem. Soc. A*, 724 (1967).
2 B. Sarkar and Y. Wigfield, *J. Biol. Chem.*, *242*, 5572 (1967).
3 D. R. Williams, *J. Chem. Soc. Dalton*, 790 (1972).
4 G. Brookes and L. D. Pettit, *J. Chem. Soc. Dalton*, 1918 (1977).
5 V. Srivastava, K. B. Lal and H. L. Nigam, *J. Indian Chem. Soc. LIX, April*, 497 (1982).

TABLE I. Polarographic Characteristics of some Mixed-Aminoacid Complexes of Copper(II) at Different Temperatures: h = 40 cm, $[Cu^{2+}]$ = 1 m*M*, KNO_3 = 0.5 *M*, gelatin = 0.005%, pH = 6.5 ± 0.1.

Complexes	Temp. (°C)	$-E_{1/2}$ (V *vs.* SCE)	i_d (μA)		$D \times 10^7$ ($cm^2\ sec^{-1}$)	$Kr \times 10^4$ (cm sec^{-1})	Q_D (kcal)	Q_e (kcal)
Cu–histidine–aspartic acid	25	0.189	0.90	0.2766	2.086	6.195		
	30	0.170	0.76	0.3405	1.488	9.743	7.889	7.5733
	35	0.178	1.02	0.2724	2.680	8.768		
Cu–histidine–alanine	25	0.183	0.845	0.3575	1.840	7.979		
	30	0.178	0.920	0.3367	2.181	9.455	5.2690	4.4329
	35	0.178	1.28	0.3347	4.221	12.78		
Cu–histidine–threonine	25	0.183	0.89	0.2570	2.041	6.616		
	30	0.193	1.20	0.2647	3.710	7.413	10.474	2.3312
	35	0.194	1.40	0.2431	5.049	8.230		
Cu–histidine–serine	25	0.203	0.96	0.2483	2.374	4.793		
	30	0.200	1.10	0.2425	3.118	5.779	6.487	3.9574
	35	0.197	1.31	0.2674	4.442	7.519		