ELECTRODICS AND ELECTROBIOLOGY

COMPLEXATION OF COPPER (II) BY GLYCINE IN FRESH AND SEA WATER MEDIA

S JAYA, T PRASADA RAO and G PRABHAKARA RAO

Central Electrochemical Research Institute, Karaikudi-623 006

The stability constants of Cu'(II) glycine complexes in 0.7 M $NaClO_4$ and 0.7M $NaNO_3$ media were evaluated using Cu (II) ion selective electrode. The stability constant data are consistent with earlier reports of other metal ion complexes of glycine. The distribution level of Cu (II) - glycine complexes in presence of other complexing ligands of marine environment has also been numerically evaluated.

Key words : Cu (II) - glycine complexes, stability constant, marine environment

INTRODUCTION

The toxicity of heavy metals and metalloids, present at trace levels in the environment, such as mercury, lead and cadmium is well known [1,2]. On the other hand, elements belonging to the category of biochemically essential e.g. copper, zinc, selenium etc. also tend to be toxic when the concentration limits exceed certain threshold values [2].Further, the uptake of heavy metals depends on their speciation in aquatic environment. In view of this, the measurement of a nutrient or toxic is of little or no use. Hence, besides the knowledge of total concentration of a particular metal in a given environment, its distribution among various species is also of great interest [3-5].

The distribution of a particular metal among various species in an aquatic system depends on the equilibria existing between various inorganic and organic ligands and the metal ion. This distribution can be evaluated in principle, if all data needed are known including the corresponding stability constant values. In view of the fact that many parts of ocean contains little of particulate material, it is often advantageous to study speciation only in dissolved state [3].

This paper concerns with speciation of copper by aminoacids as they are main constituents of dissolved organic matter in fresh and sea water. To elucidate the specific influence of the salinity components of sea water on the complexation of copper, the measurements are performed in non-complexing medium like 0.7 M $NaClO_4$. The stability constants are arrived at by using potentiometric rather than voltammetric approaches as the former is dependent on a fewer factors thus making interpretation easier, particularly in media containing adsorbable compound and when ligands are not in excess [6]. The complexation properties are obtained by copper sensing ion-selective electrodes (ISE) as it offers a more reliable measurement than single point potentiometric determinations. Such studies were carried out for chemical speciation for copper by humic acid [7,8] but no report appeared for speciation of metals in presence of aminoacids. This paper describes the chemical speciation of copper in fresh and sea water media in presence of varying amounts of glycine.

EXPERIMENTAL

The potentials were measured with an accuracy of ±0.1mV with a chemtrix digital pH meter. The e.m.f. readings were taken when

a drift was less than 0.1mV in 2 min. The ISE used was ORION copper ISE Model 94-29. The combined (glass and calomel) electrode was used both as reference electrode during equilibrium measurement and as pH measuring device to maintain the pH during titration.

All chemicals were of BDH, AR grade. Standard solutions of copper and stock solution of $NaClO_4$ were prepared from BDH and Loba, AR grade chemicals respectively. The pH of the solution was adjusted to 6 with 5 x 10^{-3}M boric acid and 5 x 10^{-4}M sodium hydroxide.

RESULTS AND DISCUSSION

Evaluation of stability constants

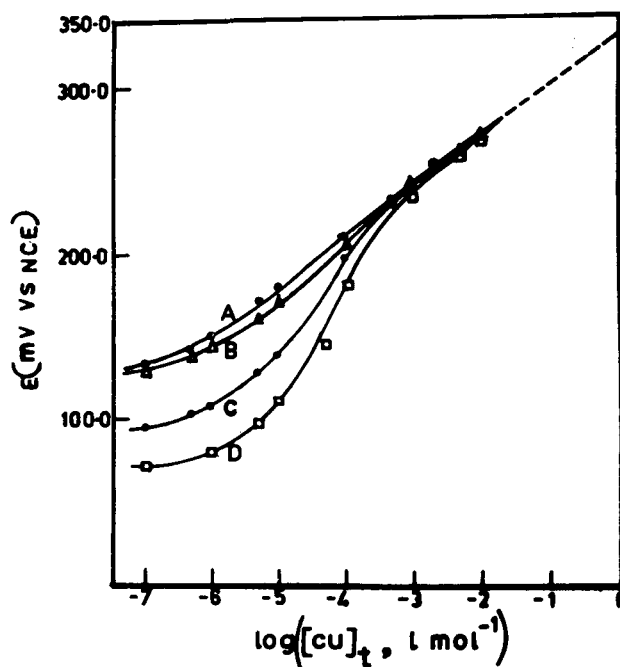The copper ISE responds to copper [11] in Nernstian manner in

Fig. 1: Response of copper ion-selective electrode to varying concentrations of copper in the range 5 x 10^{-7} to 10^{-1}M in presence of O, 5 x 10^{-5}, 3 x 10^{-4} and 5 x 10^{-4} M glycine (curves A, B, C and D respectively)

the range 5×10^{-7} to 10^{-1} M in 0.7 M sodium perchlorate medium. The standard electrode potential (E_0') and slope (s) values are found to be 334 and 31 mV respectively. The concentration of copper in sea water and variety of natural water samples lie in the range of 5×10^{-7} to 5×10^{-6} M. In view of the fact that copper ISE responds in Nernstian manner only upto 5×10^{-7} M of copper, the experiments were conducted with 5×10^{-6} M of copper in order to arrive at reliable stability constant data.

Fig. 1 shows the response of copper ISE with varying concentrations of copper ranging from 5×10^{-7} to 10^{-1}M at different concentrations of glycine viz. 0.5×10^{-5}, 3×10^{-4} and 5×10^{-4} (curves A, B, C and D respectively). It is clear that the degree of complexation is dependent not only on concentration of glycine but also on copper concentration. Further, a qualitative picture of degree of complexation of copper with varying concentrations of glycine is clearly discernible from the Figure 2. The calculation of stability constants of copper glycine complexes was possible from these data [6], but was not considered as it leads to values which are not precise.

An approach suggested for determining stability constants using ISE [6-8] is to measure the response for a fixed concentration of metal at varying concentrations of ligand. Fig. 2 shows the typical plot of response of copper ISE vs glycine concentration, when copper concentration and pH are maintained at 5×10^{-6}M and 6.3 respectively.
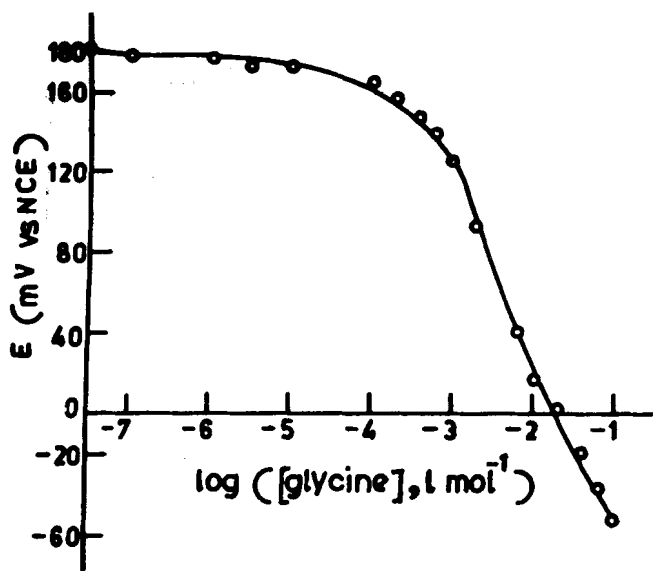

Fig. 2: Response of copper ion-selective electrode for 5×10^{-6} M of copper in presence of varying amounts of glycine

The stability constants β_1' and β_2' were evaluated (assuming the formation of only 1:1 and 1:2 complexes) by plotting α-1/L_t vs L_t (cf. Fig.3) as per relation

$$\frac{\alpha - 1}{L_t} = \beta'_1 + \beta'_2 L_t$$

where L_t is the total ligand (glycine) concentration. The β'_1 and β'_2 values in 0.7M $NaClO_4$ medium were calculated to be 4×10^7 and 2×10^{14} respectively. By adopting the same procedure, the stability constants calculated in 0.7M $NaNO_3$ medium are of same order as in case of 0.7M $NaClO_4$.
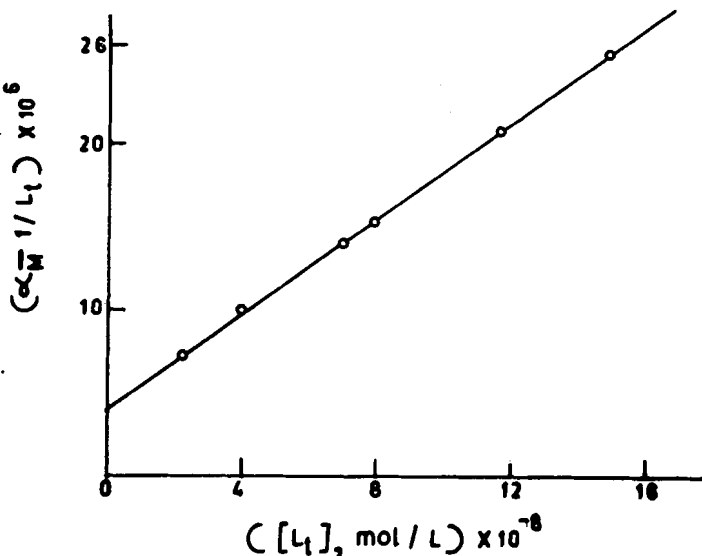

Fig. 3: Plot of $(\alpha - 1)/(L_t)$ vs (L_t)

Studies were then directed to simulate sea water conditions and observe the effect of the presence of associated major inorganic cations and anions on the speciation of copper as its glycine complexes. Thus, by the addition of 0.01M K^+, 0.05M Mg^{2+}, 0.01M Ca^{2+} or 0.03M SO_4^{2-} did not alter the equilibria of the copper-glycine complexes as evidenced by the identical EMF values obtained with copper ISE. This observation indicates that K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} have negligible effect on speciation of copper by glycine. On the other hand addition of 0.5 M chloride resulted in sluggish response characteristics for copper ISE resulting in inaccurate measurements.

The distribution of copper species

Using the stability constants of copper-glycine complexes and those of other copper species existing in sea water (see Table I) the distribution of copper among various species has been evaluated. The results shown in Fig. 5 are valid for sea water containing glycine as only organic ligand or another ligand with similar stability constant value. The distribution depends on the ligand concentration, as (i) the stability constants used are stoichiometric stability constants valid for sea water medium and (ii) the fact that inorganic components and salinity of sea water remain practically same. The percent distribution of $CuCl^+$, $CuCl_2$, $Cu(glycine)^+$, $Cu(glycine)_2$ and uncomplexed Cu^{2+} with varying concentrations of glycine by using the software developed suitably for this purpose (available on request) was arrived at. As seen from Fig. 4, copper exists mainly as $CuCl_2$ or $Cu(glycine)_2$ at lower or higher concentrations of glycine respectively.

TABLE-I: Stability constants of various complexes present in sea water with relevance to chelation of copper with glycine

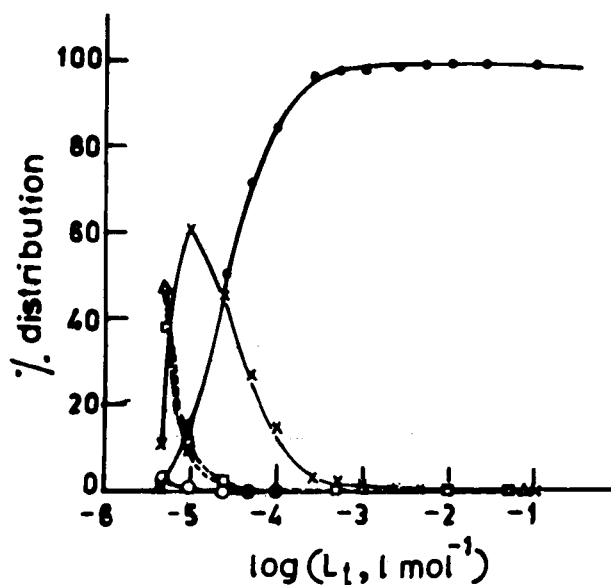| Cation	Ligand	Stability constant $\beta/(1\ mol^{-1})^n$	Experimental conditions	References
Cu^{2+}	Cl^-	6.3×10^2	18°, variable	
		2.5×10^4	9	
	OH^-	2.95×10^4	zero ionic strength	9
	CO_3^{2-}	3.98×10^8	zero ionic strength	9
	SO_4^{2-}	1.9×10^2	zero ionic strength	~9
	glycine	4×10^7	0.7M $NaClO_4$	
			or	Present work
		2×10^{14}	0.7M $NaNO_3$	
Ca^{2+}	glycine	11.0	0.7M NaCl, 20°	10
Mg^{2+}	glycine	20.0	0.7M NaCl, 20°	10
Cd^{2+}	glycine	1.08×10^4	sea water, 20°	11
		1.94×10^7		
Zn^{2+}	glycine	2.0×10^4	0.7 M NaCl, 20°	10
		6.8×10^7		
Pb^{2+}	glycine	2.95×10^5	zero ionic strength, 25°	9
		7.2×10^8		

Fig. 4 : Distribution pattern of copper in simulated sea water medium (pH 6.3) in presence of varying amounts of glycine, o-o-o free copper, $\triangle$-$\triangle$-$\triangle$ (CuCl)$^+$, $\square$-$\square$-$\square$-CuCl$_2$, x-x-x Cu (glycine)$^+$, ●-●-● Cu (glycine)$_2$
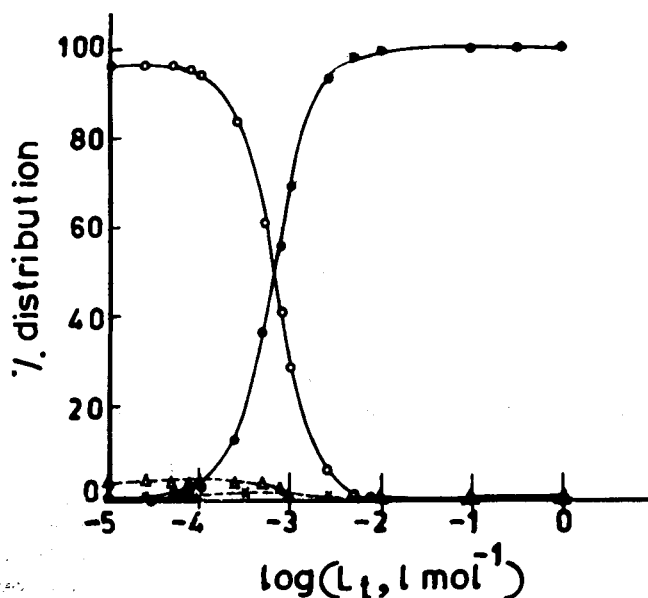
Fig. 5: Distribution pattern in fresh water medium (Cl$^-$ = 2 x 10^{-3} M pH 6.3) in presence of varying amounts of glycine $\triangle$-$\triangle$-$\triangle$(CuCl)$^+$, o-o-o CuCl$_2$, x-x-x Cu(glycine)$^+$, ●-●-● Cu (glycine)$_2$

For fresh waters, containing smaller amounts of competing ions, especially chloride, the formation of copper-glycine complex occurs at much lower concentration of glycine. Taking into account the dependence of stability constants on the ionic strengths, the stability constants of copper-glycine complexes in fresh water (2 x 10^{-3}M chloride, pH 6.3) are calculated to be 1.265 x 10^8 and 6.311 x 10^{14} respectively. The distribution pattern of copper in fresh water obtained by using the procedure described for sea water, is shown in Fig.5. From the Figs.5 and 6 it is clear that the speciation of copper as its glycine complexes, at naturally occurring levels, is negligible. However, these charts are useful in understanding the distribution pattern of copper among various species, in the presence of higher concentration of glycine or any other amino acid with similar stability constants arising due to local activity, in fresh or sea water samples.

REFERENCES

1. M B Jacobs, *The analytical toxicology of industrial inorganic poisons,* Interscience Publishers, New York (1967)

2. D W Sundstrom and H E Clei, *Waste water treatment,* Prentice Hall, New Jersey (1979)

3. T M Florence and G E Bately, *Talanta,* **24** (1971) 151

4. T M Florence and G E Bately, *C.R.C. critical reviews in Anal Chem,* **9** (1980) 219

5. P A Krenkel, *Heavy metals in aquatic environment,* Pergamon Press, New York (1974)

6. J Buffle in *Speciation of trace metals in natural waters by means of electroanalytical methods,* I.U.P.A.C. Commission V.5

7. J Buffle, P Deladoey and F L Greter, *Anal Chim Acta,* **116** (1980) 255

8. J Buffle, F L Greter and W Haerdi, Anal Chem, **49** (1977) 216

9. J Bjerrum, G Schwarzenbach and L G Sillen, *Stability constants, Chem Soc Publ,* **6** (1957)

10. M L S Simoes Goncalves and P Valenta, *J Electroanal Chem,* **132** (1982) 357

11. M L S Simoes Goncalves, P Valenta and H W Nurenberg, *J Electroanal Chem,* **149** (1983)