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Potentiometric, Spectroscopic and Polarographic Studies on Cu(II)–Prometone–D-Glucosamine Ternary System

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Our recent work on Cu(II) complexes with prometone herbicide (2-methoxy-4,6-bis(isopropylamino)-s-triazine) [1] and D-glucosamine [2] (see also refs. 3–5), have shown that both organic molecules act as relatively strong ligands in a neutral medium, with s-triazine being more effective in slightly acidic solutions and aminosugar more potent in the basic solutions ($\{O^-, NH_2\}$ chelate formation).

Since the natural environment, expected for example in the soil, may favorize the mixed ligand complex formation (e.g. ternary), we have carried out potentiometric and spectroscopic studies on the Cu(II)–prometone–D-glucosamine system.

D-glucosamine, subunit of, among others, the potent metal binding polymers like chitine or its derivative chitosan (poly(β-1,4-D-glucosamine)), may play an important role in the essential metal transport process [6]. Thus the formation of the mixed ligand species metal ion–D-glucosamine–herbicide could be used as a simple model system for plant and soil chemistry.

Experimental

Potentiometric titrations were carried out on a Taccussel ISIS 20000 pH-meter with TB/HA and C8 electrodes at 25 ± 0.03 °C for the molar ratios shown in Table I. Stability constants were calculated with a SUPERQUAD program [8] adapted to IBM-PC microcomputer.

All the solutions were prepared under argon atmosphere in deionized and bi-distilled water. Carbonate free 0.1013 M NaOH was prepared in 0.15 M NaCl and standardized against phtalate (N.B.S.). HCl solution was standardized with 0.1013 M NaOH. Puretronic cupric chloride was dissolved in HCl solution with 0.2 M concentration of Cu(II) checked with EDTA. Prometone (Pr) (Ciba Geigy) and D-glucosamine (GA) (Sigma) were used as obtained. The stock solutions of ligands were prepared in 0.15 M NaCl. A small amount of methanol (1% *v*/*v*) was added to solubilise the prometone samples. The quantities of ligands and protons introduced into a potentiometric vessel were verified by SUPERQUAD [8] and PKA SIMPLEX [9] programs.

TABLE I. The Quantities (μmol) of Cu(II), Prometone and D-glucosamine used in the Titrations

Cu	Prometone	D-glucosamine
0	12	0
0	0	12
0	12	12
1	12	12
2	12	12
4	12	12
2	8	12
2	20	12
2	12	8
2	12	20

EPR measurements were carried out on a Varian E 109 spectrometer at 9.3 GHz at 77 K. Absorption spectra were recorded on a Beckman Acta 7 spectrophotometer. For the spectroscopic measurements the Cu(II) concentration of 5×10^{-3} M in 0.15 M $NaClO_4$ was used.

Polarographic studies were performed on a Radelkis OH-105 polarograph. Polarograms were recorded at 25 °C under argon in 0.15 M $NaClO_4$ electrolyte.

Results and Discussion

The species distribution and the respective stability constants obtained with SUPERQUAD are given in Fig. 1 and Table II, respectively. According to previous results [1, 2] obtained for the binary systems in an acidic medium, pH 4–6.3, the major complex species is $Cu(Pr)_2$ ((1200) in Table II). In the pH range 6–8.5 two ternary complexes (1110) and (111-1) are present with the latter species reaching 50% in pH ~7.2. The Cu–D-glucosamine complex (102-2) with two $\{NH_2, O^-\}$ chelates [2] predominates at pH > 7.8 according to expectations. The EPR spectra which clearly indicated the formation of binary and ternary systems in the investigated solutions were very useful in this study (Table II). The EPR parameters of (1200) species, $g_\parallel = 2.350$ and $A_\parallel = 150$ Gauss and its stability constants log $\beta_{1200} = 6.90$ correspond well to a $Cu(Pr)_2$ complex [1]. The other two species are formed at

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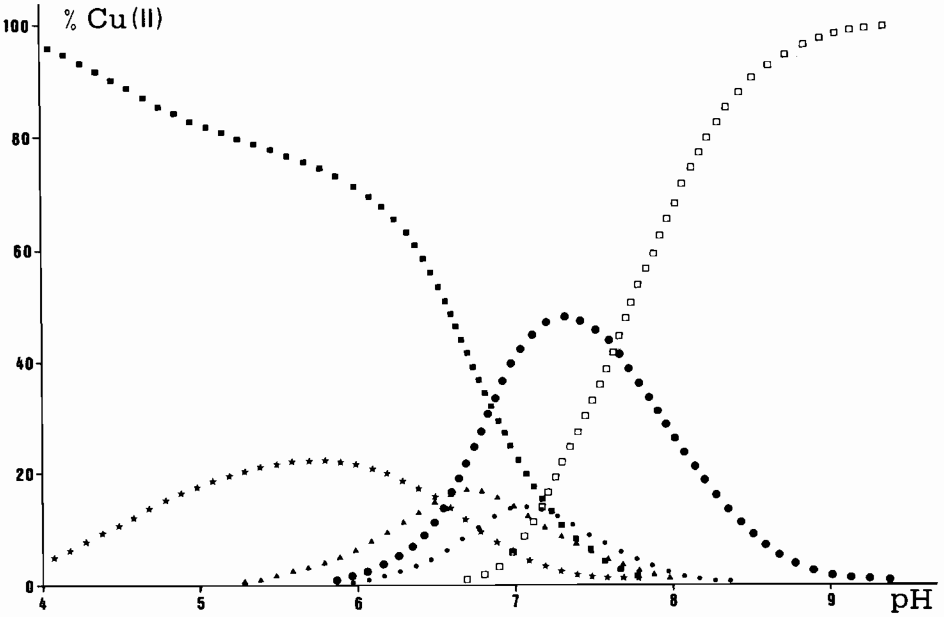

Fig. 1. The species distribution in the Cu(II)–prometone–D-glucosamine solutions as a function of pH. ■, (1000) (unbound Cu(II)); ★, (1200); ▲, (1110); •, (1020); ●, (111-1); □, (102-2) (for the species assignment see Table II).

TABLE II. Log Values of Stability Constants log β_{pqrs} and EPR Parameters for the Complex Species Observed in Ternary Cu(II)–Prometone–D-glucosamine System, $M_pPr_qGA_rH_s$, in 0.15 M NaCl at 25 °C

p	q	r	s	log β_{pqrs}	EPR	
					$g_{\parallel}$	$A_{\parallel}$ (Gauss)
1	2	0	0	6.90	2.350	150
1	1	1	0	8.18	2.323	150
1	0	2	0	9.02	2.293	145
1	1	1	−1	1.66	2.260	170
1	0	2	−2	−5.26	2.255	175

pH ~5.8. Their EPR parameters suggest that (1020) complex is a $Cu(GA)_2$ species (Table II) as log β_{1020} = 9.02 [2]. The other EPR spectrum overlapped with those two must then be derived from the ternary species (Table II, species (1110)). The log β_{1110} value (8.18) corresponds very well to the statistically evaluated stability constant [7] value from log β for $Cu(Pr)_2$ (log β = 6.9) and $Cu(GA)_2$ (log β = 9.02) (calc. log β = 8.26).

The (111-1) complex species dominant at pH 7.3 has the EPR parameters close to those of (102-2) species (CuL_2H_{-2}, L = D-glucosamine in ref. 2) and is hardly seen in the EPR spectra at pH >8.

The relative intensity variation of the EPR spectra of the respective complexes obtained in the studied solutions corresponds well to the species distribution scheme presented in Fig. 1. This could be used as evidence in support of the SUPERQUAD calculation made for the potentiometric data.

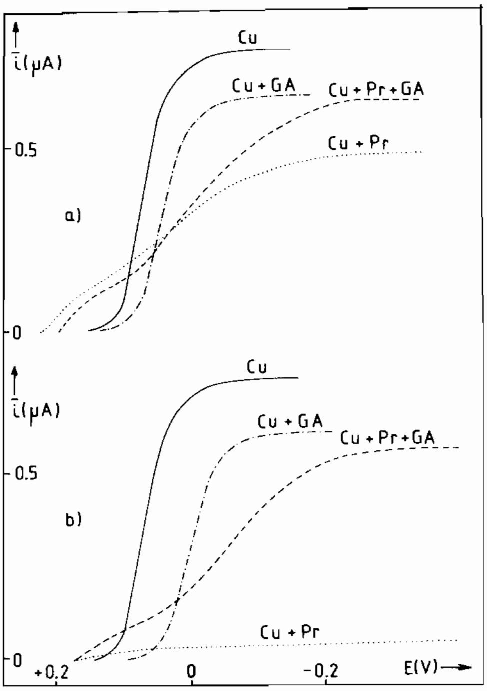

Fig. 2. Polarograms for Cu(II)–GA, Cu(II)–Pr and Cu(II)–GA–Pr solutions at pH (a) 6.65 and (b) 7.3 in 0.15 M $NaClO_4$ $c_{Cu(II)} = 10^{-4}$ M dm^{-3}, $c_{GA} = 2 \times 10^{-3}$ M dm^{-3}, $c_{Pr} = 2 \times 10^{-3}$ M dm^{-3}.

The presence of the ternary species could also be followed by polarography. The polarographic study

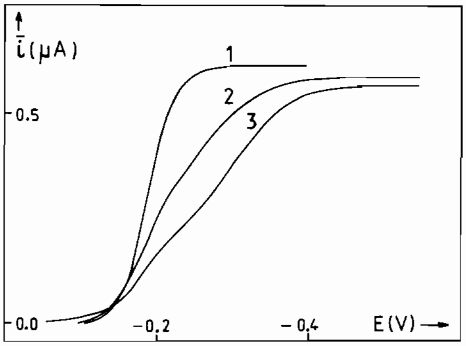

Fig. 3. Polarograms of Cu(II)–GA and Cu(II)–GA–Pr solutions at pH 9.5 in 0.15 M $NaClO_4$ with $c_{Cu(II)} = 10^{-4}$ M dm^{-3}, $c_{GA} = 7 \times 10^{-3}$ M dm^{-3} and $c_{Pr} = 0$ (1), 5×10^{-4} M dm^{-3} (2) and 10^{-3} M dm^{-3} (3).

on the Cu(II)–prometone system was described earlier [1]. The polarograms of Cu(II)–prometone–D-glucosamine solutions are considerably different to those of Cu(II)–Pr or Cu(II)–GA (Fig. 2). In Cu(II)–GA system at pH >9 (Fig. 3) the reduction of the binary complex $Cu(GA)_2$ is a reversible process with $E_{1/2} = -0.185$ V. The addition of prometone to the Cu(II)–GA solutions causes the formation of a new polarographic wave at more negative potential (−0.32 V, slope 0.07 V) which describes the irreversible reduction process of the ternary system. The increase of Pr to GA molar ratio causes the latter wave to become more pronounced (Fig. 3).

Conclusions

The formation of the ternary complex in the Cu(II)–prometone–D-glucosamine system is possible according to the statistical rules due to which the major complex at pH range 6.8–7.5 is (111-1) with prometone and chelating glucosamine via $\{NH_2, O^-\}$ donors. This complex is stable enough to keep bound herbicide ligand in the soluble phase at pH >7 which was not the case in the Cu–prometone binary system [1].

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