

Metal Complex Formation by Glyphosate

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Complex formation between several divalent metal ions and the herbicide glyphosate [*N*-(phosphonomethyl)glycine] was examined by differential pulse polarography and spectrophotometry in aqueous media. One Cu(II)-glyphosate complex with a half-wave potential ($E_{1/2}$) of -0.26 V and two Cd(II)-glyphosate complexes with an $E_{1/2}$ of -0.72 and -0.94 V were determined by polarography. A log K stability constant of 4.25 was estimated for the Cu(II)-glyphosate complex based on a 1:1 ratio. The UV absorption spectrum of the Cu(II)-glyphosate complex, which was formed by agitating metallic CuO with aqueous solutions of glyphosate, showed a strong absorption band at 226 nm that was interpreted as a ligand-to-metal charge-transfer band. The IR spectra of the glyphosate complex and the sodium salt of glyphosate exhibited similar vibrations; however, the bands for the complex were more intense and less hydrogen bonded. It was suggested that the complex formed as a result of a surface interaction between glyphosate and copper at the liquid/solid interface.

Glyphosate [*N*-(phosphonomethyl)glycine], a widely used herbicide in agriculture, has been found to alter several vital biochemical processes in plants and microorganisms, such as amino acid, protein, and nucleic acid biosyntheses, photosynthesis, and respiration; however, the primary mechanism of action has not been clearly established (Hoagland and Duke, 1982). It was suggested that chelation or complexation of metal cations may be affecting plant metabolism and physiology at any of the many points dependent on metal cations.

In a study with soils, Sprankle et al. (1975) showed that additions of Fe(III) and Al(III) cations reduced the degradation of glyphosate in a sandy loam. They postulated that the cations formed new adsorption sites in the soil, which conversely made glyphosate less available for microbial degradation. From the infrared spectra of some cation-saturated montmorillonites and glyphosate, Shoval and Yariv (1979) inferred the occurrence of some complexes between anionic glyphosate and the Fe(III) and Al(III) cations. The formation of metal complexes of glyphosate has been inferred in other soil and plant studies (Sprankle et al., 1975; Stahlman and Phillips, 1979).

The complex-forming properties of a large number of aminophosphonic acid compounds, similar to glyphosate, have been described by Kabachnick et al. (1974); however, no such information has been reported on glyphosate itself. Chang and Foy (1982), using polarography and spectrophotometry, reported the formation of Cu(II) and Fe(III) complexes between several pyridine carboxylic acids, including the herbicide picloram. In the present work, the formation of complexes between glyphosate and several divalent metal ions was investigated in aqueous media by using polarography, ultraviolet (UV) and infrared (IR) spectrophotometry, and liquid chromatography.

EXPERIMENTAL SECTION

Chemicals. Analytical-grade glyphosate (97% purity) was obtained from Monsanto Chemical Co., St. Louis, MO, and used without further purification. All other chemicals were reagent grade and used without further purification.

Preparation of Complexes. Two different procedures were used to prepare the complexes that were studied in this investigation. In the first procedure, 25-mL aliquots of glyphosate solution ranging in concentration from 20

to 800 $\mu\text{g/mL}$ were combined with 1-g quantities of pulverized cupric oxide [black wire ground to small particles (0.2–0.4 mm)]. The mixtures were agitated in polypropylene tubes for 1 h at room temperature, centrifuged, and passed through filter paper. The Cu(II) concentrations in the liquid phases were determined by atomic absorption spectrometry and a colorimetric method using 2,2'-bichinchonic acid (Diehl and Hach, 1982). Both UV and visible spectral analyses were made of the Cu(II) complex solution, and an infrared spectral analysis using KBr pellets was made on the residue that remained after the removal of water by lyophilization. In the second procedure, 25-mL aliquots of stock solutions of $\text{Cu}(\text{NO}_3)_2$, $\text{Pb}(\text{NO}_3)_2$, CdSO_4 , and ZnSO_4 prepared in 0.1 M KCl were mixed with weighed quantities of crystalline glyphosate. The pH of the mixtures was adjusted with dilute sodium hydroxide. The concentrations of metal ions and glyphosate were in the range of 0.25–2.60 and 1.0–50.0 mM, respectively. The metal complexes that formed by combining glyphosate with these divalent ions were characterized by differential pulse polarography (DDP) using a dropping mercury electrode (DME).

The composition of the Cu(II)-glyphosate complex was determined by the method of continuous variation, where the concentrations of Cu(II) ions and glyphosate were varied, but the sum of the concentrations was constant. A 6.4 mM solution of Cu(II) ions (400 $\mu\text{g/mL}$) prepared by $\text{Cu}(\text{NO}_3)_2$ and an equimolar solution of glyphosate (1082 $\mu\text{g/mL}$) were prepared in distilled water and adjusted to pH 5 before combining. Absorbance measurements were made at 226 nm, the wavelength at which the complex was found to absorb. An apparent stability constant was obtained for the Cu(II)-glyphosate complex by direct measurement of the free glyphosate remaining in solution after complexation. Attempts to measure free Cu(II) in solution with an ion-selective electrode were unsuccessful because the analyzer did not function properly in the presence of the complex presumably due to some interaction with the electrode.

Instrumentation. DPP was performed with a PAR Model 174A polarographic analyzer, which was connected to a Model 174/50 drop timer assembly and a three-electrode configuration cell. The working electrode was a DME with a drop time of 0.5 s. The polarograms were recorded on a Houston Instrument Model 2000 X-Y recorder. The UV and visible spectra were obtained with a Beckman DU-8 spectrophotometer, and the infrared spectra were obtained with a Perkin-Elmer Model 1320

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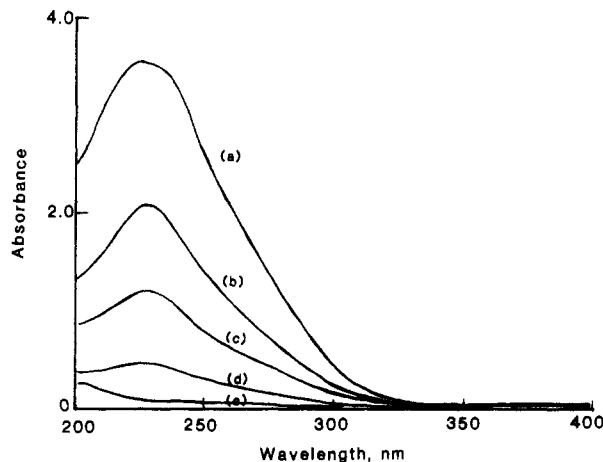


Figure 1. Absorption spectra of the Cu(II)-glyphosate complex (λ_{\max} 226 nm) resulting from the interaction of cupric oxide (1 g) with various concentrations of glyphosate: (a) 200 $\mu\text{g}/\text{mL}$; (b) 100 $\mu\text{g}/\text{mL}$; (c) 50 $\mu\text{g}/\text{mL}$; (d) 20 $\mu\text{g}/\text{mL}$; (e) 0 $\mu\text{g}/\text{mL}$. Solution pH 5.

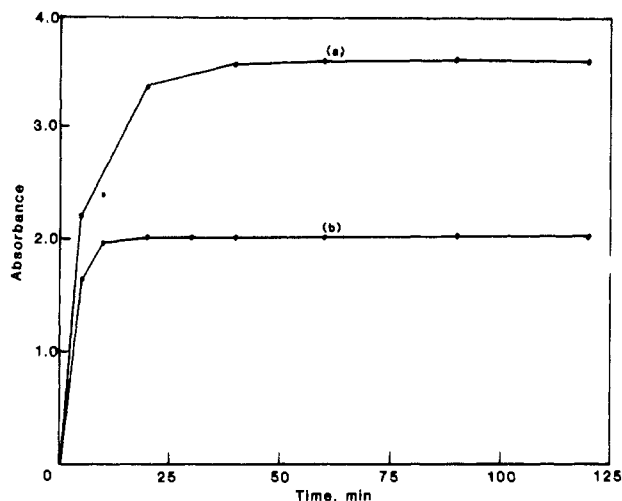


Figure 2. Formation of absorption band of the Cu(II)-glyphosate complex at 226 nm resulting from the interaction of cupric oxide (1 g) with glyphosate solutions at (a) 200 and (b) 100 $\mu\text{g}/\text{mL}$.

infrared spectrophotometer. A Spectra-Physics high-performance liquid chromatograph (HPLC) was used to quantitate glyphosate. Details of the HPLC method for determining glyphosate in aqueous media were described in an earlier paper (Glass, 1983). Measurements of pH were performed on a Fisher Accument Model 750 selective ion analyzer utilizing a Fisher combination electrode. Atomic absorption analyses were performed on a Perkin-Elmer Model 5000 atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Complex Formation from CuO. The UV spectra in Figure 1 show the absorption that resulted from agitating pulverized cupric oxide with varying concentrations of glyphosate at pH 5. The maximum absorption band occurred at 226 nm, where the absorbance increased from near 0.5 to 3.5 in glyphosate solutions ranging from 20 to 200 $\mu\text{g}/\text{mL}$. Neither glyphosate nor CuO gave UV spectra alone. Figure 2 shows a plot of the rate of formation of this absorption band at 226 nm with time, indicating that the interaction is completed within 15 min. The 226-nm band is interpreted as a ligand-to-metal charge-transfer (CT) band, resulting from the transfer of an electron from an electron-donating group in glyphosate to the electron-accepting metal. It is uncertain where the electron comes

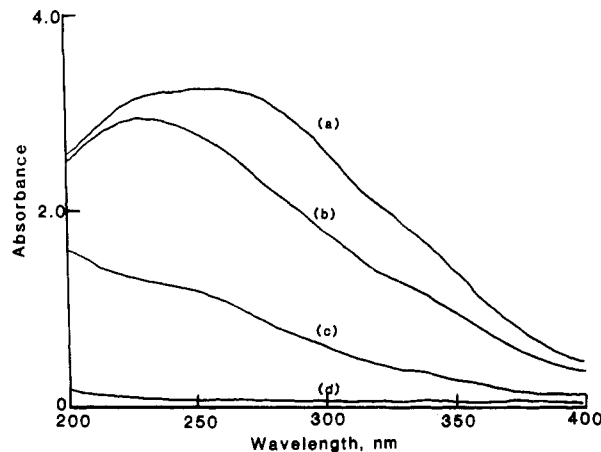


Figure 3. Absorption spectra of the Fe(III)-glyphosate complex (λ_{\max} 233 nm) resulting from the interaction of ferric oxide (1 g) with various concentrations of glyphosate: (a) 200 $\mu\text{g}/\text{mL}$; (b) 100 $\mu\text{g}/\text{mL}$; (c) 50 $\mu\text{g}/\text{mL}$; (d) 0 $\mu\text{g}/\text{mL}$. Solution pH 4.

from, but the lone-pair electrons on the secondary amine of glyphosate are probably involved in the process. In contrast to the CT process in the Cu(II)-glyphosate complex, the electron transfer in the complex formed in solution between glyphosate and the transition metal manganese apparently is complete or irreversible because the reduction of permanganate ($\text{Mn}^{7+} \rightarrow \text{Mn}^{4+}$) was observed in the presence of glyphosate (unpublished results).

Additional evidence for the ligand-to-metal CT process was obtained from the extinction coefficient of the complex, which was estimated as 4.5 ($\log \epsilon$) based on the formation of a 1:1 Cu(II)-glyphosate complex. Extinction coefficients ($\log \epsilon$) generally fall in the range of 3–5 for electronically allowed CT transitions (Lever, 1974). In Figure 3, the UV spectra that resulted from agitating ferric oxide with solutions of glyphosate (pH 4) show an absorption band (λ_{\max}) at 233 nm, which was interpreted also as a ligand-to-metal CT band. Details of this investigation, which indicates that glyphosate also complexes trivalent metal ions, will be presented in a later report.

The development of blue color in the glyphosate solutions in the present investigation was additional evidence for complex formation. A broad band ranging from 700 to 800 nm in the visible spectra (not shown) was attributed to an electronic d-d transition typical of most copper complexes. Chang and Foy (1982) did not observe the development of a blue color in the complex formation between Cu(II) and picloram but reported the development of a pink color, resulting from the complex formation between picloram and Fe(II). The formation of a weaker complex with a smaller extinction coefficient may account for the absence of the blue color. Another difference between the Cu(II) complexes of glyphosate and picloram was the charge assigned to the two complexes. A positively charged complex, $[\text{Cu(II)-picloram}]^+$, was reported in the earlier work; however a negatively charged complex, $[\text{Cu(II)-glyphosate}]^-$, was concluded from the present investigation. The evidence for the assignment follows: (1) the complex dissolved in NaOAc at pH 5 moved anodically when analyzed by paper electrophoresis (unpublished results) and (2) the complex was retained by bicarbonate-saturated anion-exchange resin (Bio-Rad AG 1-X8) and was released by chloride ions. The number of charges on the anionic Cu(II)-glyphosate complex is uncertain.

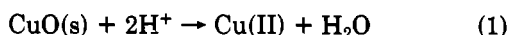
Table I shows additional data on the absorbance measurements at 226 nm and the concentration of Cu(II) ions produced as a function of pH and glyphosate concentration. A greater amount of the complex formed at lower

Table I. Cu(II) Ions, Free Glyphosate Concentrations and Absorbance Measurements (λ_{\max} 226 nm) Resulting from the Interaction of Glyphosate Solutions (25 mL) with Cupric Oxide (1 g) as a Function of Concentration and pH at 27 °C

initial solution, glyphosate		complex solutions				
$\mu\text{g/mL}$	pH	glyphosate ^a		Cu(II) ions, $\mu\text{g/mL}$		absorbance ^b
		$\mu\text{g/mL}^b$	pH ^c	colorimetry ^{b,d}	AA ^{b,e}	
0	3		5.29	36.41 \pm 0.93	<i>f</i>	0.71 \pm 0.01
	3		6.26	3.06 \pm 0.13		0.59 \pm 0.04
	5		6.18	2.72 \pm 0.02		0.26 \pm 0.01
	9		6.99	0		0.03 \pm 0.02
20	5		7.01		9.79 \pm 0.18	0.58 \pm 0.06
	5		7.26		23.17 \pm 0.18	1.31 \pm 0.03
100 (0.6 mM)	3	det.	5.71	38.29 \pm 1.90		1.92 \pm 0.02
	5	det.	6.86	34.13 \pm 0.00	42.30 \pm 0.07	2.01 \pm 0.02
	9	det.	9.80	25.86 \pm 1.02		2.06 \pm 0.01
200	3	4.73 \pm 0.53	5.20	74.32 \pm 0.93		3.64 \pm 0.04
	5	4.47 \pm 0.27	6.66	64.92 \pm 2.05	80.53 \pm 1.68	3.44 \pm 0.00
	9	60.00 \pm 5.22	9.28	28.82 \pm 2.84		1.72 \pm 0.01
400	3	9.50 \pm 1.94	4.94	143.89 \pm 6.51		6.39 \pm 0.50
	5	8.87 \pm 2.01	7.78	113.84 \pm 7.43	133.38 \pm 3.88	7.40 \pm 0.20
	9	188.20 \pm 19.70	9.23	28.57 \pm 2.71		2.70 \pm 0.10
800	3	74.95 \pm 11.00	7.28	611.52 \pm 47.32	566.50 \pm 24.5	16.90 \pm 0.90
	5	141.92 \pm 21.99	6.85	209.12 \pm 8.92	210.00 \pm 9.0	11.60 \pm 0.60
	9	551.65 \pm 71.95	11.36	91.91 \pm 0.91	93.0 \pm 5.70	5.08 \pm 0.37

^aThe fluorescent derivative was prepared from 2- to 5-mL aliquots and measured by HPLC. The minimum level of detection was near 2 $\mu\text{g/mL}$ without a cleanup step. ^bMean \pm standard deviation of a minimum of four determinations. ^cMean of final pH values. ^dA purple cuprous derivative (λ_{\max} nm) was prepared by adding 2 mL of Na_2SO_3 (7.9 mM) to 1-mL aliquots of the complex solutions and subsequently adding 1 mL of disodium 2,2'-bichinchoninate (12.5 mM). The accuracy of the method was found to be 55% with standard cupric chloride solutions. Data shown for the colorimetric method have been corrected. ^eAA denotes atomic absorption. ^fAll blanks indicate that determinations were not made.

pH values. The pH of the glyphosate solutions increased 2–3 units after complexing with copper, demonstrating consumption of hydrogen ions during the process. In an earlier study on copper oxide, Schindler (1967) demonstrated that the solubility of copper oxide in aqueous medium was dependent on the hydrogen ion concentration as illustrated in eq 1:



The effect of pH on the proposed complex formation is not fully understood, but the data show that the Cu(II) concentrations increase with higher quantities of glyphosate, suggesting some type of surface reaction between glyphosate and CuO. Chang and Matijevic (1983) recently reported that such chelating agents as EDTA and HEDTA were responsible for releasing ferric species from the iron oxide hematite and proposed two mechanisms for the phenomena. In the first mechanism, the ferric ions are released from the bare surface and react with either hydroxide or chelating ions in solution, causing a further release of the metal ion from the solids. In the second mechanism, which is more related to (1) the surface properties of the oxide, (2) the pH of the medium, and (3) the chelating power of the complexing agent, the chelating agent becomes bound to the lattice metal ion and the entire complex is then released into solution as the lattice bond breaks. In a recently published study of the reduction and dissolution of manganese(III, IV) oxide suspensions by hydroquinone, Stone and Morgan (1984) reported that the dissolution rate was first order with respect to the reductant, hydroquinone, and postulated the formation of hydroquinone-oxide surface complexes prior to the electron-transfer process. The results of the two studies and the evidence obtained from the present investigation indicate that complex formation is an essential step in the reduction and dissolution of metal oxides by organics.

The infrared spectra of a dry residue from the Cu(II)-glyphosate complex and the sodium salt of glyphosate in KBr pellets are shown in Figure 4. Absorption bands appear at 3413, 3186, and 2912 cm^{-1} in the spectrum of the complex and a broad absorption band appears in that of

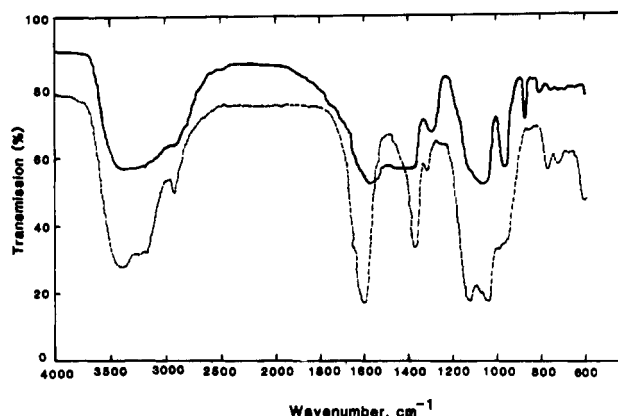


Figure 4. Infrared spectra of the sodium salt of glyphosate (—) and a residue from the Cu(II)-glyphosate complex solution (---) prepared in KBr pellets.

the salt. The poor resolution in the spectrum of the salt of glyphosate is attributed to N–H stretching vibrations of the secondary amine of glyphosate. The strong bands observed at 1605 and 1371 cm^{-1} in the complex are assigned to asymmetrical and symmetrical C=O stretching vibrations of the carboxylate. The broad band with its center at 1575 cm^{-1} in the spectrum of the salt is attributed also to the C=O vibrations of the carboxylate. Absorption bands also appear at 1131, 1044, 770, and 720 cm^{-1} in the complex and at 1050, 960, and 870 cm^{-1} in the salt. The bands at 1131 and 1044 cm^{-1} are believed to be due to PO_3 vibrations of the phosphono group of glyphosate. Very strong absorption bands with similar frequencies were observed in the IR spectra of several transition metal coordination compounds of (2-aminoethyl)phosphonic acids (Menke and Walmsley, 1976). These bands were assigned to stretching modes of the PO_3 group. Coordination was interpreted as occurring through the PO_3 group in the complex. There are insufficient data to determine what the coordination sites are in the Cu(II)-glyphosate complex, but I propose that Cu(II) ion is coordinated through the carboxylate, the amino and the phosphono groups of glyphosate, and a water molecule. This explanation is

Table II. Half-Wave Potentials^a and Limiting Currents (i_d) from the Polarographic Reduction of Free Metal Ions and Metal Complexes of Glyphosate at 27 °C

metal ion ^b concn, mM	glyphosate ^c	pH	$-(E_{1/2})_M$, ^d V	i_d , mA	$-(E_{1/2})_C$, ^d V	i_d , mA	$-(E_{1/2})_C$, V	i_d , mA
Cd(II)								
1.0	0.0	7.5	0.62	1.6				
	1.0	7.5	0.62	1.5	0.72	D ^e	0.92	0.26
1.3	2.0	7.5	0.62	1.2	0.72	D	0.92	0.37
	12.5	8.6	ND ^e		0.76	0.6	1.03	0.63
1.3 ^f	25.0	10.6	ND		0.76	0.4	1.05	0.22
2.0	1.0	7.5	0.64	1.65	0.72	D	0.92	0.58
	2.0	7.5	0.64	0.64	0.72	D	0.92	0.47
2.6	12.5	6.5	0.64	2.20	0.72	D	0.94	0.60
	25.0	6.5	0.64	1.84	0.72	D	0.96	0.81
	50.0	6.5	ND		0.72	0.9	0.96	1.14
Cu(II)								
0.25	0.0	5.2	0.09	0.40				
1.0	2.5	11.0	ND		0.26	0.05		
	5.0	11.0	ND		0.26	0.05		
	10.0	11.0	ND		0.28	0.14		
Pb(II)								
2.0	0.0	3.0	0.42	1.07				
	6.0	4.0	0.43	0.49	ND		ND	
	25.0	4.0	0.43	0.25	ND		ND	
Zn(II)								
0.5	0.0	5.0	1.07	0.39				
	50.0	5.0	1.08	0.40	ND		ND	
	0.0	11.0	1.64	0.16				
	50.0	11.0	1.64	0.03	ND		ND	

^a $-(E_{1/2})$, volts, vs. SCE. ^bAll metal ion solutions were prepared in 0.1 M KCl as the supporting electrolyte, except where otherwise indicated. ^cSolutions were adjusted to a given pH after glyphosate was added. ^dHalf-wave potentials of free metal ions $-(E_{1/2})_M$ and metal complexes $-(E_{1/2})_C$. ^eD and ND denote detectable and nondetectable, respectively. ^fSupporting electrolyte was 0.1 M NaHCO₃.

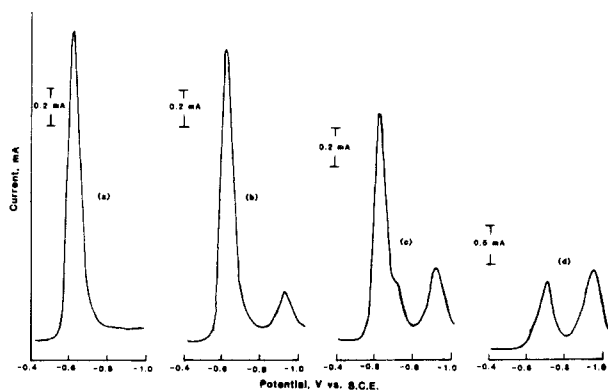


Figure 5. Polarograms of 1.0 mM Cd(II) in 0.1 M KCl with varying concentrations of glyphosate at pH 7.5: (a) 0.0 mM; (b) 1.0 mM; (c) 2.0 mM. Polarogram d represents 2.6 mM Cd(II) and 50 mM glyphosate at pH 7.5.

supported by the recent investigation by Fonong et al. (1983), who concluded that the structure of some 1:1 and 2:1 Ca(II) complexes of several diphosphonates consisted of an intricate network of hydrogen bonds and ligand-bridges coordination complexes.

Complex Formation in Solution. Polarography and UV spectrophotometry were used to characterize the metal complexes of glyphosate that formed in aqueous media. Copper and cadmium were the only two transition metals that formed new polarographic waves in the presence of glyphosate. Glyphosate itself was found to be polarographically inactive as reported earlier by Bronstad and Friestad (1976). Figure 5 shows the polarograms of free Cd(II) ions whose half-wave potential appear at -0.62 V and complexed Cd(II) whose half-wave potential is -1.04 V. Additional data in Table II show that a second wave begins to appear near -0.7 V and continues to increase in wave height with higher concentrations of glyphosate. At 50 mM glyphosate, the free Cd(II) wave completely disappears, and the remaining two waves at -0.7 and -1.04 V are assigned to two separate Cd(II)-glyphosate com-

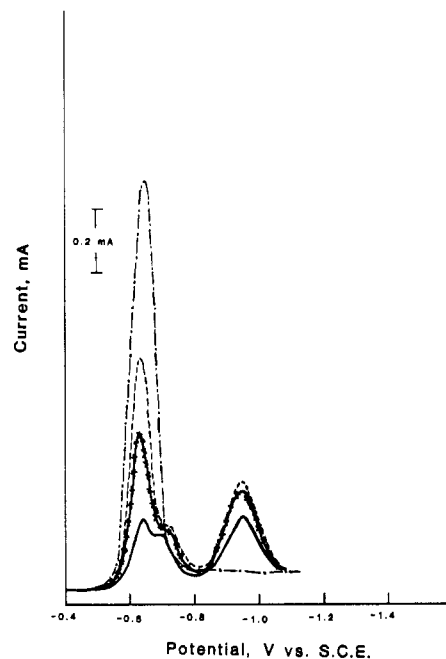


Figure 6. Polarograms of 2.6 mM Cd(II) in 0.1 M KCl with 25 mM glyphosate at various pHs (---) pH 5.5; (-·-) pH 6.5; (×) pH 7.5; (—) pH 8.5.

plexes. The large difference in the limiting currents (i_d) of free Cd(II) ions and Cd(II) complexes indicates that a large proportion of the complex is not reduced in the applied potential range. The polarograms in Figure 6 demonstrate that the reduction of the cadmium complex is pH dependent.

The free Cu(II) ions gave a wave with a half-wave potential of -0.09 V and the Cu(II) complex produced one wave at a half-wave potential of -0.26 V in the presence of glyphosate (Table II). The reduction of the Cu(II) complex was also pH dependent similar to what was found with cadmium. With Zn(II) and Pb(II) ions, no new po-

Table III. Apparent Stability Constants (log *K*) for the Cu(II) Complex of Glyphosate^a

sample	Cu(II) ions added, M	pH	glyphosate found, M	log <i>K</i>
1	1.28×10^{-3}	5	0.7×10^{-4}	4.34
2	0.6×10^{-4}	5	1.4×10^{-4}	4.21
3	0.32×10^{-4}	5	2.6×10^{-4}	4.17
				$\bar{X} \pm \text{SD}: 4.24 \pm 0.07$

^aInitial glyphosate concentration was 1.2×10^{-3} M (200 $\mu\text{g}/\text{mL}$).

larographic waves were formed, but there was a decrease in the limiting currents of these ions in the presence of glyphosate (Table II), suggesting that the electroactivities of the ions were affected by glyphosate. The precipitation of the free metal ions as hydroxides was observed at higher pH values (>pH 9), but no precipitation occurred at the higher pH values in the presence of glyphosate, providing further evidence that glyphosate is a complexing agent (unpublished results).

In a continuous variation plot for the Cu(II)-glyphosate complex (not shown), the absorbance at 226 nm was plotted against the mole fraction of Cu(II). The maximum absorbance was observed at a mole fraction of 0.5, which corresponded to a 1:1 complex. An apparent stability constant (log *K*) of 4.24 ± 0.07 as shown in Table III was obtained at pH 5 by direct measurement of free glyphosate in solution and an estimation of free Cu(II) based on the difference between the amount of Cu(II) ions added and the amount tied up in the 1:1 complex. The stability constants for the 1:1 picloram complexes of Fe(III) and Cu(II) were estimated as 6.5 and <5.0, respectively (Chang and Foy, 1982).

SUMMARY AND CONCLUSION

The results from the polarographic study demonstrate that glyphosate exhibit fairly strong complexing properties toward divalent metal ions. Cadmium and cupric ions formed stable complexes that led to the formation of new polarographic waves. Aqueous solutions of glyphosate were found to interact with metallic CuO and Fe₂O₃ presumably at the solid/liquid interface to form UV absorption bands at 226 and 233 nm, respectively, which were interpreted as ligand-to-metal charge-transfer bands. Based on these findings and other spectral data, it was concluded that a 1:1 Cu(II)-glyphosate complex formed that gave an estimated log *K* stability constant of 4.25. The present findings are significant in relation to the chemistry of glyphosate; however, advanced studies with ESR and NMR are needed for establishing the structures of these complexes and the mechanisms of the interactions.

The complexing ability of glyphosate probably accounts for the corrosiveness of this substance to iron and galvanized steel. The formation of complexes has been inferred in the loss of herbicidal activity and in the adsorption of glyphosate by soil components, and it is likely that the complexation occurs via the same mechanisms as witnessed here in the complexing of cupric ions from CuO. The hydrous metal oxides, which are abundant in soils, are the likely species for metal complex formation.

Complex formation and chelation of metal ions were dismissed by Rubin et al. (1982) for causing 95% inhibition of the enzyme DAHP synthase-Co in glyphosate-treated mung beans. In agreement with these authors, glyphosate inhibition most likely is not due to cobalt chelation but probably due to competition between glyphosate and one or more of the substrates for active sites on the enzyme. Glyphosate may also be complexing the enzyme-bound metal by displacing the weaker ligand substrates already present on the enzyme that have smaller stability constants for the metal. Since glyphosate has such strong affinity for copper, complex formation with some of the cuproprotein enzymes in plants, such as phenolase, ascorbate oxidase, laccase, or amine oxidase, may be a prime target for herbicidal action.

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