INFLUENCE OF CITRIC ACID AND GLYCINE ON THE ADSORPTION OF MERCURY (II) BY KAOLINITE UNDER VARIOUS pH CONDITIONS

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Abstract—This investigation was carried out to study the effect of different concentrations of citric acid and glycine, which are common in freshwaters, on the kinetics of the adsorption of Hg by kaolinite under various pH conditions. The data indicate that Hg adsorption by kaolinite at different concentrations of citric acid and glycine obeyed multiple first order kinetics. In the absence of the organic acids, the rate constants of the initial fast process were 46 to 75 times faster than those of the slow adsorption process in the pH range of 4.00 to 8.00. Citric acid had a significant retarding effect on both the fast and slow adsorption process at pHs of 6.0 and 8.0. It had a significant promoting effect on the fast and slow adsorption process at pH 4.00. Glycine had a pronounced enhancing effect on the rate of Hg adsorption by kaolinite during the fast process. The rise in pH of the system further increased the effect of glycine on Hg adsorption. The magnitude of the retarding/promoting effect upon the rate of Hg adsorption was evidently dependent upon the pH, structure and functionality of organic acids, and molar ratio of the organic acid/Hg. The data obtained suggest that low-molecular-weight organic acids merit close attention in studying the kinetics and mechanisms of the binding of Hg by sediment particulates and the subsequent food chain contamination.

Key Words—Adsorption, Kaolinite, Kinetics, Mercury, Organic acids, pH, PZC, Speciation.

INTRODUCTION

Interactions between sediment particulates and metals play an important role in the regulation of dissolved metal concentrations in freshwaters (Solomons and Forstner 1984). It has been estimated that 90–99% of the total Hg in the freshwater system is sorbed by the particulates (Lindberg et al. 1975; Ramamoorthy and Rust 1976; Kudo et al. 1977; Reeder et al. 1979). The extent of the association of Hg with sediment particulates is controlled by the nature and properties of sediments and ionic factors including organic ligands (Moore and Ramamoorthy 1984; Lindqvist 1991a, 1991b; Wang et al. 1991). The speciation of metals in solution may enhance the adsorption if ligands themselves are adsorbed onto the mineral surface. Conversely, speciation may hinder or prevent the adsorption if the complexing ligands form strong complexes with metals and these complexes are not adsorbed on the mineral surface (Solomons and Forstner 1984). The surface properties of the sediments, the dissociation of the organic ligands and the formation of metal-organic complexes in natural waters is strongly pH-dependent (Stumm and Morgan 1981; Stumm 1987).

Citric acid and glycine are among the organic ligands commonly present in natural water systems. Gardner (1974) calculated the concentration of Hg complexed by different ligands in a model system containing 15 organic ligands which are present in the natural water. The results indicated that besides cysteine and other sulphur containing organic acids, citric acid and glycine seem to be most strongly associated with mercury. Lindberg et al. (1975) indicated that a greater proportion of dissolved Hg is complexed by the <500 molecular weight organic fraction due to its relatively greater total acidity. The nature and reactivity of these complexes is not well understood although functional groups such as -COOH, -NH$_2$ and -SH are reported to be responsible for the formation of Hg complexes (Ramamoorthy and Kushner 1975). This study, using well defined organic acids, is particularly relevant to understanding the influence of natural organics on Hg adsorption by mineral surfaces because these acids contain functional groups similar to those occurring in the natural water (Gjessing 1976).

Kaolinite is commonly present in freshwater sediments (Oscarson et al. 1981). It has a small negative charge due to broken edges and structural imperfections (Grim 1968). Kaolinite has the ability to adsorb organic acids onto its surface, because of structural imperfections (Grim 1968; Mortland 1986).

The objective of this study was to investigate the kinetics of the adsorption of Hg species by kaolinite under different concentrations of citric acid and glycine at various pH conditions. This information is essential to understand the impact of different organic

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Table 1. Stability constants of complexes of Hg(II) with hydroxyl, glycine and citric acid used in the computation of Hg speciation.

Ligands	Log K_{f1}†	Log K_{f2}‡
Hydroxyl	10.91§	11.80§
Citric acid	10.90§	
Glycine	10.50#	8.60#
Hydroxyl-glycine	9.90#	

† K_{f1} stands for 1:1 Hg-ligand complexes.
‡ K_{f2} stands for 1:2 Hg-ligand complexes.
§ Martell and Smith (1979).
# Reid and Podanyi (1988).

acids, which have different structures and functional groups, on the dynamics of Hg in the freshwater system and subsequent food chain contamination.

MATERIALS AND METHODS

Preparation of Kaolinite

A kaolinite sample from the Birch Pit near Macon, Georgia, U.S.A. was obtained from Wards Natural Science Establishment Inc., New York. It was ultrasonified (Genrich and Bremner 1972) and the <2 μm size fraction was separated by sedimentation (Jackson 1979). The kaolinite surface was saturated with 10^{-1} M $CaCl_2$ and subsequently washed with water until free of Cl.

Point of Zero Charge (PZC) of Kaolinite

The surface charge of the kaolinite sample was determined by the potentiometric method. One tenth gram of kaolinite was suspended and equilibrated in 25 mL of 10^{-2}, 10^{-1} and 1.0 M NaCl solutions in which 0.25 mL of 10^{-1} M HCl was added. The suspension was titrated with 10^{-1} M NaOH by an automatic Metrohm 672 titroprocessor. The point of zero charge (PZC) was taken at the pH where the titration curves, which were obtained in the presence of different concentrations of NaCl, intersected each other.

Kinetics of Hg Adsorption as Influenced by Citric Acid and Glycine

One tenth gram of the <2 μm kaolinite was suspended in 50 ml of 10^{-5} M Hg as $Hg(NO_3)_2$ solution containing 0, 10^{-3}, 10^{-2} and 10^{-1} M citric acid or glycine. The initial pH of the citrate-$Hg(NO_3)_2$ and glycine-$Hg(NO_3)_2$ solutions, as well as the kaolinite suspension, was adjusted to 4.0, 6.0 and 8.0. After mixing the clay suspension with respective solutions, the pH of the suspensions was also adjusted to 4.00, 6.00 and 8.00. Two drops of toluene were added to each suspension to prevent microbial activity. The flasks that contained the suspensions were shaken in a constant temperature water bath at 25°C for 0.5, 1, 2, 4, 8, 24, 48 and 96 h. The reaction period was limited to 96 h.

because a significant loss of Hg could occur after a longer reaction period (Newton and Ellis 1974).

The pH of the suspensions was determined at the end of each reaction period by using a pH combination electrode. The Eh of the suspension was measured by a Pt electrode (vs. an AgCl reference electrode in 4 M KCl solution). The suspensions were centrifuged at 1600 g for 30 minutes and were then filtered through a 0.45 μm Millipore membrane at the end of selected reaction periods.

Aliquots of the supernatant were taken for total Hg analysis by a UV mercury analyzer at the wavelength of 253.7 nm utilizing the cold vapor technique for total Hg determination (U.S. Environmental Protection Agency 1974).

Adsorption of Citric Acid and Glycine by Kaolinite

One tenth gram of kaolinite sample was suspended in 50 mL of 10^{-2} M solution of citric acid or glycine. The initial pH of the solution was adjusted to either 4.00, 6.00 or 8.00, in a 125 mL flask. The suspension was shaken in a constant temperature water bath at 25°C for 1 and 24 h. At the end of each reaction period, the suspension was filtered through 0.45 μm Millipore membrane and washed with water. The organic carbon content of the kaolinite sample before and after the reaction with citric acid or glycine was determined using infrared spectrophotometry (Tocomaster Model 915B, total organic carbon computation system).

Calculations for Hg Speciation

Calculations for the Hg speciation at various citric acid or glycine to Hg molar ratios at pHs of 4.00, 6.00 and 8.00 were carried out by the GEOCHEM program originally developed by Sposito and Mattigod (1979) and modified by Parker et al. (1987) for IBM PC. For the calculations, the same Hg, citric acid and glycine concentrations at pHs of 4.00, 6.00 and 8.00 were used as per the adsorption studies. The stability constant values of various Hg(II) complexes used in the computation are presented in Table 1. The model uses the Debye-Hückel equation for activity coefficients calculation and was run under the condition (Eh, dissolved gases and ionic strength) which was the same as used in the experiment. Calculations were carried out at 0.003 atm concentration of dissolved carbon dioxide.

RESULTS

Kinetics of Hg Adsorption as Influenced by Citric Acid

The time dependence of Hg adsorption by kaolinite as influenced by various concentrations of citric acid at pHs of 4.00, 6.00 and 8.00 is shown in Figure 1. The data indicate that the Hg adsorption in these systems obeyed multiple first order kinetics, because the
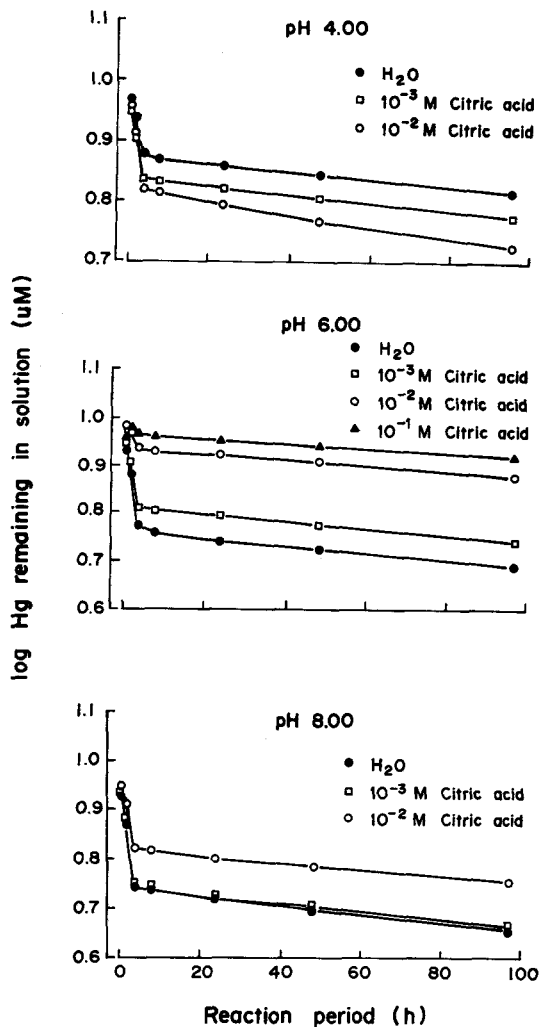
Figure 1. Rate curves of mercury adsorption by kaolinite as influenced by citric acid. All fast and slow reactions are fitted to respective linear equations with $r^2 \geq 0.99$ and $P < 0.01$.

Table 2. The rate constants of Hg adsorption by kaolinite under various citric acid concentrations in the pH range of 4.00 to 8.00.

Concentration of citric acid (M)	Rate constants† $(hr^{-1}) \times 10^3$		Final suspension‡	
	Step I	Step II	pH	Eh (mv)
		pH 4.00		
0	68 ± 3	1.49 ± 0.08	3.85	485
10^{-3}	93 ± 4	1.54 ± 0.04	3.92	520
10^{-2}	104 ± 2	2.40 ± 0.12	3.90	510
		pH 6.00		
0	131 ± 4	1.75 ± 0.08	6.05	470
10^{-3}	106 ± 3	1.65 ± 0.03	5.90	530
10^{-2}	37 ± 1	1.20 ± 0.05	5.95	515
10^{-1}	19 ± 1	1.09 ± 0.05	5.85	505
		pH 8.00		
0	142 ± 4	2.10 ± 0.01	8.05	485
10^{-3}	146 ± 2	1.97 ± 0.08	7.90	515
10^{-2}	101 ± 2	1.69 ± 0.08	7.85	510

† Log Hg (μM) remaining in the solution was plotted versus time (hr) in calculating the rate constants. Step I stands for the fast reactions and Step II stands for the slow reactions.

‡ The degrees of the precision of the pH value is ± 0.15 and the Eh value is ± 60 mv. The measurements were carried out at the end of the reaction periods.

8.0, but it had a significant promoting effect on the fast and slow adsorption processes at pH 4.00. At pH 8.00, the rate of Hg adsorption almost remained the same both in the presence of 10^{-3} M citric acid and in the absence of citric acid. The results show the rate of Hg adsorption during the fast process at different concentrations of citric acid varied with pH (Figure 2). In the presence of 10^{-2} M citric acid, the rate of Hg adsorption during the fast adsorption process was minimum at pH 6.00 (Figure 2). Adsorption increased sharply with the increase or decrease of the pH value.

The data on the adsorption of citric acid by kaolinite sample are presented in Table 3. The data show that

regression analysis revealed two distinct rate curves. The initial rapid adsorption occurred within 4 h. and was followed by the slow adsorption process. The rate constants of both the fast and slow adsorption processes are tabulated in Table 2. In the absence of citric acid, the initial adsorption process was 46 to 75 times faster than the slow process. In the absence of citric acid, the Hg adsorption in the fast process was: 1) 1.4 and 1.5 times slower than in the presence of 10^{-3} and 10^{-2} M citric acid at pH 4.00; 2) 1.2, 3.5 and 6.9 times faster than that in the presence of 10^{-3}, 10^{-2} and 10^{-1} M citric acid at pH 6.00; and 3) 1.4 times faster than that in the presence of 10^{-2} M citric acid at pH 8.00. The same trend was observed for the slow adsorption process of Hg. Citric acid at a concentration of 10^{-2} M had a significant retarding effect on the rapid and slow adsorption of Hg by kaolinite at pHs of 6.0 and
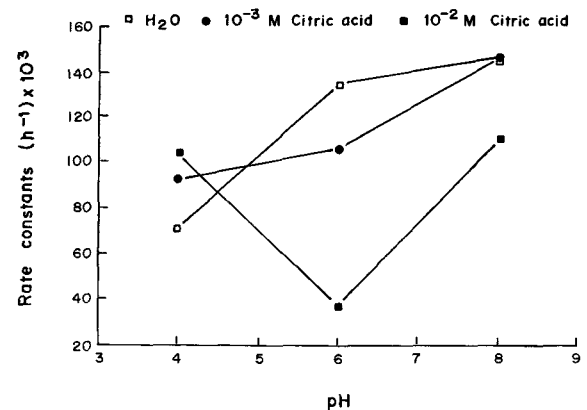

Figure 2. Effect of pH on the rate constants of Hg adsorption at varying concentrations of citric acid in the fast adsorption process.
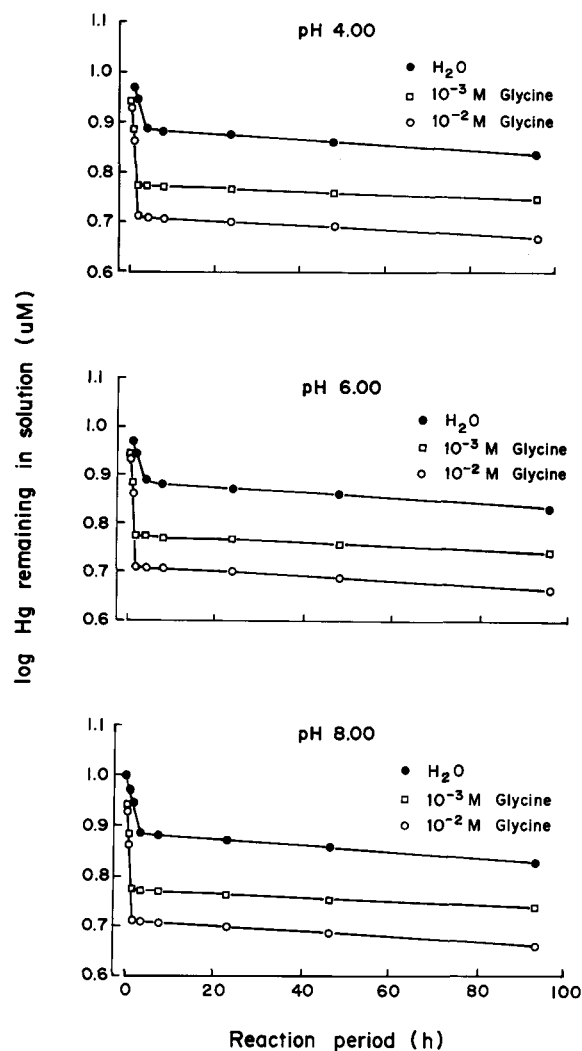
Figure 3. Rate curves of mercury adsorption by kaolinite as influenced by glycine. All fast and slow reactions are fitted to respective linear equations with $r^2 \geq 0.99$ and $P < 0.01$. The differences in the Hg adsorption level between the absence of glycine (Figure 3) and the absence of citric acid (Figure 1) are attributable to the heterogeneity of the kaolinite sample studied.

the adsorption of citric acid by kaolinite virtually remained constant between the 1 and 24 hours reaction period. The adsorption was greatest at pH 4.00 and substantially less at pHs of 6.00 and 8.00.

Kinetics of Hg Adsorption as Influenced by Glycine

The time dependence of Hg adsorption by the kaolinite at various concentrations of glycine is illustrated in Figure 3. The results show that the sorption of Hg by kaolinite obeyed multiple first order kinetics. There was an initial fast adsorption that was followed by a slow sorption. Separation of the adsorption rate

Table 3. The amount of citric acid adsorbed by kaolinite at 10^{-2} M citric acid as influenced by pH.

	μg of citric acid adsorbed/g of kaolinite	
pH	1 hr	24 hr
4.00	84 ± 7	81 ± 5
6.00	6 ± 1	5 ± 2
8.00	4 ± 1	4 ± 1

data into the fast or slow process was based on the relative rate of Hg uptake.

The rate constants for both the fast and slow adsorption processes are shown in Table 4. The data of the fast sorption process showed that the presence of glycine in solution substantially increased the rate of the Hg adsorption. The rate of Hg adsorption in the presence of glycine during the slow adsorption process became very slow. The rate constants of the fast process are 54 to 75 times higher in the absence of glycine and 309 to 438 times higher in the presence of glycine than the slower adsorption process. As the concentration of glycine increased, the rate constants of Hg adsorption during the fast adsorption process increased significantly. In the fast adsorption process, increasing the glycine concentration from 0 to 10^{-2} M, the rate of Hg adsorption increased by 4.9 times at pH of 4.00, 3.8 times at pH 6.00 and 4.1 times at pH 8.0. Figure 4 showed that the rate of Hg adsorption consistently increased with the increasing concentration of glycine for the pH range of 4.00 to 8.00 during the fast adsorption process. The adsorption of glycine by kaolinite surface is presented in Table 5. The data

Table 4. The rate constants of Hg adsorption by kaolinite under various glycine concentrations in the pH range of 4.00 to 8.00.

Concentration of glycine (M)	Rate constant† (hr⁻¹) × 10³		Final suspension‡	
	Step I	Step II	pH	Eh (mv)
	pH 4.00			
0	68 ± 3	1.25 ± 0.05	3.96	475
10^{-3}	258 ± 4	0.74 ± 0.03	3.95	510
10^{-2}	331 ± 4	1.07 ± 0.02	4.00	525
	pH 6.00			
0	131 ± 4	1.75 ± 0.10	6.05	465
10^{-3}	460 ± 2	1.05 ± 0.06	5.90	520
10^{-2}	496 ± 3	1.20 ± 0.07	5.95	515
	pH 8.00			
0	135 ± 2	2.00 ± 0.07	7.95	485
10^{-3}	510 ± 15	1.24 ± 0.06	7.90	535
10^{-2}	556 ± 6	1.51 ± 0.04	7.90	540

† Log Hg (μM) remaining in the solution was plotted versus time (hr) in calculating the rate constants. Step I stands for the fast reactions and Step II stands for the slow reactions.

‡ The degrees of the precision of the pH value is ±0.15 and the Eh value is ±75 mv. The measurements were carried out at the end of the reaction periods.
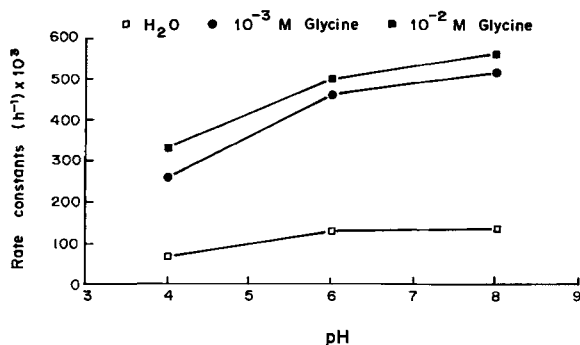
Figure 4. Effect of pH on the rate constants of Hg adsorption at varying concentrations of glycine in the fast adsorption process.

Table 5. The amount of glycine adsorbed by kaolinite at 10^{-2} M glycine as influenced by pH.

pH	μg of glycine adsorbed/g of kaolinite	
	1 hr	24 hr
4.00	46 ± 2	48 ± 1
6.00	72 ± 2	74 ± 3
8.00	78 ± 4	79 ± 3

show that the adsorption of glycine increased with the increasing pH of the system but the increase of the adsorption from 1 to 24 h. was not substantial.

DISCUSSION

The adsorption of Hg-organic ligand complexes on a kaolinite surface can be described by various adsorption processes (Solomons and Forstner 1984). The PZC of the kaolinite sample determined during the present study is 4.5. This value is close to the reported PZC value of 4.6 by Stumm and Morgan (1981). At the pH below the PZC of kaolinite, it carries a net positive charge, but at the pH above its PCZ, it carried a net negative charge.

In the aqueous solution, Hg^{2+} reacts with water to form $Hg(OH)^+$ and $Hg(OH)_2$. Theoretical calculations carried out by using the GEOCHEM computer program at 10^{-5} M Hg concentration show that at pH values of 4.00, 6.00 and 8.00 in the absence of other complexing ligands, $Hg(OH)_2$ is the dominant species in aqueous solution, although the concentration of $Hg(OH)^+$ and Hg^{2+} increased with the decreasing pH (Figure 5).

The rate of Hg adsorbed by the kaolinite surface in the absence of the organic acids (Table 2) and the PZC of the kaolinite sample indicated that $Hg(OH)_2$ can be adsorbed by the kaolinite surface irrespective of net positive and negative charges on the surface. Rogers et al. (1984) reported that Hg adsorption by hydrous oxides of Al, Fe, Mn and Si was neither related to their specific surface nor to their cation exchange capacity. Therefore, the ion exchange reaction would not be the predominant mechanism for the $Hg(OH)_2$ adsorption by the kaolinite. A hydroxyl ligand coordinated to Hg(II) may function as a bridging ligand (Johanssen 1971) and form a strong covalent bond between the kaolinite surface and the Hg(II) ion. However, as the pH decreases from 8 to 4, the concentration of the Hg species, $Hg(OH)^+$ and Hg^{2+}, increases significantly (Figure 5). Since the kaolinite

surface carries a net positive charge at pH 4.00, repulsion between the positively charged Hg species and the positively charged kaolinite surface would result in slower Hg adsorption (Table 2).

Effect of Citric Acid on Hg Adsorption

Citric acid has three COOH functional groups with pK_1 of 3.15, pK_2 of 4.76 and pK_3 of 6.40 (Martell and Smith 1979). Therefore at pH 4.00, one of the COOH groups is largely dissociated, but at pH 6.00, more than 50% of the second COOH group is dissociated and all three of the COOH groups are largely dissociated at pH 8.00. These dissociated COOH groups at all pH values of 4.00, 6.00 and 8.00 may result in the formation of 1:1 and 1:2 types of Hg citrate complexes. Calculations based on the GEOCHEM computer program predict that: 1) 97.90 to 100% of the Hg is present as Hg citrate in the presence of 10^{-3} to 10^{-1} M citric acid at pH of 4.0; 2) 66.7 to 99.5% of the Hg is present as Hg citrate in the presence of 10^{-3} to 10^{-1} M citric acid at pH of 6.00; and 3) 0.00 to 2.00% of the Hg is present as Hg citrate in the presence of 10^{-3} to 10^{-1} M citric acid concentrations at pH of 8.0 (Table 6). In the presence of 10^{-3} and 10^{-2} M citric acid at pH 4.00, Hg is present mainly as Hg citrate complexes. The kaolinite surface carries a net positive charge at pH of 4.00, thus the Hg citrate complexes can be rapidly adsorbed by kaolinite. Also, citrate is adsorbed onto the kaolinite surface and the residual COOH group of the citrate (Table 3) may serve as new adsorption sites for the mercury. Davis and Leckie
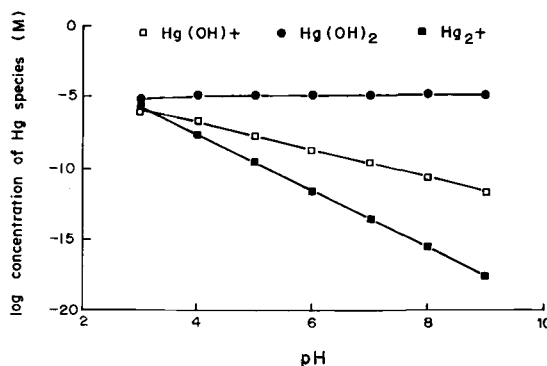

Figure 5. Hydroxy species of Hg at 10^{-5} M Hg as influenced by pH.

Table 6. Influence of citric acid on Hg speciation at 10^{-5} M Hg in the pH range of 4.00 to 8.00.

pH	Concentration of citric acid (M)	% Fraction of Hg	
		$Hg(OH)_2$	Hg-Citrate†
4.00	0	100.00	0.00
	10^{-5}	73.90	25.90
	10^{-4}	18.70	81.30
	10^{-3}	2.10	97.90
	10^{-2}	0.20	99.80
	10^{-1}	0.00	100.00
6.00	0	100.00	0.00
	10^{-5}	98.00	2.00
	10^{-4}	83.10	16.70
	10^{-3}	33.10	66.70
	10^{-2}	4.70	95.30
	10^{-1}	0.50	99.50
8.00	0	100.00	0.00
	10^{-5}	100.00	0.00
	10^{-4}	100.00	0.00
	10^{-3}	100.00	0.00
	10^{-2}	99.50	0.50
	10^{-1}	95.10	2.00

† Hg citrate species refers to 1:1 Hg citrate complex.

Table 7. Influence of glycine on Hg speciation at 10^{-5} M Hg in the pH range of 4.00 to 8.00.

pH	Concentration of glycine (M)	% Fraction of Hg	
		$Hg(OH)_2$	Hg-Glycinate†
4.00	0	100.00	0.00
	10^{-5}	88.5	3.60
	10^{-4}	66.30	27.80
	10^{-3}	15.80	82.8
	10^{-2}	0.70	99.30
6.00	0	100.00	0.00
	10^{-5}	98.0	2.00
	10^{-4}	82.6	17.40
	10^{-3}	23.4	76.60
	10^{-2}	0.70	99.30
8.00	0	100.00	0.00
	10^{-5}	98.1	1.90
	10^{-4}	82.7	17.30
	10^{-3}	23.9	76.10
	10^{-2}	0.70	99.30

† Hg glycinate species includes the sum of 1:1 and 1:2 Hg glycinates as well as hydroxy Hg-glycinate.

(1978) suggested that the functional groups of an adsorbed ligand may serve as new adsorption sites for trace metals at the surface. They further postulated that the presence of an adsorbing complexing ligand in an oxide suspension can change the chemical microenvironment at the surface. Therefore, the rate of Hg adsorption by kaolinite increases with increasing citric acid concentration at pH 4.00 (Table 2). At pHs of 6.00 and 8.00, the kaolinite surface will carry a net negative charge and Hg citrate complexes also apparently have a negative charge. Therefore, the rate of the adsorption of Hg decreases in the presence of citric acid (Table 2). The amount of citric acid adsorbed by the kaolinite is also minimal (Table 3) due to the repulsion of the negatively charged surface of kaolinite and citrate in this pH range. The higher rate constants of Hg adsorption at pH 8.00, as compared with those at pH 6.00, are attributed to the species of Hg available for the adsorption. At pH 8.00, Hg is largely present as $Hg(OH)_2$ even in the presence of 10^{-2} M citric acid (Table 6). Whereas at pH 6.00, most of the Hg is in the form of Hg citrate in the citric acid concentration of 10^{-3} to 10^{-1} M. Therefore, the rate of Hg adsorption at pH 8.00 is controlled by $Hg(OH)_2$ rather than by the Hg citrate species. The data in Table 2 clearly show the increased adsorption of Hg in the presence of citric acid at pH 4.00 and the decreased adsorption of Hg in the presence of citric acid at pHs of 6.00 and 8.00. This differential effect of citric acid on the adsorption of Hg has considerable environmental significance. The data obtained suggest that the citric acid-mercury interaction should play an important role in influencing the distribution of mercury between the solid and the solution phases, and the mobility of Hg in freshwater environments.

Effect of Glycine on Hg Adsorption

Glycine carries one carboxyl and one amino functional groups. Therefore, the ionization of glycine can be described by two pK values. The pK_1 for the COOH group is 2.34 and the pK_2 for the $-NH_3^+$ is 9.60 (Lehninger 1980). Mercury forms both 1:1 and 1:2 types of mercury-glycinate complexes as well as hydroxy Hg-glycinate complexes (Reid and Podanyi 1988). The speciation calculations carried out by using the GEOCHEM program at various concentrations of glycine are presented in Table 7. Calculations show that the fraction of mercury as Hg-glycinate is substantial in the pH range of 4.00 to 8.00 at glycine concentrations higher than 10^{-4} M. At 10^{-2} M glycine concentration, 99.3% of Hg is present as Hg-glycinate in the pH range studied. At glycine concentrations between 10^{-2} and 10^{-5} M in the pH range of 4.00 to 8.00, a series of Hg-glycinate complexes is present (Figure 6). These Hg-glycinate complexes apparently carry a net positive charge because of a protonated amino group. The rate of the fast adsorption of Hg by kaolinite significantly increased as the concentration of glycine increased from 0.00 to 10^{-2} M over the pH range of 4.00 to 8.00 (Table 4), indicating that compared with $Hg(OH)_2$, the Hg-glycinate species has a higher affinity toward the surface of kaolinite. At pHs of 6.00 and 8.00, the Hg-glycinate complex ions apparently carry a positive charge because the amino group is protonated. The kaolinite surface has a net negative charge in this pH range. This results in the increased rate of Hg adsorption in the presence of glycine. However, at pH 4.00, kaolinite carries a net positive charge. Therefore, the adsorption of positively
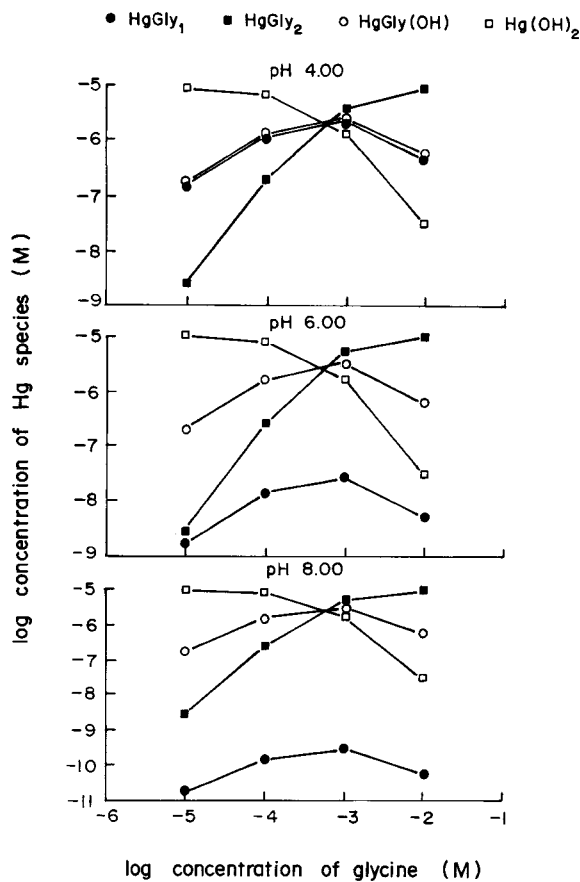
Figure 6.　Effect of glycine on the formation of Hg-glycinate complexes at 10^{-5} M Hg in the pH range of 4.00 to 8.00. HgGly$_1$ stands for 1:1 Hg-glycinate complex, HgGly$_2$ stands for 1:2 Hg-glycinate complex, and HgGly (OH) stands for 1:1 hydroxy Hg-glycinate complex.

charged hydroxy Hg-glycinate complex ions is apparently due to some negative sites present on kaolinite surfaces at pH 4.00. Furthermore, at pH 4.00, kaolinite surface carries a net positive charge and the COOH group of glycine is dissociated (Lehninger 1980). This results in the significant adsorption of glycine on the kaolinite surface (Table 5). At pHs 6.00 and 8.00, kaolinite surface carries a net negative charge and the amino group of glycine is protonated and thus carries a positive charge. Therefore, glycine can be adsorbed on the kaolinite surface through amino groups (Table 5). The adsorbed glycine molecules may act as a new adsorption site. The functional group of the adsorbed organic ligand may serve as a new adsorption site of certain metals, which may be more reactive than the isolated oxide surfaces (Davis and Leckie 1978). This could also contribute toward the higher rate of Hg adsorption in the presence of glycine at pHs of 6.00 and 8.00.

The initial fast reaction followed by the slow reaction in the adsorption processes of Hg by kaolinite both in the absence and presence of citric acid or glycine is attributed to the geometric and energetic heterogeneity of the kaolinite surfaces. The data indicated that organic acids such as citric acid and glycine substantially modify both fast and slow adsorption kinetics of Hg and may influence the subsequent transformation and dynamics of Hg in the freshwater environment. If the ligands are adsorbed on the surfaces of sediment particles and can then complex with Hg, or if Hg-ligand complexes are adsorbed more strongly than Hg(OH)$_2$, the Hg adsorption is enhanced. However, if the ligands blanket the surface, or are able to keep the Hg in solution, the adsorption is reduced. Therefore, the main factors expected to control the influence of organic ligands on the adsorption of Hg include the nature and concentration of ligands, the Hg-ligand formation constant, pH, the nature and properties of sediment particulates and the other ionic factors.

Although the concentration of citric acid and glycine in the water columns in the freshwater environment is lower than that used in this experiment, these organic acids are continuously produced in a localized zone through microbial and other biological activities. In the immediate vicinity of the sites of the decomposition of plant materials and the plant rhizosphere where biological activities are intense, the concentration of organic acids could be higher than 10^{-3} M (Stevenson and Fitch 1986; Fox and Comerford 1990). Therefore, the influence of organic acids on Hg dynamics in pore water of freshwater sediments and aquatic plant rhizosphere warrants in-depth research.

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