AGRICULTURE

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TEMPERATURE DEPENDENCE OF ZINC SORPTION BY GOETHITE

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ABSTRACT

Sorption of Zn by synthetic goethite [surface area 95.2m^2 g^{-1}, pH(ZPC) 7.9] was studied in equilibrium conditions as functions of temperature and pH.

Two sets of isotherms of Zn sorption by goethite were conducted at 25°C and 44°C, each at pH 5.4, 6.2, 7.0 and .5. At each pH level, the initial Zn concentration ranged from 0.025 to 7.0 mg Zn L^{-1} (i.e., from 3.82 x 10^{-7} to 1.07 x 10^{-4} mol Zn L^{-1}).

Zinc sorption by goethite increased with an increase in both temperature and pH. The maximum Zn sorption experimentally achieved at 25°C at pH 5.4, 6.2, 7.0 and 8.5 were, respectively, 14, 54, 185 and 370 umol Zn g^{-1}. Sorption of Zn was markedly endothermic at all pH levels, and the temperature-induced increase in sorption was generally most pronounced at low pH and high-system loadings.

Mean $\Delta\bar{G}^{o}$ values ranged from -47 kJ mol^{-1} at pH 8.5 to -38 kJ mol^{-1} at pH 5.4; $\Delta\bar{H}^{o}$ from 27 kJ mol^{-1} at pH 8.5 to 61 kJ mol^{-1} at pH 5.4; and $\Delta\bar{S}^{o}$ from 242 J mol^{-1} deg^{-1} at pH 8.5 to 322 J mol^{-1} deg^{-1} at pH 5.4. Isosteric heats of Zn sorption, Q_r, ranged from 4 to 113 kJ mol^{-1}, and were generally higher at low pH than high pH.

Keywords: enthalpy, entropy, goethite, isosteric heats, sorption, zinc

INTRODUCTION

Goethite is often the most common iron oxide mineral in soils. Synthetic goethite is usually used in studies to understand the chemistry of interactions of ions with iron oxides in soils. following the work of Grimme [11] and the suggestion by Jenne [13] that iron oxides could control the concentrations of heavy metals in soils, several studies have been conducted into the interaction zinc (Zn) with goethite (1,5,6,7,8 i 15, 20].

Sorption studies with Zn are needed because the element may be deficient in some soils, but may also be present at toxic levels in others as a result of management practices such as spreading of sewage sludge [18]. Studies of Zn interaction with goethite are therefore of interest from the point of view of soil fertility and environmental science.

Most studies of Zn interaction with goethite have been done at room temperatures. In tropical soils, which usually contain large amounts of goethite, soil temperatures may exceed 40^{oC} during some parts of the year. The study of the influence of temperature on the interaction of Zn with goethite may therefore have relevance for tropical soils.

The work reported here was undertaken to investigate the influence of temperature on the sorption of Zn by goethite, and to estimate some thermodynamic parameters associated with the interaction.

MATERIALS AND METHODS

Goethite Preparation and Characteristics

Goethite (-FeOOH) was prepared from 10% NaOH and 0.2 M Fe(NO$_3$)$_3$. The gel was aged for ten days, with continuous stirring, at pH 11.7 at room temperature. The residue was washed repeatedly in deionized distilled water until pH 7 was reached, and excess water at the end of each washing cycle was removed with filter candles. The sample had the following properties: surface area (ethylene glycol), 95.2m^2 g^{-1}; principal X-ray diffraction peak, 4.17 A; ratio of oxalate-soluble iron/total iron, 0.015; endothermic differential thermal analysis peak, 285°C; colour, yellow (10 YR 7/8); crystal shape, needlelike; crystal size, about 0.4 um long.

Sorption Procedure

Equilibrium sorption isotherms were conducted at two temperature: 25°C in a constant-temperature room, and 44^{oC} in a thermostated water-bath shaker. At each of the two temperatures, isotherms were conducted at four pH levels: 5.4, 6.2, 7.0, and 8.5; at each pH level, the initial Zn concentration ranged from 0.025 to 7.0 mg Zn L^{-1} (i.e., from 3.82 x 10^{-7} to 1.07 x 10^{-4} mol Zn L^{-1}).

An amount of 0.05g goethite in 200 mL suspension containing Zn as the nitrate, and maintained at a constant ionic strength at 1.0 x 10^{-3} M with NaNO$_3$ in a narrow-mouth 500-mL polyethylene bottle was gently shaken (about 120 cycles min^{-1}) for 54 hours. [Preliminary kinetic experiments showed that the time required to attain "equilibrium" was about 40 h at low pH, and shorter at high pH (Fig.1)]

The pH was checked once in twelve hours, and adjusted when necessary with 0.1 M NaOH and 0.1 M HNO_3. During shaking, purified CO_2-free nitrogen gas was continuously flushed through the suspension to eliminate carbon dioxide, which would otherwise alter the pH.

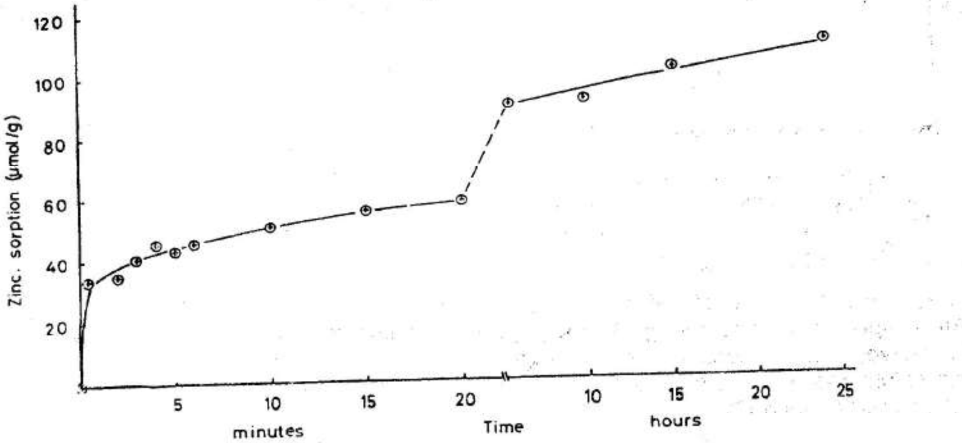

Fig.1: Kinetics of Zn sorption by goethite at pH 7.0 and 25°C. Weight of goethite = 100 mg; suspension volume = 400 ml; initial Zn concentration = 30.6 umol Zn L^{-1} (2 mg Zn L^{-1})

The suspension was filtered with a Millipore micropore (0.22-um pore size) filter paper of 25 mm diameter in size, held in Swinnex filter holders. [Duplicate samples of suspensions were also ultracentrifuged at 16,000 rpm (30 900 relative centrifugal force) for 20 min with a Sorvall Superspeed RC-2B centrifuge; a comparison of the filtrate and the centrifuged supernatant showed no difference in metal concentration from the same suspension.] The amount of Zn sorbed was calculated from the difference between the initial and final Zn concentrations in solution. Solution Zn concentrations above 0.02 mg Zn L^{-1} were determined by a flame atomic absorption method, and lower concentrations by a flameless carbon rod atomizer method, all using a Varian-Techtron Model 1200 (with a Model 63 carbon-rod flameless atomizer). An air-acetylene flame was used for all flame analyses, and in all cases, standards were prepared to contain $NaNO_3$ at 1.0×10^{-3} M and HNO_3 at 0.12 M.

Calculations

The standard partial molar thermodynamic parameters were calculated from the variation of the thermodynamic distribution oefficient, K_o, with changes in temperature. $\Delta \bar{G}^{o}$, the standard partial molar Gibbs free energy change for Zn sorption on goethite, was computed from the equations [9]:

$$\Delta \bar{G}^{o} = -2.303RT \log K_o \qquad (1)$$

$$K_o = a_{2,s}/a_{2,b} \qquad (2)$$

where, R is the gas constant, T the absolute temperature, and $a_{2,s}$ and $a_{2,b}$ are the activities of solute in ug per one mL of solvent, respectively, in the sorbed and bulk phases. Although the activities of the solute in the sorbed phase cannot be measured directly, the corresponding concentration ratio (using the same units as the activities) $c_{2,s}/c_{2,b}$ for any point on the isotherm can be computed. As the bulk solution concentration and amount sorbed approach zero, the corresponding activity coefficients, $Y_{2,s}$ and $Y_{2,b}$, approach unity, and one can write:

$$\lim_{c_{2,s} \text{ or } c_{2,b} \to 0} (c_{2,s}/c_{2,b}) = a_{2,s}/a_{2,b} = K_o \qquad (3)$$

A value for log Ko was obtained by plotting log $(c_{2,s}/c_{2,b})$ on the ordinate venus $c_{2,s}$ on the abssissa and extrapolating to zero $c_{2,s}$ (Fig.2)

The value for $c_{2,s}$ (the ug of Zn sorbed per mL of solvent in contact with the goethite surface) was calculated by the equation [9]:

$$c_{2,s} = \frac{(d_1/M_1)A_1}{\dfrac{S}{N(x/m)} - \dfrac{A_2}{M_2 \times 10^6}} \qquad (4)$$

where, d_1 is the density of solvent (ug/mL), M_1 and M_2 are respective molecular weight (g/mole) of solvent and solute, A_1 and A_2 are respective cross-sectional areas (cm2/molecule) of solvent molecule and solute molecule, N is Avogadro's number (6.02×10^{23} molecules/

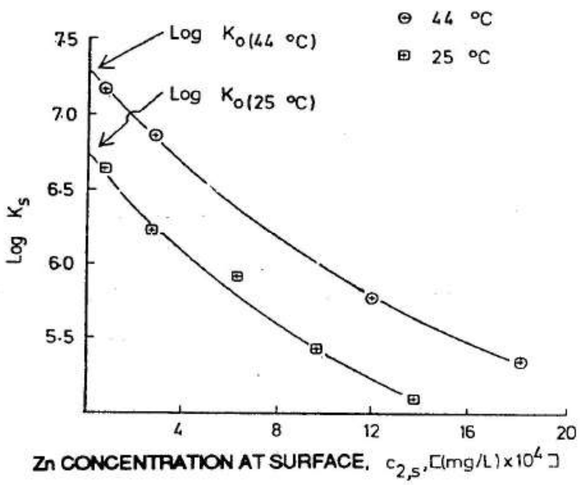

Fig.2: Log K_s, the distribution coefficient, as a function of $c_{2,s}$, the concentration of Zn at goethite surface, at pH 6.2. Extrapolation to find log K_o (= K_s at $c_{2,s}$ of zero)

mole). S is surface area of sorbent (cm²/g), and x/m is specific sorption (ug/g). A_1 and A_2, the respective cross-sectional areas of the solvent and solute molecules were estimated by the generalized equation [14]:

$$A_i = 1.091 \times 10^{-16} \left[\frac{M_i \times 10^{24}}{N d_i} \right]^{2/3} \qquad (5)$$

where, M_i and d_i are, respectively, the molecular weight (g/mole) and density (g/mL) of the solvent (H_2O) or soute (Zn).

The standard partial molar ethalpy change for Zn sorption, $\Delta \bar{H}^{o}$, was estimated by an integrated form of the van't Hoff equation:

$$\Delta \bar{H}^{o} = 2.303 \frac{RT_2T_1}{T_2-T_1} \log[\left[\frac{K_o, T_2}{K_o, T_1}\right] \qquad (6)$$

where . K_o, T_2 and K_o, T_1 are distribution coefficients at two temperatures.

With $\Delta \bar{G}^{o}$ and $\Delta \bar{H}^{o}$ estimated, the corresponding standard entropy change, $\Delta \bar{S}^{o}$ · was estimated by the Gibbs-Helmholtz equation in the form:

$$\Delta \bar{S}^{o} = \frac{1}{T} \left(\Delta \bar{H}^{o} - \Delta \bar{G}^{o} \right) \qquad (7)$$

where $\Delta \bar{G}^{o}$ represents the average of the two $\Delta \bar{G}^{o}$ values at T_2 and T_1, and T equals[$(T_2 + T_1)/2$] in degrees Kelvin.

The isosteric heat of adsorption, Q_r, defined as the differential heat of adsorption at constant interfacial tension (i.e., constant sorbed amount), was calculated from isotherm data by an equation analogous to the Clausius-Clapeyron equation:

$$Q_r = 2.303 \frac{RT_2T_1}{T_2-T_1} \log [c_b, T_2/c_2, T_1] \qquad (8)$$

where c_b, T_2 and c_b, T_1 are the respective equilibrium solute concentrations in the bulk solution at temperature T_2 and T_1 at the constant surface coverage (r). Values of Q_r were plotted against values of x/m. amount sorbed, to show how Q_r varied with the surface coverage.

RESULTS AND DISCUSSION

Effect of Temperature on Zn Sorption by Goethite

The sorption of Zn by goethite was endothermic, being markedly higher at 44°C than at 25°C. Endothermicity of cation adsorption by soil materials and soils has also been reported by other workers. For example, an endothermic adsorption of Co^{2+} on montmorillonite was reported by Hodgson et al [12] and of Co^{2+} by Fe_2O_3, Al_2O_3 and MnO_2 by Tewari et al [22], and Barrow [4] reported increases in Zn retention by soil with increasing temperature of incubation of the soil with $Zn(NO_3)_2$.

Figures 3 and 4 present sorption isotherms at the two temperatures at pH 5.4 and 8.5, respectively. (The shapes of isotherms at pH 6.2 and 7.0 were similar to those at pH 5.4 and 8.5 with corresponding intermediate magnitudes of sorption). The maximum Zn sorption achieved in this work at the various pH levels at 25°C and 44°C, respectively, were: pH 5.4, 14 and 33 umol g⁻¹; pH 6.2, 54 and 72 umol g⁻¹; pH 7.0, 185 and 245 umol g⁻¹; pH 8.5, 370 and 370 umol g⁻¹. The temperature-induced sorption enhancement

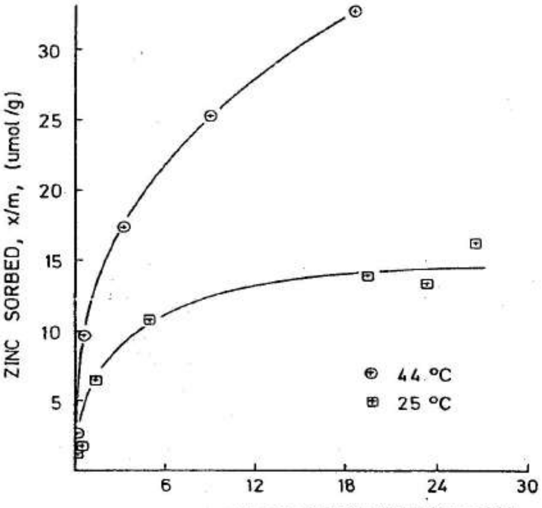

Fig.3: Isotherms for Zn sorption by goethite at pH 5.4 showing the effect of temperature. Weight of goethite = 50 mg; suspension volume = 200 mL.

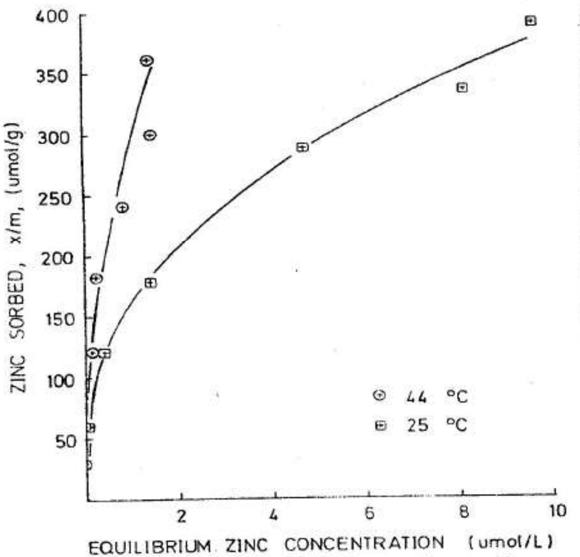

Fig.4: Isotherms for Zn sorption by goethite at pH 8.5 showing the effect of temperature. Weight of goethite = 50 mg; suspension volume = 200 mL.

was more marked at low pH than at high pH at any given initial solution Zn level, and, generally, more marked at high Zn levels than at low Zn levels (Fig.5). The influence of pH and temperature on Zn sorption by goethite is apparent in Figure 6.

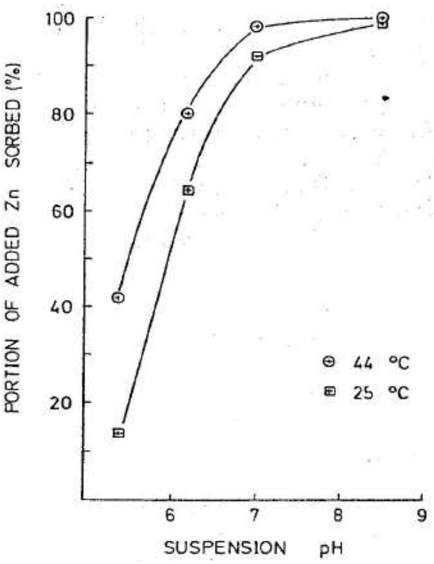

Fig. 6: Percentage of initial solution Zn of 1.00 mg mg L^{-1} sorbed by goethite as a function of pH and temperature.

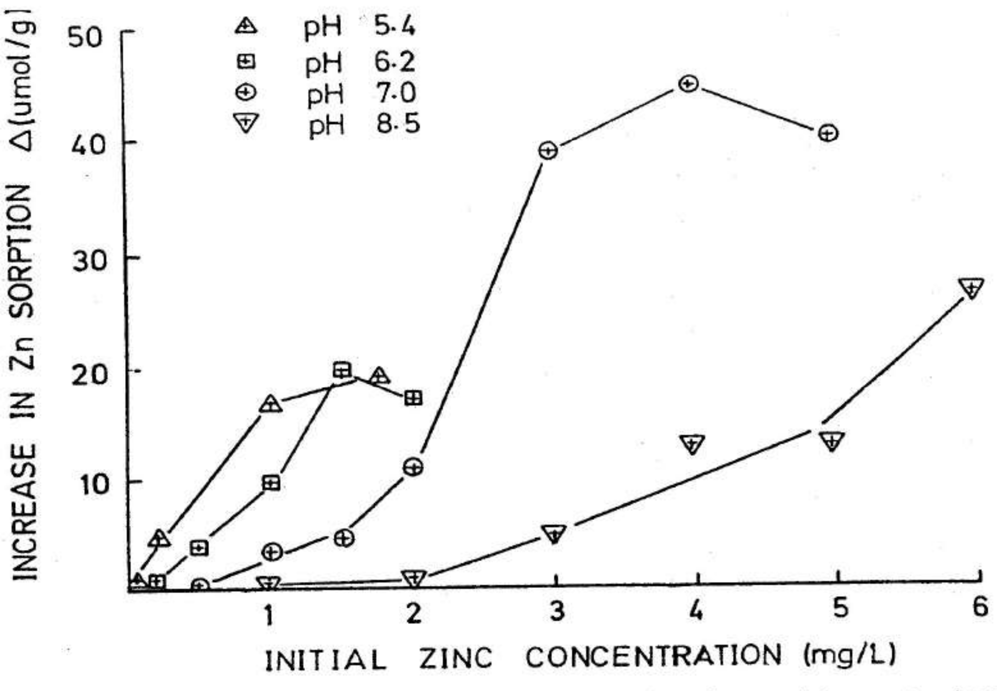

Fig.5: Absolute increases in Zn sorption by goethite induced by an increase in temperature from 25°C to 44°C as a function of initial solution Zn concentration and pH.

The relatively lower effect of temperature on Zn sorption at low solution Zn and high pH levels suggested that even at 25°C, high-affinity sites already existed on the goethite surface at these low Zn coverages and high pH, resulting in near-100 per cent sorption of added Zn. the relatively low effect of temperature on Zn sorption at high pH could also be attributed to the fact that even at 25°C, a relatively high concentration of $ZnOH^{+}$ ions probably already existed at the high pH; the $ZnOH^{+}$ ion is the form of Zn that may be sorbed by goethite [5]. The hydrolytic reaction, $Zn^{2+} + H_2O = ZnOH^{+} + H^{+}$, increases with an increase in temperature (Sillen and Martell [21] reported pK_1 values as 9.7-9.0 at 25°C, 8.6 at 36°C, and 8.4 at 42°C); therefore, a high proportion at $ZnOH^{+}$ ions, as would exist at high pH, would act to reduce the effect of temperature on the reaction.

It is suggested that the generally marked increases in Zn sorption with increase in temperature could be ascribed mainly to an enhanced hydrolysis of Zn [5, 21], and a reduced pH of zero point of charge of the goethite. Parks [17] cited literature that indicated that the zero point or charge [pH(ZPC)] of natural goethite samples decreased from 6.7 at 25°C to 6.0 at 60°C, and to 3.2 at 100°C. A reduced pH(ZPC) would mean that at any given pH, the area of goethite surface bearing negative charges would be larger at 44°C than at 25°C, and the reduction in the electrostatic potential of the surface at the higher temperature would favour the adsorption of a positively-charged Zn ion.

Thermodynamic Parameters

The values of the standard partial molar free energy change, $\Delta\bar{G}^{o}$, which were negative, indicated that goethite positively sorbed Zn from solution, and the greater the negativity of the $\Delta\bar{G}^{o}$ value, the higher the degree of spontaneity of the sorption reaction [3]. For example, at pH 5.4, sorption of Zn proceeded more readily at 44°C ($\Delta\bar{G}^{o}$ = -41.6 kJ mol⁻¹) than at 25°C ($\Delta\bar{G}^{o}$ = -34.5 kJ mol⁻¹), and at 25°C it proceeded more readily at pH 8.5 ($\Delta\bar{G}^{o}$ = -44.2 kJ mol⁻¹) than at pH 5.4 ($\Delta\bar{G}^{o}$ = 34.5 kJ mol⁻¹) (Table 1).

The positive nature of the $\Delta\bar{H}^{o}$ values (enthalpies) (Table 1) indicated that Zn sorption by goethite was endothermic, and also that the partial molar enthalpies for the sorbed Zn in its standard state were greater than the molar enthalpies of the Zn in solution. The increase in temperature presumably increased the energy content of the sorbing Zn species relative to that of the displaced surface moiety. The higher $\Delta\bar{H}^{o}$ values at the low pH would suggest that at 25°C, much weaker forces were binding the Zn to the goethite surface, or that the Zn was not in a form suitable for strong interaction with the surface at these low pH levels; appreciable proportions of the appropriate form of Zn were apparently created and built up by the heat input. The appropriate form of Zn is the $ZnOH^{+}$ [4], the production of which (through hydrolysis of Zn) is an endothermic process [2, 21].

The standard partial molar entropy change for Zn sorption, $\Delta\bar{S}^{o}$ was positive at all pH levels, and highest at low pH. The sorbed Zn species could be considered, then, to possess a higher degree of orientation and stability at high pH (with lower $\Delta\bar{S}^{o}$ values) than at low pH (with higher $\Delta\bar{S}^{o}$ values) (Table 1).

The values of the isosteric heats (Q_r) associated with Zn sorption by goethite were all positive and were, at the lowest Zn coverages obtained in this work, 113, 84, 4, and 25 kJ mol⁻¹ at pH 5.4, 6.2, 7.0, and 8.5, respectively

Table 1: The Values of the Standard Thermodynamic Parameters of Zn Sorption by Goethite

pH	Temp °C	log K_o	$\Delta\bar{G}^{o}$	Mean $\Delta\bar{G}^{o}$	$\Delta\bar{H}^{o}$	$T\Delta\bar{S}^{o}$	$\Delta\bar{S}^{o}$
			kJ mol⁻¹				J mol⁻¹ deg⁻¹
5.4	25	6.11	-34.5	-38.1	60.6	99.1	322.2
5.4	44	6.85					
6.2	25	6.74	-38.2	-41.3	46.0	87.6	284.9
6.2	44	7.31	-44-4				
7.0	25	7.41	-41.9	-44.1	16.5	61.0	198.2
7.0	44	7.61	-46.3				
8.5	25	7.81	-44.2	-46.9	27.2	74.4	241.8
8.5	44	8.14	-49.5				

(Fig.7). As a comparison, for the endothermic sorption of Co(II) on oxides, Tewari et al [22] reported Q_r values of 26 to 31 kJ mol^{-1} for Fe_2O_3, 62 to 86 kJ mol^{-1} for Al_2O_3, and 60 to 93 kJ mol^{-1} for MnO_2. The positive nature of the Q_r values emphasizes the endothermic nature of Zn sorption of goethite. The relative magnitude of the Q_r values, according to Roy et al [19], may reflect the number of bonds, or more generally, the strength of bonding between sorbed Zn and goethite. At pH 5.4, 6.2, and 7.0, the Q_r values rose to a maximum and then dropped. At pH 8.5, however, Q_r values continued to rise, though slowly, beyond a Zn coverage of 180 umol Zn g^{-1}. The drop in Q_r (or decrease in the endothermicity of the sorption reaction) after rising to a peak at pH 5.4, 6.2, and 7.0 might be explained as: 1) if active sites are assumed to exist on the goethite, and if these sites are taken up by the first additions of sorbed Zn species, then the binding of later additions must occur on less active sites, and, accordingly, the strength of binding falls off [3]; 2) the increase in mutual repulsion among sorbed Zn species at high loadings operates to oppose the additions of further Zn species [3, 16]; in fact, according to Kuo and Lotse [16], at increasing surface coverage, the sorption may change gradually from "specific" to "nonspecific." The increasing demand for thermal energy at pH 8.5 as coverage increased (Fig. 7) may be explained as a result of the energy needed for hydrolyzing Zn, and rearrangement of the hydroxy species into clusters on the goethite surface, which could result in their nucleation/precipitation into $Zn(OH)_2$ crystals.

The interpretation of heats of sorption data must be approached with caution, because the Q_r values, unfortunately, cannot be assigned to any given reaction; it is probably more accurate to view the Q_r values as heats of the overall reaction [19]. As suggested by Griffin and Jurinak [10], the Q_r includes the summation of the energies involved in the desorption of solvent molecules from the sorption sites, the partial dehydration of sorbed ion, the lateral interaction energy between sorbed ions on the sorbent surface, in addition to the interaction of the sorbate with the sorbent surface sites.

CONCLUSION

The study showed that Zn sorption by goethite increased with an increase in temperature and pH; the thermodynamic parameters of Zn sorption were estimated to show the extent of endothermicity of the reaction. It was suggested that the $ZnOH^+$ ion was the main form of Zn that might be sorbed by goethite, and that the formation of this ion was favoured by high pH and temperature. The increased Zn sorption at the high pH and temperature was attributed, therefore, to the increased concentration of the $ZnOH^+$ ion the adsorption of which was favoured by the temperature induced reduction in the electrostatic potential of the goethite surface.

The abrupt increase in Zn sorption (Fig.6) and the increasing demand for thermal energy (Fig.7) at pH 8.5 were attributed to the hydrolysis of Zn and the rearrangement of the hydroxy species into clusters on the goethite surface, that would lead to their nucleation/precipitation into $Zn(OH)_2$ crustals.

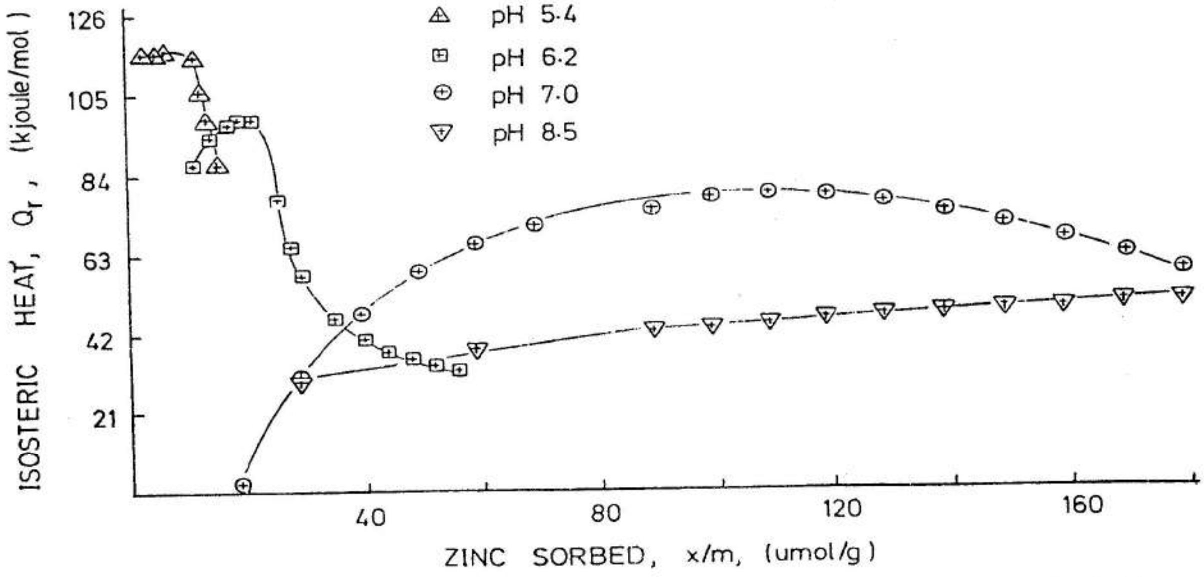

Fig. 7: Isosteric heat (Qr) of Zn sorption by goethite as a function of amounts of Zn sorbed and pH.

Tropical soils usually contain large amounts of goethite and also experience high soil temperatures. The high sorption of Zn by goethite with increasing pH and temperature, as revealed in this study, suggests that this reaction may play a very significant role in the reduction of soil solution Zn levels and its subsequent unavailability to crops when soils in the lowland humid tropics are excessively limed.

ACKNOWLEDGEMENT

I thank the University of Ghana for the sponsorship of this study.

REFERENCES

1. *Akomah, A.B. 1975; On the Interaction of Zinc with a Ferric Oxyhydroxide, PhD Dissertation. University of California, Davis, U.S.a. Dissertation Abstracts International, June 1976, Volume 36, No.12, Part 1, page 5896-B.*
2. *Baes, C.f. and R.E. Mesmer, 1976. The Hydrolysis of Cations. John Wiley and Sons, New York.*
3. *Barrow, G.M. 1966. Physical Chemistry. 2nd ed. McGraw-Hill Book Company , new York.*
4. *Barrow, N.J. 1986. Testing a mechanistic model. II. The effects of time and temperature on the reaction of zinc with a soil. J.Soil Sci. 37:277-286*
5. *Barrow, N.J, J.W. Bowden,A.M. Posner, and J.P. Quirk. 1981. Describing and adsorption of copper, zinc, and lead on a variable charge mineral surface. Aust. J.Soil Res. 19:309-321.*
6. *Bolland, M.D.A., A.M. Posner, and J.P.Quirk. 1977.Zinc adsorption by goethite in the absence and presence of phosphate. Aust. J. Soil Res. 15:279-286.*
7. *Bowden, J.W., M.D.A. Bolland, A.M. Posner, and J.P. Quirk. 1973. Generalized model for anion and cation adsorption at oxide surfaces. Nature Physical Science (London) 245:81-83.*
8. *Forbes, E.A., A.M. Posner, and J.P. Quirk,. 1976. The specific adsorption of divalent Cd., Co, Pb , and Zn on goethite. J. Soil Sci.. 27:154-166.*

9 *Fu, Y., R.S. Hansen, and F.E. Bartell. 1948. Thermodynamics of adsoption from solutions: 1. The mobility and activity coefficients of adsorbed layers. J. Phys. Chem.52:374-386.*

10. *Griffin, R.A. and J.J. Jurinak. 1973. The interaction of phosphate with calcite. Soil Sci. Soc. Am. Proc. 37:847-850.*
11. *Grimme, H. 1969. Die adsorption von Mn. Co., Cu und Zn durch goethite aus verdunnten losungen. Z. flanzenemahr. Dung., Bodenkunde. 121:58-65.*
12. *Hodgson, J.F., K.G. Tiller, and M. Fellows. 1964. The role of hydrolysis in the reaction of heavy metals with soil-forming materials. Soil Sci. Soc. Am. Poc. 28:42-46.*
13. *Jenne, E.A. 1968. Controls on Mn. Fe, Co, Ni, Cu and Zn concentrations in soils and water. The significant role of hydrous Mn and Fe oxides. Adv. Chem. Ser. 73:337-387.*
14. *Kodera, K. and Y. Onishi. 1959. The molecular cross-sectional areas of solids. I. Carbon black. Bulletin of Chem. Soc. Japan. 32:356-361*
15. *Kuo, S. 1986. Concurrent sorption of phosphate and zinc, cadmium, or calcium by a hydrous ferric oxide. Soil Sci. Soc. Am. J. 50:1412-1419.*
16. *Kuo, S. and E.G. Lotse. 1974. Kinetics of phosphate adsorption and desorption by lake sediments. Soil Sci. Soc. Am. Proc. 38:50-54.*
17. *Parks, G.A.. 1965. The isoelectric points of solid oxides, solid hydroxides and aqueous hydroxo complex systems. Chem. Rev. 65:177-198.*
18. *Pulford, I.D. 1986. Mechanisms controlling zinc solubility in soils. J.Soil Sci. 37:427-438.*
19. *Roy, W.R., J.J. Hassett, and R.A. Griffin. 1989. Quasi - thermodynamic basis of competitive-adsorption coefficients for anionic mixtures in soils. J. Soil Sci. 40:9-15.*
20. *Shuman, L.M. 1977. Adsorption of Zn by Fe and Al hydrous oxides as influenced by aging and pH. Soil Sci. Soc. Am. J. 41:703-706.*
21. *Sillen, L.G. and A.E. Martell. 1964. 2nd ed. Stability Constants of Metal-Ion Complexes, Spec. Publ. No.17, The Chemical Soc. Lond. p.754.*
22. *Tewari, P.H., A.B. Campbell, and Woon Lee. 1972. Adsorption of Co^{2+} by oxides from aqueous solution. Can. J. Chem. 50:1642-1648.*