BRAZILIAN RED LATOSOL A TYPIC SOIL AS AN EXCHANGER: A THERMODYNAMIC STUDY INVOLVING Cu, Zn, Cd, Hg, Pb, Ca AND Na

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Abstract—The thermodynamic cationic exchange process involving divalent (Cu, Zn, Cd, Hg, Pb and Ca) and monovalent (Na) cations in Brazilian red Latosol soil was studied. Using a batchwise method, the exchange was monitored as a function of the added cation concentration and the aqueous suspension of the soil at different temperatures. The isotherm series obtained were adjusted to a modified Langmuir equation, whose results were compared with the proposed Rawat method. The cationic exchange equilibria constants (ln K) vary from 1.97 to 9.80 for the Langmuir equation and 7.06 to 13.50 for the Rawat method. The variation in enthalpies obtained by applying the van't Hoff equation gave, for Langmuir and Rawat procedures, exothermic values for Cu (65.5 and 97.3), Cd (36.9 and 45.6) and Pb (43.0 and 50.7) kJ mol^{-1}, and endothermic values for Zn (40.8 and 30.5), Hg (15.0 and 11.3), Ca (30.4 and 40.0) and Na (32.7 and 42.3) kJ mol^{-1}. The exchanges proceed spontaneously, as indicated by the free energy values: Cu (14.2 and 27.2), Zn (21.6 and 32.0), Cd (16.1 and 23.2), Hg (13.8 and 22.9), Pb (22.6 and 28.3), Ca (17.0 and 25.9) and Na (9.9 and 19.3) kJ mol^{-1} at 323 K. These results suggest that the interaction occurs by complex formation between the organic matter of the soil matrix and the cations dispersed in aqueous solution.

**Key Words**—Adsorption, Ionic Exchange, Isotherm, Langmuir Method, Red Latosol Soil.

INTRODUCTION

The ionic exchange process in the soil-water interface system depends directly on soil exchanged properties, which normally include some degree of humus derived from the natural organic matter and the mineral matrix. The organic matter plays an important role in forming aggregates to control the acidity, cycling the nutrient elements and decontaminating pollutants, which are related to the growing plants (Lobartini et al. 1992). During the ionic exchange process, ion isomorphic substitution on the matrix surface causes rupture of bonds on the clay mineral edges with dissociation of organic matter protons (Moniz 1972; Sposito 1989). For example, carboxylic and phenolic compounds dissociate within pH 3.0 to 4.8. Alternatively, much of the solid material in soil is composed of inorganic compounds that establish the framework of the natural matrix (Sposito 1989). Thus, the majority of ions are firmly held onto the soil surface of the solids and are available to solid/liquid interface phenomena or are distributed among the arrays of the silicates in the bulk (Patzkó and Dékány 1993). In some cases, their determinations can predict environmental toxicity (Baker and Amacher 1980), where the bioassessibility and migration are related to pH and solubility (Harter 1983).

The presence of ions at the solid/liquid interface is due to the ionization of the hydroxyl groups bonded to silicon in clay minerals and those coming from dissociation of organic matter, which are highly dependent upon pH. Thus, its increase favors the dissociation of protons in the medium, resulting in ionic interaction with cations present in the aqueous solution. This process increases the total cationic capacity. The cations adsorbed in the bulk are not static with respect to the ionic bond formed, but present a continuous activity (Moniz 1972). In this context, the reactive organic functional groups originating on the surface create a distribution of possible charges in the heterogeneous matrix (Moniz 1972). However, the nature of the available surface groups and the characteristic of the cations determine system selectivity (Marinsky 1966; Bunzl et al. 1976; Jorge and Chagas 1988).

The ionic exchange process causes mobility of the cations in the solid/liquid interface. The dynamics of this phenomenon can be represented by the following general chemical equilibrium equation:

$$n\bar{A}^{m+} + mB^{n+} = nA^{m+} + m\bar{B}^{n+} \qquad [1]$$
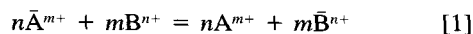
where A and B are positive species with $m+$ and $n+$ charges in the exchanged phase ($\bar{A}^{m+}$ and $\bar{B}^{n+}$) and in solution (A^{m+} and B^{n+}).

In this process, the cations in solution are exchanged with an equivalent quantity in the bulk. This operation depends on the exchanger properties and the cationic or anionic species present in solution, which are largely associated with the pH of the solution. In principle, 2 features must be considered: the degree of dissociation of the functional groups attached to the exchanger and the presence of H^+ and OH^- in solu-

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tion, which can compete with the other exchangeable ions. Therefore, the influence of the functional group related to the acid-basic character must be taken into account (Oliveira and Airoldi 1993).

In the present case, the interactions between cations and basic centers on the exchanger surface were focused. The main objectives were to determine the thermodynamic parameters K, ΔH, ΔG, ΔS from the experimental isotherms. Although these isotherms fit the Langmuir model well (McGlashan 1979), the mechanisms of the ionic exchange/adsorption processes are not well known due to the heterogeneity of the adsorbate. The parameters K, ΔH, ΔG, ΔS refer to the heterogeneous system containing red Latosol soil and divalent (Cu, Zn, Cd, Hg, Pb and Ca) or monovalent (Na) cations. The thermodynamic values obtained from variations of temperature were compared with another proposed method (Rawat et al. 1990).

METHOD

Composed samples were collected from soil covered by bush vegetation on the campus of the Universidade Estadual de Campinas at a depth of 5 to 10 cm, after removal of the top layer. This collection procedure is well established (Camargo et al. 1986; Keith 1988).

The soil was air-dried for 3 mo and sieved at 0.59 mm to separate root fragments and large particles. It was then sieved at 0.149 mm to maintain nearly homogeneous particle size and stored in polyethylene bags at 293 ± 5 K. The characterization used routine methods. The water content of 1.3% per g of soil was determined by drying the sample to constant mass. The organic matter content of 3.3% per g of soil was determined by titrating soil samples in an acidic medium, following the end point by a redox reaction. The pH of 5.2 was obtained in strong electrolyte, 1.0 M $CaCl_2$, in a proportion of 1:2.5 for soil:solution. The total acidity corresponding to H^+ plus Al^{3+} was 1.4 meq/100 g of soil, as determined by percolating 5.0 g of dry fine soil in air with 0.10 L of 2.0 M calcium acetate at pH 7.0, and titrating the eluate with sodium hydroxide. The cation exchange capacity of 3.4 meq/ 100 g of soil was determined from the sum of the extractable bases and the total acidity. The total extractable bases of 2.0 meq/100 g of soil were obtained by extracting the percolate fraction of 10.0 g of the soil with 0.10 L of 0.05 M nitric acid solution (Critter et al. 1994). The specific area of 37.3×10^4 cm^2 g^{-1} was determined by a BET method.

Reagent grade chemicals were used to prepare $CuCl_2$, $ZnCl_2$, $CdCl_2$, $HgCl_2$, $CaCl_2$, NaCl and $Pb(NO_3)_2$ solutions for the ionic exchange processes in a batchwise system with controlled temperature. Thus, in a given sequence of experiments for the ionic exchange, 0.25 g of soil samples were suspended in 25.0 cm^3 of cation solutions of different concentrations and

mechanically stirred for 2 h. The adsorption time was previously established for an identical series of stirring samples containing cation solutions in order to reach constant adsorption values. After centrifuging for 10 min at 2000 rpm, the amount of supernatant divalent cations was determined through atomic absorption spectrometry in a model 5000 Perkin-Elmer instrument, with cations (source) of: Cu (λ = 324.8), Zn (λ = 213.9), Cd (λ = 228.8), Hg (λ = 228.8), Pb (λ = 217.2) and Ca (λ = 422.7) nm (Prince 1979). The sodium was analyzed by flame photometry, where a calibration curve was previously obtained. The cations and the corresponding linear ranges were: Cu (0–5), Zn (0–1), Cd (0–2), Hg (0–300), Pb (0–20), Ca (0–5) and Na (0–10) μg cm^{-3} (1 ppm corresponds to 1 mg dm^{-3}) (Price 1979). The pH supernatant was measured at the end of the operation. For each sample analyzed, at least 1 duplicate run was performed to check the reproducibility.

Under equilibrium conditions, the exchange process at the solid/liquid interface can be characterized by the number of moles exchanged, N_f, on the soil, which was calculated by applying the expression:

$$N_f = (C_a - C_e)V/m \qquad [2]$$

where C_a and C_e are the initial and equilibrium number of cations in solution (M), respectively, m is the mass (g) of soil assayed and V is the volume (dm^3) of solution (Airoldi and Santos 1994).

RESULTS AND DISCUSSION

The sample soil, among the richest in organic content of natural Latosols, is thus excellent for cultivation. The chemical composition is high in iron, mainly in the form of magnetite, 50% kaolinite and 40% gibbsite, with an SiO_2/Al_2O_3 ratio of 1:1 to the clay fraction (Oliveira et al. 1979). The high proton concentration proceeding from the humic components allied to the participation of an effective hydrolyzable aluminum makes this soil acidic, reflected in the high cation exchange capacity (CEC). This demonstrates the ability of the soil suspension to retain cations on the surface, and therefore to act as an exchanger. The pH of the Latosol soil suspension was measured in the presence of salt to reduce the electric double layer; in this condition, the pH of the particle surface approaches that of the bulk of solution (Klute 1986).

Figure 1 shows a typical illustration of the ionic exchange kinetic for Pb, using 2 distinct concentrations, where the number of cations exchanged, N_f, is plotted against time. This series of experiments confirms a time scale of a few h for the exchange. As observed the increase in time caused the appearance of a defined saturation after 2 h. These results, expressed in time dependence of the moles of charge of exchangeable Pb^{2+} in red Latosol soil, indicated a relatively rapid kinetic of cation exchanged, allowing 2
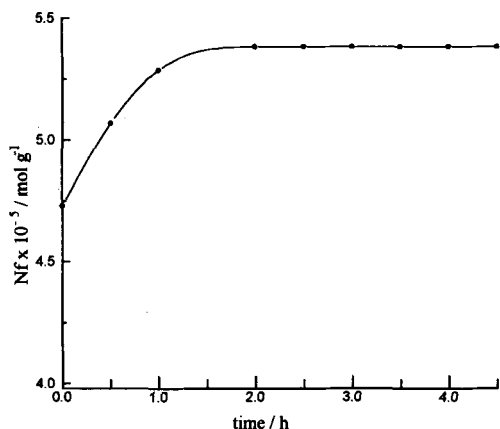
Figure 1. Number of exchanged moles of Pb as a function of time. Each sample of 1.0 g of latosol soil was mechanically stirred in 25.0 cm^3 of 2.28 $\times$ 10^3 of lead nitrate solution.

h to be chosen as a time scale to perform the experiments.

Extension of the ionic exchange equilibria for such heterogeneous systems implies a concomitant cation interaction with the organic matter and a proton release from the matrix, which should alter the pH of the medium. This is illustrated for Cu by plotting the number of moles of the exchanged cations, N_f, and the variation in pH against the concentration of the available moles of cation. These concentrations, C_e, and pH values were determined in the supernatant aqueous solution after centrifuging the suspension following 2 h of the exchanged process, as shown in Figure 2. The continuous increase in cation promoted the exchange as follows: 1) due to a low concentration of cations, a pronounced enhancement in N_f values established a defined plateau; 2) consequently pH values decreased abruptly from 6.5 to 4.5 where a plateau is also outlined, possibly due to the free organic matter proton.

The ionic exchange data were collected for all cations at least 3 different temperatures. The curve profile resulting from the N_f versus C_e plot presents an exchange saturation that defines a plateau for all cations, which is fitted to a modified Langmuir model (Equation 3), as shown in Figure 3 for Pb. The isotherms showed that a temperature increase caused a marked increase in reaction rate. These series of curves were classified by Giles as "H" form for the adsorption phenomena, where a strong interaction occurs between the exchanged surface of the soil and the cation added (Giles et al. 1960). Therefore, the ionic exchange is treated here as adsorption, due to the similarity in behavior. This relationship can be established because the most important chemical processes affecting the behavior and bioavailability of metals in soils involve adsorption of metals from the liquid phase onto the solid phase. This process controls the concentration of cations and complexes in the soil solution and influ-
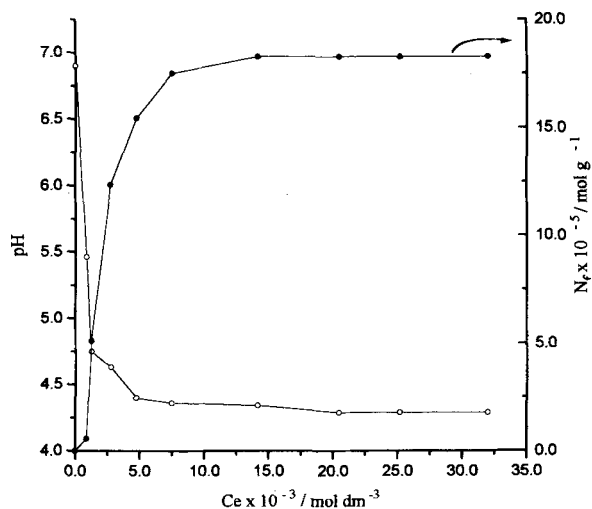

Figure 2. Number of exchanged moles of Cu (●) and the respective pH (○) of solution versus the Cu concentration in the end of the ionic exchange process. Each sample having 1.0 g of latosol soil was mechanically stirred with variable copper chloride solution.

ences the uptake by plant roots (Kabata-Pendias and Pendias 1984). The adsorption of metals includes cation exchange, organic complexation and co-precipitation. In the present case, each generic isotherm represents the ionic exchange/adsorption, whose linearization can be obtained by plotting C_e/N_f versus C_e, as follows:

$$C_e/N_f = 1/Kb + C_e/b \qquad [3]$$

where K is a constant of equilibrium and b is a constant of maximum adsorption (mol g^{-1}). The linearized
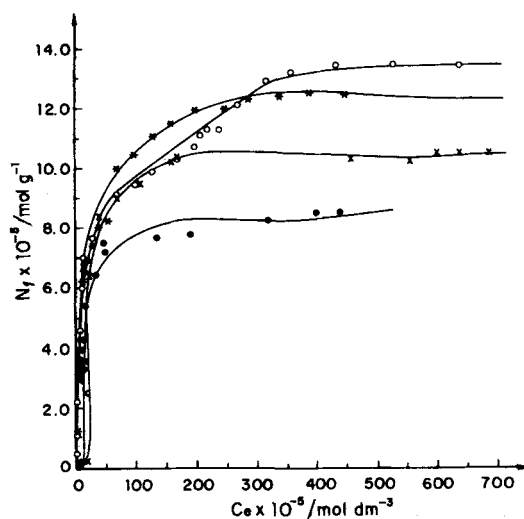

Figure 3. Ionic exchange isotherms of Pb^{2+} in red Latosol soil at (●) 295, (×) 305, (*) 315 and (○) 323 K versus the concentration of the cation in equilibrium.
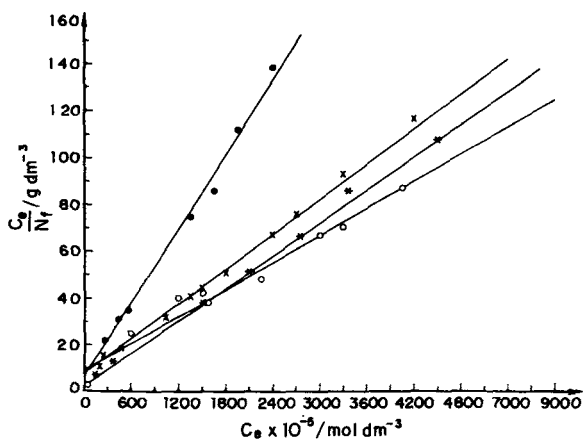
Figure 4. Linearization of the ionic exchange isotherms of Cu^{2+} in red Latosol soil at (●) 295, (×) 307, (*) 315 and (○) 323 K.

form of the copper adsorption is presented in Figure 4, where $b = 1/\alpha$ and $K = \alpha/\beta$ are obtained from angular and linear coefficients, respectively.

Solution pH variation, metal retention and organic matter content of the matrix are important chemical features to be analyzed in the ionic exchange process. The solubility of cations in soil is directly affected by the variation in pH, which favors the availability of cations in soil for plants (Harter 1983). Cations are also retained by organic matter at given pH values, although no direct correlation between them for a variety of soils was found. However, a better correlation could be related to the content of active organic matter (Harter 1983). The nature of cations can affect ionic exchange, since any degree of hydrolization or cation-anion couple solubility is altered. In the present case, the divalent cations were dissolved in an aqueous solution at pH 5.2 and some hydrolysis started to occur at pH above 6.0. However, the anions were chosen to avoid the formation of any insoluble compounds, and their concentrations were also extremely low.

The negative charges of the organic compounds interact with the acid soil surface. This mechanism of interaction could include cation bridging the clay and organic part or exchanging the hydroxyl groups of the organic compounds with the oxides present in the final extremity of the clay surface (Baham and Sposito 1994). These natural organometallic-minerals can also be formed by dissociation of the organic matter, when the free proton interacts with the minerals of soil and promotes its decomposition (Sposito 1989). Thus, the importance of organic matter in the adsorption mechanism can involve 3 main possibilities: 1) the exchange of ligands between functional groups like carbonyl, hydroxyl and phenol as well as cations during the formation of complexes in the soil matrix; 2) diffusion of organic compounds weakly adsorbed in

aqueous solution; and 3) the dissociable organic groups and the cation (Sposito 1989).

From the isotherm linearization results, K values were calculated using the Langmuir model and also a method proposed by Rawat. Only the adsorption process of the cation on the surface was considered, and the chemical reaction can be represented:

$$S^{2-} + M^{2+} \rightarrow SM \qquad [4]$$

S^{2-} is the soil surface and M^{2+} is the cation added to the system. The exchanger activity coefficient is assumed as unity, because only molecule interactions of the same species are considered. These $\gamma\pm$ coefficients for ions are unity due to low concentrations and negligible ionic strength, in accordance with the Debye-Huckel equation (McGlashan 1979).

The equilibrium constant can be represented as follows:

$$K = \bar{a}_M/a_M \qquad [5]$$

$\bar{a}_M$ and a_M are the activity of the cation in the exchanger phase and in solution, respectively. The activity is related to the concentration, C, by the expression:

$$a = \gamma \pm C \qquad [6]$$

$\gamma\pm$ is equal to 1, as previously shown; and Equation [5] can be rewritten as (Rawat et al. 1990):

$$K = C_s/C_e \qquad [7]$$

C_s is the concentration (mol g^{-1}) of the cation in the exchanger phase and C_e is the concentration (M) after equilibrium is reached. In this ionic exchange process, it is also assumed that: 1) a monolayer of solute is formed on the solid; and 2) the measured exchanger area is completely covered by solvent molecules. In this medium, the solute molecule does not occupy space. This assumption is adjusted to dilute solutions, as described previously.

Using Rawat's method, C_s values were calculated, providing the number of moles of cation added per volume in contact with the solid surface:

$$C_s = \rho ANN_f/MS \qquad [8]$$

ρ is the water density (1.0 g cm^{-3}), A is the area of molecule (cm^2 molecule^{-1}), N is the Avogadro constant (6.023 × 10^{23} molecule), N_f is the number of fixed moles (mol of solute per gram of solid), M is the molecular mass of solvent (g) and S is the superficial area of the solid (cm^2 g^{-1} of solid), which is related to many physical and chemical properties of materials.

After determining K values by using both methods, the variation of enthalpy was calculated using the van't Hoff equation:

$$\partial\ln(K)/\partial\ln(1/T) = \Delta H/R \qquad [9]$$

T is the absolute temperature (K) and R is the ideal gas constant (8.31 Jmol K^{-1}). It is worth mentioning

Table 1. Comparative enthalpic values obtained by the van't Hoff equation and by Rawat's proposed method in red Latosol soil.

Ion M^{n+}	ΔH/kJ mol^{-1}	
	Langmuir	Rawat
Cu	-65.5 ± 1.3	-97.3 ± 3.9
Cd	-36.9 ± 1.1	-45.6 ± 1.8
Pb	-43.0 ± 1.3	-50.7 ± 2.0
Zn	40.8 ± 1.2	30.5 ± 1.2
Hg	15.0 ± 0.5	11.3 ± 0.5
Ca	30.4 ± 0.9	40.0 ± 1.6
Na	32.7 ± 0.9	42.3 ± 1.7

that thermodynamic features of reactions occurring in soil systems are scarce. However, the enthalpic values were calculated for both methods and are compiled in Table 1. The exothermic series of values for Cu, Cd and Pb contrast with the endothermic ones for other cations. With the exception of Cu and Hg, the other enthalpic values are in the 30.0 to 66.0 kJ mol^{-1} range, indicating a chemisorption process. Therefore, it is expected that the ligand attached to organic matter complexes the cations in solution. However, other effects such as surface deprotonation, organic matter transference from the bulk to the interfacial phase of the mineral surface and surface conformational change can accompany the main phenomenon (Gu et al. 1994; Kowalska et al. 1994).

Variations of the free energy and entropy were calculated using Equations [10] and [11], respectively, and these results were combined with the K values in Tables 2 and 3:

$$\Delta G = -RT \ln K \qquad [10]$$

$$\Delta S = \Delta H - \Delta G/T \qquad [11]$$

The exothermic free energy data illustrate a spontaneous process, whose values for Langmuir and Rawat methods range from $-$ (5.1 to 24.0) and $-$ (14.7 to 33.1) kJ mol^{-1} ranges, for the listed values in Tables 2 and 3. The values for Na, Ca and Zn increase with the temperature, while Pb and Cd remain practically constant with the change in temperature. In following the variation in enthalpy, Zn, Hg, Ca and Na are entropically favorable in these processes, due to exothermic values presented.

CONCLUSION

The study of adsorption onto soil surfaces gives information about the exchange capacity of the matrix, where the highest adsorption comprises a higher exchange capacity. This parameter is related to the actual highest capacity of the matrix in exchanging. It is characteristic of the surface, which could be specified by the number of available sites, the content of organic matter, the amount of exchangeable cations, the natural pH of the soil and also the properties of the ion ana-

Table 2. Thermodynamic results of cation exchange processes at different temperatures in red Latosol soil using van't Hoff equation.

M^{n+}	T (K)	ln K	ΔS (J K^{-1} mol^{-1})	$-\Delta G$ (kJ mol^{-1})
Cu	295.0 ± 0.1	6.81 ± 0.14	-279 ± 14	16.7 ± 0.8
	307.0 ± 0.1	5.73 ± 0.11	-261 ± 11	14.6 ± 0.6
	315.0 ± 0.1	6.63 ± 0.13	-263 ± 6	17.4 ± 0.2
	323.0 ± 0.1	5.27 ± 0.10	-247 ± 9	14.2 ± 0.4
Cd	298.0 ± 0.1	7.19 ± 0.14	-64 ± 3	17.8 ± 0.7
	309.0 ± 0.1	5.95 ± 0.12	-70 ± 3	15.3 ± 0.5
	323.0 ± 0.1	6.00 ± 0.12	-64 ± 2	16.1 ± 0.3
Pb	295.0 ± 0.1	9.80 ± 0.20	-64 ± 2	24.0 ± 0.5
	305.0 ± 0.1	9.30 ± 0.19	-64 ± 2	23.6 ± 0.4
	315.0 ± 0.1	8.50 ± 0.17	-66 ± 3	22.3 ± 0.6
	323.0 ± 0.1	8.40 ± 0.17	-63 ± 2	22.6 ± 0.4
Zn	298.0 ± 0.1	5.90 ± 0.12	186 ± 9	14.6 ± 0.5
	307.0 ± 0.1	6.44 ± 0.13	187 ± 10	16.5 ± 0.7
	324.0 ± 0.1	8.00 ± 0.16	193 ± 7	21.6 ± 0.5
Hg	298.0 ± 0.1	4.66 ± 0.10	89 ± 4	11.5 ± 0.4
	308.0 ± 0.1	4.98 ± 0.10	90 ± 4	12.8 ± 0.4
	323.0 ± 0.1	5.14 ± 0.10	89 ± 4	13.8 ± 0.5
Ca	298.0 ± 0.1	5.39 ± 0.11	147 ± 7	13.4 ± 0.6
	310.0 ± 0.1	7.00 ± 0.14	156 ± 7	18.1 ± 0.7
	323.0 ± 0.1	6.34 ± 0.13	147 ± 6	17.0 ± 0.7
Na	298.0 ± 0.1	2.75 ± 0.06	133 ± 6	6.8 ± 0.3
	309.0 ± 0.1	1.97 ± 0.04	122 ± 5	5.1 ± 0.2
	322.0 ± 0.1	3.70 ± 0.07	132 ± 5	9.9 ± 0.2

Table 3. Thermodynamic results of cation exchange processes at different temperatures in red Latosol soil obtained through Rawat's method.

M^{n+}	T (K)	ln K	ΔS (J K^{-1} mol^{-1})	$-\Delta G$ (kJ mol^{-1})
Cu	295.0 ± 0.1	13.50 ± 0.32	−217 ± 2	33.1 ± 0.5
	307.0 ± 0.1	12.00 ± 0.25	−218 ± 2	30.6 ± 0.3
	315.0 ± 0.1	11.16 ± 0.24	−216 ± 2	29.2 ± 0.3
	323.0 ± 0.1	10.11 ± 0.28	−217 ± 2	27.2 ± 0.3
Cd	298.0 ± 0.1	10.05 ± 0.17	−70 ± 1	24.9 ± 0.2
	309.0 ± 0.1	9.36 ± 0.12	−70 ± 1	24.1 ± 0.1
	323.0 ± 0.1	8.62 ± 0.07	−70 ± 1	23.2 ± 0.1
Pb	295.0 ± 0.1	12.60 ± 0.56	−67 ± 1	30.9 ± 0.5
	305.0 ± 0.1	11.79 ± 0.37	−68 ± 1	29.9 ± 0.4
	315.0 ± 0.1	11.85 ± 0.12	−63 ± 1	31.0 ± 0.1
	323.0 ± 0.1	10.54 ± 0.26	−69 ± 1	28.3 ± 0.3
Zn	298.0 ± 0.1	10.95 ± 0.18	193 ± 2	27.1 ± 0.2
	307.0 ± 0.1	11.05 ± 0.22	191 ± 2	28.2 ± 0.2
	324.0 ± 0.1	11.88 ± 0.21	193 ± 2	32.0 ± 0.3
Hg	298.0 ± 0.1	8.15 ± 0.13	106 ± 1	20.2 ± 0.1
	308.0 ± 0.1	8.52 ± 0.04	107 ± 1	21.8 ± 0.1
	323.0 ± 0.1	8.52 ± 0.10	106 ± 1	22.9 ± 0.1
Ca	298.0 ± 0.1	8.41 ± 0.28	204 ± 2	20.8 ± 0.3
	310.0 ± 0.1	9.17 ± 0.14	205 ± 2	23.6 ± 0.2
	323.0 ± 0.1	9.66 ± 0.03	204 ± 2	25.9 ± 0.1
Na	298.0 ± 0.1	5.92 ± 0.09	191 ± 2	14.7 ± 0.1
	309.0 ± 0.1	7.06 ± 0.06	196 ± 2	18.1 ± 0.1
	322.0 ± 0.1	7.21 ± 0.03	191 ± 2	19.3 ± 0.1

lyzed, which includes the ionic radius and its degree of hydration.

The increase in temperature causes an increase in the exchange, indicating that this variable disturbs the conditions of cation exchangeability and the surface. The calculated enthalpy obtained by the variation in temperature provides the average values. In this case, there is no ideal method for calculating thermodynamic parameters for this kind of heterogeneous system.

Individual enthalpic value depends upon the temperature and also the thermal effect. Moreover, any fraction of ion exchanged is associated with a correspondent exchange enthalpy, whose value is directly related to the amount of cations added to the system. Thus, the energy associated with the process depends upon the number and type of interactions caused by the cation in the system. Additions of cations in a heterogeneous system with distinct types of sites in the attached ligands affects the variation in enthalpy. These changes can be explained by the influence of the following factors: 1) the degree of hydration of the cations can be altered due to the change in the energy of the process; 2) the functional groups involving the sites of the ligands can be deformed; 3) the acid organic groups of the matrix can be deprotonated; 4) the matrix changes with probable decomposition of the minerals, which are easily leached, and also the organic matter (Sposito 1989). This occurs with low molar mass organic acids held in the matrix, which are liberated due to the decrease of the interactive forces with increased temperature. Consequently, the numbers of sites in ligands and the conformation of the polymeric matrix are altered. Thus, the water molecules presented in the first sphere of coordination are more easily exchanged, permitting the formation of complexes with cations of transition metals.

In attempting to explain the ion exchange process for heterogeneous systems, especially when accompanied by the formation of complexes, the following energetic contributions should be determined: the enthalpy of coordination bonding between metal and the matrix ligand groups, the enthalpy of dehydration of matrix ligand groups, the exchanged matrix of water in the first sphere of cation coordination and the enthalpy of deformation of polymeric matrix and minerals in the soil (Hajiev et al. 1989).

ACKNOWLEDGMENT

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