Energy relationships between constant charge soils and cations

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Abstract

This paper described the relationships of energies between the constant-charge soils (yellow-brown, and black soils) and five kinds of cations (K^+, NH_4^+, Ca^{2+}, Cd^{2+}, Cr^{3+}) as inferred from the Wien effect measurements in suspensions. The results showed that the mean free binding energies, ΔG_{bi}, of K^+ and NH_4^+ to the two soils were in the range of 6.3 to 7.0 kJ/mol, the binding energies of K^+ being larger than those of NH_4^+. The range of binding energies of divalent cations to both soils was 7.2-9.4 kJ/mol. As for the same cation, the binding energies were of the order yellow-brown soil < black soil. The mean free binding energies of Cr^{3+} to both soils were smaller than those of all divalent cations. The mean free adsorption energies, ΔG_{ad}, of monovalent cations to both soils at the same field strength, such as 150 kV/cm, showed that the adsorption energies of K^+ and NH_4^+ to yellow-brown (0.88-0.90 kJ/mol) were near the same, but the adsorption energy of NH_4^+ for black soil was more than that of K^+ by 0.1 kJ/mol. The range of adsorption energies of divalent cations to both soils was 1.4-2.2 kJ/mol.

Key words

Electrical conductivity, field strength, mean free energy

Introdution

Chemical phenomena in soils are the appearance of various forms of energies and their transformation (Yu, 1976). Soil chemists usually explain the interactions between various ions and clay minerals/soil particles in terms of the affinity parameter of a best-fitted Langmuir isotherm, whether the assumptions behind the originally derived Langmuir model are applicable or not (Ajwa and Tabatabai, 1997). Since the fifties of last century, to investigate the nature of soil chemical phenomena on basis of the energy relationship became an active research field (Yu, 1976) because the energies between ions and soil particles can be used for characterizing interactions of ions with soil particles, which is very interesting and useful for the investigations of plant nutrition and soil environmental protection. Critter and Airoldi (2003) experimentally determined the ion-exchange equilibrium on cationic latosol soils/aqueous solution interface and calculated the Gibbs free energy by linearization of the Langmuir equation. However, the investigation of energy relationship between cations and soil particles in the second half of the 20th century was based on indirect deduction, rather than on direct measurement. Since there is no break-through in methods to determine the binding energy of cations to soil particles (Yu, 1963; 1976), up to now the experimental results in the aspect have been little reported, and there is still no conspicuous advance.

Recently, a novel method for evaluating the interactions of ions with charged colloidal particles, based on measurements of the Wien effect in suspensions, has been developed (Li *et al.*, 2005). The binding and the adsorption energies of cations with soil particles can be determined on basis of the new method. In the present report we applied the new method to investigate the energy relationships between two constant charge soils (yellow-brown and black soils) and five kinds of cations (K^+, NH_4^+, Ca^{2+}, Cd^{2+}, and Cr^{3+}).

Materials and methods

Soil Samples

The tested yellow-brown soil (Alfisol) and black soil (Mollisol), which were expected to carry only negative charge, were collected from a depth of about 1m in Nanjing and Haerbin, respectively. The organic matter content of yellow-brown and black soils was 5.4, and 13.6g/kg, respectively. The clay fraction of <2 μm in diameter was separated by sedimentation, dried, and ground. The positive and negative charge densities of the clay fractions of the two soils at different pH values are presented in Figure 1.

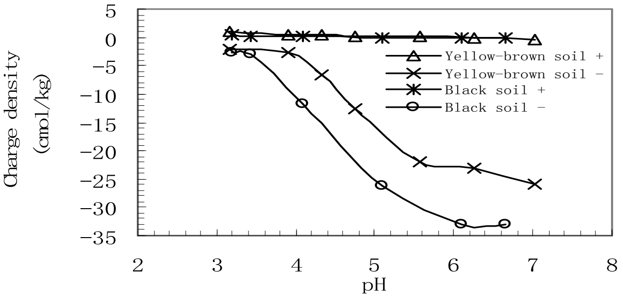

Figure 1. Variation of negative and positive charge densities of the soils with pH

Preparations of Homoionic Soil Samples and Suspensions

The clay fractions of the two soils were saturated with various cations by three sequential equilibrations with 1 mol L^{-1} solutions of chlorides of these cations. After the free chlorides contained in the clay samples were thoroughly removed, the chloride-free clay fractions were dried and ground. Suspensions were prepared by adding deionized water to soil samples in plastic bottles to achieve a solid concentration of 10g/L. The suspensions were allowed to stand for about 7-10 days prior to the Wien effect measurements.

Wien Effect Measurement Procedure

The procedure of Wien effect measurements was described in a previous paper (Li *et al*., 2005). The data presented in Figure 2 are the means of two sets of measurements; the standard errors were usually smaller than the symbols on the graphs. All the reported measurements were made at a constant temperature of 25°C.

Equations evaluating binding and adsorption energies

The equation evaluating the binding energy (Li *et al*., 2005) is given by

$$\Delta G_{bi}=RT\ln(2\cdot CEC\cdot C_p\cdot\lambda/EC_0) \qquad (1)$$

The adsorption energy evaluation is according to the following equation

$$\Delta G_{ad}=RT\ln(EC/EC_0) \qquad (2)$$

The application of equation (2) to a series of Wien effect measurements may provide a spectrum of the cation adsorption energies. All binding/adsorption energies will be assigned positive signs in this paper.

Results and discussion

Mean Gibbs free binding energy

The parameters needed for calculating mean Gibbs free binding energy according to equation (1) are presented in Table 1 along with the mean free binding energies. The mean free binding energies were of the order $Ca^{2+} > Cd^{2+} > K^+ > NH_4^+ > Cr^{3+}$, and $Ca^{2+} > Cd^{2+} > Cr^{3+} > K^+ = NH_4^+$ for yellow-brown and black soils, respectively. The binding energy of K^+ to yellow-brown soil calculated from K^+ ion activity in the suspension of pH 5.33, which was determined with potassium ion-selective electrode by Xuan *et al*. (1965), was 7.25 kJ/mol, that is closed to the value (6.71 kJ/mol) calculated from EC_0. The binding energies of divalent cations are larger than those of monovalent cations by 0.45~2.40 kJ/mol. The sequence of mono- and divalent cations is reasonable (Diatta, 2004), but it was somewhat unexpected that the mean free binding energy of Cr^{3+} for both soils was smaller than those of all divalent cations. This may be due to that the high degree of hydrolysis of Cr^{3+} in water resulted in its transformation into divalent $Cr(OH)^{2+}$ and monovalent $Cr(OH)_2^+$, together with H^+ cations. The hydrolysis constant (p*K*) of Cr^{3+} (3.9) is much smaller than those of Ca^{2+} (12.5) and Cd^{2+} (9.7) (Wen *et al*., 1977). It is notable that the ΔG_{bi} values of yellow-brown soil were smaller than those of black soil, probably because of the higher organic matter content in the black soil.

Table 1. The parameters necessary to evaluation of mean Gibbs free binding energies (ΔG_{bi})

	Yellow-brown soil					Black soil				
	K^+	NH_4^+	Ca^{2+}	Cd^{2+}	Cr^{3+}	K^+	NH_4^+	Ca^{2+}	Cd^{2+}	Cr^{3+}
pH	5.35	5.29	4.97	4.60	4.24	6.44	6.39	5.74	5.38	4.53
CEC (mol/kg)	0.199	0.192	0.156	0.103	0.0504	0.333	0.334	0.311	0.288	0.181
λ (mS·L/cm·mol)	73.52	73.55	59.50	54.00	67.0	73.52	73.55	59.50	54.00	67.0
$CEC\cdot C_p\cdot\lambda$ (mS/m)	0.146	0.141	0.0928	0.0556	0.0338	0.245	0.246	0.185	0.156	0.121
EC_0/100 (mS/cm)	1.95	2.26	0.693	0.621	0.769	2.90	2.91	0.828	0.796	0.823
ΔG_{bi} (kJ/mol)	6.71	6.26	8.16	7.16	5.39	7.01	7.01	9.42	9.10	8.39

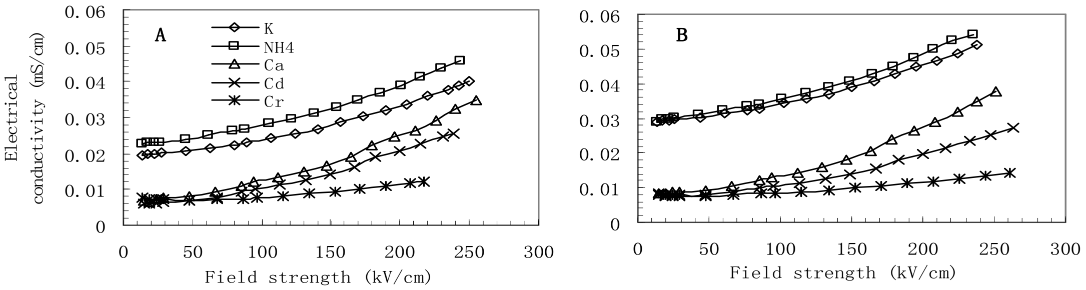

Figure 2. Dependence on field strength of electrical conductivities of suspensions (10 g/L) of yellow-brown soil (A), and black soil (B) saturated with different cations in deionized water

EC-Field strength relationships

The effects of field strength on the electrical conductivities of the suspensions of yellow-brown and black soils saturated with various cations are shown in Figure 2A and B, respectively. With weak fields (about 15 kV/cm), the EC values of the suspensions ranged from 0.006 to 0.029 mS/cm, and the EC values of various suspensions increased with increase in field strength. The changes in EC values of suspensions of the two soils with cations at the same field strength are in the same order $NH_4^+ > K^+ > Ca^{2+} > Cd^{2+} > Cr^{3+}$.

Mean Gibbs free adsorption energy

The mean Gibbs free adsorption energies of all cations released at a given applied field, evaluated via equation 2, are presented in Figure 3. In the range of low field of 15~80 kV/cm the adsorption energies of mono- and divalent cations were not different, but as field strength is more than 100 kV/cm, the ΔG_{ad} values of divalent cations is obviously larger than those of monovalent cations. The ΔG_{ad} values among various cations descend in the order $Ca^{2+} > Cd^{2+} > NH_4^+ > K^+ > Cr^{3+}$. It is not well known that ΔG_{ad} values of Cr^{3+} to the soil particles are lower than those of mono- and divalent cations, and this will be further investigated.

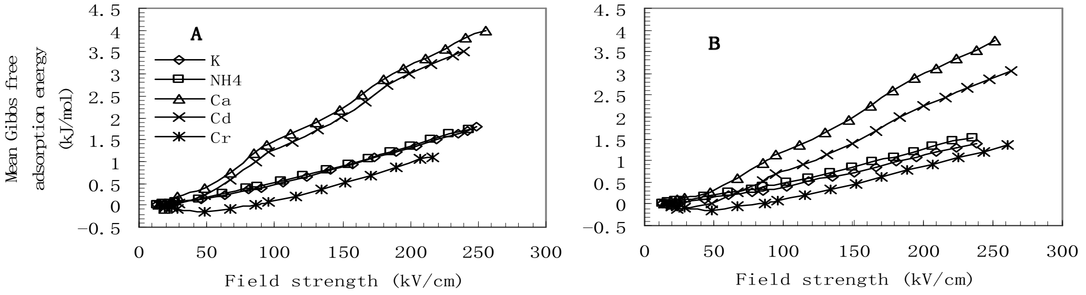

Figure 3. Mean Gibbs free adsorption energies as a function of field strength for yellow-brown soil (A), and black soil (B) saturated with different cations in deionized water (10 g/L)

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