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Humic acid-divalent cation interactions

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Abstract

The adsorption behavior of divalent cations M^{2+} (Cu, Ni, Co and Zn) with commercial humic acid (HAAl) and also with an extracted fraction of peat soil (HAPs) was followed in aqueous solution. The series of adsorption isotherms were fitted to a modified Langmuir equation. The maximum number of moles adsorbed gave: 0.55 ± 0.02, 0.66 ± 0.02, 0.54 ± 0.02, 0.40 ± 0.02 mmol per gram for HAAl and 0.63 ± 0.03, 0.61 ± 0.06, 0.55 ± 0.02, 0.54 ± 0.03 mmol/g for solid HAPs, for copper, nickel, zinc and cobalt, respectively. The same interaction followed calorimetrically gave endothermic values: 2.4 ± 1.0, 8.4 ± 0.9, 18.3 ± 0.9, 10.6 ± 0.9 kJ mol^{-1} and 18.4 ± 1.2, 15.9 ± 1.4, 15.4 ± 1.2, 15.0 ± 1.2 kJ mol^{-1} for HAAl and HAPs, respectively, for the same sequence. Because all Gibbs free energies were negative. Complexation must be accompanied by an increase in entropy.

Keywords: Humic acid; Thermodynamic data; Divalent cations; Adsorption

1. Introduction

Brown and black biopolymers associated with soil, sediment and particulates suspended in water consist of material derived from the degradation of animals and plants and are called humic substances. The mobility and transport of heavy metal ions in the environment is affected by the presence of humic substances [1,2].

Humic acid (HA) is one of the main components of the organic mass in soils and also of the dissolved organic carbon in natural aquatic environments [3]. These substances are a mixture of weak-acid polyelectrolytes, organic macromolecules exhibiting a large range of molar-mass distribution, substructures and functionalities [4,5]. Cation complexation by humic acids reduces bioavailability and toxicity [1]. The nature of the interaction between HA and cations in the environment is therefore of considerable importance [6,7]. However, the physical-chemistry of such interactions, are poorly understood, due to the complex structure and heterogeneity of humic acids [8], which leads to a distribution of types and number of metal binding sites [9].

Thermodynamic data on cation-humic acid interactions aid in understanding the effects that occur in this interaction. Thus, calorimetric determination the enthalpy and entropy changes of cation adsorption by humic acid are useful understanding these interactions.

The present investigation deals with the adsorption of several divalent cations (Cu, Ni, Co and Zn) onto two distinct humic acids, one being the extracted fraction from peat soil and the other being from a commercial source.

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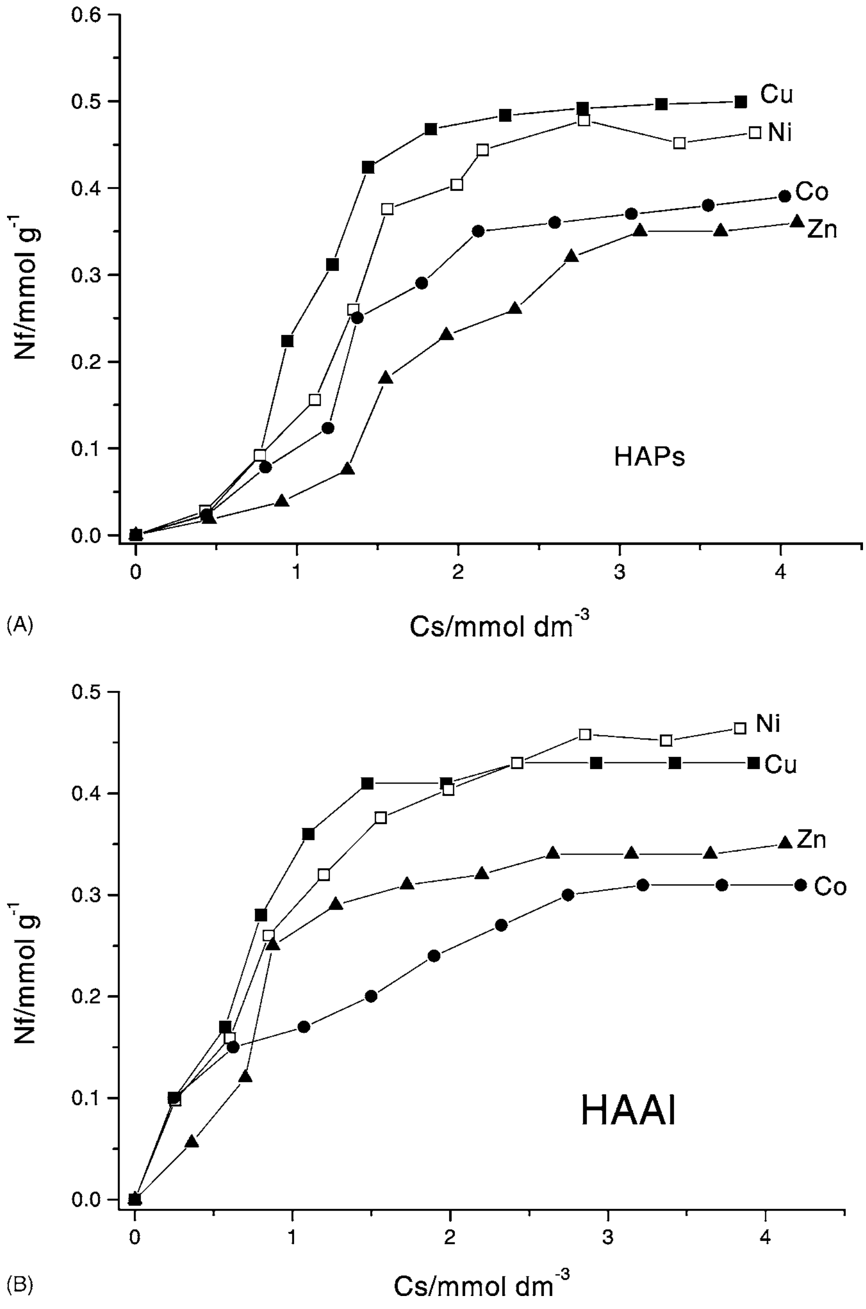

Fig. 1. Isotherms of adsorption of divalent cations Cu (■), Ni (□), Co (●) and Zn (▲) on humic acid samples HAPs (A) and HAAl (B).

2. Experimental

2.1. Samples

The humic acids were selected from two different origins: (a) commercial product from Aldrich (HAAl) and (b) obtained from Brazilian peat soil (HAPs) [10].

2.2. Purification of the commercial humic acids

HAAl samples were suspending in water and dialyzed in order to reduce the salt content [4]. The external water was twice replaced in the first 5 h period and then every 12 h until no chloride could be detected in the dialysate by dialysis tubing [11]. The resulting solid was then dried in vacuum for 4 h at 55 °C. The total acidity and carboxylic acidity were determined by potentiometric titration [12], as recommended, with some modification of the original procedure [12,13].

2.3. Adsorption isotherms

The adsorption isotherms were obtained by the batchwise method, in which a series of samples of 50.0 mg of humic acid were suspended in 20.0 cm^3 of aqueous solution with the cation concentration, varying from 2.0 to 12.0 mmol dm^{-3}. The ionic strength was controlled with KCl at 0.1 mol dm^{-3}, and Clark/Lubs buffer was used to maintain pH 5. The samples were mechanically stirred for 4 h at 298 ± 1 K and the solid separated by centrifugation and filtration. The adsorbed cation content was determined by difference by sampling the filtrated supernatant, using a Perkin Elmer 3000 DV ICP-AES [14].

2.4. Calorimetry

Calorimetric titrations were done on a differential, isothermal LKB 2277 microcalorimetric system. The titration consisted of suspending approximately 20.0 mg of humic acid in 2.50 ml of solution. In a steel ampoule, which was vigorously stirred at 298.15 ± 0.02 K. After thermal equilibration, the cation solution was incrementally added with a microsyringe. For each increment, the total thermal effect ($\Delta_{tit}Q$) was recorded, as indicated by zero baseline at the end of the reaction. The same procedure was employed to monitor the thermal effect of cation dilution ($\Delta_{dil}Q$) without the solid and also of adding the water to the humic acid, which gave a null value. By combining these two heat outputs, the net value ($\sum \Delta_r Q$) can be determined by the expression $\sum \Delta_r Q = \sum(\Delta_{tit}Q) - (\Delta_{dil}Q)$ [15,16].

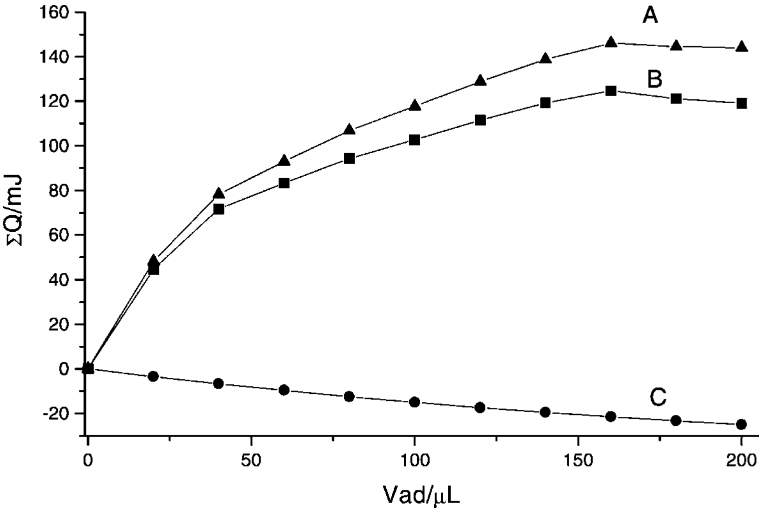

Fig. 2. Calorimetric titration of divalent copper into an HAPs sample. The curve (A) represents the measured thermal effect $\sum Q_{res}$, (B) $\sum Q_{tit}$ (B) and (C) $\sum Q_{dil}$.

3. Results

The carboxylic and total acidity gave 2.54 ± 0.06 and 4.94 ± 0.05 mmol and 2.33 ± 0.02 and 5.07 ± 0.03 mmol/g of HAAl and HAPs, respectively. The ability of the humic acid to adsorb cations from water was evaluated by measuring the sorption isotherms the divalent cations of copper, nickel, zinc and cobalt. The number of moles adsorbed (N_f), for one gram of the solid, was obtained from the initial number of moles of cation (n_i) added to the system and free cation at equilibrium (n_s) for a mass (m) of the support, by applying the expression: $N_f = (n_i - n_s)/m$.

The adsorption isotherms for all cations are represented in Fig. 1. The maximum adsorption values differ with the cation.

The data are described by the general equation for the Langmuir model: $(C_s/N_f) = (C_s/N_s) + (1/N_s b)$.

C_s is the concentration of solution in equilibrium (mol dm^{-3}), N_f as defined before (mol g^{-1}), N_s the

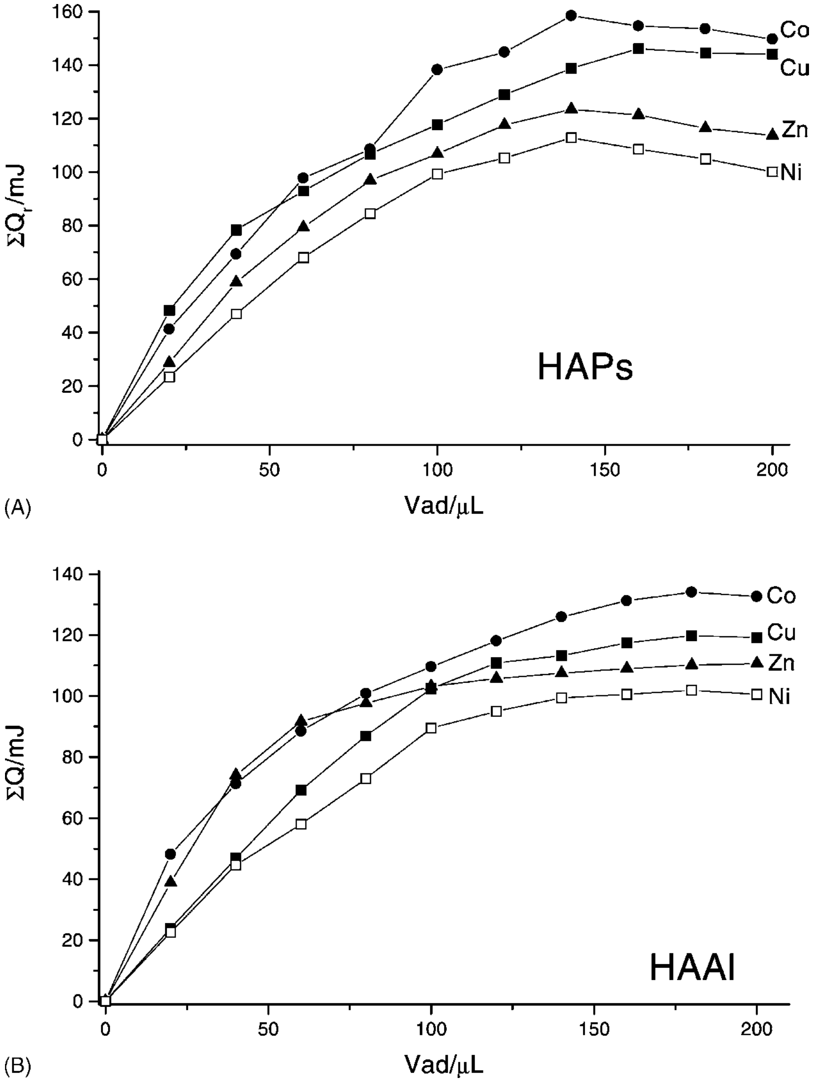

Fig. 3. Thermal effect of the interaction of the divalent cations Cu (■), Ni (□), Co (●) and Zn (▲) with humic acid samples HAPs (A) and HAAl (B).

Table 1
Maximum adsorbed amounts of divalent cations (M^{2+} = Cu, Ni, Co and Zn), Ns (mmol) per gram (g) of humic acid, at 298 ± 1 K

Sample	Cu	Ni	Co	Zn
HAPs	0.63 ± 0.03	0.61 ± 0.06	0.55 ± 0.02	0.54 ± 0.03
HAAl	0.55 ± 0.02	0.66 ± 0.02	0.40 ± 0.02	0.54 ± 0.02

maximum amount of solute adsorbed per gram of adsorbent ($\mathrm{mol\,g^{-1}}$), which depends on the number of adsorption sites, and b is a constant. All further data are derived from this linearized form of the adsorption isotherm, i.e. from plots of C_s/N_f as a function of $C_s N_s$ and b values were obtained from the slope and intercept of the linearized form. Ns values are listed in Table 1. These data show the adsorption followed the sequence Cu > Ni > Co > Zn for HAPs and Ni > Cu > Zn > Co for HAAl, respectively.

The thermal effect of the adsorption reaction was obtained from the calorimetric results, with the values obtained expressed by $\sum \Delta_r Q = \sum(\Delta_{\mathrm{tit}} Q) - (\Delta_{\mathrm{dil}} Q)$. The data for copper is shown in Fig. 2.

The thermal effect values for the adsorption reaction ($\sum \Delta_r Q$) for all interactions between divalent cations and humic acid samples are presented in Fig. 3. Fitting these data to a modified Langmuir Eq. (2) [15,16], the integral enthalpies involved in the formation of a monolayer per unit mass of adsorbate $\Delta_{\mathrm{mono}} H$ were calculated, as shown in Fig. 4.

$$\frac{\sum X}{\sum \Delta_r H} = \frac{1}{(K-1)\Delta_{\mathrm{mono}} H} + \frac{\sum X}{\Delta_{\mathrm{mono}} H} \qquad (2)$$

In this equation, $\sum X$ is the total mole fraction of the cation in solution after adsorption, X values are obtained for each addition of titrant, by using the modified Langmuir equation, whose behavior was shown to be a good adjustable model for such heterogeneous systems [15,16]. $\Delta_r H$ the integral enthalpy of adsorption ($\mathrm{J\,g^{-1}}$) obtained through the net thermal effect of adsorption and the number of moles of the adsorbate, K the proportionality constant that also includes the equilibrium constant. By using the slope and linear values from the $\sum X/\Delta_r H$ versus $\sum X$ plot, $\Delta_{\mathrm{mono}} H$ and the enthalpy of adsorption $\Delta_{\mathrm{ads}} H$ values can be calculated by means of the expression $\Delta_{\mathrm{ads}} H = \Delta_{\mathrm{mono}} H / N_s$. Gibbs free energies were calculated from K values by the expression: $\Delta G = -\mathrm{RT} \ln \mathrm{K_{eq}}$, and the entropy value calculated through $\Delta G =$

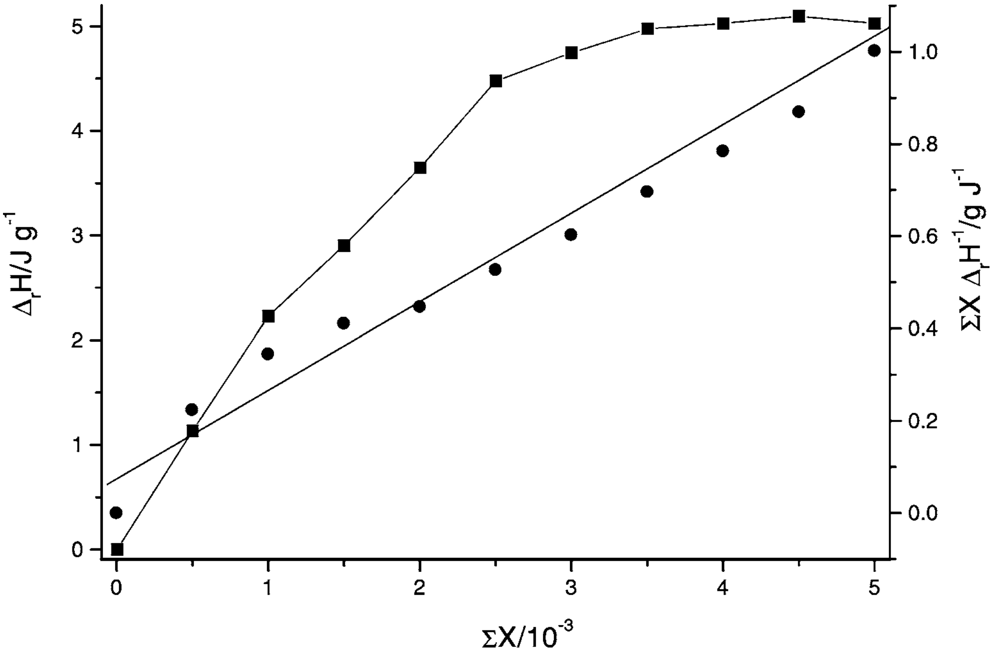

Fig. 4. Calorimetric titration isotherm of HAAl with cobalt at 298.15 ± 0.02 K; the straight line is the linearized form of the isotherm.

$\Delta H - T\Delta S$. All thermodynamic data are listed in Table 2.

Table 2
Thermodynamic data for the interaction of divalent cations (M^{2+} = Cu, Ni, Co and Zn) with the humic acid samples HAPs and HAAl at 298.15 ± 0.02 K

Sample	M^{2+}	$-\Delta G$ (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
HAPs	Cu	16.1 ± 0.8	18.4 ± 1.2	116 ± 1
HAPs	Ni	15.4 ± 0.8	15.9 ± 1.4	105 ± 1
HAPs	Co	15.7 ± 0.8	15.4 ± 1.2	104 ± 1
HAPs	Zn	15.2 ± 0.8	15.0 ± 1.2	101 ± 1
HAAl	Cu	18.3 ± 0.7	12.4 ± 1.0	103 ± 1
HAAl	Ni	22.1 ± 0.8	8.4 ± 0.9	102 ± 1
HAAl	Co	19.0 ± 0.8	18.3 ± 0.9	125 ± 1
HAAl	Zn	18.5 ± 0.8	10.6 ± 0.9	98 ± 1

4. Discussion

Humic acid samples have the ability to adsorb divalent cations. The humic acid extracted from peat soil presented higher cation adsorptions than those observed for the commercial product. The adsorption processes for both humic acids were spontaneous in nature although they presented an endothermic enthalpy for the interaction, resulting in an entropically favored process. *This fact can be explained by liberation of more than one proton for each adsorbed cation, causing a typical chelate effect, which is entropically favored*.

The increase in entropy can be interpreted by considering the release of (i) protons during the interactive process, and (ii) solvent molecules that were previously bonded to the solute involved in the replacement ion exchange process. Such increases in species in solution contribute to favorable conditions for such general solid/liquid interface reactions.

Based on structural features associated with the humic acid, an adsorption of the soluble aqueous species is expected, mainly due to nitrogen or oxygen atoms, present in the basic amine or oxygen centers dispersed over all the biopolymer surface [9].

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