Chemistry for Sustainable Development **14** (2006) 367–373

Humic Acids: Interaction with Metal Ions, Features of Structure and Properties of Metal Humic Complexes

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(Received November 10, 2005)

Abstract

The mechanism of processes involved in the interaction of humic acids with heavy metal ions, as well as the features of structure and properties of metal humic complexes (MHC) are investigated with the help of EPR spectroscopy and TGA. The topography of distribution of functional groups on the surface of the powders of humic acids and MHC is investigated by means of adsorption of acid-base indicators. The stability of MHC in aqueous medium and the mobility of heavy metals are studied with the help of HCl leaching method.

INTRODUCTION

Humic acids (HA) are high-molecular polyfunctional and polyconjugated systems. The composition of their functional groups and the structure of molecular fragments depend both on the genesis of humic raw material and on the method of isolation and purification [1, 2]. Investigation of the mechanism of the interaction of HA with metal ions (especially polyvalent ones) seems very urgent not only for the prediction of the redistribution of humic compounds, heavy metals (HM) in the environment but also for the development of methods for active control of the migration of pollutants in natural environment, for obtaining new materials to be used in environmental protection, and for verification of the schemes of utilization of worked out humic sorbents of HM.

The goal of the present work was to study the mechanism of the interaction of HA with HM ions in aqueous medium, including the analysis of physicochemical factors providing the stability of metal humic complexes (MHC).

EXPERIMENTAL

Humic acids extracted with the aqueous solutions of NaOH from the high-moor peat with the decomposition degree of 40–45 % [3] and subjected to preliminary fractionation [4] according to the parameters of molecular mass distribution and physicochemical properties were the subject of investigation. Metal humic complexes were obtained by the interaction of HA under static conditions with HM ions in the monoionic solutions of $MeSO_4$ (pH $\leq$ 4). The solution of $MeSO_4$ and HA was kept for 24 h under periodic mixing at a temperature of 20 °C. Thus obtained insoluble MHC were separated by centrifuging, the precipitate was washed from free HM ions with distilled water. After washing, MHC were dried at a temperature of 25 and 105 °C, then triturated and again dried. The concentration of HM ions in MHC was determined according to the procedure described in [5] by means of incineration at a temperature of 700 °C, followed by the dissolution of ash in concentrated HCl.

Analysis of active centres on the surface of particles of the powdered MHC was carried out using the indicator procedure [6] based on the ability of acid-base indicators to change their colour during the interaction with the active centres on particle surface. The samples under investigation, with a mass of 0.02 g, were placed into the aqueous solutions of indicators. The degree of indicator conversion into the acid or basic form was determined on the basis of changes in the optical density of indicator solutions. A set of 20 indicators was used for the analysis.

The stability of MHC to dissolution in water and in HCl solutions was determined under static conditions. Concentrations of HM ions in solutions were determined according to the procedure described in [5].

Thermogravimetric examination of HA and MHC was carried out with OD-103 derivatograph in nitrogen within temperature range 20–800 °C, at the heating rate of 10 °C/min, with DTA sensitivity equal to 1/10, DTG 1/5.

To investigate the structure of HA and MHC, electron paramagnetic resonance (EPR) was used, due to the high sensitivity of this method to the specific features of the structure of organic matter in the compounds of natural polymers with the metals of variable valence [7]. It should be stressed that the paramagnetism of HA is due not to the nature of free radicals stabilized in a rigid high-molecular matrix (as some researchers [8, 9] suppose) but to the energy gain from the formation of supramolecular aggregates (as a consequence of synergism in the interaction of aromatic fragments and functional groups of HA with the participation of hydrogen bonds) [10]. The procedure of EPR spectra recording and processing was described in [11].

The concentration of carboxyl groups in HA and in MHC was determined using the barium acetate procedure [12].

RESULTS AND DISCUSSION

It was established that the static exchange capacity (SEC) for HA fractions with respect to Cu^{2+} and Ni^{2+} ions is directly dependent on the concentration of carboxylic groups in HA for pH £ 4 (Fig. 1), that is, under the conditions when no hydroxides of these polyvalent metal ions are formed [13]. One can see that under these conditions the SEC values for Cu^{2+} and Ni^{2+} are almost identical.

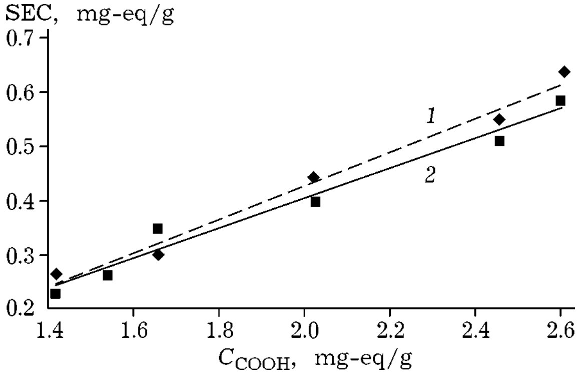

Fig. 1. Dependence of carboxylic group content of HA fractions on SEC for Cu^{2+} (*1*) and Co^{2+} (*2*) ions for pH £ 4. $SEC_{Cu^{2+}} = 0.3102C_{Cu^{2+}} - 0.194$, $R^2 = 0.9877$; $SEC_{Ni^{2+}} = 0.2767C_{Ni^{2+}} - 0.1487$, $R^2 = 0.9759$.

It was established by means of adsorption of acid-base indicators on the surface of powdered MHC that Cu^{2+} ions interact both with strongly acidic and with weakly acidic functional groups of HA (Fig. 2).

The low selectivity of HA functional groups in the interaction with Cu^{2+} ions is due to the high complexing ability of Cu^{2+} ions even in the acid medium, which is also characteristic of Cr^{3+} ions. In this situation, Cu^{2+} ions are able to form organic mineral compounds both with carboxyl and with hydroxyl groups of HA [14, 15]. Ni^{2+} ions more clearly exhibit selectivity of the interaction with HA: these ions mainly interact with functional groups characterized by low pK_a values, and only insignificantly interact with the functional groups characterized by high pK_a. The intensity of recording functional groups for which $pK_a = 4–8$ changes only slightly. According to the data shown in Fig. 2, Co^{2+} ions are able to interact only with the carboxylic groups of HA with low pK_a. At the same time, it follows from the data shown in Fig. 2 that dry MHC powder contains a sufficient amount of vacant sorption centres, especially with $pK_a > 9$. On the basis of the presence of free exchange centres, the investigated powders of humic preparations can be rated as a sequence: H–HA > Co–HA > Ni–HA > Cr–HA ³ Cu–HA.

The strength of the interaction inside complex organometallic compounds to which MHC

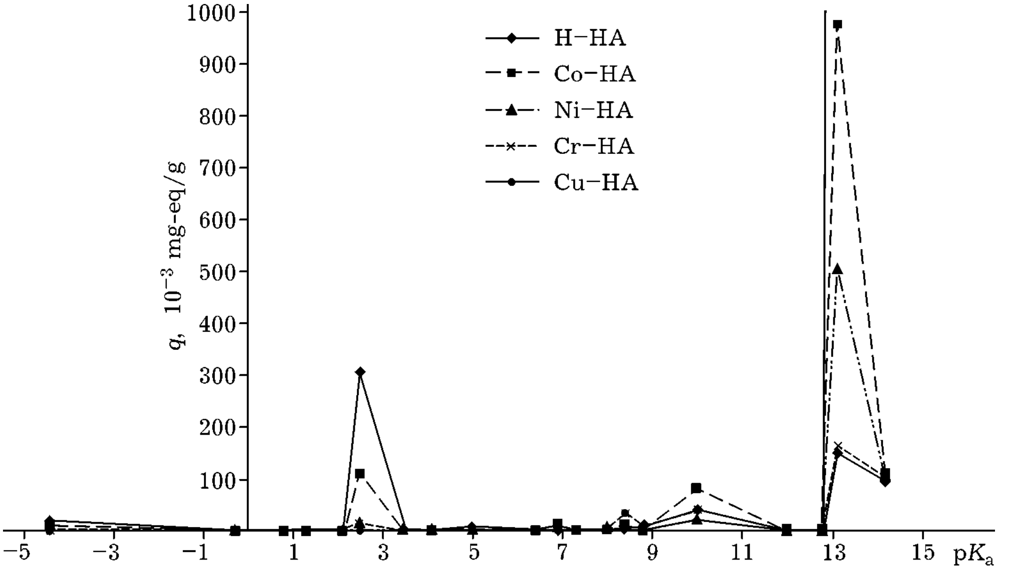

Fig. 2. Spectra of the distribution of acid-base centres on the surface of MHC powder particles.

and HA belong can be estimated on the basis of thermal stability by means of DTA. According to the data shown in Fig. 3, among the investigated humic compounds, H–HA possess the maximal stability to thermal destruction within the range 20–350 °C, while MHC are ranged as Co–HA > Ni–HA > Cr–HA > Cu–HA. Comparative analysis of the obtained results together with the data shown in Fig. 2 allows us to conclude that the thermal stability of MHC compounds increases with an increase in the number of free ion exchange (functional) centres. Within temperature range 80–140 °C, a small endothermic effect is observed on DTA curves *1*–*5* (see Fig. 3). For H–HA (curve *1*), it is connected with the removal of physically and, in part, chemically bound water; for MHC, its maximum shifts and depends on the cation included in a MHC. According to [16], changes in the position of the endothermic maximum are caused by the destruction of crystal hydrates. The stage of the intensive mass los is observed at a temperature starting from 170 °C (see Fig. 3); its rate reaches maximum at 255 °C.

According to the data reported in [7], within temperature range 150–190 °C, mass loss is due to the primary reactions of decomposition of organic compounds. Water removal from HA as a result of decarboxylation can proceed up to 200 °C [18], that is, HA decarboxylation is the process prevailing within this temperature range. At a temperature of 370 °C, the destruction

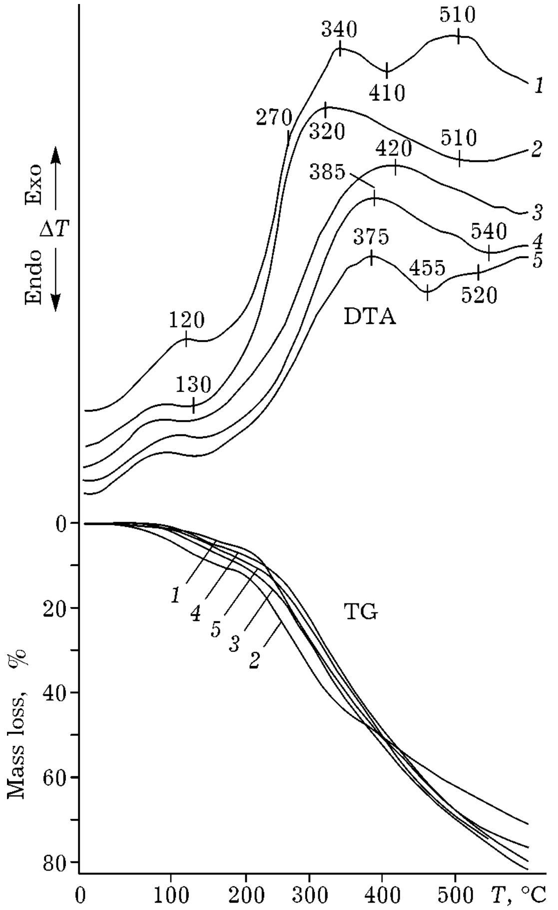

Fig. 3. Derivatograms of HA in the H-form (*1*) and MHC with ions: Cu^{2+} (*2*), Co^{2+} (*3*), Cr^{3+} (*4*), Ni^{2+} (*5*).

of aliphatic constituents of peripheral HA fragments is almost complete, along with decarboxylation. According to [18], phenol groups are more stable; however, even they are completely decomposed below 400 °C. With further temperature rise, thermal destruction processes take place in the "nucleus" of HA. An intense MHC mass loss is over at 500 °C. Further temperature rise does not cause any substantial changes in the sample mass because the stage of active pyrolysis is over, and this process takes place either in the carbon framework or in the mineral component.

The interaction of water-soluble HA fractions with HM ions in aqueous medium results in the formation of sedimentation-unstable MHC which usually precipitate. Metal humic complexes are water-saturated (W = 70–90 mass %) gels with weakly acid or neutral medium. It is known that the stability of MHC is determined by the acidity of the medium: the higher the latter, the less the strength of bonding in Me–HA complexes; therefore, the mobility of a metal increases along with its trend to migratory transport together with moisture to the adjacent media.

In comparison with Cu^{2+} and Cr^{3+}, Ni^{2+} and Co^{2+} ions form less stable MHC which can be easier decomposed in aqueous medium. The transition of HM from MHC into solution finished when the equilibrium is achieved; afterwards, this process is almost independent of the acidity of solution (Fig. 4). Among the MHC samples subjected to analysis, the most stable complexes are characteristic of Zn (see Fig. 4), which is in agreement with the data reported in [19, 20]. The authors of [20] demonstrated by means of ultrafiltration that the stability constants of Zn–HA complexes for a number of HA fractions are higher than those of Cu–HA. So, the metals under investigation can be ranged in the following sequence according to the stability of MHC to decomposition (HM washout): Zn > Cr = Cu > Ni = Co.

A rise in the temperature of drying MHC preparations causes a decrease in the washout degree of HM ions (see Fig. 4). In this situation we observe principal differences between MHC with the metals of variable valence (Cu, Cr, Ni) and stable one (Zn): drying conditions have a strong effect on the former for any concentration of HCl solutions, while in the case of MHC containing Zn the effect of drying temperature is insignificant for high HCl concentration.

No substantial changes occur in the composition of functional groups of HA within the studied range of drying temperatures [21]. So, we used EPS spectroscopy to explain the obtained results.

The parameters of the EPR signal of HA (Table 1) are typical for the HA of high-moor peat [11]. Sorption of Zn^{2+} ions causes some broadening of the spectrum and a shift of g factor, which is due to partial delocalization of the unpaired electron on Zn^{2+} ion [22].

Sorption of the metals of variable valence on HA causes a decrease in the intensity of the EPR signal of MHC. Some researchers sup-

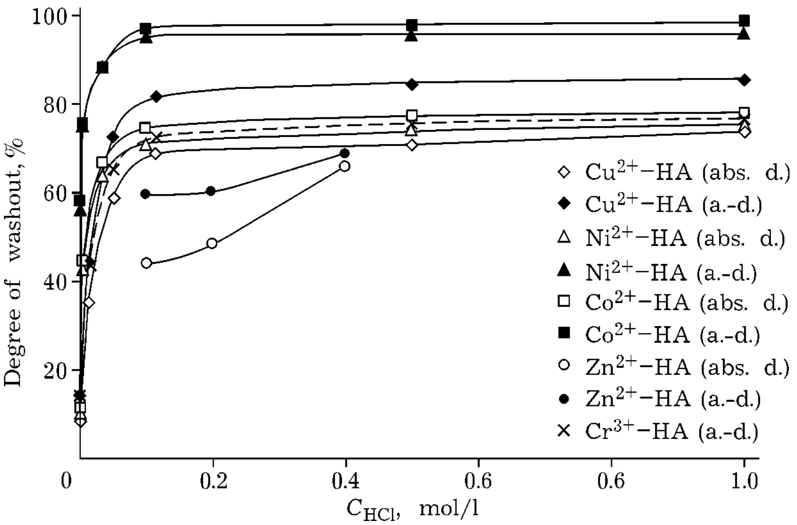

Fig. 4. Degree of HM washout from MHC with aqueous solutions of HCl.

TABLE 1

Parameters of EPR spectra of HA and MHC

Sample	Sample material	HM content of MHC, mg-eq/g HA	Organic PMC					Metal ions	
			$\Delta H_{0.1\ \mathrm{mW}}$, Gs	$\Delta H_{50\ \mathrm{mW}}$, Gs	g-factor	A/A_0	I, 10^{17} sp/g	ΔH, Gs	$I_{rel} \times 10^8$
H–HA	a.-d.	–	3.8	4.3	2.0034	2.5	4.8	n/r	n/r
	abs. d.		3.2	4.0	2.0031	1.9	8.5	n/r	n/r
Zn–HA	a.-d.	0.47	4.1	4.3	2.0036	1.6	4.9	n/r	n/r
	abs. d.		4.3	5.3	2.0034	1.7	9.5	n/r	n/r
Cu–HA	a.-d.	0.63	4.9	5.2	2.0030	4.9	0.3	280	10.5
	abs. d.		5.4	6.0	2.0029	5.4	1.2	290	5.0
Cr–HA	a.-d.	0.45	5.4	6.1	2.0033	5.3	1.7	510	2.7
	abs. d.		6.7	7.0	2.0033	10.0	2.3	810	3.9
Ni–HA	a.-d.	0.57	3.8	4.3	2.0036	5.3	3.9	n/r	n/r
	abs. d.		4.1	4.5	2.0033	6.5	3.6	n/r	n/r
Co–HA	a.-d.	0.43	3.6	4.1	2.0034	5.3	2.6	n/r	n/r
	abs. d.		3.8	4.5	2.0035	4.5	9.1	n/r	n/r

Note. abs. d. – absolutely dry, a.-d. – air-dry material; n/r – not registered; A/A_0 – ratio of the amplitudes of EPR signals recorded at 50 and 0.1 mW, respectively.

pose that the reason is chemical interaction of free radicals with HM ions [23–25]. However, the transformation of the parameters of EPR signal provides evidence that its attenuation is connected with the features of the physical (magnetic dipole-dipole) interaction of organic SMC with Me^{n+} [26, 27]. Differences in the degree of their influence is due to substantial differences in relaxation times for Me^{n+}, which is exhibited in EPR spectra of the latter (see Table 1).

A rise in MHC drying temperature causes an increase in the intensity of the EPR signal of H–HA and Zn–HA almost by a factor of 2, which is likely to be due to the formation of more compact supramolecular structures [28]. For MHC with the metals of variable valence, transformation of both the spectra of organic SMC and the spectra of metal ions is observed during dehydration.

In literature, a decrease in the intensities of the EPR signals of Cu forms of carboxylic cationites and HA is explained by the transition of Cu^{2+} into the diamagnetic state [29, 30]. However, the authors of [26, 27] consider the reason of this fact to be the formation of the groups of Me^{n+} ions located closely to each other ("exchange pockets") characterized by very short relaxation time, which causes non-recordable broadening of the EPR spectra of ions and weakening of their effect on the signal of organic SMC. It is evident that the destruction of hydrate shells with an increase in drying temperature [31] promotes the formation of these groups also in the case of MHC of other metals of variable valence.

An increase in the stability of MHC at high drying temperature is due to the compact aggregation of the supramolecular structure of MHC, removal of water molecules, which brings about steric hindrance for HM ion washout. For Zn–HA, the stability to the "leaching" action of the acid (with an increase in its concentration) is determined by the steric factors of the structure, which diminish the effect of drying conditions on the degree of ion washout from MHC. The conservation of differences in the stability of MHC with the metals of variable valence at any HCl concentration is due to the destruction of hydrate shells of HM, which promotes their rapprochement because the exchange interaction between paramagnetic ions becomes possible. This interaction holds Me^{n+} ions close to each other. At the same time, an increase in the effective charge of the formed exchange associates enhances their interaction with negatively charged regions of HA radicals, which makes steric hindrance for HM washout from MHC.

CONCLUSIONS

The results obtained in the present investigation provide evidence that the SEC of HA toward HM ions (Cu^{2+}, Ni^{2+}) is directly dependent on the COOH group content of HA. The maximal sorption capacity of H−HA toward HM ions is exhibited by the carboxylic groups of its aliphatic fragments (pK_a ~ 2.56); the carboxylic groups of aromatic structures (pK_a ~ 5) and hydroxyl groups of phenols (pK_a ~ 8.4) are somewhat less active; even lower activity is exhibited by the aliphatic hydroxyls of alcohols (pK_a ~ 13). The minimal ability to complexing with HM ions is characteristic of the functional groups with pK_a ~ 10 which can be related to the hydroxyl groups of phenols with donor substituents in the benzene ring [32].

It is shown experimentally that the binding strength of Me−HA complexes is determined mainly by the mechanism of interaction between a HM ion and functional groups of HA. The thermal stability of MHC is directly dependent on the concentration of free sorption centres (first of all COOH groups) that can be ranged in a sequence: H−HA > Co−HA > Ni−HA > Cr−HA £ Cu−HA. The effect of drying conditions on the stability of Me−HA complexes to washout depends on the magnetic properties of metal ion.

The data obtained allow us to develop a direct approach to the validation of regulations of technological processes, both for the production of sorption materials and for the purification of industrial waste water from HM ions with the help of HA and HA-based sorbents, and to use them as geochemical barriers suppressing migratory transport of HM with ground water to adjacent media, for example, around the areas where industrial and household wastes containing HM are stored.

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