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Effect of pH and ionic strength on the interaction of humic acid with aluminium oxide

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Abstract The effect of pH and neutral electrolyte on the interaction between humic acid/humate and γ-AlOOH (boehmite) was investigated. The quantitative characterization of surface charging for both partners was performed by means of potentiometric acid–base titration. The intrinsic equilibrium constants for surface charge formation were $\log K_{a,1}^{int} = 6.7 \pm 0.2$ and $\log K_{a,2}^{int} = 10.6 \pm 0.2$ and the point of zero charge was 8.7 ± 0.1 for aluminium oxide. The pH-dependent solubility and the speciation of dissolved aluminium was calculated (MINTEQA2). The fitted (FITEQL) pK values for dissociation of acidic groups of humic acid were $pK_1 = 3.7 \pm 0.1$ and $pK_2 = 6.6 \pm 0.1$ and the total acidity was $4.56\,\mathrm{mmol\,g^{-1}}$. The pH range for the adsorption study was limited to between pH 5 and 10, where the amount of the aluminium species in the aqueous phase is negligible (less than $10^{-5}\,\mathrm{mol\,dm^{-3}}$) and the complicating side equilibria can be neglected. Adsorption isotherms were determined at pH ~ 5.5, ~8.5 and ~9.5, where the surface of adsorbent is positive, neutral and negative, respectively, and at 0.001, 0.1, 0.25 and $0.50\,\mathrm{mol\,dm^{-3}}$ $NaNO_3$. The isotherms are of the Langmuir type, except that measured at pH ~ 5.5 in the presence of 0.25 and $0.5\,\mathrm{mol\,dm^{-3}}$ salt. The interaction between humic acid/humate and aluminium oxide is mainly a ligand-exchange reaction with humic macroions with changing conformation under the influence of the charged interface. With increasing ionic strength the surface complexation takes place with more and more compressed humic macroions. The contribution of Coulombic interaction of oppositely charged partners is significant at acidic pH. We suppose heterocoagulation of humic acid and aluminium oxide particles at pH ~ 5.5 and higher salt content to explain the unusual increase in the apparent amount of humic acid adsorbed.

Key words Humic acid · Aluminium oxide · Adsorption · Heterocoagulation · Surface complexation

Introduction

Interactions between hydrous oxides and naturally occurring organic materials such as humic and fulvic acids are of great importance in environmental processes. Natural soil and water systems, and relatively simple models of them (e.g. dispersions of metal oxides in organic acid solutions), have been examined by a number of researchers. Comprehensive reviews of this work are to be found in the books by Sposito [1, 2] and Buffle [3]. Most such investigations are related to the pH dependence of the interactions since the soil and water equilibria are largely pH-dependent, but less attention has been paid to the effect of the ionic strength.

The surface OH groups of hydrous aluminium oxides have amphoteric character. The reaction of surface $\underline{\mathrm{Al}}$-OH sites with H^+ or OH^- ions from dissolved acids or bases leads to the formation of positive ($\underline{\mathrm{Al}}\text{-}OH_2^+$) or negative ($\underline{\mathrm{Al}}\text{-}O^-$) charges on the surface, depending on the pH [4–8]. At pHs lower than the point of zero charge (PZC), where the sum of the positive and negative charges is zero, the surface has a net positive charge and a positive surface potential. At pHs above the PZC, the surface charge and surface potential are negative. The pH-dependent and ionic-strength-dependent surface charge formation process can be described by various model approximations, the most widely accepted of them being the site-binding electrostatic model [9, 10]. The surface charge development can be affected by the solubility of the solid [11], which is often neglected in the models.

From both chemical and structural points of view, humic substances are inherently composite materials. They consist of multifunctional aromatic components linked together by a variety of aliphatic constituents [12]. Their characteristic polar functional groups are -COOH, -OH, -C=O and $-NH_2$. Hydrophobic moieties, such as the long alkyl side chains of fatty acid residues, provide amphiphilic character for humic molecules. Because of the randomness of formation, uniform behavior cannot be expected for the polydisperse product, but only trends can be predicted for different properties [13]. The dissociation of (mainly) acidic groups in aqueous media leads to the spontaneous formation of an electric double layer (EDL); therefore, electrostatic interactions play a determining role in the conformation and aggregation of individual humic macroions as well as in their interaction with charged solid particles such as clay minerals and metal oxides. At high pH and low ionic strength, when the functional groups are fully ionized, the charges linked by organic structures tend to move as far away from each other as possible; however, the expansion of the network is limited by the chemical cross-links and, therefore, the extent of expansion and compression of the cross-linked humic nanospheres is much smaller than that for linear polyelectrolytes [13]. The expanded or collapsed networks are totally or partially penetrable by water molecules, while the formation of water-impenetrable units can be assumed in the process of the precipitation of humic acid. The sensitivity of humate solutions to electrolytes depends greatly on the size and acidic group density of the humic nanospheres. Based on this feature, electrolyte-induced spontaneous fractionation of multicomponent humic acid solutions can be predicted [14] similarly to the selective coagulation taking place in mixed colloidal dispersions [15]. Adsorption on mineral surfaces, dissolution and precipitation of humic materials under changing solution conditions are common processes in soils and natural waters [13].

The interaction of humic substances with aluminium-bearing minerals and the structure of the resulting complexes, a wide range of which are found in nature, have long been a subject of scientific interest. Aluminium can act as a bridging cation for the binding of humic substances to clay minerals, thereby affecting the physical properties of soil [1].

The ability of humic substances to form stable complexes with aluminium can be accounted for by their high content of oxygen-containing functional groups (-COOH, phenolic, enolic and alcoholic OH and =C=O). More than 40 types of binding sites in humic substances have been reported in the literature as reviewed by Stevenson and Vance [1]. The binding of aluminium by humic substances can occur through water bridges, electrostatic (Coulombic) attraction, formation of a coordinate link with a single donor group and formation of a chelate complex. In addition, aluminium can bridge between two or more humic molecules, i.e. intermolecular chelation is also possible. The cross-linking of humic substances to clay and oxide particles through aluminium and other cations is believed to be important in the formation of stable aggregates in soil [1].

According to Buffle [3] natural organic materials (e.g. humic or fulvic acids) are polyfunctional complexants for which the secondary effects, such as polyfunctional properties, conformational changes and polyelectrolyte properties are important; therefore, complex formation is influenced by the electric field and the conformation of the macroions.

Kummert and Stumm [16] found that the adsorption of aromatic acids on γ-Al_2O_3 can be described quantitatively by surface coordination processes. Their calculations indicated that salicylic acid has exactly the same ability to form surface complexes on γ-Al_2O_3 as to form soluble aluminium complexes. The presence of strong complex-forming agents is well known to prevent the precipitation of aluminium hydroxide and oxyhydroxide crystals, and the weathering of aluminium-bearing rocks and minerals is normally enhanced by the presence of a complexing agent [1]. The aluminol OH groups on the surface of aluminium oxides and hydroxides can be replaced by carboxyl groups of humic substances from soil solutions, and the resulting bonds weaken the Al-O bonds in the solid [1]. It is obvious that the solubility of alumina is controlled not only by the pH of the medium but also by the presence of complex-forming ligands [17, 18]. The adsorption of simple organic acids on alumina is similar to that of fulvic acids: it is controlled by both electrostatic and specific interactions; in principle, it is a ligand-exchange reaction which takes place at a charged interface [16, 19].

The present article reports an investigation of the pH and ionic strength dependence of the interaction between dissolved humic acid and aluminium oxide particles. The main goal is to study the effect of the charges of the interacting partners; therefore, the pH was chosen so that the interaction of particles with the same or opposite sign of charge as well as uncharged oxide and charged humate could be studied.

Experimental

Materials

Aluminium oxide was an analytical grade reagent (Brockmann) from Reanal (Hungary). To reduce the particle size, a 40 g/100 g aqueous suspension was ground for 1 h in an agate ball mill. The crystal structure of the Brockmann alumina was determined with a Philips PW 1830/PW 1820 X-ray diffractometer, $\lambda(\mathrm{Cu}_{\mathrm{K}\alpha}) = 0.1542\,\mathrm{nm}$ and identified as mainly boehmite (γ-AlOOH). The specific surface area (a_{BET}) determined by N_2 adsorption [Brunauer–Emmett–Teller (BET) method, Micromeritics Gemini II 2375 surface area analyzer] was $107\,\mathrm{m}^2\,\mathrm{g}^{-1}$. The surface-charging properties of the adsorbent were determined by potentiometric acid–base titrations at 0.01, 0.1 and $1\,\mathrm{mol\,dm}^{-3}$ concentrations of the background electrolyte, KNO_3. The pH of the PZC could be obtained from acid–base titrations since the electrolyte, KNO_3, was proven to be indifferent.

Humic acid was obtained from brown coal (Dudar, Hungary) by a traditional alkaline extraction procedure using $0.1\,\mathrm{mol\,dm}^{-3}$ NaOH solution. It was purified in the usual way [20]. The ash content of raw humic acid was reduced by HF/HCl treatment. The dried, ground humic acid was extracted with benzene/ethanol in a Soxhlet apparatus for 72 h to remove tar components.

The sodium humate solution was prepared from the dried humic acid sample (in a vacuum oven at 60 °C) by dissolution in the amount of $0.1\,\mathrm{mol\,dm}^{-3}$ NaOH calculated to be equivalent to the total acidity of humic acid measured by potentiometric acid–base titration. The electrolyte-free humic acid solution was prepared by cation exchange, passing the sodium humate solution through a column of regenerated cation-exchange resin (Varion KSM, Hungary) washed free of Cl^-. The concentrations of the humic acid and sodium-humate solutions are given in units relating to the number of acidic groups in the unit volume. The number of acidic groups in a unit mass of the sample is equal to the total acidity of humic acid ($4.56\,\mathrm{mmol\,g}^{-1}$).

Solutions and suspensions were prepared, stored and processed in carefully cleaned vessels. Chromium sulfuric acid was used to oxidize organic impurities. The water was obtained directly from a Millipore apparatus. All chemicals were analytical reagent grade (Reanal, Hungary).

Methods

The pH-dependent surface charge was determined by potentiometric acid–base titration under a CO_2-free atmosphere. An indifferent background electrolyte (NaCl for humic acid and KNO_3 for alumina) was used to maintain a constant ionic strength ranging between 0.001 and $1\,\mathrm{mol\,dm}^{-3}$. A portion of stock suspension of ground aluminium oxide was dialyzed against $0.01\,\mathrm{mol\,dm}^{-3}$ KNO_3 solution. A given amount of equilibrated suspension containing 1 g aluminium oxide was diluted with KNO_3 solution to give a volume of $0.05\,\mathrm{dm}^3$ and ionic strengths of 0.01, 0.1 and $1\,\mathrm{mol\,dm}^{-3}$. Portions of electrolyte-free humic acid solution 0.015 g humic acid were diluted with NaCl solution to give a volume of $0.05\,\mathrm{dm}^3$ at ionic strengths of 0.001, 0.01 and $0.1\,\mathrm{mol\,dm}^{-3}$. Before titration, the suspensions or solutions were stirred and bubbled by purified nitrogen for 1 h. Equilibrium titration was performed by means of a self-developed titration system (GIMET1) with 665 Dosimat (Metrohm) burettes, nitrogen bubbling, a magnetic stirrer and a high-performance potentiometer. The whole system (millivolt measurement, stirring, bubbling, amount and frequency of titrant) was controlled by an IBM PS/1 computer using AUTOTITR software. A Radelkis OP-0808P (Hungary) combination pH electrode was calibrated for three buffer solutions to check the Nernstian response. The hydrogen ion activity versus concentration relationship was determined from a reference solution titration so that the electrode output could be converted directly to the hydrogen ion concentration instead of to activity.

The net proton surface excess amount (Δq, moles per gram) is defined as the difference between $\mathrm{H}^+(\Gamma_{\mathrm{H}^+})$ and $\mathrm{OH}^-(\Gamma_{\mathrm{OH}^-})$ surface excess amounts related to unit mass of solid, $\Delta q = \Gamma_{\mathrm{H}^+} - \Gamma_{\mathrm{OH}^-}$. The surface excess amount defined for the adsorption [21] is determined from the initial and equilibrium concentration of solute. The values of Γ_{H^+} and Γ_{OH^-} were calculated at each point of titration from the electrode output using the actual activity coefficients from the slope of the straight lines of $\mathrm{H}^+/\mathrm{OH}^-$ activity versus concentration functions from the corresponding background electrolyte titration. The surface excess concentration of H^+ or OH^- was calculated as a function of pH. The number of charged sites, defined as the net proton surface excess ($\Delta q = \Gamma_{\mathrm{H}^+} - \Gamma_{\mathrm{OH}^-}$), was related to unit mass of alumina or humic acid and was plotted as a function of pH. Net proton surface excess versus pH curves are shown in Figs. 1 and 2.

The humic acid/humate adsorption isotherms at different pHs were determined by the depletion method. A given amount of aluminium oxide stock suspension was equilibrated for 24 h with the series of humic acid/humate solutions in closed test tubes at room temperature. The concentration of the humic compounds was related to the number of acidic functional groups in the solutions, and their initial values varied between 0 and $2\,\mathrm{mmol\,dm}^{-3}$. The stock solution of humic acid was used to prepare the series at acidic pH (pH $\sim$ 5) and that of sodium humate was used to prepare the series at alkaline pH (pH $\sim$ 8.5 and $\sim$9.5). The suspension concentration was constant ($2.5\,\mathrm{g\,dm}^{-3}$). The concentration of electrolyte, $NaNO_3$, was held constant at 0.001, 0.1, 0.25 or $0.5\,\mathrm{mol\,dm}^{-3}$. The pH was adjusted to the desired value of pH $\sim$ 5, $\sim$8.5 or $\sim$9.5 with NaOH or HNO_3 solutions. The pH was checked after the solutions had stood for 24 h. The equilibrium concentration of humic acid/humate was determined using a spectrophotometer (Uvikon 930) measuring the absorbance of humate solutions at 450 nm, after separation of the solid particles by

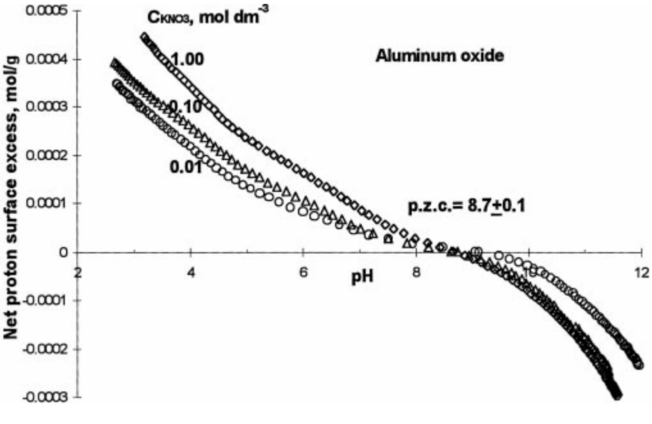

Fig. 1 Net surface proton excess of aluminium oxide (boehmite) in the presence of an indifferent electrolyte (KNO_3). Equilibrium constants: $\log K_1 = 6.7 \pm 0.2$, $\log K_2 = 10.6 \pm 0.2$ calculated using the Stumm extrapolation method

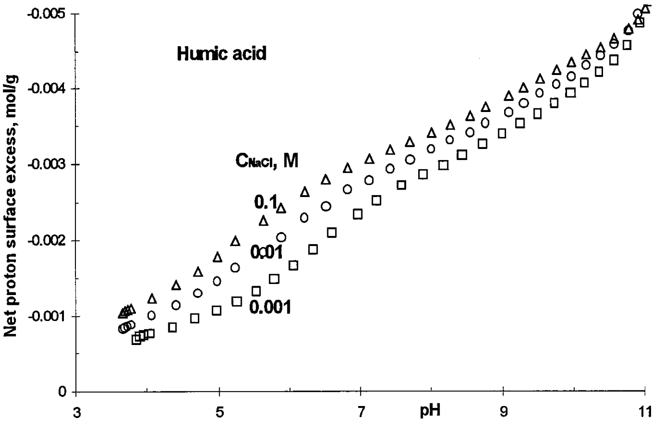

Fig. 2 pH and ionic strength dependence of net proton excess of humic acid in the presence of NaCl. Total acidity: 4.56 mmol g^{-1}; intrinsic dissociation constants: $pK_1 = 3.7 \pm 0.1$, $pK_2 = 6.6 \pm 0.1$ fitted using FITEQL (two pKs, diffuse double layer)

centrifugation (Sorvall RC B5 Plus supercentrifuge, 20000 rpm for 40 min).

Results and discussion

The interaction between humic substances and charged solid particles such as amphoteric aluminium oxide in aqueous media is essentially influenced by the pH and ionic strength and depends on the charge of both the solute molecules and the solid particles. An EDL formed spontaneously around the particles due to the reaction with H^+/OH^- ions of the aqueous medium. The quantitative characterization of the surface charge is of crucial importance. The pH dependences of surface-charging for both aluminium oxide and humic acid are characterized by potentiometric acid–base titration.

Surface reactions of boehmite

Aluminium oxide is an amphoteric solid material; its pH-dependent net proton surface excess amount (Δq) at different concentrations of an indifferent electrolyte (KNO_3) is seen in Fig. 1. The net proton surface excess is proportional to the surface charge ($\sigma_0 = F\Delta q/a^s$, where F is the Faraday constant and a^s is the specific surface area) since this solid can develop charges only due to the specific adsorption of H^+ and OH^- [4–8] and the present electrolyte (KNO_3) is indifferent [6]. The PZC was determined as the intersection point of the Δq versus pH curves at different ionic strengths. At $pH = 8.7 \pm 0.1$ its value was in the usual range known for aluminium oxide [6]. The following reactions of the surface $\underline{Al}$-OH groups with either H^+or OH^- ions represent the charge formation on the surface:

$$1.\ \underline{\mathrm{Al}}\text{-OH} + H^+ \Leftrightarrow \underline{\mathrm{Al}}\text{-OH}_2^+ \quad K_{a,1}^{app} = \frac{[\underline{\mathrm{Al}}\text{-OH}_2^+]}{[\underline{\mathrm{Al}}\text{-OH}][H^+]} \ . \tag{1}$$

$K_{a,1}^{app}$ is the apparent association constant of protons on $\underline{Al}$-OH.

$$2.\ \underline{\mathrm{Al}}\text{-OH} \Leftrightarrow \underline{\mathrm{Al}}\text{-O}^- + H^+ \tag{2}$$

$$\underline{\mathrm{Al}}\text{-OH} + OH^- \Leftrightarrow \underline{\mathrm{Al}}\text{-O}^- \tag{3}$$

The proton association equilibrium of negatively charged surface sites is

$$\underline{\mathrm{Al}}\text{-O}^- + H^+ \Leftrightarrow \underline{\mathrm{Al}}\text{-OH} \quad K_{a,2}^{app} = \frac{[\underline{\mathrm{Al}}\text{-OH}]}{[\underline{\mathrm{Al}}\text{-O}^-][H^+]} \ . \tag{4}$$

$K_{a,2}^{app}$ is the apparent association constant of H^+.

The apparent association constants depend significantly on the surface charge density (σ_0); therefore, intrinsic equilibrium constants (K_a^{int}) for surface charge formation can be determined by means of extrapolation methods such as suggested by Stumm and Hohl [23, 24].

$$\lim_{(\sigma_0 \to 0)} \log K_a^{app} = \log K_a^{int} \ . \tag{5}$$

The intrinsic equilibrium constants of aluminium oxide were determined by extrapolation to zero charge density, and their values were $\log K_{a,1}^{int} = 6.7 \pm 0.2$ and $\log K_{a,2}^{int} = 10.6 \pm 0.2$. These values are in good agreement with several literature data [7, 25] and correlate well with the observed PZC ($pH_{PZC} = 8.7 \pm 0.1$) according to the relation [7, 25] $PZC = 0.5(\log K_{a,1}^{int} + \log K_{a,2}^{int})$.

The farther the pH of the solution from the pH of the PZC, the higher the charge density of aluminium oxide particles. Since the surface charge density of the aluminium oxide particles is proportional to the net proton surface excess amounts, the pH and ionic strength dependence given in Fig. 1 show the charge at changing solution conditions. The number of positively or negatively charged sites on the surface increases with increasing ionic strength.

Below pH ~ 4 and above pH ~ 10, the dissolution of the amphoteric solid becomes perceptible [26]. Under acidic conditions the dissolution of alumina and the formation of various hydrolysis products were also taken into consideration by calculating the pH-dependent dissolution (Fig. 3) and the distribution of hydrolysis products (Fig. 4). As the adsorbent was boehmite, the solubility of this crystalline phase was calculated by taking into consideration the following equation and equilibrium constant:

$$\mathrm{AlO(OH)}\ \text{(boehmite)} + 3H^+ - 2H_2O = Al^{3+}$$
$$\log K = 8.13\,[27] \ . \tag{6}$$

Figure 3 shows the amount of dissolved Al^{3+} as a function of pH as well as that of one of the characteristic

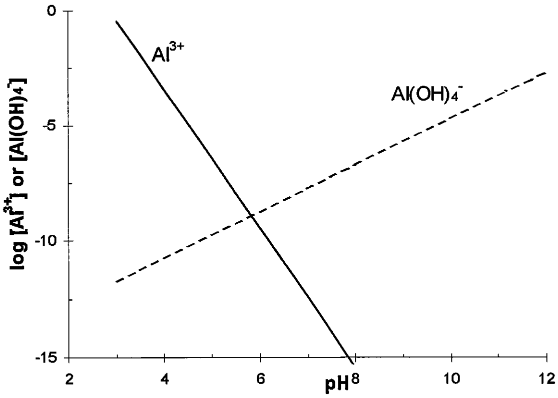

Fig. 3 Solubility product of boehmite, calculated concentration of Al^{3+} and $Al(OH)_4^-$ ions at different pH

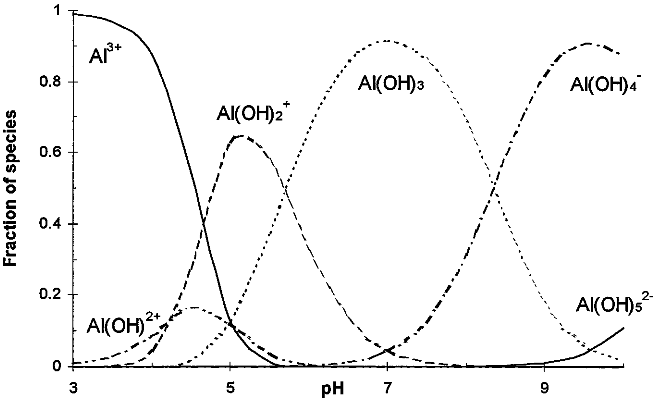

Fig. 4 Distribution of aluminium species calculated using MINTEQA2 as a function of pH

mononuclear aluminium species, $Al(OH)_4^-$, which form at higher pH. The concentration of spontaneously formed hydrolysis products at pH = 5–10 remains below 10^{-5} mol dm^{-3}. The formation of different mononuclear aluminium species was also calculated using the MICROQL-UCR program [28] using chemical speciation and equilibrium constants from the literature [29]. The distribution of different mononuclear aluminium species changes significantly with increasing pH (Fig. 4) but the concentration of the different aluminium species in the aqueous phase is negligible (less than 10^{-5} mol dm^{-3}) between pH 5 and 10. The pH for the humic acid/humate adsorption measurements was varied between pH 5 and 10, where the complicating side equilibria can be neglected. Considering the charging behavior of the aluminium oxide in aqueous electrolyte solutions (Fig. 1), three particular pH values were chosen for the adsorption study:

1. pH around $pH_{PZC} = 8.7 \pm 0.1$.
2. $pH < 7$, positively charged oxide ($\Delta q > 0.05$ mmol g^{-1}, $|\sigma_0| > 0.05$ C m^{-2}).
3. $pH > 9$, negatively charged oxide ($|-\Delta q| > 0.01$ mmol g^{-1}, $|-\sigma_0| > 0.01$ C m^{-2}).

Dissociation of humic acid

Humic acids develop negative charges and form EDLs spontaneously due to the dissociation of the acidic groups. The pH dependence of the net proton surface excess, which is the equivalent of the number of negatively charged surface sites, is shown in Fig. 2. The humic acid particles become more negatively charged with both increasing pH and ionic strength, and the maximum value, the total acidity (4.56 mmol g^{-1}) of the sample, was attained at a pH of about 10.5. Above this pH, the net proton consumption started to become independent of ionic strength and increased infinitely, approaching pH ~ 11, due to the alkaline hydrolysis [30].

Equilibrium constants (K, or $pK = -\log K$) characterize any dissociation process. In the case of humic acids, only apparent pK values can be given without considerations of the influences of the electrostatic field. The effect of ionic strength on proton binding has been interpreted somewhat differently, but it is mainly an electrostatic effect which can be described by introducing an electrostatic correction term [31, 32]. It may be strongly affected by the polydispersity and conformation of humic substances [33]. Among the numerous models available to describe the electrostatic effect, we have chosen the diffuse double layer (DDL) approach (details given in Refs. [13, 34]).

We assume the existence of two dissociation steps related to the stronger (1) and weaker (2) acidic groups of humic acid. The net proton surface excess curves at different ionic strengths were fitted using the FITEQL(v.3.2) [35] software choosing the option of two pKs and the DDL electrostatic model. The sum of the stronger and weaker acidic groups calculated from the fitted curves agrees relatively well with the measured values at pH ~ 10.5. The calculated pK values are $pK_1 = 3.7 \pm 0.1$ and $pK_2 = 6.6 \pm 0.1$.

The electrostatic field inside and around the humic macroions shows considerable pH and ionic strength dependence. The results of our previous model calculations [13, 14, 34] clearly predict that the repulsion between the charged part (either inter- or intraparticular) of humic acid decreases with both decreasing pH and increasing ionic strength. In parallel, the measured particle sizes also decrease. The extent of the conformational changes (expansion or compression) of the humic macroions is much smaller than that for linear polyelectrolytes since the expansion of the network is limited by the cross-links of the humic molecules. The sensitivity of humic acid solutions to salt concentration depends

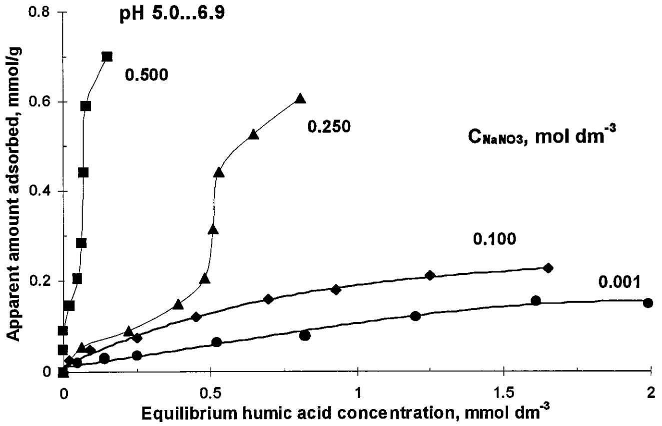

Fig. 5 Ionic strength dependence of interaction between humic acid and positively charged aluminium oxide at room temperature (*ordinate*: apparent amount adsorbed, calculated from the difference between the initial and equilibrium concentration after centrifugation; *abscissa*: equivalent concentration of humic acid in millimoles of acidic groups per liter)

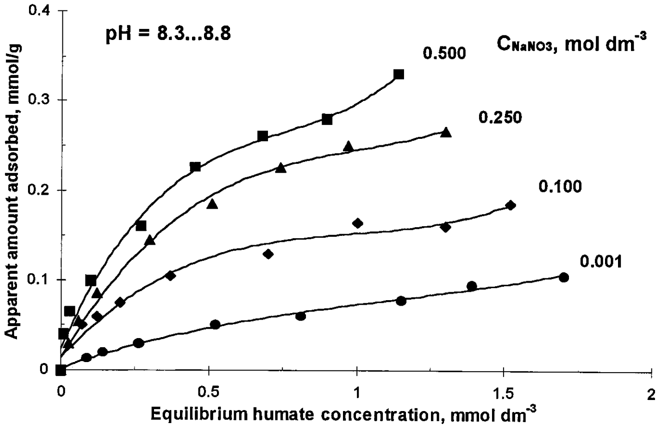

Fig. 6 Ionic strength dependence of interaction between sodium-humate and uncharged aluminium oxide at room temperature (*ordinate*: apparent amount adsorbed, calculated from the difference between the initial and equilibrium concentration after centrifugation; *abscissa*: equivalent concentration of sodium humate in millimoles of acidic groups per liter)

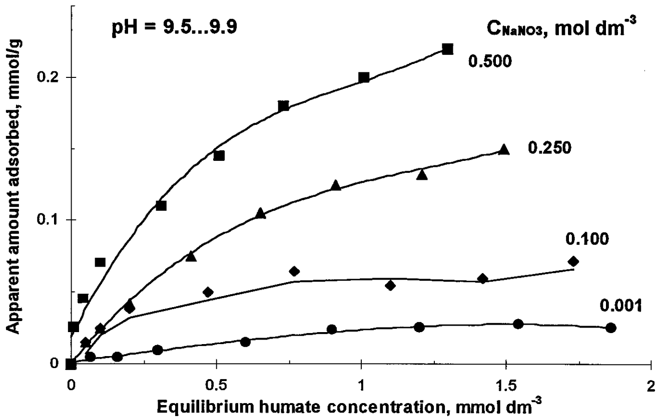

Fig. 7 Ionic strength dependence of interaction between sodium humate and negatively charged aluminium oxide at room temperature (axes as in Fig. 6)

greatly on the size and acidic group density of the molecules. At low pH a relatively small amount of salt can induce the precipitation of organic matter, whereas the colloidal stability increases strongly with increasing pH. Any traditionally prepared sample is a mixture of qualitatively different humic acid molecules which show different colloidal stability and, thus, fractionation will take place at different solution conditions.

Adsorption studies

Adsorption isotherms of humic acid at pH ~ 5.5 and of sodium humate at pH ~ 8.5 and ~9.5 on aluminium oxide were determined in dilute systems containing 0.001, 0.1, 0.25 and 0.5 mol dm^{-3} $NaNO_3$ (Figs. 5–7), respectively. The isotherms seem to be Langmuir type according to the classification of Giles et al. [36], except two of them measured at pH ~ 5.5 and higher electrolyte concentrations. Monolayer adsorption capacities calculated from the linearized form of the Langmuir equation are summarized in Table 1 and are plotted in Fig. 8 as a function of pH. The most significant trend is the increase in the apparent amounts adsorbed with increasing ionic strength independent of pH. This is most pronounced in the acidic region. The same effect of indifferent electrolytes was observed for the interaction of humic substances with different clays (mainly montmorillonite) [37, 38].

At the lowest ionic strength of 1 mmol dm^{-3} the adsorption of the anionic material decreases with increasing pH. The plateau values reach 0.143 mmol g^{-1} at pH ~ 5.5, 0.107 mmol g^{-1} at pH ~ 8.6 and 0.027 mmol g^{-1} at pH ~ 9.7 (Table 1). This trend is expected since the humate macroions are negatively charged at each pH (Fig. 2), while the surface charge of aluminium oxide changes from positive to negative with increasing pH (Fig. 1). Under acidic conditions, the positively charged aluminium oxide (the number of positive surface sites is about 0.1 mmol g^{-1} at pH ~ 5.5, Fig. 1) adsorbs about 0.14 mmol g^{-1} acidic groups of humic acid (Table 1). The charge balance is commensurable, especially if we consider that humic acid is only partially dissociated at pH ~ 5.5 (Fig. 2). Thus, the Coulombic interaction between the polyanions and the positively charged surface is dominant under acidic condition; however, simple electrostatic attraction between humate and aluminium oxide cannot be assumed at higher pHs

Table 1 Evaluation of adsorption isotherms: humic acid/humate – aluminium oxide systems, room temperature, linearized Langmuir equation

Conditions	Adsorption capacity (n_m^σ) (mmol g^{-1})^a					
	pH ~ 5.0–6.9 $\sigma_0 \sim +0.20$–0.05 C m^{-2} $\Delta q \sim 0.25$–0.05 mmol g^{-1}		pH ~ 8.3–8.8 $\sigma_0 \sim 0$ (+/–0.01) C m^{-2} $\Delta q \sim 0$ (+/–0.01) mmol g^{-1}		pH ~ 9.5–9.9 $\sigma_0 \sim -0.01$–0.08 C m^{-2} $\Delta q \sim -0.01$–0.08 mmol g^{-1}	
c_{NaNO_3} (mol dm^{-3})	Langmuir (regression)	Measured	Langmuir (regression)	Measured	Langmuir (regression)	Measured
0.001	0.135 (0.94)	0.143	0.097 (0.98)	0.107	0.058 (0.99)	0.027
0.100	0.243 (0.99)	0.222	0.145 (0.96)	0.183	0.088 (0.99)	0.077
0.250	–	0.606	0.265 (0.99)	0.264	0.22 (0.99)	0.154
0.500	–	0.7	0.35 (0.99)	0.33	0.245 (0.98)	0.222

^{a} Adsorption capacity is related to the number of acidic groups of humic acid calculated from the total acidity (4.56 mmol g^{-1})

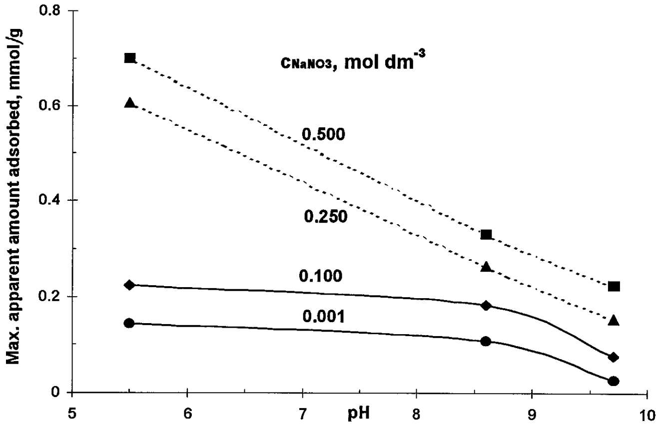

Fig. 8 pH dependence of maximum apparent amount of humate adsorbed on aluminium oxide at different ionic strength

(above $pH_{PZC} \sim 8.7$) where the oxide surface is uncharged or even negatively charged.

The pH of systems changed during the adsorption process (1 day stand) as was the case for adsorption of humic and polyacrylic acids on alumina reported elsewhere [39]. At pH ~ 5.5 and a low concentration of humic acid the pH increased by about 0.5–1 pH units, but at higher concentrations it decreased by about 0.1–0.3 pH units in the adsorption series. To explain this observation, two processes can be assumed [1, 3, 16–19, 40]. One is a ligand-exchange reaction (surface complexation) between the surface site $\underline{Al}$-OH and the dissociated form (A^-) of humic acid (HA) which should result in an increase in pH:

$$\underline{Al}\text{-OH} + A^- \Leftrightarrow \underline{Al}\text{-A} + OH^- \ . \qquad (7)$$

The other is an anion-exchange reaction of humic acid with the protonated $\underline{Al}$-OH_2^+ sites in which the pH should slightly decrease due to the formation of a strong acid (HNO_3) from a weak one (humic acid):

$$\underline{Al}\text{-}OH_2^+ \ldots NO_3^- + HA \Leftrightarrow \underline{Al}\text{-}OH_2^+ \ldots A^- + H^+ + NO_3^+ \ . \qquad (8)$$

These processes contribute simultaneously to the overall change in pH during adsorption, and an increasing contribution of Eq. (8) can be assumed with increasing concentration of humic acid.

Under weakly alkaline conditions, at both pH ~ 8.6 and pH ~ 9.7, the pH of the suspensions decreased by some tenths of a pH unit during adsorption. The ligand exchange reaction (Eq. 7) should also lead to an increase in pH in alkaline media. Probably, a side reaction can take place simultaneously on the surface of alumina in alkaline solution

$$\underline{Al}\text{-OH} + OH^- \Leftrightarrow \underline{Al}\text{-}O^- + H_2O \qquad (9)$$

in which hydroxyl ions from the ligand-exchange reaction are consumed. This process results in the formation of negatively charged surface sites. When all OH^- ions are consumed, the pH should remain constant; therefore, the small decrease in the bulk pH cannot be explained in this way. Although the measurements were performed in closed systems, dissolution of CO_2 from the atmosphere, as a pH-lowering effect, cannot be fully excluded.

The increase in ionic strength in the adsorption systems enhanced the apparent amount adsorbed at each pH studied. The surface charge density of alumina particles and the dissociation of acidic groups of humic acid are enhanced by increasing ionic strength due to the charge-screening by counterions (Figs. 1, 2). In addition, electrolytes also induce conformational changes of cross-linked humic nanoparticles. The size of the humic macroions decreases with increasing electrolyte concentration due to the charge-screening effect of salts [12]. The salt effect is much more pronounced at low pH, where the dissociation of acidic groups is also suppressed, and an intraparticle contraction is often followed by an interparticle aggregation resulting in coagulation of humic acid [13, 14].

The apparent amounts of humate adsorbed roughly double when the concentration of $NaNO_3$ in the adsorption systems is raised from 0.001 to 0.1 mol dm^{-3} at each pH (Figs. 5–7, Table 1). This increase in humate adsorption can be interpreted by the conformational changes, since such an extent of the contraction of humic macroions due to charge-screening seems to be reliable. We could show [41] that the size of a fractionated humate sample decreases to half its value when the salt concentration is raised from 0.001 to 0.1 mol dm^{-3} at pH ~ 9. A further decrease in size at higher $NaNO_3$ concentrations (0.25 and 0.50 mol dm^{-3}) can be a reason for the further increase in adsorption (Figs. 5–7, Table 1), except for the systems measured at pH ~ 5.5.

For interpretation of the adsorption of an organic compound onto a solid, the Langmuir approach is often used [3]. Evaluation of the adsorption isotherms of humic acid/humate on aluminium oxide led to the data summarized in Table 2. The average equilibrium quotient, $\tilde{K}^{\mathrm{a}}$, is almost the same for all systems, except for acidic systems with high salt content. We conclude that the same adsorption mechanism is operative in most systems, i.e. mainly surface complexation with humate macroions being compressed more and more as the ionic strength increases. At low pH, electrostatic attraction promotes accumulation of humic macroions in the interfacial layer. The parameter $\tilde{Q}^{\mathrm{a}}$ calculated from the adsorption data at low coverage is comparable with the measured adsorption capacities. The significant increase in the distribution coefficient, $[\mathrm{P}]_s/[\mathrm{P}]$, between the bulk solution and the "surface volume" with increasing salt concentration is related to the narrowing of the EDL in which the more-and-more compressed humate units are accumulated.

An additional mechanism for humic acid–oxide interaction seems to occur at pH ~ 5.5 and higher amounts of salt. These systems can be considered as exceptions compared to the others examined. We tested the colloidal stability of humic acid solution alone at pH 5.5. Homocoagulation of humic acid particles could not be observed at the same salt concentration (up to 0.5 mol dm^{-3}). Although the concentration of the dissolved aluminium species (Figs. 3, 4) is very low at pH ~ 5.5, complexation with these dissolved aluminium species resulting in insoluble aluminium humate complexes over the range of pH from 4 to 7 [1] may contribute to the significant increase in the apparent amount adsorbed. Besides this, we suppose that heterocoagulation of humic units with aluminium oxide particles can also take place in a similar way as has been found for humic acid and montmorillonite [37, 38]. The probability of heterocoagulation was calculated for the interaction of humic substances with montmorillonite [38]. In the present systems, heterocoagulation of the organic and inorganic particles is also probable. This process may involve an electrolyte-induced spontaneous fractionation of the multicomponent humic acid solutions [14] similarly to the selective coagulation taking place in mixed colloidal dispersions [15].

Conclusion

The aluminol OH groups on the surface of alumina can be replaced by complex-forming ligands of humate [1, 3]. The accumulation of solute ions in the solid/liquid interfacial layer is influenced by the electrostatic field around the particle: this interaction can be considered as a ligand-exchange reaction taking place at a charged interface. According to our previous results [40], chelating anions such as salicylate are adsorbed at the uncharged $\underline{\mathrm{Al}}$-OH groups in larger amounts than on the positively charged surface sites because the density of uncharged sites is much higher than that of charged ones especially at a pH around the PZC. The surface complexation of a limited number of aluminol sites harmonizes with the measured Langmurian type iso-

Table 2 Interaction parameters for humic acid/humate adsorption on aluminium oxide at room temperature. $\tilde{K}^{\mathrm{a}}$ is the average equilibrium quotient and is defined by $\tilde{K}^{\mathrm{a}} = {}^{\mathrm{P}}\tilde{\Theta}/(1 - {}^{\mathrm{P}}\tilde{\Theta})[\mathrm{P}]$, where ${}^{\mathrm{P}}\tilde{\Theta} = \tilde{n}^{\mathrm{a}}/\tilde{n}^{\mathrm{a}}_{\mathrm{max}}$ is the fraction of the surface area occupied by P and $\tilde{n}^{\mathrm{a}}(\tilde{n}^{\mathrm{a}}_{\mathrm{max}})$ is the quantity (maximum) of adsorbed P. The parameter $\tilde{Q}^{\mathrm{a}}$ is defined by $\tilde{Q}^{\mathrm{a}} = \tilde{K}^{\mathrm{a}}\tilde{n}^{\mathrm{a}}_{\mathrm{max}} = \mathrm{constant}$. It corresponds to the slope of the straight line $\tilde{n}^{\mathrm{a}} = f([\mathrm{P}])$ under conditions $\tilde{n}^{\mathrm{a}} \ll \tilde{n}^{\mathrm{a}}_{\mathrm{max}}$. Since in natural systems $\tilde{n}^{\mathrm{a}}_{\mathrm{max}}$ is not always measurable, the parameter $\tilde{Q}^{\mathrm{a}}$ is a comparable quantity. $[\mathrm{P}]_S/[\mathrm{P}]$ is the distribution coefficient of P between the "surface volume" and the bulk solution

Conditions	pH ~ 5.0–6.9 σ_0 ~ +0.20–0.05 C m^{-2} Δq ~ 0.25–0.05 mmol g^{-1}				pH ~ 8.3–8.8 σ_0 ~ 0 (+/–0.01) C m^{-2} Δq ~ 0 (+/–0.01) mmol g^{-1}				pH ~ 9.5–9.9 σ_0 ~ –0.01–0.08 C m^{-2} Δq ~ –0.01–0.08 mmol g^{-1}			
$c_{\mathrm{NaNO_3}}$ (mol dm^{-3})	$\tilde{K}^{\mathrm{a}}$ (dm^3 mmol^{-1})	$\tilde{Q}^{\mathrm{a}}_{\mathrm{V}}$ (dm^3 g^{-1})	n^{σ}_{m} (mmol g^{-1})	$\frac{[\mathrm{P}]_s}{[\mathrm{P}]}$	$\tilde{K}^{\mathrm{a}}$ (dm^3 mmol^{-1})	$\tilde{Q}^{\mathrm{a}}_{\mathrm{V}}$ (dm^{3}g^{-1})	n^{σ}_{m} (mmol g^{-1})	$\frac{[\mathrm{P}]_s}{[\mathrm{P}]}$	$\tilde{K}^{\mathrm{a}}$ (dm^3 mmol^{-1})	$\tilde{Q}^{\mathrm{a}}_{\mathrm{V}}$ (dm^{3}g^{-1})	n^{σ}_{m} (mmol g^{-1})	$\frac{[\mathrm{P}]_s}{[\mathrm{P}]}$
0.001	2.1	0.074	0.135	274	1.9	0.097	0.097	176	0.8	0.022	0.058	43
0.100	3.1	0.207	0.243	7214	6.5	0.192	0.145	9076	2.7	0.077	0.088	2283
0.250	3.1	0.349	~0.61	28630	4.4	0.401	0.265	17830	1.3	0.165	0.22	4441
0.500	25.6	2.928	~0.70	387899	4.6	0.433	0.35	34633	3.9	0.261	0.245	20596

therms. A limited increase in humate adsorption with increasing ionic strength is interpreted by conformational changes of the humic macroions; a moderate compaction of the humate network due to charge-screening was proven [34, 41]. Heterocoagulation of the dissimilar (organic and inorganic) particles is also probable, which may involve an electrolyte-induced spontaneous fractionation of the multicomponent humic acid solutions [14] similarly to the selective coagulation taking place in mixed colloidal dispersions [15].

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