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ORIGINAL CONTRIBUTION

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Aluminium ions at polyelectrolyte interfaces. I. Mechanism of polyacrylic acid/aluminium oxide and humic acid/kaolinite complex formation

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Abstract Understanding adsorption phenomena involving humic acids and clays is a difficult challenge owing to their complex nature. Thus, to progress in the study of such systems, attempts were made to replace natural systems by polyacids and oxides of simpler chemical and morphological structure. Since the present investigation was dedicated to determine some characteristics of acidic soils which contain traces of aluminium ions, these ions were added to the adsorbent/polyacid systems as trace constituents. Phenomena related to the interactions of humic or polyacrylic acid with aluminium oxide and kaolinite clay have been investigated and the well-differentiated interfacial behaviour of the oxide and kaolinite was determined and discussed. The results of electrophoretic mobility measurements demonstrated the huge time-dependent effect of polymeric layers adsorbed on oxides and modified clays.

Key words Adsorption of humic acid on oxide · Adsorption of humic acid on kaolinite · Adsorption of polyacrylic acid on oxides · Adsorption of polyacrylic acid on kaolinite · Amphiphilic polymer

Introduction

Agricultural soils are composed of agglomerates of clays and particulate matter of various sizes and shapes, of crystalline or amorphous nature [1]. The cohesion of soil aggregates results from combined effects of inorganic and organic materials. The latter constituents were determined to be responsible for the stability of agglomerated fine particles, such as oxides and clays, which in turn ensure the cohesion of the ensemble on larger scales [2, 3]. The ionic composition of soils depends on a great number of parameters and we were especially interested in studying the effects of aluminium ions, which remain as the major ionic component of acidic soils when other ions of smaller valence have been washed out by acid rain [4, 5]. In order to progress in the understanding of the complex roles of aluminium ions and humic acids in the cohesion of soil agglomerates, we investigated a synthetic system (polyacrylic acid/aluminium oxide) and a mixed system (humic acid/aluminium oxide) before extending the investigations to a natural system (humic acid/kaolinite clay).

First of all, it should be noted that we do not consider the synthetic and mixed systems to serve as model systems for the natural system, a priori [6]. Actually, the surface charge characteristics of aluminium oxide and kaolinite and the interaction with aluminium ions are expected to be very different. Conversely, the situation of the hydrosoluble synthetic or natural materials appeared to be less controversial since carboxylic acid groups are present as the sole or major ionisable group, respectively. Accordingly, aluminium ions were expected to interact similarly with the two polymeric materials in acidic and neutral media and to form ionic complexes of quite identical nature under these conditions [7].

Secondly, within these limitations, we expected relative and absolute concentrations of adsorbent, adsorbate and aluminium ions to be major parameters of the study. Since the relative concentrations of adsorbent and adsorbate limit the degree of surface area coverage, they govern the interfacial conformation of the adsorbed macromolecules and its evolution with time. The relative concentrations of polymer and aluminium ions limit the degree of complexation of acidic groups and thus govern the solubility parameters of the complex. The relative concentrations of aluminium ions and oxide or clay fix the ion transfer or exchange characteristics between solid and liquid phases. In addition, the absolute concentration of aluminium ions determines the relative concentration of the different positive, negative or neutral species present in solution at a given pH.

Thirdly, the role of pH in adsorption processes involving charged adsorbents and adsorbates has been recognised as being essential [8, 9, 10, 11, 12]; therefore, this parameter was set to 5.0 at time zero for suspensions and solutions but was allowed to vary with time when the variation was consecutive to the formation of binary or ternary complex systems. This method was estimated to be adapted to soil conditions where the characteristics of the solid constituents may be considered as being pH-controlling factors, owing to the very high surface-to-liquid volume ratio. Therefore, despite the fact that the complex systems were formed in dilute aqueous suspension, the investigations were performed in such a way as to obtain information on concentrated colloidal systems (aggregates) of structures comparable to that formed in wet acidic soils by clays and humic acids.

Finally, different methods of investigation of the interactions governing the stability and cohesion of soil aggregates have been described in the literature [13, 14, 15]. The objectives of the present method were to interpret the adsorption mechanism in terms of the electrochemical characteristics of the complex systems.

Materials and methods

Aluminium oxide

The α-alumina samples of industrial origin (Aluminium-Péchiney) were partially soluble at pH 5 and at 25 °C and contained different major impurities, such as Na_2O, SiO_2, Fe_2O_3 and CaO. The evolution with time of the pH of the different samples initially suspended in 10^{-3} mol/l KCl solutions at pH 3.5, each at an oxide concentration preserving a constant surface area to volume ratio, was found to be greatly sample-dependent, but the final hydrogen and aluminium ion concentrations in the supernatant solution depended slightly on the sample. In the case of the sample employed in this study, the characteristics of the supernatant differed little between incubation periods of 2 and 24 h despite the fact that this did not correspond strictly to the equilibrium situation. Two successive dissolution rates were measured in acidic media (pH 2), indicating the existence of a more soluble layer at the oxide surface corresponding to aluminium hydrates as indicated by electron spectroscopy for chemical analysis (ESCA). The underlying and only slowly soluble material was aluminium oxide. ESCA also gave information about the nature of the surface impurities, and we determined that Ca (0.1%) could be fully extracted, while Mg (0.3%) remained after treatment in acidic or salt media.

KCl at a constant concentration of 10^{-3} mol/l was used to set the ionic strength at a relatively fixed value, to favour usual Al/OH interactions and to avoid Al/Cl ones. The dissolution of the aluminium oxide in 10^{-3} mol/l aqueous KCl solution provided 10^{-4} mol/l aluminium ions at the equilibrium pH of 5.0. These concentrations of hydrogen and aluminum ions were established instantaneously when 0.4 g dry alkaline oxide powder was suspended in 50 ml water containing 10^{-3} mol/l KCl and 10^{-4} mol/l $AlCl_3$ at pH 4.06. Acid–base titration of the colloid suspended in electrolyte solutions of different concentrations showed the point of zero charge to lie at pH 9.1. Therefore, the solid/liquid interface corresponds to a surface network of positively charged aluminium hydrates in "equilibrium" with the "synthetic supernatant" at pH 5.0 containing 10^{-3} mol/l KCl and 10^{-4} mol/l $AlCl_3$. The alumina particles had a mean size of 1.54 μm and a specific surface area determined from the Brunauer–Emmett–Teller adsorption isotherm of 3.0 m^2/g.

Kaolinite

The clay was a kaolinite-type material of French origin (Kaolin des Charentes, code type name GZA IV). The morphology, composition and surface area characteristics of the clay are given in Table 1.

One basal face of the kaolinite platelet contains hydroxyl groups, while the other contains oxygen groups. The silicon surface is poorly hydrated in aqueous media and the pH-independent negative charge, which forms a great part of the total charge, is ascribable to isomorphous substitution, some of the neutral SiO_2 groups being replaced by negatively charged AlO_2^- groups. The lateral surface charge is a function of the pH of the suspending medium, the point of zero net proton charge being close to 7. At pH 5.0 the basal and lateral faces are oppositely charged and aggregates of card-house structures may exist in concentrated suspensions [16, 17].

Table 1 Morphological and chemical characteristics of the kaolinite clay

Plate diameter	0.21 μm		
Plate thickness[a]	0.04 μm		
Lateral specific area[a]	8.3 m^2/g		
Basal specific area[b]	18.5 m^2/g		
Size distribution	Finer than 0.10 μm	12%	
	Finer than 0.16 μm	50%	
	Coarser than 10 μm	Negligible	
Cation-exchange capacity	9 mEq/100 g		
Loss on ignition	13.9 wt%		
Chemical composition			
SiO_2	46 wt%	MgO	0.24 wt%
Al_2O_3	36 wt%	Na_2O	0.03 wt%
Fe_2O_3	1.23 wt%	K_2O	0.75 wt%
MnO	0.1 wt%	TiO_2	1.39 wt%

[a] Derived from granulometric analysis (Sedigraph and Andreasen methods)

[b] Calculated using the results of gas adsorption

The clay suspended in aqueous solution at pH 3.5 (0.5 g/l) was fractionated by sedimentation. Particles of very large sizes were allowed to settle out by gravity and were discarded, this operation being repeated 5 times.

Polyacrylic acid

Polyacrylic acid was synthesised at 60 °C by polymerisation of acrylic acid using potassium persulphate as initiator. The polymer was fractionated by membrane dialysis in water to eliminate the low-molecular-weight material and a sample of mean molecular weight of 9.6×10^5 was used as the synthetic polymeric material.

Humic acids

The peat-derived humic substance was supplied as sodium humate by Aldrich Chimie and some characteristics are given by Ochs et al. [10]. Extraction of the soluble phase from the product immersed in water at pH 1.5 indicated the presence of fulvic acid at a concentration of 8%. For simplicity, this mixture of fulvic and humic acids is called humic acid. The humate powder dissolved in water gave an alkaline solution of pH 8 and the nonsoluble constituents were centrifuged. Stock solutions at a concentration of 1 g/l in 10^{-3} mol/l aqueous KCl solutions at pH 5.0 appeared coloured. Acid–base titration of the humic acids showed the equivalent concentration of acid groups to be 0.003 mol/g. The titration curve showed the presence of two different weak acidic groups with different acid strengths at concentrations of 0.73 (weak acidic strength) and 0.27 (very weak acidic strength). These characteristics were previously determined by Barak and Chen [18]. Turbidity measurements at 500 nm on solutions with varying polymer concentrations showed the organic substance to be soluble in aqueous solution at pH 5 and 25 °C in the presence of aluminium ions below a threshold concentration of 2×10^{-4} mol/l $AlCl_3$.

System characteristics

The apparent degree of dissociation, α, of carboxylic acid groups is defined as follows:

$$\alpha = \frac{[R\mathrm{COO}^-]}{[R\mathrm{COOH}]} \ , \tag{1}$$

where $R\mathrm{COO}^-$ and $R\mathrm{COOH}$ are the dissociated carboxylic acid and total (neutral plus dissociated) carboxylic groups of the polyelectrolyte, respectively. The brackets indicate concentrations in moles per litre. At pH 5.0 α was determined to be 0.10. An important parameter of the system is the degree of complexation, α_{comp}, which is defined by

$$\alpha_{\mathrm{comp}} = \frac{[(R\mathrm{COO})_3\mathrm{Al}]}{3[R\mathrm{COOH}]} \ . \tag{2}$$

The brackets correspond to concentrations of initial aluminium ions [Al] in the absence of adsorbents and nonadsorbed aluminium ions $[\mathrm{Al}_{\mathrm{free}}]$ in the presence of kaolinite and complexed carboxylic groups $[(R\mathrm{COO})_3\mathrm{Al}]$. $[R\mathrm{COOH}]$ is the total concentration of polyacrylic or humic acid.

Reduced electrophoretic mobility

Measurements of electrophoretic mobility of the bare, complexed and polyacrylic or humic acid coated kaolinite and alumina particles were carried out using a Malvern Zeta Sizer III. In all situations, the experiments were carried out at 25 °C. The precision and accuracy of the experimental results were checked using a standard colloid suspended in a given standard buffer, for which the mobility should be reproduced with an error smaller than ±10%.

Results and discussion

Influence of the aluminium ion concentration on the ion speciation in solution

The positive net valence, n^+, of aluminium ions in aqueous KCl solution at pH 5.0 was derived from titration of $AlCl_3$ at 25 °C [19]. From the small differences in the titration curves obtained in the range 10^{-4}–10^{-3} mol/l $AlCl_3$ we derived the variation of the n^+ as a function of the aluminium ion concentration (Fig. 1).

At pH 5.0 the increase in n^+ with dilution results from the increase in the concentration of the Al^{3+} form to the detriment of all other ionic forms, such as $Al(OH)^{2+}$, $Al(OH)_2{}^+$ and $Al(OH)_3$. One may further assume that when the concentration tends to be close to zero, only the Al^{3+} form will be present in solution.

Interaction of aluminium ions with carboxylic acid groups

The concentrations of free and complexed carboxylate groups present on the polyacrylic acid were determined by acid–base titration using correlations between the amount of NaOH added to the solution to ionise the

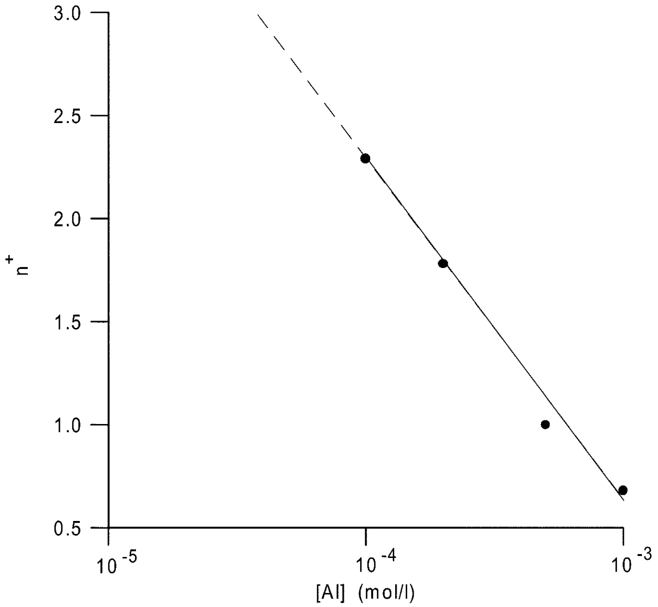

Fig. 1 Mean valence, n^+, of the soluble aluminium ions as a function of the ion concentration in solution

carboxylic acid groups (between pH 4 and 9) and that of the initial aluminium ion of known concentration. This correlation is shown in Fig. 2 (note that concentrations are expressed in equivalent-grams per litre in this figure). The concentration of aluminium ion–polyelectrolyte complexes is also determined by titration of the ionisable constituents between pH 8 and 10 in the case of polymer excess and in the range pH 7–10 when the free aluminium ions are in excess. Ionisation of the neutral form was found to be negligible over the pH range concerned. The linear correlation between the amount of NaOH reagent used to obtain the corresponding pH shift and the concentration of aluminium ions initially present in the polyelectrolyte solution is also shown in Fig. 2. With regard to the coexistence of complexed and free polyelectrolyte segments and its effect on the concentration of the reagent added, linear correlations between the NaOH concentration and the dissociated and complexed carboxylic acid groups were established, which serve to calculate the unknown concentrations of these constituents. The concentration of free polyelectrolyte was determined by taking into account the concentration of complexed aluminium ions and the total polymer concentration.

Addition of polyacrylic or humic acids to aqueous solutions containing 10^{-3} mol/l KCl, 10^{-5} mol/l HCl and $AlCl_3$ at various concentrations induced rapid pH drops, the amplitude of which is a function of the polyelectrolyte and aluminium ion concentrations, as represented in Figs. 3 and 4, respectively. Figure 3 shows the shift in hydrogen ion concentration resulting from addition of various amounts of polyacrylic acid to aqueous electrolyte solutions only differing initially by the aluminium ion concentration, which was successively equal to 0, 10^{-5}, 3×10^{-5} and 10^{-4} mol/l. Figure 4 represents the shift in hydrogen ion concentration resulting from addition of various amounts of humic acid to aqueous aluminium chloride solutions at concentrations of 0, 10^{-5}, 2.5×10^{-5}, 5×10^{-5} and 10^{-4} mol/l.

The increasing part of the hydrogen ion concentration as a function of the humic acid concentration displays two domains of strong and low variations, which may be attributed to the existence of two acidic groups of different strengths.

The degree of complexation, α_{comp}, may be derived by taking into account the positive net valence of the aluminium ions and the neutral and dissociated acidic groups. Determination of the progress of the reactions expressed in Eqs. (3) and (4) leads to Eq. (5) for the degree of complexation defined by Eq. (2)

$$Al(OH)^{n^+}_{(3-n^+)} + (3 - n^+)H^+ \leftrightarrow Al^{3+} + (3 - n^+)H_2O \ , \tag{3}$$

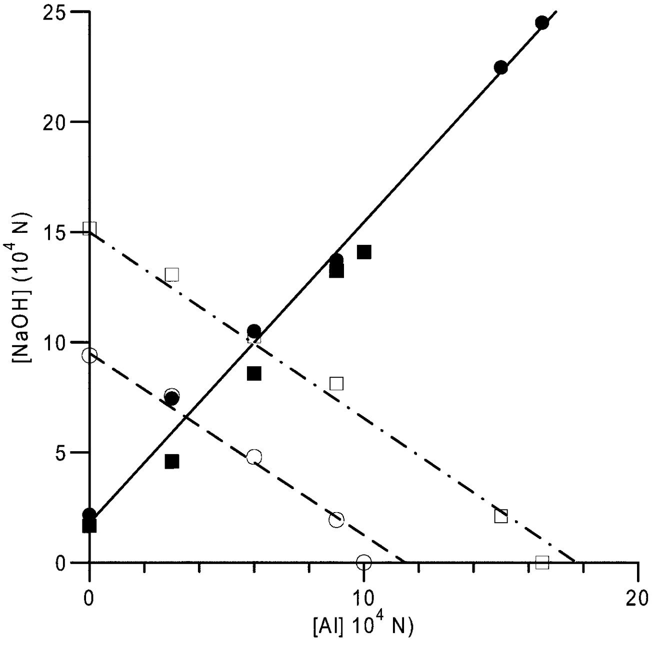

Fig. 2 Correlation between the initial concentration of aluminium ions and the NaOH concentration added to the solution to titrate the free polyacrylic acid in the presence of 1.414×10^{-3} N (○) and 2.228×10^{-3} N (□) and the complexed groups in the presence of 1.414×10^{-3} N (●) and 2.228×10^{-3} N (■). (N means equivalent grams per litre)

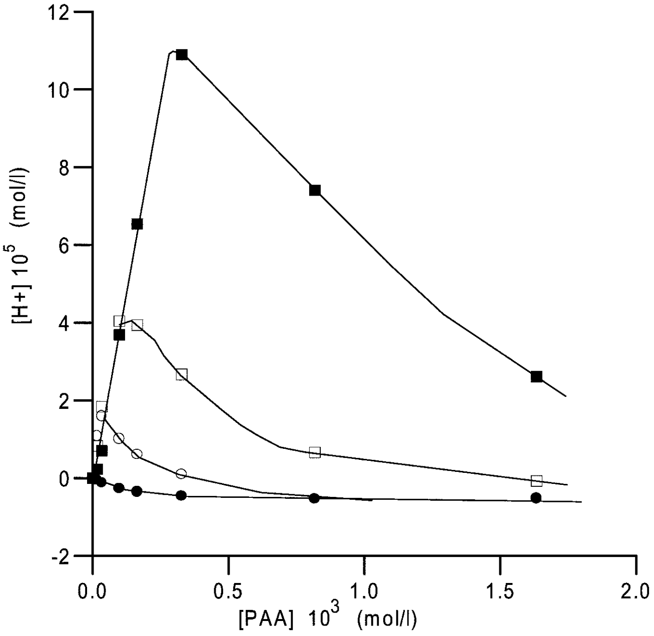

Fig. 3 Shift in the hydrogen ion concentration induced by complexation of the carboxylic groups of polyacrylic acid as a function of the polyelectrolyte concentration for various concentrations of aluminium ions: 0(●); 10^{-5} (○); 3×10^{-5} (□); 10^{-4} (■). The initial pH was 5.0

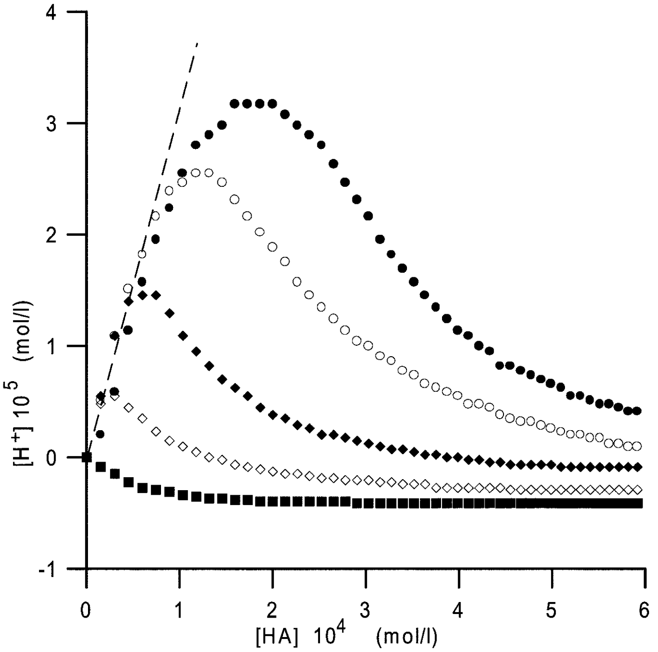

Fig. 4 Shift in the hydrogen ion concentration induced by complexation of the acidic groups of humic acid as a function of the polyelectrolyte concentration for various concentrations of aluminium ions: 0 (■); 10^{-5} (◇); 2.5 × 10^{-5} (◆); 5 × 10^{-5} (○); 10^{-4} (●). The initial pH was 5.0

$$Al^{3+} + 3\alpha R\text{COO}^- + 3(1-\alpha)R\text{COOH} \leftrightarrow Al(R\text{COO})_3 + 3(1-\alpha)H^+ \ , \quad (4)$$

$$\alpha_{\text{comp}} = \frac{3}{(n^+ - 3\alpha)} \frac{[H^+]}{[R\text{COOH}]} \ . \quad (5)$$

Equation (5) expresses the degree of complexation, α_{comp}, as a function of the production of hydrogen ions, the initial degree of dissociation, α, and the positive net valence, n^+, of the aluminium ions at pH 5.0. Equation (5) is valid at and on the right-hand side of the maximum of the curves shown in Figs. 3 and 4. For concentrations of humic and polyacrylic acids smaller than those corresponding to the maximum, we expected the mean degree of carboxylic acid complexation obviously to remain at the level determined for the maximum hydrogen ion production, whereas the corresponding lower production of hydrogen ions is correlated to the smaller polymer concentration and to the presence of residual aluminium ions. The application of Equation (5) to the results obtained for polyacrylic and humic acids shows the maximum degree of complexation to be close to 0.60 and 0.28 (±0.02), respectively, and to be independent of the aluminium ion concentration. The results shown in Fig. 2 relative to the polyacrylic acid/aluminium oxide system indicate the concentration of reagent required to titrate the free acid groups (for $[Al] = 0$) to be equal to the concentration of aluminium ions which is necessary to complex the polymer (no free polyelectrolyte). From this we obtain that the maximum α_{comp} should be close to 0.6. The fact that the value of the maximum α_{comp} is higher for the synthetic polyelectrolyte than for the natural one leads us to conclude that complexed polyacrylic acid presents a greater portion of neutral chain segments than complexed humic acid does. The greater concentration of Al-complexed neutral $Al(R\text{COO})_3$ groups within the synthetic coil may result from the greater flexibility of the synthetic polymer compared to that of the natural one. Actually, the branched structure of the natural macromolecule is supposed to be additionally strengthened by intramolecular hydrogen and hydrophobic bonds [20, 21].

Therefore, like amphoteric polymers, complexed polyacrylic and humic acids contain neutral, positively and negatively charged chain segments and assemblies of chain segments, owing to the various reactions of carboxylic acid groups with the aluminium ions of different valences.

Interaction of aluminium ions with aluminium oxide and kaolinite clay

The point of zero charge of aluminium oxide α-Al_2O_3 determined by titration of the oxide in KCl suspensions was found to be 9.10 ± 0.05, in agreement with other results in the literature [22] and no specific adsorption of Cl^- was determined to occur. When the oxide is suspended in 10^{-3} mol/l KCl, the supernatant becomes slightly modified owing to the partial dissolution of the oxide and aluminium ions were determined to be present at a concentration of 10^{-4} mol/l at pH 5.0. At that pH, the oxide bears a net positive charge as revealed by electrophoretic mobility measurements and the resulting potential calculated using Smoluchwoski's equation is 55 ± 3 mV. From the crystallographic point of view, the surface of the suspended oxide is not well defined and may contain amorphous AlOOH and crystalline $Al(OH)_3$ regions. ESCA analysis showed the O/Al ratio to be close to 3.5, greater than the value expected for corundum and, therefore, the oxide surface is expected to present surface and hydration characteristics of the hydroxide gel.

The situation is different for the kaolinite clay, which is not soluble in the aqueous supernatant at pH 5.0. Addition of $AlCl_3$ to the 10^{-3} mol/l KCl aqueous suspension at pH 5.0 promotes interfacial ion exchange and adsorption. The residual concentration of aluminium in solution is shown in Fig. 5 as a function of the clay dose. At a dose of 0.2, the

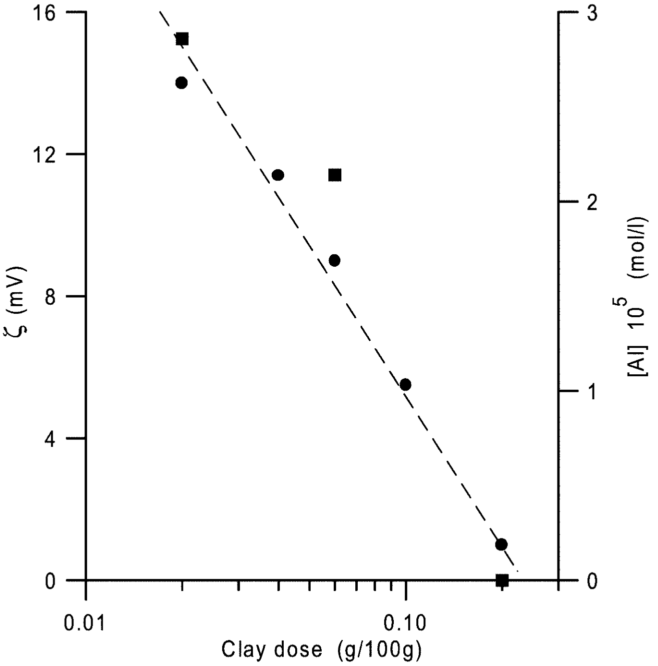

Fig. 5 *Right ordinate*: Residual aluminium ion concentration as a function of the kaolinite clay dose (log scale) (■). *Left ordinate*: ζ potential (●) of kaolinite modified by adsorption of aluminium ions subsequent to immersion in 50 ml aqueous (10^{-4} mol/l $AlCl_3$, 10^{-3} mol/l KCl and 10^{-5} mol/l HCl) solution of kaolinite at the doses given on the abscissa

supernatant is free of aluminium ions. Therefore, the valence characteristics of the soluble aluminium ions depend on the clay dose and near the threshold value of 0.2 only Al^{3+} ions will be present in the supernatant, as derived from Fig. 1. Adsorption occurs mainly on the basal silica surface at the AlO_2^- sites since the net charge of the ionisable groups of the lateral face is already positive and the other basal face contains chemically neutral hydrogen-bonded aluminol groups [16, 17, 23–28]. The left ordinate of Fig. 5 shows the ζ potential of the clay in the presence of aluminium ions as a function of the clay dose. At pH 5.0 a negative value of −17.5 mV was determined for the bare clay, whereas above a surface concentration of three Al sites per square nanometre of the basal silica face the ζ potential becomes positive. Actually, the potential seems to level at 15 mV and the surface density of adsorbed aluminium ions derived from the balance between the initial and the residual aluminium ion concentration appears to be compatible with the low cation-exchange capacity of the kaolinite clay [17, 23, 24, 29–34]. This modification of the surface charge indicates that the aluminium ions interact strongly with the basal AlO_2^- sites and that electrostatic interactions occur, which involve the aluminium ions of different valences.

Hydrogen ions produced by adsorption of polyacrylic and humic acids on aluminium oxide and kaolinite clay

Addition of synthetic or natural polymer to the aluminium oxide suspension at a dose of 0.8 g/100 g aqueous suspension KCl and $AlCl_3$ at a concentration of 10^{-3} and 10^{-4} mol/l, respectively, produces rapid pH drops. Conversely to the previous situation leading to the formation of binary complexes where the pH remained constant after the drop, for the ternary systems we determined that the pH increases very slowly after the initial fast drop. For the two systems and at the various concentrations of the carboxylic acid groups, the difference in the maximum hydrogen ion productions in the presence and in the absence of aluminium oxide was attributed to adsorption phenomena and is represented in Fig. 6. The similar shape of the two curves indicates that interfacial phenomena should be identical but of different magnitude.

The interpretation of these effects is based on the observation that the production of hydrogen ions which immediately results from mixing oxide and polyacrylic acid or oxide and humic acid results from the complexation of carboxylic acid groups by surface and solute aluminium ions. The aluminium ions involved in the complexation reactions only differ by their degree of protonation, n^+, which takes the mean value of 2.3 for

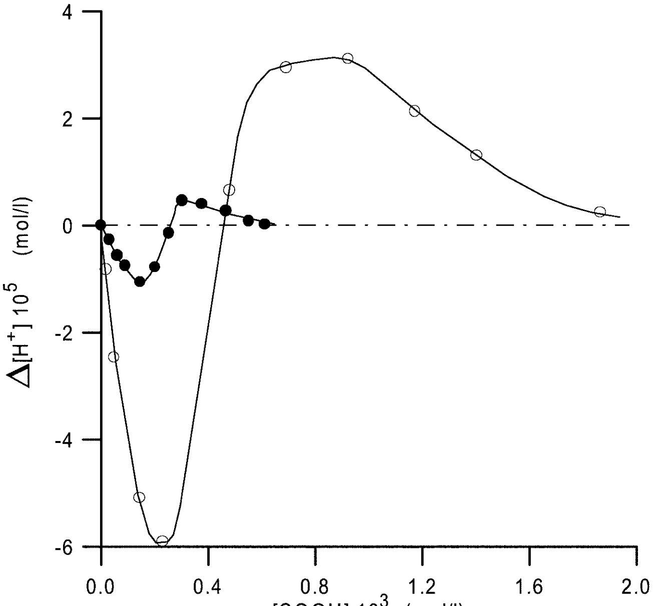

Fig. 6 Difference in the shift of the hydrogen ion concentrations generated in the absence and in the presence of aluminium oxide by addition to an aqueous (10^{-4} mol/l $AlCl_3$, 10^{-3} mol/l KCl and 10^{-5} mol/l HCl) solution of polyacrylic acid (○) and humic acids (●) as a function of the carboxylic acid concentration

solute aluminium ions, whereas it should be significantly less than this value for surface groups owing to their inclusion in the oxide crystalline network. Therefore, according to Eq. (5) complexation of carboxylic acid up to a given value of α_{comp} by Al surface groups produces fewer hydrogen ions than complexation by solute aluminium ions. We consider the two following situations:

1. When the relative number of carboxylic acid groups is small, complexation and adsorption produces fewer hydrogen ions than complexation alone. At a given concentration, the number of aluminium ions required to induce the maximum complexation should be similar in the presence and in the absence of oxide; however, in the presence of oxide, surface groups are involved in the process and the lower production of hydrogen ions depends on the adsorption amount. We previously determined the concentration of free, noncomplexed aluminium ions to be greater in the presence of the oxide than in the absence of oxide when only complexation by solute aluminium ions occurs [35]. These two results establish the existence of interfacial complexation phenomena between positively charged aluminium sites of the oxide and carboxylic acid groups [10, 36]. For Al^+ surface groups (characterised by n^+ equal to 1), complexation produces neutral ion pairs.
2. When the relative number of carboxylic acid groups is great, complexation and adsorption produces more hydrogen ions than complexation alone. At all concentrations, the maximum degree of complexation is not achieved and addition of aluminium oxide to the solution is equivalent to adding surface aluminium groups obviously characterised by a reduced degree of protonation. Adsorption thus contributes to slightly increase the degree of complexation and thus the production of hydrogen ion.

The situation is totally different when humic acid is added to the kaolinite in the presence of aluminium ion. The maximum pH drop accompanying the addition of humic acid to kaolinite clay suspension was determined for different polymer concentrations and clay doses and compared to that resulting from the complexation of the acidic groups in the absence of kaolinite.

The results in Fig. 7 show the change in the hydrogen ion concentration as a function of the concentration of aluminium ion. This concentration is determined by the number of aluminium ions added to the pure solution (in the absence of clay) and it corresponds to the residual concentrations of aluminium ions in the solution as set by the different clay doses. The change in the hydrogen ion concentration is shown to be similar in the presence and in the absence of clay; therefore, we conclude that interfacial complexation does not occur during the initial adsorption period responsible for the pH drop and that hydration of the aluminium ion may be responsible for the absence of surface complexation. Therefore, only effects due to electrostatic attraction are responsible for the adsorption. Thus, complexation in solution and adsorption at the solid/liquid interface may be viewed as being two independent processes, at least in that initial period of 1 or 2 h.

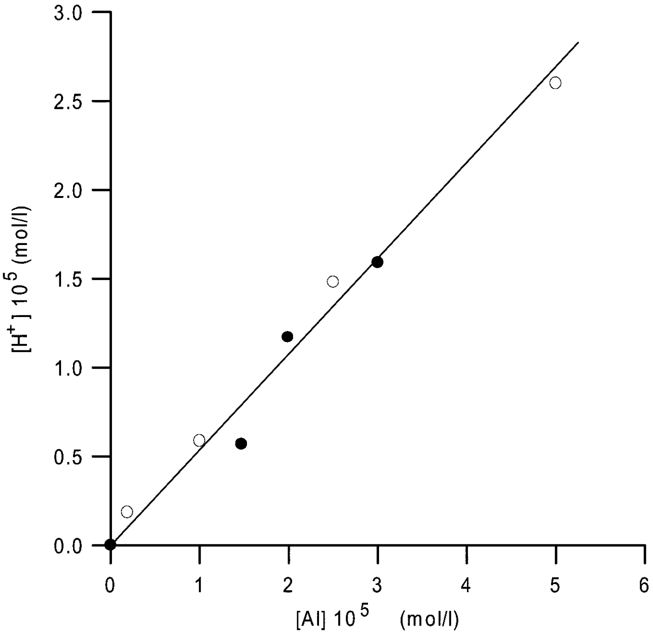

Fig. 7 Shift in the hydrogen ion concentration induced by humic acid complexation as a function of the initial (○) (in the absence of kaolinite) and the residual concentration of aluminium ions (●) in the solution, as fixed by the different doses of kaolinite

For the aluminium oxide systems, we conclude that the complexation reaction and the concomitant dehydration of the oxide surface sites lead to the formation of a thin, electrically neutral surface zone. Conversely, electrostatic charge–charge interactions exerted between the aluminium ions (which are counterions of the permanent AlO_2^- sites) and the positively (complexed) and negatively (dissociated) charged carboxylic acid groups predominate at the clay–humic acid interface, thus inducing long-range electric interactions in the adsorbed polymer layer.

Short-term modifications in the interfacial layer induced by adsorption of polyacrylic acid at the oxide surface and humic acids at the oxide or kaolinite clay surfaces.

We note that the dry alkaline oxide powder was suspended in the synthetic supernatant (10^{-3} mol/l KCl, 10^{-4} mol/l $AlCl_3$ at pH 4.06) so that a stable pH of 5.0 was established instantaneously. The polymer solution at pH 5.0 was then added to the suspension

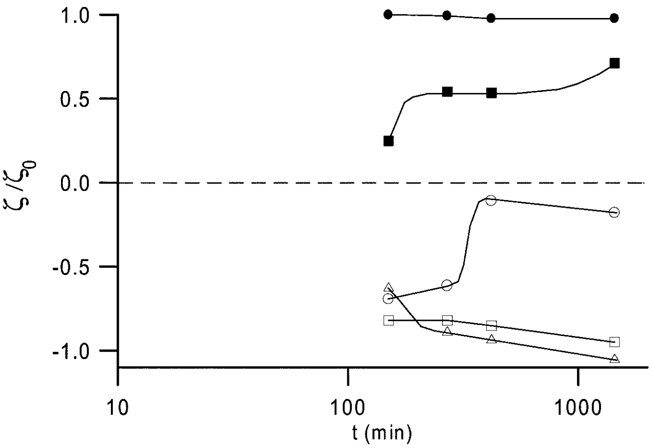

Fig. 8 Polyacrylic acid in the presence of aluminium oxide suspended in aqueous (10^{-3} mol/l KCl, 10^{-4} mol/l $AlCl_3$) solution at the initial pH of 5.0. Reduced ζ potential as a function of time for polyelectrolyte concentrations of 0 (●); 0.6×10^{-3} mol/l (■); 1.33×10^{-3} mol/l (○); 1.8×10^{-3} mol/l (□) and 2.66×10^{-3} mol/l (△)

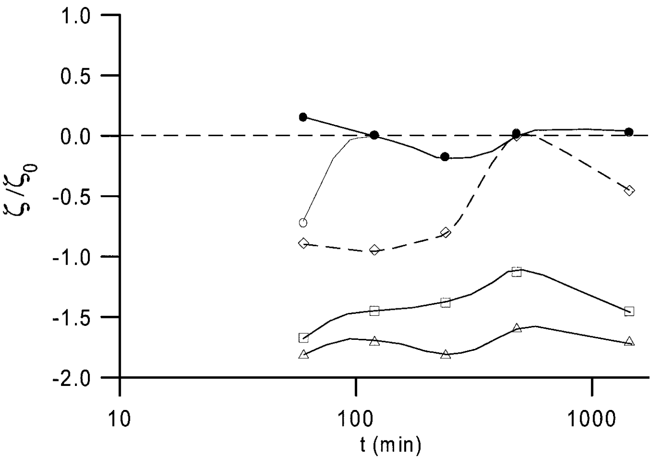

Fig. 10 Humic acids in the presence of kaolinite at a dose of 0.06 suspended in aqueous (10^{-3} mol/l KCl, 10^{-4} mol/l $AlCl_3$) solution at the initial pH of 5.0. Reduced ζ potential as a function of time for humic acid concentrations of 0.12×10^{-4} mol/l (●); 0.3×10^{-4} mol/l (○); 0.6×10^{-4} mol/l (◇); 2.4×10^{-4} mol/l (□) and 3×10^{-4} mol/l (△)

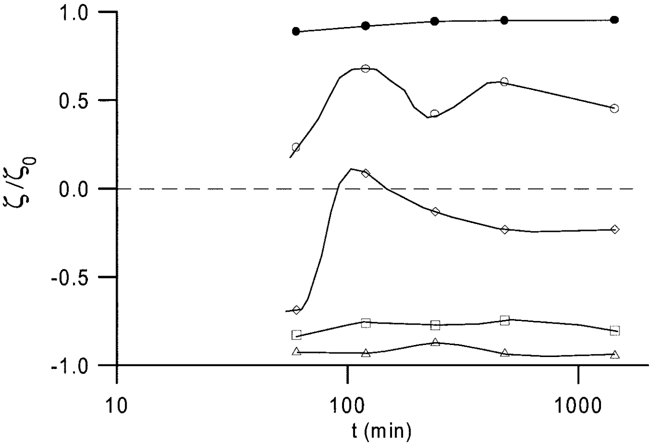

Fig. 9 Humic acid in the presence of aluminium oxide suspended in aqueous (10^{-3} mol/l KCl, 10^{-4} mol/l $AlCl_3$) solution at the initial pH of 5.0. Reduced ζ potential as a function of time for humic acid concentrations of 0.57×10^{-4} mol/l (●); 1.14×10^{-4} mol/l (○); 2.46×10^{-4} mol/l (◇); 3.45×10^{-4} mol/l (□) and 4.68×10^{-4} mol/l (△)

under stirring to reach a final dose of 0.8 g/100 g. For the kaolinite system, various amounts of humic acid were added to suspensions containing 0.06 g clay per 100 g suspension. In this situation, the residual concentration of aluminium ion is 0.21×10^{-4} mol/l, while 0.79×10^{-4} mol/l is adsorbed on the clay surface and the pH of the suspension is 5.0. Hydrogen ion transfer and the reduced electrophoretic mobility (the mobility of the bare oxide serving as a reference) were determined as a function of time and the results concerning the electrophoretic mobility are reported in Figs. 8, 9 and 10 for polyacrylic and humic acids.

The electrophoretic mobility of the oxide suspended at pH 5.0 and of the kaolinite modified by adsorption of aluminium ions, determined before addition of humic acids, was taken as a reference. Changes in the electrophoretic mobility determined for the polyacrylic acid/oxide system (Fig. 8) were previously correlated with the modifications in the total amount of polymer adsorbed and in the degree of complexation of the adsorbed polymer [19]. For the humic acid/oxide (Fig. 9) or humic acid/kaolinite systems (Fig. 10) the changes with time are globally comparable, but to a greater extent in the case of the clay system. It is assumed that within a period of 24 h these modifications can be attributed to changes in the adsorption amounts and also in the degree of polyacid complexation. It is worth noting that humic acid at great concentrations changed the electrophoretic mobility by a factor close to -1.5.

It may be concluded that macromolecules of various molecular weights and degrees of complexation compete for the available surface area during the formation of the interfacial layer. This phenomenon as investigated using surface-area-exclusion chromatography [37] will be presented elsewhere as will be the long-term variation due to the presence of aluminium ions.

Conclusion

In the presence of aluminium ions the synthetic and the natural substances display typical behaviour of charged macromolecules despite the great difference in molecular weight. It is therefore possible that intermolecular links contribute to aggregate the natural substance and are responsible for the macromolecule behaviour which is responsible for time-dependent effects on the surface charge density. The aluminium oxide/polyacrylic acid synthetic system is inappropriate to fully serve as a model for the kaolinite/humic acid natural system despite the fact that the apparent effect on the electrophoretic mobility of the complex systems is quite similar. The aluminium ions belonging to aluminium oxide and kaolinite surfaces induce very different interaction modes with synthetic and natural polyelectrolytes. The aluminium sites of the oxide surface are engaged in interfacial complexation reactions with dissociated or neutral acidic groups located near the surface. This locally promotes the formation of neutral hydrophobic –Al(OH_2)OOC– moieties. Conversely, for the kaolinite clay, the aluminium ions of the basal silica faces were determined not to exert short-range interactions with acid groups, such as complexation. Apparently, during the initial step of the adsorption, the positively charged counterions of the basal silica face were found not to interact with acid groups of the polyelectrolytes.

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References

1. Jennings JE, Knight K (1957) Proceedings of the Fourth International Conference on Soil Mechanics and Foundation Engineering, London, p 316
2. Colom J, Wolcott AR (1967) Plant Soil 26:261
3. Dennett KE, Sturm TW, Amirtharajah A, Mahmood T (1998) Water Environ Res 70:268
4. Pierzynski GM, Sims JT, Vance GF (1994) Soils and environmental quality. Lewis, London, pp 249–261
5. Berggren D, Muller J (1995) Cosmochim Acta 20:4167
6. Pefferkorn E (1997) Adv Colloid Interface Sci 73:127
7. Mahiuddin S, Suryanarayan I, Dutta NN, Borthakur PC (1992) Colloids Surf A 64:177
8. Ben-Hur M, Malik M, Letey J, Mingelgrin U (1992) Soil Sci 153:349
9. Tiller C, O Melia CR (1993) Colloids Surf A 73:89
10. Ochs M, Cosovic B, Stumm W (1994) Geochim Cosmochim Acta 58:639
11. Vermeer AWP, van Riemsdijk WH, Koopal LK (1998) Langmuir 14:2810
12. Tombacz E, Dobos A, Szekeres M, Narres HD, Klumpp E, Dekany I (2000) Colloid Polym Sci 278:337
13. Chaney K, Swift RS (1984) Soil Sci 35:223
14. Chaney K, Swift RS (1986) Soil Sci 37:337
15. Le Bissonnais Y, Arrouays D (1997) Eur J Soil Sci 48:39
16. Theng BKG (1979) Formation and properties of clay–polymer complexes. Development in soil science series, vol 9. Elsevier, Amsterdam
17. Schofield RK, Samson HR (1954) Discuss Faraday Soc 18:135
18. Barak P, Chen Y (1992) Soil Sci 154:184
19. Ringenbach E, Chauveteau G, Pefferkorn (1993) J Colloid Interface Sci 161:223
20. Schulten HR (1995) Fresenius J Anal Chem 351:62
21. Schulten HR, Schnitzer M (1997) Soil Sci 162:115
22. Yopps JA, Fuerstenau DW (1964) J Colloid Sci 19:61
23. Bolland MDA, Posner AM, Quirk JP (1976) Aust J Soil Res 14:197
24. Street N, Buchanan AS (1956) Aust J Chem 9:450
25. Flegman AW, Goodwin JW, Ottewill RH (1969) Proc Br Ceram Soc 13:31
26. Goodwin JW (1971) Trans J Br Ceram Soc 70:65
27. Follet EAC (1965) J Soil Sci 16:334
28. Weiss A, Russov J (1963) Proc Int Clay Conf Stockholm 1:203
29. van Olphen H (1977) An introduction to clay colloid chemistry. Wiley, New York
30. Grim RE (1968) Clay mineralogy. McGraw-Hill, New York
31. Ferris AP, Jepson WB (1975) J Colloid Interface Sci 51:245
32. Fripiat JJ (1957) Bull Groupe Fr Argiles 4:23
33. Cashen GH (1959) Trans Faraday Soc 55:477
34. Cashen GH (1966) J Soil Sci 17:303
35. Ringenbach E, Chauveteau G, Pefferkorn E (1995) Colloids Surf A 99:161
36. Buleva M, Peikov V, Pefferkorn E, Petkanchin IB (in press) Colloids Surf A
37. Pefferkorn E, Elaissari A, Huguenard C (1999) In: Pefferkorn E (ed) Interfacial phenomena in chromatography. Dekker, New York, pp 329–386