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CHARACTERIZATION AND INTERACTION OF HUMIC ACIDS WITH METAL IONS AS A FUNCTION OF SOLUTION pH

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Abstract. This study examines the solubility of humic acids as a function of solution pH and their interactions with di- and trivalent metal ions at different pH values. It has been observed that humic acids and their salts interact with divalent transition metal ions in aqueous solutions at low pH values. The results demonstrate that the amount of metal ions – specifically copper, cobalt, and nickel – bound to humic acids increases almost linearly with their initial concentration. Moreover, the amount of bound metal ions rises as the pH of the medium increases. Investigations into the interactions of iron, aluminum, and chromium ions with humic acids at varying pH levels show that, at low pH values and low metal ion concentrations, the amount of metal ions bound to humic acids is directly proportional to their concentration in the aqueous solution.

Keywords: humic acids, copper, cobalt, nickel, iron, aluminum, chromium, ions, pH.

1. Introduction

Humic acids are the primary organic component of soil and play an important role in soil fertility.[1] From a chemical perspective, humic acids are high-molecular-weight aromatic hydroxycarboxylic acids, often containing additional functional groups such as carbonyl and methoxy groups[1–5]. In alkaline solutions, they form humate salts. Humic compounds derived from household waste[2–4] can be utilized in agriculture[5–8], and the environmental conditions of any region are closely linked to humic substances, as they influence the stability of land, water resources, and soils. Soil protection against water erosion is associated with the formation of insoluble humic compounds with inorganic materials, in particular those contaminated with heavy metals[9–16]. Mine waste soils not only contain elevated levels of toxic metals but also exhibit poor physical properties, high acidity, and low nutrient content[12]. To remediate anthropogenic mine soils, appropriate soil management strategies should be implemented to reduce metal bioavailability and dispersion, thereby minimizing exposure to humans and other organisms.

Sodium salts of humic acids are widely used in industry to stabilize mineral dispersions. Humic acids are complex polyelectrolytes with a broad range of molecular weights, containing carboxyl, hydroxyl, and amino functional groups[5], which make them polydentate ligands. Among these, the carboxyl groups are dominant, forming strong bonds with metal cations, particularly heavy metal ions. Given their environmental significance, it is essential to study how environmental conditions influence the interaction of humic acids with metal ions. Humic acids effectively bind various inorganic ions, including aluminum[6, 7] and iron[8].

Studies on the interaction between metal dications and humic acids have shown that the amount of bound metal dications depends on their nature[9]. Research on the adsorption of copper ions by biowaste containing humic acids indicates that the amount of copper ions bound to humic acids decreases as the pH of the mixture increases[9, 10]. Furthermore, the amount of copper ions bound to humic acids increases linearly with their initial concentration[6]. Iron and calcium ions bound to humic substances immobilized on silica gel can form hydrophobic and hydrophilic surfaces, respectively[6]. The ability of humic acids to form chemical bonds with free metal ions in highly diluted aqueous solutions follows the order $Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ [6, 16, 17]. This trend is attributed to the chelating activity of phenolic and carboxyl groups in humic acids, as well as the coordination behavior of metal ions.

Given the ecological challenges related to land and water resources, soil erosion, heavy metal contamination, high levels of toxic metals, soil acidity, and nutrient depletion, it is crucial to investigate the properties of humic acids in relation to environmental pH and their capacity to form chemical bonds with metal ions.

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Therefore, the objective of this study is to examine the characteristics and interactions of humic acids with di- and trivalent metal ions as a function of pH.

2. Experimental

2.1. Materials

To investigate the interaction between humic acids and di- and trivalent metal ions at different pH values, chemically pure salts of $CuSO_4$, $CoCl_2$, $NiSO_4$, $Fe_2(SO_4)_3$, $Al(NO_3)_3$, $Cr(NO_3)_3$ were used without further purification. Humic acids, containing 1.02 % nitrogen, 49.10 % carbon, and 5.15 % hydrogen, were obtained from the Olaine Chemical Reagents Factory. The humic acids used in this study are dark brown in color and exhibit low water solubility. Potentiometric titration determined the acid group content to be 3.6 mmol/g of humic acids.

2.2. Methods

To investigate the interaction of humic acids with metal ions, a dispersion of humic acids or a solution of their sodium salts was mixed with a metal salt solution and stirred for 24 hours. The resulting mixture was then centrifuged at 8000 s^{-1} for 20 min, separating the metal salt solution from the precipitate of the metal salts of humic acid. At pH < 5, the concentration of humic acids in the solution after centrifugation did not exceed the experimental error.

The concentration of metal ions in the solution, following the precipitate removal, was determined by spectrophotometric analysis of ammonia complexes of copper (II) and cobalt (II) at wavelengths of 540 nm and 490 nm, respectively. The amount of bound metal ions was calculated as the difference between the initial metal ion concentration in the mixture and the concentration remaining in the solution after the precipitate removal.

The interaction of humic acids with trivalent metal ions was studied as follows. Pre-prepared mixtures of humic acids with ferric sulfate, aluminum sulfate, or chromium nitrate were obtained by adding a calculated volume of a 2–15 % aqueous metal salt solution to a 2–10 % aqueous solution or dispersion of humic acids at 18 °C under continuous stirring. The pH of the dispersion was adjusted using hydrochloric acid or sodium hydroxide solutions. The dispersion was stirred for 2 hours at 18 °C before a final pH adjustment. The experiment was repeated one or two times. Once the pH remained stable for 4 hours, the dispersion was centrifuged.

The initial concentrations of metal ions and humic acids in the mixtures were calculated based on the total volume, ranging from 0.5 to 200 mmol/L for metal ions and from 1 to 50 g/L for humic acids. The concentration of humic acids in water after centrifugation (10,000 s^{-1}, 30 min) was determined using gravimetric and colorimetric methods. The optical density of the solution was measured at 400 nm using a Specord 40 spectrophotometer. The discrepancy between the results obtained by these two methods did not exceed 5 %.

The concentration of metal ions in the solution at pH 3 was determined colorimetrically after centrifugation. For iron ions, ammonium rhodanide was added to form an iron-rhodanide complex, whose optical density was measured at 364 nm. The concentration of chromium ions was determined after oxidation with perchloric acid, followed by the formation of a complex with 1,5-diphenylcarbazide, which was analyzed at 540 nm. The amount of bound metal ions was calculated as the difference between the initial metal ion concentration and the concentration remaining in the solution after centrifugation.

3. Results and Discussion

Studies of the interaction between humic acids and divalent metal ions at different pH values were carried out by the potentiometric titration method and spectrophotometrically. Depending on the pH value, the solubility of humic acids in water increases with increasing pH of the medium from 3 to 8, reaching a maximum. A decrease in pH below 3 leads to a slight increase in dissolution, which is obviously due to the presence of amino groups in its structure. The titration curve of humic acids with an alkali solution shows the presence of both free acid groups, which are titrated at pH 7, and acid groups bound to amino groups of the humic acids, which are titrated at pH 11. On the reverse titration curve of the ammonium salt of humic acids, an inflection point is observed at pH 7. Hence, the calculated amount of free and bound acid groups is, respectively, 1.9 and 1.7 mmol/g of humic acids.

Humic acids in aqueous dispersion exhibit ion-exchange properties. When their dispersion is mixed with a solution of NaCl or $CaCl_2$, a significant decrease in pH is observed. The pH of the solution after separation of the humic acid precipitate is nearly identical to that of the initial dispersion, obviously indicating the binding of humic acid particles with metal ions. Potentiometric titration of a humic acid dispersion with NaCl or $CaCl_2$ solutions (Fig. 1) shows that the inflection points of the titration curves correspond to the maximum binding capacity of the humic acids for sodium and calcium ions. The metal chloride-to-humic acid ratios at these inflection points are 7.9 and 25 mmol/g for Na^+ and Ca^{2+}, respectively.

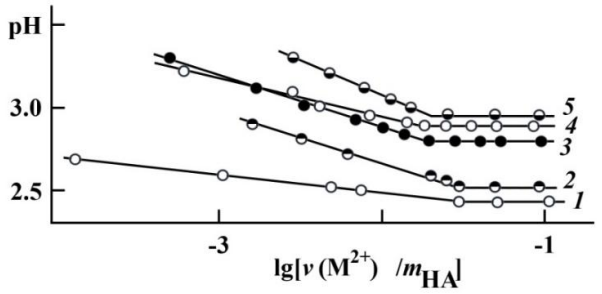

Fig. 1. Potentiometric titration curves of humic acid dispersions with $CaCl_2$ (1, 2, 5) and NaCl (3, 4) $\nu(M^{2+})/m_{HA}$ (mol/g). Metal chloride concentration is 10 %. Humic acid dispersion concentrations (%): 1 – 10, 2, 3 – 5, and 4, 5 – 2

At a pH close to 3, mixed calcium salts with humic acid carboxyl groups and chloride ions, such as R-COOCaCl, are likely to form. It should be noted that not all acid groups of humic acids participate in interactions with metal ions in NaCl and $CaCl_2$ solutions, as the total acid group content determined by sodium hydroxide titration is 3.6 mmol/g.

Titration of a $CuSO_4$ solution with a humic acid dispersion at pH 2.8 reveals that the minimum pH value during titration is nearly equal to the initial pH of the humic acid dispersion (Fig. 2, curve 2). The inflection point occurs at a ratio of $\nu(CuSO_4)/m_{HA}$ = 1.6 mmol/g, which is higher than for NaCl and $CaCl_2$. Notably, the position of the inflection point is independent of the initial pH of the humic acid dispersion or its sodium salts (Fig. 2, curves 2 and 3). However, increasing the initial pH of the humic acid solution raises the minimum pH observed on the titration curve.

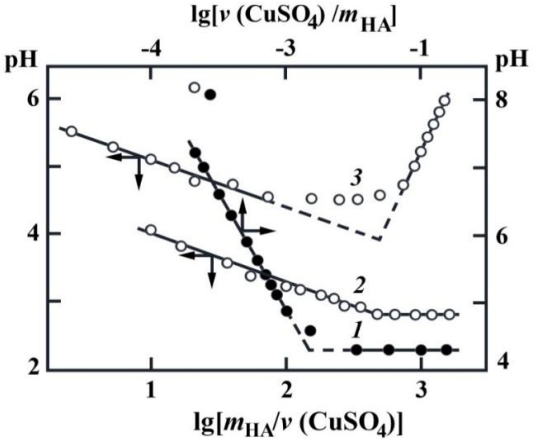

Fig. 2. Curves of potentiometric titration of (1) a solution of sodium salts of humic acids (pH 7.8) with $CuSO_4$, (2) a solution of $CuSO_4$ with a dispersion of humic acids (10 %, pH 2.8), and (3) a solution of $CuSO_4$ with a solution of sodium salts of humic acids (pH 7.6). $\nu(CuSO_4)$/mHA represents the ratio of $CuSO_4$ to humic acid (mol/g). $CuSO_4$ concentrations (%): 1 – 7.9, 2 – 1.9, 3 – 3.95. Concentrations of sodium salt of humic acids (%): 1 – 1; 2, 3 – 5

When titrating a solution of the sodium salt of humic acids (pH 7.9) with $CuSO_4$, the minimum pH observed aligns closely with that of a copper (II) salt solution, ranging between 3.8 and 4.6 due to salt hydrolysis. Despite the difference in pH, the $\nu(CuSO_4)/m_{HA}$ value at the inflection point remains consistent with previously observed values. At the inflection point, precipitation of the copper salt of humic acids occurs.

The relationship between the amount of Cu^{2+} ions bound to humic acids after centrifugation and the initial $CuSO_4$ concentration in the mixture was also studied. Results show a linear increase in the quantity of bound Cu^{2+} with increasing initial copper salt concentration. This linearity indicates an equilibrium interaction, as confirmed by a proportional relationship between the concentration of bound copper ions and their concentration in solution (Fig. 3).

An increase in the pH of the mixture from 4.0 to 4.6 promotes the formation of the copper salts of humic acids, as evidenced by the increased slope of the straight lines (Fig. 3, curves 1 and 2). At pH values close to 7 and low copper concentrations, water-soluble humic acid salts are formed that cannot be precipitated. However, at higher Cu^{2+} concentrations and near-neutral pH, precipitates of both copper (II) hydroxide and the copper salts of humic acids form.

The excess amount of bound copper ions – up to 40 mmol/g of humic acids – compared to the 3.64 mmol/g of acid groups in the humic acids indicates the formation of poorly soluble basic copper salts.

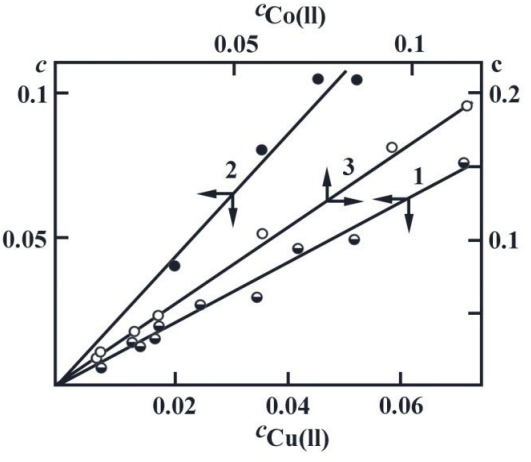

Fig. 3. Effect of the amount of copper (II) $c_{Cu(II)}$ (1, 2) and cobalt (II) $c_{Cu(II)}$ ions (3) bound by humic acids on their concentration in solution c (mol/L). Initial humic acid concentrations (g/L): 1 and 3 – 2.5; 2 – 1.25. pH of the mixture: 1 – 4.0; 2 and 3 – 4.6

The potentiometric titration curves of cobalt (II) and nickel (II) salts with sodium salts of humic acids (pH 7.6) exhibit a profile similar to that observed for

copper (II) sulfate (Fig. 4). At low concentrations of humic acids, a marked decrease in pH occurs, attributed to the reaction of metal cations with free carboxyl groups and partial complexation with amino groups. This reaction leads to the release of acid anions and protons into the solution. As titration proceeds, a plateau is observed on the pH curve. The minimum pH value of the mixture increases in accordance with the metal ion series in which the pH required for the precipitation of metal hydroxides increases: copper (II) < cobalt (II) < nickel (II).

The inflection points of the titration curves are close and correspond to ratios ($\nu(M^{2+})/m_{HA}$) of 1.6, 2.0, and 1.4 mmol/g for Cu^{2+}, Co^{2+} and Ni^{2+}, respectively. The plateau region in the titration curves is likely due to the formation of basic metal salts of humic acids. An increase in the concentration of sodium salts of humic acids leads to a progressive elevation in the pH of the mixture. The study of the binding of cobalt(II) ions with sodium salts of humic acids as a function of Co^{2+} concentration in aqueous solution at pH 4.6 revealed a linear relationship (Fig. 3, curve 3), similar to that observed for copper(II) ions.

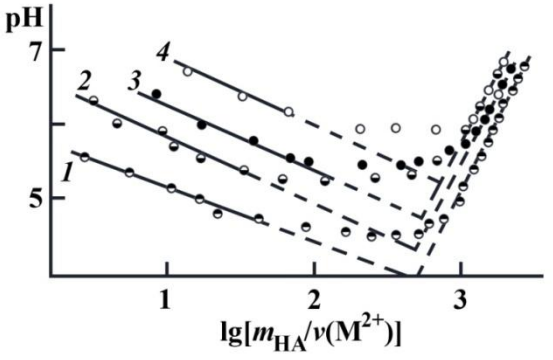

Fig. 4. Potentiometric titration curves of $CuSO_4$ (1), $CoCl_2$ (2, 3), and $NiSO_4$ (4) solutions with a solution of sodium salts of humic acids (initial pH 7.6) $\nu(M^{2+})/m_{HA}$ (mol/g). Metal salt concentrations (%): $CuSO_4$ – 0.395 (1), $CoCl_2$ – 2.0 (2) or 0.25 (3), and $NiSO_4$ – 0.25 (4). Concentration of sodium salts of humic acids is 5 % (1) or 10 % (2–4)

For cobalt (II) ions, the slope of the straight-line dependence is 1.67, which is lower than that observed for copper (II) ions. This indicates that the decomposition of basic cobalt salts with humic acids occurs to a greater extent than that of copper salts under the same pH conditions. This behavior aligns with the higher pH required for the transition of cobalt (II) and copper (II) salts into their respective hydroxides in water and supports the previously proposed hypothesis regarding the formation of basic metal salts with humic acids.

An analysis of these results, along with the findings from our previous studies[15], suggests that the solubility of humic acids depends significantly on the pH of the solution. Upon the addition of sodium hydroxide to a dispersion of humic acids at an initial pH of approximately 3, the solubility of the humic acids increases, reaching a maximum near pH 8, where they are almost completely dissolved. A decrease in pH below 3 results in a slight increase in solubility, likely due to the presence of amino groups in the structure of the humic acids.

The study of humic acid solubility at pH 6.8, upon the addition of aluminum, chromium, and iron salts, showed that dispersions are formed at salt concentrations below 1 mmol/L. Increasing the salt concentration leads to a corresponding increase in dispersed phase content. After centrifugation and separation of the precipitate, the concentration of humic acids in the supernatant decreases (Fig. 5), while the concentration of metal salts in the mixture prior to centrifugation increases.

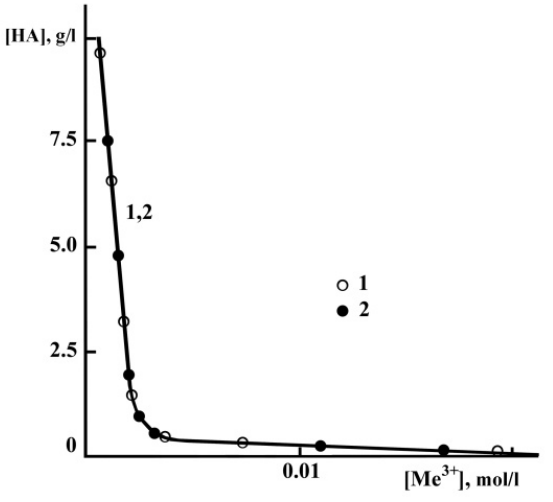

Fig. 5. Effect of the initial concentration of chromium (1) and aluminum ions (2) on the humic acid concentration (the initial humic acid concentration is 12.5 g/L and pH 6.8)

A significant portion of the humic acids precipitates when 40 mmol/L of chromium or aluminum salts is added. At this point, the molar ratio of metal salt to the acidic functional groups of humic acids approaches 3, and the pH of the solution decreases to about 4. In mixtures of humic acids with ferrous sulfate, the pH drops to 3 when the concentration of trivalent iron salts is about 30 mmol/L. Under these conditions, humic acids become practically insoluble.

The solubility of humic acids is strongly dependent on the pH of the solution. When sodium hydroxide is added to a dispersion of humic acids at an initial pH of around 3, their solubility increases significantly, and they become almost fully soluble at pH values approaching 8 (Fig. 6, curve 1). In contrast, the addition of a trivalent metal salt to the dispersion decreases the solubility of

humic acids. In the presence of the aluminum salt, humic acids remain practically soluble at pH values above 10, likely due to the formation of sodium aluminate and sodium humate in this pH range (Fig. 6, curve 2).

When iron salts are present, the solubility of humic acids increases above pH 7; however, even at pH 11, no more than 60 % of the humic acids are in solution (Fig. 6, curve 3). In this case, insoluble iron salt particles form and become adsorbed onto the macromolecules of the humic acids.

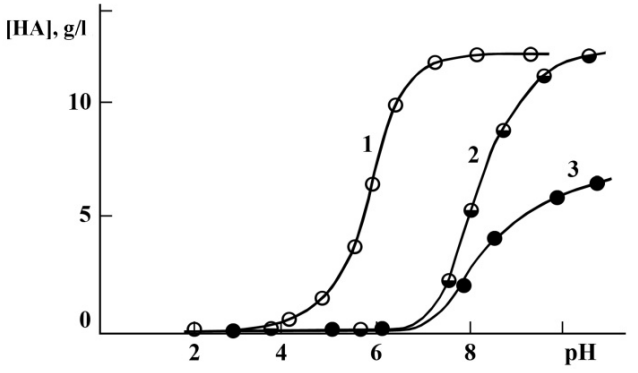

Fig. 6. Dependence of humic acid concentration in solution on pH, at an initial humic acid concentration of 12.5 g/L: without added metal ions (1), with aluminum ions at 62 mmol/L (2), and with iron ions at 58 mmol/L(3)

A study of metal ion interactions with humic acids at pH 3.2 (Fig. 7) revealed that the amount of metal ions bound to humic acids is proportional to the metal ion concentration in solution. At low initial concentrations of iron ions, their concentration in solution approaches zero. Within the pH range of 3 to 6.8, the initial pH of humic acid dispersions remains practically unchanged regardless of the amount of bound iron ions (Fig. 7, curves 1 and 2).

The ratio of bound iron ions to the acidic functional groups of humic acids reaches 1.5 at a metal ion concentration of 40 mmol/L, suggesting that not all iron ions are chemically bound to acidic sites – some are likely adsorbed onto the macromolecular structure, contributing to particle formation. In comparison, the concentration of chromium ions bound to humic acids is lower than that of iron ions (Fig. 7, curve 3).

The ratio of chromium ions bound to humic acids to the concentration of acidic functional groups of humic acids in the mixture remains below 1 when the concentration of chromium ions in solution is about 60 mmol/L. The observed difference in the interaction of humic acids with chromium and iron ions may be attributed to differences in the degree of hydrolysis of their respective salts. In our experiments, dilute metal salt solutions were used, which were partially hydrolyzed prior to interaction with humic acids. Thus, the reactions occurred between humic acids and the hydrolysis products of the metal salts.

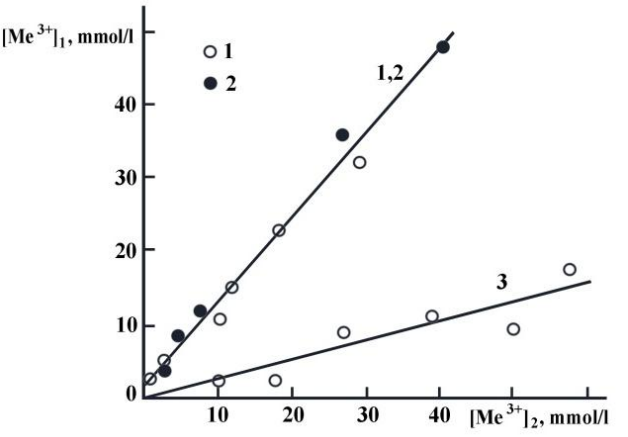

Fig. 7. Relationship between the amount of metal ions bound to humic acids and their concentration in aqueous solution at pH 3.2 for iron ions (curves 1 and 2) and chromium ions (curve 3). The initial pH of the humic acid dispersion is 6.8 for curve 1 and 3.2 for curves 2 and 3. The concentration of humic acids is 10–15 g/L

A study of the pH of aqueous metal salt solutions provides insight into the mechanism of the initial stage of humic salt formation. Hydrolysis of trivalent metal salts can proceed according to the following reactions:

$$[Me(H_2O)_6]^{3+}=[Me(OH)(H_2O)_5]^{2+}+H^+, \quad (1)$$

$$2[Me(H_2O)_6]^{3+}=[Me_2(OH)(H_2O)_9]^{5+}+H^++2H_2O, \quad (2)$$

$$2[Me(H_2O)_6]^{3+}=[Me_2(OH)_2(H_2O)_8]^{4+}+2H^++2H_2O. \quad (3)$$

The formation of aqua-cationic dimers through hydrolysis of trivalent metal salts has been described elsewhere[6, 17–20].

From reactions (1)–(3), the following equations were derived to relate pH to the initial concentration of metal ions at equilibrium:

$$-pH=\frac{1}{2}\lg\left(K_p\right)+\frac{1}{2}\lg\left(\left[Me\left(H_2O\right)_6\right]_6^{3+}-\left[H^+\right]\right) \quad (4)$$

$$-pH=\frac{1}{2}\lg\left(K_p\left[H_2O\right]^2\right)+\frac{1}{2}\lg\left(\left[Me\left(H_2O\right)_6\right]_6^{3+}-2\left[H^+\right]\right) \quad (5)$$

$$-pH=\frac{1}{3}\lg\left(K_p\left[H_2O\right]^2\right)+\frac{2}{3}\lg\left(\left[Me\left(H_2O\right)_6\right]_6^{3+}-2\left[H^+\right]\right) \quad (6)$$

where K_p is the equilibrium constant and $\left[Me\left(H_2O\right)_6\right]_6^{3+}$ is the initial concentration of metal ions.

As shown in Eqs. (4)–(6), the coefficients preceding the logarithmic terms differ, making it possible to determine the dominant hydrolysis reaction based on experimental data on the pH dependence of the initial metal salt concentration.

Experimental results for the hydrolysis of aluminum sulfate, chromium nitrate, and iron sulfate

follow linear trends according to Eqs. (4)–(6) (Fig. 8). The slopes of the corresponding lines are approximately 1.0 for aluminum and chromium salts, and 0.75 for iron salts. Therefore, the dominant hydrolysis reaction is reaction (2) for aluminum and chromium salts, and reaction (3) for iron salt.

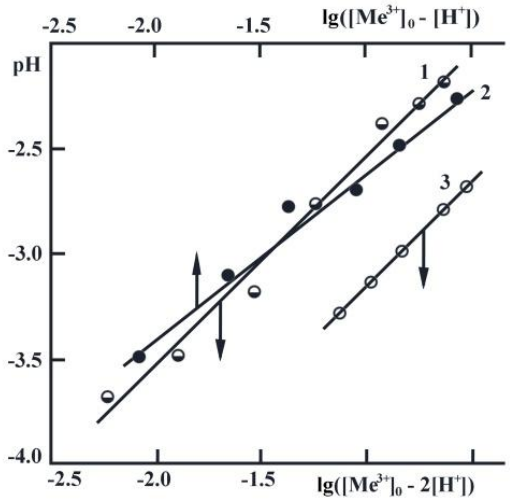

Fig. 8. Dependence of solution pH on the concentration of chromium nitrate (1), iron sulfate (2), and aluminum sulfate (3). Curves (1) and (3) are described by Eq. (5), and curve (2) by Eq. (6)

Straight-line fits based on Eq. (5) for aluminum and chromium salts, and Eq. (6) for iron salt are shown in Fig. 8. The correlation coefficients are 0.996, 0.991, and 0.988, respectively. The slopes of the fitted lines are 1.01 ± 0.07 for aluminum, 0.98 ± 0.08 for chromium, and 0.77 ± 0.10 for iron salts.

The logarithms of the equilibrium constants, calculated using Eq. (5), are –4.31 ± 0.08 L^2/mol^2 for aluminum and –3.15 ± 0.16 L^2/mol^2 for chromium salts. For iron salt, the logarithm of the equilibrium constant calculated using Eq. (6) is –2.39 ± 0.19 L^3/mol^3, which is close to the known value of –2.91 reported elsewhere[18–22].

4. Conclusions

Humic acids in aqueous dispersions exhibit ion-exchange properties. The pH of the solution after the precipitation of humic acids remains close to that of the initial dispersion, indicating the binding of metal ions by humic acid particles.

Humic acids and their salts bind transition metal ions in aqueous solutions within a pH range of 3 to 5. The amount of metal ions bound increases with rising pH, particularly from 4.0 to 4.6.

The inflection point on the potentiometric titration curves of divalent metal salt solutions shows minimal dependence on the initial pH of the humic acids or their sodium salts. These inflection points correspond to 1.6, 2.0, and 1.4 mmol/g of humic acid for copper(II), nickel(II), and cobalt(II) ions, respectively.

The addition of trivalent metal salts to humic acid dispersions decreases their solubility. In the presence of aluminum salt, humic acids are practically soluble at pH values above 10, likely due to the formation of sodium aluminate and sodium humate. In contrast, in the presence of iron salt, humic acid solubility increases at pH values above 7; however, even at pH 11, no more than 60 % of the humic acids are dissolved.

Studies of humic acid interactions with trivalent metal ions at pH 3.2 indicate that the amount of metal ions bound is proportional to their concentration in solution. At low initial concentrations of iron ions, their residual concentration in solution approaches zero. Moreover, the initial pH value of humic acid dispersions (within the range of 3–6.8) remains largely unaffected by the amount of bound iron ions.

The binding capacity of humic acids for chromium ions is lower than for iron ions. This difference may be attributed to variations in the degree of hydrolysis of their respective salts.

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ХАРАКТЕРИСТИКА ТА ВЗАЄМОДІЯ ГУМІНОВИХ КИСЛОТ З ІОНАМИ МЕТАЛІВ ЗАЛЕЖНО ВІД pH СЕРЕДОВИЩА

Анотація. *Досліджено розчинність гумінових кислот залежно від pH розчину, а також взаємодію іонів дво- та тривалентних металів з гуміновими кислотами за різних значень pH середовища. Встановлено, що гумінові кислоти та їхні солі взаємодіють з іонами двовалентних перехідних металів у водному розчині за низьких значень pH. Показано, що кількість зв'язаних з гуміновими кислотами іонів двовалентних металів міді, кобальту та нікелю зростає практично лінійно зі збільшенням їхньої початкової концентрації. Кількість зв'язаних іонів металу також збільшується зі зростанням pH середовища. Під час дослідження взаємодії іонів заліза, алюмінію та хрому з гуміновими кислотами за різних значень pH суміші встановлено, що кількість іонів металу, зв'язаних з гуміновою кислотою, пропорційна до концентрації іонів металу у водному розчині за низьких значень pH і низьких концентрацій іонів металів.*

Ключові слова: *гумінові кислоти, іони міді, кобальту, нікелю, заліза, алюмінію, хрому, pH.*