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Copper(II) and lead(II) complexation by humic acid and humic-like ligands

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Abstract: The stability of metal–humate complexes is an important factor determining and predicting speciation, mobility and bioavailability of heavy metals in the environment. A comparative investigation of the complexation of Cu(II) and Pb(II) with humic acid and humic-like ligands, such as benzoic and salicylic acid, was performed. The analysis was realized at pH 4.0, a temperature of 25 °C and at an ionic strength of 0.01 mol dm⁻³ (NaCl) using the Schubert ion-exchange method and its modified form. The stability constants were calculated from the experimental data by the Schubert method for complexes with benzoic and humic acid. A modified Schubert method was used for the determination of the stability constants of the complexes with salicylic acid. It was found that Cu(II) and Pb(II) form mononuclear complexes with benzoic and humic acid while with salicylic acid both metals form polynuclear complexes. The results indicate that Pb(II) has a higher binding ability than Cu(II) to all the investigated ligands. The Cu(II)–salicylate and Pb(II)–salicylate complexes showed noticeable higher stability constants compared with their complexes with humic acid, while the stabilities of the complexes with benzoic acid differed less. Salicylic and benzoic acids as humic-like ligands can be used for setting the range of stability constants of humic complexes with Cu(II) and Pb(II).

Keywords: copper; lead; benzoic acid; salicylic acid; humic acid; Schubert's method.

INTRODUCTION

Heavy metals introduced into soil and natural waters are involved in a number of chemical, physical, and biological processes that determine their concen-

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trations. The bioavailability of a metal depends on its chemical form, which is strongly affected by the presence of natural and anthropogenic ligands. The complexation of metals with ligands can drastically change the physico-chemical and biological properties of the metal species.¹

The binding or complexing of metal ions by humic substances (HS), as widely distributed natural ligands in soil and natural waters, is an important factor determining metal toxicity, bioavailability and transport.²⁻⁴ Humic and fulvic acids, as fractions of humic substances, are the most important HS components that, due to their high structural complexity, contribute to the overall fate of trace metal cations, such as Pb(II), Cu(II), Zn(II) and Cd(II), in environment.⁵⁻⁷ They contain a variety of functional groups which may react with metal ions. Humic acid (HA) with its hydroxyl, phenoxyl and carboxyl reactive groups can form coordination compounds with metals. The large number of ionizable sites in the humic acid molecule, mainly phenolic and carboxylic groups, provide the appreciable ability to form stable complexes and chelates with heavy metal cations (Pb(II), Cu(II), Zn(II) and Cd(II)).⁸

The mobility of humic-metal complexes in soils and aquifers strongly depends on their charging behavior which is influenced by the ambient pH value.² Metal ion binding to HA depends on the competition between metal ions and protons for the available binding sites and the electric charge of the humic macromolecule.^{9,10} As the pH increases, the macromolecule becomes increasingly negatively charged attracting the positively charged metal ions and protons. Thus, in defining the ion binding process of humic substances, it is necessary to specify the pH value of the system.¹¹

The study of Cu(II) and Pb(II) interactions with HS is of great interest in terms of the environmental impact of metals due to the ability of HS to immobilize these ions by sorption processes.^{12,13} Humic matter-metal ion stability constants have been determined by a variety of different analytical techniques,¹⁴ such as potentiometric titration,¹⁵ equilibrium dialysis,¹⁶ ion selective electrode (ISE) techniques,¹⁷ scanned stripping voltammetry and dynamic light scattering techniques.¹⁸ The Schubert ion-exchange method is a popular method for determining the stability constants of metal ions and humic acid.^{19,20} This method is based on the competition of a metal to bind to a ligand or resin, which lead to its distribution between solution and solid phase. The concentration of metal is measured in the presence and absence of a dissolved ligand.²¹

In this study, benzoic and salicylic acid were used, as discrete ligand models, for the study of complexation properties of humic acid. Their structure is a simplified form of the humic structure, which can be seen in Fig. 1.

The understanding of complexation process is hindered by the fact that humic acids are assemblage of large polyfunctional molecules, such as lipids, carbohydrates, aromatics, *etc.* having a great variety of functional groups and metal

binding sites. Thus, a full and detailed description of metal binding is hard to obtain. However by using “simpler” and stoichiometrically defined ligands of known chemical structure and with similar binding sites to those of humic in the context of chemical composition, electronic and steric effects, a prediction of humic–metal binding can be performed.¹⁷ Considering the fact that the major binding sites of humic acid are attributed to the oxygen-containing functional groups, *i.e.*, carboxylic and phenolic groups, the employment of benzoic and salicylic acids as humic model ligands is justified.¹⁵

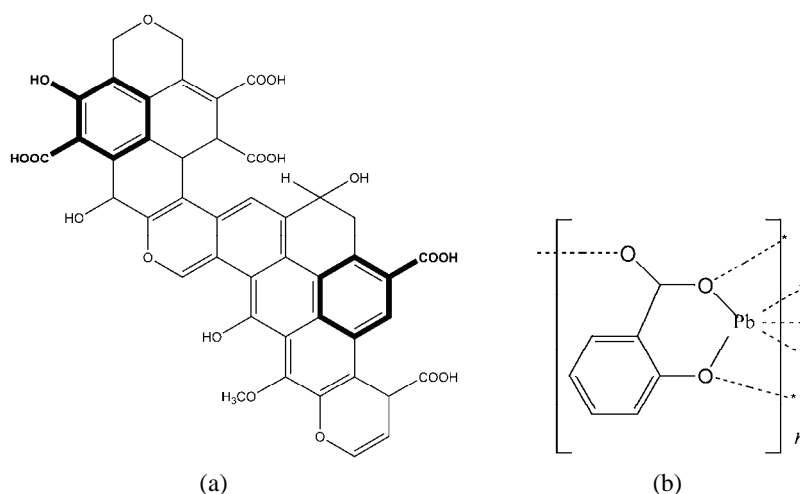


Fig. 1. a) Proposed structural formula of humic acid with possible ion binding sites indicated; b) interaction of oxygen donor groups in salicylic acid with Pb(II) ion.

The information obtained using benzoic and salicylic acids can be useful in the difficult task of evaluation of the nature and the contribution of the donor sites of humic acid to complexation.

EXPERIMENTAL

Chemical reagents, instrumentation and resin preparation

All the used chemicals were of analytical grade purity and purchased from Merck ($\text{Pb}(\text{NO}_3)_2$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, benzoic acid, salicylic acid) and Aldrich (HA, catalog H1, 675-2 lot No. S15539-264). Stock metal solutions of Cu(II) and Pb(II) (1000 mg L^{-1}) were prepared by dissolving appropriate amount of the metal salts in 0.1 M HCl . Aldrich HA was purified by the same procedure that is recommended for purification of HA isolated from soil, in order to remove ash content, residual fulvic acids and heavy metals. Its main characteristics are summarized in Table I. Three different concentrations of ligands were used (0.005 , 0.01 and 0.015 mol L^{-1} for benzoic and humic acid, 0.005 , 0.0075 and 0.015 mol L^{-1} for salicylic acid). All solutions were prepared using double deionized water (conductivity less than $0.1 \mu\text{S cm}^{-1}$). Metal ion solutions were adjusted to pH 4.0 by the addition of 0.1 M NaOH or HCl with a constant ionic strength of 0.01 mol dm^{-3} .

Measurements of pH were made with a Hach Sension 3 pH-meter (precision 0.1 mV or 0.001 units of pH) using a Hach gel-filled combination glass electrode (51935-00). All experiments were performed at 25 ± 1 °C.

TABLE I. Main characteristics of the humic acids used in this study

Elementary analysis	Content, %	Functional group	Concentration, mmol g ⁻¹
C	54.47	Total acidity	6.48
H	3.82	COOH	3.94
N	0.75	Phenolic OH	2.54
S	3.80	–	–
O	29.26	–	–
Ash content	3.7	–	–
Moisture content	4.2	–	–

The prepared solutions were analyzed by flame atomic absorption spectroscopy (AAS) using an AAnalyst 300 (Perkin Elmer) instrument.

For each experiment, Dowex 50WX8, 100–200 mesh, Na-form cation exchange resin was used. Approximately 50 g of the resin was stirred with deionized water. Fine particles were decanted off and the resin was transferred to glass column containing deionized water. Then, the resin was rinsed with 2 L of deionized water, followed by 2 L of 2 M HCl, 2 L of 2 M NaOH, and rinsed with 2 L of deionized water. The resin was converted into the Na-form by passing 2 L of 2 M NaCl, followed by a 2 L rinse with deionized water. The resin was air-dried for 24 h, and then stored in an air-tight polyethylene container.

The time to attain equilibrium was investigated for both metal ions by taking an accurately known amount of Na-saturated cation exchange resin and 50.0 ml of metal ion solution. Samples were shaken and period to attain equilibrium was determined by measuring the concentration of the respective metal ions in the supernatant. Equilibrium was achieved after 1 h.

Experimental procedure for establishing metal/ion-exchange isotherms (D_0)

Ion-exchange isotherms were measured at pH 4.0 for each metal Cu(II) and Pb(II). For each measurement, metal solutions were prepared by adding different volumes of metal stock solutions to 50.0 mL volumetric flask together with 0.01 M NaCl, and the pH was adjusted by the addition of 0.1 M NaOH and/or 0.1 M HCl. Accurately weighed, 100.0 mg of cleaned, Na-saturated cation exchange resin was added to 50.0 mL of the prepared metal solutions. All samples were shaken at constant temperature for 2 h at 25 °C.

Experimental procedure for the determination of the conditional stability constant of the metal–ligand complexes (D)

The ion-exchange procedure used to determine stability constants for ligands and divalent metal ion was similar to the procedure used to establish the distribution coefficient, D_0 , with difference that the solution contained ligand.²²

Each solution contained variable concentration of metal ions, from 5 to 20 mg L⁻¹ for Cu(II) and Pb(II), and a concentration of organic acid (benzoic, salicylic or humic acid), from 5 to 15 mol L⁻¹, at pH 4.0, with 100 mg of Dowex 50WX8 (100–200 mesh) resin in the Na-form and was shaken for 2 h at 25 °C. The total concentration of free metal ion and complexed metal ion remaining in the equilibrium solution was determined in the supernatant by flame AAS.

RESULTS AND DISCUSSION

The isotherms for both metal ions at 25 °C temperature and pH 4.0 were investigated. The experiments were performed at pH 4.0 to avoid hydrolysis of the metal ions and carbonate formation. The linear range was obtained from each isotherm curve to estimate the D_0 in order to choose the appropriate concentrations for both metal ions to avoid the effect of metal loading.

The distribution coefficient, D_0 , between the resin and solution phase for metal ion in the absence of ligand and the distribution coefficient, D , between resin and solution phase for metal ion in presence of ligand was calculated from the equilibrium ratio:

$$D_0 = \frac{\alpha_0 V}{(100 - \alpha_0) m_r} \quad (1)$$

where α_0 is percentage of total metal bound to the exchange resin; $(100 - \alpha_0)$ is percentage of the total metal remaining in solution; V is volume of solution (mL) and m_r is mass of the exchange resin (g).

The number of equivalents of complexing agent, n , combined with a particular metal ion was found from the slope of the linear function:

$$\log \left(\frac{D_0}{D} - 1 \right) = \log \beta_{mn} + n \log c_L \quad (2)$$

where c_L is the concentration of ligand (mol L^{-1}).

Equation (2) was used to determine conditional stability constants for the mononuclear complexes. Possible problems with the Schubert method can occur when the complex, $M_m L_n$, is not mononuclear ($m \neq 1$). Equation (3) presents the equation for the modified Schubert method, which was used to eliminate this source of error and presents the modified method of data treatment and analysis:

$$\log M_c = \log \left(\frac{D_0}{D} - 1 \right) = \log m + \log \beta_{mn} + (m - 1) \log M + n \log c_L \quad (3)$$

Equation (3) was used to calculate $\log \beta_{mn}$ for polynuclear complexes.²²⁻²⁵ Equation (2) is a reduced form of Eq. (3) for the case of $m = 1$, when a mononuclear complex is present. The metal-ligand ratios were obtained from the slopes of the curves $\log (D_0/D - 1)$ vs. $\log c_L$ (Fig. 2) according to the Schubert method, and $\log M_c$ vs. $\log c_L$ (Fig. 3) according to the modified Schubert method. The slopes of these plots give the composition of the complexes, which when close to unity indicate a 1:1 metal:ligand ratio. Values of n near 1.5 indicate that the stoichiometry of the complexes is 2:3.

The percentage of total metal bound to the exchange resin, α_0 , the values of the slope, n , and stability constants, $\log \beta_{mn}$, obtained for Cu(II) complexes (at 5

mg L⁻¹ Cu(II) concentration) with the investigated ligands, at pH 4.0 are summarized in Table II.

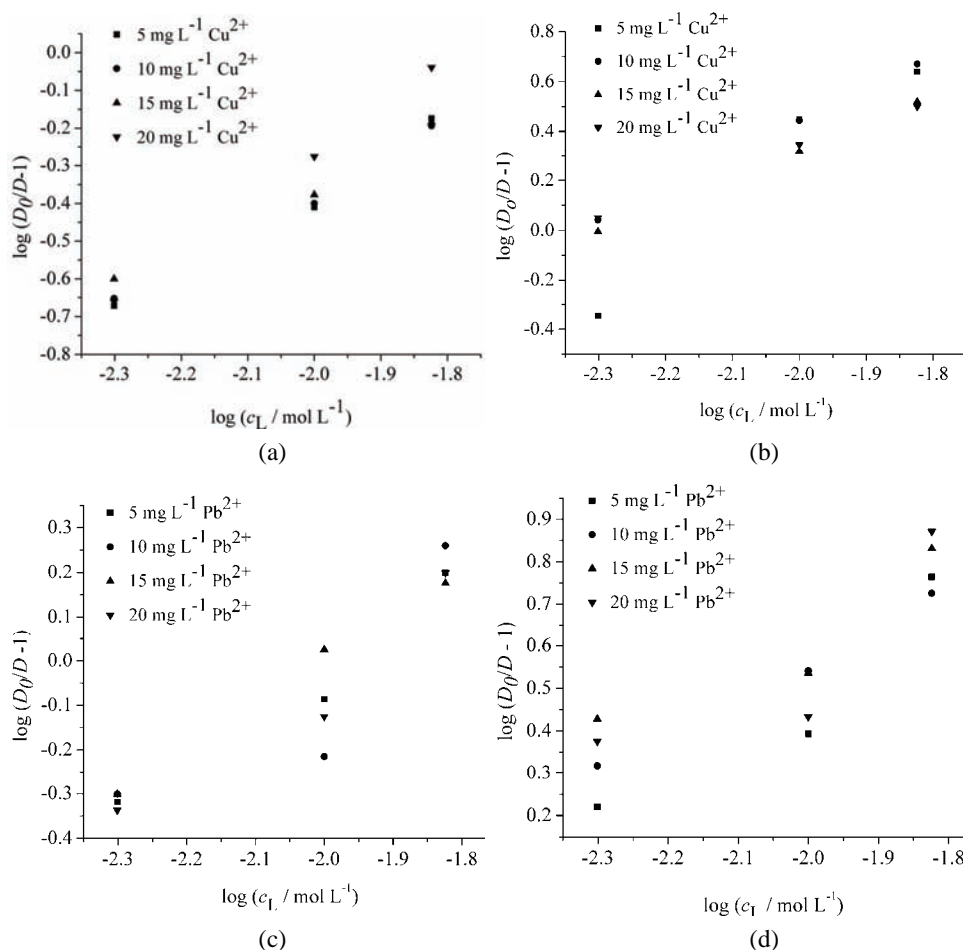


Fig. 2. Plots of $\log(D_0/D-1)$ vs. $\log c_L$ for a) Cu(II)–benzoic acid; b) Cu(II)–humic acid; c) Pb(II)–benzoic acid and d) Pb(II)–humic acid, obtained by the Schubert method.

These results show that percentage of total metal bound to the exchange resin, α_0 , for Cu(II)–salicylate was 54.76 %, which was the highest when compared to the percentage for Cu(II)–humate (49.28 %) and Cu(II)–benzoate (53.70 %). This trend was even more pronounced in the presence of higher humic acid concentrations, that is, more metal was in the solution phase than on the resin, confirming the stronger and multi-site binding and multifunctional characteristics of the humate ligand.

Since the values of n should be an integer, values of $n \approx 1$ indicate that the complexation of Cu(II) with benzoic and humic leads to the formation of 1:1 complexes. In addition, it was noticed that for Cu(II)–salicylate, n was 1.6, and the stoichiometry 2:3 was assigned in this case.

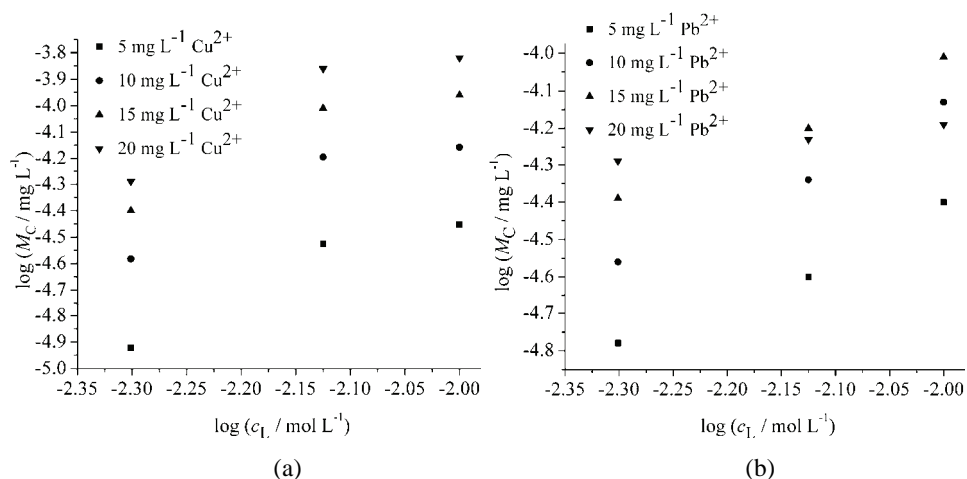


Fig. 3. Plots of $\log M_C$ vs. $\log c_L$ for a) Cu(II)–salicylic acid and b) Pb(II)–salicylic acid, obtained by the modified Schubert method.

TABLE II. Experimentally determined percentages of the total metal bound to the exchange resin, α_0 , distribution coefficients, D_0 , metal–ligand ratios and logarithms of conditional stability constant, $\log \beta_{mn}$, for complexes between Cu(II) (5 mg L^{-1}) and benzoic, salicylic and humic acid, at pH 4.0 and ionic strength of $I = 0.01 \text{ mol dm}^{-3}$, determined by the Schubert method

Acid	$c_L \times 10^3$ mol L^{-1}	α_0	D_0	D	$D_0/D-1$	n	Mole ratio Cu:L	$\log \beta_{mn}$	$\log \beta_{mn}$ (mean)
Benzoic	0	58.52	705.4	–	–	–	–	–	1.62
	5.0	53.70	–	581.53	0.213	–	–	1.63	
	10.0	50.40	–	507.85	0.389	–	–	1.59	
	15.0	45.65	–	422.39	0.670	1.02	1:1	1.65	
Salicylic	0	58.52	705.4	–	–	–	–	–	10.53 ^a
	5.0	54.76	–	605.22	0.16	–	–	11.05	
	7.5	51.52	–	531.35	0.33	–	–	10.49	
	10.0	46.56	–	435.63	0.62	1.60	2:3	10.06	
Humic	0	58.52	705.4	–	–	–	–	–	2.33
	5.0	49.28	–	485.80	0.45	–	–	2.25	
	10.0	27.00	–	184.93	2.81	–	–	2.45	
	15.0	20.84	–	131.63	4.36	1.13	1:1	2.29	

^aObtained by the modified Schubert method

The stability constants obtained for Cu(II)–benzoate, –salicylate and –humate complexes are given in Table II. The most stable complex was the Cu(II)–

–salicylate complex with $\log \beta_{mn}$ 10.53, which corresponds to literature data.²⁶ For determination of these stability constants, the modified Schubert method was applied. The stability constant of the Cu(II)–humate complex was between the stabilities of Cu(II)–salicylate and –benzoate complexes. Stability constants of Cu(II)–humate complexes can differ because of the origin of the humic ligand, but the obtained values were similar and comparable. Variation of stability constants values in humic complexation studies is not uncommon due to differences in the elemental composition of the humics, their chemical structure and period of genesis during the humification process.²⁷

The percentage of total metal bound to the exchange resin, α_0 , the slope values, n , and stability constants, $\log \beta_{mn}$, obtained for the Pb(II) complexes (at a 5 mg L^{-1} Pb(II) concentration) with the investigated ligands, at pH 4.0 and 25°C , are presented in Table III. It was found that percentage of total metal bound to the exchange resin for Pb(II)–benzoate was higher than for Cu(II)–salicylate and Cu(II)–humate in the total metal and ligand concentration range. This is in accordance with the number of binding sites in the ligands. In addition, the differences between the percentages of the total metal bound to the resin for same ligand were greater with increasing concentration of ligand. The values of stability constants presented in Table III show that stability constant of Pb(II)–humate complex was higher than that of the Pb(II)–benzoate complex. Moreover, the Pb(II)–salicylate complex was the most stable, with a value of 10.90 for $\log \beta_{mn}$.

TABLE III. Experimentally determined percentages of the total metal bound to the exchange resin, α_0 , distribution coefficients, D_0 , metal–ligand ratios and logarithms of conditional stability constant, $\log \beta_{mn}$, for complexes between Pb(II) (5 mg L^{-1}) and benzoic, salicylic and humic acid, at pH 4.0 and ionic strength of $I = 0.01 \text{ mol dm}^{-3}$, determined by the Schubert's method

Acid	$c_L \times 10^3$ mol L^{-1}	α_0	D_0	D	$D_0/D-1$	n	Mole ratio Pb:L	$\log \beta_{mn}$	$\log \beta_{mn}$ (mean)
Benzoic	0	52.56	553.96	–	–	–	–	–	1.97
	5.0	42.80	–	374.12	0.48	–	–	1.98	
	10.0	37.80	–	303.86	0.82	–	–	1.92	
	15.0	30.00	–	214.29	1.58	1.05	1:1	2.02	
Salicylic	0	52.56	553.96	–	–	–	–	–	10.90 ^a
	5.0	34.96	–	268.76	1.06	–	–	11.41	
	7.5	30.76	–	222.13	1.49	–	–	10.85	
	10.0	25.60	–	172.04	2.21	1.24	2:3	10.44	
Humic	0	52.56	553.96	–	–	–	–	–	2.50
	5.0	29.40	–	208.21	1.66	–	–	2.52	
	10.0	24.20	–	159.63	2.47	–	–	2.39	
	15.0	14.00	–	81.39	5.81	1.07	1:1	2.59	

^aObtained by the modified Schubert method

According to Table II and III, the results show that the system Cu(II) without ligand had higher value of the percentage of total metal bound to exchange resin than the Pb(II) system.

The stability constants, $\log \beta_{mn}$, and the metal–ligand ratio for the Cu(II) and Pb(II) complexes with all the investigated ligands, shown in Figs. 1 and 2, are summarized in Table IV.

Table IV. Stability constants, $\log \beta_{mn}$, and metal–ligand ratios for complexes between Cu(II) and Pb(II) with benzoic, salicylic and humic acid, at pH 4.0 and ionic strength $I = 0.01 \text{ mol dm}^{-3}$, determined by the Schubert method

Acid	Cu					Pb				
	<i>c</i> mg L ⁻¹	M:L	$\log \beta_{mn}$	$\log \beta_{mn}$ (mean)	Literature value ^{ref}	<i>c</i> mg L ⁻¹	M:L	$\log \beta_{mn}$	$\log \beta_{mn}$ (mean)	Literature value ^{ref}
Benzoic	5	1:1	1.62	1.65	1.60 ²⁸	5	1:1	1.97	1.96	2.00 ²⁸
	10	1:1	1.63			10	1:1	1.90		
	15	1:1	1.65			15	1:1	2.01		
	20	1:1	1.71			20	1:1	1.95		
Salicylic	5	2:3	10.53	10.34 ^a	10.60 ²⁶	5	2:3	10.90	10.51 ^a	–
	10	2:3	10.22			10	2:3	10.60		
	15	2:3	10.10			15	2:3	10.44		
	20	2:3	10.49			20	3:1	10.12		
Humic	5	1:1	2.33	2.35	1.95 ¹² 3.70 ²² 5.28 ²¹	5	1:1	2.50	2.58	2.76 ¹² 3.66 ²¹ 4.78 ²⁴
	10	1:1	2.42			10	1:1	2.57		
	15	1:1	2.32			15	1:1	2.64		
	20	1:1	2.34			20	1:1	2.60		

^aObtained by the modified Schubert method

A comparison of the obtained results for the stability constants and stoichiometry of Cu(II) with benzoic and salicylic acid with literature data indicate that values were approximately the same. The obtained values of the stability constants for the Pb(II)–benzoate complexes were similar with literature data,²⁸ while the values of the stability constant for Pb(II)–salicylate complexes are not available in the literature.

The obtained results, which were derived using the Schubert method and its modified form, indicate that the conditional stability constant, $\log \beta_{mn}$, for the Pb(II)–humate complex was greater than that of Cu(II)–humate at pH 4.0. Pb(II) was found to form the most stable complex with the oxygen-carrying donor groups of humic acid. An explanation for the established stabilities of the Pb(II)– and Cu(II)–humate complexes can be given within the concept of hard/soft acids and bases. Since oxygen, as the donor atom in carboxylic and phenolic groups, exhibits hard base properties (a highly electronegative atom), a strong bond will be formed with hard acids (Pearson's rule). Bearing in mind that the electronic configuration of the Pb(II) ion $18(n-1)e^- + 2ne^-$ classifies it in the borderline metal acids, while Cu(II) ion, the electronic configuration $(n-1)d^9$, classifies it as a soft

metal acid, the greater stability of the Pb(II)–humate complex compared to the complexes with copper can be expected.

The established trend of the stabilities of the metal–humate complexes can be used for predicting the strength of interaction between the donor atoms and the metal ions, as well as to predict their competition in binding to humate ligand. The obtained results indicate that there may be competition between Pb(II) ions and Cu(II) ions in the binding for carboxyl and phenolic binding sites of humate macromolecules. Therefore, under conditions of increased concentrations of Pb(II) ions in the natural environment, Pb(II) may displace Cu(II) ions, which can lead to increasing mobility and bioavailability of copper.

The present results provide important information on the interaction of Cu(II) and Pb(II) with benzoic, salicylic and humic acid, and demonstrate that not only are carboxyl groups involved in metal binding, but also other groups, like phenolic groups, must be involved.

CONCLUSIONS

The Schubert ion-exchange method is applicable for the determination of conditional stability constants of mononuclear complexes while for polynuclear complexes, a modified Schubert ion-exchange method should be applied. The obtained stoichiometry values indicate that humic and benzoic acid form mononuclear complexes with Cu(II) and Pb(II), while salicylic acid forms polynuclear complexes with both metals.

Phenolic acids comprise a significant part of the chemical structure of humic substances showing an important role in complexation properties of HA. Salicylic and benzoic acids, as humic-like ligands, can be used for setting the range of stability constants of humic complexes with Cu(II) and Pb(II). The binding of Pb(II) by HA is stronger than that for Cu(II). The results of this study are important for understanding the mobility and fate of Cu(II) and Pb(II) in the environment.

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ИЗВОД

КОМПЛЕКСИРАЊЕ БАКАР(II) И ОЛОВО(II) ЈОНА ХУМИНСКОМ КИСЕЛИНОМ И МОДЕЛОМ ХУМИНСКОГ ЛИГАНДА

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Стабилност метал–хуматног комплекса представља важан фактор у одређивању и предвиђању специјације, мобилности и биорасположивости тешких метала у животној средини.

У овом раду вршена су упоредна испитивања комплекса Cu(II) и Pb(II) са хуминском киселином и моделом хуминског лиганда, као што су бензоева и салицилна киселина. Испитивања су вршена на рН 4,0 и температури од 25 °C и при јонској јачини од 0,01 mol dm⁻³ (NaCl), помоћу класичне и модификоване Шубертове јоноизмењивачке методе. Константе стабилности за комплексе са бензоеном и хуминском киселином израчунате су помоћу експерименталних података добијених класичном Шубертовом методом. Модификована Шубертова метода је коришћена за одређивање константе стабилности комплекса са салицилном киселином. Утврђено је да Cu(II) и Pb(II) јони формирају мононуклеарне комплексе са бензоеном и хуминском киселином. Такође, утврђено је и да оба метала формирају полинуклеарне комплексе са салицилном киселином. Резултати указују на то да Pb(II) јон има већу способност везивања од Cu(II) јона са свим испитиваним лигандима. Олово и бакар салицилатни комплекси показују већу константу стабилности у поређењу са хуматним комплексима, док се стабилности ових комплекса мање разликују од стабилности комплекса са бензоеном киселином. Салицилна и бензоева киселина се могу користити као модели хуминског лиганда за одређивање опсега константи стабилности комплекса Cu(II) и Pb(II) јона са хуминском киселином.

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