Scientific paper

COMPARATIVE STUDY OF BINDING STRENGTHS OF HEAVY METALS WITH HUMIC ACID

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Abstract

The complexation of humic acid with certain heavy metal ions (Co(II), Ni(II), Cu(II), Zn(II) and Pb(II)) was investigated. The stability constants of humate complexes were determined by method which is based on distribution of metal ions between solution and resin in the presence and the absence of ligand, known as Schubert's ion exchange method. Experiments were performed at 25 °C, at pH 4.0 and ionic strength of 0.01 mol dm^{-3}.

It was found that the 1:1 complexes were formed between metal ions and humic acid. Obtained results of the stability constants, log β_{mn}, of complexes formed between the metal ions and humic acid follow the order Co(II) < Ni(II) < Cu(II) > Zn(II) which is the same like in the Irving-Williams series for the binding strength of divalent metal ion complexes. Stability constant of complex between Pb(II) ions and humic acid is greater than stability constants of other investigated metal-humate complexes.

The investigation of interaction between heavy metal ions and humics is important for the prediction of the distribution and control of the migration of heavy metals in natural environment.

Key words: heavy metal pollution, humic acid, stability constant

Introduction

Heavy metals contamination of the environment is the threat to all living organisms. Since the metals are not biodegraded and that many of them are soluble in water, they can become more available for living systems and can accumulate in the environment [1]. Defining the factors that affect their bioavailability, leaching and toxicity in soil/water systems is of crucial importance.

Industrial discharge to the atmosphere, soil and water is the most important source that contributes to increased concentrations of heavy metals in the environment. The greatest heavy metal dispersion is observed in the areas with metallurgy industries. During processing of the ore, the heavy metals, which occur in nature at very low concentrations, are released to the environment in high concentrations [2]. Around 100 times more lead (Pb), 13 times more copper (Cu) and 21 times more zinc (Zn) are emitted to the atmosphere by human activities than by natural processes. Those industrial areas can be considered as risk areas with regard to trace metals and need to have discharge control or in some cases remediation strategy. These metal ions under certain conditions favor the interaction with the functional groups, such as carboxylic, phenolic, alcoholic, enolic-OH and amino groups. All this shows the necessity for improving the knowledge about heavy metals behavior in soils and waters in order to make accurate risk assessments for human health, define long-term ecological effects, set limit values and identify priorities in remediation of contaminated sites [3].

Heavy metals can be involved in a series of complex chemical and biological interactions. Factors which affect their mobility through soil/water system are pH, redox status of the environment, sorbent nature, presence and amount of organic and inorganic ligands, including humic and fulvic acids, root exudates and nutrients [4].

Humic acid has natural and powerful adsorbent properties and are deeply related to the transportation and accumulation of heavy metals [5,6]. They are widely distributed in soils/waters and the type and structure of their functional groups depend on their genesis but also on method of their isolation and purification [7,8]. They control behavior of heavy metals in the environment and their interactions with metals are complex, depending on the characteristics of humic acid, concentration of metal ions, pH value, *etc* [9]. The complexation of humic acid with metals can affect the fate of metals in soils and waters, thus speciation of metals is affected by these complexes as well as oxidation-reduction reactions. Humic acid can serve as carrier of toxic metals, forming complexes that are stable and enhance transport of toxic metals in waters [10-12].

Environmental implication of humic-metal binding depends on the possibility whether metal ions form soluble humic complexes that can potentially contaminate groundwater and retain the metal in soil solution or metal ions form insoluble humic complexes that will result in a reduction of bioavailability and ecotoxicity of the metals [12,13]. Studies of interactions between humic substances and heavy metals are mainly focused on estimating stability constants at a specific pH and ionic strength [8,9]. Thus, complexation of heavy metals in the very environment is usually assumed or extrapolated for the complex natural system that involve a huge number of different parameters (presence of competition ions, dissolved and particular organic matter, *etc*.). Therefore, investigation of the mechanism of interaction between heavy metal ions and humics is very important for the prediction of the distribution and control of the migration of heavy metals in natural environment [12-14].

Humic matter-metal ion stability constants are determined by a variety of different analytical techniques such as: centrifugation-depletion, equilibrium dialysis, ultrafiltration, chromato-

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graphy, diffusive gradients in thin films, *etc*. Competitive methods are Schubert's method, competing dissolved ligand and kinetic discrimination [15].

The aim of this paper is to predict the behavior of heavy metals regarding the presence of humic acid in the environment, based on the strength of formed complexes. We have determined stability constants of five transition metals by using Schubert's cation exchange equilibrium method. The results confirm that Schubert's method can be used not only for stoichiometrically defined ligands but also for complexes of polyfunctional and stoichiometrically undefined ligands, such humic ligands are. The finding of relative order of metal-humic complexes stabilities can help in estimation of the fate transport and distribution of heavy metals through different compartments of the environment [16-18].

Experimental

Chemical reagents and instrumentation

Stock solutions of each metal were prepared from metal salts ($Pb(NO_3)_2$, $CuCl_2 \cdot 2H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(SO_4)_2 \cdot 6H_2O$). All metal salts were of analytical grade purity (purchased from Merck, Germany). Humic acid was purchased from Aldrich (HA, catalog H1, 675-2 lot No. S15539-264). All solutions were prepared using deionized water (conductivity less than 0.1 $\mu S\ cm^{-1}$). Measurements of pH were made with sensION MM 374 (precision 0.01 units of pH) using a HACH gel-filled glass electrode (LZW5010t.97.002). pH electrode was standardized using commercially prepared pH 4.1, pH 7.0 and pH 10.0 buffers. The prepared solutions were analyzed by Flame Atomic Absorption Spectroscopy (FAAS) using an AAnalyst 300 (Perkin Elmer) instrument.

Experimental procedure of resin preparation

The cation-exchange resin used in determination of stability constants was Dowex 50WX8, 100-200 mesh, Na-form, having an exchange capacity of 1.7 meq cm^{-3}. About 30 g of the resin was prepared by transferring to a glass column, and sequentially rinsing with 2 dm^3 of deionized water, 2 dm^3 of 2 mol dm^{-3} HCl, 2 dm^3 of 2 mol dm^{-3} NaOH and finally with 2 dm^3 of deionized water. The resin was changed in Na-form by passing 2 dm^3 of 2 mol dm^{-3} NaCl, followed by rinse of 2 dm^3 deionized water. The resin was then air-dried for 24 h, and then stored in an air-tight polyethylene container.

Experimental procedure for establishing metal(II) ion-exchange isotherms (D$_0$) and determination of conditional stability constant of metal-ligand complexes

Ion-exchange isotherm was measured at pH 4.0 for each metal (Cu(II), Pb(II), Ni(II), Zn(II) and Co(II)). Metal concentration solutions ranged from 5 mg dm^{-3} to 20 mg dm^{-3}. For each measurement, metal solutions were prepared by adding different volumes of metal stock solutions to 50.0 cm^3 volumetric flask along with 0.01 mol dm^{-3} NaCl, and adjustment of pH with the addition of 0.1 mol dm^{-3} NaOH and/or 0.1 mol dm^{-3} HCl. Accurately weighed, 0.100 g of cleaned, Na-saturated cation exchange resin Dowex 50WX8 (100-200 mesh) was added to 50.0 cm^3 of the prepared metal solutions. All samples were shaken for 2 hours, at constant temperature of 25 °C.

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. Each solution contained variable concentration of metal ions, from 5 to 20 mg dm^{-3} for each metal, and concentration of humic acid, from 0.005 to 0.015 mol dm^{-3}. The solution was adjusted to pH 4.0, 0.100 g of resin in the Na-form was added and

solutions were equilibrated under the same conditions as previous. Each determination was carried out in triplicate.

Results and discussion

The ion-exchange equilibrium method originally develop by Schubert and first applied to water soluble organic matter complexes by Miller and Ohlrogge is the most attractive procedure for the determination of stability constants [19,20]. The equilibrium reaction for chelate or complex formation can be written as (Eq. 1):

$$M + nL \rightarrow ML_n \tag{1}$$

$$K = \frac{[M] \cdot [L]^n}{[ML_n]} \tag{2}$$

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 the resin and solution phase for metal ion in the presence of ligand was calculated by equilibrium ratio (3):

$$D_0 = \frac{\alpha_0 V}{(100 - \alpha_0) m_r} \tag{3}$$

where α_0 is percentage of total metal bound to exchange resin; $(100 - \alpha_0)$ is percentage of total metal remaining in solution; V is volume of solution (cm^3) and m_r is weight of 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 (4):

$$\log\left(\frac{D_0}{D} - 1\right) = \log \beta_{mn} + n \log c_L \tag{4}$$

Parameter c_L is the concentration of ligand (mol dm^{-3}).

Equation (4) is used to determine conditional stability constants for mononuclear complexes. Possible problems with the Schubert's method occurrs when complex, M_mL_n, is not mononuclear

($m \neq 1$). The following Eq. (5) is equation of the modified Schubert's method and that is used to eliminate this source of errors and presents the modified method of data treatment and analysis:

$$\log M_c = \log\left(\frac{D_0}{D} - 1\right) = \log m + \log \beta_{mn} + (m-1)\log M + n \log c_L \qquad (5)$$

Eq. (5) is used to calculate the $\log \beta_{mn}$ for polynuclear complexes. The eq. (4) is a reduced form of eq. (5) for the case when $m = 1$, when a mononuclear complex is present [21-23].

The isotherms for each metal ion were investigated at 25 °C temperature and pH 4.0 in order to avoid hydrolysis of metal ions and carbonate formation. Humic acid was characterized in detail in the previous paper [24].

The isotherm linear range was obtained for each metal in order to estimate D_0 and choose the appropriate concentrations for preventing the effect of metal loading [21-24].

Table 1. gives a summary of the percentage of total metal bound to exchange resin, α_0, distribution coefficient between the resin and solution phase for metal ion in the absence (D_0) and presence (D) of ligand for each of five metals, and values of stability constants, $\log \beta_{mn}$. The presented results show the obtained parameters only for 5 mg dm^{-3} metal ions concentration, while the investigations were done at 10, 15 and 20 mg dm^{-3} metal ions concentrations, also.

Table 1.

The results in Table 1. show that percentage of total metal bound to exchange resin, α_0, for Co(II) is 61.14% and is the highest comparing to other metal ions Cu(II) (58.52%), Pb(II) (52.56%), Zn(II) (31.04%) and Ni(II) (12,48%). For each metal ion, percentage of total metal bound to exchange resin, α_0, decreases with increase of humic acid concentration. This trend was expected because by increasing humic acid concentration, the number of binding sites increases and therefore, the amount of metal absorbed on the resin is reduced.

Figure 1 presents plots of $\log (D_0/D-1)$ vs. $\log c_L$ for each metal ion at four concentrations.

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Figure 1.

The slopes of plots which are presented in Figure 1 give the composition of complexes. Values of *n* close to unity indicate that metal ligand ratio in these complexes is 1:1. Also, Figure 1 shows that the stability sequence of the metal ions under the given conditions is: $Co(II) < Ni(II) < Zn(II) < Cu(II) < Pb(II)$. All those transition metals tend to favor formation of a covalent or coordination bond with the humic ligand with partial or total breakdown of the hydration sphere of the metal. Thus, the investigated metals are more tightly held preferably creating inner sphere complexes than for example, alkali and alkaline earth metals which tend to favor creation of outer sphere complexes, with bonds of purely electrostatic nature, where metal retain their hydration spheres [20].

The stability constants, log β_{mn}, and metal-ligand ratios for complexes between each concentration of Pb(II), Cu(II), Zn(II), Ni(II) and Co(II) ions with humic acid are summarized in Table 2.

Table 2.

The obtained stability constants, log β_{mn}, show that the investigated divalent ions follow the Irving-Williams series type: $Co(II) < Ni(II) < Cu(II) > Zn(II)$ for the binding strength of divalent metal ion complexes in complexation with humic acid, therefore to interact according to the basic principles of the formation of the complex. The Irving–Williams order is based on empirical observation and related to both the increase of effective nuclear charge and increase of atomic number. The position of Cu(II) in Irving-Williams order is considered out-of-line ($Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)$) probably as a consequence of the fact that Cu(II) often forms distorted octahedral complexes. The different affinity of Pb(II), Cu(II), Zn(II), Ni(II) and Co(II) can be explained by their chemical properties such as the size of ion radius ($r_{M^{2+}}$), charge (*z*) of the metal ion, that is ionic potential, $Ip = z/r$, the electronegativity of the element, ligand

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field stabilization energy effects and classification which is based on the electron configuration of the cations and the concept of hard/soft acids and bases (HSAB theory) [23,24].

Stability constants obtained for complexes between Cu(II), Zn(II), Ni(II) and Co(II) and humic acid were founded to be smaller than stability constant obtained for Pb(II) humate complex, which can be explained with HSAB theory. Humic acids behave as weak acid polyelectrolyte with a variety of oxygen containing functional groups such as carboxylic, hydroxyl, phenolic and carbonyl, with oxygen as a donor atom hows hard base properties (high electronegative atom) and makes strong bonds with hard acids. According to the HSAB theory, cations Pb(II) and Cu(II) form stronger complexes with humic acids than with Co(II) and Zn(II). The affinity of the metals to humic acid can also be expected to increase in line with increasing electronegativity. This seems to be true for Cu(II), Ni(II), Zn(II) and Co(II), but not for Pb(II). Tendency of cations to form inner-sphere complexes with humic acid increases with increasing ionic potential (Ip). For the group of divalent metal ions this means that the smaller the radius of the ion is, the more likely it is to be found in an inner-sphere complex. Inner-sphere complexes are usually much stronger than outer-sphere complexes associated with a hydrated cation and an anion held by long-range electrostatic forces [23,25].

Despite its low Ip, the Pb(II)-ion great affinity to humic acid may be explained by their borderline acid properties. Electronic configuration of Pb(II) ion is (n-1) 18e- + n 2e- and this classifies lead ion as the borderline metal acids and gives greater stability of Pb(II)-humate complex comparing to other complexes, while Cu(II) and Zn(II) are classified as soft acids, and they don't form stable complexes with O-donor ligands although should have high ability to coordinate with bases which contain N and/or S as donor ligands. According to this rule, the stability constant of complexes between these ions and humic acid is lower than stability constant of Pb(II)-humate

complex. Due to the large ion size of Pb(II), the electrons are easily polarized and to a lesser degree retained by the nucleus [25].

Comparison of the obtained results for stability constants and stoichiometry of complexes Pb(II), Cu(II), Zn(II), Ni(II) and Co(II) with humic acid with literature data, indicate that values are approximately equal. Variation of stability constants values in humic complexation studies is not uncommon due to differences in humic's elemental composition, their chemical structure and period of genesis during humification process [20-22, 26].

The established trend of metal-humate complexes stabilities can be used for predicting the strength of interaction between the humics and metal ions, as well as to predict their competition in binding to humate ligand. Obtained results indicate that there may be competition between these metal ions in the binding for humate macromolecules. Therefore, in conditions of increased concentrations of metal ion in the natural environment, the metal ion may displace other ions, which can lead to increasing mobility and bioavailability of other metal ions.

The investigation reveals that humic acid can effectively bind heavy metals and due to this have potential to be used in remediation methods. For example, it can use in wastewater treatment for heavy metal removal, as metal detoxification agent for industrial and domestic effluents which contain high levels of such heavy metals. Due to the ability to form complexes, humic acid also promotes retention and accumulation of heavy metals and thus, can be used in fito remediation processes.

Conclusion

Our results provide information on the interaction of Pb(II), Cu(II), Zn(II), Ni(II) and Co(II) with humic acid and distribution of those heavy metals through soil/water natural systems. The Schubert's method can be used not only for stoichiometrically defined ligands but also for complexes of polyfunctional and stoichiometricaly undefined ligands, such humic ligands are. The obtained results derived using the Schubert's method, indicate that the stability constant, $\log \beta_{mn}$, for the Pb(II)-humate complex was greater than of other investigated humate complexes at pH 4.0. All investigated humic complexes show 1:1 stoichiometry.

The established trend of metal-humate complexes stabilities, that follows Irving-Williams series can be used for predicting the strength of interaction between the humics and metal ions, thus for predicting mobility and bioavailability of metal ions.

Acknowledgement

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Izvod

UPOREDNA ISPITIVANJA JAČINE VEZIVANJA JONA TEŠKIH METALA SA HUMINSKOM KISELINOM

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(Naučni rad)

Kontaminacija životne sredine teškim metalima predstavlja opasnost za žive organizme. Pošto metali nisu biorazgradivi, ali su rastvorljivi u vodi, oni mogu postati dostupni živim organizmima i može doći do njihove akumulacije u životnoj sredini. Najveća kontaminacija životne sredine teškim metalima javlja se u blizini industrije metala.

Teški metali mogu učestvovati u složenim hemijskim i biološkim procesima. Faktori koji utiču na njihovu pokretljivost kroz zemljišne i vodene sisteme su pH, redoks potencijal, priroda sistema, prisustvo različitih materija koje mogu imati ulogu sorbenta, prisustvo i količina organskih liganda, uključujući huminske i fulvo kiseline, prisustvo neorganskih liganda.

Procesi vezivanja, transporta, biodostupnosti i mobilnosti jona metala u zemljištu i vodenim sistemima u velikoj meri zavise od interakcije sa huminskim supstancama. Joni metala mogu nagraditi rastvorne komplekse sa huminskim supstancama i tako prouzrokovati kontaminaciju površinskih i podzemnih voda, usled zadržavanja metala u zemljišnom rastvoru. Takođe, može doći i do stvaranja nerastvornih kompleksa, i akumulacije metala u zemljištu i sedimentima.

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U ovom radu vršena su uporedna ispitivanja kompleksa jona teških metala (Co(II), Ni(II), Cu(II), Zn(II) i Pb(II)) sa huminskom kiselinom. Vrednosti konstanti stabilnosti formiranih kompleksa određene su pomoću Šubertove jonoizmenjivačke metode, koja se zasniva na raspodeli količine metala između smole i vodene faze u sistemima sa i bez prisustva liganda. Ispitivanja su vršena na pH 4.0, temperaturi od 25 °C i pri jonskoj jačini 0.01 mol dm^{-3}.

Utvrđeno je da joni ispitivanih metala sa huminskom kiselinom grade mononuklearne komplekse, 1:1. Dobijene vrednosti konstante stabilnosti formiranih kompleksa prate redosled Co(II) < Ni(II) < Cu(II) > Zn(II), koji odgovara rasporedu u Irving-Vilijamsovoj seriji jačine vezivanja, koja je određena za dvovalentne jone. Vrednost konstante stabilnosti dobijene za kompleks formiran između Pb(II) jona i huminske kiseline veća je u odnosu na vrednosti konstanti stabilnosti ostalih ispitivnih kompleksa.

Rezultati dobijeni ispitivanjem interakcije jona teških metala sa huminskom kiselinom mogu se koristiti za predviđanje distribucije i kontrolu migracije teških metala u prirodnom okruženju.

Table caption

Table 1. Experimentally determined percentage of total metal bound to exchange resin, α_0, distribution coefficients, D_0, metal-ligand ratio and logarithm of conditional stability constant, log β_{mn}, for complexes Pb(II), Cu(II), Zn(II), Ni(II)and Co(II) (5 mg dm^{-3}) with humic acid, at pH 4.0 and ionic strength of $I = 0.01$

Table 2. Stability constants, log β_{mn}, and metal-ligand ratio for complexes of Pb(II), Cu(II), Zn(II), Ni(II) and Co(II) with humic acid, at pH 4.0 and ionic strength of $I = 0.01$

Naslovi tabela

Tabela 1. Eksperimentalno određene vrednosti procenta metala vezanog za smolu u odnosu na ukupnu koncentraciju metala, α_0, distribucionog koeficijenta, D_0, metal-ligand odnosa, i logaritma konstante stabilnosti, log β_{mn}, za komplekse Pb(II), Cu(II), Zn(II), Ni(II)i Co(II) (5 mg dm^{-3}) jona sa humiskom kiselinom, pri vrednosti pH 4.0 i jonske jačine $I = 0.01$

Tabela 2. Konstante stabilnosti, log β_{mn},i odnos metal-ligand za komplekse između Pb(II), Cu(II), Zn(II), Ni(II)i Co(II) jona sa huminskom kiselinom, pri vrednosti pH 4.0 i jonskoj jačini $I = 0.01$

Figure caption

Figure 1. Schubert's plots of the ratio of complexed metal to free metal (log (D_0/D-1) versus log c_{HA} for Pb(II), Cu(II), Zn(II), Ni(II) and Co(II) ions with humic acid and concentration of metal ion a) 5 mg dm^{-3}; b) 10 mg dm^{-3}; c) 15 mg dm^{-3}; d) 20 mg dm^{-3}

Potpisi ispod slika

Slika 1. Šubertov dijagram odnosa kompleksiranog i slobodnog metalnog jona prema logaritmu koncentracije huminske kiseline za komplekse Pb(II), Cu(II), Zn(II), Ni(II) i Co(II) sa huminskom kiselinom, pri koncentraciji metalnih jona a) 5 mg dm^{-3}; b) 10 mg dm^{-3}; c) 15 mg dm^{-3}; d) 20 mg dm^{-3}

Table1.

Metal ion	$c_{HA} \cdot 10^{-3}$ (mol dm^{-3})	α_0	D_0	D	$\log (D_0/D\text{-}1)$	M:L	$\log \beta_{mn}$	$\overline{\log \beta_{mn}}$
Co(II)	0	61.14	786.67					
	5	50.36		507.25	-0.259	1:1	2.04	1.95
	10	46.46		433.88	-0.090		1.91	
	20	41.78		358.81	0.076		1.89	
Ni(II)	0	12.48	71.30					
	5	6.94		37.29	-0.040	1:1	2.26	2.24
	10	4.84		25.43	0.256		2.26	
	20	4.10		21.37	0.368		2.19	
Cu(II)[*]	0	58.52	705.4					
	5	49.28		485.80	-0.347	1:1	2.25	2.33
	10	27.00		184.93	0.449		2.45	
	20	20.84		131.63	0.639		2.29	
Zn(II)	0	31.04	225.06					
	5	18.74		115.31	-0.021	1:1	2.28	2.25
	10	14.46		84.522	0.221		2.22	
	20	11.02		61.924	0.421		2.24	
Pb(II)[*]	0	52.56	553.96					
	5	29.40		208.21	0.220	1:1	2.52	2.50
	10	24.20		159.63	0.393		2.39	
	20	14.00		81.39	0.764		2.59	

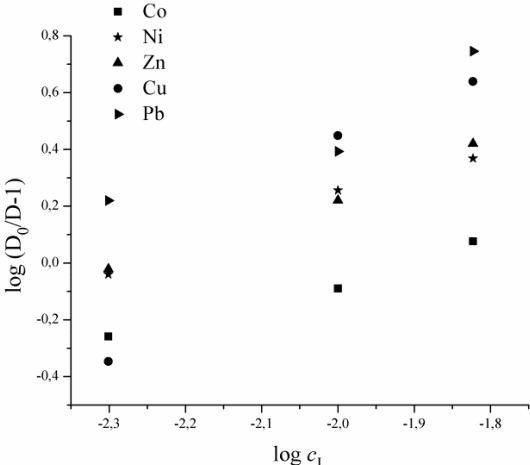[*] Results for Cu(II) and Pb(II) are previously reported and are taken from reference [24]

Table 2.

| Metal ion | M:L | $\log \beta_{mn}$ | | | $\overline{\log \beta_{mn}}$ | Literature values [22, 23, 26-30] |
| | | $c_{HA} \cdot 10^{-3}$ (mol dm^{-3}) | | | | |
		5	10	15		
Co(II)	1:1	1.96	1.91	1.93	1.93	2.82 - 6.05
Ni(II)	1:1	2.21	2.17	2.18	2.19	1.56 - 3.20
Cu(II)*	1:1	2.31	2.39	2.36	2.35	1.95 - 5.28
Zn(II)	1:1	2.24	2.23	2.30	2.26	2.74 - 4.70
Pb(II)*	1:1	2.64	2.47	2.62	2.58	2.76 - 5.32

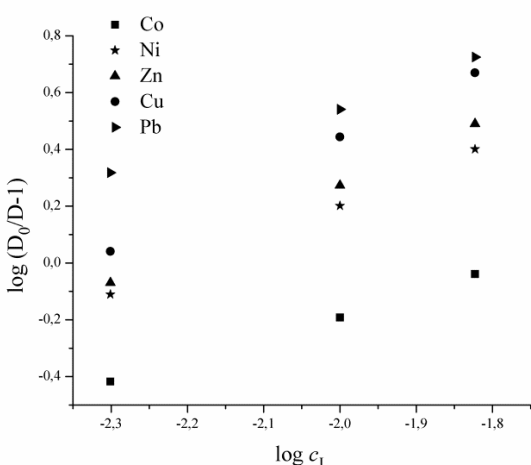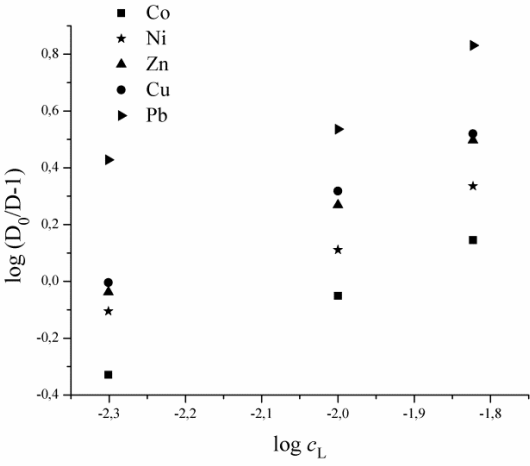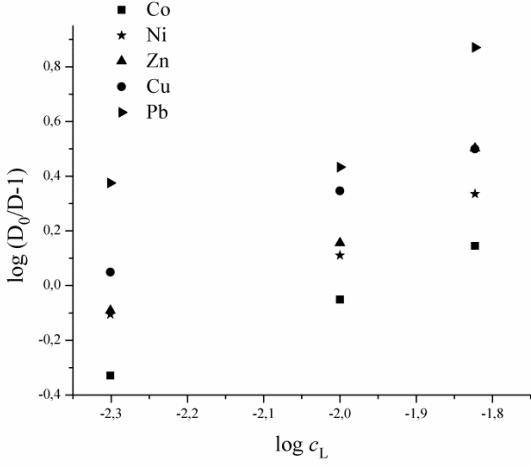* Results for Cu(II) and Pb(II) are previously reported and are taken from reference [24]

Figure 1.

a)

b)

c)

d)

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