Research Article

Measurement of Complex Formation Process of Nickel (II) with Freshwater Fulvic Acids Using the Solubility Method

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Abstract: The complex formation process between Ni(II) and fulvic acids has been studied through the solubility method at pH = 9.0. The old suspension of $Ni(OH)_2$ is used as a solid phase. Fulvic acids are isolated from Paravani lake by the adsorption-chromatographic method. The activated charcoal is used as a sorbent. The concentration of fulvic acids in model solutions changes from 1.1×10^{-5} mol/L to 4.4×10^{-5} mol/L. The value of molar mass of fulvic acids at pH = 9.0 was taken into consideration for the calculation of molar concentrations of fulvic acids. Before adding the ligand the initial concentration of nickel was 3.8×10^{-6} mol/L. This article has shown that, during complex formation process every 0.25 part of an associate of fulvic acids (Mw = 7610), inculcates into nickel's inner coordination sphere as an integral ligand, so it may be assumed, that the average molecular weight of the associate of fulvic acids which takes part in complex formation process equals to 1903. This part of the associate of fulvic acids was conventionally called the "active associate". The average molecular weight of the "active associate" was used for determining the concentration of free ligand and average stability constant (1:1), which equals to $\beta = 1.07 \times 10^7$ ($\lg\beta = 7.03$).

Keywords: fulvic acids, nickel dihydroxy fulvate complex, average stability constant, active associate

1. Introduction

Macromolecular Organic Substances-Fulvic Acids (FA) are natural organic complexing agents, found in the environment that originates from chemically and microbially modified plant and animal matter. They are the major organic matter of natural waters. FA concentrations ranges from less than 1 mg/L to more than 100 mg/L.[1-6] The chemical structure of FA has not been finalized yet. The elemental composition (%) of FA is isolated from natural waters changes C 46.7~59.7; H 4.1~5.5; O 31.8~49.7; N 0.74~3.3 and S 0.4~1.7.[1,7-10]

FA form stable complexes with heavy metals and radionuclides[1,11-21] and stipulate migration forms thereof in natural waters and soils.[1,3,22-27] Therefore, FA may affect the transport, accumulation, bioavailability, and toxicity of metals in the environment.

The carboxylic and phenolic groups of FA take an active part in complex formation and sorption processes, proceeding in natural waters, bottom sediments and soils.[1,28-31] $pK_{H,COOH}$ changes from 4.1 to 4.9, and $pK_{H,Ph-OH}$ (the dissociation constant of phenolic group of fulvic acids) changes from 9.3 to 10.6.[1,4,5,29,32] The participation of carboxylic

or phenol hydroxide groups depends not only on the value of pH (which determines the dissociation degree of carboxylic and phenol groups), also on the nature of metals. For example Al, Pb, Hg, and Cr, which are preferentially bound to the phenolic sites of the fulvic ligand; Ca, Mg, Cd, Fe(II), and Mn, which display a greater effective affinity for carboxylic sites, in contrast to what would be expected from their individual complexation parameters; and Fe(III), Cu, Zn, and Ni, for which phenolic and carboxylic distributions are overlapped.[29]

In spite of researches, the experimental data on stability constants (β) of complex compounds of FA with nickel (as in the case of other metals) is heterogeneous and it differs in several lines from each other.[33-40] This condition is mainly stipulated by ignoring the average molecular weight (Mw) of the associates of FA, which value in its turn depends on the value of pH and finally causes the wrong results. Therefore, it's difficult to investigate complex formation processes, taking place in natural waters, identify migration forms of nickel and evaluate and assess chemical-ecological condition of natural waters.

Objective of the work is to investigate complex formation process between the pure samples of FA, isolated from natural water and to calculate the average stability constant of nickel fulvate complex. Complex formation process has been studied at pH = 9.0 by the solubility method. While practically using this method, in case of choosing correctly the solid phase, polynuclear hydrolysis is impossible and is easy for the determining the exact composition and stability constants of complex. The old suspension of $Ni(OH)_2$ was used as a solid phase.

2. Materials and methods

For obtaining pure samples of FA, after filtration through membrane filters (0.45 μm pore size), the water of Paravani lake was concentrated by the frozen method. The concentrated water samples were acidified with 6 M HCl to pH 2 and was put for 2 hours on water bath at 60°C for coagulation of humin acids. Then the solution was centrifuged for 10 min at 8000 rpm (Centrifuge T-23). The adsorption-chromatographic method was used for isolating FA from centrifugate. Charcoal was used as a sorbent. Desorption of amino acids and carbohydrates was performed by means of 0.1 M HCl. 90% acetone water solution was used for desorbing polyphenols. The elution of the fraction of FA was performed with 0.1 N sodium hydroxide solution.[1,41] Obtained alkalic solution of FA, for the purification was passed through a cation-exchanger (KU-2-8). For the determination of the concentration of FA in the obtained solution was used gravimetric method, the part of the solution was dried under vacuum until the constant weight was obtained. Elemental composition of standard samples of FA was isolated from natural waters and average value of dissociation constants respectively equals to C-53.75%, H-4.29%; O-40.48%, N-0.68%, S-0.50%; P-0.01%; ashing 0.35; $pK_{H,COOH}$ = 4.37, $pK_{H,Ph-OH}$ = 10.4. Then, model solutions of FA were prepared. The solution of fulvate complexes was obtained by the solubility method. 0.1 ml suspension of old nickel hydroxide and the increasing quantity of standard solution of FA were placed in 15 ml capacity fluoroplastic cylinders. The concentration of FA in model solutions changes from 1.1×10^{-5} mol/L to 4.4×10^{-5} mol/L. Before adding ligand the initial concentration of nickel was 3.8×10^{-6} mol/L. pH = 9.0, ionic strength μ = 0.01 (KNO₃), v = 10 ml. The concentration of hydrogen ions was regulated by the addition of 0.01 M HNO₃ acid or 0.01 M NaOH (pH meter pH 2006). Then, it was stirred in a mechanical mixer for 100 hours, until the balance was achieved and then suspension was filtered through the membrane filters (0.45 μm pore size). In filtrates, the concentration of nickel was measured by atomic absorption spectrophotometer (Perkin Elmer 200).

3. Results and discussion

The data has shown that in line with the increasing of concentration of FA in solution, the concentration of nickel increases for several times as well due to the formation of fulvate complex (Table 1). During the calculation of molar concentrations of FA, the fact that they (FA) form associates in water solutions was taken into consideration. While the investigation of water solutions of FA by the gel chromatographic method was established, that in the interval pH 4~11, there is a line dependence of the average molecular weight FA (Mw) and the value of pH, which is expressed in the following way: Mw = 1350 pH - 4540.[1] At pH = 9, Mw(FA) = 7610.

In the diluted water solutions, the forms of nickel (β_{NiOH^+} = 5.5 × 10⁴, $\beta_{Ni(OH)_2^0}$ = 5.4 × 10¹⁴)[42] were calculated

through the following formulas (1-3):

$$\text{Ni}^{2+}\% = 100/(1 + \beta_{1.1}[\text{OH}^-] + \beta_{1.2}[\text{OH}^-]^2) \tag{1}$$

$$\text{NiOH}^+\% = \beta_{1.1}[\text{OH}^-]100/(1 + \beta_{1.1}[\text{OH}^-] + \beta_{1.2}[\text{OH}^-]) \tag{2}$$

$$\text{Ni(OH)}_2^0\% = \beta_{1.2}[\text{OH}^-]^2100/(1 + \beta_{1.1}[\text{OH}^-] + \beta_{1.2}[\text{OH}^-]^2) \tag{3}$$

Where $\beta_{1.1}$-the stability constant of MeOH^+, $\beta_{1.2}$-the stability constant of Me(OH)_2.
As the results show, nickel dihydroxy complex Ni(OH)_2^0 is the dominant form at pH = 9.0.
The reaction between nickel dihydroxy complex and the anions of FA may be written in the following way:

$$\text{Ni(OH)}_2^0 + m\,\text{FA} = \text{Ni(OH)}_2(\text{FA})_m \tag{4}$$

$$\beta = [\text{Ni(OH)}_2\text{FA}_m]/\{[\text{Ni(OH)}_2^0][\text{FA}]^m\} \tag{5}$$

In solution, the concentration of nickel dihydroxy fulvate complex equals to the difference between final $[\text{Ni(II)}_{\text{total}}]$ and initial $[\text{Ni(II)}_{\text{free}}]$ concentrations of nickel received after formation of complex:

$$[\text{Ni(OH)}_2\,\text{FA}_m] = [\text{Ni(II)}_{\text{total}} - \text{Ni(II)}_{\text{free}}] \text{ and } [\text{Ni(OH)}_2^0] = [\text{Ni(II)}_{\text{free}}]. \tag{6}$$

Put these values in (5)

$$\beta = [\text{Ni(II)}_{\text{total}} - \text{Ni(II)}_{\text{free}}]/\{[\text{Ni(II)}_{\text{free}}][\text{FA}]^m\} \tag{7}$$

From (7) equation

$$\beta[\text{Ni(II)}_{\text{free}}] = [\text{Ni(II)}_{\text{total}} - \text{Ni(II)}_{\text{free}}]/[\text{FA}]^m \tag{8}$$

At the fixed pH, the left part of the equation (8) is a permanent value and we mark it as K'.

$$K' = [\text{Ni(II)}_{\text{total}} - \text{Ni(II)}_{\text{free}}]/[\text{FA}]^m \tag{9}$$

The logarithm of this equation (9) is:

$$\lg K' = \lg[\text{Ni(II)}_{\text{total}} - \text{Ni(II)}_{\text{free}}] - m\lg[\text{FA}] \tag{10}$$

The numeral value (m) of the stoichiometric coefficient or the number of ligands in the inner coordination sphere of complex equals to tangent of tilt angle of straight line built in coordinates

$$\lg[\text{Ni(II)}_{\text{total}} - \text{Ni(II)}_{\text{free}}] - \lg[\text{FA}_{\text{total}}]$$

For the calculation of the exact value of tangents tilt angle of straight line, was used the least square method:

$$m = \text{tg}\alpha = (n\Sigma x_i y_i - \Sigma x_i \Sigma y_i)/(n\Sigma x_i^2 - (\Sigma x_i)^2). \tag{11}$$

where

$$x_i = \lg[FA_{total}] \text{ and } y_i = \lg[Ni(II)_{total} - Ni(II)_{free}] \tag{12}$$

After the calculation, was obtained the numeral value of m (Mw(FA) = 7610) which equal to 0.98 (Table 1-2), most likely can be said that the complex obtained at pH = 9 in the system Ni(OH)$_2$(solid)-Ni(II)(solution)-FA-H$_2$O is the nickel dihydroxy fulvate, with the structure 1:1.

So the complex formation reaction (pH = 9.0) may be written:

$$Ni(OH)_2^0 + FA = Ni(OH)_2FA \tag{13}$$

Therefore, the formula for the stability constant can be expressed in the following way:

$$\beta = [Ni(OH)_2FA]/\{[Ni(II)_{free}][FA]\} = [Ni(II)_{total} - Ni(II)_{free}]/\{[Ni(II)_{free}][FA]\}. \tag{14}$$

Table 1. The dependence of the solubility of nickel hydroxide on the concentration of FA and the necessary data for the determination the composition of nickel Dihydroxy fulvate complexes pH = 9.0; Mw(FA) = 7610; [Ni(II)$_{free}$] = 3.8 × 10^{-6} mol/L

Mol/L			$[Ni_{total}]:[FA_{total}]$	$\lg[FA_{total}]$	$\lg[Ni(OH)_2FA]$
$[FA_{total}]$	$[Ni_{total}]$	$[Ni(OH)_2FA]$			
1.11 × 10^{-5}	4.64 × 10^{-5}	4.26 × 10^{-5}	1 : 0.23	-4.9547	-4.3706
1.66 × 0^{-5}	6.64 × 10^{-5}	6.26 × 10^{-5}	1 : 0.25	-4.7799	-4.2034
2.22 × 10^{-5}	9.00 × 10^{-5}	8.62 × 10^{-5}	1 : 0.25	-4.6536	-4.0645
2.77 × 10^{-5}	11.08 × 10^{-5}	10.62 × 10^{-5}	1 : 0.25	-4.5575	-3.9739
3.33 × 10^{-5}	12.40 × 10^{-5}	12.02 × 10^{-5}	1 : 0.27	-4.4775	-3.9201
3.88 × 10^{-5}	15.68 × 10^{-5}	15.30 × 10^{-5}	1 : 0.25	-4.4112	-3.8153
4.44 × 10^{-5}	17.60 × 10^{-5}	17.22 × 10^{-5}	1 : 0.25	-4.3526	-3.7640

Table 2. The calculation of the composition of nickel fulvate dihydroxy complex by the least square method, Mw(FA) = 7610; pH = 9.0. $X_i = \lg[FA_{total}]$, $Y_i = \lg[NiFA_m]$

X_i	Y_i	X_iY_i	X_i^2
-4.9547	-4.3706	21.6550	24.5490
-4.7799	-4.2034	20.0918	22.8474
-4.6536	-4.0645	18.9145	21.6560
-4.5575	-3.9739	18.1110	20.7708
-4.4775	-3.9201	17.5522	20.0480
-4.4112	-3.8153	16.8300	19.4587
-4.3526	-3.7640	16.3832	18.9451

$\sum X_i = -32.187$; $(\sum X_i)^2 = 1036.0029$; $\sum Y_i = -28.1118$; $\sum X_i^2 = 148.275$; $\sum X_iY_i = 129.5377$; m = 0.98

The complexation of FA to metal ions cannot be described in strict frames because of the ill-defined nature of FA in contrast to the complexation of single ligands. So in order to make it succeed the calculation of stability constants of fulvate complexes, it is necessary to make some assumptions.

Table 3. The necessary data for the calculation of conditional stability constants of nickel fulvate complex by the leden method, pH = 9.0; Mw(FA) = 1903, $[Ni(II)_{free}] = 3.8 \times 10^{-6}$ mol/L; $F(FA) = [Ni(OH)_2FA]/([Ni(II)_{free}][FA_{free}])$; $[FA_{free}] = [FA_{total}] - [Ni(OH)_2FA]$; $[Ni(OH)_2FA] = [Ni(II)_{total}] - [Ni(II)_{free}]$

Mol/L				F(FA)
$[FA_{total}]$	$[Ni(II)_{total}]$	$[Ni(OH)_2FA]$	$[FA_{free}]$	
4.44×10^{-5}	4.64×10^{-5}	4.26×10^{-5}	0.18×10^{-5}	6.26×10^6
6.66×10^{-5}	6.64×10^{-5}	6.26×10^{-5}	0.40×10^{-5}	4.12×10^6
8.88×10^{-5}	9.00×10^{-5}	8.62×10^{-5}	0.26×10^{-5}	8.72×10^6
11.10×10^{-5}	11.08×10^{-5}	10.62×10^{-5}	0.48×10^{-5}	5.83×10^6
13.32×10^{-5}	12.40×10^{-5}	12.02×10^{-5}	1.30×10^{-5}	2.43×10^6
15.54×10^{-5}	15.68×10^{-5}	15.30×10^{-5}	0.24×10^{-5}	16.77×10^6
17.76×10^{-5}	17.60×10^{-5}	17.22×10^{-5}	0.54×10^{-5}	8.40×10^6

Table 4. The calculation of conditional stability constant of nickel fulvate complex by the least square vethod. Mw(FA) = 1903; pH = 9.0; $X_i = [FA_{free}]$; $Y_i = F(FA)$

X_i	Y_i	X_iY_i	X_i^2
0.18×10^{-5}	6.26×10^6	11.27	0.0324×10^{-10}
0.40×10^{-5}	4.12×10^6	16.48	0.1600×10^{-10}
0.26×10^{-5}	8.72×10^6	22.672	0.0676×10^{-10}
0.48×10^{-5}	5.83×10^6	27.984	0.2304×10^{-10}
1.30×10^{-5}	2.43×10^6	31.59	1.6900×10^{-10}
0.24×10^{-5}	16.77×10^6	40.248	0.0576×10^{-10}
0.54×10^{-5}	8.40×10^6	45.36	0.2916×10^{-10}

$\sum X_i = 3.4 \times 10^{-5}$; $(\sum X_i)^2 = 11.56 \times 10^{-10}$; $\sum Y_i = 52.53 \times 10^6$; $\sum X_i^2 = 2.5296 \times 10^{-10}$; $\sum X_iY_i = 195.604$; $\beta = 1.07 \times 10^7$

In the balanced solutions, correlation $[Ni(II)_{total}]:[FA_{total}]$ on average equals to 1:0.25 (Table 1). This means that during the complex formation process, the associate of FA, which Mw at pH = 9.0 equals to 7610, divides and every 0.25 part of this associate inculcates into nickel's (II) inner coordination sphere, as an integral ligand. So it may be assumed that Mw of the associate of FA which takes part in the complex formation process equals to 1903. This part of the associate of FA was conventionally called the "active associate".[43] The meaning of Mw of the "active associate" of FA (Mw = 1903) was used for determining the concentration of free ligand $[FA_{free}]$ and average stability constant.

For the calculation of average stability constant of nickel fulvate at pH = 9.0 was used Leden function F(L).[44]

$$\text{Function } F(L) = F(FA) = [Ni(OH)_2FA]/\{[Ni(II)_{free}][FA_{free}])\} =$$

$$= ([Ni(II)_{total}] - [Ni(II)_{free}])/([Ni(II)_{free}][FA_{free}]) = \beta_1 + \beta_2[FA_{free}], \tag{15}$$

where

$$[FA_{free}] = [FA_{total}] - [Ni(OH)_2FA] = [FA_{total}] - \{[Ni(II)_{total}] - Ni(II)_{free}]\} \tag{16}$$

Under the solubility method, the concentration of [Ni(II)$_{free}$] equals to the initial concentration of metal before adding ligand in solution. It should be emphasized, using average molecular weights of "active associates" in the given systems is both real and forced, because as it is shown from data (Table 1), with the solubilty method, in any point the molar concentration of fulvate complex exceeds the molar concentration of total associate, which average molecular weight at pH = 9.0 is big enough. Therefore, free ligand cannot be calculated. Without it, it is impossible to determine the stability constant of fulvate complex.

When [FA$_{free}$] aspires to zero, β could be found by the graphical method. The m section which is cut on the ordinate by the straight line built in coordinates F(FA)-[FA$_{free}$] equals to the stability constant. The value of β is calculated by the square method:

$$\beta = (\Sigma y_i - a\Sigma x_i)/n \tag{17}$$

where

$$a = (n\Sigma x_i y_i - \Sigma x_i \Sigma y_i)/[(n\Sigma x_i^2 - (\Sigma x_i)^2)] \tag{18}$$

$$x_i = [FA_{free}] \tag{19}$$

and

$$y_i = F(FA) \tag{20}$$

The necessary data, for calculating the conditional stability constants of nickel dihydroxy fulvate complex are given in Tables 3 and 4.

$$\beta(Ni(OH)_2FA) = 1.07 \times 10^7 \tag{21}$$

$$\lg \beta = 7.03 \tag{22}$$

4. Conclusion

Calculations have approved that in diluted water solutions nickel dihydroxy complex Ni(OH)$_2^0$ is the dominant form at pH = 9.0. It was shown that, during the complex formation process, an associate of FA, which Mw at pH = 9.0 equals to 7610 divides and every 0.25 part of this associate inculcates into nickel's inner coordination sphere, as an integral ligand. This part of the associate of FA was conventionally called the "active associate". The value of Mw of the "active associate" of FA (Mw = 1903) was used for determining the concentration of free ligand and average stability constant. It has shown that using average molecular weights of "active associates" in the given systems is both real and forced.

It was established, that in the Ni(OH)$_2$(solid)-Ni(II)(solution)-FA-H$_2$O system at pH = 9.0, dominates the nickel dihydroxy fulvate complex with the structure 1:1, which average stability constant $\beta = 1.07 \times 10^7$, $\lg \beta = 7.03$.

Acknowledgments

Conflict of interest

The authors declare no competing financial interest.

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