The Determination of Average Stability Constant of Nickel-FA Complex at pH = 8.0 by the Solubility Method

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Abstract: At pH = 8, the complex formation process of Ni(II) ions with FA was studied by the solubility method. FA were separated from the river Mtkvari by the adsorption-chromatographic method. The charcoal (BAU, Russia) was used as a sorbent. The old suspension of Ni(II) hydroxide was used as the solid phase, on which was added the increasing quantity of standard solution of FA. In diluted solutions, at pH = 8.0 the dominant form of Ni(II) is nickel dihydroxocomplex $\text{Ni}(\text{OH})_2^0$. It was established that in the $\text{Ni}(\text{OH})_2(\text{solid})\text{-Ni}(\text{OH})_2^0(\text{solution})\text{-FA}^{2-}\text{-H}_2\text{O}$ system dominates nickel dyhydroxofulvate complex with the structure 1:1, $[\text{Ni}(\text{OH})_2\text{FA}]^{2-}$. The average stability constant of nickel dyhydroxofulvate complex was calculated based on experimental data $\beta_{\text{Ni}(\text{OH})_2\text{FA}^{2-}} = 5.3 \times 10^5$.

Key words: Nickel, FA, average stability constant, nickel fulvate, water.

1. Introduction

FA (fulvic acids) have the functional groups, so they take an active part in complexing and sorption processes, proceeding in natural waters, suspended substances, bottom sediment and soils. They form stable complexes with heavy metals and radionuclides and stipulate migration forms thereof in natural waters and soils [1-12].

The carboxylic and phenolic groups take part in fulvate complex formation processes [12-16]. $pK_{\text{H,COOH}}$ changes from 4.1 to 4.8, and $pK_{\text{H,Ph-OH}}$ changes from 9.3 to 10.5 [12, 17, 18].

In spite of researches, experimental data on stability constants of complex compounds of FA are heterogeneous. One of the reasons to this is application of various average molecular weights of FA associates. In its turn, this puts the correctness of calculation of stability constants of fulvic complexes under question.

Therefore, it is difficult to investigate complexing and sorption processes taking place in natural waters and soils, identify migration forms of heavy metals and radio nuclides, evaluate and assess chemical-ecological condition of natural waters and soils.

The authors' objective was to obtain pure samples of FA, to study complex formation processes between heavy metals and FA, to determine the structure and average stability constants of fulvic complexes.

In this paper, the authors discuss the complex formation process of nickel fulvate. According to the data, found in the literature, stability constants (β) of nickel fulvic complexes differ in several lines from each other. Value of $\lg \beta$ changes from 3.3 to 7.1 [19-22].

The complex formation process was studied at pH = 8.0 by the solubility method. The suspension of old nickel hydroxide was used as the solid phase.

2. Experiment Methodology

To obtain pure samples of FA, the authors

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concentrated the water of the river Mtkvari by the frozen method. Filtered water samples were acidified to pH 2 and were put for 2 h on water bath at 60 °C, for coagulation of humin acids. Then, the solution was centrifuged for 10 min at 8,000 rpm. To isolate FA from centrifugate, the adsorption-chromatographic method was used. The charcoal (BAU, Russia) was used as a sorbent. Desorption of amino acids and carbohydrates were performed by means of 0.1 N HCl. For the desorption of polyphenols, the 90% acetone water solution was used. The elution of FA fraction was performed with 0.1 N NaOH solution [23, 24]. The obtained alkalic solution of FA for the purification was passed through a cation-exchanger (KU-2, Russia) and dried under the vacuum until the constant mass was obtained. Then, model solutions of FA was prepared. The required pH was adjusted by the addition of hydrochloric acid or sodium hydroxide.

0.1 mL old suspension of nickel hydroxide and increasing quantity of standard solution of FA were placed in 15 mL capacity fluroplastic cylinders. pH = 8.0, $\mu = 0.01$ (KNO₃), $V = 10$ mL. Solution containing the sediment was placed in thermostat at 25 °C. Then, it was stirred in a mechanical mixer for 60 h (until the balance was achieved) and then suspension was filtered through the membrane filters (Sinpor N6, diameter of phores 400 nm). In filtrates, nickel was measured by atomic absorption spectrophotometer (Perkin almer 200).

3. Results and Discussion

The data (Table 1) show that in line with the increase of concentration of FA in the solution, the concentration of nickel increases for several times as well due to formation of fulvic complex.

During the calculation of molar concentrations of FA, the fact, that FA form associates in water solutions, which value of average molecular mass (M_w) depends on pH: $M_w = 1,350$ pH-4,540 (pH ≥ 4) [24] was taken into consideration.

In the diluted water solutions the forms, of nickel in % were calculated through Eqs. (1)-(3).

$$\text{Ni}^{2+}\% = 100/(1+\beta_{\text{NiOH}}[\text{OH}^-]+\beta_{\text{Ni(OH)}_2}[\text{OH}^-]^2) \quad (1)$$

$$\text{NiOH}^+\% = \beta_{\text{NiOH}}[\text{OH}^-]100/(1+\beta_{\text{NiOH}}[\text{OH}^-]+\beta_{\text{Ni(OH)}_2}[\text{OH}^-]^2) \quad (2)$$

$$\text{Ni(OH)}_2^0\% = \beta$$

$$\text{Ni(OH)}_2^0[\text{OH}^-]^2100/(1+\beta_{\text{NiOH}}[\text{OH}^-]+\beta_{\text{Ni(OH)}_2}[\text{OH}^-]^2) \quad (3)$$

$$\beta_{\text{NiOH}} = 5.5 \times 10^4 \quad \beta_{\text{Ni(OH)}_2}^0 = 5.5 \times 10^{14} \quad [25]$$

As the calculations show ((Fig. 1), in balanced solutions at pH = 8, practically the whole Ni(II) is in the form of nickel dihydroxocomplex Ni(OH)_2^0 .

So the complex formation reaction (pH = 8.0) may be written in Eq. (4).

In Ref. [26], the method of calculation of the stability constant of fulvic complexes was described in detail, so in this paper the item will be discussed briefly. The numeral meaning (m) of the stechiometral coefficient or the ligands number in the inner coordination

Table 1 The data (mol/L) required for calculating stability constants of nickel fulvic complex (pH = 8.0; $\mu = 0.01$ (KNO₃), $t = 25$ °C, M_w (FA) = 6,260, $C'_{\text{Ni}} = 7.9 \times 10^{-6}$).

C_{FA}	$C_{\text{Ni}} - C'_{\text{Ni}}$	$[\text{FA}^{2-}]$	$\beta = [C_{\text{Ni}} - C'_{\text{Ni}}]/\{[C'_{\text{Ni}}][\text{FA}^{2-}]\}$
6.2×10^{-5}	5.0×10^{-5}	1.2×10^{-5}	5.3×10^5
7.2×10^{-5}	5.9×10^{-5}	1.3×10^{-5}	5.8×10^5
9.3×10^{-5}	7.4×10^{-5}	1.9×10^{-5}	4.9×10^5
1.1×10^{-4}	8.9×10^{-5}	2.1×10^{-5}	5.4×10^5
1.2×10^{-4}	9.7×10^{-5}	2.3×10^{-5}	5.3×10^5
1.7×10^{-4}	13.8×10^{-5}	3.2×10^{-5}	5.5×10^5
2.0×10^{-4}	16.0×10^{-5}	4.0×10^{-5}	5.1×10^5

$$\beta_{\text{Ni(OH)}_2\text{FA}^{2-}} = 5.3 \times 10^5.$$

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Fig. 1 The distribution diagram of the forms of Ni(II) in diluted water solutions (in %).

Table 2 The data to calculate the meaning of m by the least square method.

x_i $\lg C_{FA}$	y_i $\lg [C_{Ni} - C'_{Ni}]$	x_i^2	$x_i y_i$
-4.2076	-4.3010	17.7038	18.0968
-4.1426	-4.2291	17.1611	17.5194
-4.0315	-4.1307	16.2529	16.6529
-3.9586	-4.0506	15.6705	16.0347
-3.9208	-4.0132	15.3726	15.7349
-3.7695	-3.8601	14.2091	14.5506
-3.6989	-3.7958	13.6818	14.0402

$$\Sigma x_i = -27.7295, \Sigma y_i = -28.3805, \Sigma x_i^2 = 110.0518, \Sigma x_i y_i = 112.6295, (\Sigma x_i)^2 = 768.9251, \Sigma x_i \Sigma y_i = 786.9770, m = 0.99.$$

sphere of complex equals to tangens of tilt angle of straight line built in coordinates:

$$\lg [C_{Ni} - C'_{Ni}] \text{ — } m \lg C_{FA} \quad (5)$$

where, C'_{Ni} is the initial concentration of nickel, C_{Ni} is the final concentration of nickel, received after formation of complex and C_{FA} is concentration of FA in solution.

To calculate the exact value of tangens, tilt angle of straight line was used the least square method (Table 2):

$$m = \text{tg} \alpha = (n \Sigma x_i y_i - \Sigma x_i \Sigma y_i) / (n \Sigma x_i^2 - (\Sigma x_i)^2) \quad (6)$$

$$x_i = \lg C_{FA} \text{ and } y_i = \lg [C_{Ni} - C'_{Ni}]$$

After the calculations we obtained the numeral

meaning of stoichiometrical coefficient (m), which equals to 0.99, which demonstrates that complex with the structure 1:1 dominates in the $\text{Ni}(\text{OH})_2\text{-H}_2\text{O-FA}$ system. Therefore, the formula for calculating the stability constant can be expressed in the following way:

$$\beta = [C_{Ni} - C'_{Ni}] / \{ [C'_{Ni}] [\text{FA}^2] \} \quad (7)$$

where,

$$[\text{FA}^2] = C_{FA} - [C_{Ni} - C'_{Ni}] \quad (8)$$

Taking into account the average molecular mass of associate at pH = 8, ($M_w = 1,350$ pH-4,540 [24]), the average stability constant of nickel fulvic complex

was calculated on the basis of experimental data (Table 1).

So, in Ni(OH)_2 (solid)- Ni(OH)_2^0 (solution)- FA^{2-} - H_2O system at pH = 8 dominates the nickel dyhydroxofulvic complex with the structure 1:1, $[\text{Ni(OH)}_2\text{FA}]^{2-}$, which average stability constant is: $\beta_{\text{Ni(OH)}_2\text{FA}^{2-}} = 5.3 \times 10^5$.

4. Conclusions

So, in Ni(OH)_2 (solid)- Ni(OH)_2^0 (solution)- FA^{2-} - H_2O system at pH = 8 dominates the nickel dyhydroxofulvic complex with the structure 1:1, $[\text{Ni(OH)}_2\text{FA}]^{2-}$, which average stability constant is: $\beta_{\text{Ni(OH)}_2\text{FA}^{2-}} = 5.3 \times 10^5$.

References

- [1] Zhang, H. In-Situ Speciation of Ni and Zn in Freshwaters: Comparison between DGT Measurements and Speciation Models. *Environmental Science and Technology* **2004**, 38, 1421-1427.
- [2] Town, R. M.; Van Leeuwen, H. P.; Buffle, J. Chemodynamics of Soft Nanoparticulate Complexes: Cu(II) and Ni(II) Complexes with FA and Aquatic Humic Acids. *Environmental Science and Technology* **2012**, 46, 10487-10498.
- [3] Liping, W.; Willem, H.; Van, R.; Tjisse, H. Cu^{2+} and Ca^{2+} Adsorption to Goethite in the Presence of Fulvic Acids. *Geochimica et Cosmochimica Acta* **2008**, 72, 5857-5870.
- [4] Esterves, S. J. C. G.; Machado, A. S. C.; Pinto, S. S. D. Fluorescence Quenching of Anthropogenic FA by Cu(II), Fe(III) and UO_2^{2+} . *Talanta* **1998**, 45, 1155-1165.
- [5] Shizuko, H. Stability Constants for the Complexes of Transition-Metal Ions with Fulvic and Humic Acids in Sediments Measured by Gel-Filtration. *Talanta* **1981**, 28, 809-815.
- [6] Buckau, G.; Kim, J. I.; Klenze, R.; Rhee, D. S.; Wimmer, H. A Comparative Spectroscopic Study of the Fulvate Complexation of Trivalent Transuranium Ions. *Radiochim. Acta* **1992**, 57, 105-111.
- [7] McCarthy, J. F.; Czervinski, K. R.; Sanford, W. E.; Jardine, P. M.; Marsh, J. D. Mobilization of Transuranic Radionuclides from Disposal Trenches by Natural Organic Matter. *J. of Contaminant Hydrology* **1998**, 30, 49-77.
- [8] Claret, F.; Schaver, T.; Rabung, T.; Wolf, M.; Bauer, A.; Buckau, G. Differences in Properties and Cm(III) Complexation Behavior of Isolated Humic and Fulvic Acid Derived from Opalinus Clay and Callovo-Oxfordian Argillite. *Applied Geochemistry* **2005**, 20, 1158-1168.
- [9] Glaus, M. A.; Hummel, W.; Van Loon, L. R. Trace Metal-Humate Interaction. I. Experimental Determination of Conditional Stability Constants. *Applied Geochemistry* **2000**, 15, 953-973.
- [10] Cheam, V.; Gamble, D. S. Metal-Fulvic Acid Chelation Equilibrium in Aqueous NaNO_3 Solution Hg(II), Cd(II) and Cu(II) Fulvate Complexes. *Can. J. Soil Science* **1974**, 54, 413-417.
- [11] Makharadze, G. A.; Supatashvili, G. D.; Varshal, G. M. The Research of the Forms of Copper in Surface Waters. *Hydrochemical Materials* **1988**, 103, 3-16.
- [12] Varshal, G. M.; Velyukhanova, T. K.; Koshcheeva, I. Y.; Dorofeeva, V. A.; Buachidze, N. S.; Kasimova, O. G.; et al. Investigation of Chemical Forms of Elements in Surface Water. *Journal of Analytical Chemistry* **1983**, 38, 1590-1599.
- [13] Buffle, J.; Deladoey, P.; Greter, F. L.; Haerdi, W. Study of the Complex Formation of Copper(II) by Humic and Fulvic Substances. *Analitica Chimica Acta* **1980**, 116, 255-274.
- [14] Joris, W. J.; Van, S.; Dan, B. K.; Jon, P. G. Acid-Base and Copper-Binding Properties of Three Organic Matter Fractions Isolated from a Forest Floor Soil Solution. *Geochimica et Cosmochimica acta* **2010**, 74, 1391-1406.
- [15] Rey-Castro, C.; Mongin, S.; Huidobro, C.; David, C.; Salvador, J.; Garces, J.; et al. Effective Affinity Distribution for the Binding of Metal Ions to a Generic Fulvic Acid in Natural Waters. *Environmental Science and Technology* **2009**, 43, 7184-7191.
- [16] Orsetti, S.; Marco-Brown, J. L.; Andrade, E. M.; Molina, F. V. Pb(II) Binding to Humic Substances: An Equilibrium and Spectroscopic Study. *Environmental Science and Technology* **2013**, 47, 8325-8333.
- [17] Lenoir, T.; Manceau, A. Number of Independent Parameters in the Potentiometric Titration of Humic Substances. *Langmuir* **2010**, 26, 3998-4003.
- [18] Makharadze, G. A.; Supatashvili, G. D.; Varshal, G. M. Humic Acids in Surface Waters of Georgia. *Hydrochemical Materials* **1989**, 106, 22-30.
- [19] Schnitzer, M.; Hansen, E. H. An Evaluation of Methods for the Determination of Stability Constants of Metal-Fulvic Acid Complexes. *Soil Science* **1970**, 109, 333-340.
- [20] Schnitzer, M.; Skinner, S. I. M. Stability Constants of Pb, Ni, Mn, Co, Ca and Mg Fulvic Acid Complexes. *Soil Science* **1967**, 103, 247-252.
- [21] Mantoura, R. F. C.; Dixon, A.; Rilly, J. P. The

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- Speciation of Trace Metals with Humic Compounds in Natural Waters. *Thalassia Jugoslavica* **1978**, 14, 127-145.
- [22] Goncharova, T. O.; Kolosov, I. V.; Kaplin, B. T. Hydrolysis and Complexation of Nickel Ions in Solutions of FA. *Hydrochemical Materials* **1978**, 71, 64-72.
- [23] Varshal, G. M.; Kosheeva, I. Y.; Sirotkina, I. S.; Velukhanova, T. K.; Intskirveli, L. N.; Zamokina, N. C. The Study of Organic Substances in Surface Waters and Their Interaction with Metal Ions. *Geochemistry* **1979**, 4, 598-607.
- [24] Revia, R.; Makharadze, G. Cloud-Point Preconcentration of Fulvic and Humic Acids. *Talanta* **1999**, 48, 409-413.
- [25] Nazarenko, V. A.; Antonovich, V. N.; Nevskaya, E. M. *The Hydrolise of Metal Ions in Diluted Solutions*; Moscow, 1979, p 190.
- [26] Makharadze, G.; Makharadze, T. Method of Calculation of Stability Constants of Fulvic Complexes on the Example of Copper. *Journal of Chemistry and Chemical Engineering* **2014**, 8, 108-111.