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MOLECULAR SIZE DISTRIBUTION OF NP(V)-HUMATE

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Yoshiaki SAKAMOTO, Seiya NAGAO and Tadao TANAKA

日本原子力研究所
Japan Atomic Energy Research Institute

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Molecular Size Distribution of Np(V)-humate

Yoshiaki SAKAMOTO, Seiya NAGAO and Tadao TANAKA

Department of Environmental Safety Research

Tokai Research Establishment

Japan Atomic Energy Research Institute

Tokai-mura, Naka-gun, Ibaraki-ken

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Molecular size distributions of humic acid and Np(V)-humate were studied as a function of pH and an ionic strength by an ultrafiltration method. Small particle (10,000-30,000 daltons) of humic acid increased slightly with increases in solution pH. The ion strength dependence of the molecular size distribution was clearly observed for humic acid. The abundance ratio of humic acid in the range from 10,000 to 30,000 daltons increased with the ionic strength from 0.015 M to 0.105 M, in place of the decreasing of that in range from 30,000 to 100,000 daltons.

Most of neptunium(V) in the 200 mg/l of the humic acid solution was fractionated into 10,000-30,000 daltons. The abundance ratio of neptunium(V) in the 10,000-30,000 daltons was not clearly dependent on pH and the ionic strength of the solution, in spite of the changing in the molecular size distribution of humic acid by the ionic strength. These results imply that the molecular size distribution of Np(V)-humate does not simply obey by that of the humic acid. Stability constant of Np(V)-humate was measured as a function of the molecular size of the humic acid. The stability constant of Np(V)-humate in the range from 10,000 to 30,000 daltons was highest value comparing with the constants in the molecular size ranges of 100,000 daltons-0.45 μ m, 30,000-100,000, 5,000-10,000 daltons and under 5,000 daltons.

These results may indicate that the Np(V) complexation with humic acid is dominated by the interaction of neptunyl ion with the humic acid in the specific molecular size range.

Keywords: Neptunium(V), Humic Acid, Molecular Size Distribution, pH, Ionic Strength

ネプツニウム (V) - フミン酸錯体の分子量分布

日本原子力研究所東海研究所環境安全研究部

坂本 義昭・長尾 誠也・田中 忠夫

(1996年10月1日受理)

フミン酸及びネプツニウム (V) - フミン酸錯体の分子量分布のpH及びイオン強度依存性を限外濾過法により調べた。フミン酸の分子量分布はpHとともに、若干小さい成分の割合が増加した。一定のpHにおけるイオン強度依存性を調べた結果では、溶液のイオン強度の増加とともに、30,000~100,000 daltonsの成分の割合が減少し、より小さな10,000~30,000 daltonsの成分の割合が増加する結果となった。

一方、フミン酸が200mg/l存在する系でのネプツニウム (V) の分子量分布は、10,000~30,000 daltonsが主要な成分であった。このようなネプツニウム (V) の分子量分布は、フミン酸の場合と異なり、pH及びイオン強度のどちらに対しても大きな依存性が見られなかった。これらの結果は、ネプツニウム (V) - フミン酸錯体の分子量分布は、単純にフミン酸の分子量分布に従うのではないことを示している。

更に、ネプツニウム (V) - フミン酸錯体の錯形成定数をいくつかのpHにおいて、種々の分子量毎に調べた結果、10,000~30,000 daltonsの分子量におけるフミン酸との錯形成定数が大きい結果となり、特定の分子量にあるフミン酸とネプツニウム (V) との反応がネプツニウム (V) - フミン酸錯体の形成において重要であることが示唆された。

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1. Introduction

Humic acids are most widely distributed organic material in natural water. A study on formation of actinides pseudocolloid with nucleus of humic acid may be an important for understanding a migration behavior of actinides in ground water. The colloidal phase formation is influenced as enhancement of retardation factor of actinides by a filtration effect in soil layer and/or as a formation of moving phase due to low sorption ability of the colloidal phase onto geological material[1]. Gutierrez et al. suggested a presence of freely moving Np(V) species with humic substances rather than other species of Np(V) at a granitic core column experiment[2]. Tanaka and Senoo reported that the complexation of americium(III) with humic acid was based on the interaction of humic acid in a specific molecular size range[3][4]. Sakamoto et al. have shown that the formation of the colloidal Np(V)-humate over 5,000 daltons is recognized in pH range from 5 to 10 under humic acid concentrations of 32, 140 and 320 mg/l[5]. Molecular size distribution of actinides complexed with humic acid will be an important for understanding the migration behavior of actinides in the presence of humic acids.

The objective of this work was to study the colloidal formation and the complexation of Np(V) with humic acid, especially effects of ionic strength on the colloidal formation. The molecular size distributions of humic acid and Np(V)-humate have been measured as a function of pH and ionic strength using an ultrafiltration method, because the molecular size distribution of humic acid will be influenced by pH and ionic strength[6]. In addition to the molecular size distributions, a stability constants of Np(V)-humate are determined in some kinds of the molecular size to study the interaction between Np(V) and the humic acid.

2. Experiments

2.1 Humic Acid

Humic acid purchased from Aldrich Co. was purified, protonated and freeze-dried, whose procedure is described in the previous work[5]. The proton exchange capacity was 5.1 meq/g[5].

2.2 Molecular Size Determination by Ultrafiltration

1. Introduction

Humic acids are most widely distributed organic material in natural water. A study on formation of actinides pseudocolloid with nucleus of humic acid may be an important for understanding a migration behavior of actinides in ground water. The colloidal phase formation is influenced as enhancement of retardation factor of actinides by a filtration effect in soil layer and/or as a formation of moving phase due to low sorption ability of the colloidal phase onto geological material[1]. Gutierrez et al. suggested a presence of freely moving Np(V) species with humic substances rather than other species of Np(V) at a granitic core column experiment[2]. Tanaka and Senoo reported that the complexation of americium(III) with humic acid was based on the interaction of humic acid in a specific molecular size range[3][4]. Sakamoto et al. have shown that the formation of the colloidal Np(V)-humate over 5,000 daltons is recognized in pH range from 5 to 10 under humic acid concentrations of 32, 140 and 320 mg/l[5]. Molecular size distribution of actinides complexed with humic acid will be an important for understanding the migration behavior of actinides in the presence of humic acids.

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2. Experiments

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2.2 Molecular Size Determination by Ultrafiltration

2.2.1 Np(V) in the presence of humic acid

Neptunium(V)-237 solution of 6×10^{-6} M containing the humic acid was prepared at pH range from 5 to 10. Ionic strength of this solution was adjusted to 0.105 M using NaClO₄ solution. The humic acid concentration was 200 mg/l. A glass vessel including the solution was tightly sealed and was shaken in oven at 25°C to achieve an equilibrium between the humic acid and Np(V). After shaking it for 7 days, the solution was filtrated using a 0.45 μm Millipore Millex filter. The filtrated solution was fractionated into four kinds of filtering membranes of Millipore Ultrafree-CL with a nominal molecular size of 100,000, 30,000, 10,000 and 5,000 daltons. The nominal molecular sizes of the cutoff membrane filters were calibrated with a protein of known composition. Concentration of ²³⁷Np in each fraction was measured by a liquid scintillation counting (Packard Tri-Carb Model 2500TR/AB). The percentages of Np(V) among the molecular size fractions were calculated from the radioactivity concentration in each fraction.

The molecular size distribution of Np(V)-humate was also obtained in the ionic strength of 0.055 and 0.015 M solutions to study its ionic strength dependence.

All experiments were carried out under ambient aerobic conditions.

2.2.2 Humic acid

The humic acid solution of 200 mg/l was also fractionated into the 0.45 μm filter and four kinds of ultrafilter. The molecular size distribution of the humic acid was studied by the same manner as mentioned above. The humic acid concentration was determined from absorbance at 280 nm by using an UV-VIS spectrophotometer (Shimazu UV-3100).

2.2.3 Reproducibility of size fraction of humic acid and Np(V)-humate

The ultrafiltration method was selected to obtain the molecular size distribution of Np(V)-humate due to the handling with radioactive samples. Because sorption of the humic acid and Np(V) on the filters may affect on the results of their molecular size distributions, reproducibility of the fractionation with the ultrafilter has been confirmed by following manner. The 0.1 M NaClO₄ solution including ²³⁷Np(V) of 6.0×10^{-6} M and 200 mg/l humic acid was prepared at pH, 5.5, 7.1, and 8.4. The procedure of the size fractionation of Np(V) and humic acid was same as described above. The measurements of the molecular size distribution of them were carried out in triplicate under each pH conditions.

The results for the humic acid and Np(V) are listed in Table 1. Uncertainty of the

percentage fraction is within $\pm 3\%$ for the humic acid and is $\pm 6\%$ for Np(V). The uncertainty for Np(V) is larger than that of the humic acid. A contribution of radioactivity counting error to the uncertainty, which was approximately 5% in this work, is probably one of the reasons for this difference in the uncertainty between the humic acid and Np(V). From this results, it is probably that the measurements of the molecular size distribution of the humic acid and Np(V) have been carried out within $\pm 6\%$ by the ultrafiltration method in this work.

2.3 Measurements of Stability Constant of Np(V)-humate in Some Kinds of Molecular Size

Stability constant of Np(V)-humate with the humic acid in some kinds of molecular size has been obtained to study the interaction between Np(V) and the humic acid. The stability constant in 0.1 M NaClO₄ solution was determined with absorption spectra using the UV-VIS -NIR spectrophotometer. The concentration of ²³⁷Np in the solution containing the humic acid was fixed as 1×10^{-4} M, and the concentration of the humic acid was varied between 60 and 600 mg/l. The solution pH was adjusted to 6.9, 7.2 and 8.7. Ten ml of Np(V) solution containing the humic acid was sealed in a glass tube and shaken at 25°C. After 7 days, the solution was filtered by 0.45 μm Millex filter. Subsequently, the solution was fractionated into four kinds of the ultrafilter with nominal molecular size of 100,000, 30,000, 10,000 and 5,000 daltons. The concentrations of NpO₂⁺ and NpO₂HA in each fractionated solutions were determined by the spectrophotometer at 982.2nm and 990.7nm, respectively[5]. The concentration of the humic acid in each solutions was also measured by the UV-VIS spectrophotometer at 280 nm.

Using with the concentrations of NpO₂⁺, NpO₂HA and the humic acid, the overall stability constant of Np(V)-humate is obtained. A complexation between NpO₂⁺ and the functional groups of the humic acid is estimated to be 1:1 according to Kim and Sekine[7] and Sakamoto et al. [5]. Then, the overall stability constant of Np(V)-humate (β_1) is expressed as follows[5]:

$$\beta_1(\text{eq/l}) = [\text{NpO}_2\text{HA}] / [\text{NpO}_2^+] / [\text{HA}] \quad (1)$$

$$\log([\text{NpO}_2\text{HA}] / [\text{NpO}_2^+]) = \log \beta_1 + \log [\text{HA}] \quad (2)$$

Then, the β_1 can be calculated from the linear correlation of [HA] versus [NpO₂HA]/[NpO₂⁺] on the logarithm scale.

In this work, the stability constants of Np(V)-humate in four kinds of molecular size(100,000 daltons-0.45 μm, 30,000-100,000 daltons, 10,000-30,000 daltons and 5,000-10,000 daltons) were obtained on the following supposition;

- 1) The humic acid in each molecular size has no interaction each other.
- 2) Np(V)-humate in each molecular size has no interaction each other.
- 3) The ratio of the humic acid and Np(V)-humate in each molecular size is not changed by the fractionation by the ultrafilters.

The concept of the calculation of the stability constant of Np(V)-humate in each molecular size is shown in Fig.1. The stability constant of Np(V)-humate in the solution under 5,000 daltons is expressed as:

$$\beta_{1(5)} = [\text{NpO}_2\text{HA5}]/[\text{NpO}_2^+]/[\text{HA5}] \quad (3)$$

where $\beta_{1(5)}$ (eq/1) is the stability constant of Np(V)-humate under 5,000 daltons, $[\text{NpO}_2\text{HA5}]$ is concentration of Np(V)-humate under 5,000 daltons and $[\text{HA5}]$ is the uncomplexed concentration of the humic acid under 5,000 daltons. In the case of the molecular size from 5,000-10,000 daltons, the overall stability constant ($\beta^*_{1(4)}$) in the molecular size from 5,000-10,000 daltons is expressed as;

$$\beta^*_{1(4)} = ([\text{NpO}_2\text{HA4}] + [\text{NpO}_2\text{HA5}])/[\text{NpO}_2^+]/([\text{HA4}] + [\text{HA5}]) \quad (4)$$

$$= (\beta_{1(4)} [\text{NpO}_2^+] [\text{HA4}] + \beta_{1(5)} [\text{NpO}_2^+] [\text{HA5}])/[\text{NpO}_2^+] ([\text{HA4}] + [\text{HA5}]) \quad (5)$$

$$= (\beta_{1(4)} [\text{HA4}] + \beta_{1(5)} [\text{HA5}])/([\text{HA4}] + [\text{HA5}]) \quad (6)$$

where $\beta_{1(4)}$ is the stability constant of Np(V)-humate in the molecular size from 5,000 to 10,000 daltons, and $[\text{HA4}]$ is the concentration of the humic acid in the molecular size from 5,000 to 10,000 daltons. The values of $\beta_{1(5)}$ have been obtained from the equation (3) for the case of under 5,000 daltons. The $[\text{HA4}]$ was calculated by the subtracting $[\text{HA5}]$ and $[\text{NpO}_2\text{HA4}] + [\text{NpO}_2\text{HA5}]$ from total humic acid concentration in the solution under 10,000 daltons. The overall stability constant ($\beta^*_{1(4)}$) have been calculated by the equation (2) with the concentrations of $[\text{HA4}] + [\text{HA5}]$, $[\text{NpO}_2^+]$ and $[\text{NpO}_2\text{HA4}] + [\text{NpO}_2\text{HA5}]$ that were obtained from the absorbance by the UV-VIS-NIR spectrophotometer. Then, the stability constant of Np(V)-humate in the molecular size from 5,000 to 10,000 daltons ($\beta_{1(4)}$) was calculated from the equation (4) with $\beta^*_{1(4)}$, $\beta_{1(5)}$, $[\text{HA4}]$ and $[\text{HA5}]$. This calculation was repeated to determine the stability constants of Np(V)-humate in the molecular size from 10,000 to 30,000 daltons, in that from 30,000 to 100,000 daltons and in that from 100,000 daltons to $0.45 \mu\text{m}$ by following equation:

$$\beta^*_{1(n)} = (\beta_{1(n)} [\text{HAn}] + \sum_{m=n}^5 \beta_{1(m)} [\text{HAM}]) / (\sum_{m=n}^5 [\text{HAM}]) \quad (7)$$

n=3; molecular size from 10,000 to 30,000 daltons

=2; molecular size from 30,000 to 100,000 daltons

=1; molecular size from 100,000 daltons to $0.45 \mu\text{m}$

3. Results and Discussion

3.1 pH Dependence of Molecular Size Distribution

Figure 2 shows the pH dependence of the molecular size distribution of humic acid at the ionic strength of 0.105 M. The 40-50 % of the humic acid is fractionated into 10,000-30,000 daltons at pH 5-10. The humic acid in 30,000-100,000 daltons is present as over 20% below pH 6, but the percentages of humic acid in the fractions of 100,000 daltons-0.45 μ m, 5,000-10,000 daltons and less than 5,000 daltons are approximately constant as below 20%.

Figure 3 shows the result of the molecular size distribution of Np(V) in the absence of humic acid. Most of Np(V) is detected in the fraction of less than 5,000 daltons. According to speciation of Np(V) calculated by MINTeq[5] with thermodynamic data obtained by Neck et al. [8][9], the major chemical form of Np(V) in the absence of humic acid is cationic form, NpO_2^+ in aerobic condition up to pH 9. Then, the results in Figure 3 shows that most of Np(V) is in only cationic form in the absence of the humic acid.

Figure 4 shows the pH dependence of the molecular size distribution of Np(V) in the presence of humic acid of 200 mg/l. In this case, Np(V) is mainly present in the fractions of 10,000-30,000 daltons and less than 5,000 daltons. The percentage of the fraction of 10,000-30,000 daltons is larger than that of less than 5,000 daltons above pH 7. These fractions show the reverse trend with increasing in pH.

A logarithm of a stability constant of Np(V) with humic acid increases approximately linearly with pH[5][7][10] because the stability constant for phenolate group is about two times larger in logarithm than that for carboxylate group[10]. On the basis of these results, an abundance of Np(V)-humate in solution is expected to increase with pH instead of NpO_2^- , $\text{NpO}_2\text{CO}_3^-$ as reported by Sakamoto et al. [5]. In addition, because humic acid is mainly present in the fraction of 10,000-30,000 daltons as shown in Figure 1, the increasing in the Np(V) fraction of 10,000-30,000 daltons with pH in Figure 3 corresponds probably to the change in the chemical form from NpO_2^+ to Np(V)-humate.

3.2 Ionic Strength Dependence of Molecular Size Distribution

The ionic strength dependence of the molecular size distribution of humic acid and Np(V) was studied at pH 8.4. This pH region is dominant for the formation of colloidal Np(V)-humate (Figure 4) and the formation of other species of Np(V) is negligible on the

molecular size distribution as shown in Figure 3.

Figure 5 shows the molecular size distribution of humic acid and Np(V) in the presence of 200 mg/l humic acid as a function of the ionic strength. The fractions in less than 5,000 daltons, 5,000-10,000 daltons and 100,000 daltons-0.45 μ m are not shown in Figure 4 because the percentages in these fractions for both of humic acid and Np(V) were approximately constant as below 10-20% in the ionic strength from 0.015 to 0.105 M.

The percentage of humic acid in 10,000-30,000 daltons shows slight increase with the ionic strength, and on the contrary the percentage in 30,000-100,000 daltons decreases significantly with the ionic strength. This result indicates that relative amounts of small molecular size of humic acid and large one are different with the ionic strength of the solution. Nagao and Senoo suggested the same trend for molecular size distribution of Aldrich Chemical's humic acid with using a high performance gel permeation chromatography[11].

Variation of Np(V) fraction in 10,000-30,000 daltons is almost similar with that of humic acid(Figure 5), on the other hand, the percentage of Np(V) fraction in 30,000-100,000 daltons is remained constant with increasing in the ionic strength. Then, most of Np(V)-humate is in the fraction of 10,000-30,000 daltons in spite of the existence of the humic acid fraction of 30,000-100,000 daltons under low ionic strength condition.

Moriyama et al. reported the ionic strength dependence on the stability constant of Np(V)-humate[10]. The apparent stability constant of Np(V) for carboxylate groups of humic acid was $10^{2.69 \pm 0.08}$ at ionic strength 0.1 M and $10^{2.89 \pm 0.05}$ at ionic strength 0.01 M[10]. This result indicates that the apparent interaction of Np(V) with humic acid is in same degree in different ionic strength solution. From the result in Figure 4, however, practical interaction between Np(V) with the humic acid is assumed to be not same in different kinds of the ionic strength solution because the molecular size of humic acid is changed by changing in ionic strength. In the measurement of the stability constant, the complexation reaction is usually supposed to be related with functional group of whole humic acid. However, the result in Figure 4 may suggest that Np(V) interacts strongly with humic acid in the specific molecular size of 10,000-30,000 daltons. The whole functional groups of humic acid may not always be available for the complexation reaction for Np(V)-humate. The complexation reaction may relate to the molecular size distribution of humic acid.

3.3 Stability Constant of Np(V)-humate in Some Kinds of Molecular Size

The value of $\log[\text{NpO}_2\text{HA}]/[\text{NpO}_2^-]$ at pH 7.2 is plotted in Figure 6 as a function of $\log[\text{HA}]$ for four kinds of molecular size humic acid. The $[\text{NpO}_2\text{HA}]$ under 5,000 daltons was negligible small to calculate the stability constant. From these plots, the stability constants of Np(V)-humate in the each molecular size were calculated according to eq. (2)~(7). The logarithm of the stability constant at pH 7.2 is listed in Table 2. The $\log \beta_1$ in the molecular size from 10,000-30,000 daltons shows highest value which is about 3.3 times of the value in the molecular size from 10,000-30,000 daltons.

The pH dependence of the stability constant is shown in Figure 7. The logarithm of the stability constant increased linearly with pH in each molecular size. In the pH range from 7 to 9, the stability constant in the molecular size from 10,000-30,000 daltons is higher than the constants in other molecular size range, and the stability constants in all molecular size range shows similar pH dependency. This results imply that the complexation of Np(V) with the humic acid in the molecular size from 10,000 to 30,000 daltons is superior to that in other molecular size, and will support the difference of molecular size distribution between Np(V)-humate and the humic acid, as shown in Figure 5.

3.4 Interaction of Np(V) with Humic Acid

The molecular size distribution of humic acid structure varies with pH and ionic strength[6] by changing into an acidic nature as a result of ionization of the functional groups such as the COOH and phenolic OH groups[6]. The changing in the molecular size distribution of humic acid might lead the difference in the degree of molecular interactions between cationic radionuclides and humic acids. Tanaka and Senoo reported that the americium(III) complexation with humic acid was related to humic acid in molecular size of 30,000-100,000 daltons, and the interaction was influenced by steric hindrance around the functional groups due to the large hydrated ionic size of americium(III)[3].

In the case of Np(V), the effect of the hydrated ionic size must be considered to explain the specific interaction, moreover, geometry of NpO_2^+ may be also important. The neptunium atom of neptunyl ion is an environment of oxygen atoms, so that the coordination by the functional groups of humic acid may be influenced by a strongly electronegative oxygen atom[12]. Tochiyama et al. pointed out that the steric characteristics are important for the complexation of Np(V) with organic compounds[13]. The steric characteristic related to Np(V) structure is probably one of the reasons why the Np(V) ionic complexation with humic acid is connected to the interaction with humic acid in the specific molecular size.

4. Conclusion

From the results of the molecular size distribution of Np(V)-humate with the ultrafiltration method, Np(V) in the presence of humic acid 200 mg/l was mainly present in the specific molecular size fraction of 10,000-30,000 daltons. These results were supported by the measurements of the stability constants of Np(V)-humate in some kinds of molecular size. The specific interaction is considered Np(V) selectivity complexes with the humic acid in the specific molecular size due to the steric characteristics. The molecular size distribution of humic acid is an important to understand the complexation of Np(V) with humic acid and the characteristics of Np(V)-humate.

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Table 1 Molecular size distribution of humic acid and Np(V) in the presence of humic acid(200mg/l) by the ultrafiltration method

	pH	0.45 μ m -100,000 daltons (%)	100,000 -30,000 daltons (%)	30,000 -10,000 daltons (%)	10,000 -5,000 daltons (%)	5,000 daltons under (%)
Humic acid	8.4 \pm 0.10	7 \pm 3	14 \pm 2	42 \pm 1	17 \pm 2	20 \pm 1
	7.1 \pm 0.03	8 \pm 2	17 \pm 2	39 \pm 3	17 \pm 3	20 \pm 1
	5.5 \pm 0.02	10 \pm 2	29 \pm 2	31 \pm 2	12 \pm 3	19 \pm 2
Np(V) in the presence of humic acid	8.4 \pm 0.10	6 \pm 2	7 \pm 2	44 \pm 3	8 \pm 2	35 \pm 1
	7.1 \pm 0.03	1 \pm 4	11 \pm 3	39 \pm 3	5 \pm 6	44 \pm 4
	5.5 \pm 0.02	1 \pm 3	9 \pm 4	31 \pm 3	5 \pm 5	54 \pm 4

Ionic strength:0.105M

Table 2 Stability constant of Np(V)-humate in four kinds of molecular size

Molecular size	$\log\beta_1$
100,000 daltons-0.45 μ m	2.48
30,000-100,000 daltons	2.12
10,000-30,000 daltons	2.64
5,000-10,000 daltons	2.34

Ionic strength:0.105M, pH:7.2

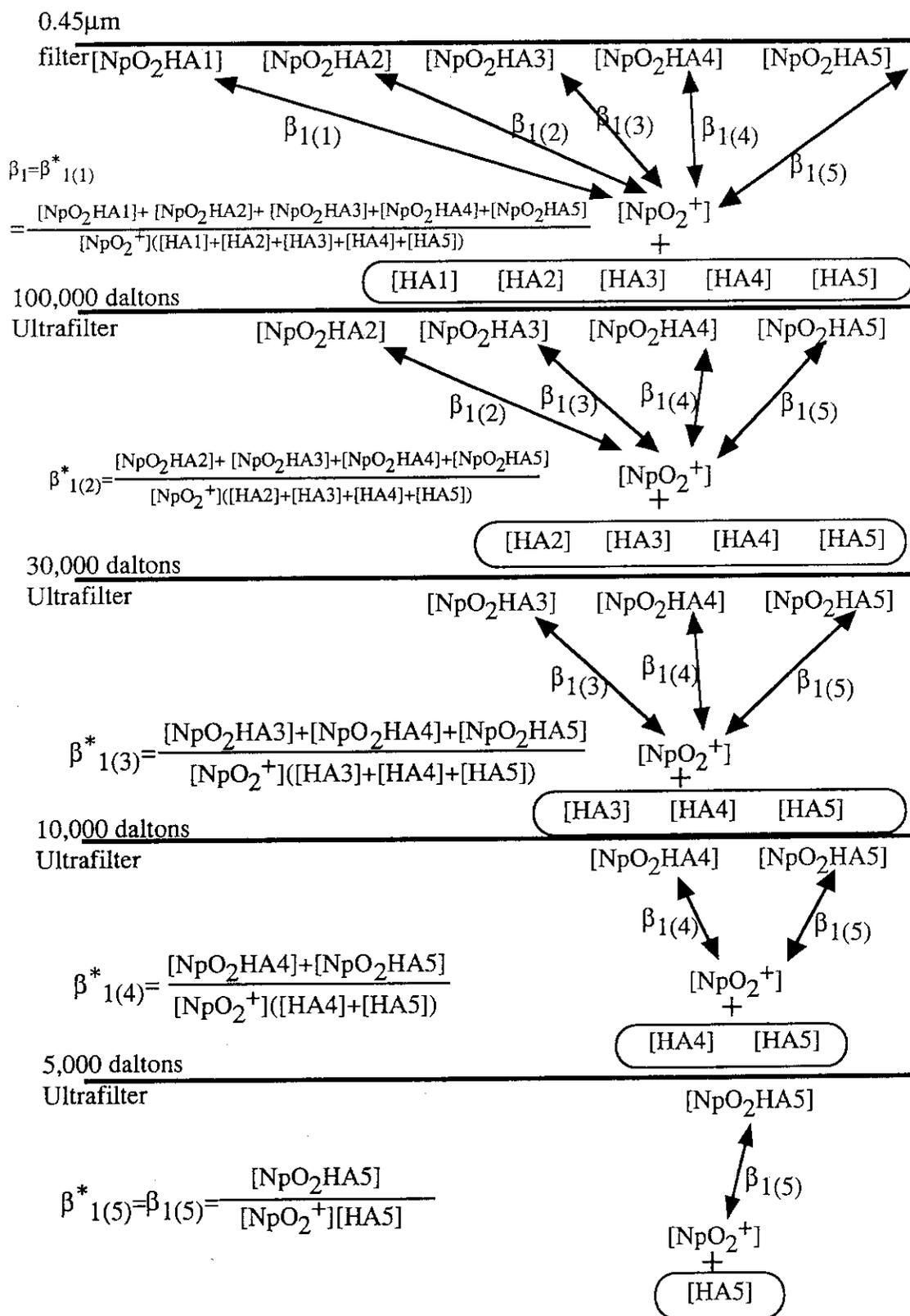


Figure 1 Concept of measurement of the stability constants of Np(V)-humate in some kinds of molecular size

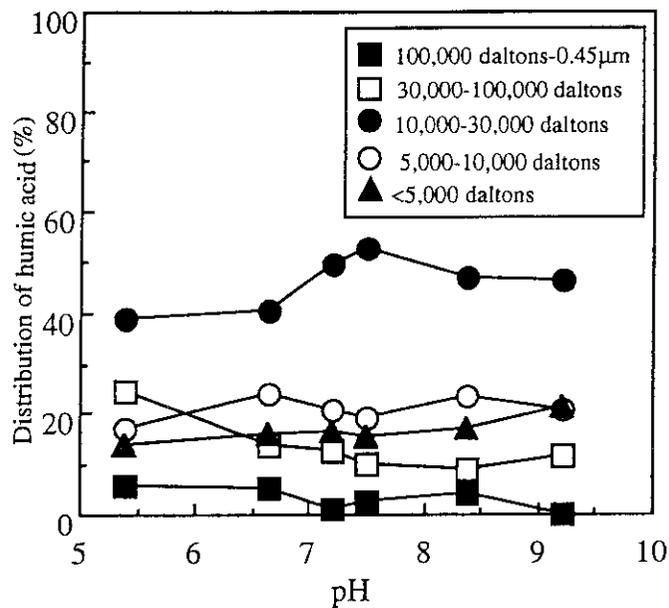


Figure 2 Effect of pH on the molecular size distribution of humic acid with 200 mg/l at the ionic strength of 0.105M

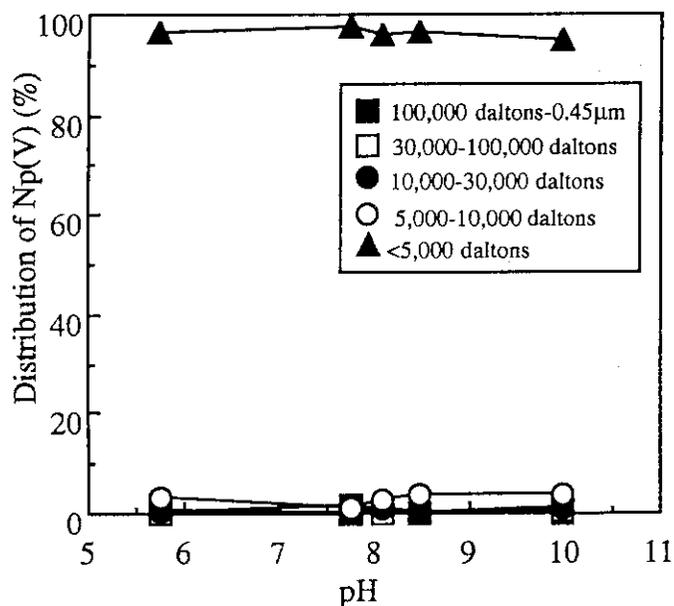


Figure 3 Effect of pH on the molecular size distribution of Np(V) in the absence of humic acid at the ionic strength of 0.105M

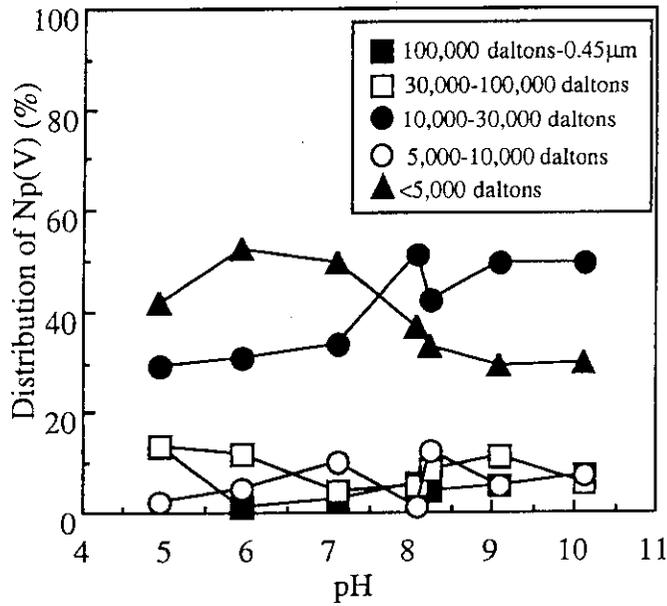


Figure 4 Effect of pH on the molecular size distribution of Np(V) in the presence of humic acid of 200 mg/l at the ionic strength of 0.105M

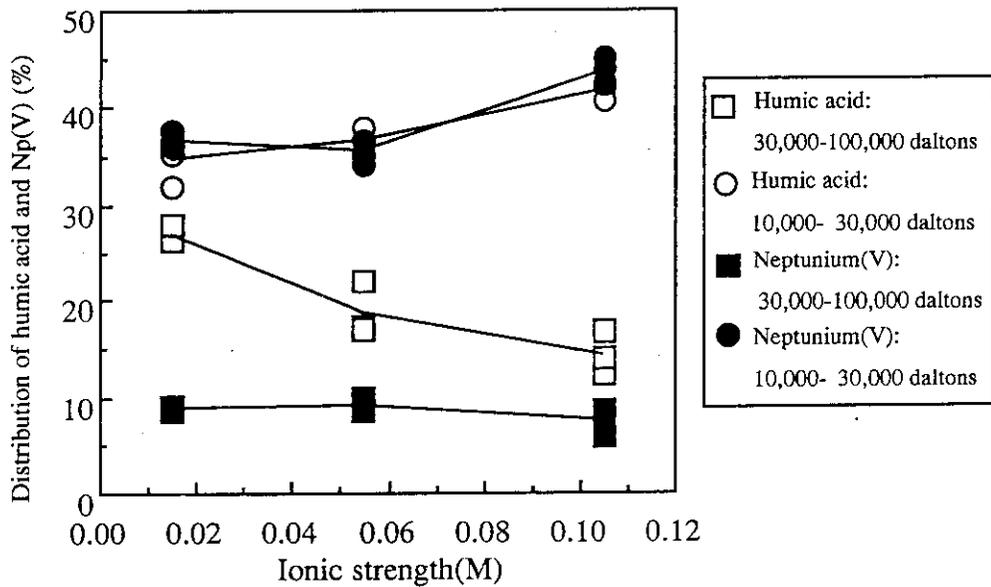


Figure 5 Effect of the ionic strength on the molecular size distribution of humic acid and Np(V) in the presence of humic acid of 200mg/l at pH 8.4

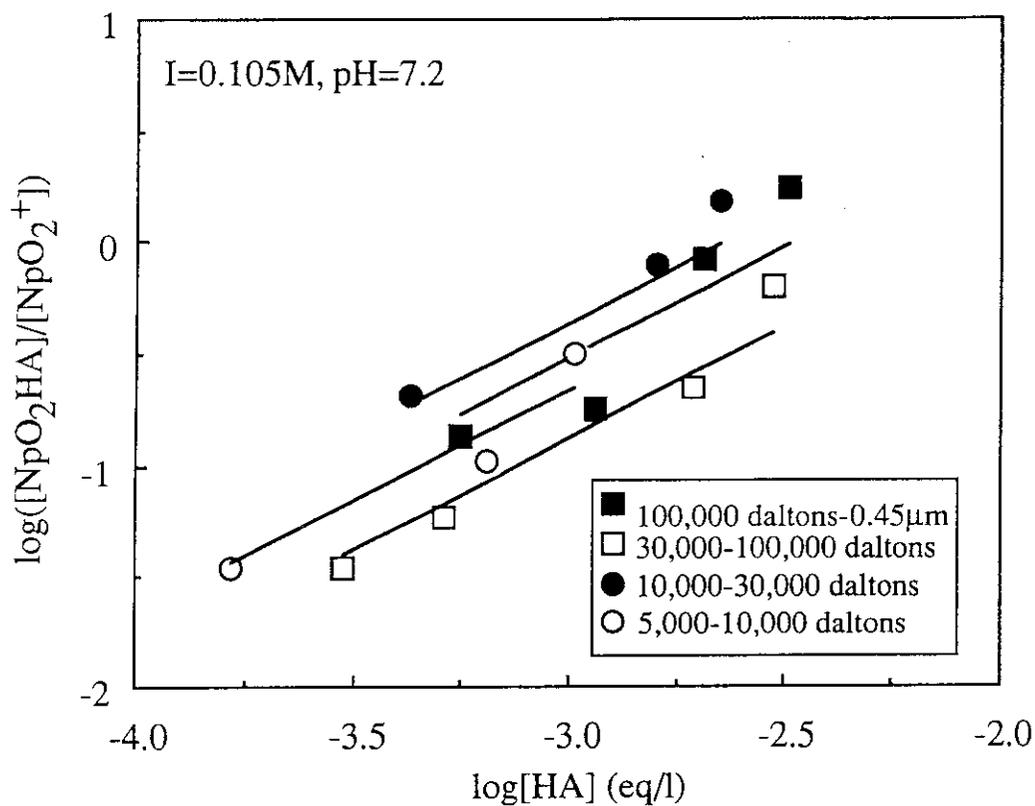


Figure 6 Relationship between $[NpO_2HA]/[NpO_2^+]$ ratio and concentration of uncomplexed functional group of the humic acid

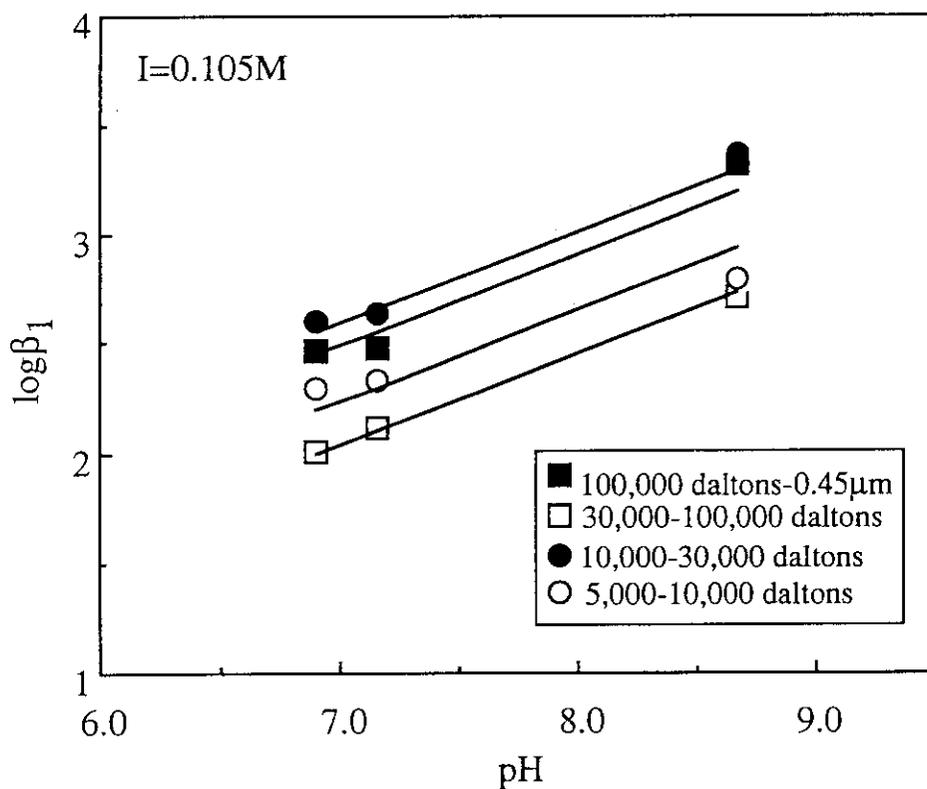


Figure 7 The pH dependence of the stability constant of Np(V)-humate in four kinds of molecular size