

フミン酸およびポリアクリル酸による鉄(II)の錯生成

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地下水中のフミン物質は、放射性核種と可溶性コロイド錯体を形成することにより、それらの移行挙動に影響を与えると考えられている。核種とフミン物質の相互作用を理解するためには、地下水中にもともと含まれている競争イオンによる影響をも評価しておく必要がある。この目的で、Fe(II)とアルドリッチ社製フミン酸との錯生成をイオン交換法により検討した。フミン酸の組成不均質性と高分子電解質性による影響を分離して評価するために、組成が均質な高分子弱酸であるポリアクリル酸(分子量 90000)についても同様の検討を行い、pH, イオン強度, 金属イオン濃度が錯生成に及ぼす影響を比較した。みかけの錯生成定数を $\beta_a = [ML]/([M][R])$ ($[M]$: 遊離 Fe^{2+} イオン濃度, $[ML]$: 錯生成している Fe^{2+} イオン濃度, $[R]$ は $C_R\alpha$ で, C_R はプロトン交換サイトの全濃度で α は解離度である)と定義し、pH 4.6 から 5.5, イオン強度 0.1 および 1.0 M NaCl Fe(II) 濃度 $\sim 10^{-8}$ から $\sim 10^{-4}$ M の溶液条件で $\log\beta_a$ の値を求めた。ポリアクリル酸錯体およびフミン酸錯体のいずれについても $\log\beta_a$ は解離度とともに増加しイオン強度とともに減少した ($I = 0.1$ M NaCl でポリアクリル酸錯体では 2.26 ($\alpha = 0.32$) から 2.59 ($\alpha = 0.47$), フミン酸錯体では, 4.66 ($\alpha = 0.58$) から 4.83 ($\alpha = 0.70$) $I = 1.0$ M NaCl でポリアクリル酸錯体では 0.53 ($\alpha = 0.49$) から 0.98 ($\alpha = 0.71$), フミン酸錯体では 3.31 ($\alpha = 0.59$) から 3.62 ($\alpha = 0.71$)). $\log\beta_a$ の $\log\alpha$ に対する依存性は両者で同程度であり, イオン強度依存性はフミン酸錯体の方がやや小さい。ポリアクリル酸錯体の $\log\beta_a$ は Fe(II)濃度の変化によらず一定であるが, フミン酸錯体の $\log\beta_a$ は, フミン酸の組成の不均質性のために, Fe(II)濃度が低くなると著しく上昇した ($I = 0.1$ M NaCl, $\alpha = 0.68$ で 3.21 ($C_{Fe} = 4 \times 10^{-4}$ M) から 4.79 ($C_{Fe} = 6 \times 10^{-8}$ M)), $I = 1.0$ M NaCl, $\alpha = 0.68$ で 2.35 ($C_{Fe} = 4 \times 10^{-4}$ M) から 3.58 ($C_{Fe} = 6 \times 10^{-8}$ M))。

Keywords: Fe(II), 錯生成, フミン酸, ポリアクリル酸, イオン交換

Humic substances in groundwater are expected to affect the migration behavior of radionuclides by forming soluble colloid complexes with radionuclides. In order to understand the interaction between radionuclides and humic substances, it is also important to estimate the effect of the competing cations originally present in the groundwater. In this connection, the complex formation of Fe(II) with Aldrich humic acid has been investigated by ion exchange method. To evaluate the effect of heterogeneous composition and of polyelectrolyte nature of humic acid, the complex formation of Fe(II) with homogeneous polymeric weak acid, polyacrylic acid ($MW = 90000$ Dalton) has been also examined to compare the effect of pH, ionic strength and metal-ion concentration on the complex formation. By defining the apparent formation constant as $\beta_a = [ML]/([M][R])$, where $[M]$ and $[ML]$ are the concentrations of free and bound Fe^{2+} ion, and $[R] = C_R\alpha$ (C_R is the total concentration of proton exchange sites and α is the degree of dissociation of humic or polyacrylic acid), the values of $\log\beta_a$ have been obtained at pH 4.6 to 5.5 in 0.1 and 1.0 M NaCl at the concentration of Fe(II) from $\sim 10^{-8}$ to $\sim 10^{-4}$ M. For both humate and polyacrylate complexes, $\log\beta_a$ increased with the degree of dissociation and decreased with ionic strength (at $I = 0.1$ M NaCl, from 2.26 ($\alpha = 0.32$) to 2.59 ($\alpha = 0.47$) for Fe(II)-polyacrylate and from 4.66 ($\alpha = 0.58$) to 4.83 ($\alpha = 0.70$) for Fe(II)-humate, and at $I = 1.0$ M NaCl, from 0.53 ($\alpha = 0.49$) to 0.98 ($\alpha = 0.71$) for Fe(II)-polyacrylate and from 3.31 ($\alpha = 0.59$) to 3.62 ($\alpha = 0.71$) for Fe(II)-humate). The dependence of $\log\beta_a$ of humate on $\log\alpha$ was similar to that of polyacrylate and that of humate on ionic strength was slightly less than that of polyacrylate. While the variation of Fe(II) concentration had no appreciable influence on $\log\beta_a$ of Fe(II)-polyacrylate, $\log\beta_a$ of Fe(II)-humate appreciably increased at lower Fe(II) concentrations due to the heterogeneous composition of the humic acid (at $I = 0.1$ M NaCl, $\alpha = 0.68$, from 3.21 ($C_{Fe} = 4 \times 10^{-4}$ M) to 4.79 ($C_{Fe} = 6 \times 10^{-8}$ M) and at $I = 1.0$ M NaCl, $\alpha = 0.68$, from 2.35 ($C_{Fe} = 4 \times 10^{-4}$ M) to 3.58 ($C_{Fe} = 6 \times 10^{-8}$ M)).

Keywords: Fe(II), Complex formation, Humic acid, Polyacrylic acid, Ion exchange

1 Introduction

In the safety assessment of underground disposal of radioactive wastes, one of the key mechanisms in retarding the possible transport of radionuclide from a disposal facility to the biosphere through groundwater flow is the sorption of radionuclide onto host rocks in geological barrier system. In this process, however, when high concentrations of dissolved organic materials exist in groundwater, they could have a strong detrimental effect on the sorption. Since organic materials such as humic (and fulvic) acids have high binding strengths to metal cations and tendency to exist as colloids in solution [1-3], radionuclides sorbed onto host rocks will be redissolved into the groundwater as complexes with the humic acids and mobilized in the groundwater flow [4,5]. Because of the widespread existence of humic acids in groundwater (around 1ppm or more),

the parameters affecting on the humic acids-radionuclides interaction should be studied in detail for understanding of migration behavior of radionuclides.

One of the main reasons for the difficulty in clarifying this interaction is that humic acids are mixtures of various ill-defined organic macromolecules with different compositions, structures and molecular weights and their complex-forming characteristics cannot be treated as those of simple molecules[1,6-7]. Due to the complication introduced by the heterogeneous composition and polyelectrolyte nature of humic acid, dependences of the interaction between metal ions and humic acids upon ionic strength, pH and metal-ion concentration are still unclear. Our previous studies on the complex formation of NpO_2^+ [8], Eu^{3+} [9], and Ca^{2+} [10] with Aldrich humic acid revealed that the apparent formation constants of humate complexes increases with pH and decreases with ionic strength mainly due to the polyelectrolyte nature of the humic acid. More importantly, the constants considerably increase with the decrease in metal-ion concentrations. This fact implies that the effect of foreign cations originally present in groundwater on the complex formation is dependent not only

Complex Formation of Fe(II) with Humic Acid and Polyacrylic Acid, by: Budi Setiawan, Kouichi Tanaka, Yuichi Niibori and Osamu Tochiyama (osamu.tochiyama@qse.tohoku.ac.jp)

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on the concentration of the concerned metal ion itself but also on the concentrations of foreign cations. To understand the effect of competing cations originally present in groundwater, the complex formation of Fe(II) with Aldrich humic acid has been investigated as a function of pH, ionic strength and Fe(II) concentration. In the anaerobic condition in deep underground, iron predominantly exists in divalent state. Although concentrations of iron in groundwater are low (around 10^{-7} to 10^{-4} M[1]), they are still comparable to the concentrations of dissolved organic materials. To separately estimate the effect of heterogeneous composition and that of polyelectrolyte nature each other, the complex formation of Fe(II) with the homogeneous polymeric weak acid, PAA (polyacrylic acid, $[-CH_2CH(COOH)-]_n$), has been also examined and compared with the humic acid.

Usually, the formation constant of a metal complex is defined as,

$$K = \frac{[ML]}{[M][L]} \quad (1)$$

where [L] is the concentration of free ligand, [M] and [ML] denote the concentrations of free and bound metal ion, respectively. However, in the complex formation of metal ion with humic acid or polyacrylic acid, functional groups which bind to metal ions are fixed to a macromolecule and we do not know how many functional groups coordinate to a single metal ion. This makes the estimation of [L] impossible. Although various definitions have been used[11-21], the present study takes the following definition of the apparent complex formation constant.

$$K_a = \frac{[ML]}{[M][R]} = \frac{[ML]}{[M] C_R \alpha} \quad (2)$$

where [M] and [ML] are the concentration of free and bound Fe^{2+} ion, and [R] is the concentration of free dissociated proton exchanging sites. When the amount of dissociated proton exchanging sites consumed in making the complex is negligible as compared to the total amount of the dissociated functional groups, [R] can be approximated by $C_R \alpha$ where C_R is the total concentration of proton exchange sites and α is the degree of dissociation of humic or polyacrylic acid. The advantage by using this definition is that the values of C_R and α can be independently determined by the potentiometric titration of humic or polyacrylic acid. The effect of polyelectrolyte nature and heterogeneous composition can be disclosed by examining the change in β_α with pH, ionic strength and metal-ion concentration.

Ion exchange method has been used to study the complex formation of Fe(II) with humic and polyacrylic acids. As compared with solvent extraction, ion exchange method has a limitation in the point that the ion exchanger (gel) phase cannot be completely separated from the aqueous phase due to the wetting of the gel phase. Since the concentration of the metal ion in the exchanger phase cannot be directly measured, it is obtained as a difference between the initial added concentration of the metal ion and that remained in the aqueous phase at equilibrium. This makes the range of the measurable

distribution ratio rather limited, and as a result, the concentration of the complexing ligand cannot be varied in a wide range. However, when we have tried to apply the solvent extraction method to the study of the complex formation of Fe(II) with polyacrylic acid, some unknown side reaction occurred at high ligand concentrations. In the solvent extraction system, the coexistence of the extracting reagent is unavoidable and this is undesirable to the present case where the oxidation of Fe(II) is worried. For this reason, ion exchange method has been applied because the method does not introduce any foreign reagents other than the concerned metal ion and ligand.

2 Experimental

2.1 Reagents

Radiotracer ^{59}Fe (specific radioactivity 37MBq/ml, carrier 0.56mg Fe/ml, radionuclide purity 99.00%) obtained from NEN[®] Life Science Products, Inc. was diluted to about 1.4×10^{-6} M by 0.01M HCl and kept in a polyethylene bottle as a stock solution. 25wt% aqueous solution of polyacrylic acid ($MW=90000$ Daltons) from Polysciences Inc. was used as received. Aldrich humic acid was purified by the procedure based on the description given in the references[3, 22-23]. A sample of 5g of Aldrich humic acid was dissolved in 5L solution containing 0.1 M NaOH and 1g NaF. After adjusting the pH of the solution to 7 by the addition of HCl, the solution was stirred overnight with N_2 bubbling. Solution containing dissolved HA was passed through 0.45 μ m membrane filter (Advantec) to separate macro-size particles and then the filtrate solution was acidified with 2M HCl to pH1. After standing the solution for several hours, the supernatant was discarded and the precipitate was dissolved again into 0.1 M NaOH. Then the solution was acidified again to pH1 and the procedure was repeated for 3 times. The suspension was centrifuged (3000rpm, 15min.) and the precipitate was washed with 0.1 M HCl repeatedly until $[Na^+]$ becomes ≤ 10 mg/l in supernatant. The precipitate was then freeze-dried (Eyela FDU-810), washed with distilled water and centrifuged. The precipitate was washed repeatedly until ion meter reading of $[Cl^-]$ is less than 50mg/l in supernatant. The precipitate was freeze-dried and stored in a desiccator.

The synthetic organic cationic resin, Amberlite 200CT (Na-type) with exchange capacity 4.3meq/g was used because of its applicability to a broad pH range of 0 to 14. The resin was settled in a column and purified by passing successively 1M HCl and 1M NaCl. The cycle was repeated three times. Finally, the resin was equilibrated with 0.16 M NaCl. After rinsing with distilled water, the resin was spread in a thin layer on a tray for air-drying.

Other chemicals were obtained from Dojindo Laboratories or Wako Pure Chemical Industries and were used without further purification.

2.2 Procedures

The calibration of the electrode for pcH measurements (pcH is the negative logarithms of hydrogen ion concentrations) were conducted as described previously[24]. In order to estimate the concentration of dissociated functional groups, [R] in eq. (2), the titration curves of Aldrich humic acid and polyacrylic acid were obtained at $I = 0.1$ and 1.0M NaCl in the same way as described previously [24, 8]. Maximum proton exchange capacities (C_R) were obtained to be $4.95\sim 5.10\text{meq/g}$ for the humic acid and 12.88 meq/g for polyacrylic acid. The concentration of dissociated functional group at each pcH was calculated by applying the following relation to the titration results:

$$[\text{H}^+] + [\text{NaOH}]_{\text{added}} = [\text{OH}^-] + [\text{R}] \quad (3)$$

$$[\text{R}] = C_R \quad (4)$$

where $[\text{H}^+] = 10^{-\text{pcH}}$, $[\text{OH}^-] = 10^{\text{pK}_w - \text{pcH}}$ and $\text{pK}_w = 13.78$ ($I = 0.1$), 13.69 (0.4), 13.71 (1.0) [25].

For the determination of complex constants, the resin was contacted in a glass tube with 5 ml of aqueous phase containing a variable concentration of humic or polyacrylic acid, 0.02M hydroxyl ammonium chloride, 0.1 or 1.0M NaCl, buffer reagents (a mixture of 0.02M of 2-(N-morpholino) ethanesulfonic acid and tris(hydroxymethyl) aminomethane, varied from pcH 4.6 to 5.5) and Fe(II) (varied from $\sim 10^{-8}$ to $\sim 10^{-4}\text{M}$) labeled with ^{59}Fe . The tube was capped with rubber cap and shaken by using reciprocal shaker for 150min at $25 \pm 1^\circ\text{C}$. After the centrifugation (2000rpm , 10min.), activity of 1 ml of the aqueous phase was measured with a well-type of NaI(Tl) scintillation counter. The distribution coefficient K_d was calculated by,

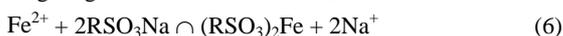
$$K_d = \frac{A_T - A_{\text{eq}}}{A_{\text{eq}}} \frac{V}{m} \quad (5)$$

where A_T and A_{eq} are the activities of 1 ml of the aqueous phase in the absence and presence of the ion exchange resin, respectively, V is the volume (ml) of the aqueous phase, and m is the mass (g) of the resin. The remaining part of the aqueous phase was used for the pH measurement.

3 Results and discussions

3.1 Distribution of Fe(II) in the absence of humic or polyacrylic acid

The ion exchange reaction of Fe(II) in the absence of any complexing reagents can be described as,



where Fe^{2+} and Na^+ are free ions in the aqueous phase, RSO_3Na and $(\text{RSO}_3)_2\text{Fe}$ are Na^+ and Fe^{2+} ions bound to the resin. Equilibrium constant for eq.(6) becomes,

$$K_{\text{ex}} = \frac{([\text{Fe}^{2+}]_R [\text{Na}^+]^2)}{([\text{Fe}^{2+}] [\text{Na}^+]_R^2)} \quad (7)$$

Brackets with subscript R indicate the concentration of Fe(II) in the resin (mmol/g) and without subscript in the solution (mmol/ml). K_{ex} is the conditional constant which changes with the solution condition such as ionic strength (due to the changes in the activity coefficients of the ionic species in the aqueous and resin phases). The distribution coefficient, K_d , of a metal ion is defined as,

$$K_d^0 = \frac{[\text{Fe}^{2+}]_R}{[\text{Fe}^{2+}]} = K_{\text{ex}} \frac{([\text{Na}^+]_R)^2}{([\text{Na}^+])^2} \quad (8)$$

To check the applicability of the ion exchange system to the study of complex formation, the effects of the shaking time, the ratio of the resin mass to the solution volume, pcH and ionic strength on the distribution of Fe(II) were examined. K_d^0 values for the shaking time from 30 to 150minutes were obtained and 90minutes was confirmed to be enough for the Fe(II) distribution to reach equilibrium. The shaking time of 150minutes was adopted for the experiments. For 5ml of the aqueous solution, from 0.01 to 0.05g of the resin was confirmed to give a constant K_d^0 value and the experiments have been carried out in this range of the mass to volume ratio. As for pcH of the solution, K_d^0 was constant in the range of pcH 4.2 – 5.6 as suggested by eq.(6). Beyond pcH 5.6, the K_d^0 value increased with pcH probably due to the hydrolysis of ferrous iron in the solution. For the present study, pcH range used for the complexation experiments was 4.6 to 5.5. Figure 1 shows the dependence of $\log K_d^0$ on the ionic strength. At the ionic strengths of 0.1, 0.4 and 1.0 M NaCl, values of $\log K_d^0$ were obtained to be 2.79, 1.78 and 1.09, respectively. These values indicate that $\partial \log K_d^0 / \partial \log [\text{Na}^+] \cong -1.7$, not exactly -2 as expected from eq.(8). This is considered due to the changes in the activity coefficients of Fe^{2+} and Na^+ in the aqueous and resin phases. Since the distribution of Fe(II) is considered to follow eqs. (6) and (7), the result can be considered to be indicating that the ion exchange reaction between the iron ion of charge +2 and sodium ion of charge +1 given by eq. (6) is taking place without any side reaction. Thus, it can be concluded that iron ion exists predominantly as Fe^{2+} ion under the condition used in the experiments.

3.2 Determination of $\log \beta_n$ by the ion exchange method

In the presence of humic or polyacrylic acid, the distribution coefficient of Fe(II) decreases from K_d^0 to K_d due to the complex formation of Fe(II) with humic or polyacrylic acid.

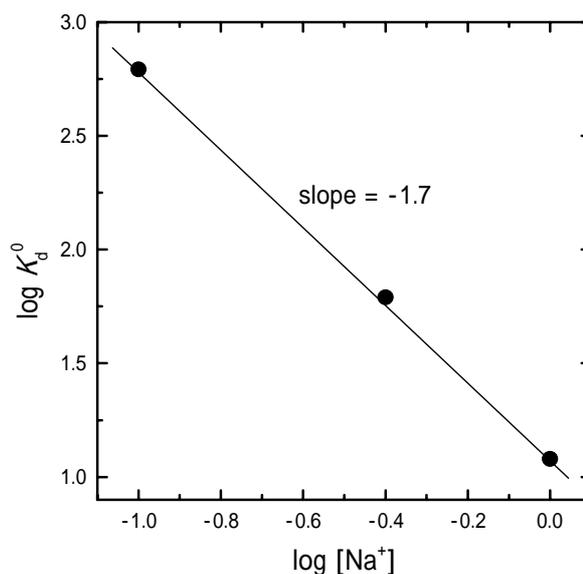


Fig. 1 The distribution of Fe(II) as a function of ionic strength in the absence of any complexing agents.

$$K_d = \frac{[\text{Fe}^+]_R}{[\text{Fe}^{2+}] + [\text{FeL}]} = \frac{K_d^0}{1 + \frac{K_d^0}{C_R}} \quad (9)$$

where β_α is the apparent complex formation constant defined by eq.(2). By measuring K_d values as a function C_R at a fixed pcH and comparing them with K_d^0 , β_α can be estimated. To obtain a complex formation constant, eq.(9) can be transformed into the following linear relationship famously called as Schubert's method [26],

$$\frac{1}{K_d} = \frac{1}{K_d^0} + \frac{1}{K_d^0} [\text{R}] \quad (10)$$

By plotting $1/K_d$ against $[\text{R}]$, $1/K_d^0$ and β_α/K_d^0 will be obtained as an intercept and a slope. This linear equation is simple and easy to grasp the validity of the assumed reactions from the obtained data. On the other hand, the measurements of K_d were carried out so as to the errors in the values of $\log K_d$ (calculated from the α -activities of ^{59}Fe in the solutions in the presence and absence of humic or polyacrylic acid) were nearly equal in these experiments. Therefore, for the calculation of $\log \beta_\alpha$, an optimum set of $\log K_d^0$ and $\log \beta_\alpha$ were obtained by a nonlinear least-squares fitting which minimized the sum of the squares of residuals between $\log K_d$ (observed) and $\log K_d$ (calculated),

$$S = \{\log K_d(\text{observed}) - \log K_d(\text{calculated})\}^2 \quad (11)$$

where

$$\log K_d(\text{calculated}) = \log K_d^0 - \log(1 + 10^{\log \beta_\alpha + \log [\text{R}]}) \quad (12)$$

In practice, the fittings of the data to eq.(10) and to eq.(12) did not give any appreciable differences in the calculated $\log \beta_\alpha$. Therefore, the results will be shown by the form of the plots of $1/K_d$ against $[\text{R}]$.

Typical examples of the experimental results for the complex formation of Fe(II) with polyacrylic acid are given in Figs. 2 and 3 in the form of the plots of $1/K_d$ against $[\text{R}]$. When pcH and ionic strength are fixed constant, the plots give a linear relationship between K_d and $[\text{R}]$ (the straight lines are the result of the fitting by eqs.(11) and (12)), indicated the validity of the assumed reaction given by eq.(10). Figures 2 and 3 also indicated that the slope varies with pcH and with ionic strength, i.e. $\log \beta_\alpha$ defined by eq.(2) is not constant but varies with pcH and ionic strength. Similar experiments were conducted at different sets of pcH, ionic strength and Fe(II) concentration, and the results are summarized in Table 1. The deviations given for the values of $\log \beta_\alpha$ and $\log K_d^0$ are the standard deviations σ which were estimated from the data. The systematic errors arising from the flaw in the design of the experiment, in the preparation of the reagents and solutions, in the estimation of α , etc. are considered larger than these values of σ , and the uncertainties of the values of $\log \beta_\alpha$ are estimated to be 0.05 to 0.1. As expected from the charge of Fe^{2+} ion, the values of $\log \beta_\alpha$ are not very large.

3.3 Complex formation of Fe(II) with polyacrylate

Table 1 shows the values of $\log \beta_\alpha$ of Fe(II)-polyacrylate obtained at various conditions. The variation of Fe(II) concentration has no influence on the value of $\log \beta_\alpha$ of

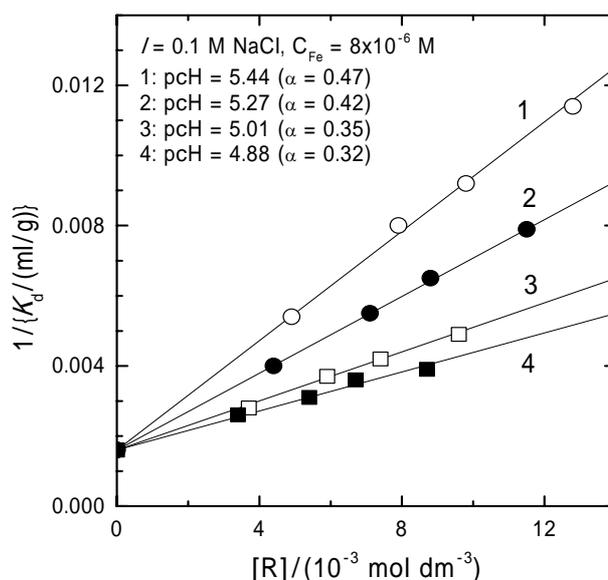


Fig. 2 Distribution of Fe(II) as a function of polyacrylate concentration at $I = 0.1 \text{ M}$, $C_{\text{Fe}} = 8 \times 10^{-6} \text{ M}$.

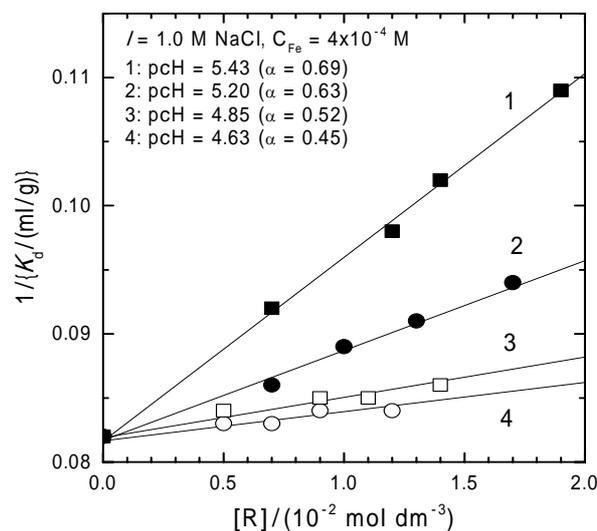


Fig. 3 Distribution of Fe(II) as a function of polyacrylate concentration at $I = 1.0 \text{ M}$, $C_{\text{Fe}} = 4 \times 10^{-4} \text{ M}$.

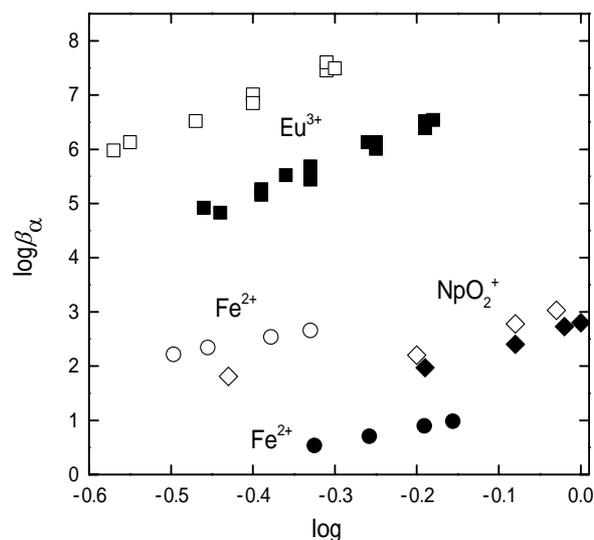
Fe(II)-polyacrylate. This is reasonable because polyacrylic acid is a homogeneous polymeric acid and the ligand species in the complex is the same at all Fe(II) concentrations. On the other hand, $\log \beta_\alpha$ changes with α and with ionic strength. Since, in the definition of eq.(2), the concentration of the dissociated monomeric unit, $[\text{R}] = C_R \alpha$, is simply used in place of the concentration of the true ligand species, $\log \beta_\alpha$ would increase with α if more than one carboxylate groups coordinate to a single Fe^{2+} ion, because the dependence of the concentration of multidentate unit (a set of two or more dissociated adjacent carboxylate groups) on pH ($\partial \log [\text{L}] / \partial \text{pH}$) is larger than $[\text{R}]$. This may be understood when one considers, for example in the oxalic acid, the increase in $[\text{C}_2\text{O}_4^{2-}]$ with pH as compared to that of the simple anionic charge. As a result, $\log \beta_\alpha$ increases with α , reflecting the number of carboxylate groups coordinating to each metal ion. In Fig.4, the dependences of $\log \beta_\alpha$ on $\log \alpha$ are

Table 1 Apparent formation constant of Fe(II)-polyacrylate complex

I/M	C_{Fe}/M	pcH	α	$\log\beta_\alpha$	$\log K_d^0$
0.1	6×10^{-8}	4.89	0.32	2.26 ± 0.03	2.79 ± 0.01
		5.07	0.37	2.36 ± 0.05	2.79 ± 0.01
		5.32	0.44	2.67 ± 0.02	2.79 ± 0.01
		5.46	0.47	2.59 ± 0.04	2.79 ± 0.01
8×10^{-6}	8×10^{-6}	4.88	0.32	2.23 ± 0.01	2.79 ± 0.01
		5.01	0.35	2.33 ± 0.01	2.79 ± 0.01
		5.27	0.42	2.53 ± 0.01	2.79 ± 0.02
		5.44	0.47	2.68 ± 0.02	2.79 ± 0.02
4×10^{-4}	4×10^{-4}	4.77	0.29	2.14 ± 0.03	2.79 ± 0.01
		4.97	0.34	2.30 ± 0.03	2.79 ± 0.01
		5.20	0.40	2.66 ± 0.03	2.79 ± 0.01
		5.46	0.48	2.97 ± 0.03	2.79 ± 0.02
0.4	8×10^{-6}	4.87	0.44	1.23 ± 0.01	1.78 ± 0.01
		5.05	0.49	1.38 ± 0.01	1.79 ± 0.01
		5.31	0.57	1.54 ± 0.01	1.79 ± 0.01
		5.48	0.62	1.63 ± 0.01	1.78 ± 0.01
1.0	6×10^{-8}	4.76	0.49	0.53 ± 0.10	1.09 ± 0.01
		5.01	0.57	0.72 ± 0.01	1.09 ± 0.01
		5.28	0.65	0.86 ± 0.04	1.09 ± 0.01
		5.49	0.71	0.98 ± 0.04	1.09 ± 0.01
8×10^{-6}	8×10^{-6}	4.72	0.47	0.54 ± 0.01	1.09 ± 0.01
		4.96	0.55	0.67 ± 0.01	1.09 ± 0.01
		5.26	0.64	0.89 ± 0.01	1.09 ± 0.01
		5.44	0.70	0.98 ± 0.01	1.09 ± 0.01
4×10^{-4}	4×10^{-4}	4.63	0.45	0.45 ± 0.02	1.09 ± 0.01
		4.85	0.52	0.59 ± 0.01	1.09 ± 0.01
		5.20	0.63	0.93 ± 0.01	1.09 ± 0.01
		5.43	0.69	1.25 ± 0.01	1.09 ± 0.01

compared for Fe(II), Eu(III) [9, 27] and Np(V)-polyacrylates [8, 24]. The dependences are in the order of $Eu^{3+} > NpO_2^+ \cong Fe^{2+}$, indicating that the number of carboxylates coordinating to a single metal ion is somewhat larger for Eu(III) and similar for Fe(II) and Np(V) despite the difference in the formal charge of Fe^{2+} and NpO_2^+ . In the case of NpO_2^+ ion, NpO_2^+ is the dioxo ion and the charge density on the central neptunium atom is higher than its formal charge of +1. Thus, the above order suggests that the higher charge density on the central neptunium atom contributes to some extent to the complex formation of Np(V) with polyacrylate.

The effect of ionic strength on $\log\beta_\alpha$ discloses the polyelectrolyte nature of polyacrylic acid. The changes in $\log\beta_\alpha$ of Fe(II), Eu(III) and Np(V)-polyacrylate with ionic strength are much larger than expected from the changes in the activity coefficients of Fe^{2+} , Eu^{3+} and NpO_2^+ ions in the aqueous solution. This may be explained by the consideration of the structure of the electrical double layer around the polyacrylate [10]. Since anionic carboxylate groups in polyacrylate are fixed to a macromolecular matrix, they give fairly high charge

**Fig. 4** Apparent formation constants of Eu(III), Fe(II) and Np(V)-polyacrylate as a function of $\log\alpha$.

□ : $I = 0.1 M$, ◻ : $I = 1.0 M$,
 ◻ : Eu(III)-polyacrylate, ◻ : Fe(II)-polyacrylate,
 ◻ : Np(V)-polyacrylate

density. Thus, in the surrounding of dissociated polyacrylic acid, a part of the surface charge is neutralized by Na^+ ions attracted by the crowded negative charge. Therefore the concentration of Fe^{2+} , Eu^{3+} or NpO_2^+ in the close vicinity of polyacrylate is controlled by the competition between Na^+ and Fe^{2+} , Eu^{3+} or NpO_2^+ to this zone. In other words, some part of the complex formation of metal ion-polyacrylate proceeds via an ion exchange between Na^+ and the metal ion. However, in the present definition of β_α , Na^+ ions are assumed not to be complexed no matter what they are close to or apart from the polyanion. As a result, $\log\beta_\alpha$ is expected to change with the concentration of background salt. In Fig.4, $\log\beta_\alpha$ of Fe(II), Eu(III) and Np(V)-polyacrylates are compared. As expected from the above-considered ion exchange reaction in the electrical double layer formed in the close vicinity of the polymeric anion, the effect of ionic strength is in the order of the charge of the metal ions, i.e. $Eu^{3+} \square Fe^{2+} > NpO_2^+$.

3.4 Complex formation of Fe(II) with humate

In the same manner as in the study of Fe(II)-polyacrylate, the values of $\log\beta_\alpha$ were obtained for Fe(II)-humate. Typical examples of the experimental results for the complex formation of Fe(II) with humic acid are given in Figs 5 and 6, and all the results are summarized in Table 2. Similarly to Fe(II)-polyacrylate, the plots give a linear relationship between K_d and $[R]$, indicating the validity of this ion exchange method. The value of $\log\beta_\alpha$ varies with α and with ionic strength in a similar manner as in Fe(II)-polyacrylate. A distinct difference can be seen in the effect of Fe(II) concentration.

In Fig.7, the effect of Fe(II) concentration on $\log\beta_\alpha$ of Fe(II)-humate is compared with that of Fe(II)-polyacrylate in the form of the plots of $\log\beta_\alpha$ against $\log\alpha$. It clearly indicates

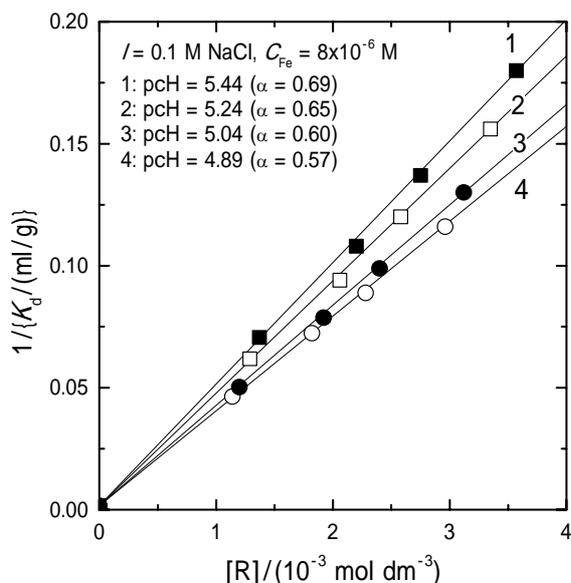


Fig. 5 Distribution of Fe(II) as a function of humate concentration at $I = 0.1 \text{ M}$, $C_{\text{Fe}} = 8 \times 10^{-6} \text{ M}$.

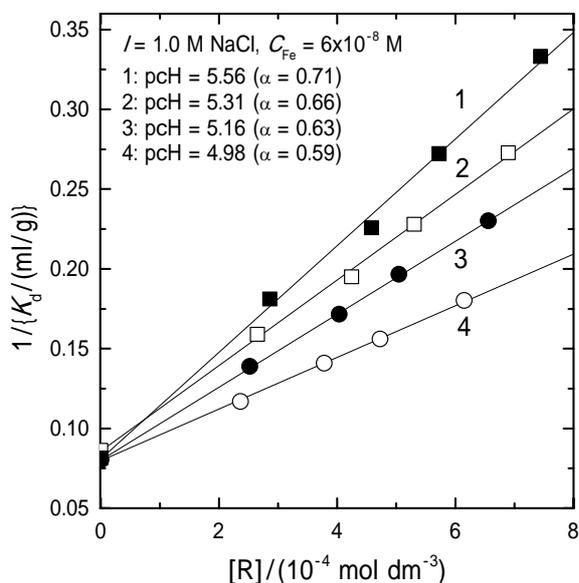


Fig. 6 Distribution of Fe(II) as a function of humate concentration at $I = 1.0 \text{ M}$, $C_{\text{Fe}} = 6 \times 10^{-8} \text{ M}$.

that $\log \beta_{\alpha}$ of Fe(II)-humate is much higher than polyacrylate at a lower Fe(II) concentration and decreases with Fe(II) concentration. Higher $\log \beta_{\alpha}$ values at lower metal ion concentrations are in accordance with our previous results on Np(V)-humate[8], Eu(III)-humate[9] and Ca(II)-humate[10]. This is considered due to the heterogeneous composition of the humic acid. Since humic acids are mixtures of various organic macromolecules with different compositions, they contain weaker and stronger binding sites. At a lower metal-ion concentration, minor but stronger sites are preferentially used to form stronger complex. With the increase in the metal-ion concentration, these sites are occupied and weaker sites will be used to form weaker complex.

As shown in Fig.7, the effect of $\log \alpha$ on $\log \beta_{\alpha}$ in Fe(II)-humate is similar to Fe(II)-polyacrylate in contrast to a large difference in the value of $\log \beta_{\alpha}$. Since humic acid is

Table 2 Apparent formation constant of Fe(II)-humate complex

I/M	C_{Fe}/M	pcH	α	$\log \beta_{\alpha}$	$\log K_d^0$
0.1	6×10^{-8}	4.93	0.58	4.66 ± 0.05	2.79 ± 0.13
		5.12	0.62	4.77 ± 0.05	2.79 ± 0.02
		5.39	0.68	4.79 ± 0.05	2.79 ± 0.02
		5.48	0.70	4.83 ± 0.04	2.79 ± 0.02
	8×10^{-6}	4.89	0.57	4.38 ± 0.08	2.79 ± 0.13
		5.04	0.60	4.41 ± 0.05	2.79 ± 0.02
		5.24	0.65	4.46 ± 0.05	2.79 ± 0.02
		5.44	0.69	4.49 ± 0.05	2.79 ± 0.02
	4×10^{-4}	5.10	0.62	3.17 ± 0.45	2.79 ± 0.05
		5.15	0.63	3.19 ± 0.44	2.79 ± 0.03
		5.39	0.68	3.21 ± 0.42	2.79 ± 0.03
		5.56	0.71	3.22 ± 0.41	2.79 ± 0.02
1.0	6×10^{-8}	4.97	0.59	3.31 ± 0.04	1.08 ± 0.06
		5.16	0.63	3.45 ± 0.03	1.08 ± 0.01
		5.31	0.66	3.49 ± 0.03	1.08 ± 0.01
		5.56	0.71	3.62 ± 0.02	1.08 ± 0.01
	8×10^{-6}	4.74	0.54	2.88 ± 0.06	1.11 ± 0.03
		4.96	0.59	3.02 ± 0.05	1.11 ± 0.05
		5.20	0.64	3.15 ± 0.04	1.11 ± 0.05
		5.42	0.68	3.27 ± 0.04	1.11 ± 0.06
	4×10^{-4}	4.69	0.53	2.04 ± 0.19	1.15 ± 0.01
		4.92	0.58	2.24 ± 0.15	1.15 ± 0.01
		5.20	0.64	2.33 ± 0.13	1.15 ± 0.01
		5.42	0.68	2.35 ± 0.12	1.15 ± 0.01

heterogeneous in composition, the increase of α of humic acid means not only the increase of the concentration of dissociated functional groups but also the dissociation of weaker acidic sites (more basic and stronger complexing sites). Therefore, the increase in $\log \beta_{\alpha}$ with $\log \alpha$ may be due both to the multidentate coordination and the participation of more basic sites. However, since the dependences of $\log \beta_{\alpha}$ on $\log \alpha$ at three different Fe(II) concentrations are similar, the influence of

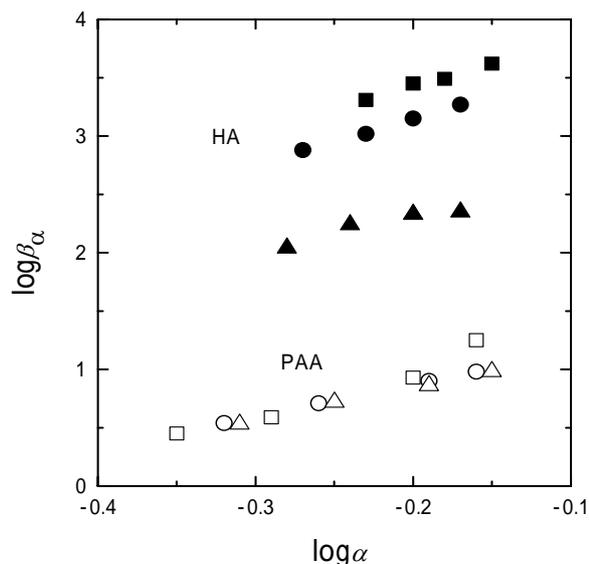


Fig. 7 The effect of Fe(II) concentration on the plots of $\log \beta_{\alpha}$ vs. $\log \alpha$.

: Fe(II)-humate, : Fe(II)-polyacrylate
 : $C_{\text{Fe}} = 6 \times 10^{-8} \text{ M}$, : $C_{\text{Fe}} = 8 \times 10^{-6} \text{ M}$
 : $C_{\text{Fe}} = 4 \times 10^{-4} \text{ M}$

heterogeneous composition is considered small and the increase in $\log\beta_\alpha$ with $\log\alpha$ is supposed mainly due to the multidentate coordination.

In Fig.8, the effect of ionic strength on $\log\beta_\alpha$ of Fe(II)-humate is compared with that of Fe(II)-polyacrylate. For both complexes, the effects are larger than expected from the change in the activity coefficient of Fe^{2+} ion in the aqueous phase, indicating the polyelectrolyte effect in both polyacrylate and humate. The higher dependence of $\log\beta_\alpha$ of Fe(II)-polyacrylate than Fe(II)-humate suggests that the charge density around polyacrylate is higher than around humate, which is consistent with their proton exchange capacities ($C_R = 4.95\sim 5.10\text{ meq/g}$ for the humic acid and $C_R = 12.88\text{ meq/g}$ for polyacrylic acid).

4 Conclusions

The apparent formation constant ($\log\beta_\alpha$) of Fe(II)-humate and Fe(II)-polyacrylate were obtained at pcH 4.6 to 5.5 and $I = 0.1$ and 1.0 M NaCl by using the ion exchange method. The result indicated that $\log\beta_\alpha$ of both complexes increased with the degree of dissociation (α) and decreased with the ionic strength due to their polyelectrolyte nature. These effects are considered to be the effects on a certain single complex formation constant $\log\beta$ and may be estimated if their polyelectrolyte nature and multidentate coordination are properly taken into consideration. On the other hand, while $\log\beta_\alpha$ of Fe(II)-polyacrylate is independent of the change in Fe(II) concentration, $\log\beta_\alpha$ of Fe(II)-humate increases with the decrease in Fe(II) concentration due to the existence of different

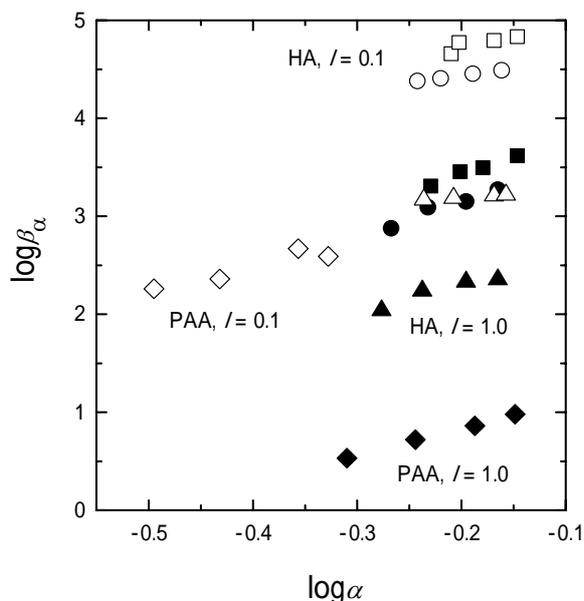


Fig. 8 The effect of ionic strength on the plots of $\log\beta_\alpha$ vs. $\log\alpha$.

Fe(II)-humate at $I = 0.1$ () and 1.0 M ();
 $C_{\text{Fe}} = 6 \times 10^{-8}\text{ M}$ (), $8 \times 10^{-6}\text{ M}$ (), $4 \times 10^{-4}\text{ M}$ ().
 Fe(II)-polyacrylate at $I = 0.1$ () and 1.0 M (),
 $C_{\text{Fe}} = 4 \times 10^{-4}\text{ M}$.

strengths of complexing sites in the humic acid. This effect of the metal ion concentration on $\log\beta_\alpha$ due to the heterogeneous composition of the humic acid disables the use of a single constant of $\log\beta$, that is, if we have a mixture of two complex forming reagents, we have no way to represent the complex formation of a metal ion with this mixture with a single complex formation constant. Thus, in order to consider the competition of the radionuclides with the metal ions such as Fe(II) originally existing in the underground water, we are confronted with the formidable task of treating the variable (conditional) complex formation constants which change with the metal ion concentration.

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