

## Evaluation of Distribution Coefficient of a Metal Ion in the Presence of a Chelating Agent

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### Abstract

A mathematical model has been developed for an analytical calculation of distribution coefficient ( $K_D$ ) in the presence of a chelating agent. The newly formulated  $K_D$  is given as a function of the mole fraction of a free metal ion in the solution,  $\beta$ , and will serve as an alternative for the tedious individual measurements of  $K_D$ . This formulation will be used to analyze the effects of the presence of chelating agents on the adsorption capacity of geologic media such as clay minerals and soils. The present method may be a significant progress for the evaluation of the transport phenomena and separation processes of metal ions (or radionuclides) in the presence of chelating agents.

### INTRODUCTION

Radionuclides adsorption properties are extremely important in order to minimize the movement of radionuclides from a radioactive waste disposal site into the environment and eliminate the radioactive contaminants resulting from nuclear reactors and other nuclear facilities.

The utilization of clay minerals for retaining radioactive ions from liquid radioactive wastes as an adsorbing medium has been proposed because of their high sorption capacity and thermal resistance<sup>1,2</sup>. Also these clay minerals have been proposed as a suitable buffer or backfill material for disposal of radioactive waste disposal in the subsurface<sup>3,4</sup>. Many soils and rocks present in a subsurface radioactive waste disposal site contain these clay minerals and influence the migration behaviors of the radionuclides of various forms from the site into the environment<sup>5,6</sup>. It has been stated that the adsorption of the radionuclides on the clay minerals is significantly influenced by the presence of chelating agents<sup>7-9</sup>. Also it has been noted<sup>7,8,10</sup> that complex formation of the radionuclides (especially, <sup>60</sup>Co) with chelating agents found

in groundwater such as synthetic chelating agents (e.g., ethylenediamine tetraacetic acid (EDTA) and diethylenetriaminepenta acetic acid (DTPA) used in clean up and decontamination operations at nuclear facilities) and natural chelating agents (e.g., humic acid and fulvic acid) greatly accelerate the migration rate of the radionuclides.

Therefore, in this study, the effects of the presence of organic chelating agent on the adsorption capacity of natural adsorbing media such as clay minerals and soils for the radioactive metal ions are analyzed by developing a calculation model for the extended distribution coefficient incorporating the complexation reaction of a metal ion.

### MODEL DEVELOPMENT

#### Chelated Complex Formation

For the expression of chelate (or complex) formation, we introduce the concept of the apparent equilibrium constant and use the conditional stability constant as an equilibrium constant for the complex formation reaction<sup>11</sup>. The general form of the overall conditional stability constant is given by

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

where  $[M']$  denotes the apparent metal concentration, i.e., the concentration not only the free metal ion but also of all the metal ion solution that has not reacted with the chelating agent. Similarly,  $[L']$  represents the apparent ligand concentration, i.e., the concentration of the free ligand but also of all species of the chelating agent not bound to the metal M and  $[ML']$  is the apparent concentration of the complex formed, i.e., the concentration of all complexes including M and L.  $K'_{ML}$  is the overall conditional stability constant of the complex formed.

The relationship between the apparent and free metal ion concentration is given by using side reaction coefficient,  $\alpha$

$$E \frac{[M']}{[M]} = 1 + [Y]\gamma_1 + [Y]^2\gamma_2 + \dots = \alpha_{M(Y)}, \quad (2)$$

where Y is an interfering complexant which reduces the free metal ion concentration,  $\gamma_n$  the overall stability constant of the complexes formed in the side reaction. The quantity  $\alpha_{M(Y)}$  is called the side-reaction coefficient or  $\alpha$ -coefficient for M reacting with Y. The alpha coefficients are measures of the extent of side reactions, and it might be appropriate to refer to them as side reaction coefficients. If M reacts only with L in accordance with the reaction scheme on which the analytical method is based, then  $\alpha_M = 1$ , but if M is involved in side reactions with other species present, then  $\alpha_M > 1$ .  $\alpha_L$  can be explained in the same way of  $\alpha_M$ .

The ratio  $[L']/[L]$  can be similarly calculated for the side reaction of L with B

$$\frac{[L']}{[L]} = 1 + [B]\gamma_1 + [B]^2\gamma_2 + \dots = \alpha_{L(B)}, \quad (3)$$

And the ratio of the total concentration of 1:1 complex to that of the normal metal-ligand complex is given by

$$\begin{aligned} \frac{[ML']}{[ML]} &= \frac{[ML] + [MHL] + \dots + [MYL]}{[ML]} \\ &= 1 + [H]K_{MHL} + \dots + [Y]K_{MYL} = \alpha_{ML'} \quad (4) \end{aligned}$$

Therefore, the overall conditional stability constant can be calculated by using the side reaction coefficients,  $\alpha$ 's.

$$K'_{ML} = \frac{\alpha_{ML}}{\alpha_M \alpha_L} K_{ML} \quad (5)$$

where

$$K_{ML} = \frac{[ML]}{[M] [L]} K_{ML} \quad (6)$$

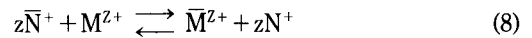
or

$$\log K'_{ML} = \log K_{ML} + \log \alpha_{ML} - \log \alpha_M - \log \alpha_L \quad (7)$$

### Calculation of Distribution Coefficient

In order to investigate the effects of chelating agents on the adsorption of radionuclides ion exchange adsorption model is introduced since the natural clay minerals acts as inorganic ion exchangers. From the ion exchange model we can obtain a distribution coefficient ( $K_d$ ) of the radioactive metal ions<sup>12,13</sup>. Many workers have studied the adsorption of metal ions on the clay minerals by using an ion exchange model<sup>12-15</sup>. In these studies, it is usually assumed that the ion exchanger was initially loaded with univalent alkali ions such as  $Na^+$  since the use of alkali ions simplifies the theoretical treatment and does not form complexes with most chelating agents.

The ion exchange process can be expressed by



where  $M^{Z+}$  and  $\bar{M}^{Z+}$  are the radioactive metal ions with a positive charge Z in the solution and in the exchanger, respectively.  $N^+$  and  $\bar{N}^+$  are the alkali metal ions with a univalent charge in the solution and in the exchanger, respectively.

The distribution coefficient of the radioactive metal ion  $M^{Z+}$  between the solution phase and solid exchanger phase,  $K_d$ , at any concentration is defined by

$$K_d = \frac{[\bar{M}^{Z+}]}{[M^{Z+}]} \quad (9)$$

$K_d$  can be calculated by applying mass balance

to the ion exchange equilibrium and using the selectivity coefficient<sup>13,15</sup>.

In an actual application, the distribution coefficient alone does not give any information about the proportion of a metal adsorbed or not adsorbed by an ion exchanger. To determine the proportion consideration must be given also to the amount of exchanger (i.e., the amount of the solid clay minerals) and to the amount of the solution. Therefore, from the Eq. (9), it follows that

$$\frac{\text{amount of metal ion in the exchanger}}{\text{amount of metal ion in the solution}} = \frac{[\bar{M}^{z+}]G}{[M^{z+}]V} = K_d \frac{G}{V} \quad (10)$$

where  $G$  is the amount of exchanger in grams and  $V$  is the amount of the solution in  $\text{cm}^3$ . Further we define the fraction of the adsorbed metal ions as follows:

$$P = \frac{\text{amount of the metal ion in the exchanger}}{\text{total amount of the metal ion}} = \frac{K_d}{K_d + v} \quad (11)$$

and the distribution coefficient  $K_d$  is given by

$$K_d = \frac{Pv}{1-P} \quad (12)$$

where  $v = V/G$ .

The effect of a complexation reaction on the ion exchange properties is closely connected with the charge of the species formed. Larger changes in the exchange properties, result if a complexation reaction leads to a change in the charge of a metal ion. The most significant alteration of exchange properties may result when the ionic charge of a metal ion changes its sign. If a metal cation is quantitatively transformed by some chelating anion into a complex ion of negative charge, a cation exchanger will take up only extremely small amount of the metal ion.

In this study, it is assumed that no positively charged complexes between radioactive metal ions and chelating agents are formed. This assumption may be appropriate for the complexation of most

metal ions with synthetic chelating agents such as EDTA<sup>11</sup>. Also the charge is omitted in order to treat the mathematical equations easily.

In the presence of chelating agents in the solution, the distribution coefficient in Eq. (12) based on the free radioactive metal ion concentration should be corrected to consider the contribution of complexed metal ions. Thus a new distribution coefficient based on the total concentration of the radioactive metal ions in the solution is defined as follows:

$$K_D = \frac{[\bar{M}]}{TC} \quad (13)$$

where  $TC$  is the total concentration of the radioactive metal ion in the solution whether it is complexed or not and can be expressed by

$$TC = [M'] + [ML'] \quad (14)$$

If we consider the amount of the complexed metal ions (i.e., the amount of complexes formed), it can be obtained following mass balance equations can be obtained for the amounts of metal ions and chelating agents

$$[M_0] = [M'] + [ML'] + \frac{[\bar{M}]}{v} \quad (15)$$

and

$$[L_0] = [L'] + [ML'] \quad (16)$$

Here  $[M_0]$  and  $[L_0]$  are initially loaded concentrations of the radioactive metal ions and chelating agents, respectively.

Inserting Eq. (14) into the Eq. (15),

$$[\bar{M}] = v([M_0] - TC) \quad (17)$$

and  $TC$  can be given by combining Eqs. (13) and (17)

$$TC = \frac{v[M_0]}{K_D + v} \quad (18)$$

Since, from the Eq. (16),

$$[ML'] = [L_0] - [L'] \quad (19)$$

$[L']$  can also be given by inserting Eq. (19) into Eq. (1) and rearranging for  $[L']$  gives

$$[L'] = \frac{[L_0]}{K'_{ML}[M'] + 1} \tag{20}$$

By using the Eq. (19) and (20),  $[ML']$  is given by

$$[ML'] = \frac{K'_{ML}[M'] [L_0]}{K'_{ML}[M'] + 1} \tag{21}$$

Therefore, TC can be given by inserting Eq. (21) into Eq. (14)

$$TC = \frac{K'_{ML}[M']^2 + (1 + K'_{ML}[L_0])[M']}{K'_{ML}[M'] + 1} \tag{22}$$

By equating Eqs. (18) and (22) and rearranging for  $K_D$  we can express the distribution coefficient in the presence of chelating agents as follows:

$$K_D = v \left( \frac{K'_{ML}[M_0] \beta + 1}{K'_{ML}[M_0] \beta^2 + K'_{ML}[L_0] \beta + \beta} - 1 \right) \tag{23}$$

where

$$\beta = \frac{[M']}{[M_0]} \tag{24}$$

If we let

$$K'_{ML} [M_0] = M^* ; K'_{ML} [L_0] = L^* \tag{25}$$

then  $K_D$  can be given on a sample form:

$$K_D = v \left( \frac{M^* \beta + 1}{M^* \beta^2 + L^* \beta + \beta} - 1 \right) \tag{26}$$

If there is no chelating agent, since  $M^* = L^* = 0$  and  $\beta = 1 - P$ ,  $K_D$  would be equal to  $K_d$

$$K_D = \frac{v P}{1 - P} = K_d \tag{27}$$

Therefore, in this model, a controlling factor for the evaluation of the distribution coefficient in the presence of chelating agents may be  $\beta$ , which represents the concentration ratio of the uncomplexed metal ions to the initial loading metal ions.

The calculation results of Eq. (23) are shown in Figs. 1 and 2 with varying value of  $\beta$  for some values of the initial loading concentrations of a chelating agents,  $[L_0]$  and the conditional stability constant,  $K'_{ML}$ , respectively.

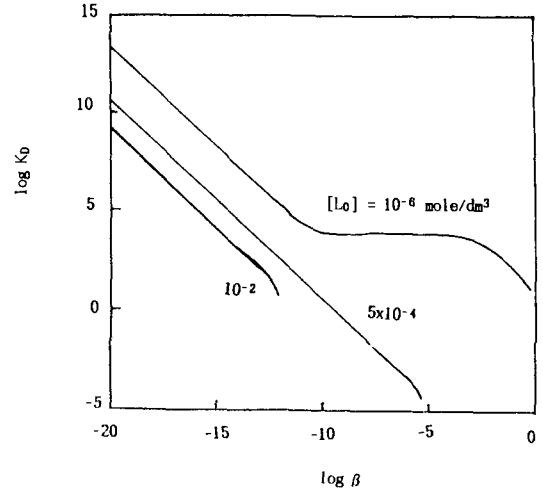


Fig. 1. The calculation results of the distribution coefficient,  $K_D(\text{cm}^3/\text{g})$ , from the Eq. (23) when  $[M_0] = 5 \times 10^{-4} \text{ mole}/\text{dm}^3$ ,  $K'_{ML} = 10^{13.9} \text{ dm}^3/\text{mole}$ , and  $v = 20 \text{ cm}^3/\text{g}$ .

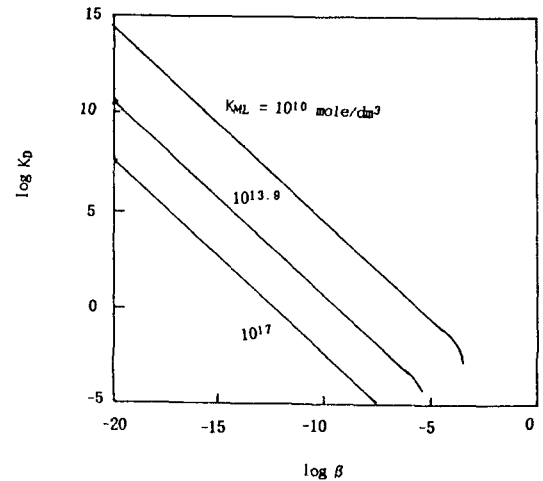


Fig. 2. The calculation results of the distribution coefficient,  $K_D(\text{cm}^3/\text{g})$ , from the Eq. (23) when  $[M_0] = 5 \times 10^{-4} \text{ mole}/\text{dm}^3$ ,  $[L_0] = 5 \times 10^{-4} \text{ mole}/\text{dm}^3$ , and  $v = 20 \text{ cm}^3/\text{g}$ .

### CONCLUSION

In this study, we developed a simple calculation model of the distribution coefficient of a metal ion in the presence of a chelating agent. If we know the mole fraction of a free metal ion in the solution,  $\beta$  we can calculate the distribution coefficient,  $K_D$ , in the presence of a chelating agent.

Thus, the newly formulated  $K_D$  as a function of the  $\beta$  will serve as an alternative for the tedious individual measurements of  $K_D$ . The above procedure is also very useful for the adsorption system of a metal ion in the presence of a chelating agent and will allow simple calculation of  $K_D'$ .

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