Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Distribution Coefficient of a Metal in the Presence of a Chelating Agent

M. H. Baik[a]; K. J. Lee[b]
[a] DEPARTMENT OF NUCLEAR ENGINEERING, KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY, TAEJON, KOREA [b] Radwaste Disposal Research Department Kaeri, Nuclear Environment Management Center, Taejon, Korea

To cite this Article Baik, M. H. and Lee, K. J.(1995) 'Distribution Coefficient of a Metal in the Presence of a Chelating Agent', Separation Science and Technology, 30: 2, 247 — 261
To link to this Article: DOI: 10.1080/01496399508015837
URL: http://dx.doi.org/10.1080/01496399508015837

SEPARATION SCIENCE AND TECHNOLOGY, 30(2), pp. 247–261, 1995

Distribution Coefficient of a Metal in the Presence of a Chelating Agent

---

M. H. BAIK* and K. J. LEE
DEPARTMENT OF NUCLEAR ENGINEERING
KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY
373-1 KUSONG-DONG, YUSONG-GU, TAEJON 305-701, KOREA

ABSTRACT

A linear adsorption model has been developed to investigate the effect of chelating agents on the adsorption of metal ions by introducing an extended concept of the distribution coefficient. In addition, batch adsorption experiments were performed on the cobalt/EDTA/bentonite adsorption system in order to analyze the effect of chelating agent and to validate the developed adsorption model. The experimental results showed a linear adsorption isotherm, thus validating the assumption of a constant distribution coefficient. Also, the concentrations of all species participating in the adsorption/chelation reaction could be determined by the developed model. The results of this study showed that adsorption of a metal solute was greatly affected by the presence of chelating agents, even in a small amount, by increasing the total solubility of the metal and reducing the distribution coefficient up to more than two orders of magnitude.

INTRODUCTION

Adsorption properties of radioactive solutes are extremely important to minimize the movement of radionuclides from a radioactive waste disposal site into the environment and to 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 (1, 2). These clay

---

* Current address: Nuclear Environment Management Center, Radwaste Disposal Research Department, Kaeri, P.O. Box 105, Yusong-Gu, Taejon 305-600, Korea

minerals have also been proposed as a suitable buffer or backfill material for the disposal of radioactive wastes in the subsurface (3, 4). Many soils and rocks present in subsurface radioactive waste disposal sites contain these clay minerals and influence the migration behavior of the radionuclides with various forms from the disposal site into the environment (5, 6).

It has been stated that adsorption of radionuclides on geologic porous media such as clay minerals, soils, and rock matrix is significantly influenced by the presence of a chelating agent (7–9). It has also been noted (7–10) that chelate formation of radionuclides (especially ^{60}Co) with chelating agents found in groundwater greatly accelerates the migration rate of the radionuclides. Synthetic chelating agents such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and diethylenetriaminepentaacetic acid (DTPA) have been used extensively by a variety of industries (9, 10). Specifically, these chelating agents have been widely applied to the nuclear industry and decontamination of reactors and equipments. Hundreds of kilograms of chelating agents may be employed in a single decontamination operation (11). Decontamination wastes generated by the decontamination operations are then solidified and disposed of. Disposal of such decontamination wastes will constitute an introduction of chelating agents to the environment if they are not decomposed prior to disposal, or if they are not easily chemically or biochemically degraded by natural processes in the environment.

In the equilibrium adsorption processes, it is generally assumed that there is a functional relationship between the concentrations of the solute in the solution and solid phases, respectively, which may be expressed as

$$\overline{C}_i = f(C_i) \tag{1}$$

where $\overline{C}_i$ is the concentration of a solute i adsorbed on the solid phase (mol/g) and C_i is the concentration of the solute i in the solution phase (mol/dm^3). Such a relationship is termed a sorption function or a sorption isotherm. The simplest and most widely used equilibrium sorption isotherm is generally given as a linear form. In the linear isotherm, it is assumed that the amount of the solute adsorbed by the solid phase and the concentration of the solute in the solution are related by a linear relationship:

$$\overline{C}_i = K_{di}C_i \tag{2}$$

where K_{di} (dm^3/g), the distribution coefficient of the solute i, is a measure of the solute retention by the solid matrix, and the upper bar denotes the solid phase.

Engineers and geologists have traditionally used the concept of a distribution coefficient to describe quantitatively the transport of contaminants undergoing reversible sorption and ion-exchange processes. The linear isotherm model of Eq. (2) has also been used to describe the adsorption of nonradioactive solutes by the soil matrix (12, 13).

Although the distribution coefficient approach is conceptually and computationally simple, it is technically valid only under the assumptions of local chemical equilibrium and a linear sorption isotherm. Several investigations, including those of Miller and Benson (14) and Valocchi et al. (15), have cautioned against the use of distribution coefficients in problems involving multicomponent ion-exchange reactions where the isotherms are nonlinear. However, they also mentioned that it is possible to describe adsorption behaviors of radionuclides using the distribution coefficient model based upon simple mass balance if the effect of hydrodynamic dispersion and the concentration of a radionuclide is not so significant as to induce nonlinear sorption behaviors.

Therefore, in this study we assume that adsorption behaviors of a metal solute in the presence of chelating agents can also be described by the linear sorption model using the distribution coefficient concept. Accordingly, the effect of synthetic organic chelating agents on the adsorption capacity of natural adsorbing media such as clay minerals will be analyzed by developing an adsorption model based upon the distribution coefficient incorporating the chelate formation reaction. In addition, batch adsorption experiments will be performed on the cobalt/EDTA/bentonite chelation/adsorption system in order to analyze the effect of chelating agent and validate the adsorption model developed.

MODEL DEVELOPMENT

Chelate Formation

In order to simplify the calculation of complex formation, Schwarzenbach introduced a concept of an apparent constant in complexometry (16). Ringbom has given this concept a somewhat broader significance and has used it to calculate the influence of a whole series of side reactions (17). He introduced the term "conditional stability constant" for this concept to stress that the constant is not constant but depends on the experimental conditions. It is emphasized that conditional stability constants can be used not only when considering the equilibrium of a complexation reaction but also when dealing with neutralization, precipitation, and redox reactions.

To keep the equilibrium equation in a simple form, an equilibrium stability constant considering the influence of all side reactions in which metal solute M and chelating agent L take part is introduced and defined as follows:

$$\mathrm{M} + \mathrm{L} \leftrightarrow \mathrm{ML} \tag{3}$$

and

$$K'_{\mathrm{ML}} = \frac{C'_{\mathrm{ML}}}{C'_{\mathrm{M}}C'_{\mathrm{L}}} \tag{4}$$

where C'_{M} denotes an apparent concentration of the metal M (mol/dm^3), i.e., concentration not only of the free metal ion (C_{M}) but also of all metals in solution that have not reacted with the chelating agent L. Similarly, C'_{L} represents the apparent concentration of the chelating agent L (mol/dm^3), i.e., concentration not only of the free chelating agent (C_{L}) but also of all species of the chelating agent not bound to the metal M. Also, C'_{ML} is the apparent concentration of the chelate ML (mol/dm^3) whether it is protonized or hydroxized. K'_{ML} is the conditional stability constant of the chelate ML (dm^3/mol).

The relationship between the apparent concentration and the free metal concentration can be given by using an α-coefficient for each species. It is defined as (16)

$$\alpha_{\mathrm{M}} = \frac{C'_{\mathrm{M}}}{C_{\mathrm{M}}}; \qquad \alpha_{\mathrm{L}} = \frac{C'_{\mathrm{L}}}{C_{\mathrm{L}}}; \qquad \alpha_{\mathrm{ML}} = \frac{C'_{\mathrm{ML}}}{C_{\mathrm{ML}}} \tag{5}$$

The α-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 $\alpha_{\mathrm{M}} = 1$, but if M is involved in side reactions with other species present, then $\alpha_{\mathrm{M}} > 1$. α_{L} and α_{ML} can be explained in the same way.

Extended Concept of Distribution Coefficient

The effect of chelate formation on adsorption properties, such as those in an ion-exchange reaction, is closely related with the charge of the species formed. Larger changes in the adsorption properties result if chelate formation leads to a change in the charge of the chelate formed. The most significant alteration of adsorption properties may result when the ionic charge of the metal solute changes its sign. If a cationic solute is quantitatively transformed by some chelating anions into a chelated solute with a negative charge, the adsorbent will take up only an extremely small amount of the solute. Therefore, in this study it is assumed that no positively charged chelates are formed between the metal solutes and chelating agents and thus the chelates will not be adsorbed onto the solid phase. This assumption may be appropriate for the chelation of most metal solutes with synthetic chelating agents such as EDTA (18).

In the presence of chelating agents in the solution, the distribution coefficient of a metal solute based upon the presence of only free metal solutes should be corrected to consider the contribution of the chelating agents. Thus, in this study an extended concept of distribution coefficient is introduced in order to consider the contribution of the chelating agents and can be defined as

$$K_D = \frac{\overline{T_M}}{T_M} \cong \frac{\overline{C_M}}{T_M} \tag{6}$$

where $\overline{T_M}$ is the total concentration of the metal solute M including the concentration of the chelated solute ML adsorbed onto the solid phase (mol/g), $\overline{C_M}$ is the concentration of the free metal solute M adsorbed onto the solid phase (mol/g), T_M is the total concentration of the metal solute M in the solution whether it is chelated or not (mol/dm^3), and K_D is the distribution coefficient of the metal solute M between the solid and solution phases, respectively, in the presence of a chelating agent (cm^3/g). Since the chelated solute ML would not adsorb onto the solid phase according to the assumption, $\overline{T_M}$ will be equal the concentration of the free metal solute adsorbed, $\overline{C_M}$, i.e., $\overline{T_M} \approx \overline{C_M}$.

In an actual application, the distribution coefficient alone does not give any information about the proportion of solute adsorbed or not adsorbed by an adsorbent. To determine the proportion, consideration must also be given to the amount of adsorbent (or adsorbing solid) and to the amount of solution. Therefore, from Eq. (6) it follows that

$$\frac{\text{the amount of metal solute on the solid}}{\text{the amount of metal solute in the solution}} = \frac{\overline{C_M}G}{T_M V} = K_D \frac{G}{V} \tag{7}$$

where G is the amount of solid in grams and V is the amount of the solution in dm^3. Further, we define the fraction of the adsorbed solute as follows:

$$P = \frac{\text{the amount of metal solute on the solid}}{\text{total amount of metal solute}} = \frac{K_D}{K_D + \upsilon} \tag{8}$$

where $\upsilon = V/G$ is usually referred as a solution to solid ratio. Therefore, the distribution coefficient, K_D, can be expressed as

$$K_D = \frac{P\upsilon}{1 - P} \tag{9}$$

Calculation Procedure

If we consider the amount of chelated metal solute (i.e., the amount of chelates formed), we can obtain the following mass balance equations for the amount of metal solutes and chelating agents:

$$C_{M0} = C'_M + C'_{ML} + \frac{\overline{C_M}}{\upsilon} = T_M + \frac{\overline{C_M}}{\upsilon} \tag{10}$$

and

$$C_{L0} = C'_L + C'_{ML} = T_L \tag{11}$$

where

$$C'_M + C'_{ML} = T_M \tag{12}$$

Here C_{M0} and C_{L0} are initially loaded concentrations of the metal solute M (mol/dm^3) and chelating agent L (mol/dm^3), respectively, and T_L is the total concentration of the chelating agent L (mol/dm^3) in the solution whether it is chelated or not.

By rewriting Eq. (10), $\overline{C_M}$ can be expressed as

$$\overline{C_M} = \upsilon(C_{M0} - T_M) \tag{13}$$

and T_M can be given by inserting Eq. (13) into Eq. (6):

$$T_M = \frac{\upsilon C_{M0}}{K_D + \upsilon} \tag{14}$$

It can be noticed that if K_D is known, T_M can be easily determined from Eq. (14). In other words, if T_M is given by experiment or other work, K_D can be directly calculated by

$$K_D = \frac{\upsilon(C_{M0} - T_M)}{T_M} \tag{15}$$

Since from Eq. (11)

$$C'_{ML} = C_{L0} - C'_L \tag{16}$$

C'_L can be given by inserting Eq. (16) into Eq. (4) and rearranging for C'_L:

$$C'_L = \frac{C_{L0}}{1 + K'_{ML}C'_M} \tag{17}$$

By introducing Eq. (17) into Eq. (16), C'_{ML} is given by

$$C'_{ML} = \frac{K'_{ML}C'_M C_{L0}}{1 + K'_{ML}C'_M} \tag{18}$$

Therefore, T_M can be given by inserting Eq. (18) into Eq. (12):

$$T_M = \frac{K'_{ML}C'^2_M + (1 + K'_{ML}C_{L0})C'_M}{1 + K'_{ML}C'_M} \tag{19}$$

By expanding and rearranging Eq. (19) for C'_M, a quadratic form of equation is obtained as

$$K'_{ML}C'^2_M + (1 + K'_{ML}C_{L0} - K'_{ML}T_M)C'_M - T_M = 0 \tag{20}$$

The above equation can be solved analytically, and the resulting solution is

$$C'_M = \frac{(K'_{ML}\,T_M - K'_{ML}C_{L0} - 1) + \sqrt{(1 + K'_{ML}C_{L0} - K'_{ML}T_M)^2 + 4K'_{ML}T_M}}{2K'_{ML}} \tag{21}$$

C'_{ML} is then determined by inserting Eq. (21) into Eq. (12) and rewriting for C'_{ML}:

$$C'_{ML} = \frac{(K'_{ML}\,T_M + K'_{ML}C_{L0} + 1) - \sqrt{(1 + K'_{ML}C_{L0} - K'_{ML}T_M)^2 + 4K'_{ML}T_M}}{2K'_{ML}} \tag{22}$$

Also, C'_L can be determined from the mass balance of L, Eq. (11), using Eq. (22).

When the apparent concentrations of the participating species (i.e., C'_M, C'_L, and C'_{ML}) are determined, the real concentrations of the species (i.e., C_M, C_L, and C_{ML}) can be calculated by using the α-coefficients for each species (i.e., α_M, α_L, and α_{ML}) which are defined in Eq. (5). α_M, α_L, and α_{ML} values will be different for different reaction systems. Thus, when a reaction system is determined, α-coefficients for the species would be calculated. However, these α-coefficients can be readily calculated by referring to the literature (17).

Furthermore, by equating Eqs. (14) and (19) and rearranging for K_D, we can express the distribution coefficient in the presence of a chelating agent as follows:

$$K_D = \nu\left(\frac{K'_{ML}C_{M0}\beta + 1}{K'_{ML}C_{M0}\beta^2 + K'_{ML}C_{L0}\beta + \beta} - 1\right) \tag{23}$$

where

$$\beta = C'_M/C_{M0} \tag{24}$$

If we let

$$M^* = K'_{ML}C_{M0} \quad \text{and} \quad L^* = K'_{ML}C_{L0} \tag{25}$$

then K_D can be given as a simple form:

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

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

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

Therefore, in this model there may be two controlling parameters for the evaluation of the distribution coefficient in the presence of chelating agents. One is T_M, which represents the total concentration of the radioactive solutes in the solution. The other is β, defined in Eq. (24). Although both T_M and β can determine the distribution coefficient K_D, T_M can be more easily determined than β since the value of β may be extremely low in the presence of a chelating agent. Thus, if we know T_M, which can be readily measured by an experimental procedure, we can calculate the distribution coefficient, K_D, and the real concentrations of the participating species, C_M, C_L, and C_{ML}.

EXPERIMENT

Adsorption System and Materials

A batch adsorption experiment was conducted in order to validate the developed adsorption model and to investigate the effect of chelating agent on the adsorption of a metal solute. In this experiment, cobalt(II)/EDTA/bentonite is considered as a representative chelation/adsorption system. A bentonite clay which was purchased from Industrial Minerals of Korea Co. was used as an adsorbing solid medium. The Korean bentonite, named Geko-Standard, is a 100% activated bentonite in a sodium form. The physical characteristics are listed in Table 1. The chemical composition of the Korean bentonite is listed in Table 2.

TABLE 1
Physical Characteristics of Korean Bentonite

Characteristics	Range of values
Moisture content	8–12%
Loose bulk density	0.75–0.85 g/cm^3
Residue on 0.063 mm/230 mesh	25%
Montmorillonite content	70%
Cation-exchange capacity	100 meq/100 g

TABLE 2
Composition of Korean Bentonite

	Composition (%)
SiO_2	63.6
Al_2O_3	17.6
Fe_2O_3	3.1
CaO	3.0
MgO	Tr.[a]
Na_2O	3.4
K_2O	0.5
Ignition loss	5.8

[a] Tr. = tracer quantity.

Cobalt metal was selected as an adsorbing solute because it is one of the predominant species released from nuclear power plants as a low-level radioactive waste (^{60}Co) and can easily form a metal-chelate with most conventional chelating agents. However, in this work a stable cobalt ion with a bivalent charge, Co^{2+}, was used. Thus, the adsorption behavior of cobalt metal would be observable in a relatively high concentration according to the measuring methods. In order to minimize the co-ion effects and side reactions, only cobalt chloride ($CoCl_2$) was used.

Disodium-EDTA (Na_2EDTA) was selected as the chelating agent reacting with cobalt metal. Disodium-EDTA dissociates into sodium ions and negative free EDTA, and then free EDTA forms a Co-EDTA chelate with the cobalt metal in the solution. That is, EDTA, formally represented as a 4-anion, although this is pH dependent, will chelate with cobalt metal in solution:

$$Co^{2+} + EDTA^{4-} \leftrightarrow Co\text{-}EDTA^{2-} \tag{28}$$

Apparatus and Analytical Method

The adsorption experiments were carried out by the batch technique in 250 mL polyethylene bottles. All experiments were performed at an ambient temperature of 20 ± 5°C. A bentonite sample of 1 g was simultaneously reacted with 50 mL cobalt chloride solution and 50 mL disodium-EDTA solution, and then the pH of the resultant was adjusted. The resultant was shaked for 7 days for all reactants to achieve equilibrium. After equilibrium was reached, complete separation of the two phases, solution and solid, was achieved by centrifugation.

The amount of cobalt metal in the separated supernant solution was analyzed by an atomic absorption spectrometer (AAS, Perkin-Elmer

3100). When an AAS measures the amount of cobalt metal, it measures the total amount of cobalt metal present in the solution, T_M. This is because the metal-chelate is more detectable than the free metal ion (19).

The samples were adjusted to about pH 8.0 with 0.1 N HCl and NaOH solutions as measured by an Orion pH meter. Shaking was carried out with a domestic shaker for 7 days. Centrifugation was done for 20 minutes at 12,000 rpm with a Beckman J2-21M/E centrifuge.

RESULTS AND DISCUSSION

Distribution Coefficient (Adsorption Isotherm)

Experimentally observed values of T_M are listed in Table 3 for several cases with variation of C_{MO}. This experiment was conducted at pH 8.0 ± 0.1, $\nu = 100$ cm^3/g, and $t_c = 7$ days. Cobalt can be added at different stages so that differences in the adsorption behavior of cobalt between free cobalt ion and chelated cobalt may be shown. In order to investigate this effect, cobalt and EDTA were reacted to form chelated cobalt, and bentonite was added after 7 days. Almost all cobalt metal will be present as the chelated form when cobalt and EDTA are added to bentonite after 7 days because cobalt metal forms a strong chelate with EDTA. In addition, in order to study the effect of chelating agent on adsorption, two cases are compared. One is the case of no chelating agent and the other is the case with chelating agent. Therefore, the cases considered in this experimental study are:

TABLE 3
Observed Values of Total Concentration of Cobalt Metal in Solution, T_M, at pH = 8.0 ± 0.1, $\nu = 100$ cm^3/g, and $t_c = 7$ days

	T_M (ppm)		
C_{M0} (ppm)	$C_{L0} = 0$	$C_{L0} = 5 \times 10^{-4}$ (mol/dm^3)	$C_{L0} = 5 \times 10^{-4a}$ (mol/dm^3)
0.25	0.01	0.24	0.24
0.5	0.02	0.48	0.48
1.0	0.04	0.96	0.96
2.0	0.04	1.88	1.85
4.0	0.04	3.78	3.72
8.0	0.39	7.48	7.32
15.0	0.97	13.82	13.40
30.0	5.92	27.06	26.43

[a] Bentonite added 7 days after the reaction of cobalt with EDTA.

Case I. $C_{L0} = 0$ (no chelating agent): only cobalt added to bentonite.
Case II. $C_{L0} = 5 \times 10^{-4}$ mol/dm^3: cobalt, EDTA, and bentonite are added simultaneously.
Case III. $C_{L0} = 5 \times 10^{-4}$ mol/dm^3: cobalt and EDTA are first reacted in advance and then bentonite is added after 7 days.

The calculated results are listed in Table 4. They show that the presence of EDTA appears to have a significant effect on cobalt adsorption. Therefore, it can be suggested that EDTA may reduce the adsorption capacity of bentonite. However, comparison of Case II with Case III shows a negligible difference, suggesting that the effect of chelating agent on metal adsorption can be significant regardless of the chemical state of the metal.

Adsorption isotherms for the three cases are shown in Fig. 1. Figure 1 shows that the isotherms in the presence of EDTA (Cases II and III) are more linear than the case of no chelating agent (Case I). This may be due to the fact that the adsorption isotherm is almost linear when the concentration of adsorbing solute is extremely low. In our experimental condition (i.e., $C_{L0} > C_{M0}$), most cobalt metals will be present as a Co-EDTA chelate which may not be adsorbed onto the bentonite, thus free cobalt metal will be present in an extremely low concentration. This will be proved in Table 7 which shows the calculated concentrations of the participating species. Accordingly, the experimental results of Fig. 1 validate the aforementioned assumption that the distribution coefficient of a metal, K_D, in the presence of a chelating agent is constant.

TABLE 4
Calculated Distribution Coefficient, K_D, Using the Experimental Data from Table 3

	K_D (cm^3/g)		
C_{M0} (ppm)	$C_{L0} = 0$ (mol/dm^3)	$C_{L0} = 5 \times 10^{-4}$ (mol/dm^3)	$C_{L0} = 5 \times 10^{-4}$ [a] (mol/dm^3)
0.25	2400.06	4.17	4.17
0.5	2399.99	4.17	4.17
1.0	2399.96	4.16	4.16
2.0	4900.07	6.38	8.11
4.0	9900.15	5.82	7.53
8.0	1951.32	6.95	9.29
15.0	1451.43	8.54	12.30
30.0	406.77	10.87	13.51

[a] Bentonite added 7 days after the reaction of cobalt with EDTA.

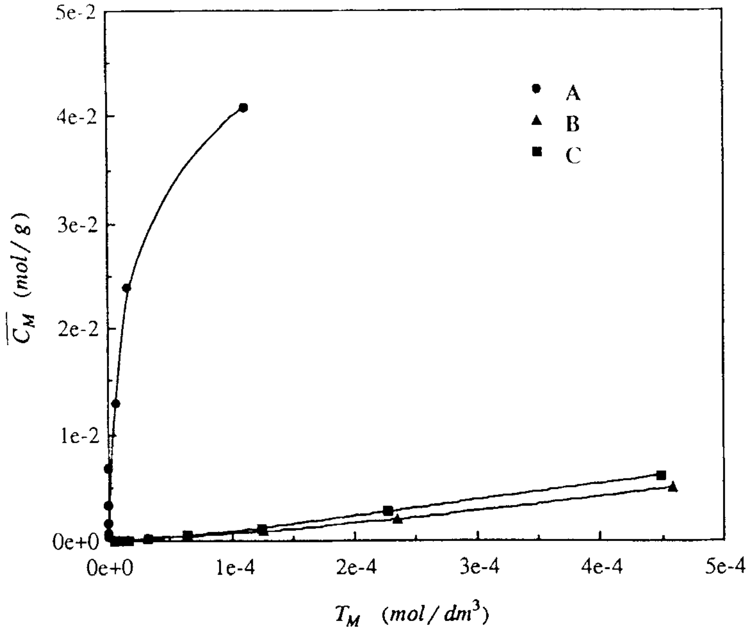

FIG. 1 Adsorption isotherms for the three cases considered. A, B, and C refer to Cases I, II, and III, respectively.

Effect of Chelating Agent

Table 5 shows the variation of the distribution coefficient for cobalt metal with increasing concentration of EDTA. The distribution coefficient, K_D, decreases as the concentration of EDTA, C_{L0}, increases. However, the total concentration of cobalt in solution, T_M, increases with increasing C_{L0}.

The effect of chelating agent on adsorption was analyzed by introducing a new parameter a, defined as C_{L0}/C_{M0}, which represents the fraction of the amount of chelating agent with respect to that of metal (or degree of chelate formation). As shown in Table 5, K_D decreases abruptly at a = 1, meaning that an equivalent amount of cobalt reacts with EDTA. When $a > 1$, the distribution coefficient does not decrease nearly as much. On the other hand, when $a < 1$ (a = 0.2), the effect of chelating agent is much less than when $a \geq 1$. These results are easily explained by a titrational approach for the chelate formation reaction (17, 19).

Any complexing agent that reduces the proportion of uncomplexed metal solute in a given reaction system increases the total solubility of the

TABLE 5
Effect of Concentration of Chelating Agent EDTA, C_{L0} (mol/dm^3), When C_{M0} = 5.0 × 10^{-5} mol/dm^3, pH = 8.0 ± 0.1, ν = 100 cm^3/g, and t_c = 7 days

C_{L0} (mol/dm^3)	$C_{L0}/C_{M0} = a$	T_M (mol/dm^3)	K_D (cm^3/g)
None	0	1.3575×10^{-6}	3583.33
1.0×10^{-5}	0.2	1.5611×10^{-5}	220.29
5.0×10^{-5}	1	4.5306×10^{-5}	10.36
1.0×10^{-4}	2	4.6324×10^{-5}	7.94
5.0×10^{-4}	10	4.6833×10^{-5}	6.76
1.0×10^{-3}	20	4.7511×10^{-5}	5.24

metal, i.e., the sum of complexed and uncomplexed metal concentration in a saturated solution (17). The total solubility of metal solute in the presence of chelating agent can be given by the value of T_M. In Table 5, T_M shows a trend similar to K_D. The largest increase in T_M is observed when chelating agent is present and the second largest when a = 1. Therefore, it can be concluded that the presence of chelating agent significantly in-

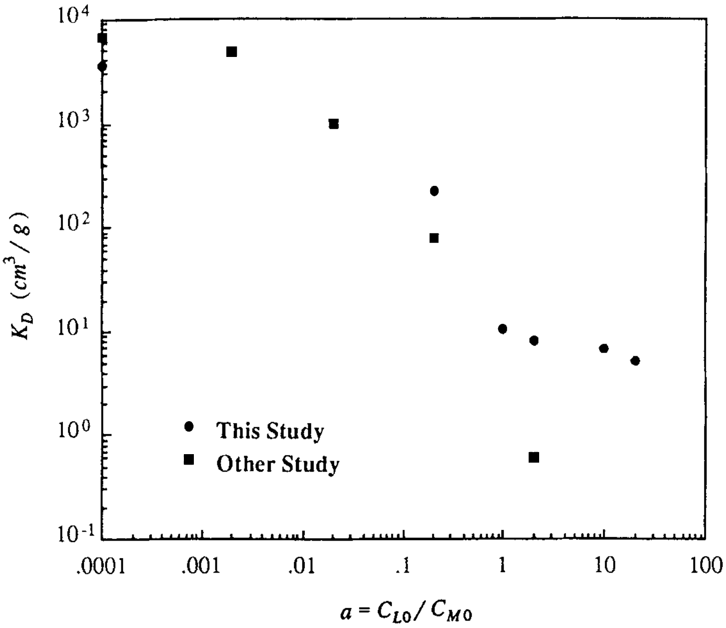

FIG. 2 Comparison of the experimental results of this study with those from another study.

TABLE 6
Calculated Conditional Stability Constant, K'_{CoEDTA} (dm^3/mol), for Co-EDTA Chelate Formation at pH 8 Literature Data

log K_{CoEDTA}	log α_{CoEDTA}	log $\alpha_{\mathrm{Co(OH)}}$	log $\alpha_{\mathrm{EDTA(H)}}$	log K'_{CoEDTA}
16.31	$= \log(1 + C_{\mathrm{H}} \cdot K_{\mathrm{CoHL}})$ $= \log(1 + 10^{-8} \times 10^{3.1}) \cong 0$	0.1	2.3	13.91

creases the total solubility of a metal solute, and this increase of total solubility is closely related to the distribution coefficient.

The experimental results of this study as listed in Table 5 were also compared with the experimental results from another study, as shown in Fig. 2. The other experimental study was conducted at pH 8.0, $\nu = 20$ cm^3/g, and $C_{\mathrm{M0}} = 2.5 \times 10^{-4}$ mol/dm^3 for the adsorption of cobalt onto illitic soil in the presence of EDTA (10). In spite of being different reaction systems, these two studies show similar behavior. However, a somewhat different behavior is shown at $a > 1$. This may be due to the higher initial loading concentration of cobalt, C_{M0}, in the other study.

Concentrations of the Species

Since cobalt metal Co(II) may be present in the form of CoHL and CoL under our experimental conditions, protonation of the chelating agent EDTA should be taken into account (17). Here H means hydrogen ion and L is the ligand of EDTA. Co(II) will also be present as Co(OH)$_2$ at pH 8 but may be a small quantity, as shown in Table 6. The conditional stability constant, K'_{ML}, in our experimental conditions can be obtained from the literature as $10^{13.9}$ dm^3/mol. However, for this study K'_{ML} was calculated by using necessary data such as K_{ML} and α-coefficients obtained from the literature (17). The necessary data and calculated K'_{ML} for Co-EDTA are presented in Table 6. Notice that the calculated value of K'_{ML} ($= 10^{13.91}$) is consistent with the value from the literature.

TABLE 7
Calculation Results for the Concentrations of Participating Components Using the Data Given in Tables 5 and 6

a	C_{M} (mol/dm^3)	C_{L} (mol/dm^3)	C_{ML} (mol/dm^3)
0	1.0783×10^{-6}	0	0
0.2	4.4570×10^{-6}	5.0119×10^{-7}	1.0000×10^{-5}
1	9.4322×10^{-14}	2.5059×10^{-7}	4.5306×10^{-7}
2	8.4339×10^{-15}	5.0119×10^{-7}	4.6324×10^{-5}
10	1.0099×10^{-15}	2.5059×10^{-6}	4.6833×10^{-5}
20	4.8746×10^{-16}	5.0119×10^{-6}	4.7511×10^{-5}

The real concentrations of the reacting species in our system (C_M, C_L, and C_{ML}) were calculated by using the experimental data from Table 5 and the parameter values listed in Table 6. The calculated concentrations for cobalt (M), EDTA (L), and Co-EDTA chelate (ML) are shown in Table 7. Table 7 shows that the concentration of free cobalt metal, C_M, is extremely low when $a \geq 1$. By comparing Tables 5 and 7, it is seen that T_M is almost equal to C_{ML}. This may be due to the negligibly low concentration of free cobalt metal with respect to that of Co-EDTA chelate and the unit value of α_{ML}, i.e., $T_M = C'_M + C'_{ML} \cong C'_{ML} = C_{ML}$.

ACKNOWLEDGMENT

This work was supported by the Korea Science and Engineering Foundation.

REFERENCES

1. S. Ahman and I. H. Qureshi, *Sep. Sci. Technol.*, *24*, 56 (1989).
2. S. Ahmad, A. Mannan, and I. H. Qureshi, *Ibid.*, *27*, 523 (1992).
3. D. G. Brookins, *Geochemical Aspects of Radioactive Waste Disposal*, Springer-Verlag, New York, 1984.
4. G. W. Beall and B. Allard, *Nucl. Technol.*, *59*, 405 (1982).
5. I. Neretnieks, "The Importance of Sorption Processes in Retarding Radionuclide Migration in the Geosphere," in *Fundamentals of Adsorption*, AIChE, 1983.
6. K. L. Erickson, "Radionuclide Sorption Studies on Abyssal Red Clays," in *Radioactive Waste in Geological Storage*, American Chemical Society, Washington, D.C., 1979.
7. L. Means, D. A. Crerar, and J. O. Duguid, *Science*, *200*, 1477 (1978).
8. M. Cleveland and T. F. Rees, *Ibid.*, *212*, 1506 (1981).
9. C. F. Bell, *Principles of Application of Metal Chelation*, Clarendon Press, Oxford, 1977.
10. M. A. Bangash, J. Hanif, and M. A. Ahan, *Waste Manage.*, *12*, 29 (1992).
11. J. A. Ayres, *Decontamination of Nuclear Reactors and Equipment*, Ronald Press, New York, 1970.
12. C. W. Miller and L. V. Benson, *Water Resour. Res.*, *19*, 381 (1983).
13. A. J. Valocchi, R. L. Street, and P. V. Roberts, *Ibid.*, *17*, 1517 (1981).
14. L. Means and C. A. Alexander, *Nucl. Chem. Waste Manage.*, *2*, 183 (1981).
15. D. P. Mellor, *Chelating Agents and Metal Chelates*, Academic Press, New York, 1964.
16. G. Schwarzenbach, *Complexometric Titrations*, Interscience, New York, 1957.
17. A. Ringbom, *Complexation in Analytical Chemistry*, Wiley-Interscience, New York, 1963.
18. J. M. Tiedje, *Appl. Microbiol.*, *30*, 327 (1975).
19. G. D. Christian, *Analytical Chemistry*, Wiley, New York, 1980.

Received by editor April 5, 1994