

# Study of the diffusion of metals and metals-EDTA complexes in water by capillary method

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**Abstract.** EDTA can complex with radionuclides (RNs) to form negatively charged complexes, making it difficult for clay minerals to retard the diffusion of RNs waste. The diffusion coefficient of RNs in water ( $D_w$ ) is an important parameter for the safety assessment of the repository. In this study, the effects of EDTA on the diffusion of metal ions ( $\text{Cu}^{2+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Lu}^{3+}$  and  $\text{Zn}^{2+}$ ) were investigated by a capillary method. The experimental results showed that  $[\text{Cu-EDTA}]^{2-}$ ,  $[\text{Sm-EDTA}]^{-}$  and  $[\text{La-EDTA}]^{-}$  have higher  $D_w$  than the  $\text{Mn}^{2+}$ . Whereas,  $[\text{Nd-EDTA}]^{-}$  and  $[\text{Zn-EDTA}]^{2-}$  have lower  $D_w$  than  $\text{Nd}^{3+}$  and  $\text{Zn}^{2+}$  cations. The  $D_w$  is consistent with the literatures, indicating the validity of the capillary method to determine the diffusion coefficients. According to Stokes-Einstein relation, the ionic radius and ionic potential of the ion are in disproportional to the  $D_w$  value. Cu-, Sm- and La-EDTA complexes have smaller molecular size than the uncomplexed metal ions, indicating that the  $\text{M}^{n+}$  ions might be associated with many water molecules to form hydrated ions with larger ionic radius. Whereas the  $[\text{Nd-EDTA}]^{-}$  and  $[\text{Zn-EDTA}]^{2-}$  have larger molecular size than  $\text{Nd}^{3+}$  and  $\text{Zn}^{2+}$  cations.

## 1. Introduction

Ethylenediaminetetraacetate (EDTA) is often used as a chelate for agricultural and industrial applications, resulting in an increase of EDTA concentrations in various water sources. It may complex with free heavy metal ions to form soluble complexation, thus enhancing the transportation of  $\text{M-EDTA}^{(Z-4)+}$  complexes in water and clays barrier systems<sup>1-3</sup>. The effect of EDTA on the transportation of metal ions has been attracted a lot of attention, such as  $^{85}\text{Sr-EDTA}^{2-}$  in sediments<sup>4</sup>,  $\text{Cd/Co-EDTA}^{2-}$  in saprolite<sup>5</sup>, and  $\text{Eu-EDTA}^{-}$  in hard clay rock<sup>6</sup>. EDTA can decrease the adsorption of metal ions on minerals and enhance their transportation not only due to the formation of negatively charge complexes<sup>7, 8</sup>, but also due to the reducing of the clay specific surface area<sup>9</sup>. For example, equimolar EDTA inhibited the sorption of U(VI) on montmorillonite due to the formation of negatively charged  $\text{UO}_2\text{HEDTA}^{-}$ ,  $(\text{UO}_2)_2\text{OHEDTA}^{-}$  and  $(\text{UO}_2)_2\text{EDTA}^{4-}$ <sup>7</sup>. The transportation of  $\text{Th}^{4+}$  through sands was enhanced by EDTA due to the formation of  $\text{Th}(\text{OH})(\text{EDTA})_2^{2-}$  and  $\text{Th}(\text{OH})(\text{EDTA})^{-2}$ .

In order to retard the transportation of radionuclidewaste, it often uses porous materials with low permeability such as clay rock and compacted bentonite as backfill material for the repository. Diffusion is the predominant behavior of radionuclide ions. Diffusion coefficient of RNs in water ( $D_w$ ) is one

of the most important parameters to predict the diffusion behavior of RNs in backfill material and the surrounding rock. The diffusion cell method is often used in determining the diffusion coefficient of RNs in water<sup>1,10</sup> and in minerals<sup>6,11</sup>. EDTA can alter diffusion of RNs by complexation reaction or by the modification of the properties of minerals. Due to the large molecular size of EDTA, the diffusion coefficient of  $\text{M-EDTA}^{(Z-4)+}$  complexes in water was found to be similar among various metal ions<sup>1</sup>. Descostes et al. (2017) reported that EDTA increase the diffusion of RNs in clays due to the formation of negatively charged complexes. Anionic exclusion of  $[\text{Eu-EDTA}]^{-}$  was found in the rock clay. However, to the best of our knowledge, only a few studies related to the effect of EDTA on the diffusion of RNs were reported due to the long experimental period<sup>1,6,9</sup>.

Tri-valent lanthanides were often used as the surrogates of tri-valent actinides to avoid the operation of radioactivity experiments. In this study, the effect of EDTA on metals ions ( $\text{Cu}^{2+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Lu}^{3+}$  and  $\text{Zn}^{2+}$ ) were investigated by a capillary method. The aim is to verify this method to the classic conductivity method and diffusion cell method. Some new diffusion coefficients of ions were also provided. We wish to have more knowledge of the diffusion properties of  $\text{M-EDTA}^{(Z-4)+}$  complexes before the diffusion experiment in clay starts.

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## 2. Materials and Methods

### 2.1 Experiments

#### 2.1.1 Materials

The diffusion experiments were conducted at aerobic condition. Reagent-grade  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ ,  $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,  $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$  (Aaladdin) and ethylenediaminetetraacetic acid disodium salt ( $\text{Na}_2\text{EDTA}$ , Aaladdin). The solution was prepared in Milli-Q (18  $\text{M}\Omega/\text{cm}$ ) water.

The aqueous chemical speciation of M-EDTA<sup>(Z-4)+</sup> complexes were calculated by using HySS (Hyperquad Simulation and Speciation) computer program. The stability constants from literature were used for calculations<sup>12</sup>. All  $\text{M}^{n+}$  cations was mainly formed with EDTA as soluble M-EDTA<sup>(Z-4)+</sup> complexes with almost 100% in 0.5 M NaCl solution due to the large stability constantes of M-EDTA<sup>(Z-4)+</sup> complexes.

#### 2.1.2 Diffusion experiment

The diffusion behavior of  $\text{M}^{n+}$  and M-EDTA<sup>(Z-4)+</sup> complexes in water will be investigated by a capillary method with single element solution (Fig.1). A working solution of  $\text{Cu}^{2+}$  was prepared by dissolving solid metal chlorides in 0.5 M NaCl solution. 0.1 mol/L of  $\text{Cu}^{2+}$  stock solution was prepared by adding some  $\text{Cu}^{2+}$  working solution in 0.5 mol/L of NaCl solution. The pH was adjusted to  $7.0 \pm 0.2$  by adding minor HCl or NaOH. The 5.0 ml vials were filled with 4.0 ml of tracer free NaCl solution. After a capillary was fit into an opening in the cap of the vial, the glass open-ended capillary (diameter ca. 0.85 mm) was filled with 25  $\mu\text{L}$   $\text{Cu}^{2+}$  at a length of ca. 4.7 cm, and then a parafilm membrane sealed the upper end of the capillary. The bottom end of the capillary immersed into 0.5 mol/L of NaCl solution (Fig. 1A). The out-diffusion of  $\text{Cu}^{2+}$  from the capillary into the solution started. After a certain time interval, the capillary was removed from the solution. The concentration of copper in vials was measured by an inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer, Optima 7000 DV). The same experimental procedures were conducted for the other metal ions ( $\text{Sm}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Zn}^{3+}$  and  $\text{Lu}^{3+}$ ) and M-EDTA<sup>(Z-4)+</sup> complexes.

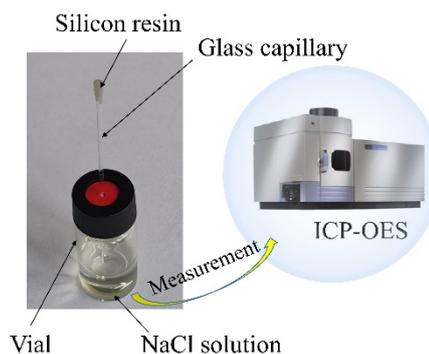


Fig.1 The diffusion set-up for the capillary method.

### 2.2 Computational methods

#### 2.2.1 Determination of the diffusion coefficients of free metal ions

The diffusion coefficient ( $D_w$ ) for a metal ion in NaCl solution was obtained by fitting the concentration of the metal ion in vials as a function of time by the following equation<sup>13</sup>:

$$\frac{C}{C_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-(2n+1)^2 \cdot \pi^2 \cdot D_w \cdot t / 4L^2\right] \quad (1)$$

where  $C$  (mol/L) is the concentration of the metal ion in the vials.  $C_0$  (mol/L) is the initial concentration of the metal ion.  $L$  (m) is the filled length of metal ions solution in the capillary. It was 0.047 m in this study.

$D_w$  is related to the diffusion coefficients of  $\text{M}^{n+}$  and M-EDTA<sup>(Z-4)+</sup> complexes ( $D_{w,\theta}$ ) and NaCl ion ( $D_{w,e}$ ) in diluted solution as follows<sup>14</sup>:

$$D_w = \frac{Z_1^2 c_1 + Z_2^2 c_2}{Z_1^2 c_1 / D_{w,e} + Z_2^2 c_2 / D_{w,\theta}} \quad (2)$$

where  $D_{w,Na+}$  is  $1.33 \times 10^{-9} \text{ m}^2/\text{s}$ <sup>14</sup>.

#### 2.2.2 Calculation of ionic radius of $\text{M}^{n+}$ and M-EDTA<sup>(Z-4)+</sup> complexes

The ionic radius of the diffusing species ( $r$ , Å) is calculated by the classic Stokes-Einstein relation as follows:

$$r = \frac{kT}{6\pi\eta D_w} \quad (3)$$

where  $k$  ( $1.380649 \times 10^{-23} \text{ Pa}\cdot\text{m}^3/\text{K}$ ) is the Boltzmann constant,  $T$  (K) is the temperature and  $\eta$  (Pa·s) is the viscosity of the medium, which is  $0.9365 \times 10^{-3} \text{ Pa}\cdot\text{s}$  in 0.5 mol/L of NaCl solution<sup>15</sup>.

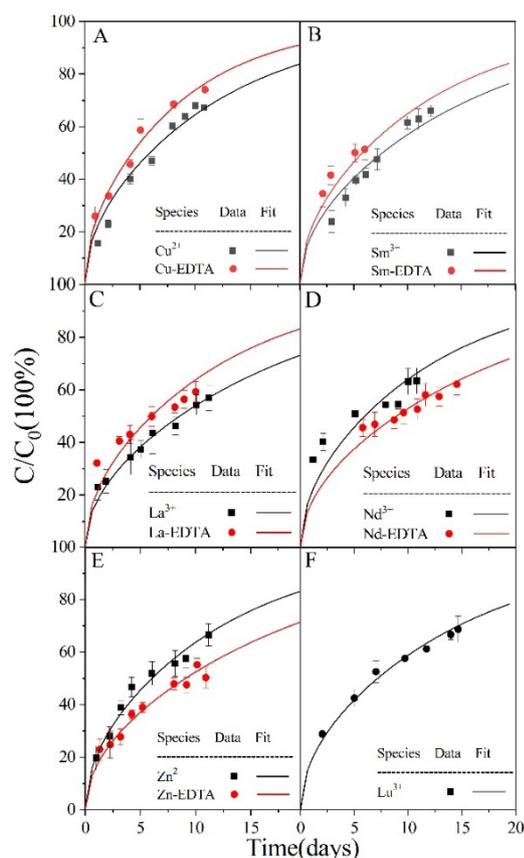
The ionic potential ( $I_p$ ) is defined as:

$$I_p = |z| / r \quad (4)$$

where  $z$  is the charge of ion and  $r$  is the ionic radius (Å).

### 3. Results & Discussion

Fig. 2 shows the diffusion profile of  $M^{n+}$  and M-EDTA $^{(Z-4)+}$  complexes in 0.5 M NaCl solution. Due to the large stability constants of M-EDTA $^{(Z-4)+}$  complexes, almost 100% complexes were formed in 0.5 M NaCl solution. The concentration ratio of  $M^{n+}$  and M-EDTA $^{(Z-4)+}$  complexes increased with increasing time. The concentration ratio of M-EDTA $^{(Z-4)+}$  (M = Cu $^{2+}$ , Sm $^{3+}$  and La $^{3+}$ ) complexes are higher than that of  $M^{n+}$ , indicating that the complexes diffuse faster than the metal ions. Whereas, the ratio of M-EDTA $^{(Z-4)+}$  (M = Nd $^{3+}$  and Zn $^{2+}$ ) complexes are lower than that of  $M^{n+}$ , implying a higher diffusion velocity of metal ions than that of the complexes.



**Fig.2** The diffusion profile of  $M^{n+}$  and M-EDTA $^{(Z-4)+}$  complexes in 0.5 M NaCl solution. T = 20 °C,  $C_0(M^{n+}) = 1.0 \times 10^{-3}$  mol/L.

The diffusion coefficients, the ionic radii and the ionic potentials ( $I_p$ ) of  $M^{n+}$  and M-EDTA $^{(Z-4)+}$  complexes were summarized in Table 1. The results were compared with the  $D_w$  measured by diffusion cell method and the limiting molar ionic conductivities using the Nernst-Einstein equation<sup>1, 10, 14, 16</sup>. The diffusion coefficient was obtained by fitting the experimental data as shown in Fig.1 by Eq.(1). The ionic radius was calculated by Eq.(3) in this work and for the literatures.  $I_p$  was calculated by Eq.(4). The  $I_p$  from literatures are listed in the round bracket in Table 1. The diffusion coefficients of  $M^{n+}$  ions in diluted water are calculated by Eq.(2), which are consistent with the  $D_w$  from literatures, indicating the validity of the capillary method to determine the diffusion coefficients. However, the  $D_w$  of M-EDTA $^{(Z-4)+}$  complexes were higher in this work than in literature. Since multi-element solution was employed to determine the diffusion coefficient by diffusion cell method as reported by Furukawa et al. (2007), the discrepancy could be explained by the co-complexation reaction of ions and EDTA.

According to Stokes-Einstein relation as shown in Eq.(1), the diffusion coefficient of ion is in disproportion to the ionic radius. For Cu $^{2+}$ , Sm $^{3+}$  and La $^{3+}$ , the ionic radius of M-EDTA $^{(Z-4)+}$  complexes are smaller than that of  $M^{n+}$ , indicating that the  $M^{n+}$  ions might be associated with many water molecules to form hydrated ions with larger ionic radius. Whereas, the ionic radius of [Nd-EDTA] $^-$  and [Zn-EDTA] $^-$  are larger than that of Nd $^{3+}$  and Zn $^{2+}$ . The  $D_w$  of [Nd-EDTA] $^-$  and [Zn-EDTA] $^-$  are in good agreement with that of Furukawa, et al. (2008), who reported that the  $D_w$  of Ln-EDTA $^{(Z-4)+}$  complexes were in the range of  $5.43 \times 10^{-10} - 5.76 \times 10^{-10}$  m $^2$ /s, which is close to that of H $_2$ EDTA $^{2-}$ . Since the molecular size of EDTA is much larger than that of metal ions, the diffusion of metal ions lose their characteristics by the complexation. However, the diffusion coefficient of [Cu-EDTA] $^{2-}$ , [Sm-EDTA] $^-$  and [La-EDTA] $^-$  were higher. More experiments will be conducted to clarify the discrepancy of the diffusion coefficient due to the multi-element solution and single element solution.

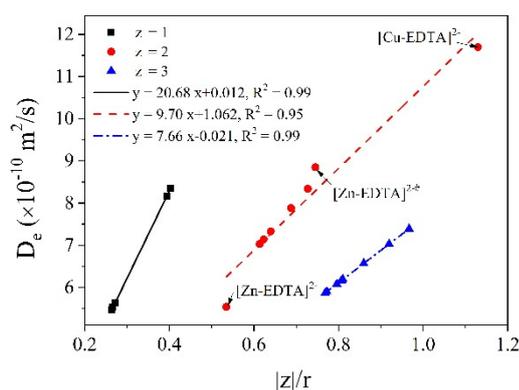
**Table 1** The diffusion coefficients and molecular radii and of  $M^{n+}$  and M-EDTA $^{(Z-4)+}$  complexes in 0.5 M NaCl solution. T = 20 °C,  $C_0(M^{n+}) = 1.0 \times 10^{-3}$  mol/L.

Species	$D_w(\times 10^{-10}$ m $^2$ /s)	RSD%	$D_{w,0}(\times 10^{-10}$ m $^2$ /s)	$r(\text{\AA})$	$I_p$	Reference
Cu $^{2+}$	7.88	5.24	7.84	2.91	0.69 (2.74*)	This work
Cu $^{2+}$			7.14	3.21	0.62 (2.95)	Li, et al. (1974)
Cu $^{2+}$			7.33	3.13	0.64	Vanysek (2000)
Sm $^{3+}$	6.57	5.47	6.53	3.49	0.86	This work
Sm $^{3+}$			6.08	3.77	0.80	Vanysek (2000)
La $^{3+}$	5.87	5.43	5.84	3.90	0.77 (2.78*)	This work
La $^{3+}$			6.19	3.70	0.81 (2.47)	Vanysek (2000)
Nd $^{3+}$	7.39	5.44	7.35	3.10	0.97	This work

Nd <sup>3+</sup>			6.16	3.72	0.81	Vanysek (2000)
La <sup>3+</sup>			6.17	3.71	0.81	Li, et al. (1974)
Zn <sup>2+</sup>	8.34	5.46	8.3	2.75	0.73 (2.70*)	This work
Zn <sup>2+</sup>			8.85	2.68	0.75	Li, et al. (1974)
Zn <sup>2+</sup>			7.03	3.26	0.61	Vanysek (2000)
Lu <sup>3+</sup>	7.03	5.44	6.99	3.26	0.92	This work
Lu <sup>3+</sup>			5.9	3.88	0.77	Furukawa (2008)
[Cu-EDTA] <sup>2-</sup>	11.7	5.47	11.7	1.77	1.13	This work
[Sm-EDTA] <sup>-</sup>	8.16	5.51	8.1	2.54	0.39	This work
[Sm-EDTA] <sup>-</sup>		4.50	5.53	3.75	0.27 (1.6)	Furukawa (2007)
[La-EDTA] <sup>-</sup>	8.35	5.58	8.29	2.48	0.40	This work
[La-EDTA] <sup>-</sup>			5.47	3.79	0.26 (1.6)	Furukawa (2007)
[Nd-EDTA] <sup>-</sup>	5.63	5.44	5.57	3.68	0.27	This work
[Nd-EDTA] <sup>-</sup>			5.53	3.75	0.27	Furukawa (2007)
[Zn-EDTA] <sup>2-</sup>	5.54	5.56	5.48	3.74	0.53	This work

\* Data from Nordstrom (1997)

Fig.3 shows the diffusion coefficients of  $M^{n+}$  and M-EDTA<sup>(Z-4)+</sup> complexes as a function of ionic potentials. It is defined as  $|z|/r$ , where  $z$  is the charge of ion and  $r$  is the ionic radius (Å). It shows a linear relationship between the diffusion coefficients and ionic potentials. The intercepts decrease with increasing the charge of ions. The ionic potentials of are lower than 1.2, which is in accordance with the anions reported by Li and Gergory (1974). However, cations have the lower ionic potentials in this work than in literatures<sup>1, 10, 16</sup>. It can be explained that the ionic radii of  $M^{n+}$  ions are larger due to the formation with water molecules to form hydrated ions in this work. The  $I_p$  is in proportional to the  $D_w$  when combined Eq.(2) and Eq. (3), indicating that the ions with high ionic potentials diffuse faster in the water.



**Fig.3** The diffusion coefficients of  $M^{n+}$  and M-EDTA<sup>(Z-4)+</sup> complexes in 0.5 M NaCl solution as a function of ionic potentials.

## 4. Conclusions

The results of this work indicate that EDTA can alter the diffusion behavior of the metal ions. The diffusion coefficients of ions is in disappropotional to the molecular size and ionic potential of metal ions. The

ions with smaller molecular sizes and ionic potentials have higher diffuion ability. Most of M-EDTA<sup>(Z-4)+</sup> complexes have similar diffusion velocities with the  $D_w$  values of  $\sim 5.5 \times 10^{-10}$  m<sup>2</sup>/s. Due to the heterogeneity of RNs, the M-EDTA<sup>(Z-4)+</sup> complexes do not show similar diffusion behavior. This work provides a simple method to determine the diffusion coefficients of RNs.

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