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

Zilong Geng¹, Hui Chen¹, Chenyu Yang¹, Qiang Shen¹, Tao Wu*¹

¹Department of Engineering, Huzhou University, 313000 Huzhou, P. R. China

Abstract. EDTA can complex with radionuclides (RN) 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 (Dw) is an important parameter for the safety assessment of the repository. In this study, the effect of EDTA on the diffusion of metal ions (Cu²⁺, Sm³⁺, Nd³⁺, Lu³⁺ and Zn²⁺) were investigated by a capillary method. The experimental results showed that [Cu-EDTA]²⁺, [Sm-EDTA]³⁺ and [La-EDTA]⁴⁺ have higher Dw than Mn²⁺. Whereas, [Nd-EDTA]²⁺ and [Zn-EDTA]²⁺ have lower Dw than Nd³⁺ and Zn²⁺ cations. The Dw is consistent with the literature, 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 Dw value. Cu-, Sm- and La-EDTA complexes have smaller molecular size than the uncomplexed metal ions, indicating that the metal ions might be associated with many water molecules to form hydrated ions with larger ionic radius. Whereas the [Nd-EDTA]²⁺ and [Zn-EDTA]²⁺ have larger molecular size than Nd³⁺ and Zn²⁺ 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 solublecomplexation, thus enhancing the transportation of M-EDTA(2-4)⁺ complexes in water and clays barrier systems.¹-³ The effect of EDTA on the transportation of metal ions has been associated with many water molecules to form hydrated ions with larger ionic radius. Whereas the [Nd-EDTA]²⁺ and [Zn-EDTA]²⁺ have larger molecular size than Nd³⁺ and Zn²⁺ cations.

Typically, the transport of radionuclides in the environment is of the most important parameters to predict the 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 and in minerals⁴-⁷. 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 M-EDTA(2-4)⁺ complexes in water was found to be similar among various metal ions. Descostes et al. (2017) reported that EDTA increased the diffusion of RNs in clays due to the formation of negatively charged complexes. Anionic exclusion of [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.¹, ⁶, ⁹

Tri-valent lanthanides were often used as the surrogates of tri-valent actinides to avoid the operation of radioactivity experiments. In this study, the diffusion of EDTA on metal ions (Cu²⁺, Sm³⁺, Nd³⁺, Lu³⁺ and Zn²⁺) were investigated by a capillary method. The aim is to verify this method to the classical 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 M-EDTA(2-4)⁺ complexes before the diffusion experiment in clay starts.

Corresponding author: twu@zjhu.edu.cn

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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 CuCl₂·H₂O, SmCl₃·6H₂O, LaCl₃·6H₂O, NdCl₃·6H₂O, ZnCl₂, LuCl₃·6H₂O (Aaladdin) and ethylenediaminetetraacetic acid disodium salt (Na₂EDTA, Aaladdin). The solution was prepared in Milli-Q (18 MΩ/cm) water.

The aqueous chemical speciation of M-EDTA(Z-4)+ complexes were calculated by using HySS (Hyperquad Simulation and Speciation) computer program. The stability constants from literature were used for calculations. All M⁹⁺ cations was mainly formed with EDTA as soluble M-EDTA(Z-4)+ complexes with almost 100% in 0.5 M NaCl solution due to the large stability constants of M-EDTA(Z-4)+ complexes.

2.1.2 Diffusion experiment

The diffusion behavior of M¹⁺ and M-EDTA(Z-4)+ complexes in water will be investigated by a capillary method with single element solution (Fig. 1). A working solution of Cu²⁺ was prepared by dissolving solid metal chlorides in 0.5 M NaCl solution. 0.1 mol/L of Cu²⁺ stock solution was prepared by adding some CuCl₂ working solution in 0.5 mol/L of NaCl solution. The pH was adjusted to 7.0 ± 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 µL Cu²⁺ 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 Cu²⁺ 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 (Sm³⁺, La³⁺, Nd³⁺, Zn³⁺ and Lu³⁺) and M-EDTA(Z-4)+ complexes.

2.2 Computational methods

2.2.1 Determination of the diffusion coefficients of free metal ions

The diffusion coefficient (D₀) 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:

\[ \frac{C}{C_0} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[ -\frac{(2n+1)^2 \cdot \pi^2 \cdot D_0 \cdot t}{4L^2} \right] \]

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.

\( D_0 \) is related to the diffusion coefficients of M⁹⁺ and M-EDTA(Z-4)+ complexes (\( D_{w,e} \)) and NaCl ion (\( D_{w,0} \)) in diluted solution as follows:

\[ D_v = \frac{Z_v^2 c_v + Z_{w,e}^2 c_{w,e}}{Z_v^2 c_v / D_{w,e} + Z_{w,e}^2 c_{w,e} / D_{w,0}} \]

where \( D_{w,Na^{+}} \) is 1.33 × 10⁻⁹ m²/s.

2.2.2 Calculation of ionic radius of M¹⁺ and M-EDTA(Z-4)+ complexes

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

\[ r = \frac{kT}{6\pi \eta D_v} \]

where \( k \) (1.380649 × 10⁻²³ Pa·m³/K) is the Boltzmann constant, \( T \) (K) is the temperature and \( \eta \) (Pa·s) is the viscosity of the medium, which is 0.9365 × 10⁻³ Pa·s in 0.5 mol/L of NaCl solution.

The ionic potential (\( I_f \)) is defined as:

\[ I_f = |z| / r \]

where \( z \) is the charge of ion and \( r \) is the ionic radius (Å).
3. Results & Discussion

Fig. 2 shows the diffusion profile of $\text{M}^{n+}$ 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 $\text{M}^{n+}$ and M-EDTA($^{(Z-4)+}$) complexes increased with increasing time. The concentration ratio of M-EDTA($^{(Z-4)+}$)($\text{M} = \text{Cu}^{2+}, \text{Sm}^{3+}$, and $\text{La}^{3+}$) complexes are lower than that of $\text{M}^{n+}$, indicating that the complexes diffuse faster than the metal ions. Whereas, the ratio of M-EDTA($^{(Z-4)+}$)($\text{M} = \text{Zn}^{2+}$ and $\text{Nd}^{3+}$) complexes are larger than that of $\text{M}^{n+}$, implying a higher diffusion velocity of metal ions than that of the complexes.

The diffusion coefficients, the ionic radii and the ionic potentials ($I_p$) of $\text{M}^{n+}$ 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 $1, 10, 14, 16$. 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 $\text{M}^{n+}$ 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 disproportionional to the ionic radius. For $\text{Cu}^{2+}, \text{Sm}^{3+}$ and $\text{La}^{3+}$, the ionic radius of M-EDTA($^{(Z-4)+}$) complexes are smaller than that of $\text{M}^{n+}$, indicating that the $\text{M}^{n+}$ ions might be associated with many water molecules to form hydrated ions with larger ionic radius. Whereas, the ionic radius of $[\text{Nd-EDTA}]^-$ and $[\text{Zn-EDTA}]^-$ are larger than that of $\text{Nd}^{3+}$ and $\text{Zn}^{2+}$. The $D_w$ of $[\text{Nd-EDTA}]^-$ and $[\text{Zn-EDTA}]^-$ 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 $H_2\text{EDTA}^2$.

Since the molecular size of EDTA is much larger than metal ions, the diffusion of metal ions lose their characteristics by the complexation. However, the diffusion coefficient of $[\text{Cu-EDTA}]^2$, $[\text{Sm-EDTA}]^-$ and $[\text{La-EDTA}]^-$ were higher. More experiments will be conducted to clarified the discrepancy of the diffusion coefficient due to the multi-element solution and single element solution.

![Fig.2](https://example.com/image2)

**Fig.2** The diffusion profile of $\text{M}^{n+}$ and M-EDTA($^{(Z-4)+}$)complexes in 0.5 M NaCl solution. $T = 20^\circ\text{C}$, $C_{0}(\text{M}^{n+}) = 1.0 \times 10^{-3}$ mol/L.

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

Table 1 The diffusion coefficients and molecular radii of $\text{M}^{n+}$ and M-EDTA($^{(Z-4)+}$) complexes in 0.5 M NaCl solution. $T = 20^\circ\text{C}$, $C_{0}(\text{M}^{n+}) = 1.0 \times 10^{-3}$ mol/L.
| Ion       | D (×10⁻¹⁰ m²/s) | V (Å) | k (Å⁻¹) | Comment |
|-----------|----------------|-------|---------|---------|
| Nd³⁺      | 6.16           | 3.72  | 0.81    | Vanysek (2000) |
| La³⁺      | 6.17           | 3.71  | 0.81    | Li, et al. (1974) |
| Zn²⁺      | 8.34           | 5.46  | 0.81    | This work |
| Zn²⁺      | 8.85           | 2.68  | 0.75    | Li, et al. (1974) |
| Lu³⁺      | 7.03           | 5.44  | 0.81    | Vanysek (2000) |
| Lu³⁺      | 6.99           | 3.26  | 0.92    | This work |
| [Cu-EDTA]²⁻ | 11.7          | 5.47  | 1.13    | This work |
| [Sm-EDTA]⁻ | 8.16           | 5.51  | 0.39    | This work |
| [Sm-EDTA]⁻ | 5.53           | 3.75  | 0.27    | Furukawa (2007) |
| [La-EDTA]⁻ | 8.35           | 5.58  | 0.40    | This work |
| [La-EDTA]⁻ | 8.29           | 2.48  | 0.26    | Furukawa (2007) |
| [Nd-EDTA]⁻ | 5.63           | 5.44  | 0.27    | This work |
| [Nd-EDTA]⁻ | 5.57           | 3.68  | 0.27    | Furukawa (2007) |
| [Zn-EDTA]²⁻ | 5.54           | 5.56  | 0.53    | This work |

* Data from Nordstrom (1997)

Fig. 3 shows the diffusion coefficients of M

+ and M-EDTA(\(Z-4\)+) 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

1, 10, 16. It can be explained that the ionic radii of M\(^{3+}\) ions are larger due to the formation with water molecules to form hydrated ions in this work. The \(I_p\) is in proportion to the \(D_w\) when combined Eq.(2) and Eq. (3), indicating that the ions with high ionic potentials diffuse faster in the water.

[Image: Fig.3 The diffusion coefficients of M\(^{3+}\) and M-EDTA(\(Z-4\)+) 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 disappropotional to the molecular size and ionic potential of metal ions. The ions with smaller molecular sizes and ionic potentials have higher diffusion ability. Most of M-EDTA(\(Z-4\)+) complexes have similar diffusion velocities with the \(D_w\) values of \(~5.5 \times 10^{-10} m^2/s\). Due to the heterogeneity of RNs, the M-EDTA(\(Z-4\)+) complexes do not show similar diffusion behavior. This work provides a simple method to determine the diffusion coefficients of RNs.

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