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Organic species of lanthanum in natural environments: Implications to mobility of rare earth elements in low temperature environments

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ABSTRACT

Naturally occurring organic ligands, such as acetate, citrate, malonate, oxalate, and succinate, play important roles in mobility and accumulation of La and other rare earth elements in low temperature systems under Earth surface conditions. However, a comprehensive and consistent thermodynamic database covering the complexes of rare earth elements with those naturally occurring organic ligands is lacking. In this study, thermodynamic data of organic species of rare earth elements (REE) represented by La, with an emphasis on their aqueous complexes with organic ligands, are critically reviewed. The organic ligands covered by this study include acetate, citrate, malonate, oxalate and succinate. In this critical review, the Specific Interaction Theory (SIT) model is adopted for extrapolation to infinite dilution. This model is a reliable activity coefficient model valid for a wide range of ionic strengths. These critically reviewed data, including complex formation constants, SIT interaction coefficients and solubility product constants, would enable accurate modeling of the speciation and solubility of REE in various environments including high ionic strength environments, providing insight into mobility and enrichment of REE in various environments.

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1. Introduction

The knowledge of chemical behavior of rare earth elements (REE), represented by La, in solutions with naturally occurring organic ligands has impacts for a number of fields. The impact for fields related to geosciences includes the accurate prediction of mobility of REE under Earth surface conditions, decontamination of environments contaminated with actinides (i.e., Am), exploration for REE deposits, and nuclear waste management (Wood, 1993). In the field of nuclear waste management, in a recent critical review of complexes of U, Np, Pu and Am with organic ligands (Hummel et al., 2007), the evaluation is limited to citrate, ethylenediaminetetraacetate (EDTA), oxalate, and α-isosaccharinate (ISA). The naturally occurring, important organic ligands include acetate, citrate, malonate, oxalate and succinate. Obviously, the evaluation of Hummel et al. (2007) emphasizes the organic ligands potentially present in waste streams, but ignored other naturally occurring organic ligands such as acetate, malonate, and succinate, which could be important in natural environments because of their relatively high concentrations and relatively strong complexes with REE. For instance, acetate concentrations in some oil-field brines can be as high as ~0.07 M (Willey et al., 1975). These naturally occurring organic ligands could play an important role in the mobility of REE because of their formation of strong complexes with REE or relatively high concentrations in environments. However, a comprehensive and consistent thermodynamic model valid to high ionic strength for the complexes of REE with these naturally occurring organic ligands is not available. In this paper, thermodynamic properties including formation constants, solubility product constants and relevant specific interaction coefficients of REE complexes with naturally occurring organic ligands are critically reviewed. The emphasis of this paper is on aqueous complexes of rare earth elements with organic ligands. The Specific Interaction Theory (SIT) model which is valid for high ionic strength, is adopted in this study to extrapolate stability constants to infinite dilution.

2. Stability constants of aqueous complexes of lanthanum and other rare earth elements with organic ligands

In the following, a series of stability constants of La organic complexes and associated specific interaction coefficients are evaluated based on the SIT model.

2.1. Stability constants of acetate complexes

The chemical formula of acetic acid is $C_2H_4O_2$. In the following, acetate ligand is abbreviated as "Ac". The formation of La acetate complexes can be expressed as

$$La^{3+} + nAc^- = La(Ac)_n^{3-n} \quad (1)$$

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$$\log \beta_n^I = \log m_{La(Ac)n^{3-n}} - \log m_{La^{3+}} - n \log m_{Ac^-} \quad (2)$$

$$\log \beta_n = \log a_{La(Ac)n^{3-n}} - \log a_{La^{3+}} - n \log a_{Ac^-} \quad (3)$$

where β_n^I is the formation quotient of La^{3+} with n complexing ligands at a constant ionic strength, whereas β_n is the same formation constant at infinite dilution.

Ding and Wood (2002) determined the log β_1^I of acetate with La^{3+}, Nd^{3+}, Gd^{3+} and Yb^{3+} in a NaCl medium from 0.1 m to 2.0 m. Their values of log β_1^I of acetate with La^{3+} and Nd^{3+} are extrapolated to infinite dilution by using the SIT model. Their values for Gd^{3+} and Yb^{3+}, however, are not used in this study, as the values for these two elements at 0.1 m ionic strength do not follow the general trend developed by Byrne and Li (1995) for formation constants of rare earth elements with organic ligands at 0.1 M ionic strength.

Based on the SIT model, the $\log \beta_1$ at infinite dilution should be

$$\log \beta_1 = \log \beta_1^I + 6D + \Delta\varepsilon\ (\text{Eq. (1)}) \times (I_m) \quad (4)$$

where D is the Debye–Hückel term, and $\Delta\varepsilon$ is the stoichiometric summation of specific interaction coefficients regarding Eq. (1) in NaCl medium. They are given by the following respective expressions:

$$D = \frac{A_\gamma \sqrt{I_m}}{1 + \rho\sqrt{I_m}} \quad (5)$$

in which A_γ is the Debye–Hückel slope for activity coefficient, which is 0.5092 at 25 °C (Helgeson and Kirkham, 1974); ρ the minimum distance of approach between ions, which is taken as 1.5 (Ciavatta, 1980), and I_m ionic strength on molal scale. The detailed description of the SIT model can be found in Ciavatta (1980) and Guillaumont et al. (2003).

In Eq. (4), $\Delta\varepsilon$ (Eq. (1)) is given by the following equation in NaCl medium:

$$\Delta\varepsilon\ (\text{Eq. (1)}) = \varepsilon(LaAc^{2+}, Cl^-) - \varepsilon(La^{3+}, Cl^-) - \varepsilon(Na^+, Ac^-) \quad (6)$$

In Fig. 1, $\log \beta_1$ is determined as 2.52 ± 0.08 with a $\Delta\varepsilon = -0.11 \pm 0.04$. In Fig. 1, the negative slope of the plot is $\Delta\varepsilon$. According to $\Delta\varepsilon = -0.11 \pm 0.04$ derived in this study, $\varepsilon(La^{3+}, Cl^-) = 0.22 \pm 0.02$ from Ciavatta (1980), and $\varepsilon(Na^+, Ac^-) = 0.0399 \pm 0.006$ from Xiong (2006), $\varepsilon(LaAc^{2+}, Cl^-)$ is derived as 0.15 ± 0.05 (Table 1).

The $\log \beta_1$ derived from experimental studies in a $NaClO_4$ medium is 2.56 ± 0.14 (Fig. 2) with $\varepsilon(LaAc^{2+}, ClO_4^-) = 0.31 \pm 0.05$ which is derived from $\Delta\varepsilon$ of -0.20 ± 0.04 based on the following equation:

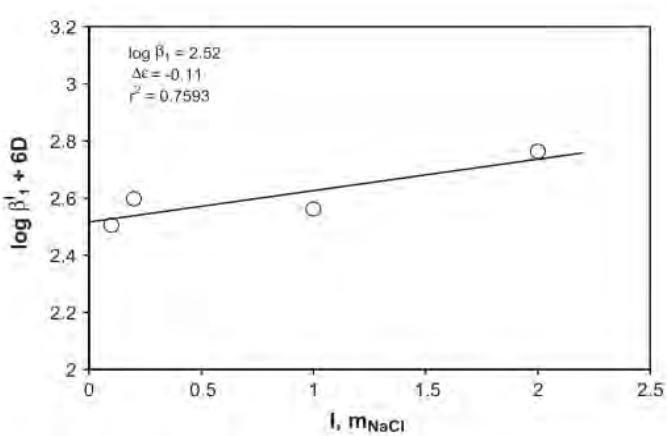

Fig. 1. A plot showing $\log \beta_1^I$ of $LaAc^{2+}$ as a function of ionic strength in NaCl medium. Experimental data are from Ding and Wood (2002).

$$\Delta\varepsilon\ (\text{Eq. (1)}) = \varepsilon(LaAc^{2+}, ClO_4^-) - \varepsilon(La^{3+}, ClO_4^-) - \varepsilon(Na^+, Ac^-) \quad (7)$$

In the derivation, $\varepsilon(La^{3+}, ClO_4^-) = 0.47 \pm 0.03$ and $\varepsilon(Na^+, Ac^-) = 0.0399 \pm 0.006$ are from Ciavatta, 1980 and Xiong (2006), respectively. The $\log \beta_1$ of 2.56 ± 0.14 in $NaClO_4$ medium is in excellent agreement with the above value determined in a NaCl medium. Therefore, this study recommends an average value of 2.54 ± 0.16 as the stability constant of $LaAc^{2+}$. This recommended value is very close to the value of 2.58 suggested by Ding and Wood (2002) based on the extrapolation to zero ionic strength according to their expression of ionic strength dependence of experimental quotients.

Similarly to the procedure for obtaining the $\log \beta_1$ for $LaAc^{2+}$, the $\log \beta_1$ for $NdAc^{2+}$ is obtained as 2.86 ± 0.06 (Fig. 3 and Table 1). According to $\Delta\varepsilon = -0.12 \pm 0.04$ obtained in this study, using $\varepsilon(La^{3+}, Cl^-) = 0.22 \pm 0.02$ from Ciavatta (1980) as an analog to $\varepsilon(Nd^{3+}, Cl^-)$, and $\varepsilon(Na^+, Ac^-) = 0.0399 \pm 0.006$ from Xiong (2006), $\varepsilon(NdAc^{2+}, Cl^-)$ is derived as 0.14 ± 0.03 (Table 1).

Wood et al. (2000) determined $\log \beta_1^I$ of $NdAc^{2+}$ in 0.1 m NaCl at 25 °C as 2.10 ± 0.13. This datum is not used in the above regression for $\log \beta_1$ for $NdAc^{2+}$. As an independent check, this value is also extrapolated to infinite dilution. By using the SIT coefficients mentioned above, the $\log \beta_1$ extrapolated by using the SIT model should be 2.75 ± 0.15. This value would be in good agreement with 2.86 ± 0.06 (Table 1), recommended by this study.

Regarding the formation constant for $La(Ac)_2^+$ determined in a $NaClO_4$ medium,

$$La^{3+} + 2Ac^- = La(Ac)_2^+ \quad (8)$$

the $\log \beta_2$ is expressed as:

$$\log \beta_2 = \log \beta_2^I + 10D + \Delta\varepsilon\ (\text{Eq. (8)}) \times (I_m) \quad (9)$$

$$\Delta\varepsilon\ (\text{Eq. (8)}) = \varepsilon(La(Ac)_2^+, ClO_4^-) - \varepsilon(La^{3+}, ClO_4^-) - 2 \times \varepsilon(Na^+, Ac^-) \quad (10)$$

In Fig. 4, and Table 1, $\log \beta_2$ and $\varepsilon(La(Ac)_2^+, ClO_4^-)$ are evaluated as 3.93 ± 0.24 and 0.12 ± 0.09, respectively.

Similarly, regarding the formation constant for $La(Ac)_3^0$ determined in $NaClO_4$ medium,

$$La^{3+} + 3Ac^- = La(Ac)_3^0 \quad (11)$$

the $\log \beta_3$ is expressed as:

$$\log \beta_3 = \log \beta_3^I + 12D + \Delta\varepsilon\ (\text{Eq. (11)}) \times (I_m) \quad (12)$$

$$\Delta\varepsilon\ (\text{Eq. (11)}) = \varepsilon(La(Ac)_3^0, Na^+, ClO_4^-) - \varepsilon(La^{3+}, ClO_4^-) - 3 \times \varepsilon(Na^+, Ac^-) \quad (13)$$

In Fig. 5, Table 1, $\log \beta_3$ and $\varepsilon(La(Ac)_3^0, Na^+, ClO_4^-)$ are evaluated as 4.72 ± 0.28 and 0.10 ± 0.10, respectively.

2.2. Stability constants of citrate complexes

The chemical formula of citric acid is $C_6H_8O_7$. In the following, the citrate ligand is abbreviated as "Cit". Daniele et al. (1985) determined the stability constant of La-citrate complex in 0.1 M $NaClO_4$ as 7.17 in log units. According to the SIT model, we have,

$$La^{3+} + Cit^{3-} = LaCit^0 \quad (14)$$

Its stability constant is expressed as,

$$\log \beta_1 = \log \beta_1^I + 18D + \Delta\varepsilon\ (\text{Eq. (14)}) \times (I_m) \quad (15)$$

$$\Delta\varepsilon\ (\text{Eq. (14)}) = \varepsilon(LaCit^0, Na^+, ClO_4^-) - \varepsilon(La^{3+}, ClO_4^-) - \varepsilon(Na^+, Cit^{3-}) \quad (16)$$

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Table 1
Stability constants of aqueous complexes of La and other rare earth elements with organic ligands at infinite dilution at 25 °C and 1 bar, and associated specific interaction coefficients derived in this study.

Reactions	ε or $\Delta\varepsilon$ ($\pm 2\sigma$)	$\log\beta$ or $\log K$ ($\pm 2\sigma$)	Reference and remarks
$La^{3+} + Ac^- = LaAc^{2+}$	$\varepsilon(LaAc^{2+}, Cl^-) = 0.15 \pm 0.05$ $\varepsilon(LaAc^{2+}) = 0.31 \pm 0.05$	2.54 ± 0.16	This study
$Nd^{3+} + Ac^- = LaAc^{2+}$	$\varepsilon(NdAc^{2+}, Cl^-) = 0.14 \pm 0.03$	2.86 ± 0.06	This study
$La^{3+} + 2Ac^- = La(Ac)_2^+$	$\varepsilon(La(Ac)_2^+, ClO_4^-) = 0.12 \pm 0.09$	3.93 ± 0.24	This study
$La^{3+} + 3Ac^- = La(Ac)_3^0$	$\varepsilon(La(Ac)_3^0, Na^+, ClO_4^-) = 0.10 \pm 0.10$ $\varepsilon(Na^+, HCit^{2-}) = -0.083 \pm 0.03$ $\varepsilon(Na^+, Cit^{3-}) = -0.10 \pm 0.04$	4.72 ± 0.28	This study
$La^{3+} + Cit^{3-} = LaCit^0$	$\varepsilon(Na^+, H_2Cit^-) = -0.056 \pm 0.02$; $\varepsilon(Na^+, HCit^{2-}) = -0.083 \pm 0.03$; $\varepsilon(Na^+, Cit^{3-}) = -0.10 \pm 0.04$	9.11 ± 0.24	This study
$La^{3+} + Mal^{2-} = LaMal^+$	Using $\Delta\varepsilon = -0.62 \pm 0.10$ for $EuMal^+$ in $NaClO_4$ medium as an analog	4.79 ± 0.23	This study
$La^{3+} + 2Mal^{2-} = La(Mal)_2^-$	Using $\Delta\varepsilon = -1.19 \pm 0.04$ for $Eu(Ox)_2^-$ in $NaClO_4$ medium as an analog	7.18 ± 0.12	This study
$La^{3+} + HMal^- = LaHMal^{2+}$	Using $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$; and employing $\varepsilon(EuMal^+, ClO_4^-) = -0.12 \pm 0.11$ as an analog to $\varepsilon(La(HMal)_2^+, ClO_4^-)$	2.48 ± 0.30	This study
$La^{3+} + HMal^- + Mal^{2-} = LaH(Mal)_2^0$	Using $\varepsilon(La^{3+}, ClO_4^-) = 0.47 \pm 0.03$; $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$; $\varepsilon(Na^+, Mal^{2-}) = 0.03 \pm 0.04$; and utilizing $\varepsilon(La(Ac)_3^0, Na^+, ClO_4^-) = 0.10 \pm 0.10$ as an analog to $\varepsilon(LaH(Mal)_2^0, Na^+, ClO_4^-)$	6.59 ± 0.40	This study
$Eu^{3+} + Mal^{2-} = EuMal^+$	$\varepsilon(EuMal^+, ClO_4^-) = -0.12 \pm 0.11$; $\varepsilon(Na^+, Mal^{2-}) = 0.03 \pm 0.04$	5.49 ± 0.11	This study
$La^{3+} + Ox^{2-} = LaOx^+$	$\Delta\varepsilon = -0.69 \pm 0.06$	6.00 ± 0.40	Cetiner and Xiong (2008)[a]
$La^{3+} + Suc^{2-} = LaSuc^+$	Using $\Delta\varepsilon = -0.62 \pm 0.10$ for $LaMal^+$ in $NaClO_4$ medium as an analog	4.34 ± 0.11	This study
$La^{3+} + HSuc^- = LaHSuc^{2+}$	Using $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$; $\varepsilon(LaAc^{2+}, ClO_4^-) = 0.31 \pm 0.05$ as an analog to $\varepsilon(LaHSuc^{2+}, ClO_4^-)$	2.21 ± 0.10	This study
$La^{3+} + 2HSuc^- = La(HSuc)_2^+$	Using $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$ as an analog to $\varepsilon(Na^+, HSuc^-)$; $\varepsilon(EuMal^+, ClO_4^-) = -0.12 \pm 0.11$ as an analog to $\varepsilon(La(HSuc)_2^+, ClO_4^-)$	3.80 ± 0.17	This study
$H_2Mal = H^+ + HMal^-$	$\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$	-2.90 ± 0.05	This study
$HMal^- = H^+ + Mal^{2-}$	$\varepsilon(Na^+, Mal^{2-}) = 0.03 \pm 0.04$	-5.62 ± 0.07	This study

[a] In Cetiner and Xiong (2008), the uncertainties of the SIT interaction coefficient and formation constant were not given. In this study, the respective uncertainties are provided.

Based on dissociation constants of citric acid in $NaClO_4$ medium from Choppin et al. (1996), and $\varepsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$ from Ciavatta (1980), $\varepsilon(Na^+, Cit^{3-})$ is derived as -0.10 ± 0.04. Therefore, using $\varepsilon(La(Ac)_3^0, Na^+, ClO_4^-)$ determined in this study as an analog to $\varepsilon(LaCit^0, Na^+, ClO_4^-)$, $\varepsilon(La^{3+}, ClO_4^-) = 0.47 \pm 0.03$, and $\varepsilon(Na^+, Cit^{3-}) = -0.10 \pm 0.04$, the $\log\beta_1$ is evaluated as 9.11 ± 0.24 based on the SIT model (Table 1). This value is similar to the formation constant of $AmCit^0$ evaluated by Hummel et al. (2007) ($\log\beta_1 = 8.55 \pm 0.20$) and in the Waste Isolation Pilot Plant (WIPP) thermodynamic model ($\log\beta_1 = 8.80$) (Xiong et al., 2010).

2.3. Stability constants of malonate complexes

The chemical formula of malonic acid is $C_3H_4O_4$. In the following, the malonate ligand is abbreviated as "Mal". In this study, the stability constants of La in $NaClO_4$ medium are evaluated by using the SIT model. The first association constant of malonate with La is expressed as:

$$La^{3+} + Mal^{2-} = LaMal^+ \quad (17)$$

Based on the SIT model, the $\log\beta_1$ at infinite dilution should be

$$\log\beta_1 = \log\beta_1^I + 12D + \Delta\varepsilon\ (\text{Eq. } (17)) \times (I_m) \quad (18)$$

$\Delta\varepsilon$(Eq. (17)) is given by the following equation:

$$\Delta\varepsilon\ (\text{Eq. } (17)) = \varepsilon(LaMal^+, ClO_4^-) - (\varepsilon(La^{3+}, ClO_4^-) - (\varepsilon(Na^+, Mal^{2-}) \quad (19)$$

Dellien and Grenthe (1971) determined $\log\beta_1^I$ in 1.0 M $NaClO_4$ as 3.07. Abdullah and Monk (1985) obtained a similar value of 2.88 in 1.0 M $NaClO_4$. As some of the specific interaction coefficients defined in Eq. (19) are not known, the interaction coefficients for $EuMal^+$ are derived in this study to be used as analogs for $LaMal^+$.

Similar to the equations for $LaMal^+$, formation reaction of $EuMal^+$ is expressed as,

$$Eu^{3+} + Mal^{2-} = EuMal^+ \quad (20)$$

Based on the SIT model, the $\log\beta_1$ at infinite dilution should be

$$\log\beta_1 = \log\beta_1^I + 12D + (\Delta\varepsilon\ (\text{Eq. } (20)) \times (I_m) \quad (21)$$

$\Delta\varepsilon$(Eq. (20)) is given by the following equation:

$$\Delta\varepsilon\ (\text{Eq. } (20)) = \varepsilon(EuMal^+, ClO_4^-) - \varepsilon(Eu^{3+}, ClO_4^-) - \varepsilon(Na^+, Mal^{2-}) \quad (22)$$

According to Fig. 6, the $\log\beta_1$ for $EuMal^+$ is evaluated as 5.49 ± 0.11 at infinite dilution, with a $\Delta\varepsilon$ (Eq. (20)) $= -0.62 \pm 0.11$. Using this $\Delta\varepsilon$ (Eq. (20)) $= -0.62 \pm 0.11$ as an analog to $\Delta\varepsilon$ (Eq. (17)), $\log\beta_1$ for $LaMal^+$ is calculated as 4.79 ± 0.23 according to Eq. (18) (Table 1). This is the average value based on the extrapolation to infinite dilution of the conditional formation constants of Dellien and Grenthe (1971) and Abdullah and Monk (1985) in 1.0 M Na ClO_4 as mentioned before. In this study, the strength of La Mal^+ differs from that of $EuMal^+$ by 0.7 logarithmic units. This difference is similar to that observed in the evaluation of Wood (1993), which is 0.6 logarithmic units.

As $\varepsilon(Na^+, Mal^{2-})$ and $\varepsilon(EuMal^+, ClO_4^-)$ are not available in the literature, it is worthwhile deriving them based on $\Delta\varepsilon$ (Eq. (20)) $= -0.62 \pm 0.11$ and $\varepsilon(La^{3+}, ClO_4^-) = 0.47 \pm 0.03$ as an analog to $\varepsilon(Eu^{3+}, ClO_4^-)$. In order to obtain $\varepsilon(Na^+, Mal^{2-})$, the dissociation constants of malonic acid in $NaClO_4$ are evaluated.

In Fig. 7A and B, equilibrium quotients of malonic acid in $NaClO_4$ medium at 25 °C are evaluated by using the SIT model. In Fig. 7A, according to $\Delta\varepsilon = 0.10 \pm 0.02$, $\varepsilon(Na^+, HMal^-)$ is derived as -0.04 ± 0.03 based on $\varepsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$ (Ciavatta, 1980). In Fig. 7B, according to $\Delta\varepsilon = 0.21 \pm 0.03$, $\varepsilon(H^+, ClO_4^-) = 0.14 \pm 0.02$ and the above derived $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$, $\varepsilon(Na^+, Mal^{2-})$ is derived as 0.03 ± 0.04. It is worth mentioning that $\varepsilon(Na^+, HMal^-)$ and $\varepsilon(Na^+, Mal^{2-})$ derived in this study have a magnitude similar to $\varepsilon(Na^+, HOx^-) = -0.03 \pm 0.02$ and $\varepsilon(Na^+, Ox^{2-}) =$

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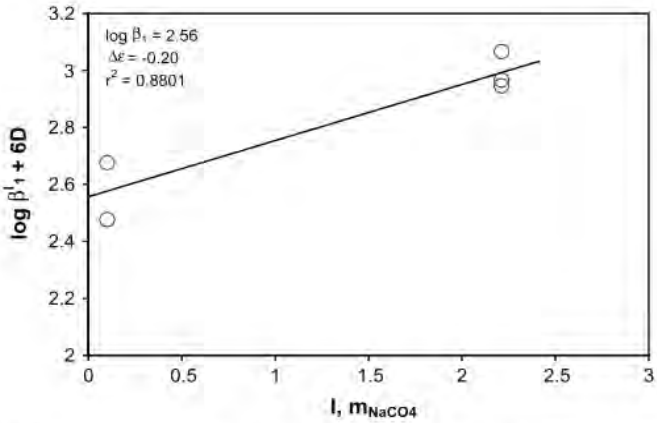

Fig. 2. A plot showing $\log \beta_1^I$ of $LaAc^{2+}$ as a function of ionic strength in $NaClO_4$ medium. Experimental data are from Sonesson (1958), Kolat and Powell (1962), Kovar and Powell (1966), Migal' and Chebotar (1967), and Bukietynska and Mondry (1984).

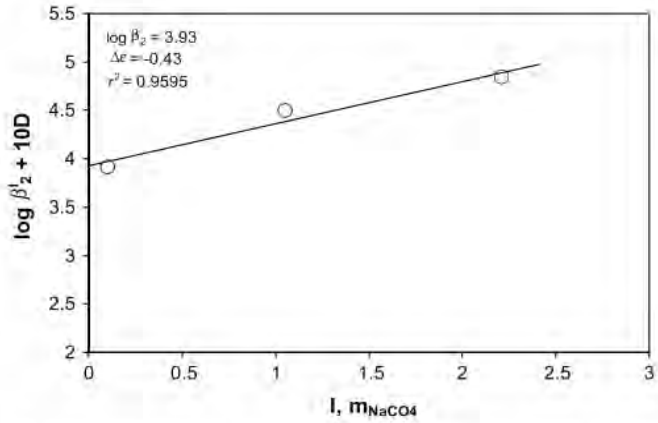

Fig. 4. A plot showing $\log \beta_2^I$ of $La(Ac)_2^+$ as a function of ionic strength in $NaClO_4$ medium. Experimental data are from the compilation of NIST (Smith and Martell, 2004).

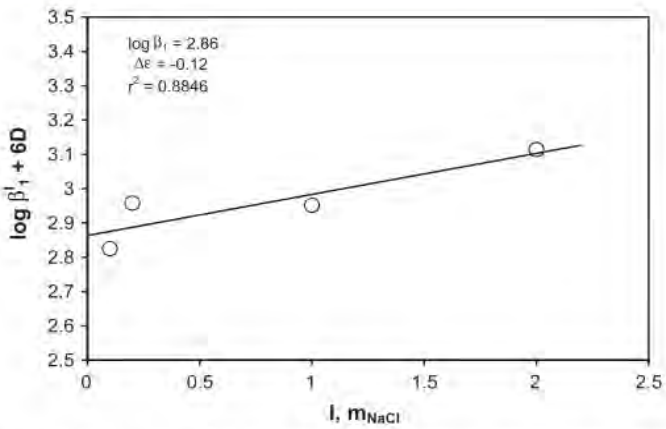

Fig. 3. A plot showing $\log \beta_1^I$ of $NdAc^{2+}$ as a function of ionic strength in NaCl medium. Experimental data are from Ding and Wood (2002).

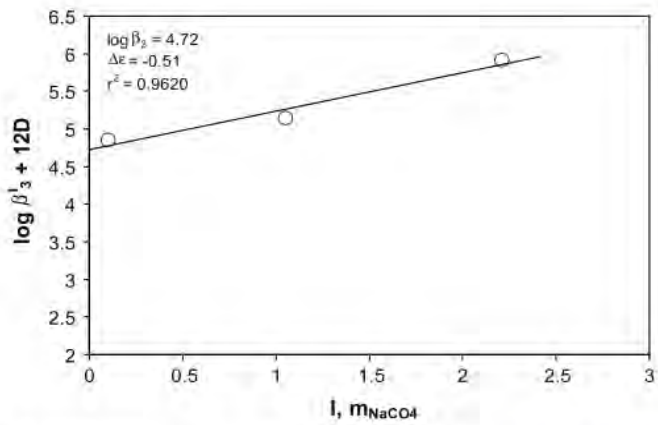

Fig. 5. A plot showing $\log \beta_3^I$ of $La(Ac)_3^0$ as a function of ionic strength in $NaClO_4$ medium. Experimental data are from the compilation of NIST (Smith and Martell, 2004).

-0.02 ± 0.04 recommended by Xiong (2009). In addition, this study also recommends the first and second dissociation constants of malonic acid at infinite dilution as -2.90 ± 0.05 and -5.62 ± 0.07, respectively, based on the SIT model for extrapolation to infinite dilution (Table 1).

Based on $\varepsilon(Na^+, Mal^{2-}) = 0.03 \pm 0.04$ and $\Delta\varepsilon = -0.62 \pm 0.10$, $\varepsilon(EuMal^+, ClO_4^-)$ is derived to be -0.12 ± 0.11 in accordance with Eq. (22).

The second cumulative association constant of malonate with La is expressed as:

$$La^{3+} + 2Mal^{2-} = La(Mal)_2^- \tag{23}$$

Based on the SIT model, the $\log \beta_2$ at infinite dilution should be

$$\log \beta_2 = \log \beta_2^I + 16D + \Delta\varepsilon\ (\text{Eq. (23)}) \times (I_m) \tag{24}$$

$\Delta\varepsilon$(Eq. (23)) is given by the following equation for $\log \beta_2^I$ determined in $NaClO_4$ medium:

$$\Delta\varepsilon\ (\text{Eq. (23)}) = \varepsilon(Na^+, La(Mal)_2^-) - \varepsilon(La^{3+}, ClO_4^-) - 2 \times \varepsilon(Na^+, Mal^{2-}) \tag{25}$$

Dellien and Grenthe (1971) determined $\log \beta_2^I$ in 1 M Na ClO_4 at 25 °C as 5.14 ± 0.04. Cetiner and Xiong (2008) derived $\Delta\varepsilon$ for $Eu(Ox)_2^-$ in $NaClO_4$ medium as -1.19 ± 0.04. By using this $\Delta\varepsilon$ for $Eu(Ox)_2^-$ as an analog to $\Delta\varepsilon$ (Eq. (23)), this study recommends a value of 7.18 ± 0.12 for $\log \beta_2$ of $La(Mal)_2^-$ (Table 1).

In addition, Dellien and Grenthe (1971) determined stability constants of La with bimalonate. Formation reactions regarding La with bimalonate can be expressed as:

$$La^{3+} + HMal^- = LaHMal^{2+} \tag{26}$$

$$La^{3+} + HMal^- + Mal^{2-} = LaH(Mal)_2^0 \tag{27}$$

The $\log \beta_{1,HMal^-}^I$ and $\log \beta_{1,HMal^-,Mal_2^-}^I$ in 1.0 M $NaClO_4$ at 25 °C were determined as 1.37 ± 0.20 and 4.11 ± 0.30, respectively (Dellien and Grenthe, 1971). Based on the SIT model, the $\log \beta_{1,HMal^-}$ regarding Reaction 26 should be:

$$\log \beta_{1,HMal^-} = \log \beta_{1,HMal^-}^I + 6D + \Delta\varepsilon\ (\text{Eq. (26)}) \times (I_m) \tag{28}$$

$\Delta\varepsilon$(Eq. (26)) is given by the following equation:

$$\Delta\varepsilon\ (\text{Eq. (26)}) = \varepsilon(LaHMal^{2+}, ClO_4^-) - \varepsilon(La^{3+}, ClO_4^-) - \varepsilon(Na^+, HMal^-) \tag{29}$$

Using $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$ derived in this study as an analog to $\epsilon\ (Na^+, HSuc^-)$, $\varepsilon(LaAc^{2+}, ClO_4^-) = 0.31 \pm 0.05$ as an analog to $\varepsilon(LaHMal^{2+}, ClO_4^-)$, and $\varepsilon(La^{3+}, ClO_4^-) = 0.47 \pm 0.03$ as mentioned before, $\log \beta_{1,HMal^-}$ is calculated as 2.48 ± 0.30 (Table 1).

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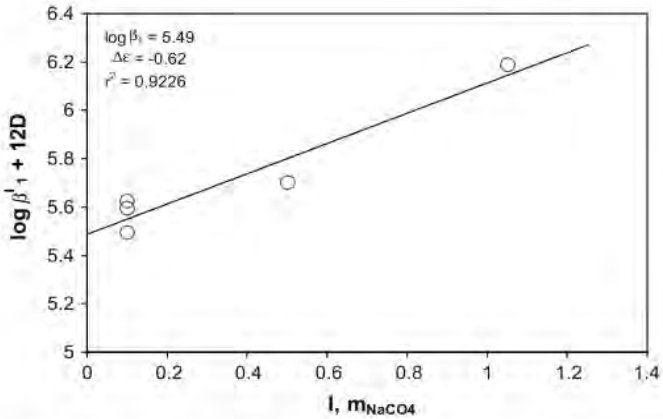

Fig. 6. A plot showing $\log \beta_1^I$ of $EuMal^+$ as a function of ionic strength in NaCl medium. Experimental data are from Powell et al. (1968), Dellien and Grenthe (1971), Shanbhag and Choppin (1982), Choppin et al. (1986), and Wang et al. (2000).

Similarly, based on the SIT model, the $\log \beta^I_{1,HMal^-,Mal^{2-}}$ regarding Reaction 27 should be:

$$\log \beta_{1,HMal^-,Mal^{2-}} = \log \beta^I_{1,HMal^-,Mal^{2-}} + 14D + \Delta\varepsilon\ (\text{Eq. (27)}) \times (I_m) \quad (30)$$

$\Delta\varepsilon$(Eq. (27)) is given by the following equation:

$$\Delta\varepsilon\ (\text{Eq. (27)}) = \varepsilon(LaH(Mal)^0_2, Na^-, ClO^-_4) - \varepsilon(La^{3+}, ClO^-_4) - \varepsilon(Na^+, HMal^-) - \varepsilon(Na^+, Mal^{2-}) \quad (31)$$

Using $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$ and $\varepsilon(Na^+, Mal^{2-}) = 0.03 \pm 0.04$ derived in this study, $\varepsilon(La(Ac)^0_3, Na^+, ClO^-_4) = 0.10 \pm 0.10$ as an analog to $\varepsilon(LaH(Mal)^0_2, Na^+, ClO^-_4)$, and $\varepsilon(La^{3+}, ClO^-_4) = 0.47 \pm 0.03$ as mentioned before, $\log \beta^I_{1,HMal^-,Mal^{2-}}$ is calculated as 6.59 ± 0.40 (Table 1).

2.4. Stability constants of oxalate complexes

The chemical formula of oxalic acid is $C_2H_2O_4$. The oxalate ligand is abbreviated to "Ox" in the following. In the study of Cetiner and Xiong (2008), the stability constant of La with oxalate has been evaluated with the SIT model. The $\log \beta_1$ of 6.00 ± 0.40 from their work is adopted in this study (Table 1). This value is similar to the value of 5.87 obtained by Schijf and Byrne (2001), which was obtained by using a variant extended Debye–Hückel equation for extrapolation.

2.5. Stability constants of succinate complexes

The chemical formula of succinic acid is $C_4H_6O_4$. For simplicity, succinate ligand is abbreviated as "Suc" in the following. The first association constant of La with succinate is expressed as:

$$La^{3+} + Suc^{2-} = LaSuc^+ \quad (32)$$

Based on the SIT model, the $\log \beta_1$ at infinite dilution should be

$$\log \beta_1 = \log \beta^I_1 + 12D + \Delta\varepsilon\ (\text{Eq. (32)}) \times (I_m) \quad (33)$$

$\Delta\varepsilon$(Eq. (32)) is given by the following equation:

$$\Delta\varepsilon\ (\text{Eq. (32)}) = \varepsilon(LaSuc^+, ClO^-_4) - \varepsilon(La^{3+}, ClO^-_4) - \varepsilon(Na^+, Suc^{2-}) \quad (34)$$

Regarding the stability constant of La with succinate, Choppin et al. (1986) determined a value of 3.09 ± 0.02 for $\log \beta^I_1$ in 0.1 M $NaClO_4$.

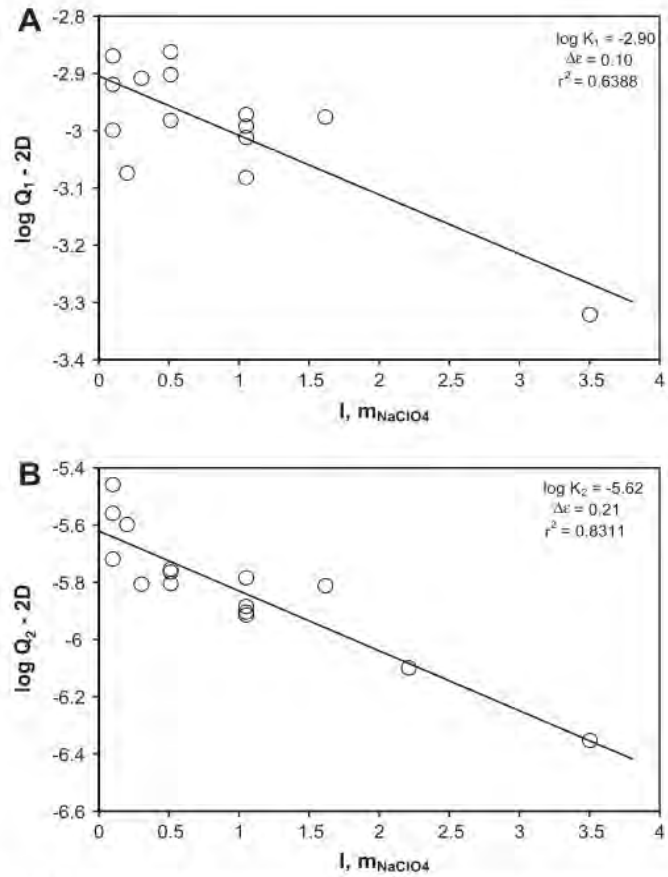

Fig. 7. A plot showing dissociation constants of H_2Mal as a function of ionic strength in $NaClO_4$ medium. A. First dissociation constants; B. Second dissociation constants. Experimental data are from the compilation of NIST (Smith and Martell, 2004).

As $LaSuc^+$ and $LaMal^+$ are identical in charge, $\Delta\varepsilon$ (Eq. (20)) of -0.62 ± 0.10 determined above for the complex of La with malonate can be used as an analog to $\Delta\varepsilon$ (Eq. (32)) for the complex of La with succinate. When the SIT model is applied for extrapolation of the values of Choppin et al. (1986) to infinite dilution, $\log \beta_1$ is 4.34 ± 0.11. The value of 4.34 ± 0.11 is similar to the value of 3.96 (uncertainty not given) obtained by Peacock and James (1951) with the Davies equation for extrapolation of their experimental data to infinite dilution. Therefore, this study selects the value of 4.34 ± 0.11 as the $\log \beta_1$ of $LaSuc^+$ (Table 1).

In addition, Ke et al. (1968) determined stability constants of La with bisuccinate. Formation reactions regarding La with bisuccinate can be expressed as:

$$La^{3+} + HSuc^- = LaHSuc^{2+} \quad (35)$$

$$La^{3+} + 2HSuc^- = La(HSuc)^+_2 \quad (36)$$

The $\log \beta^I_{1,HSuc}$ and $\log \beta^I_{2,HSuc}$ in 0.15 M $NaClO_4$ at 25 °C were determined as 1.48 ± 0.08 and 2.63 ± 0.12, respectively. Based on the SIT model, the $\log \beta_{1,HSuc}$ regarding Reaction 35 should be:

$$\log \beta_{1,HSuc^-} = \log \beta^I_{1,HSuc^-} + 6D + \Delta\varepsilon\ (\text{Eq. (35)}) \times (I_m) \quad (37)$$

$\Delta\varepsilon$(Eq. (35)) is given by the following equation:

$$\Delta\varepsilon\ (\text{Eq. (35)}) = \varepsilon(LaHSuc^{2+}, ClO^-_4) - \varepsilon(La^{3+}, ClO^-_4) - \varepsilon(Na^+, HSuc^-) \quad (38)$$

Using $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$ derived in this study, as an analog to $\varepsilon(Na^+, HSuc^-)$, $\varepsilon(LaAc^{2+}, ClO^-_4) = 0.31 \pm 0.05$ as an analog

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to $\varepsilon(LaHSuc^{2+}, ClO_4^-)$, and $\varepsilon(La^{3+}, ClO_4^-) = 0.47 \pm 0.03$ as mentioned before, $\log \beta_{1,HSuc^-}$ is calculated as 2.21 ± 0.10 (Table 1).

Similarly, based on the SIT model, the $\log \beta_{2,HSuc^-}$ regarding Reaction 36 should be:

$$\log \beta_{2,HSuc^-} = \log \beta^I_{2,HSuc^-} + 10D + \Delta\varepsilon\ (\text{Eq. (36)})(I_m) \quad (39)$$

$\Delta\varepsilon$(Eq. (36)) is given by the following equation:

$$\Delta\varepsilon\ (\text{Eq. (36)}) = \varepsilon(La(HSuc)_2^+, ClO_4^-) - \varepsilon(La^{3+}, ClO_4^-) - 2\varepsilon(Na^+, HSuc^-) \quad (40)$$

Using $\varepsilon(Na^+, HMal^-) = -0.04 \pm 0.03$ as an analog to $\varepsilon(Na^+, HSuc^-)$, $\varepsilon(EuMal^+, ClO_4^-) = -0.12 \pm 0.11$ as an analog to $\varepsilon(La(HSuc)_2^+, ClO_4^-)$, and $\varepsilon(La^{3+}, ClO_4^-) = 0.47 \pm 0.03$ as mentioned before, $\log \beta_{2,HSuc^-}$ is calculated as 3.80 ± 0.17 (Table 1).

Byrne and Li (1995) developed the linear free energy relationships regarding formation constants of rare earth elements with organic ligands at 0.1 M ionic strength, based on literature data. The linear free energy relationships developed by them can be expressed as:

$$\log \beta^I_1(M_i) = I_{ij} + S_{ij} \times \log \beta^I_1(M_j) \quad (41)$$

where $\log \beta^I_1(M_i)$ is the formation constant of rare earth element, i, with an organic ligand at ionic strength of 0.1 M; $\beta^I_1(M_j)$ is the formation constant of the reference rare earth element, j, with the same organic ligand at ionic strength of 0.1 M; I_{ij} the intercepts of the regressions; S_{ij} the slopes of the regressions. Although those intercepts and slopes are obtained for formation constants at 0.1 M ionic strength, it is of interest to test if they are applicable to the formation constants at infinite dilution obtained in this study.

According to their regressions, when the formation constant of La is taken as a reference, the intercept and slope for the formation constant of Nd in Eq. (41) are 0.1401 and 1.0756, respectively. By using the above intercept and slope, and $\log \beta_1$ of 2.54 for $LaAc^{2+}$ at infinite dilution (Table 1) as the reference, the predicted $\log \beta_1$ for $NdAc^{2+}$ is 2.87 (Table 2), which compares well with the value of 2.86 ± 0.06 listed in Table 1.

Similarly, the intercept and slope for the expression of the formation constant of La as a reference and that of Eu as a predicted are 0.2218 and 1.1152, respectively. By using $\log \beta_1$ of 4.79 for $LaMal^+$ at infinite dilution (Table 1) as a reference, the predicted $\log \beta_1$ for $EuMal^+$ at infinite dilution is 5.56 (Table 2), which compares favorably with the value of 5.49 ± 0.11 listed in Table 1. These favorable comparisons suggest that the intercepts and slopes obtained by Byrne and Li (1995) for 0.1 M ionic strength could be applied to formation constants at infinite dilution. Therefore, by using the formation constants at infinite dilution obtained in this study as references, the formation constants of other rare earth elements are also predicted in this study (Table 2).

3. Solubility constants of rare earth elements oxalates

As oxalates of REE have low solubilities, they could be solubility-controlling phases for REE in low temperature environments. In this study, solubility constants of REE oxalates are evaluated from solubility experiments in HCl and H_2SO_4 media (Sarver and Brinton, 1927). The solubility constant of lanthanide oxalate is expressed as:

$$Ln_2Ox_3(s) + 6H^+ = 2Ln^{3+} + 3H_2Ox \quad (42)$$

Based on the SIT model, solubility constants at infinite dilution are expressed as:

$$\text{Log}K = \log Q - 12D + \Delta\varepsilon(I_m) \quad (43)$$

In HCl medium, $\Delta\varepsilon$ (Eq. (42)) has the following form:

Table 2
Predicted formation constants of rare earth elements from Ce to Lu with organic ligands at infinite dilution, 25 °C, and 1 bar.

Metal ion	Ligands						
	[A]Ac^-	[B]Cit^{3-}	[C]Mal^{2-}	[D]$HMal^-$	[E]Ox^{2-}	[F]Suc^{2-}	[G]$HSuc^-$
Ce^{3+}	2.71	9.50	5.04	2.65	6.29	4.57	2.37
Pr^{3+}	2.81	9.76	5.19	2.75	6.47	4.72	2.47
Nd^{3+}	2.87	9.94	5.29	2.81	6.59	4.81	2.52
Sm^{3+}	3.01	10.28	5.50	2.94	6.84	5.00	2.65
Eu^{3+}	3.05	10.38	5.56	2.99	6.91	5.06	2.69
Gd^{3+}	3.00	10.36	5.52	2.94	6.88	5.02	2.63
Tb^{3+}	3.03	10.56	5.61	2.96	7.00	5.09	2.65
Dy^{3+}	3.04	10.69	5.66	2.97	7.07	5.13	2.65
Ho^{3+}	3.04	10.76	5.68	2.97	7.11	5.16	2.65
Er^{3+}	3.06	10.86	5.73	2.99	7.17	5.20	2.67
Tm^{3+}	3.08	10.99	5.79	3.01	7.25	5.25	2.68
Yb^{3+}	3.13	11.11	5.87	3.06	7.34	5.32	2.73
Lu^{3+}	3.13	11.17	5.88	3.05	7.36	5.33	2.72

[A] An uncertainty of ±0.16 is applied to all predicted $\log \beta_1$ with Ac^-.
[B] An uncertainty of ±0.24 is applied to all predicted $\log \beta_1$ with Cit^{3-}.
[C] An uncertainty of ±0.11 is applied to all predicted $\log \beta_1$ with Mal^{2-}.
[D] An uncertainty of ±0.30 is applied to all predicted $\log \beta_1$ with $HMal^-$.
[E] An uncertainty of ±0.40 is applied to all predicted $\log \beta_1$ with Ox^{2-}.
[F] An uncertainty of ±0.11 is applied to all predicted $\log \beta_1$ with Suc^{2-}.
[G] An uncertainty of ±0.10 is applied to all predicted $\log \beta_1$ with $HSuc^-$.

$$\Delta\varepsilon\ (\text{Eq. (42)}) = 2 \times \varepsilon(Ln^{3+}, Cl^-) - 6 \times \varepsilon(H^+, Cl^-) \quad (44)$$

In H_2SO_4 medium, $\Delta\varepsilon$ (Eq. (42)) has the following form:

$$\Delta\varepsilon\ (\text{Eq. (42)}) = 2 \times \varepsilon(Ln^{3+}, HSO_4^-) - 6 \times \varepsilon(H^+, HSO_4^-) \quad (45)$$

The evaluated solubility constants at infinite dilution are listed in Table 3. In combination with dissociation constants of H_2Ox at infinite dilution evaluated by using the SIT model (Xiong, 2009),

$$H_2Ox = 2H^+ + Ox^{2-} \quad (46)$$

The solubility product constants (K_{sp}),

$$Ln_2Ox_3(s) = 2Ln^{3+} + 3Ox^{2-} \quad (47)$$

can be derived (Table 4). In addition, a series of interaction coefficients are also derived (Table 5). In derivation of $\varepsilon(Ln^{3+}, HSO_4^-)$, $\varepsilon(H^+, HSO_4^-)$ is calculated from the Pitzer parameter $\beta^{(0)} = 0.2065$ for the interaction between H^+ and HSO_4^- according to the estimation method of Plyasunov et al. (1998). The $\beta^{(0)}$ is from Harvie et al. (1984).

Chung et al. (1998) performed a solubility study of rare earth oxalates in oxalic and nitric acid media in two sets of experiments. One set of experiments is at a constant concentration of HNO_3 of 0.5 M with various concentrations of oxalic acid ranging from 0.035 M to 0.485 M (total ionic strength up to 1.955 M). In the other set of experiments, solubilities of rare earth oxalates were measured in solutions at a constant concentration of oxalic acid of 0.31 M with varying concentrations of NHO_3 ranging from

Table 3
Solubility constants of oxalates of La and other rare earths at infinite dilution, 25 °C and 1 bar evaluated in this study.[a]

Species	$\log K$ (±2σ) evaluated from HCl medium	$\log K$ (±2σ) evaluated from H_2SO_4 medium	Weighted average $\log K$ and associated uncertainty (±2σ)
$La_2(C_2O_4)_3$	−13.06 ± 0.28	−13.66 ± 0.52	−13.19 ± 0.35
$Ce_2(C_2O_4)_3$	−14.10 ± 0.28	−14.78 ± 0.60	−14.22 ± 0.36
$Pr_2(C_2O_4)_3$	−14.81 ± 0.34	−15.39 ± 0.60	−14.95 ± 0.42
$Nd_2(C_2O_4)_3$	−15.17 ± 0.90	−15.75 ± 0.50	−15.61 ± 0.62
$Sm_2(C_2O_4)_3$	−15.54 ± 0.70	−15.72 ± 0.70	−15.63 ± 0.70
$Gd_2(C_2O_4)_3$	−16.54 ± 0.44	−16.00 ± 0.60	−16.35 ± 0.50

[a] Evaluated from solubility data of Sarver and Brinton (1927).

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Table 4
Solubility product constants of oxalates of La and other rare earth at infinite dilution, 25 °C and 1 bar evaluated in this study [a]

Species	$\log K_{sp}$ ($\pm 2\sigma$) evaluated from HCl medium	$\log K_{sp}$ ($\pm 2\sigma$) evaluated from H_2SO_4 medium	Weighted average $\log K_{sp}$ ($\pm 2\sigma$)
$La_2(C_2O_4)_3$	−29.02 ± 0.28	−29.62 ± 0.52	−29.15 ± 0.35
$Ce_2(C_2O_4)_3$	−30.06 ± 0.28	−30.74 ± 0.60	−30.18 ± 0.36
$Pr_2(C_2O_4)_3$	−30.77 ± 0.34	−31.35 ± 0.60	−30.91 ± 0.42
$Nd_2(C_2O_4)_3$	−31.13 ± 0.90	−31.71 ± 0.50	−31.57 ± 0.62
$Sm_2(C_2O_4)_3$	−31.50 ± 0.70	−31.68 ± 0.70	−31.59 ± 0.70
$Gd_2(C_2O_4)_3$	−31.96 ± 0.44	−32.50 ± 0.60	−32.31 ± 0.50

[a] Solubility product constants are calculated by using solubility constants listed in Table 3 in combination with dissociation constants of oxalic acid at infinite dilution from Xiong (2009).

Table 5
Specific interaction coefficients of REE with HSO_4^- evaluated in this study.[a]

SIT coefficient	Value ($\pm 2\sigma$)
$\varepsilon(La^{3+}, HSO_4^-)$	0.56 ± 0.11
$\varepsilon(Ce^{3+}, HSO_4^-)$	0.51 ± 0.12
$\varepsilon(Pr^{3+}, HSO_4^-)$	0.52 ± 0.12
$\varepsilon(Nd^{3+}, HSO_4^-)$	0.54 ± 0.13
$\varepsilon(Sm^{3+}, HSO_4^-)$	0.56 ± 0.19
$\varepsilon(Gd^{3+}, HSO_4^-)$	0.54 ± 0.12

[a] Evaluated from solubility data of Sarver and Brinton (1927).

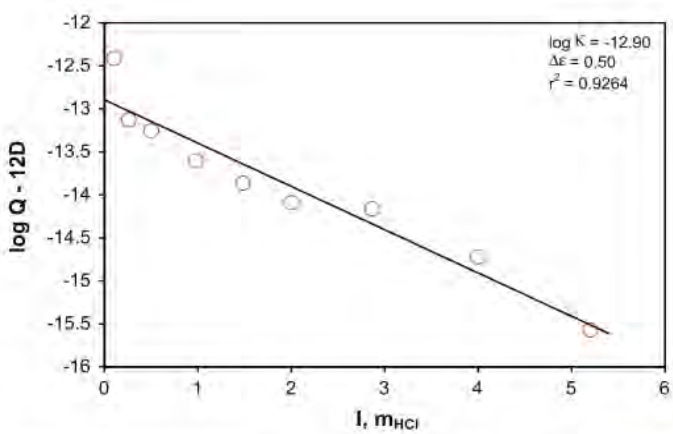

Fig. 8. A plot showing solubility constants of La oxalate (defined in Eq. (42)) as a function of ionic strength in HCl medium. Experimental data are from Sarver and Brinton (1927).

0.25 M to 2.0 M (total ionic strength up to 2.93 M). They used the Bromley model to extrapolate their experimental to infinite dilution. They obtained solubility product constants of La-, Ce-, Nd-, Sm-, and Gd-oxalates as −29.22, −30.40, −30.89, −31.35, and −31.37, respectively. These values are close to the values recommended in this study (Table 4), and the values recommended in this study are considered more reliable, as they are evaluated from a wider range of ionic strengths up to ~8 m (see Figs. 8 and 9).

In addition, Panyushkin et al. (2003) measured the standard enthalpies of formation of hydrated and anhydrous La, Sm and Ho succinates. The same research group also measured the standard enthalpies of formation of anhydrous Nd and Eu(III) succinates and malates (Shabanova et al., 2005). However, the differences between the standard enthalpies of formation of hydrated and anhydrous succinates for the same rare earth element are substantially smaller than theoretically expected. For instance,

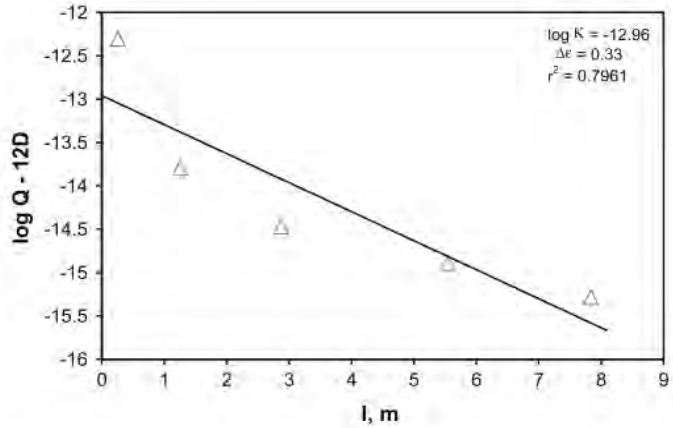

Fig. 9. A plot showing solubility constants of La oxalate (defined in Eq. (42)) as a function of ionic strength in H_2SO_4 medium. Experimental data are from Sarver and Brinton (1927).

La_2Suc_3 has a $\Delta_f H$ of −3984.7 ± 2.3 kJ mol^{-1}, while $La_2Suc_3 \bullet 5.70H_2O$ has a $\Delta_f H$ of −4089.5 ± 2.2 kJ mol^{-1}, resulting in a difference of only 104.8 kJ mol^{-1}. As is known, liquid water has a $\Delta_f H$ of −285.830 kJ mol^{-1}. Therefore, their data are not evaluated in this study. Their data will be evaluated when more data become available.

4. Summary

In this study, formation constants of La with the naturally occurring organic ligands, acetate, citrate, malonate, oxalate and succinate, are evaluated with the SIT model. As oxalates of rare earth elements have low solubilities and they are potentially the solubility-controlling phases for REE in the low temperature environments such as soil solutions, the solubility product constants of REE oxalates are also evaluated from solubilities of REE oxalates in HCl and H_2SO_4 media. The solubility product constants evaluated from both media agree with each other. In addition, a number of SIT interaction coefficients are obtained in this study. With these data, it would be possible to model the influence of naturally occurring organic ligands on the mobility of REE in various environments including those related to solutions with high ionic strength.

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