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## Effects of temperature and ionic strength on the stabilities of the first and second fluoride complexes of yttrium and the rare earth elements

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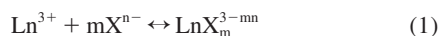
**Abstract**—The stability constants for the formation of yttrium and rare earth elements (YREEs) with fluoride



have been determined by an ion exchange method in dilute solutions as a function of temperature (5 to 45°C). The concentrations of the YREEs were measured using ICP- mass spectrometry. The values of  $\log \beta_1$  and  $\log \beta_2$  at 25.0°C are in good agreement with the work of Schijf and Byrne (1999). The effect of temperature on the stability constants has been used to determine the enthalpies of formation of  $\text{LnF}^{2+}$  and  $\text{LnF}_2^+$ . Average values of  $\Delta H_1 = +9.6 \pm 0.4$  kJ/mol and  $\Delta H_2 = +20.7 \pm 1.1$  kJ/mol were found for the enthalpies. Our results are in reasonable agreement with literature values of  $\Delta H_1$  (Paul et al., 1961; Baisden et al., 1987; Grant et al., 1988). The measurements from Luo and Byrne (2000, 2001) for the formation of  $\text{LnF}^{2+}$  as a function of ionic strength in NaCl and  $\text{NaClO}_4$  have been fitted to the Pitzer equations. These results have been used to examine the effect of ionic strength on the activity coefficients of the  $\text{LnF}^{2+}$  ions in NaCl and  $\text{NaClO}_4$  solutions. At low ionic strengths the activity coefficients of  $\text{LnF}^{2+}$  for the YREEs are independent of atomic number. Since the values of  $\Delta H_1$  do not appear to be a strong function of ionic strength, these results can be used to estimate the stability constants for the formation of  $\text{LnF}^{2+}$  complexes from 0 to 50°C and  $I = 0$  to 6 *m*. Copyright © 2004 Elsevier Ltd

### 1. INTRODUCTION

The interest in yttrium and rare earth elements (YREEs) results from their unique physical chemical characteristics. The entire group exists exclusively as trivalent ions in natural waters, and their ionic radius decreases by less than 20% across the fifteen member series. Their extremely coherent chemical properties and their similarity with actinides make them particularly useful as models to study the geochemistry and speciation of trivalent actinides in natural waters, which are radioactive and exist mainly in nuclear wastes (Menard et al., 1998). The speciation of YREEs in natural waters (Byrne and Sholkovitz, 1996) is mainly controlled by their chemical complexation with organic and inorganic ligands. The speciation can be modeled by using ionic interaction models that require reliable complexation stability constants as a function of temperature and ionic strength. The formation of complexes of YREEs ( $\text{Ln}^{3+}$ ) with various inorganic ligands (X) can be expressed as



Recent studies have shown that carbonate (Luo and Byrne, 2004), hydroxide (Klungness and Byrne, 2000), sulfate (Schijf and Byrne, 2004), fluoride (Lee and Byrne, 1993; Schijf and Byrne, 1999; Luo and Byrne, 2000), chloride (Luo and Byrne, 2001) and oxalate (Schijf and Byrne, 2001) can form complexes with the YREEs in natural waters. Wood (1990) reviewed the thermodynamic stability constants as a function of

ionic strength for YREEs' inorganic complexes and extrapolated the stability constant values to zero ionic strength. By using the Pitzer interaction model, Millero (1992) extrapolated the stability constants to infinite dilution and estimated the activity coefficients of the ion pairs  $\gamma(\text{LnX}_m^{3-mn})$  for the formation of REE complexes at 25°C with  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{CO}_3^{2-}$ . New studies (Klungness and Byrne, 2000; Luo and Byrne, 2000, 2001) on stability constants as a function of ionic strength provide more data and it is now possible to make more reliable estimates on the activity coefficients of ion pairs and the infinite dilution thermodynamic stability constants of YREEs.

The purpose of the present work was to examine the effect of temperature on the stability constants for the formation of YREEs complexes with fluoride and the effect of concentration on the complexes in  $\text{NaClO}_4$  and NaCl using the Pitzer equations. The recent works of Luo and Byrne (2000; 2001) provide reliable stability constants as a function of ionic strength that can be examined using the Pitzer equations as was done in earlier studies (Millero, 1992). By combining our new measurements with the work of Luo and Byrne (2000; 2001), we provide Pitzer parameters that can be used to calculate activity coefficients and stability constants for the formation of yttrium and rare earths fluoride complexes from 0 to 50°C and ionic strength from 0 to 6 *m*.

### 2. EXPERIMENTAL

Various experimental methods (Luo and Byrne, 2000) have been developed to examine the complexation of yttrium and rare earths with fluoride. The ion-exchange equilibration technique (Schijf and Byrne, 1999), which is based on an equilibration of YREE between the target

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ligand and cation resin, is used to determine the element speciation due to its accuracy and sensitivity. In this paper, the formation constants of YREEs fluoride complexes have been determined using batch equilibration with a cation exchange resin (Schijf and Byrne, 1999).

## 2.1. Reagents and Materials

All the chemicals were trace-metal or omnitrace-metal grade. The vessels used were made of Teflon and were acid-cleaned before use. The cation-exchange resin (Bio-Rad AG 50W-X2; hydrogen form) was cleaned (Schijf and Byrne, 1999) three times with 1M (molar, mol/L) HCl and Milli-Q water (18M $\Omega$ •cm) respectively. The extra resin was stored in acidified water and then thoroughly rinsed before use.

## 2.2. Working Vessel

Measurements were made in a 1L Teflon bottle which was set in a glass container that could be used to control the temperature of the bottle. Three holes on the cover of the bottle were made for 1) a Teflon stirrer; 2) a combination electrode (915600 ORION); and 3) titrating and taking out samples. The combination electrode was used to monitor the pH of the solution. The temperature was controlled with a Neslab water bath, which was monitored with a Guildline 9540 Platinum resistance thermometer. The measurements were made in dilute OmniTrace grade HNO<sub>3</sub> (15.78 N, EMD Chemicals Inc.) at five different temperatures: 5.2°C, 15.1°C, 25.0°C, 34.7°C and 44.5°C. The uncertainty in the temperatures is  $\pm 0.1^\circ\text{C}$ .

## 2.3. Titration and Total YREEs Analysis

For each experiment, 1.5 mL HNO<sub>3</sub> and 2.5 mL of mixed standard solution with 100 ppm YREEs (SCP Science, NY) were added to the Teflon bottle. The total volume was adjusted to 1 L with Milli-Q water. The final concentration of YREEs was 250 ppb. The final YREE concentrations ranged from 2.8  $\mu\text{M}$  for Y to 1.3  $\mu\text{M}$  for Lu. The ionic strength (I) of the solution was  $0.025 \pm 0.001$  mol/L. By gentle stirring,  $0.60 \pm 0.01$  g of resin (wet weight) was suspended to avoid grinding.

Sorption of the resin is strongly dependent on the pH and ionic strength of the solution, so fluoride ions were added as hydrofluoric acid (HF) which is weakly dissociated at low pH (Schijf and Byrne, 1999). Fluoride complexation measurements were carried out by titrating the initial solutions with HF (23.20 N, Alfa, Trace-metal grade). At 25.0°C, 34.7°C and 44.5°C, additions of 0, 200, 400, 600, 800, 1000, 1200 and 1400  $\mu\text{L}$  were made, and slightly different additions of 0, 150, 300, 450, 600, 750, 900, 1050 and 1200  $\mu\text{L}$  were made for 5.2°C and 15.1°C. Equilibrium was assumed when the potential of the glass electrode remained within  $\pm 0.1$  mV for 24 h. The EMF of the electrode system was related to the pH of the solution by

$$E = E^* + (RT/2.303 F)pH \quad (2)$$

where  $E^*$  is the apparent standard potential. The values of  $E^*$  were determined by titrating the ionic media with HCl.

After initial equilibrium (without HF), the YREEs' concentrations decreased from 250 ppb to  $\sim 1$  ppb, so more than 99.5% of each element was adsorbed onto the resin. During the entire experiment (with HF), this fraction never fell below 95%. To keep the activity coefficient of metals on the resin constant, it is essential to keep metal loading on the resin at maximum and its change on the resin at minimum. Because of the low solubility of rare earth fluorides, precipitation was avoided by keeping  $[\text{Ln}^{3+}][\text{F}^-]^3 < K_{\text{sp}}(\text{LnF}_3)$ . In this experiment, LaF<sub>3</sub> precipitation occurred only for  $[\text{F}^-]$  concentrations greater than  $1.3 \times 10^{-3}$  M (Schijf and Byrne, 1999). When equilibrium was reached, a 15 mL aliquot was transferred to a 30 mL Teflon bottle for analysis. The solution was re-equilibrated at a different temperature for 24 h, which was sufficient to re-establish a new equilibrium.

The YREEs were analyzed by using ICP-MS (HP 4500). Instrument drift was monitored by using In, Cs and Re as internal standards (Schijf and Byrne, 1999). YREEs concentrations were calibrated using five standard solutions of 2, 4, 6, 10 and 15 ppb. The RSD % was better than 2% for all elements. The detection limit was 0.001 ppb.

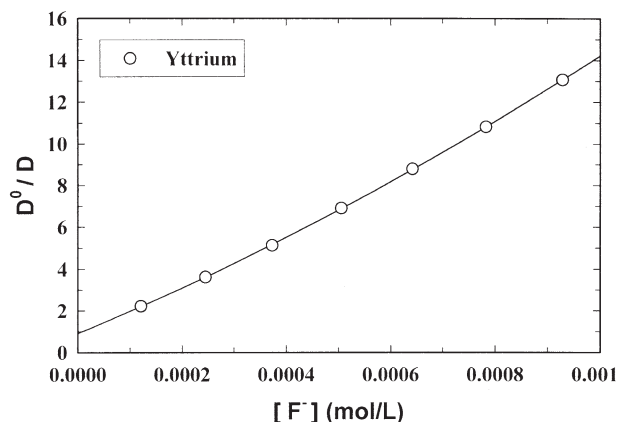


Fig. 1.  $D^0/D$  as a function of  $[\text{F}^-]$  in the solution at  $I = 0.025$  mol/L and  $44.5^\circ\text{C}$ . Measurement for yttrium was shown as an example.

## 2.4. Determination of the Stability Constants

After each HF addition,  $\text{F}^-$  complexes with free YREE ions in the solution and the concentration of free YREEs decreases. Resin responds by releasing YREEs into the solution to re-establish equilibrium. The concentration of the YREEs in the solution can be used to determine the cumulative stability constants for the formation of YREEs complexes with fluoride

$${}_F\beta_1 = [\text{LnF}^{2+}]/[\text{Ln}^{3+}][\text{F}^-] \quad (3)$$

$${}_F\beta_2 = [\text{LnF}_2^+]/[\text{Ln}^{3+}][\text{F}^-]^2 \quad (4)$$

$${}_F\beta_n = [\text{LnF}^{3-n}]/[\text{Ln}^{3+}][\text{F}^-]^n \quad (5)$$

It is assumed that the resin does not adsorb the complex species (Gomes et al., 1997). The metal ions adsorbed by the resin are in equilibrium with the metal ions in the solution. This gives

$$[\text{Ln}]_T = [\text{Ln}]_{\text{resin}} + [\text{Ln}]_{\text{solution}} \quad (6)$$

In the absence of the fluoride ligand, we have:

$$[\text{Ln}]_{\text{solution}} = [\text{Ln}^{3+}] \quad (7)$$

In the presence of fluoride, we have:

$$[\text{Ln}]_{\text{solution}} = [\text{Ln}^{3+}] + [\text{LnF}^{2+}] + [\text{LnF}_2^+] + \dots + [\text{LnF}_n^{3-n}] \\ = [\text{Ln}^{3+}](1 + {}_F\beta_1[\text{F}^-] + {}_F\beta_2[\text{F}^-]^2 + \dots + {}_F\beta_n[\text{F}^-]^n) \quad (8)$$

Distribution coefficients  $D^0$  and  $D$  in the absence and presence of  $\text{F}^-$  were defined as

$$D^0 = [\text{Ln}]_{\text{resin}}/[\text{Ln}^{3+}] \quad \text{and} \quad D = [\text{Ln}]_{\text{resin}}/[\text{Ln}]_{\text{solution}} \quad (9)$$

Combining Eqn. (8) and (9), we have

$$D^0/D = 1 + {}_F\beta_1[\text{F}^-] + {}_F\beta_2[\text{F}^-]^2 + \dots + {}_F\beta_n[\text{F}^-]^n \quad (10)$$

The free fluoride concentration  $[\text{F}^-]$  was calculated by

$$[\text{F}^-] = [\text{F}^-]_T / (1 + K_{\text{HF}}^*[\text{H}^+]) \quad (11)$$

where  $[\text{F}^-]_T$  is the total fluoride in the solution.

The values of  $K_{\text{HF}}^*$  at  $I = 0.025$  mol/L as a function of temperature were estimated from Pitzer equations developed by Millero and Roy (1997). The values of  $[\text{H}^+]$  were determined from the electrode measurements. A nonlinear least-squares method (Cantrell and Byrne, 1987; Schijf and Byrne, 1999) was used to determine the YREEs-fluoride stability constants. A typical run at  $44.5^\circ\text{C}$  for Y is shown in Figure 1. A second degree function is sufficient to fit the data yielding values of  ${}_F\beta_1$ ,  ${}_F\beta_2$  and the standard error of the fits.

## 3. RESULTS AND DISCUSSION

## 3.1. Effect of Temperature on YREEs-F Stability Constants

The stability constants for the formation of YREEs fluoride complexes were determined for 5.2°C, 15.1°C, 25.0°C, 34.7°C and 44.5°C from the equilibrium measurements described above. The cumulative stability constants for  $\text{LnF}_2^{2+}$ ,  $\text{LnF}_2^+$  and the ratios  $K_2/K_1 = \beta_2/\beta_1^2$  are given in Table 1 along with the standard errors. The ratios of  $K_2/K_1$  appear to be independent of temperature. Our results at 25.0°C are compared to the results of Schijf and Byrne (1999) in Figure 2. Our results are in good agreement with this earlier study, except for  $\log {}_F\beta_2$  and  $K_2/K_1$  for cerium. The abnormal behavior of  $K_2/K_1$  for cerium fluoride complexes found by Schijf and Byrne (1999) ( $0.07 \pm 0.03$  excluding Ce) was similar to that found in their oxalate paper (Schijf and Byrne, 2001). They attributed this behavior to the cerium fluoride complex being weaker than the other YREEs, and this causes values of  ${}_F\beta_2$  to be less constrained yielding a larger error. Since the errors in  ${}_F\beta_1$  and  ${}_F\beta_2$  are very strongly correlated, the ratio  $K_2/K_1$  is even more poorly confined. This might also be the cause of the differences for some heavy REEs (from Ho to Lu) (see Fig. 2). By making smaller and more HF additions in a given  $[\text{F}^-]$  range in our experiment, the values of  ${}_F\beta_2(\text{CeF}_2^+)$  appear to be more constrained and the abnormal phenomenon for  $K_2/K_1$  did not occur. Our average value of  $K_2/K_1$  ( $0.06 \pm 0.03$ ) is in good agreement with the values determined by Schijf and Byrne (1999) ( $0.07 \pm 0.03$  excluding Ce) and Lee and Byrne (1993) ( $0.09 \pm 0.03$ ).

The values of  $\log {}_F\beta_1$  and  $\log {}_F\beta_2$  at 5.2°C, 15.1°C, 25.0°C, 34.7°C and 44.5°C are shown as a function of atomic number in Figures 3 and 4. The patterns at each different temperature are very similar. There is a very distinct sequence of peaks and valleys ('tetrad effect') both for  ${}_F\beta_1$  and  ${}_F\beta_2$ . The values of  $\log {}_F\beta_1$  and  $\log {}_F\beta_2$  increase from La to Dy with small minima at Nd and Gd. It then shows a valley from Ho to Yb with a minimum at Er, and decreases from Yb to Lu. The pattern of  $\log {}_F\beta_1$  reproduced exactly the pattern observed by Schijf and Byrne (1999) (see Fig. 2).

The values of  $\log {}_F\beta_1$  and  $\log {}_F\beta_2$  increase with increasing temperature. A temperature increase from 5.2°C and 44.5°C increases  $\log {}_F\beta_1$  by  $\sim 0.22$  and  $\log {}_F\beta_2$  by  $\sim 0.47$  for the entire group. The effect of temperature on the values of  $\log {}_F\beta_1$  and  $\log {}_F\beta_2$  can be used to determine the enthalpies for the formation of  $\text{LnF}_2^{2+}$  and  $\text{LnF}_2^+$  using the van't Hoff equation

$$d\ln\beta_i/dT = \Delta H_i/R T^2 \quad (12)$$

Integrating (12),

$$\log \beta_i = A_i - C_i/T \quad (13)$$

where  $A_i$  and  $C_i$  are constants and  $\Delta H_i$  is related to  $C_i$  by

$$\Delta H_i = -R(2.303 C_i) \quad (14)$$

The values of  $\log {}_F\beta_1$  and  $\log {}_F\beta_2$  for Y, Ce and Ho as a function of  $1/T$  (K) are shown in Figure 5. The resulting enthalpies for all the metals are summarized in Table 2 and shown as a function of the atomic number in Figure 6. The

Table 1. The stability constant for the formation of  $\text{LnF}_2^{2+}$  and  $\text{LnF}_2^+$  ion complex at  $I = 0.025$  (mol/L) and different temperatures.  $K_2/K_1 = \beta_2/(\beta_1)^2$ .

REE	5.2°C			15.1°C			25.0°C			34.7°C			44.5°C		
	$\log {}_F\beta_1$	$\log {}_F\beta_2$	$K_2/K_1$	$\log {}_F\beta_1$	$\log {}_F\beta_2$	$K_2/K_1$	$\log {}_F\beta_1$	$\log {}_F\beta_2$	$K_2/K_1$	$\log {}_F\beta_1$	$\log {}_F\beta_2$	$K_2/K_1$	$\log {}_F\beta_1$	$\log {}_F\beta_2$	$K_2/K_1$
Y	3.84 ± 0.01	6.08 ± 0.02	0.03	6.22 ± 0.03	6.22 ± 0.03	0.03	3.97 ± 0.01	6.35 ± 0.03	0.03	4.02 ± 0.01	6.45 ± 0.03	0.03	4.06 ± 0.01	6.56 ± 0.04	0.03
La	2.98 ± 0.02	4.89 ± 0.03	0.08	4.98 ± 0.10	4.98 ± 0.10	0.08	3.11 ± 0.01	5.16 ± 0.13	0.09	3.18 ± 0.01	5.21 ± 0.03	0.07	3.21 ± 0.01	5.39 ± 0.10	0.09
Ce	3.15 ± 0.01	5.15 ± 0.09	0.07	5.33 ± 0.20	5.33 ± 0.20	0.08	3.29 ± 0.01	5.48 ± 0.03	0.08	3.34 ± 0.02	5.60 ± 0.18	0.08	3.40 ± 0.01	5.70 ± 0.12	0.08
Pr	3.23 ± 0.01	5.40 ± 0.01	0.09	5.49 ± 0.04	5.49 ± 0.04	0.09	3.35 ± 0.01	5.66 ± 0.05	0.09	3.43 ± 0.01	5.73 ± 0.15	0.07	3.47 ± 0.01	5.85 ± 0.05	0.08
Nd	3.17 ± 0.01	5.40 ± 0.02	0.12	5.53 ± 0.03	5.53 ± 0.03	0.12	3.29 ± 0.01	5.66 ± 0.05	0.12	3.35 ± 0.01	5.78 ± 0.04	0.12	3.38 ± 0.01	5.86 ± 0.04	0.13
Pm	3.53 ± 0.01	5.76 ± 0.02	0.05	5.90 ± 0.03	5.90 ± 0.03	0.06	3.61 ± 0.01	5.99 ± 0.04	0.06	3.67 ± 0.01	6.12 ± 0.03	0.06	3.71 ± 0.01	6.19 ± 0.04	0.06
Sm	3.63 ± 0.02	5.89 ± 0.08	0.04	6.00 ± 0.02	6.00 ± 0.02	0.05	3.72 ± 0.01	6.11 ± 0.04	0.05	3.78 ± 0.01	6.25 ± 0.03	0.05	3.81 ± 0.01	6.30 ± 0.02	0.05
Eu	3.61 ± 0.01	5.86 ± 0.02	0.04	5.97 ± 0.03	5.97 ± 0.03	0.04	3.71 ± 0.01	6.07 ± 0.02	0.05	3.75 ± 0.01	6.20 ± 0.02	0.05	3.78 ± 0.01	6.25 ± 0.02	0.05
Gd	3.73 ± 0.01	6.01 ± 0.02	0.03	6.10 ± 0.03	6.10 ± 0.03	0.03	3.83 ± 0.01	6.24 ± 0.04	0.04	3.86 ± 0.01	6.34 ± 0.02	0.04	3.90 ± 0.01	6.39 ± 0.02	0.04
Tb	3.76 ± 0.01	5.98 ± 0.02	0.03	6.11 ± 0.02	6.11 ± 0.02	0.03	3.88 ± 0.01	6.29 ± 0.03	0.03	3.93 ± 0.01	6.38 ± 0.02	0.03	3.97 ± 0.01	6.49 ± 0.03	0.03
Dy	3.66 ± 0.01	5.71 ± 0.02	0.02	5.82 ± 0.04	5.82 ± 0.04	0.03	3.78 ± 0.01	5.98 ± 0.04	0.03	3.84 ± 0.01	6.08 ± 0.03	0.03	3.88 ± 0.01	6.19 ± 0.03	0.03
Ho	3.64 ± 0.01	5.70 ± 0.02	0.03	5.75 ± 0.05	5.75 ± 0.05	0.02	3.77 ± 0.01	5.94 ± 0.04	0.03	3.81 ± 0.01	6.04 ± 0.03	0.03	3.87 ± 0.01	6.16 ± 0.05	0.03
Er	3.65 ± 0.01	5.83 ± 0.02	0.03	5.94 ± 0.03	5.94 ± 0.03	0.03	3.77 ± 0.01	6.09 ± 0.03	0.03	3.85 ± 0.01	6.20 ± 0.02	0.03	3.89 ± 0.01	6.30 ± 0.02	0.03
Tm	3.71 ± 0.01	6.03 ± 0.02	0.04	6.14 ± 0.03	6.14 ± 0.03	0.04	3.84 ± 0.01	6.31 ± 0.03	0.04	3.90 ± 0.01	6.43 ± 0.02	0.04	3.95 ± 0.01	6.56 ± 0.01	0.05
Yb	3.59 ± 0.01	5.99 ± 0.01	0.06	6.11 ± 0.02	6.11 ± 0.02	0.06	3.74 ± 0.01	6.31 ± 0.03	0.07	3.80 ± 0.01	6.42 ± 0.01	0.06	3.85 ± 0.01	6.55 ± 0.02	0.07

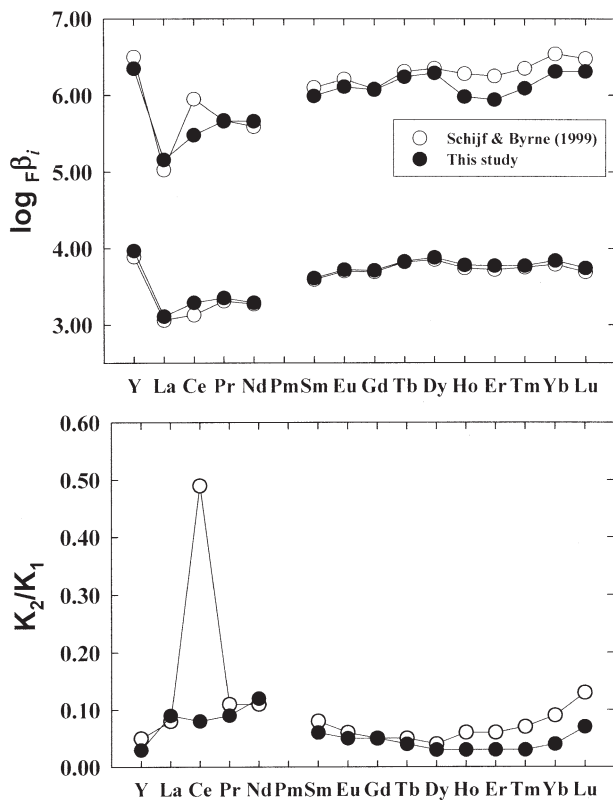


Fig. 2. A comparison of the stability constants and  $K_2/K_1$  for the formation of  $\text{LnF}^{2+}$  and  $\text{LnF}^+$  with the work of Schijf and Byrne, 1999 at 25°C and  $I = 0.025\text{M}$ . The average value of  $K_2/K_1$  in this study ( $0.06 \pm 0.03$ ) is in good agreement with the values determined by Schijf and Byrne (1999) ( $0.07 \pm 0.03$  excluding Ce).

values of  $\Delta H_1$  and  $\Delta H_2$  are reasonably constant for the YREEs ( $\Delta H_1 = +9.6 \pm 0.4$  kJ/mol and  $\Delta H_2 = +20.7 \pm 1.1$  kJ/mol). It is interesting to note that  $\Delta H_2 \approx 2 \Delta H_1$ . Since  $\log(K_2/K_1) = \log_{F}\beta_2 - 2 \log_{F}\beta_1$ , the temperature dependence of  $\log(K_2/K_1)$  is proportional to  $\Delta H_2 - 2 \Delta H_1 \approx 0$ . In other words as we found from the measurements,  $K_2/K_1$  does not depend on temperature.

The enthalpies for the formation of  $\text{LnF}^{2+}$  from this study

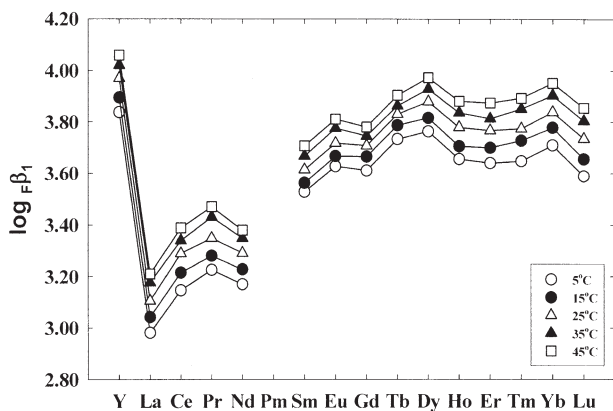


Fig. 3. Values of  $\log_{F}\beta_1$  for YREE at  $I = 0.025$  mol/L and different temperatures.

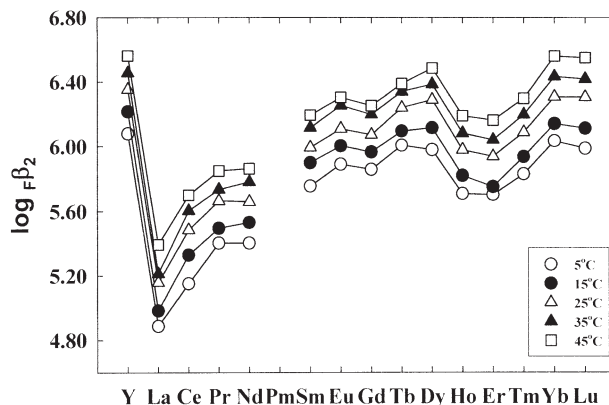


Fig. 4. Values of  $\log_{F}\beta_2$  for YREE at  $I = 0.025$  mol/L and different temperatures.

( $\Delta H_1 = +9.6$  kJ/mol) are in good agreement with the titration calorimetry values of Grant et al. (1988) in 1 mol/L  $\text{NaClO}_4$  except for Pr and Nd (see Fig. 7). The calorimetry results of Walker and Choppin (1967) (+16 to +40 kJ/mol) are much larger than our results and the results of Grant et al. (1988). The value of  $\Delta H_1$  for the formation of  $\text{YF}^{2+}$  from Paul et al. (1961) (+9.92 kJ/mol) in 0.5 mol/L  $\text{NaClO}_4$  and  $\text{EuF}^{2+}$  from Baisden et al. (1987) ( $+9.61 \pm 0.03$  kJ/mol) in 1.0 mol/L  $\text{NaClO}_4$  are in good agreement with our result at  $I = 0.025$  mol/L and the results of Grant et al. (1988) (see Fig. 7). The value of  $\Delta H_1$  for

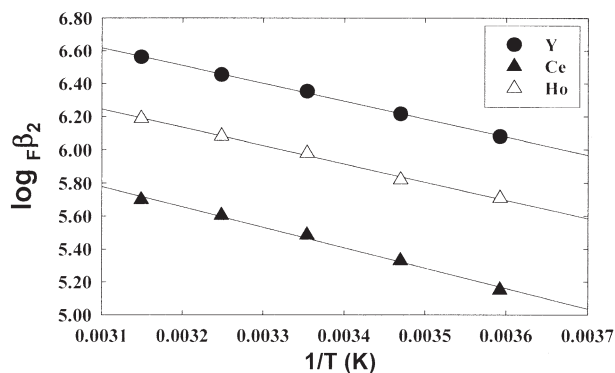
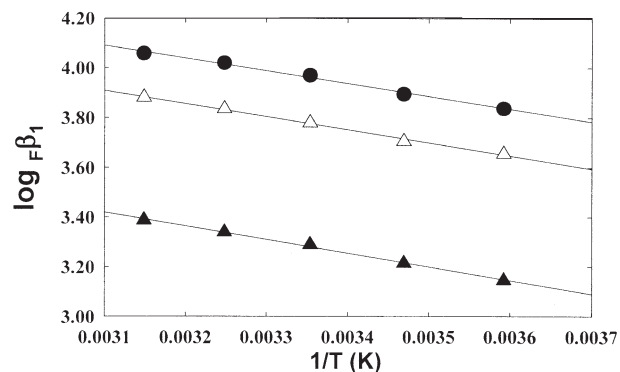


Fig. 5. Values of  $\log_{F}\beta_1$  and  $\log_{F}\beta_2$  for the formation of Y, Ce and Ho fluoride complexes as a function of temperature.

Table 2. Enthalpies for the  $\text{LnF}^{2+}$  and  $\text{LnF}_2^+$  ion complexes at 25°C.

REE	$\Delta H_1$ (kJ/mol)	$\Delta H_2$ (kJ/mol)
Y	+9.79 ± 0.46	+20.82 ± 0.37
La	+10.26 ± 0.47	+21.39 ± 1.93
Ce	+10.53 ± 0.35	+23.78 ± 1.10
Pr	+11.00 ± 0.62	+19.56 ± 1.25
Nd	+9.38 ± 0.44	+20.25 ± 0.55
Pm	-	-
Sm	+7.97 ± 0.41	+18.85 ± 0.70
Eu	+8.19 ± 0.42	+18.58 ± 1.15
Gd	+7.24 ± 0.20	+17.61 ± 0.90
Tb	+7.24 ± 0.23	+17.44 ± 1.29
Dy	+9.20 ± 0.22	+22.20 ± 1.06
Ho	+10.02 ± 0.39	+21.11 ± 0.74
Er	+10.04 ± 0.26	+20.79 ± 1.98
Tm	+10.61 ± 0.51	+20.57 ± 0.71
Yb	+10.57 ± 0.18	+23.14 ± 0.98
Lu	+11.74 ± 0.32	+24.53 ± 1.07
Mean	+9.6 ± 0.4	+20.7 ± 1.1

the formation of  $\text{YF}^{2+}$  by Aziz and Lyle (1969) (+5.04 kJ/mol) is much lower than all of these studies. From these comparisons, it appears that the values of  $\Delta H_1$  are not a strong function of ionic strength. To the best of our knowledge, no literature results are available for  $\Delta H_2$ .

### 3.2. Ionic Strength Dependence of YREEs Fluoride Complexation

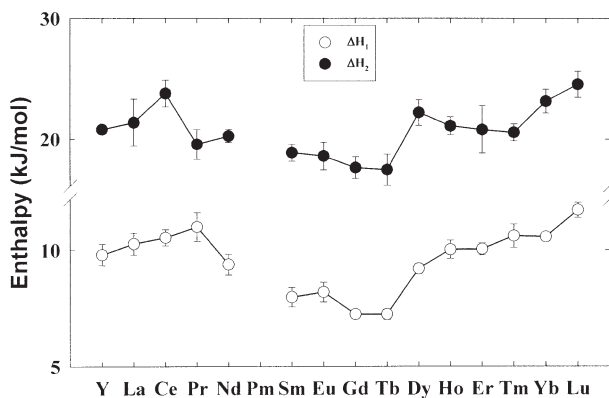
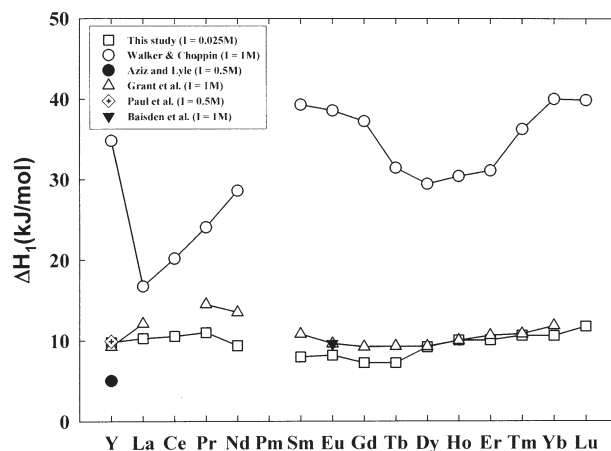
At low concentrations of YREE and fluoride, the trace activity coefficients in a  $\text{NaClO}_4$  solution can be estimated from the Pitzer equations as formulated by Millero and Pierrot (1998)

$$\ln \gamma_{\text{Ln}} = Z^2 f^\gamma + 2 m_{\text{ClO}_4} (B_{\text{LnClO}_4} + m_{\text{ClO}_4} C_{\text{LnClO}_4}) + Z^2 R + Z S \quad (15)$$

$$\ln \gamma_{\text{F}} = Z^2 f^\gamma + 2 m_{\text{Na}} (B_{\text{NaF}} + m_{\text{Na}} C_{\text{NaF}}) + Z^2 R + Z S \quad (16)$$

The Debye-Hückel term,  $f^\gamma$  is given by

$$f^\gamma = -A^\phi [I^{0.5}/(1 + 1.2 I^{0.5}) + (2/1.2) \ln(1 + 1.2 I^{0.5})] \quad (17)$$

Fig. 6. Values of the enthalpies for the formation of  $\text{LnF}^{2+}$  ( $\Delta H_1$ ) and  $\text{LnF}_2^+$  ( $\Delta H_2$ ) complexes with standard errors.Fig. 7. Comparisons of the enthalpies ( $\Delta H_1$ ) for the formation of  $\text{LnF}^{2+}$  complexes.

where  $A^\phi$  is given by Møller (1988)

$$A^\phi = 3.36901532 \times 10^{-1} - 6.32100430 \times 10^{-4} T + 9.14252359/T - 1.35143986 \times 10^{-2} \ln T + 2.26089488 \times 10^{-3}/(T - 263) + 1.92118597 \times 10^{-6} T^2 + 4.52586464 \times 10^{+1}/(680 - T) \quad (18)$$

The medium terms R and S in Eqns. (15)-(16) in  $\text{NaClO}_4$  are given by Pitzer (1991)

$$R = m_{\text{Na}} m_{\text{ClO}_4} B'_{\text{NaClO}_4} \quad (19)$$

$$S = m_{\text{Na}} m_{\text{ClO}_4} C_{\text{NaClO}_4} \quad (20)$$

The ionic strength (I) is equal to the molality of  $\text{NaClO}_4$  (m) in the solution. The second ( $B_{\text{MX}}$ ) and third ( $C_{\text{MX}}$ ) virial coefficients for 1-1, 2-1 and 3-1 electrolytes MX ( $M = \text{Na}$  or  $\text{Ln}$  and  $X = \text{F}$  or  $\text{ClO}_4$ ) are given by

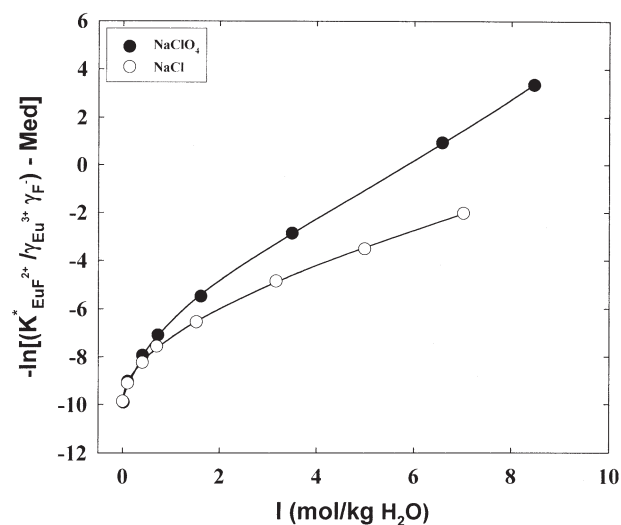
Fig. 8. Values of  $\{-\ln[(K_{\text{EuF}^{2+}}^*/\gamma_{\text{Eu}^{3+}}\gamma_{\text{F}^-})] - \text{Med}\}$  plotted as a function of  $\text{NaClO}_4$  and  $\text{NaCl}$  at 25°C. Curves are calculated from the Pitzer models.

Table 3. Pitzer coefficients ( $\beta^{(0)}$ ,  $\beta^{(1)}$  and C) for the formation of  $\text{LnF}^{2+}$  ion complexes in  $\text{NaClO}_4$  and  $\text{NaCl}$  at 25°C.<sup>a</sup>

REE	$\ln K_{\text{LnF}}^{0, 2+}$	$\beta_{\text{LnF-ClO}_4}^{(0)}$	$\beta_{\text{LnF-ClO}_4}^{(1)}$	$C_{\text{LnF-ClO}_4}$	$\beta_{\text{LnF-Cl}}^{(0)}$	$\beta_{\text{LnF-Cl}}^{(1)}$
Y	10.24 ± 0.08	0.4375	4.0849	0.0131	0.2363	3.8477
La	8.31 ± 0.16	0.5633	3.6661	-0.0126	0.2080	3.8262
Ce	8.90 ± 0.13	0.4321	4.1573	0.0024	0.1873	3.9997
Pr	8.86 ± 0.11	0.4254	4.1538	0.0048	0.1937	3.9428
Nd	8.82 ± 0.10	0.3266	4.4665	0.0181	0.1951	3.9096
Pm	—	—	—	—	—	—
Sm	9.60 ± 0.10	0.3831	4.3210	0.0155	0.2153	3.9280
Eu	9.86 ± 0.13	0.4016	4.2755	0.0156	0.2100	3.9724
Gd	9.77 ± 0.11	0.3998	4.2659	0.0159	0.2138	3.9746
Tb	10.12 ± 0.08	0.3739	4.5056	0.0191	0.2154	4.0494
Dy	10.14 ± 0.08	0.3964	4.3975	0.0177	0.2218	4.0262
Ho	9.86 ± 0.08	0.3961	4.3010	0.0177	0.2375	3.8936
Er	9.83 ± 0.08	0.4176	4.2090	0.0159	0.2336	3.8380
Tm	9.88 ± 0.08	0.3996	4.2678	0.0184	0.2347	3.8803
Yb	10.09 ± 0.08	0.4246	4.1921	0.0153	0.2317	3.8522
Lu	9.79 ± 0.07	0.3714	4.3974	0.0206	0.2312	3.8545

a)  $C_{\text{LnF-Cl}} = C_{\text{EuF-Cl}} = 0.0117$  for all elements.

$$B_{\text{MX}} = B_{\text{MX}}^0 + (B_{\text{MX}}^1/2 I) [1 - (1 + 2 I^{0.5}) \exp(-2 I^{0.5})] \quad (21)$$

$$B'_{\text{MX}} = (\beta_{\text{MX}}^1/2 I^2) [-1 + (1 + 2 I^{0.5} + 2 I) \exp(-2 I^{0.5})] \quad (22)$$

$$C_{\text{MX}} = C_{\text{MX}}^0 / (2 |Z_{\text{M}} Z_{\text{X}}|^{0.5}) \quad (23)$$

Similar equations are used for  $\text{NaCl}$  solutions where  $\text{ClO}_4^-$  is replaced by  $\text{Cl}^-$ . The values of  $\beta_{\text{MX}}^0$ ,  $\beta_{\text{MX}}^1$  and  $C_{\text{MX}}$  for  $\text{NaF}$ ,  $\text{NaCl}$ ,  $\text{NaClO}_4$ ,  $\text{Ln}(\text{ClO}_4)_3$  and  $\text{LnCl}_3$  are taken from Pitzer (1991).

### 3.3. Determination of the Pitzer coefficients for YREE complexes with $\text{F}^-$

The Pitzer coefficients were determined from the measurements of Luo and Byrne (2000, 2001) in  $\text{NaCl}$  and  $\text{NaClO}_4$  solutions as a function of ionic strengths at 25°C. The formation of complexes of YREE with  $\text{F}^-$  is given by the equation



The thermodynamic equilibrium constant ( $K_{\text{LnF}}^{0, 2+}$ ) for the formation of  $\text{LnF}^{2+}$  is given by

$$K_{\text{LnF}^{2+}}^0 = K_{\text{LnF}^{2+}}^* \{ \gamma(\text{LnF}^{2+}) / \gamma(\text{Ln}^{3+}) \gamma(\text{F}^-) \} \quad (25)$$

where  $\gamma(i)$  is the activity coefficient of  $i$  and  $K_{\text{LnF}}^* = {}_{\text{F}}\beta_1$  is the stoichiometric stability constant

$$K_{\text{LnF}^{2+}}^* = {}_{\text{F}}\beta_1 = [\text{LnF}^{2+}] / [\text{Ln}^{3+}] [\text{F}^-] \quad (26)$$

$[i]$  is the concentration of species  $i$ . From measurements of  $K_{\text{LnF}^{2+}}^*$  as a function of concentration it is possible to determine the thermodynamic constant and the activity coefficient of the ion complex. The rearrangement of the natural log of Eqn. 25 gives

$$\ln \{ K_{\text{LnF}^{2+}}^* / \gamma(\text{Ln}^{3+}) \gamma(\text{F}^-) \} = -\ln K_{\text{LnF}^{2+}}^0 + \ln \gamma(\text{LnF}^{2+}) \quad (27)$$

The value of the activity coefficient for the  $\text{LnF}^{2+}$  complex can be formulated by the same form as Eqns. 15—(16)

$$\ln \gamma(\text{LnF}^{2+}) = Z^2 f^{\gamma} + 2 m_{\text{ClO}_4} (B_{\text{LnF-ClO}_4} + m_{\text{ClO}_4} C_{\text{LnF-ClO}_4}) + Z^2 R + Z S \quad (28)$$

Combining with Eqn. 21, and taking  $z=2$ ,

$$\ln \gamma(\text{LnF}^{2+}) = \text{Med} + 2 m \beta^{(0)} + 2 m \beta^{(1)} f^1 + 2 m^2 C \quad (29)$$

where

$$f^1 = [1 - (1 + 2 I^{0.5}) \exp(-2 I^{0.5})] / 2 I \quad (30)$$

The medium term (med) is given by

$$\text{Med} = 4 f^{\gamma} + 4 R + 2 S \quad (31)$$

Combining Eqns. 27 and (29) on rearranging gives

$$-\ln \{ K_{\text{LnF}^{2+}}^* / \gamma(\text{Ln}^{3+}) \gamma(\text{F}^-) \} - \text{Med} = -\ln K_{\text{LnF}^{2+}}^0 + 2 m \beta^{(0)} + 2 m \beta^{(1)} f^1 + 2 m^2 C \quad (32)$$

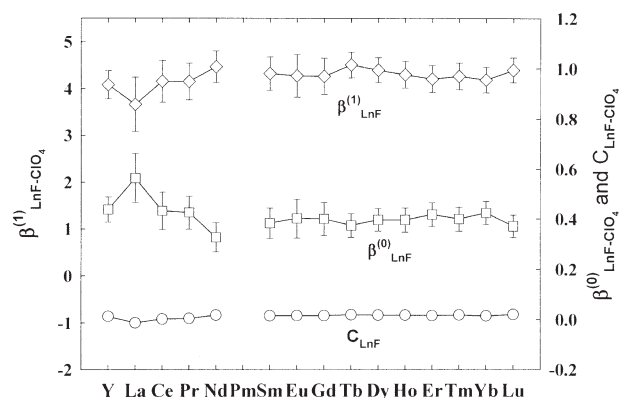


Fig. 9. Pitzer parameters for the interaction of  $\text{LnF}^{2+}$  with  $\text{NaClO}_4$ . Standard errors are shown for  $\beta_{\text{LnF}}^{(0)}$ ,  $\beta_{\text{LnF}}^{(1)}$  and  $C_{\text{LnF}}$ . Error bars for  $C_{\text{LnF}}$  are within the size of the symbols.

Table 4. A Comparison of thermodynamic constants ( $\ln K_{\text{LnF}}^{02+}$ ) extrapolated using the Pitzer equations in this study with the work of Luo & Byrne (2000) using extended Debye-Hückel equation at 25°C.

REE	Our study	Luo & Byrne	$\Delta$
Y	10.24 ± 0.08	10.27	-0.03
La	8.31 ± 0.16	8.34	-0.02
Ce	8.90 ± 0.13	8.89	0.01
Pr	8.86 ± 0.11	8.84	0.02
Nd	8.82 ± 0.10	8.80	0.03
Pm	—	—	—
Sm	9.60 ± 0.10	9.56	0.05
Eu	9.86 ± 0.13	9.83	0.03
Gd	9.77 ± 0.11	9.76	0.01
Tb	10.12 ± 0.08	10.06	0.06
Dy	10.14 ± 0.08	10.11	0.03
Ho	9.86 ± 0.08	9.86	0.00
Er	9.83 ± 0.08	9.83	0.00
Tm	9.88 ± 0.08	9.88	0.00
Yb	10.09 ± 0.08	10.11	-0.02
Lu	9.79 ± 0.07	9.79	0.01

All terms on the left-hand side of Eqn. 32 are known experimentally or can be calculated from Pitzer programs (Millero, 1992; Millero and Pierrot, 1998). A nonlinear least-squares fit of the values of the left side of Eqn. (32) as a function of  $2m$ ,  $2m f^1$  and  $m^2$  yields the infinite dilution thermodynamic stability constant ( $K_{\text{LnF}}^{02+}$ ) and the Pitzer parameters ( $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C$ ) for the rare earth fluoride ion pairs. Plots of the left side values versus molality for  $\text{EuF}^{2+}$  complexes (Luo and Byrne, 2000, 2001) in  $\text{NaClO}_4$  and  $\text{NaCl}$  are shown in Figure 8. The results of  $K_{\text{LnF}}^{02+}$ ,  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C$  in  $\text{NaClO}_4$  for YREEs along with the standard errors of the fits are given in Table 3 and Figure 9. The Pitzer coefficients for ion pairs,  $\text{LnF}^{2+}$ , are the

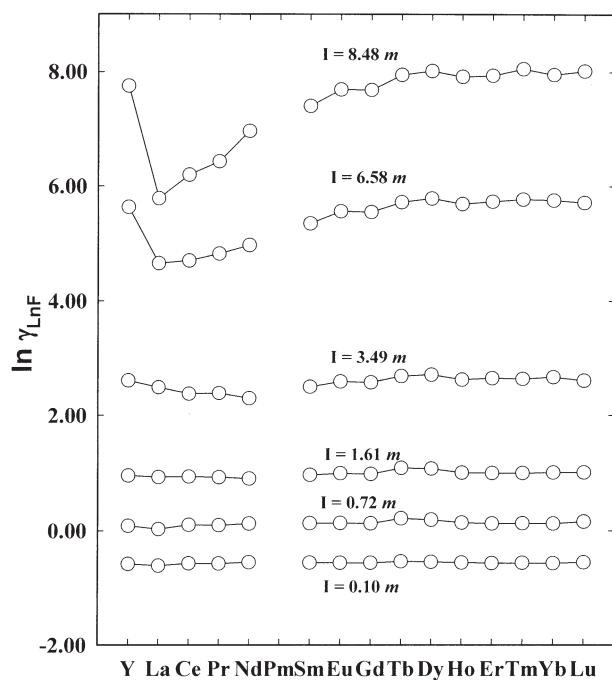


Fig. 10. Activity coefficients of  $\text{LnF}^{2+}$  in  $\text{NaClO}_4$  at different ionic strengths as a function of atomic number.

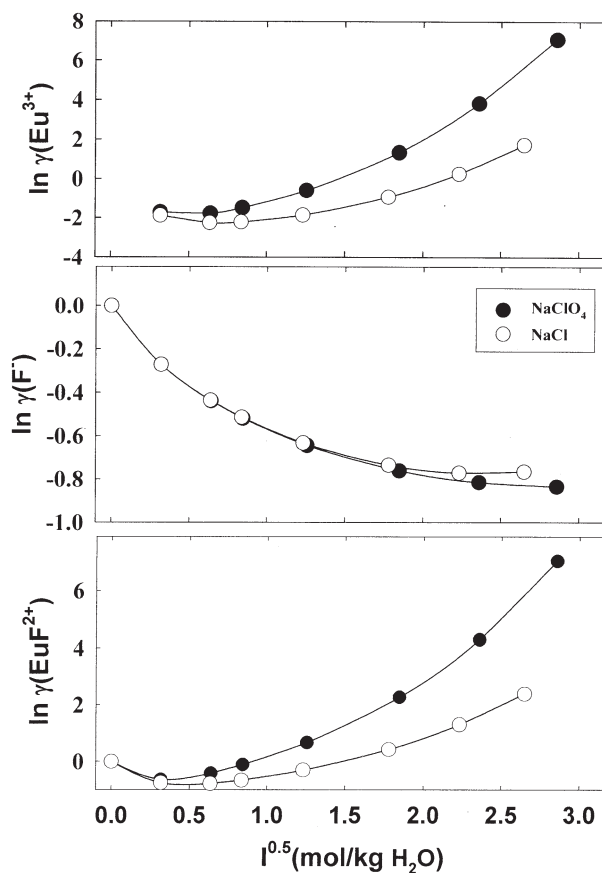


Fig. 11. Activity coefficients of  $\text{Eu}^{3+}$ ,  $\text{F}^-$  and  $\text{EuF}^{2+}$  in  $\text{NaCl}$  and  $\text{NaClO}_4$  as a function of the square root of the ionic strength.

same within experimental error for all YREEs. The standard errors of the fits for  $K_{\text{LnF}}^{02+}$  are all below 0.16 in  $\ln K_{\text{LnF}}^{02+}$  (0.07 in  $\log K_{\text{LnF}}^{02+}$ ). Similar calculations were made in  $\text{NaCl}$  solutions for  $\text{EuF}^{2+}$  complexes. Since measurements (Luo and Byrne, 2001) of the other YREEs were only made at two ionic strengths, it was not possible to independently determine the values of  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C$  in  $\text{NaCl}$  for all the metals. As the values of  $C$  in  $\text{NaClO}_4$  are quite small and constant, we have estimated the values of  $\beta^{(0)}$  and  $\beta^{(1)}$  in  $\text{NaCl}$  by assuming the values of  $C$  for all the metals are similar to the values determined for  $\text{EuF}^{2+}$  in  $\text{NaCl}$  (see Fig. 8). The resulting Pitzer coefficients in  $\text{NaCl}$  for all the ion complexes are tabulated in Table 3. The values of  $\ln K_{\text{LnF}}^{02+}$  at zero ionic strength extrapolated using the Pitzer equation are in good agreement with the extrapolations made by Luo and Byrne (2000) using an extended Debye-Hückel equation (see Table 4).

The activity coefficients for all the complexes in  $\text{NaClO}_4$  have been calculated from Eqn. 29 and are shown in Figure 10. At low ionic strengths, they are independent of the YREE ions. The activity coefficients of the YREE ion pairs are the same for a given charge type (Millero, 1992). These results indicate that below  $I = 3.5 m$ , the activity coefficients of other YREE complexes of the same charge type ( $\text{LnX}^{2+}$ ) can be estimated from the average coefficients given in Table 3. The activity coefficients of  $\text{LnF}^{2+}$  complexes at 25°C can be used to estimate the values at other temperatures because the values of  $\Delta H_i$  are

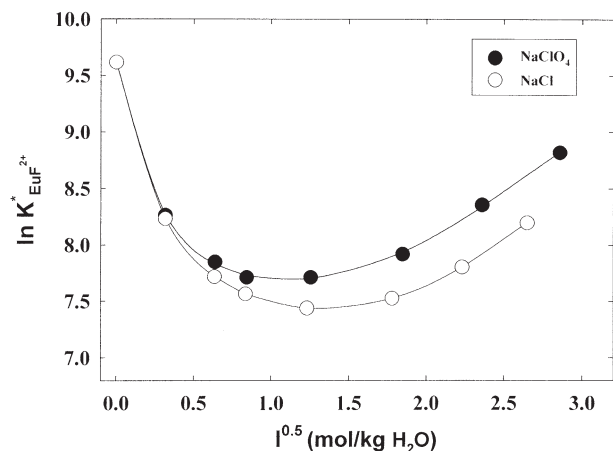


Fig. 12. The stability constants for the formation of  $\text{EuF}^{2+}$  in NaCl and  $\text{NaClO}_4$  as a function of the square root of the ionic strength. Curves are calculated from the Pitzer models.

independent of concentration (Fig. 7). It is thus possible to make reasonable estimates of the stability constants for the formation of  $\text{LnX}^{2+}$  complexes from 0 to 50°C and  $I = 0$  to 6  $m$  in  $\text{NaClO}_4$  or NaCl solutions.

As shown in Figure 11 the activity coefficients of  $\text{Eu}^{3+}$ ,  $\text{F}^-$  and  $\text{EuF}^{2+}$  in NaCl and  $\text{NaClO}_4$  solutions are different at high ionic strengths (Luo & Byrne, 2001). The differences for the activity coefficients for  $\text{F}^-$  are much smaller than those for  $\text{EuF}^{2+}$  and  $\text{Eu}^{3+}$ . These differences in the activity coefficients can lead to differences in the stability constants at high ionic strengths (see Fig. 12). Using the stability constants in  $\text{NaClO}_4$  can lead to uncertainties in the speciation of YREEs in NaCl brines. The lower stability constants in NaCl can be attributed to the formation of chloride complexes with  $\text{EuF}^{2+}$  and  $\text{Eu}^{3+}$ . If the stability constants are available for the formation of these complexes, one can correct the values of stability constants measured in  $\text{NaClO}_4$  and use them in chloride media.

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