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Effects of Ionic Strength and Charge Density on the Stability of Chloride Complexes of Trivalent Lanthanides

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The stability constants of chloride complexes of trivalent praseodymium, europium, erbium, and lutetium ($\beta^I_{\mathrm{Ln,Cl}}$ and $\beta^I_{\mathrm{Ln,2Cl}}$) were determined at 303 K in a mixture of $HClO_4$ and HCl media (ionic strength between (1 and 4) $\mathrm{mol \cdot dm^{-3}}$) by means of a solvent extraction method using dinonyl napthalene sulfonic acid. Praseodymium and erbium concentrations were measured by a VIS spectrophotometric method using xylenol orange at pH 6, whereas radioactivity measurements were undertaken for europium and lutetium. The specific ion interaction theory (SIT) was applied for the calculation of $\log_{10} \beta^0_{\mathrm{Ln,Cl}}$, and a general view of the behavior of the first chloride constants against charge density of lanthanides was obtained.

Introduction

The reactions for mononuclear complexes of lanthanides and chloride ions can be represented as follows

$$\mathrm{Ln^{3+}} + j\mathrm{Cl^-} \rightleftarrows \mathrm{LnCl}_j^{(3-j)} \tag{a}$$

where $j = 1$, 2, or 3. According to the mass-action law, the formation constants for the first and second chloride complexes at ionic strength I are, respectively

$$\beta^I_{\mathrm{Ln,Cl}} = \frac{[\mathrm{LnCl^{2+}}]}{[\mathrm{Ln^{3+}}][\mathrm{Cl^-}]} \tag{1}$$

$$\beta^I_{\mathrm{Ln,2Cl}} = \frac{[\mathrm{LnCl_2^+}]}{[\mathrm{Ln^{3+}}][\mathrm{Cl^-}]^2} \tag{2}$$

Literature data on their stability constants have been compiled and analyzed by several authors.[1–6] These inorganic complexes are one of the weakest of the lanthanides and are considered as outer sphere complexes. Extrapolation of the available low-temperature constant data indicates that the stabilities increase relatively rapidly with temperature.[7] The experimental data about the stability constants[8–23] are not necessarily related to both the first ($\mathrm{LnCl^{2+}}$) and second species ($\mathrm{LnCl_2^+}$) because of the instability of the second one. Table 1 shows the values reported in the literature for the stability constants of the first and second chloride complexes of praseodymium, europium, erbium, and lutetium.

The liquid−liquid extraction system using dinonyl naphtalene sulfonic acid (referred to as polymeric species $(\mathrm{HD})_x$) has been used to determine the stability constants of lanthanide chloride complexes and other elements (see Table 1 and refs 24 to 26). This method has been previously described in detail (see, for instance, ref 23); hence, only the main equations are included here.

The reaction for the solvent extraction of lanthanide elements by means of $(\mathrm{HD})_x$ can be represented as follows

$$\mathrm{Ln^{3+}} + \overline{(\mathrm{HD})_x} \rightleftarrows \overline{\mathrm{Ln(H}_{x-3}\mathrm{D}_x)} + 3\mathrm{H^+} \tag{b}$$

where $\overline{(\mathrm{HD})_x}$ and $\overline{\mathrm{Ln(H}_{x-3}\mathrm{D}_x)}$ represent the species in the organic phase and $\mathrm{La^{3+}}$ and $\mathrm{H^+}$ correspond to those present in the aqueous phase. The distribution coefficient is

$$D_0 = \frac{[\overline{\mathrm{Ln(H}_{x-3}\mathrm{D}_x)}]}{[\mathrm{Ln^{3+}}]} \tag{3}$$

If adequate conditions, like appropriate $\mathrm{Cl^-}$ concentration and pH, among others, are fulfilled, the complex $\mathrm{LnCl^{2+}}$ is formed, and then the distribution coefficient will be

$$D_1 = \frac{[\overline{\mathrm{Ln(H}_{x-3}\mathrm{D}_x)}]}{[\mathrm{Ln^{3+}}](1 + \beta_{\mathrm{Ln,Cl}}[\mathrm{Cl^-}])} \tag{4}$$

and the following equation can be deduced

$$\frac{1}{D_1} = \frac{1}{D_0} + \frac{\beta_{\mathrm{Ln,Cl}}}{D_0}[\mathrm{Cl^-}] \tag{5}$$

From a graph of $1/D_1$ vs $[\mathrm{Cl^-}]$, the stability constant $\beta_{\mathrm{Ln,Cl}}$ may be estimated.

When both the $\mathrm{LnCl^{2+}}$ and $\mathrm{LnCl_2^+}$ species form, the distribution coefficient, D_2, is defined as

$$D_2 = \frac{[\overline{\mathrm{Ln(H}_{x-3}\mathrm{D}_x)}]}{[\mathrm{Ln^{3+}}](1 + \beta_{\mathrm{Ln,Cl}}[\mathrm{Cl^-}] + \beta_{\mathrm{Ln,2Cl}}[\mathrm{Cl^-}]^2} \tag{6}$$

and then

$$\frac{1}{D_2} = \frac{1}{D_0} + \frac{\beta_{\mathrm{Ln,Cl}}}{D_0}[\mathrm{Cl^-}] + \frac{\beta_{\mathrm{Ln,2Cl}}}{D_0}[\mathrm{Cl^-}]^2 \tag{7}$$

In such a case, both stability constants $\beta_{\mathrm{Ln,Cl}}$ and $\beta_{\mathrm{Ln,2Cl}}$ can be estimated by a polynomial fit of the experimental data of $1/D_2$ as a function of the chloride ion concentration. Advanced

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Table 1. Data of $\beta^{I}_{\mathrm{Ln,Cl}}$ (kg·mol^{-1}) and $\beta^{I}_{\mathrm{Ln,2Cl}}$ (kg·mol^{-1})^2 from the Literature and the Present Work (PW)[a]

Ln	I^b (media); T/K	method[c]	$\beta^{I}_{\mathrm{Ln,Cl}}$	$\log_{10} \beta^{I}_{\mathrm{Ln,Cl}}$	$\beta^{I}_{\mathrm{Ln,2Cl}}$	$\log_{10} \beta^{I}_{\mathrm{Ln,2Cl}}$	ref
Pr	0; 298	EDH		0.44			17
	0; 298	PIM		0.32			4
	0; 298	S		0.3			20
	0; 303	SIT		1.5 ± 0.2			PW
	1 ($HClO_4$/HCl); 295	SE + R	0.9 ± 0.3				8
	1 ($NaClO_4$/NaCl); 298	P	1.58 ± 0.05				12
	2 ($NaClO_4$/NaCl); 303	P	0.80				22
	2 ($HClO_4$/HCl); 303	SE* + VS	1.2 ± 0.2		−		PW
			0.8 ± 0.1		−0.12 ± 0.04		
	3 ($HClO_4$ /HCl); 303	SE* + VS	1.1 ± 0.3		−		PW
			0.6 ± 0.1		0.11 ± 0.03		
	4 ($HClO_4$ /HCl); 303	SE* + VS	1.3 ± 0.6		−		PW
			0.6 ± 0.3		0.19 ± 0.09		
Eu	0; 298	IAP		0.38		0.05	20
	0; 298	EDH/S		0.34			17
	0; 298	PIM		0.28			4
	0; 298	S		0.34		0.05	20
	0; 303	SIT		1.38			21
	0; 303	SIT		1.38 ± 0.08			PW
	0.2($HClO_4$/HCl); 303	SE* + R	2.1 ± 0.1				21
	0.5($HClO_4$/HCl); 303	SE* + R	1.45 ± 0.01				21
	1 ($HClO_4$/HCl); 303	SE* + R	0.84 ± 0.07				21
	1 ($HClO_4$/HCl); 295	SE + R	0.9 ± 0.3				8
	1 ($HClO_4$/HCl); 298	SE* + R	0.79 ± 0.11		0.3 ± 0.1		9
			0.88 ± 0.1		−		
	1 ($HClO_4$/HCl); 293	II + R	0.80 ± 0.05		~0.15		10
	1 ($HClO_4$/HCl) 293	II* + R	0.95 ± 0.15				11
	1 ($HClO_4$/HCl); 303	SE* + R	0.64 ± 0.03		0.3 ± 0.03		14
	1 ($LiClO_4$) pH 1.5−3.5, 298	SE + R		0.07			15
	1 ($HClO_4$/HCl); 303	SE* + R	0.7 ± 0.06		−		PW
			0.63 ± 0.06		0.06 ± 0.005		
	2 ($HClO_4$/HCl); 303	SE* + R	0.7 ± 0.08		−		PW
			0.6 ± 0.06		0.06 ± 0.005		
	3 ($LiClO_4$) pH 0.8; 293	SE + R	0.52 ± 0.02		0.22 ± 0.02		16
	3 ($NaClO_4$/NaCl); 298	SE* + R		0.015 ± 0.05		−0.33 ± 0.22	19
	3 ($HClO_4$/HCl); 303	SE* + R	1 ± 0.1		−		PW
			0.6 ± 0.06		0.06 ± 0.005		
	4 ($HClO_4$); 298	II + R		−0.27		−0.9	13
	4 ($NaClO_4$); 298	II + R		−0.06		−0.48	13
	5 ($NaClO_4$/ $EuCl_3$)	L	0.13 ± 0.01				18
	5 ($NaClO_4$/NaCl); 298	SE* + R		0.095 ± 0.06		−0.33 ± 0.03	19
	7 ($NaClO_4$/NaCl); 298	SE* + R		0.24 ± 0.04		−	19
	9 ($NaClO_4$/NaCl); 298	SE* + R		0.42 ± 0.04		−	19
Er	0; 298	EDH		0.26			17
	0; 298	PIM		0.28			4
	0; 298	S		0.27			20
	0; 303	SIT		1.2 ± 0.5			PW
	2 ($HClO_4$/HCl); 303	SE* + VS	0.6 ± 0.2		−		PW
			0.4 ± 0.1		0.15 ± 0.11		
	3 ($HClO_4$/HCl); 303	SE* + VS	0.5 ± 0.1		−		PW
			0.4 ± 0.1		0.05 ± 0.03		
	4 ($HClO_4$/HCl); 303	SE* + VS	0.38 ± 0.08		−		PW
			0.3 ± 0.06		0.02 ± 0.01		
Lu	0; 298	EDH		0.23			17
	0; 298	PIM		−0.03			4
	0; 298	S		0.1			20
	0; 303	SIT		1 ± 0.2			PW
	1 ($HClO_4$/HCl); 295	SE + R	0.4 ± 0.02				8
	2 ($NaClO_4$/NaCl); 303	P	0.174				22
	2 ($HClO_4$/HCl); 303	SE* + R	0.8 ± 0.2		−		PW
			0.4 ± 0.1		0.16 ± 0.05		
	3 ($HClO_4$/HCl); 303	SE* + R	0.8 ± 0.2		−		PW
			0.34 ± 0.05		0.11 ± 0.02		
	4 ($HClO_4$/HCl); 303	SE* + R	0.7 ± 0.2		−		PW
			0.4 ± 0.1		0.06 ± 0.02		

[a] $\beta^{0}_{\mathrm{Ln,Cl}}$ was calculated with $Ba_j = 1$. [b] Ionic strength (I) in mol·dm^{-3}. [c] EDH: Extended Debye−Hückel expression. PIM: Pitzer interaction model. S: Selected from previous reports. IA/P: Ion association approach and specific ion approach of Pitzer. SIT: Specific ion interaction theory. IAPN: Ion-association model of Pearson and Noronha. SE: Solvent extraction. II: Ionic exchange. *: Using $(HD)_x$. R: radioactivity measurement. P: Potentiometry.VS: Visible spectrophotometry. L: Luminescence excitation spectroscopy.

general regression computational approaches have been developed, e.g., LETAGROP DISTR computer program, for this kind of calculations.[27] For simplicity, the stability constants were calculated using polynomial regression in this work.

Radiotracer methods have been frequently used (see Table 1) for the determination of the stability constants of lanthanide chlorides as in the present work for europium and lutetium. Nevertheless, the spectrophotometric method with semixylenol

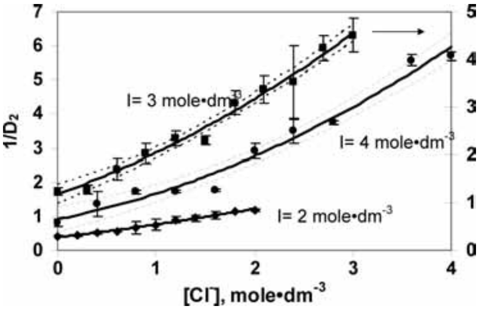

Figure 1. Graphs of $1/D_2$ vs [Cl^-], for Pr^{3+} in HCl−$HClO_4$ mixtures at (2, 3, and 4) mol·dm^{-3} ionic strength. The 95 % confidence intervals are included. The polynomial equations are given in Table 2.

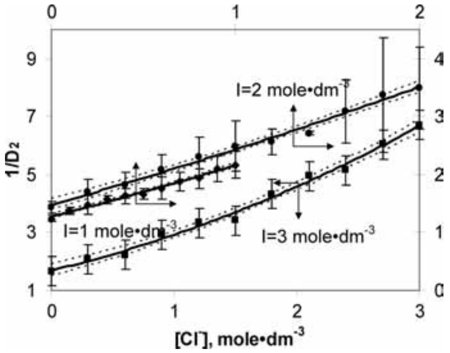

Figure 2. Graphs of $1/D_2$ vs [Cl^-], for Eu^{3+} in HCl−$HClO_4$ mixtures at (1, 2, and 3) mol·dm^{-3} ionic strength. The 95 % confidence intervals are included. The polynomial equations are given in Table 2.

orange (XO), at pH 6, is useful as well for the analysis of microgram amounts of rare earth elements.[23,28–31] This last technique was useful to measure aqueous Pr^{3+} and Er^{3+} concentrations in this research.

At present, industrial interest on lanthanides has increased, and furthermore, some of them are products of uranium nuclear fission. Regarding the chloride ion, its concentration is significantly important in some aquatic media, particularly in brines and oceans. In this sense, studies on the chloride complex formation with lanthanides are related to safe waste confinement.

The purposes of this research were (a) to determine the stability constants of Ln^{3+} complexes formed with Cl^-, at a constant temperature of 30 °C, in several ionic strength $HClO_4$ media; (b) to extrapolate to infinite dilution using the SIT (Bronsted−Guggenheim−Scatchard specific ion interaction theory) method; and (c) to know the behavior of these chloride complexes with respect to lanthanide charge densities.

Experimental Section

Materials. The details about the preparation of the solutions were given previously.[23] The oxides were obtained from heating the synthesized oxalates at the following temperatures:[32] 790 °C for praseodymium, 620 °C for europium, 720 °C for erbium, and 715 °C for lutetium. The oxides were treated with nitric acid and later with a mixture of 1:1 water/acetone, and finally, the crystals were dissolved in 10^{-3} mol·dm^{-3} nitric acid.

The lanthanide stock solutions were standardized by EDTA titration[33,34] as previously described,[23] and the concentrations were the following: $1.8\cdot10^{-3}$ mol·dm^{-3} for Pr^{3+}, $7.6\cdot10^{-5}$ mol·dm^{-3} for Eu^{3+}, $2.1\cdot10^{-3}$ mol·dm^{-3} for Er^{3+}, and $6.7\cdot10^{-5}$ mol·dm^{-3} for Lu^{3+}.

The organic phases were solutions of $(HD)_x$ in *n*-heptane whose concentrations were between (0.5 and 8) %, with initial distribution coefficients between 0.4 and 4.

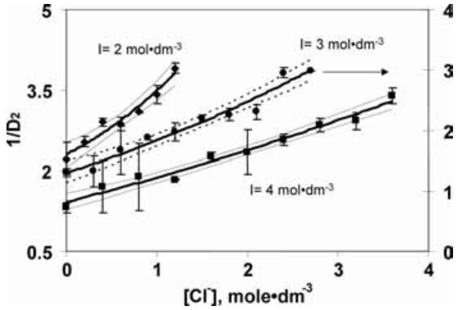

Figure 3. Graphs of $1/D_2$ vs [Cl^-], for Er^{3+} in HCl−$HClO_4$ mixtures at (2, 3, and 4) mol·dm^{-3} ionic strength. The 95 % confidence intervals are included. The polynomial equations are given in Table 2.

Procedures. (a) Lanthanide Concentration Measurements. The experimental details for the spectrophotometric[23] and radioactive[35] measurements were described elsewhere.

(B) Solvent Extraction. The experimental ionic strengths were (1, 2, 3, and 4) mol·dm^{-3}. Aqueous phases were mixtures of HCl and $HClO_4$ solutions as described elsewhere.[23] Aliquots of 2 cm^3 of each aqueous and organic phase and a determined quantity of the lanthanide stock solution were shaken for 2.5 h[21] in a water bath (Cole Parmer, Polystat) at (30 ± 0.02) °C. For these experiments, the initial lanthanide concentrations were: $[Pr^{3+}] = 8.8\cdot10^{-5}$ mol·dm^{-3}, $[Eu^{3+}] = 1.9\cdot10^{-6}$ mol·dm^{-3}, $[Er^{3+}] = 1\cdot10^{-4}$ mol·dm^{-3}, and $[Lu^{3+}] = 3.3\cdot10^{-6}$ mol·dm^{-3}. Each experiment was done at least four times.

The spectrophotometric measurements of praseodymium and erbium were carried out in aliquots of the aqueous phases before and after solvent extraction, and $1/D$ was calculated from the concentration of the element in the aqueous phase divided by that of the organic phase (initial minus final aqueous concentrations). Europium and lutetium were measured by means of the radioactivity of the isotopes $^{151m1}Eu$ and ^{177}Lu in both aqueous and organic phases, and total radioactivity was measured in an aliquot identical to the initial aqueous phase. $1/D$ was calculated from the radioactivity in the aqueous phase divided by that of the organic phase.

Results and Discussion

Absorbance measurements obeyed the law of Lambert and Beer, and the spectrophotometric calibration lines obtained at $\lambda = 577$ nm and pH 6 were

$$\text{absorbance} = 20510[\mathrm{Pr}^{3+}],\ r^2 = 0.997,\\ \text{for } 1.6\cdot10^{-6}\ \mathrm{mol\cdot dm^{-3}} < [\mathrm{Pr}^{3+}] < 2.9\cdot10^{-5}\ \mathrm{mol\cdot dm^{-3}} \qquad (8)$$

$$\text{absorbance} = 37032[\mathrm{Er}^{3+}],\ r^2 = 0.99,\\ \text{for } 3.7\cdot10^{-6}\ \mathrm{mol\cdot dm^{-3}} < [\mathrm{Er}^{3+}] < 4.9\cdot10^{-5}\ \mathrm{mol\cdot dm^{-3}} \qquad (9)$$

These molar absortivity values agree with those previously reported by Mukherji:[30] (19 000 and 37 000) dm^3·mol^{-1}·cm^{-1} for praseodymium and erbium, respectively.

Gamma spectra and half-lives of both $^{151m1}Eu$ and ^{177}Lu were verified and agreed with literature data.[36]

The graphs of $1/D_2$ vs [Cl^-] are shown in Figures 1 to 4. The sets of data were treated by means of both linear and second degree polynomial equations. The corresponding equations are given in Table 2. Attempts were undertaken to fit the results to third-order polynomial equations, but it gave negative coefficients for $[Cl^-]^3$ and [Cl^-]. The values of $\beta^{I}_{\mathrm{Ln,Cl}}$ calculated with linear equations (for example, $\beta^{I=2}_{\mathrm{Pr,Cl}} = 1.2 \pm 0.2$) and both $\beta^{I}_{\mathrm{Ln,Cl}}$ and $\beta^{I}_{\mathrm{Ln,2Cl}}$ calculated using polynomial equations ($\beta^{I=2}_{\mathrm{Pr,2Cl}} = 0.85 \pm 0.12$ and $\beta^{I=2}_{\mathrm{Pr,2Cl}} = 0.12 \pm 0.04$) are shown in

Table 1. Standard deviations of the regression equation parameters and the confidence intervals were calculated using $\alpha = 0.05$.

Values of R^2 for polynomial fitting are in general slightly higher than those for the linear ones (see Table 2). According to these results, the $LnCl_2^+$ abundance is very low and is almost undetectable. When both species are considered in the calculations, values for $\beta^I_{Ln,Cl}$ are smaller than when the second one is discarded (see Table 1). Independent of the determination method, the standard deviation values are in general high for the measurements of stability constants of chloride (see Table 1) and nitrate[37] complexes, probably because of the scarce concentration of the species formed.

For comparison purposes of the values obtained in the present research with those from previous studies, the constants should be referred to under the same experimental conditions, which is not always the case. The stability constant for $EuCl^{2+}$ in 1 $mol \cdot dm^{-3}$ has been determined several times,[8–11,14,21] and no statistical difference is appreciated when compared to the present data. Similarities were also found between the previously reported[22] values for $PrCl^{2+}$ and for $LuCl^{2+}$ in 2 $mol \cdot dm^{-3}$ and those obtained in the present work.

According to the Nuclear Energy Agency recommendation,[38] the SIT method was used for extrapolation to zero ionic strength of both $\beta^I_{Ln,Cl}$ and $\beta^I_{Ln,2Cl}$. According to this method, the values of stability constants at zero ionic strength ($\beta^0_{Ln,jCl}$) are related to the values at any ionic strength, $\beta^I_{Ln,jCl}$ by

$$\log_{10} \beta^I_{LnCl} - \Delta z^2 D = \log_{10} \beta^I_{Ln,jCl} - \Delta\varepsilon I_m \tag{10}$$

in which the ionic strength I_m must be in $mol \cdot kg^{-1}$ and $\beta^I_{Ln,jCl}$ in $(mol \cdot kg^{-1})^{-j}$. The Debye−Hückel term (D) is expressed as follows

$$D = \frac{A\sqrt[2]{I_m}}{1 + Ba_j\sqrt[2]{I_m}} \tag{11}$$

where the value of $A = 0.5131$ at 30 °C and Ba_j has had several values proposed ranging from 1.0 to 1.6. This Ba_j parameter is empirical and as such is correlated to the ion interaction coefficients ε. Δz^2 is a sum function of the squared charges of the reacting ionic species

$$\Delta z^2 = \sum z^2_{(products)} - \sum z^2_{(reactants)} = (z_{La} - jz_{Cl})^2 - z_{La}{}^2 - jz_{Cl}{}^2 \tag{12}$$

For reaction (a) and $j = 1$, $\Delta z^2 = -6$, whereas for $j = 2$, $\Delta z^2 = -10$. $\Delta\varepsilon$ is a sum function of the interaction coefficients between the reacting species and the ionic medium, and for reaction (a) in perchloric acid media and $j = 1$, it is defined by the following equation

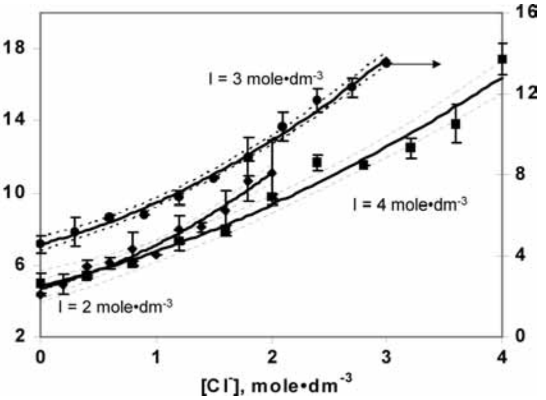

Figure 4. Graphs of $1/D_2$ vs $[Cl^-]$, for Lu^{3+} in $HCl-HClO_4$ mixtures at (2, 3, and 4) $mol \cdot dm^{-3}$ ionic strength. The 95 % confidence intervals are included. The polynomial equations are given in Table 2.

$$\Delta\varepsilon = \varepsilon(LnCl^{2+},ClO_4^-) - \varepsilon(H^+, Cl^-) - \varepsilon(Ln^{3+},ClO_4^-) \tag{13}$$

and for $j = 2$

$$\Delta\varepsilon = \varepsilon(LnCl^{2+},ClO_4^-) - 2\varepsilon(H^+, Cl^-) - \varepsilon(Ln^{3+},ClO_4^-) \tag{14}$$

Therefore, for reaction (a) and $j = 1$, eq 10 can be rewritten as

$$\log_{10} \beta^I_{Ln,Cl} + 6D = \log_{10} \beta^I_{Ln,Cl} - \Delta\varepsilon I_m \tag{15}$$

and for $j = 2$

$$\log_{10} \beta^I_{Ln,2Cl} + 10D = \log_{10} \beta^0_{Ln,2Cl} - \Delta\varepsilon I_m \tag{16}$$

According to these equations, linear relationships must be found when $\log_{10} \beta^I_{Ln,Cl} + 6D$ or $\log_{10} \beta^I_{Ln,2Cl} + 10D$ are plotted vs I_m, in which their slopes and the y-axis interceptions correspond to $-\Delta\varepsilon$ and $\log_{10} \beta^0_{Ln,jCl}$, respectively.

I_m, $\log_{10} \beta^I_{Ln,Cl}$, and $\log_{10} \beta^I_{Ln,2Cl}$ were calculated in molality units considering molarity and density of solutions.[39] Data of the present research and others from the literature were used for calculation of $\log_{10} \beta^I_{Ln,Cl} + 6D$. These data are included in Table 1, excepting those of lanthanum, which was included for a comparison and whose $\beta^I_{La,Cl}$ data were taken from the literature.[1,22,23] These data were calculated as well considering

Table 2. Linear and Polynomial Equations of the Fitting of Experimental Data, According to Equations 5 and 7[a]

		linear fitting		polynomial fitting	
Ln	I	$1/D_0 =$	R^2	$1/D_0 =$	R^2
Pr	2	$0.42 \pm 0.04\ [Cl^-] + 0.36 \pm 0.04$	0.986	$0.04 \pm 0.02\ [Cl^-]^2 + 0.33 \pm 0.03\ [Cl^-] + 0.38 \pm 0.04$	0.990
	3	$1.1 \pm 0.1\ [Cl^-] + 1 \pm 0.2$	0.976	$0.13 \pm 0.03\ [Cl^-]^2 + 0.7 \pm 0.1\ [Cl^-] + 1.2 \pm 0.2$	0.985
	4	$1.1 \pm 0.2\ [Cl^-] + 0.8 \pm 0.3$	0.979	$0.17 \pm 0.04\ [Cl^-]^2 + 0.6 \pm 0.2\ [Cl^-] + 0.9 \pm 0.4$	0.976
Eu	1	$0.88 \pm 0.07\ [Cl^-] + 1.26 \pm 0.04$	0.988	$0.08 \pm 0.07\ [Cl^-]^2 + 0.81 \pm 0.07\ [Cl^-] + 1.28 \pm 0.04$	0.988
	2	$1.02 \pm 0.08\ [Cl^-] + 1.4 \pm 0.1$	0.988	$0.06 \pm 0.04\ [Cl^-]^2 + 0.89 \pm 0.08\ [Cl^-] + 1.48 \pm 0.09$	0.989
	3	$1.5 \pm 0.1\ [Cl^-] + 1.6 \pm 0.2$	0.991	$0.22 \pm 0.04\ [Cl^-]^2 + 1 \pm 0.1\ [Cl^-] +1.7 \pm 0.2$	0.991
Er	2	$1.3 \pm 0.3\ [Cl^-] + 2.2 \pm 0.2$	0.946	$0.3 \pm 0.2\ [Cl^-]^2 + 0.8 \pm 0.3\ [Cl^-] + 2.3 \pm 0.2$	0.954
	3	$0.6 \pm 0.1\ [Cl^-] + 1.2 \pm 0.2$	0.952	$0.06 \pm 0.04\ [Cl^-]^2 + 0.5 \pm 0.1\ [Cl^-] + 1.3 \pm 0.2$	0.957
	4	$0.52 \pm 0.07\ [Cl^-] + 1.4 \pm 0.2$	0.972	$0.03 \pm 0.02\ [Cl^-]^2 + 0.43 \pm 0.07\ [Cl^-] + 1.4 \pm 0.1$	0.975
Lu	2	$3.2 \pm 0.5\ [Cl^-] + 4.2 \pm 0.6$	0.955	$0.8 \pm 0.2\ [Cl^-]^2 + 1.7 \pm 0.4\ [Cl^-] + 4.6 \pm 0.5$	0.972
	3	$3.1 \pm 0.4\ [Cl^-] + 3.9 \pm 0.7$	0.973	$0.5 \pm 0.06\ [Cl^-]^2 + 1.6 \pm 0.2\ [Cl^-] + 4.6 \pm 0.3$	0.992
	4	$2.9 \pm 0.5\ [Cl^-] + 4 \pm 1$	0.956	$0.3 \pm 0.09\ [Cl^-]^2 + 1.8 \pm 0.4\ [Cl^-] + 4.6 \pm 0.9$	0.971

[a] Mean ± $t^{0.05}_{n-2}$ standard deviation. Ionic strength (I) in $mol \cdot dm^{-3}$.

Table 3. Application of the Specific Ion Interaction Theory to $\beta^0_{\mathrm{Ln,Cl}}$[a]

Ln	n	I_m	Ba_j	$\log_{10} \beta^I_{\mathrm{Ln,Cl}} + 6D =$	R^2	refs[b]
La	6	1 to 5	1	$0.02 \pm 0.01\, I_m + 1.73 \pm 0.04$	0.89	1, 12, 22, 23
			1.5	$-0.03 \pm 0.01\, I_m + 1.44 \pm 0.05$	0.9	
			2.97	$-0.08 \pm 0.03\, I_m + 1 \pm 0.1$	0.93	
Pr	5	1 to 5	1	$0.07 \pm 0.07\, I_m + 1.5 \pm 0.2$	0.74	22, PW
			1.5	$0.01 \pm 0.06\, \mathrm{I}_m + 1.2 \pm 0.2$	0.18	
			2.98	$-0.04 \pm 0.04\, I_m + 0.8 \pm 0.1$	0.78	
Eu	13	1 to 13.6	1	$0.1 \pm 0.02\, I_m + 1.38 \pm 0.08$	0.95	8−11, 14, 19, 21, PW
			1.5	$0.07 \pm 0.06\, I_m + 1 \pm 0.3$	0.94	
			3.01	$0.04 \pm 0.01\, I_m + 0.59 \pm 0.06$	0.86	
Er	3	2 to 5	1	$0.08 \pm 0.08\, I_m + 1.2 \pm 0.5$	0.98	PW
			1.5	$0.04 \pm 0.06\, I_m + 0.9 \pm 0.2$	0.98	
			3.05	$-0.004 \pm 0.006\, I_m + 0.36 \pm 0.02$	0.997	
Lu	4	1 to 5	1	$0.1 \pm 0.06\, I_m + 1.0 \pm 0.2$	0.98	8, PW
			1.5	$0.06 \pm 0.02\, I_m + 0.77 \pm 0.08$	0.98	
			3.06	$0.01 \pm 0.02\, I_m + 0.32 \pm 0.06$	0.74	

[a] Mean ± $t^{0.05}_{n-2}$ standard deviation. Ionic strength (I) in mol·kg^{-3}. [b] Calculations were done with data taken from these references.

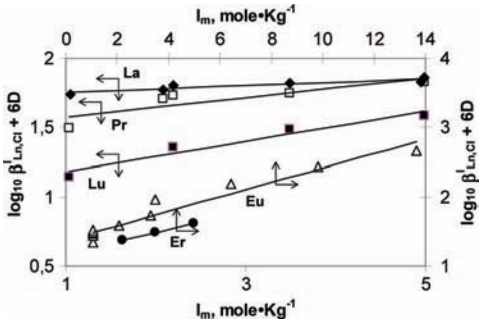

Figure 5. Application of the specific ion interaction theory to $\beta^0_{\mathrm{Ln,Cl}}$ for lanthanum,[23] praseodymium, europium, erbium, and lutetium. The value of 1 was used for Ba_j.

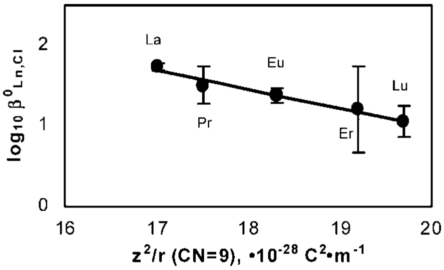

Figure 6. Graph of $\log_{10} \beta^0_{\mathrm{Ln,Cl}}$ vs charge density (z^2/r) for the elements studied in the present research and lanthanum.[23] $\mathrm{Log}_{10}\, \beta^0_{\mathrm{Ln,Cl}} = -0.23(\pm 0.07)z^2/r + 6(\pm 1)$; $R^2 = 0.98$.

the densities of hydrochloric acid solutions, and the results were compared with those reported in this paper (calculated considering the densities of perchloric acid). It was found that the differences are small and are covered by the numerical uncertainty of the constants.

Several values were considered for the Ba_j parameter (eq 11): 1, 1.5, and the products of B $(3.29 \cdot 10^7)$[38] and the hydrated ionic radii (a_j).[40] Table 3 shows the corresponding weighted least-squares regression equations. For an example, Figure 5 shows the graph of $\log_{10} \beta^I_{\mathrm{Ln,Cl}} + 6D$ as a function of ionic strength in molality, considering $\mathrm{Ba}_j = 1$. It is observed that the values of $\log_{10} \beta^0_{\mathrm{Ln,Cl}}$ (y-axis interception values of the equations) are lower as Ba_j increases.

According to the linear regression equations of Table 3, the values of $\log_{10} \beta^0_{\mathrm{Ln,Cl}}$ are in general higher than the others reported previously, which were not calculated by means of the SIT. The main difference is that the SIT includes the parameters A and Ba_j in the Debye−Hückel term, whereas the extended Debye−Hückel method is based on a plot of $\log_{10} \beta^I_{\mathrm{Ln,Cl}}$ vs $\sqrt{I}/(1+\sqrt{I})$ for low ionic strength data. Important differences are not observed between the values obtained in the present research and those reported previously for europium[21] and lanthanum,[23] which were calculated with $\mathrm{Ba}_j = 1$ and 1.5, respectively.

For the calculation of parameters $\varepsilon(\mathrm{LnCl}^{2+},\mathrm{ClO}_4^-)$, the value found in the literature[38] for $\varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) = 0.14(\pm 0.02)$ and a mean value (0.495) calculated with literature data[38] for $\varepsilon(\mathrm{Ln}^{3+},\mathrm{ClO}_4^-)$ were used. Taking into consideration the slope values of the linear equations (Table 3, $\mathrm{Ba}_j = 1$) of SIT graphs and eq 13, $\varepsilon(\mathrm{LnCl}^{2+},\mathrm{ClO}_4^-)$ values are 0.61(± 0.02), 0.56(± 0.08), 0.53(± 0.02), 0.6(± 0.1), and 0.51(± 0.06) for lanthanum, praseodymium, europium, erbium, and lutetium, respectively. The imprecision of $\varepsilon(\mathrm{Er}^{3+},\mathrm{ClO}_4^-)$ is certainly due to the scarce data available for calculation. On the other hand, according to these values, the interaction ion coefficient between perchlorate and lanthanides is quite similar along the series.

The values $\beta_{\mathrm{Ln,2Cl}}$ along the four elements considered in the present study are statistically similar in the studied ionic strength range. As proved by means of F- and t- tests, this behavior could probably be attributed to the low abundance of the LnCl_2^+ species. SIT calculations for the second constant were done; however, there are too few data about these constants (Table 1), and the statistical errors were huge. Therefore, mean values were calculated, and they were the following: $\beta^{2<I<4}_{\mathrm{Pr,2Cl}} = 0.14 \pm 0.04$, $\beta^{1<I<3}_{\mathrm{Eu,2Cl}} = 0.06 \pm 0.005$, $\beta^{2<I<4}_{\mathrm{Er,2Cl}} = 0.07 \pm 0.06$, and $\beta^{2<I<4}_{\mathrm{Lu,2Cl}} = 0.11 \pm 0.04$. These values specifically correspond to these ionic strength ranges and not necessarily to the infinite dilution.

Charge densities were calculated considering effective ionic radii with a coordination number (CN) of nine,[40] and they were $17 \cdot 10^{-28}$ C$^2 \cdot$m^{-1}, $17.5 \cdot 10^{-28}$ C$^2 \cdot$m^{-1}, $18.3 \cdot 10^{-28}$ C$^2 \cdot$m^{-1}, $19.2 \cdot 10^{-28}$ C$^2 \cdot$m^{-1}, and $19.7 \cdot 10^{-28}$ C$^2 \cdot$m^{-1}, for lanthanum, praseodymium, europium, erbium, and lutetium. A graph of $\log_{10} \beta^0_{\mathrm{Ln,Cl}}$ vs charge density for the elements studied in the present research and lanthanum is shown in Figure 6. The corresponding equation permits a prediction of $\log_{10} \beta^0_{\mathrm{Ln,Cl}}$ for other lanthanides. Chloro complexes of the light rare earth elements are more stable than those of the heavy rare earth elements. This is the opposite of the behavior of the fluoro complexes, which are predominantly electrostatic in character. Such a trend can be understood if it is recalled that Cl$^-$ is borderline to a soft ligand in the Pearson sense and thus is capable of some degree of covalent bonding. The light rare earth elements, which have larger ionic radii, are relatively more polarizable (softer) than the heavy rare earth elements and are better able to take advantage of a small degree of covalent bonding.[3]

Distribution diagrams for infinite dilution $\beta^0_{\mathrm{Ln,Cl}}$ (kg·mol^{-1}) were obtained using the MEDUSA program[41] taking into consideration for hydrolysis constants the data mentioned in ref 35. These diagrams showed that in the pH range from 0 to 7, < 3 % of the element is present as the $\mathrm{LnCl^{2+}}$ species, whereas the rest is in the form of the $\mathrm{Ln^{3+}}$ species. At higher pH, only the hydrolysis species of the lanthanides are important.

Conclusions

The stability constants for the first two chloride complexes of lanthanides ($\mathrm{LnCl^{2+}}$ and $\mathrm{LnCl_2^+}$) were determined; however, no evidence was found for the formation of the third species ($\mathrm{LnCl_3}$).

The stability constant values of the $\mathrm{LnCl^{2+}}$ species smoothly decrease as the ionic strength increases, whereas the values for $\mathrm{LnCl_2^+}$ are virtually the same, in the range studied.

The stability constants at zero ionic strength were determined by applying the SIT method to the results obtained for the $\mathrm{LnCl^{2+}}$ species and some found in the literature. These values decrease with charge density of the elements, and the acidic properties of the lanthanides may be responsible for this behavior.

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