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Stability Constants of Chloride Complexes of Lanthanum

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The stability constants of chloro complexes of La^{3+} were determined in perchloric acid media by means of a solvent extraction method. Dinonyl napthalene sulfonic acid was used as one extractant, and the lanthanum concentration was measured by an UV−VIS method using xylenol orange at pH 6. The values obtained for $\beta^{I}_{La,Cl}$ are (1 ± 0.2, 0.76 ± 0.09, and, 0.67 ± 0.15) $mol^{-1}\cdot dm^3$ for (2, 3, and 4) $mol\cdot dm^{-3}$, respectively. For $\beta_{La,2Cl}$ they are (0.2 ± 0.1, 0.09 ± 0.02, and 0.1 ± 0.03) $mol^{-2}\cdot dm^6$ for (2, 3 and 4) $mol\cdot dm^{-3}$, respectively. According to the specific ion interaction theory (SIT), $\log \beta^{0}_{La,Cl} = 1.4 \pm 0.1$ and $\epsilon(LaCl^{2+}, ClO_4^-) = 0.62 \pm 0.03$.

Introduction

Chloride ion concentration is significantly important in some aquatic media, particularly in brines and oceans. The chloride complexes are the weakest of the inorganic complexes of lanthanides,[1] but their stabilities depend on the chloride ion concentration among other parameters. At present, industrial interest on lanthanides has increased; furthermore, some of them are products of uranium nuclear fission. Therefore, deposition of non- or radioactive wastes in subsurface repositories of salt beds or oceans has generated interest in the complexes formed with chloride ions.[1−4]

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

$$La^{3+} + jCl^- \rightleftarrows LaCl_j^{(3-j)} \qquad (a)$$

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:

$$\beta^{I}_{La,Cl} = \frac{[LaCl^{2+}]}{[La^{3+}][Cl^-]} \qquad (1)$$

$$\beta^{I}_{La,2Cl} = \frac{[LaCl_2^{\ +}]}{[La^{3+}][Cl^-]^2} \qquad (2)$$

Stability constants for the species $LaCl^{2+}$ have been reported in 2 $mol\cdot dm^{-3}$ [5] and 1 $mol\cdot dm^{-3}$ [6−8] ionic strength media and at infinite dilution.[1−3,6,9,10] Stability constants for $LaCl_2^+$ and other chlorinated species at infinite dilution were reported by Haas et al.[3] Table 1 shows the values reported in the literature for the stability constants of the first and second chlorides complexes of lanthanum. Complexes with the intermediate Cl^- ion are relatively weak depending on the ionic strength and temperature, apparently Cl^- forms predominantly outer-sphere complexes with the rare earth elements. Although it is clear that lanthanum complexes with chloride ions are weak, it is difficult to compare the stability constants for the species $LaCl^{2+}$ since they have been determined in different conditions of temperature, ionic strength, and medium, as observed in Table 1. The logarithm of stability constants reported for the $LaCl^{2+}$ species are different from 0.29 to 0.64 at zero ionic strength and in general, the stability constants increase as the ionic strength decreases. In order to have a general view on the stability constants behavior, a systematic study on the stability constants of lanthanide elements would be necessary. Only two values have been reported for the $LaCl_2^+$ complex. This complex is not very stable and is probably not present to any large extent in natural waters, with the possible exception of brines with salinities greater than that of seawater. In fact, in most freshwaters, chloride complexes of the rare earth elements should be negligible.[1]

Table 1. Stability Constants of Chloride Lanthanum Complexes[a]

$I/mol\cdot dm^{-3}$ (media); T/K	method	$\beta_{La,Cl}$	$\log \beta_{La,Cl}$	$\beta_{La,2Cl}$	$\log \beta_{La,2Cl}$	ref
4; 298			−0.2		−0.6	6
4 (ClO_4/Cl); 303	SE	1.1 ± 0.8				Pw
4 (ClO_4/Cl); 303	SE	0.67 ± 0.15		0.1 ± 0.03		Pw
3 (ClO_4/Cl); 303	SE	1 ± 0.4				Pw
3 (ClO_4/Cl); 303	SE	0.76 ± 0.09		0.09 ± 0.02		Pw
2 (NaCl); 303	P	0.94				5
2 (ClO_4/Cl); 303	SE	1.6 ± 0.4				Pw
2 (ClO_4/Cl); 303	SE	1 ± 0.2		0.24 ± 0.09		Pw
1 ($NaClO_4$); 298	-		−0.1			6
1 ($NaClO_4$); 298	P	1.6 ± 0.03				7
1 (ClO_4/Cl); 295	SE	0.9 ± 0.3				8
0, 298	IA/P		0.29			2
	IA/P		0.29		−0.03	3
	EDH		0.48			1, 9
	-		0.64			10
0, 303	SIT		1.43 ± 0.12			Pw

[a] $\beta^{I}_{La,Cl}$ in $mol^{-1}\cdot dm^3$ and $\beta^{I}_{La,2Cl}$ in $mol^{-2}\cdot dm$.[6] Pw, present work; P, pH titration; SE, solvent extraction; IA/P, ion association approach and specific ion approach of Pitzer; EDH, extended Debye−Hückel expression.

The liquid−liquid extraction system using dinonyl naphtalene sulfonic acid (referred as polymeric species $(HD)_x$) has been used to determine the stability constants of lanthanide chloride complexes and other elements.[11−17] If xylenol orange is not purified, the systems are complicated by the possibility of forming more than one reaction product. It has been confirmed that semi-xylenol orange is more sensitive for the analysis of some elements.[18,19] However, it has been reported the quantitative analysis of rare earths using xylenol orange obeys the

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Lambert−Beer's law.[20,21]

The reaction for the solvent extraction of lanthanum by means of $(HD)_x$ can be represented as follows:

$$La^{3+} + \overline{(HD)_x} \rightleftarrows \overline{La(H_{x-3}D_x)} + 3H^+ \qquad \text{(b)}$$

where $\overline{(HD)_x}$ and $\overline{La(H_{x-3}D_x)}$ represent the species in the organic phase and La^{3+} and H^+ corresponding to those present in the aqueous phase. Reaction b is governed by the mass action law, and the stability constant of the complex extracted in the organic phase is defined as follows:

$$K_{La,(HD)x} = \frac{[\overline{La(H_{3-x}D_x)}][H^+]^3}{[La^{3+}][(HD)_x]} \qquad (3)$$

and the distribution coefficient of lanthanum is

$$D_0 = \frac{[\overline{La(H_{3-x}D_x)}]}{[La^{3+}]} \qquad (4)$$

From eqs 1 and 2 and taking a logarithmic expression, we get the following:

$$\log_{10} D_0 = \log_{10} K_{La,(HD)x} + \log_{10}[\overline{(HD)_x}] - 3 \log_{10}[H^+] \qquad (5)$$

If only the complex $LaCl^{2+}$ is formed, the distribution coefficient (D_1) will be

$$D_1 = \frac{[\overline{La(H_{x-3}D_x)}]}{[La^{3+}](1 + \beta_{La,Cl}[Cl^-])} \qquad (6)$$

and

$$\frac{1}{D_1} = \frac{1}{D_0} + \frac{\beta_{La,Cl}}{D_0}[Cl^-] \qquad (7)$$

A graph of $1/D_1$ versus $[Cl^-]$ is a straight line, the stability constant $\beta_{La,Cl}$ may be estimated from the slope and y-axis intersection values. On the other hand, when both the $LaCl^{2+}$ and $LaCl_2^+$ species are formed, the line of a graph of $1/D_1$ vs $[Cl^-]$ will curve upward as much as the relative amount of the second complex becomes important. The distribution coefficient (D_2) is then defined as

$$D_2 = \frac{[\overline{La(H_{3-x}D_x)}]}{[La^{3+}](1 + \beta_{La,Cl}[Cl^-] + \beta_{La,2Cl}[Cl^-]^2)} \qquad (8)$$

and

$$\frac{1}{D_2} = \frac{1}{D_0} + \frac{\beta_{La,Cl}}{D_0}[Cl^-] + \frac{\beta_{La,2Cl}}{D_0}[Cl^-]^2 \qquad (9)$$

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

Radiotracer methods have been frequently used[8,11−17] for the determination of stability constants of lanthanide chloride; nevertheless, the UV−VIS spectroscopy has been widely used as well. Mukherji[20] described a spectrophotometric method for the analysis of microgram amounts of rare earth elements with xylenol orange (XO) at pH 6. This technique was useful to measure aqueous La^{3+} concentration in this research.

The purposes of this research were to determine the stability constants of La^{3+} complexes formed with Cl^-, at a constant temperature of 303 K, in several ionic strength $HClO_4$ media: 2 mol•dm^{-3}, 3 mol•dm^{-3}, and 4 mol•dm^{-3} and moreover to extrapolate to infinite dilution using the SIT (Bronsted−Guggenheim−Scatchard specific ion interaction theory) method.

Experimental Section

Materials. All reagents were analytical grade, and deionized water was used for the preparation of solutions.

The stock solution of lanthanum was prepared as follows: Lanthanum oxalate was precipitated from the nitrate solution with a saturated oxalic acid solution. This precipitate was separated and calcined at 653 K and again at 1073 K to obtain the oxide according to the literature.[22] The oxide was treated with nitric acid and later with a mixture 1:1 water:acetone. Finally, the crystals were dissolved in 10^{-3} mol•dm^{-3} hydrochloric acid.

The lanthanum stock solution was standardized by EDTA titration.[23,24] Previously, the pH had been adjusted at 7.2 with an ammonia hydroxide solution, and then 3 drops of pyridine and 3 drops of $4.5 \cdot 10^{-4}$ mol•dm^{-3} XO (from Sigma) solution were added. The lanthanum concentration in the stock solution was $1.77 \cdot 10^{-3}$ mol•dm^{-3}.

$(HD)_x$ was purchased as a 50 % solution in *n*-heptane (from Fluka), and the concentration used for solvent extraction experiments was adjusted by dilution with the same solvent. The organic phases were solutions of the dinonyl naphthalene sulfonic acid in *n*-heptane whose concentrations were (1, 4, and 8) % for (2, 3, and 4) mol•dm^{-3} ionic strength, respectively.

A $4.5 \cdot 10^{-4}$ mol•dm^{-3}, XO solution was prepared for each set of experiments. Appropriate portions of 0.5 mol•dm^{-3} acetic acid and 1.5 mol•dm^{-3} ammonia were mixed to give a buffer of pH 6, which was measured with a pH meter.

Procedures. (a) Spectrophotometric Measurements. A standard calibration curve for the range from $2.7 \cdot 10^{-6}$ mol•dm^{-3} to $2.5 \cdot 10^{-5}$ mol•dm^{-3} of La^{3+} was obtained as follows: Appropriate aliquots of the lanthanum stock solution were added to 3 cm^3 of $4.5 \cdot 10^{-4}$ mol•dm^{-3} XO solution, and the volume was completed up to 10 cm^3 with the pH 6 buffer solution. Absorbance was measured with a UV−VIS Spectrophotometer (Perkin-Elmer) against reagent blanks adjusted to the appropriate pH.

(b) Solvent Extraction. The experimental ionic strengths were (2, 3, and 4) mol•dm^{-3}. Aqueous phases were prepared as mixtures of HCl and $HClO_4$ solutions. For instance, 2 mol•dm^{-3} ionic strength was imposed increasing the volume from (0 to 2) cm^3 of a 2 mol•dm^{-3} HCl solution and decreasing from (2 to 0) cm^3 the volume of a 2 mol•dm^{-3} $HClO_4$ solution up to complete a constant final volume of 2 cm^3. In this way, proton concentration and ionic strength were constant. The lanthanum concentration was $8.8 \cdot 10^{-5}$ mol•dm^{-3}.

The organic phase solutions of $(HD)_x$ in *n*-heptane were pre-equilibrated prior to being used by a 24-h contact with the appropriate aqueous solutions in the absence of La^{3+}. Aliquots of 2 cm^3 of each aqueous and organic phase and 100 mm^3 of the lanthanum stock solution were shaken for 2.5 h in a water bath (Cole Parmer, Polystat) at 303 ± 0.02 K. The shaking time was taken from ref 17. Other authors[11] have reported that the equilibrium is reached in less than 1 h. Each experiment was done at least four times.

Lanthanum concentration was measured in aliquots of the aqueous phase before and after solvent extraction, first the pH was adjusted to 6.0, and then 3 cm^3 of a $4.5 \cdot 10^{-4}$ mol•dm^{-3}

XO solution was added. Final volume of 10 cm^3 was completed with a pH 6 buffer solution. Spectrophotometric measurements were made as described above.

Results and Discussion

Absorbance measurements obeyed the law of Lambert and Beer in the range from ($2.7 \cdot 10^{-6}$ to $2.5 \cdot 10^{-5}$) $mol \cdot dm^{-3}$, and the spectrophotometric calibration line obtained at $\lambda = 576$ nm and pH 6 was

$$\text{absorbance} = 20519\ [\mathrm{La}^{3+}] \quad (r^2 = 0.99) \tag{10}$$

According to this equation, the molar absortivity value (20519 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$) agrees with the 20500 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ previously given by Mukherji.[20]

The set of data were treated by means of both linear and second degree polynomial equations. The linear equations were as follows:

$$\frac{1}{D_1} = 0.7(\pm 0.1)[\mathrm{Cl}^-] + 0.46(\pm 0.09), \quad r^2 = 0.98 \text{ for } I = 2\ \mathrm{mol \cdot dm^{-3}} \tag{11}$$

$$\frac{1}{D_1} = 1.2(\pm 0.3)[\mathrm{Cl}^-] + 1.2(\pm 0.4), \quad r^2 = 0.98 \text{ for } I = 3\ \mathrm{mol \cdot dm^{-3}} \tag{12}$$

$$\frac{1}{D_1} = 0.5(\pm 0.2)[\mathrm{Cl}^-] + 0.5(\pm 0.4), \quad r^2 = 0.98 \text{ for } I = 4\ \mathrm{mol \cdot dm^{-3}} \tag{13}$$

and the polynomial equations were as follows:

$$\frac{1}{D_2} = 0.12(\pm 0.04)[\mathrm{Cl}^-]^2 + 0.51(\pm 0.08)[\mathrm{Cl}^-] + 0.51(\pm 0.07), \quad r^2 = 0.99 \text{ for } I = 2\ \mathrm{mol \cdot dm^{-3}} \tag{14}$$

$$\frac{1}{D_2} = 0.12(\pm 0.03)[\mathrm{Cl}^-]^2 + 0.96(\pm 0.08)[\mathrm{Cl}^-] + 1.3(\pm 0.1), \quad r^2 = 0.99 \text{ for } I = 3\ \mathrm{mol \cdot dm^{-3}} \tag{15}$$

$$\frac{1}{D_2} = 0.07(\pm 0.01)[\mathrm{Cl}^-]^2 + 0.43(\pm 0.06)[\mathrm{Cl}^-] + 0.6(\pm 0.1), \quad r^2 = 0.99 \text{ for } I = 2\ \mathrm{mol \cdot dm^{-3}} \tag{16}$$

Attempts were undertaken to fit the results to third-order polynomial equations, but it gave negative coefficients for $[\mathrm{Cl}^-]^3$ and $[\mathrm{Cl}^-]$.

The values of $\beta^{\mathrm{I}}_{\mathrm{La,Cl}}$ calculated with eqs (11 to 13) and both $\beta^{\mathrm{I}}_{\mathrm{La,Cl}}$ and $\beta^{\mathrm{I}}_{\mathrm{La,2Cl}}$ calculated using eqs (14 to 16) are shown in Table 1. The graphs of $1/D_2$ versus $[\mathrm{Cl}^-]$ obtained for (2, 3, and 4) $mol \cdot dm^{-3}$ ionic strengths are shown in Figure 1, where second-order polynomial lines are also included.

The standard deviation values of $\beta^{\mathrm{I}}_{\mathrm{La,Cl}}$ considering linear equations are so high that no statistical difference was found among data of the present work and refs (5 to 8) in the range from (1 to 4) M ionic strength. Therefore, these data were not used for the SIT method.

According to second-order polynomial equations, both LaCl^{2+} and $\mathrm{LaCl_2}^{+}$ species were present. The value of $\beta_{\mathrm{La,Cl}}$ for 2 $mol \cdot dm^{-3}$ ionic strength is identical to the one reported in ref 5, which was obtained by a potentiometric method. The stability constant values of LaCl^{2+} smoothly tend to decrease when ionic strength increases and are higher than the values of $\beta_{\mathrm{La,2Cl}}$. These latter values are statistically similar in the studied ionic strength range. Therefore, these data were not used for the SIT method, and a mean value was calculated taking the data of the present work and one given in the literature,[6] and it was $\beta^{1<I<4}_{\mathrm{La,2Cl}} = 0.17 \pm 0.11$. Such a value corresponds to the ionic strength range from (1 to 4) mol dm^{-3} and not necessarily to the infinite dilution.

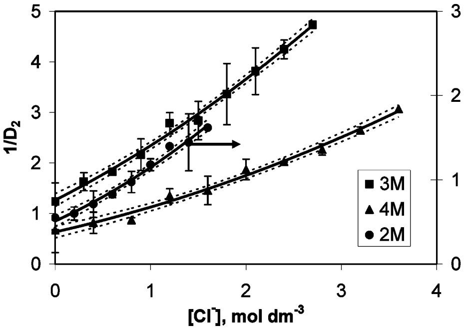

Figure 1. Graphs of $1/D_2$ vs $[\mathrm{Cl}^-]$, for La^{3+} in $\mathrm{HCl-HClO_4}$ mixtures at (2, 3, and 4) $mol \cdot dm^{-3}$ ionic strength; the 95 % confidence intervals are included. The polynomial equations are given in the text.

Thermodynamic data always refer to a selected standard state, and the Nuclear Energy Agency[25] has recommended the use of the SIT method for extrapolation to zero ionic strength. In the present work the SIT method was applied to the data of $\beta^{\mathrm{I}}_{\mathrm{La,Cl}}$. According to this method, the values of stability constants for lanthanum chlorides at zero ionic strength, $\beta^{0}_{\mathrm{La,Cl}}$, is related to the values at any ionic strength, $\beta^{\mathrm{I}}_{\mathrm{La,Cl}}$ by

$$\log \beta^{\mathrm{I}}_{\mathrm{La,Cl}} - \Delta z^2 D = \log \beta^{0}_{\mathrm{La,Cl}} - \Delta\epsilon I_{\mathrm{m}} \tag{17}$$

in which the ionic strength I_{m} and $\beta^{\mathrm{I}}_{\mathrm{La,Cl}}$ must be in $mol \cdot kg^{-1}$. The Debye–Hückel term (D) is expressed as follows:

$$D = \frac{A\sqrt[2]{I_{\mathrm{m}}}}{1 + Ba_j\sqrt[2]{I_m}} \tag{18}$$

where A and B are temperature-dependent constants, and a_j is the effective diameter of the hydrated ion j. The values of A and B at 303 K are[25] 0.5131 and $0.3291 \cdot 10^{-8}$, respectively. Several values have been proposed[25] for Ba_j ranging from 1.0 to 1.6; particularly, Scartchard proposed a value of $Ba_j = 1.5$. However, the parameter Ba_j is empirical and as such correlated to the ion interaction coefficients ϵ. ΔZ^2 is a sum function of the squared charges of the reacting ionic species:

$$\Delta z^2 = \Sigma z^2_{(\mathrm{products})} - \Sigma z^2_{(\mathrm{reactants})} = (z_{\mathrm{La}} - jz_{\mathrm{Cl}})^2 - {z_{\mathrm{La}}}^2 - j{z_{\mathrm{Cl}}}^2 \tag{19}$$

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

$$\Delta\epsilon = \epsilon(\mathrm{LaCl}^{2+}, \mathrm{ClO_4}^-) - \epsilon(\mathrm{H}^+, \mathrm{Cl}^-) - \epsilon(\mathrm{La}^{3+}, \mathrm{ClO_4}^-) \tag{20}$$

then, for reaction a and $j = 1$ eq 17 can be rewritten as

$$\log \beta^{\mathrm{I}}_{\mathrm{La,Cl}} + 6D = \log \beta^{0}_{\mathrm{La,Cl}} - \Delta\epsilon I_{\mathrm{m}} \tag{21}$$

According to eq 21, a linear relationship must be found when

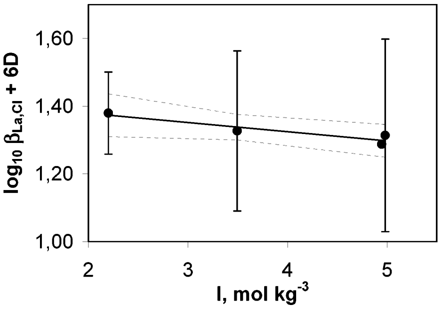

Figure 2. Log $\beta_{La,Cl} + 6D$ plotted as a function of ionic strength in molality. The values are of the present research and from ref 6. The 95 % confidence intervals are included, and the equation of the line is given in the text.

log $\beta^{I}_{La,Cl} + 6D$ is plotted versus I_m; in which the slope and the y-axis interception correspond to $-\Delta\epsilon$ and log $\beta^{0}_{La,Cl}$, respectively.

I_m and log $\beta^{I}_{La,Cl}$ were calculated in molality units considering molarity and density of solutions. A value of log $\beta^{I}_{La,Cl}$ was chosen from literature[6] considering that it was reported together with a value for the second species, just like those of the present work. Figure 2 shows the graph of log $\beta^{I}_{La,Cl} + 6D$ as a function of ionic strength in molality, considering $Ba_j = 1.5$ and weighted least-square regression. According to the linear regression equation (log $\beta^{I}_{La,Cl} + 6D = 1.43(\pm 0.12) - 0.03(\pm 0.03)I_m$; $r^2 = 0.9$ and $n = 4$), log $\beta^{0}_{La,Cl} = 1.43 \pm 0.12$. This value is quite similar to one reported for europium (1.38)[17] but higher than the others found for lanthanum.[1−3,9,10]

The values found in the literature[25] for $\epsilon(La^{3+}, ClO_4^-)$ and $\epsilon(H^+,Cl^-)$ are 0.47 and 0.12(±0.01), respectively, when the parameter $Ba_j = 1.5$. According to the slope value of the linear equation (Figure 2) $\Delta\epsilon = 0.03 \pm 0.03$ and then $\epsilon(LaCl^{2+}, ClO_4^-) = 0.62(\pm 0.03)$.

Distribution diagrams for (2, 3, and 4) mol·dm^{-3} were obtained using log $\beta^{0}_{La,Cl} = 1.43$ and log $\beta_{La,2Cl} = 0.17$ and MEDUSA program.[26] The diagrams showed that the $LaCl_2^+$ species was present in less than 1 %, the percentages of $LaCl^{2+}$ species were 65, 70, and 75, respectively, and the rest corresponded to La^{3+} species in the pH range form 0 to 7. At higher pH, the hydrolysis of lanthanum is more important.

Conclusions

The stability constants for the formation of the species $LaCl^{2+}$ were determined at different ionic strength, and it was observed that the values smoothly decreased as the ionic strength increases in the range studied. The stability constant for the species $LaCl^{2+}$ at infinite dilution was calculated using the SIT method, and it was similar to a value previously reported for europium.

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