ACIDIC AND REDOX PROPERTIES OF SOME LANTHANIDE IONS IN MOLTEN LiCl-KCl EUTECTIC

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ABSTRACT

We have studied the stability of some lanthanide(III) oxychlorides and oxides, especially those of the ceric group, in molten LiCl-KCl eutectic. Solubility products of oxychlorides and oxides have been deduced from the potentiometric titration curves of lanthanide chlorides by sodium carbonate. These values, combined with standard potentials of the Ln(III)/Ln(s) electrochemical systems determined from potentiometric and voltammetric measurements, have enabled us to establish potential-pO2 diagrams which summarize the properties of the lanthanide oxy-compounds. The possibilities of solubilizing lanthanide(III) oxychlorides and oxides by using gaseous reagents are discussed.

INTRODUCTION

The two main limiting factors for obtaining high efficiency in the electrowinning of metals from their chlorides are the presence of impurities and the metal solubility in the electrolyte. In this paper, only the first case has been taken into consideration, the second will be the subject of another paper. The major impurities are water, hydroxide and oxide anions, which can lead to the formation of metal oxychlorides and oxides (1). As a result, the physical properties of the electrolytic bath (viscosity, density, ...) change and the electrolysis yield often decreases.

So it is of primary importance for the electrowinning of lanthanide metals to study the lanthanide(III) oxychloride and oxide stabilities. The oxoacidic behavior (acceptor power towards O2- ion) of cerium(III) and yttrium(III) ions had been shown respectively in NaCl-KCl at 1000 K (2) and in NaCl at 1100 K (3), but no systematic study had been achieved previously.

We present here a study of the chemical and electrochemical stabilities of some lanthanide chlorides, oxychlorides and oxides, especially those of the ceric group, in molten LiCl-KCl eutectic.
EXPERIMENTAL RESULTS AND INTERPRETATION

- Technical.

The cell, the furnace, the programmable regulation and the preparation of the melt have already been described (4-7).

Potentials were measured by means of a reference electrode (Ag/Ag⁺ 0.75 mol.kg⁻¹). All the values are given vs. the standard chlorine electrode.

The values of $pO_2^-$ were deduced from potential measurements with an yttria-stabilized zirconia electrode, which has been shown to behave properly in the melt used. The description and the standardization procedure of this electrode were described earlier (4,8,9).

The voltammetric scans were performed with a Tacussel "PRT 30" fast-rise potentiostat coupled with a GSTP 3 function generator.

The i(E) curves were recorded on a XY Sefram TRP 10-100. The indicator electrode used was made from 0.5 mm diam. tungsten rod supplied by Johnson Matthey.

X-ray diffraction patterns were obtained with a C.G.R. diffractometer employing CoKα₁ radiation.

- Potentiometric titrations of Ln(III) by oxide ions.

Potentiometric titrations of Ln³⁺ were performed by addition of sodium carbonate, at 723 K. Fig. 1 gives the experimental curves obtained under low carbon dioxide pressures ($10^{-3}$<P(CO₂)/atm < $10^{-2}$). During these titrations, the variations of the oxide ion activity present only one equivalence point for α (mole number of CO₃²⁻ added per mole of total Ln(III)) equal to 1 for ceric lanthanides, and to 1.5 for yttrium. From that observation, we deduce that the titration reaction is the following:

$$\text{Ln}^{3+} + \text{CO}_3^{2-} + \text{Cl}^- \rightarrow \text{LnOCl}(s) + \text{CO}_2(g)$$

except in the case of yttrium for which insoluble oxide is directly obtained according to the reaction:

$$2 \text{Ln}^{3+} + 3 \text{CO}_3^{2-} \rightarrow \text{Ln}_2\text{O}_3(s) + 3 \text{CO}_2(g)$$

The precipitates obtained at the end of the titrations are colored as follows: white for lanthanum and cerium oxychlorides, pale-green for praseodymium oxychloride, grey-blue for neodymium oxychloride and white for yttrium oxide.

The conclusion from the titration curves has been confirmed by X-ray diffraction patterns of the recovered precipitates. In particular, no trace of oxide was visible on patterns for the oxychlorides.

- Electrochemical study.

The redox properties of ceric lanthanides were characterized by the joint use of several electrochemical techniques: potentiometry, (cyclic) voltammetry, chronoamperometry and current reversal...
chronopotentiometry (10). Only a part of this work is presented here.

- La$^{3+}$, Ce$^{3+}$ and Pr$^{3+}$ reduction:

Fig. 2-a shows the typical voltammograms for the reduction of lanthanum(III), cerium(III) and praseodymium(III), corrected for residual current and obtained from experiments carried out with a tungsten electrode (area A) [potential sweep rate = 0.2 V.s$^{-1}$]. These voltammograms present only one reduction peak, with a sharp variation of the current which can be interpreted as due to the formation of a metal deposit, according to the reaction:

$$
\text{Ln}^{3+} + 3e^- \rightarrow \text{Ln(s)}
$$

This is confirmed by the reoxidation peaks observed in cyclic voltammetry experiments (10). The reaction reversibility can be appreciated by semi-integral electroanalysis. Fig. 2-a shows the neopolarograms m(E) (11) which were deduced from the voltammograms by current semi-integration (12-15). The m(E) curves so obtained have been analysed by plotting the cologarithm of (m$_\infty$-m) as a function of potential (m$_\infty$ = maximum or limiting value of m). Fig. 2-b shows linear variations, the slopes of the straight lines being very close to the theoretical value for a reversible process. The numbers of faradays per mole of lanthanide (III) ion deduced from the experimental slopes are: 2.9 for lanthanum and cerium, and 3.0 for praseodymium. The voltammogram corresponding to the latter shows that the metal activity is equal to unity from the very beginning of the deposit. The diffusion coefficient values have been calculated from the limiting values m$_\infty$ of the reduction waves m(E), given by the relation:

$$
m$_\infty$ = nFAD^{1/2}|\text{Ln}^{3+}|
$$

We obtained from the experiments reported in Fig. 2: 7.2.10$^{-6}$, 5.8.10$^{-6}$ and 6.8.10$^{-6}$ cm$^2$.s$^{-1}$ respectively for D(La$^{3+}$), D(Ce$^{3+}$) and D(Pr$^{3+}$).

The standard potentials have been determined from the half-wave potentials on the m(E) curves by using the classical relations (16). The values obtained in the case of the experiments reported here are: -3.160 V, -3.155 V and -3.150 V for E° (La$^{3+}$/La(s)), E° (Ce$^{3+}$/Ce(s)) and E° (Pr$^{3+}$/Pr(s)). These values agree very well with those determined by potentiometry and other electrochemical techniques (10), given as a function of temperature in Table 1.

- Nd$^{3+}$ reduction:

Fig. 3-a shows that Nd$^{3+}$ is reduced into metal by a two-step process, differing from the one involved with the other lanthanides(III), and which has been also studied by semi-integral analysis. The neopolarogram of Fig. 3-a exhibits two waves whose relative heights do not vary with the potential sweep rate signifying that the first wave is not due to an adsorption process. So, we have to consider the existence of an intermediate oxidation state which probably corresponds to one of the neodymium sub-chlorides NdCl$_{2.37}$, NdCl$_{2.27}$ or NdCl$_{2}$ characterized by Druding and Corbett (17).
According to the value of the ratio of the limiting values $m_{1\infty}$ and $m_{2\infty}$, the two steps of Nd(III) reduction would be:

$$\text{Nd}^{3+} + e^{-} \rightarrow \text{Nd}^{2+}$$

followed by:

$$\text{Nd}^{2+} + 2e^{-} \rightarrow \text{Nd} \ (s)$$

This is confirmed by the logarithmic analysis of the neopolarogram (Fig. 3-b) according to the equation:

$$E_1 = E_1^{1/2} + \frac{RT}{F} \ln \left[ \frac{m_{1\infty} - m}{m_{1}} \right]$$

with:

$$E_1^{1/2} = E^\circ(\text{Nd}^{3+}/\text{Nd}^{2+}) + \frac{RT}{2F} \ln \frac{D(\text{Nd}^{3+})}{D(\text{Nd}^{2+})}$$

and:

$$E_2 = E_2^{1/2} + 0.5 \frac{RT}{F} \ln \left[ \frac{m_{2\infty} - m}{m} \right]$$

with:

$$E_2^{1/2} = E^\circ(\text{Nd}^{2+}/\text{Nd}(s)) + 0.5 \frac{RT}{F} \ln \left[ \frac{|\text{Nd}^{2+}|}{2} \right]$$

The experiments relative to the curves of Fig. 3 have led to the diffusion coefficient and the standard potential values:

$$D(\text{Nd}^{3+}) = 9.7 \times 10^{-6} \text{cm}^2 \cdot \text{s}^{-1} \quad ; \quad E^\circ(\text{Nd}^{3+}/\text{Nd}^{2+}) = -3.102 \ \text{V}$$

and:

$$E^\circ(\text{Nd}^{2+}/\text{Nd}(s)) = -3.123 \ \text{V}$$

Besides, by using the relation:

$$E^\circ(\text{Nd}^{3+}/\text{Nd}(s)) = \frac{1}{3} \left[ E^\circ(\text{Nd}^{3+}/\text{Nd}^{2+}) + 2 E^\circ(\text{Nd}^{2+}/\text{Nd}(s)) \right]$$

we obtained:

$$E^\circ(\text{Nd}^{3+}/\text{Nd}(s)) = -3.116 \ \text{V}$$

By experiments at various temperatures (10) we have determined the temperature-dependence of the standard potentials of the neodymium systems (table 1). The proximity of the values of the standard potentials relative to the two steps of the Nd(III) reduction is responsible for a noticeable solubility of the metal in the neodymium(III) chloride solutions according to the equilibrium:

$$\text{Nd}(s) + 2 \text{Nd}^{3+} \neq 3 \text{Nd}^{2+}$$

The constant of this equilibrium can be easily deduced from the standard potentials:

$$\log \left[ K/\text{mol.kg}^{-1} \right] = 2.51 - 1575 T^{-1}$$

in the temperature range from 650 to 850 K.

EXPLOITATION OF THE RESULTS

- **Solubility products of lanthanide(III) oxychlorides and oxides.**

  - Values deduced from the experimental titration curves. The lanthanide(III) oxychlorides and oxides can be dissolved into the melt according to the following equilibria:

$$\text{LnOCl}(s) \neq \text{Ln}^{3+} + \text{O}^{2-} + \text{Cl}^{-}$$
and:

\[ \text{Ln}_2\text{O}_3(s) \rightleftharpoons 2 \text{Ln}^{3+} + 3 \text{O}^{2-} \]

The solubility products are given by:

\[ K_s(\text{LnOCl}) = |\text{Ln}^{3+}| |\text{O}^{2-}| \]

and:

\[ K_s(\text{Ln}_2\text{O}_3) = |\text{Ln}^{3+}|^2 |\text{O}^{2-}|^3 \]

As in the case of a previous work concerning aluminum (4), we have employed a simulation method for determining the values of the solubility products. The functions \( \alpha = f(pO^{2-}) \) deduced from the equations of mass balance and mass action law are the following:

\[ \alpha = 1 + \text{Co}^{-1} \left\{ |\text{O}^{2-}| \left[ p(\text{CO}_2), K_d^{-1} + 1 \right] - K_s(\text{LnOCl}) \cdot |\text{O}^{2-}|^{-1} \right\} \] (1)

For yttrium:

\[ \alpha = 1.5 + \text{Co}^{-1} \left\{ |\text{O}^{2-}| \left[ p(\text{CO}_2), K_d^{-1} + 1 \right] - 1.5 \left[ K_s(\text{Y}_2\text{O}_3) \cdot |\text{O}^{2-}|^{-3} \right]^{1/2} \right\} \] (2)

In these expressions, \( K_d \) is the dissociation constant of \( \text{CO}_3^{2-} \) \( (K_d = p(\text{CO}_2), |\text{CO}_3^{2-}|^{-1} = 10^{-2.15} \text{ atm}) \) previously determined (4).

Titrination curves have been simulated from eq(1) and eq(2) by giving arbitrary values to the constants \( K_s \). The simulated curves which best fit the experimental points are represented on Fig. 1.

The corresponding values for \( K_s(\text{LnOCl}) \) and \( K_s(\text{Y}_2\text{O}_3) \) and the solubilities \( S \) are given in Table 2.

- Values deduced from the experimental standard potentials and from the literature thermochemical data. The equilibrium constants like the solubility products of metallic oxychlorides and oxides can be often calculated from the free energies of reactions between pure compounds, the activity coefficients of the metallic ions and oxide anion, and the activities of the components of the melt. Examples of this method of calculation can be found in the literature (18-21). We have obtained the solubility products by using (i) the activity coefficients of \( \text{Ln}^{3+} \) (collected in Table 3) derived from the standard potentials of Table 1 and from the formation free energies of pure lanthanide(III) chlorides (calculated from the literature data (22)), (ii) the activity coefficient of oxide ion determined according to the method indicated by Séon (1) and given by the relation:

\[ \log \gamma \left( \text{O}^{2-} \right) = 1.27 - 4650 T^{-1} \]

(iii) the activity of LiCl in the eutectic (23), and at last (iv) the free energies of the reactions of formation of solid oxychlorides (*) and oxides from pure metallic chlorides and lithium oxide (22, 24-29). Their values are given as a function of temperature in Table 4.

- Comparison between the values deduced from titration curve analysis (Table 2) and those calculated from thermodynamical data (Table 4) shows slight differences. This fact can be explained

(*) The temperature dependence of the heat capacities \( \text{Cp(CeOCl)} \) and \( \text{Cp(PrOCl)} \) has been estimated from data concerning the lanthanum and neodymium oxychlorides (22)
by noticing that the values obtained with the second method strongly depend on the accuracy of the thermochemical data. Yet, this method of calculation leads to pretty good predicted values: the shifts observed between them and those directly obtained from experiments are of about 5% for LaOCl, 10% for NdOCl and 14 and 20% respectively for CeOCl and PrOCl. The estimated value of $pK_s(Y_2O_3)$ presents a shift of around 15% from the experimental value.

**CONCLUSION**

The stabilities of the oxychlorides and oxides lead to a modification of the redox properties of lanthanides. This can be summarized under the form of potential-(oxo)acidity diagrams. The diagrams in Fig. 4 show the large stability domain of each oxychloride, so that it is impossible to envisage a selective precipitation or a selective chlorination of the lanthanide(III)oxychlorides.

The possibilities of solubilizing lanthanide(III) oxychlorides and oxides by using gaseous reagents, whose chlorinating powers were previously studied (9,29,30), have been examined. Only results with the gaseous HCl + H$_2$O and Cl$_2$ + O$_2$ mixtures, of an obvious interest for melt purification and lanthanide metals electrowinning, are given here. Diagrams of Fig. 5 have been established with the aid of the solubility products and in the case of the log $P$(HCl)-log $P$(H$_2$O) diagrams, the constant $K_1$ of the equilibrium:

$$2 \text{HCl}(g) + \text{O}_2^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(g) + 2\text{Cl}^-$$

is given as a function of temperature by the expression (9,29,30):

$$\log K_1 = -3.477 + 9.98 \times 10^{-3} \, T^{-1}$$

In the case of the log $P$(Cl$_2$) - log $P$(O$_2$) diagrams, the constant $K_2$ of the equilibrium:

$$\text{Cl}_2(g) + \text{O}_2^-(\text{aq}) \rightleftharpoons \frac{1}{2} \text{O}_2(g) + 2\text{Cl}^-$$

has a known value of (9,29,30):

$$\log K_2 = -0.027 + 6.912 \times 10^{-3} \, T^{-1}$$

From Fig. 5 one can note that it is possible to dissolve the oxychlorides with hydrogen chloride containing up to 80% (mol. per cent.) of water. This fact confirms the efficiency of the purification technique used for the solutions of lanthanide(III) chlorides in the melt. Fig. 5 also shows that chlorine can easily chlorinate the oxychlorides because the reaction:

$$\text{Cl}_2(g) + \text{LnOCl}(s) \rightleftharpoons \text{Ln}^{3+} + \frac{1}{2} \text{O}_2(g) + \text{Cl}^-$$

takes place even when Cl$_2$ + O$_2$ gaseous mixtures are very rich in oxygen up to 75 mol.% (value calculated for a total concentration of Ln(III) of approximately 1 mol.kg$^{-1}$, i.e. 20 wt%, currently used in classical electrolytic baths).

As final conclusions, we saw that the determination
of standard potentials and solubility products has led to interesting forecasts concerning the electrowinning of the lanthanide metals in molten LiCl-KCl eutectic. In particular, because the reduction potentials of the ceric lanthanide(III) chlorides are very close to each other and because alloys form (didymium for example), a selective electrolytic extractive method could not be envisaged. Besides, neodymium appeared to have a singular behavior among the ceric lanthanides because of the existence of the intermediate (+II) oxidation state which is responsible for the solubility of a part of the deposited metal, thus complicating the electrowinning of this metal. At last, the ceric lanthanide(III) oxychlorides have appeared not very stable, hence the evolution of chlorine at the anode, in an electrolytic process in molten chlorides, can certainly lead to a "self-purification" of the melted bath.

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Table 1: Standard potentials $E^\circ$ (V/vs.Cl$^-$/Cl$_2$ (1 atm)) of ceric lanthanide electrochemical systems in molten LiCl-KCl eutectic (molality scale, temperature range: 650 < $T$ < 850 K).

| Electrochemical systems | $E^\circ/V = A + B \cdot 10^{-4}T$ | $E^\circ/V$ at 723 K |
|-------------------------|-------------------------------------|---------------------|
| La$^{3+}$/La(s)         | -3.483 4.4                         | -3.165              |
| Ce$^{3+}$/Ce(s)         | -3.605 6.3                         | -3.150              |
| Pr$^{3+}$/Pr(s)         | -3.565 5.8                         | -3.146              |
| Nd$^{3+}$/Nd(s)         | -3.772 9.1                         | -3.114              |
| Nd$^{3+}$/Nd$^{2+}$     | -3.878 10.8                        | -3.097              |
| Nd$^{2+}$/Nd(s)         | -3.721 8.3                         | -3.121              |
| Gd$^{3+}$/Gd(s) (**)    | -3.500 5.5                         | -3.102              |
| Y$^{3+}$/Y(s) (**)      | -3.800 9.1                         | -3.142              |

Table 2: Solubility products $K_S$ and solubilities $S$ of ceric lanthanide oxychlorides and yttrium oxide (see text for definition) in molten LiCl-KCl eutectic at 723 K (molality scale).

| Initial concentration of lanthanide | $-\log K_S$ | $-\log S$ |
|-----------------------------------|-------------|-----------|
| LaOCl                             | 7.60        | 3.80      |
| CeOCl                             | 8.10        | 4.05      |
| PrOCl                             | 8.70        | 4.35      |
| NdOCl                             | 8.20        | 4.10      |
| Y$_2$O$_3$                        | 8.50        | 4.20      |
|                                  | 22.8        | 7.6       |

(*) from the work of Yang and Hudson (31)
(**) from the works of Hoshino and Plambeck (32) and Yang and Hudson (31)
Table 3: Activity coefficients $\gamma(\text{Ln}^{3+})$ of some lanthanide(III) chlorides in molten LiCl-KCl eutectic (molality scale, temperature range: $650 < T < 850$ K)

| LnCl$_3$ | $\log \gamma = A + 1000 \frac{B}{T}$ | $\log \gamma$ at 723 K |
|----------|--------------------------------------|------------------------|
| LnCl$_3$ | $-5.10$ 2.75                         | $-1.30$                |
| CeCl$_3$ | $-4.10$ 1.31                         | $-2.29$                |
| PrCl$_3$ | $-3.58$ 0.55                         | $-2.82$                |
| NdCl$_3$ | $-1.26$ -1.62                        | $-3.50$                |
| GdCl$_3$ ($\ast$) | $-4.00$ -1.06                  | $-5.47$                |
| YCl$_3$ ($\ast\ast$) | $2.02$ -7.24                      | $-7.99$                |

($\ast$) from the work of Yang and Hudson (31)

($\ast\ast$) from the works of Hoshino and Planbeck (32) and Yang and Hudson (31)
Table 4: Solubility products $K_S$ of lanthanide(III) oxychlorides and oxides (see text for definition) in molten LiCl-KCl eutectic (molality scale, temperature range: 650 < T < 850 K).

\[ -\log K_S = A + 1000 \frac{B}{T} \]

| LnOCl   | A   | B   | $-\log K_S$ at 723 K | $-\log S$ at 723 K |
|---------|-----|-----|----------------------|---------------------|
| LaOCl   | -2.69 | 7.43 | 7.59                 | 3.80                |
| CeOCl   | -1.23 | 5.91 | 6.94                 | 3.47                |
| PrOCl   | -0.86 | 5.68 | 7.00                 | 3.50                |
| NdOCl   | 1.86  | 4.12 | 7.56                 | 3.78                |
| GdOCl   | -0.84 | 5.07 | 6.17                 | 3.09                |

\[ -\log K_S = A + 1000 \frac{B}{T} \]

| Ln$_2$O$_3$ | A   | B   | $-\log K_S$ at 723 K | $-\log S$ at 723 K |
|------------|-----|-----|----------------------|---------------------|
| La$_2$O$_3$ | -1.34 | 9.05 | 11.2                 | 3.73                |
| Ce$_2$O$_3$ | 2.07  | 8.55 | 13.9                 | 4.63                |
| Pr$_2$O$_3$ | 3.37  | 7.75 | 14.1                 | 4.70                |
| Nd$_2$O$_3$ | 7.87  | 4.10 | 13.5                 | 4.51                |
| Gd$_2$O$_3$ | 2.03  | 9.35 | 15.0                 | 4.99                |
| Y$_2$O$_3$  | 12.65 | 4.81 | 19.3                 | 6.43                |
Fig. 1: Potentiometric titration curves of lanthanide(III) chlorides by sodium carbonate in molten LiCl-KCl eutectic at 723 K.

- : experimental measurements of $pO_2$^--
— : curve calculated assuming only the precipitation of stoichiometric LnOCl (Ln = La, Ce, Nd, Pr) or $Y_2O_3$. 
Fig. 2: Electrochemical study of the reduction of lanthanum(III), cerium(III) and praseodymium(III) in molten LiCl-KCl eutectic at 723 K (tungsten electrode).

a) ---- : voltammograms i(E). (v = 0.2 V.s⁻¹)
--- : corresponding "neopolarograms" m(E).

\[
\begin{align*}
|\text{La}^{3+}| &= 2.0 \times 10^{-1} \text{mol.kg}^{-1}; A = 5.1 \times 10^{-2} \text{cm}^2 \\
|\text{Ce}^{3+}| &= 9.6 \times 10^{-2} \text{mol.kg}^{-1}; A = 7.0 \times 10^{-2} \text{cm}^2 \\
|\text{Pr}^{3+}| &= 6.9 \times 10^{-2} \text{mol.kg}^{-1}; A = 5.8 \times 10^{-2} \text{cm}^2
\end{align*}
\]

b) : logarithmic analysis of m(E) curves.
Fig. 3: Electrochemical study of the reduction of neodymium(III) in molten LiCl-KCl eutectic at 723 K.

a) ---- : voltammogram $i(E)$, ($v = 0.16 \text{ V.s}^{-1}$)

+++++ : corresponding "neopolarogram" $m(E)$

------ : simulated $m(E)$ curve.

$|\text{Nd}^{3+}| = 8.54.10^{-2} \text{ mol.kg}^{-1}$

b) : logarithmic analysis of $m(E)$ curve.

----- : experimental curves

----- : theoretical slopes.
Fig. 4: Potential-pO²⁻ equilibrium diagrams of ceric lanthanides in molten LiCl-KCl eutectic at 723 K (concentration = 1 mol.kg⁻¹)
Fig. 5: Prediction of the solubilization of lanthanide(III) oxychlorides and oxides in molten LiCl-KCl eutectic at 723 K, by using gaseous HCl + H₂O and Cl₂ + O₂ mixtures.