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Calorimetric study of the reaction between lanthanoid trifluoromethanesulphonates and hexamethylphosphoramide (HMPA) in ethanolic solution

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Abstract

Compounds between trifluoromethanesulphonates and HMPA were prepared by reaction of the salt and ligand dissolved in ethanol and acetone, respectively, on water bath. The compounds are characterized by CHN, IR and TG.

From solution calorimetry and appropriate thermodynamic cycles, the standard molar enthalpies of acid–basic reaction adducts have been determined. Calorimetric measurements were performed using a Solution Calorimeter System, at 298.15 K, in ethanolic solution. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lanthanide complexes containing HMPA as ligand have been extensively studied by several authors. Emphasis has been given to the synthesis, characterization and different composition obtained [1].

This paper reports on the calorimetric study of the reactions between hydrated lanthanoid trifluoromethanesulphonates with HMPA in ethanolic solution carried out in order to determine the dissolution enthalpies and acid–base enthalpies for the reaction of the hydrated salt with HMPA.

The thermal behavior of hydrated lanthanide trifluoromethanesulfonate has been investigated by Roberts and Bykowski [2].

2. Experimental

The adducts with HMPA (Aldrich) were prepared by new route, consisting in a reaction of the trifluoromethanesulfonate salts and ligand dissolved in ethanol (Merck) and acetone (Merck) respectively, on a water bath. The mixture was then left at low temperature until precipitation. The crystals were dried in vacuo, over anhydrous calcium chloride (Reagen). The compounds obtained were $Ln(CF_3SO_3)_3 \cdot n HMPA$, where $n = 6$ for La, Nd and Gd and $n = 4$ for Tb, characterized by CNH and the metal content by complexometric titration with EDTA [3].

Calorimetric measurements were performed using a Calorimeter Solution System at 298.15 K, in ethanol solutions [4–6].

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Table 1
Standard enthalpies

Ln(III)	Equation	$\Delta H_i^\ominus$/(kJ mol^{-1})
	Eq. (1)	
La	$\Delta H_1^\ominus$	10.39 ± 0.10
Nd	$\Delta H_1^\ominus$	18.56 ± 0.19
Gd	$\Delta H_1^\ominus$	11.35 ± 0.08
Tb	$\Delta H_1^\ominus$	4.90 ± 0.04
	Eq. (2)	
HMPA	$n\Delta H_2^\ominus$	10.73 ± 0.08
	Eq. (3)	
La	$\Delta H_3^\ominus$	12.02 ± 0.08
Nd	$\Delta H_3^\ominus$	13.07 ± 0.78
Gd	$\Delta H_3^\ominus$	10.35 ± 0.01
Tb	$\Delta H_3^\ominus$	10.27 ± 1.27
	Eq. (4)	
La	$\Delta H_4^\ominus$	85.56 ± 0.08
Nd	$\Delta H_4^\ominus$	95.76 ± 0.01
Gd	$\Delta H_4^\ominus$	78.92 ± 0.06
Tb	$\Delta H_4^\ominus$	58.09±0.01
	Eq. (5)	
H_2O	$\Delta H_5^\ominus$	1.86 ± 0.10

For the enthalpy determination, the substances were sealed in very thin walled vials. After temperature and pressure equilibration ($P^\ominus = 10132$ Pa and $T^\ominus = 298.15$ K), the vials were broken.

The standard dissolution enthalpies for the following systems were determined:

$$\mathrm{LnX_3 \cdot 9H_2O_{(s)} + EtOH_{(l)} \rightarrow LnX_3 \cdot 9H_2O_{(sol)}} \quad \Delta H_{(1)}^\ominus \tag{1}$$

$$\mathrm{nHMPA_{(l)} + EtOH_{(l)} \rightarrow nHMPA_{(sol)}} \quad \Delta H_2^\ominus \tag{2}$$

$$\mathrm{LnX_3 \cdot 9H_2O_{(sol)} + nHMPA_{(l)} \rightarrow LnX_3 \cdot nHMPA_{(sol)} + 9H_2O} \quad \Delta H_3^\ominus \tag{3}$$

$$\mathrm{LnX_3 \cdot nHMPA_{(s)} + EtOH_{(l)} \rightarrow LnX_3 \cdot nHMPA_{(sol)}} \quad \Delta H_4^\ominus \tag{4}$$

$$\mathrm{9H_2O_{(sol)} + yEtOH_{(l)} \rightarrow 9H_2O_{(sol)}} \quad \Delta H_5^\ominus \tag{5}$$

where $X = F_3C–SO_3$; $n = 6$ for La, Nd, Gd and $n = 4$ for Tb.

The standard acid–base enthalpies, $\Delta H_R^\ominus$ were based on the thermodynamic cycle

$$\begin{tikzcd}
\mathrm{LnX_3.9H_2O_{(s)}} + \arrow[d, "\Delta H_1^\ominus"', "\mathrm{EtOH}"] & \mathrm{nHMPA_{(l)}} \arrow[r, "\Delta H_R^\ominus"] \arrow[d, "n\Delta H_2^\ominus"] & \mathrm{LnX_3.nHMPA_{(s)}} + \arrow[d, "\mathrm{EtOH}"', "\Delta H_4^\ominus"] & \mathrm{9\,H_2O_{(l)}} \arrow[d, "\mathrm{EtOH}"', "\Delta H_5^\ominus"] \\
\mathrm{LnX_3.9H_2O_{(sol.)}} + & \mathrm{nHMPA_{(l)}} \arrow[r, "\Delta H_3^\ominus"] & \mathrm{Ln(HMPA)_3\,.X_{3(sol.)}} + & \mathrm{9H_2O_{(sol.)}}
\end{tikzcd}$$

Thus, $\Delta H_R^\ominus = \Delta H_1^\ominus + \Delta H_3^\ominus - \Delta H_4^\ominus - 9\Delta H_5^\ominus$

ΔH in the various processes was calculated from the equation

$$\Delta H = -\omega \frac{d_r}{d_{\mathrm{cal}}}$$

where d_r and d_{cal} are the dissolution distances and the electrical calibration of the calorimeter, respectively, in the enthalprogram, and $-\omega$ is the electrical work involved in the transition between T_1 and T_2 temperatures, assuming that the calorimeter is isoperhybolic. The average values of $\Delta H_i^\ominus$ were determined by performing several measurements at different concentrations and applying the minimum square-root technique [4–6].

3. Results and discussion

Table 1 shows the enthalpies calculated for the several processes involving hydrated lanthanum, neodymium, gadolinium and terbium salts and complexes with HMPA.

Table 2 list the standard acid–base enthalpy values, $\Delta H_R^\ominus$.

Table 2
Standard acid–base enthalpies, $\Delta H_R^{\ominus}$

Ln (III)	$\Delta H_R^{\ominus}$
La	-79.89 ± 0.08
Nd	-80.87 ± 0.63
Gd	-73.96 ± 0.80
Tb	-59.25 ± 1.20

From these results, it is possible to note (Table 2) that the acidity increases from lanthanum to neodymium and then decreases, following the order: $Nd^{3+} > La^{3+} > Gd^{3+} > Tb^{3+}$.

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