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Note

Thermochemical study of the reaction between some lanthanoid trifluoromethanesulfonates and dimethylacetamide (DMA) in ethanolic solution

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Abstract

Calorimetric studies involving the reaction of lanthanoid trifluoromethanesulfonate complexes with dimethylacetamide in ethanolic solution were performed, in order to determine the dissolution standard enthalpies and acid-base enthalpies for the reaction of the hydrated salts with DMA. Comparisons with dimethylformamide (DMF) reactions were made.

INTRODUCTION

Complexes between lanthanoid trifluoromethanesulfonates and amides and thermal studies of them have been described [1–5].

In this note we report the study of a new series of trifluoromethanesulfonate complexes with dimethylacetamide (DMA) employing calorimetry in ethanolic solution to determine the dissolution standard enthalpies and acid–base enthalpies for the reaction of the hydrated salts with DMA.

EXPERIMENTAL

The hydrated trifluoromethanesulfonates were prepared as described in ref. 5. Complexes with the compositions $[Ln(DMA)_n(H_2O)_6](F_3C{-}SO_3)_3$ ($n = 3$ or 2 depending on the lanthanoid and the synthetic procedure)

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were prepared according to ref. 1. The calorimetric system and the procedures are given in ref. 5.

GENERAL CONSIDERATIONS

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

$$\begin{tikzcd}
LnX_3 \cdot 9H_2O(s) \arrow[d, "\Delta H^{\ominus} = 0"] & + n\ DMA(l) \arrow[r, "\Delta H_R^{\ominus}"] \arrow[d, "(EtOH)"', "n\Delta H_2^{\ominus}"] & {[Ln(DMA)_n(H_2O)_6]X_3(s)} \arrow[d, "(EtOH)"', "\Delta H_4^{\ominus}"] & + 3H_2O(l) \arrow[d, "(EtOH)"', "3\Delta H_5^{\ominus}"] \\
LnX_3 \cdot 9H_2O(s) & + n\ DMA(sol) \arrow[r, "\Delta H_3^{\ominus}"] & {[Ln(DMA)_n(H_2O)_6]X_3(sol)} & + 3H_2O(
\end{tikzcd}$$

in which $X = F_3C{-}SO_3$; $n = 3$ for Ln = La, Nd, Sm or Gd and $n = 2$ for Ln = Lu. Thus $\Delta H_R^{\ominus} = n\Delta H_2^{\ominus} + \Delta H_3^{\ominus} - \Delta H_4^{\ominus} - 3\Delta H_5^{\ominus}$.

In the different cases ΔH was calculated from the equation

$$\Delta H = -w \frac{d_r}{d_{calc}}$$

where d_r and d_{calc} are the dissolution distances and an electrical calibration of the calorimeter, respectively, in the enthalpogram, and $-w$ is the electrical work involved in the transition between temperatures T_1 and T_2 due to the processes, assuming that the calorimeter is isoperibolic. The average values of ΔH_i were determined by performing several measurements at different concentrations and applying the minimum square-root technique.

RESULTS AND DISCUSSION

Table 1 lists the standard enthalpies calculated for the processes involving hydrated lanthanum, neodymium, samarium, gadolinium and lutetium.

The acid–base enthalpies in ethanolic solution for the equation

$$ln(F_3C{-}SO_3)_3 \cdot 9H_2O(sol) + n\ DMA(sol) \xrightarrow{\Delta H^{\ominus}_{(EtOH)}} ln(F_3C{-}SO_3)_3(DMA)_n(H_2O)_6(sol) + 3H_2O(sol)$$

considering that

$$ln(F_3C{-}SO_3)_3 \cdot 9H_2O(s) \xrightarrow[\Delta H_1^{\ominus}]{EtOH(l)} ln(F_3C{-}SO_3) \cdot 9H_2O(sol)$$

are calculated by means of the expression

$$\Delta H^{\ominus}_{(EtOH)} = \Delta H_3^{\ominus} - \Delta H_1^{\ominus}$$

Table 2 shows the standard acid–base enthalpy values $\Delta H_R^{\ominus}$ and $\Delta H^{\ominus}_{(EtOH)}$.

TABLE 1

Standard enthalpies

Ln	Equation	$\Delta H_i^\ominus$ (kJ mol^{-1})
La	$\Delta H_1^\ominus$	10.39 ± 0.10
Nd		18.56 ± 0.19
Sm		14.51 ± 0.04
Gd		11.35 ± 0.08
Lu		12.92 ± 0.06
La	$\Delta H_3^\ominus$	4.65 ± 0.05
Nd		5.75 ± 0.07
Sm		10.38 ± 0.07
Gd		3.65 ± 0.01
Lu		21.44 ± 0.01
La	$\Delta H_4^\ominus$	58.96 ± 0.03
Nd		95.05 ± 0.95
Sm		71.37 ± 0.65
Gd		47.37 ± 0.01
Lu		40.04 ± 0.87
	$\Delta H_2^\ominus$	0.98 ± 0.01
	$\Delta H_5^\ominus$	−1.86 ± 0.01

TABLE 2

Standard acid–base enthalpies $\Delta H_R^\ominus$ and $\Delta H_{(EtOH)}^\ominus$

Ln	$\Delta H_R^\ominus$ (kJ mol^{-1})	$\Delta H_{(EtOH)}^\ominus$ (kJ mol^{-1})
La	−45.79 ± 1.03	−5.74 ± 0.11
Nd	−80.78 ± 0.95	−12.81 ± 0.20
Sm	−52.47 ± 0.65	−4.13 ± 0.08
Gd	−35.20 ± 0.03	−7.70 ± 0.08
Lu	−11.06 ± 0.87	+8.52 ± 0.06

The higher values of $\Delta H_R^\ominus$ as compared with those obtained with dimethylformamide (DMF) lanthanoid trifluoromethanesulfonate complexes (Ln = La, Nd, Gd) are attributed to the higher basicity of DMA compared with DMF [5]. It is also relevant to note that the acidity of the species follows the order $Nd^{3+} > La^{3+} > Sm^{3+} > Gd^{3+} > Lu^{3+}$.

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