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Note

CALORIMETRIC STUDY OF THE REACTION BETWEEN LANTHANOID TRIFLUOROMETHANESULPHONATES AND DIMETHYLFORMAMIDE (DMF) IN ETHANOLIC SOLUTION

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INTRODUCTION

The reaction of hydrated lanthanoid trifluoromethanesulphonates with DMF, giving rise to complexes of general composition $[Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3$, was studied [1]. The compounds were characterised by several techniques [1] including thermal decomposition [2].

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

EXPERIMENTAL

The hydrated salts of composition $Ln(CF_3SO_3)_3 \cdot 9H_2O$ were prepared by reaction of basic lanthanoid carbonates with trifluoromethanesulphonic acid in aqueous solution, followed by evaporation of the solution. The crystals were separated and stored in a desiccator over anhydrous calcium chloride. The DMF and anhydrous ethanol were Merck products.

A calorimetric system constructed at the Federal University of Rio Grande do Norte [3] was used. For enthalpy determination, the substances were sealed in very thin walled vials.

After temperature and pressure equilibration ($P^{\ominus} = 101325$ Pa and $T^{\ominus} = 298.15$ K), the vials were broken.

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GENERAL CONSIDERATIONS

The standard dissolution enthalpies for the following systems were determined:

a) $\mathrm{Ln(CF_3SO_3)_3 \cdot 9H_2O(s) + EtOH(l) = Ln(CF_3SO_3)_3 \cdot 9H_2O(sol.)}$ $\Delta H_1^{\ominus}$

b) $n\mathrm{DMF(l) + EtOH(l)} = n\mathrm{DMF(sol.)}$ $n\,\Delta H_2^{\ominus}$

c) $\mathrm{Ln(CF_3SO_3)_3 \cdot 9H_2O(s) + 3DMF(sol.)}$

$\mathrm{= [Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3(sol.) + 3H_2O(sol.)}$ $\Delta H_3^{\ominus}$

d) $\mathrm{[Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3(s) + EtOH(l)}$

$\mathrm{= [Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3(sol.)}$ $\Delta H_4^{\ominus}$

e) $n\mathrm{H_2O(l) + EtOH(l)} = n\mathrm{H_2O(sol.)}$ $n\,\Delta H_5^{\ominus}$

The standard acid–base enthalpies, $\Delta H_{\mathrm{R}}^{\ominus}$, were based on the thermodynamic cycle

$$\begin{tikzcd}
\mathrm{Ln(CF_3SO_3)_3 \cdot 9H_2O(s)} \arrow[d, "\Delta H^{\ominus} = 0"] & \mathrm{+3DMF(l)} \arrow[r, "\Delta H_{\mathrm{R}}^{\ominus}"] \arrow[d, "3\,\Delta H_2^{\ominus}"] & \mathrm{[Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3(s)} \arrow[d, "\Delta H_4^{\ominus}"'] & \mathrm{+H_2O(l)} \arrow[d, "3\,\Delta H_5^{\ominus}"'] \\
\mathrm{Ln(CF_3SO_3)_3 \cdot 9H_2O(s)} & \mathrm{+3DMF(sol.)} \arrow[r, "\Delta H_3^{\ominus}"] & \mathrm{[Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3(sol.)} & \mathrm{+H_2O(sol.)}
\end{tikzcd}$$

Thus

$$\Delta H_{\mathrm{R}}^{\ominus} = 3\,\Delta H_2^{\ominus} + \Delta H_3^{\ominus} - \Delta H_4^{\ominus} - 3\,\Delta H_5^{\ominus}$$

ΔH in the several processes was calculated from the equation

$$\Delta H = -w \frac{d_{\mathrm{r}}}{d_{\mathrm{calc.}}}$$

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 isoperhibolic. The average values of $\Delta H_i^{\ominus}$ were determined by performing several measurements at different concentrations and applying the minimum square-root technique.

RESULTS AND DISCUSSION

Table 1 lists the enthalpies calculated for the several processes involving hydrated lanthanum, neodymium, gadolinium and dysprosium salts and complexes. Table 2 shows the standard acid–base enthalpy values, $\Delta H_{\mathrm{R}}^{\ominus}$.

TABLE 1

Standard enthalpies

Ln	Equation	$\Delta H_i^\ominus$ (kJ mol^{-1})
La	a) $\Delta H_1^\ominus$	10.39 ± 0.10
Nd	$\Delta H_1^\ominus$	18.56 ± 0.19
Gd	$\Delta H_1^\ominus$	11.35 ± 0.08
Dy	$\Delta H_1^\ominus$	4.90 ± 0.04
La	c) $\Delta H_3^\ominus$	3.65 ± 0.05
Nd	$\Delta H_3^\ominus$	4.70 ± 0.07
Gd	$\Delta H_3^\ominus$	2.66 ± 0.01
Dy	$\Delta H_3^\ominus$	1.00 ± 0.5
La	d) $\Delta H_4^\ominus$	44.79 ± 0.6
Nd	$\Delta H_4^\ominus$	79.02 ± 0.01
Gd	$\Delta H_4^\ominus$	35.08 ± 0.21
Dy	$\Delta H_4^\ominus$	22.10 ± 0.10
–	b) $\Delta H_2^\ominus$	0.89 ± 0.10
–	e) $\Delta H_5^\ominus$	−1.86 ± 0.10

With these results it is possible to determine the standard acid–base enthalpies in ethanolic solution for the equation

$$\mathrm{Ln(CF_3SO_3)_3 \cdot 9H_2O(sol.) + 3DMF(sol.)}$$

$$\rightarrow \mathrm{[Ln(DMF)_3(H_2O)_6](CF_3SO_3)_3(sol.) + 3H_2O(sol.)} \qquad \Delta H^\ominus_{(\mathrm{EtOH})}$$

Thus

$$\Delta H^\ominus_{(\mathrm{EtOH})} = \Delta H_3^\ominus - \Delta H_1^\ominus \quad \text{(See Table 2)}$$

It is also possible to note from Table 2 that the acidity increases from lanthanum to neodymium and then decreases, following the order: $\mathrm{Nd^{3+}} > \mathrm{La^{3+}} > \mathrm{Gd^{3+}} > \mathrm{Dy^{3+}}$.

TABLE 2

Standard acid–base enthalpies, $\Delta H_\mathrm{R}^\ominus$ and $\Delta H^\mathrm{R}_{(\mathrm{EtOH})}$

Ln	$\Delta H_\mathrm{R}^\ominus$ (kJ mol^{-1})	$\Delta H^\ominus_{(\mathrm{EtOH})}$ (kJ mol^{-1})
La	−38.5 ± 0.62	−6.74 ± 0.11
Nd	−71.65 ± 0.16	−13.86 ± 0.20
Gd	−29.75 ± 0.26	−8.69 ± 0.08
Dy	−18.4 ± 0.53	−3.90 ± 0.50

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