Competitive Equilibria in Lanthanide Trifluoromethanesulfonate Solutions in Propylene Carbonate Containing a 15-Crown-5 Ether*

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The study of lanthanide complexes with iono-phores has been an active field of research during the last twelve years [1–2]. Despite the large number of crown ether complexes which have been reported, there is still little information concerning their behaviour in solution. In this communication, we report a competitive UV–Vis spectrophotometric investigation of the following systems (Ln = lanthanide): $Ln(CF_3SO_3)_3$ in anhydrous propylene carbonate (PC), in the presence of 15-crown-5 (15C5) or t-butylbenzo-15-crown-5 (ButB15C5) ether and of perchlorate anions. The competitive chromophore chosen was the pyridyl-2-azo-*p*-dimethylaniline (PADA) and stability constants were found by spectral simulation.

Experimental

The lanthanide triflates were synthesized from the oxides (purity ≥ 99.99%) and from trifluoromethanesulfonic acid (Fluka, purum). The white crystals were dried first in a dessicator over KOH and then under high vacuum (5×10^{-6} mm Hg) with progressive heating up to 80 °C.

The ButB15C5 ligand was synthesized according to ref. 3. The 15C5 ether (Fluka, purum) was purified by distillation and dried. PADA (*trans*-isomer, Sigma) was used without further purification. Propylene carbonate (Fluka, distilled) was purified according to ref. 4. The solutions were prepared in a glove-box (N_2 atmosphere with less than 10 ppm water) and their water content (10–40 ppm) was determined by Karl Fischer titration.

Conductivity measurements were performed at 25.0 ± 0.2 °C with a Metrohm 660 conductimeter. Absorption spectra were recorded either with a Perkin-Elmer Hitachi Model 340 or with a Perkin-Elmer Lambda-7 spectrophotometer, using calibrated cells. The reproducibility of the absorbances was ±0.002 unit. Data were analysed by means of the SPEC-FIT prpgram [5]. Standard deviations (2σ) are indicated in parentheses.

Results

The interaction between PADA and Ln(III) ions was studied first. At low ligand concentration, only 1:1 complexes were observed, while both 1:1 and 1:2 complexes had to be introduced into the model in order to fit the experimental spectra when the PADA concentration was increased. Stability constants, expressed in terms of concentrations are reported in Table I. They increase as the atomic number of the Ln(III) ion increases. Perchlorate was added to the solutions in order to maintain a constant ionic strength. It is known that this anion associates with Ln(III) ions in organic solvents [6–8]. Moreover, triflate anions have approximately the same coordinating ability as perchlorate anions, as has been demonstrated for La(III) solutions in methanol [8]. To assess the extent of anion association, conductivity measurements were performed on $Sm(CF_3SO_3)_3$ solutions 10^{-3} M in PC containing either PADA, 15C5 ether or both. The results are presented in Table II, along with the molar conductance of

TABLE I. Stability Constants at 25.0 ± 0.2 °C of the Complexes between PADA and $Ln(CF_3SO_3)_3$ [a]

	Pr[b]	Nd	Sm	Tb	Yb
Log β_1	3.50(8)	4.48(6)	4.52(4)	6.0(2)	6.3(4)
Log β_2	3.1(2)	c	c	c	c

[a] [PADA] = 5×10^{-4} M, [Ln] = 0.2–2.5×10^{-3} M, [Et_4NClO_4] = 0.1 M. [b] [PADA] = 5×10^{-3} M, [Ln] = 0.2–8×10^{-3} M, [Et_4NClO_4] = 0.1 M. [c] 1:2 complexes not observed for this ligand concentration.

TABLE II. Molar Conductivity (Ω^{-1} cm^2 mol^{-1}) at 25.0 ± 0.2 °C of Reference Salts and Samarium Triflate Solutions 10^{-3} M in Propylene Carbonate

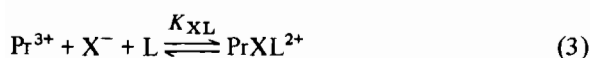| Solute	Λ_M	Type of electrolyte
Et_4NClO_4	25.2	1:1
$(Et_4N)_2[Co(SCN)_4]$	49.8	2:1
$(Et_4N)_3[Fe(SCN)_6]$	75.8	3:1
$(n\text{-}Bu_4N)_3[Fe(CN)_6]$	74.3	3:1
$Sm(CF_3SO_3)_3$	48.1	2:1
$Sm(CF_3SO_3)_3$ + 15C5(2.3×10^{-3} M)	52.9	2:1
$Sm(CF_3SO_3)_3$ + PADA(9×10^{-4} M)	46.8	2:1
$Sm(CF_3SO_3)_3$ + 15C5 + PADA	54.7	2:1

reference salts. In these solutions, $Sm(CF_3SO_3)_3$ behaves as a 2:1 electrolyte and little anion dissociation occurs upon addition of PADA or 15C5. In the presence of a supporting electrolyte, the reacting species is therefore $[LnX_n]^{(3-n)+}$, with $X = ClO_4^-$ or $CF_3SO_3^-$ and $n = 1$ or eventually 2. Indeed, the existence of macrocyclic complexes of $[LnX_2]^+$ entities is well documented, both in the solid state [1–2] and in solution [9–10]. The association constant for the $[Ln(ClO_4)]^{2+}$ species was calculated from a series of measurements on Ln(III)/PADA/15C5 or ButB15C5/ClO_4^- systems in which both the ligand and the perchlorate concentrations were varied:

$$K_{ClO_4} = [Ln(ClO_4)^{2+}]/[ClO_4^-] \cdot [Ln^{3+}]$$

Log K_{ClO_4} values of 2.08(6) and 1.84(5) were found for Ln = Pr and Sm, respectively, in good agreement with the values calculated from FT-IR spectra of $Ln(ClO_4)_3$ solutions in acetonitrile (1.8, 1.9 and 2.1 for Ln = Eu, Tb, Er [7]).

The potential of the competitive spectrophotometric method was further checked by investigating two systems containing the Pr(III) ion: Pr/ButB15C5/ClO_4^- and Pr/PADA/ButB15C5/ClO_4^-. For the first system, measurements were made on the 278 nm band of the crown ether, which shifts to 270 nm upon complexation. Using the following model with $X = ClO_4^-$ or $CF_3SO_3^-$, L = ButB15C5:

$$Pr^{3+} + X^- \underset{}{\overset{K_X}{\rightleftharpoons}} PrX^{2+} \qquad (1)$$

$$PrX^{2+} + L \underset{}{\overset{K_L}{\rightleftharpoons}} PrXL^{2+} \qquad (2)$$

$$Pr^{3+} + X^- + L \underset{\phantom{K_{XL}}}{\overset{K_{XL}}{\rightleftharpoons}} PrXL^{2+} \qquad (3)$$

one finds log $K_L = 3.34(6)$ if eqn. (2) only is taken into consideration ($[ClO_4^-]$ between 0 and 0.1 M),

and log $K_L = 3.49(11)$ if eqns. (1) to (3) are considered. For the second system, measurements were performed on the PADA bands at 430 nm (free) and 560 nm (complexed). In addition to eqns. (1) to (3), the formation of the following species was taken into consideration: $PrX(PADA)_n^{2+}$ ($n = 1$ and 2) and $PrX(PADA) \cdot L^{2+}$; the calculated log K_L value is 3.2(2), in good agreement with the above values and with the data reported by Massaux and Desreux [11] on the basis of a potentiometric determination (3.60(8)).

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