Solubilities, Solubility Products and Solution Chemistry of Lanthanon Trifluoride–Water Systems[†]

Manchery P. Menon and Jeffrey James

Department of Chemistry, Savannah State College, Savannah, Georgia, U.S.A.

Solubilities and solubility products of 14 lanthanon trifluorides $(LnF_3 \cdot 0.5H_2O)$ have been determined using conductometric, potentiometric and radiometric techniques. The solubilities and the averages of selected pK_{sp} values from literature and from our own work, that do not differ by more than one unit, show three maxima when plotted against the atomic number of lanthanons. Standard enthalpy change measured from the temperature-dependence plots of K_{sp} and the free-energy change calculated from K_{sp} of the trifluorides fall within the range 30–60 kJ mol⁻¹ and 78–103 kJ mol⁻¹, respectively, in most cases. Standard entropy change calculated from the enthalpy and free energy changes ranges from -47 to -294 J K⁻¹ mol⁻¹. The stability constants determined for the monofluoride complexes fall within the range of reported values, but those for the difluoride complexes are much higher than the fewer values that are found in literature. Lanthanon trifluorides were found to be least soluble in water at pH 3-4.

The Commission for the Solubility Data Project organized by the International Union of Pure and Applied Chemistry almost a decade ago seeks to establish a data base for the solubility of gases, liquids and solids in liquids and solids. Siekierski and Mioduski have been deputed to compile the solubility data on lanthanon halides.¹ In contrast to other lanthanon trihalides the solubility information concerning the sparingly soluble lanthanon trifluorides is generally presented in the form of the solubility product, K_{sp} .² It is not sometimes clear whether the solubility product is the true thermodynamic solubility product, K_{so} , based on activities or those computed in terms of stoichiometric concentration of ions in aqueous solution. Burgess and Kijowski² have listed several sets of pK_{sn} values for all lanthanon trifluorides (except PmF₃) reported by several authors using various techniques. However, agreement among values for a given fluoride is less than satisfactory, the difference being as high as three units (three orders of magnitude in K_{sp} in some cases. Although two sets of older data show a steady decrease in pK_{sp} from LaF₃ to LuF₃^{3,4} more recent values show an increase from LaF₃ to EuF₃ and then a decrease to ErF_3 .⁵ Furthermore, it is not very clear whether allowance for hydrolysis and/or complexation of Ln³⁺ and F⁻ ions has been made in the calculation of carlier values.^{3,4} Since thermodynamic K_{so} values of lanthanon trifluorides are very useful to solve several analytical problems including complexation of lanthanide ions addi ional data and better techniques for the measurement of K_{so} are needed.

Although the enthalpies of solution of other lanthanon trihalides in water at 25 °C are well known,² those for the dissolution of lanthanon trifluorides in water were nonexistent before the commencement of our work. This is probably due to the impracticability of direct measurement of enthalpies of solution in view of their poor solubilities in water. However, enthalpies of solution of the trifluoride can be estimated from the temperature dependence of K_{so} , using the standard van't Hoff equation. Since

[†] Paper presented at the Third International IUPAC Symposium on Solubility Phenomena, held at the University of Surrey, 23--26 August, 1988.

Solution Chemistry of Lanthanon Trifluoride–Water

the standard free energy change can also be estimated from the thermodynamic K_{so} , all the three functions, $\Delta H^{\circ}_{diss.}$, $\Delta G^{\circ}_{diss.}$ and $\Delta S^{\circ}_{diss.}$ can be computed using standard thermodynamic relations. Lanthanide ions are known to form complexes with fluoride ions in aqueous solutions, but there is considerable disagreement among values reported for the monofluoride complexes.^{6,7} There is also a paucity of information on the overall stability constants of lanthanon difluoride complexes.^{6,7}

This paper presents the final results of our measurement of the solubilities, pK_{so} values, thermodynamic functions and the stability constants of the 14 lanthanon fluoride-water systems carried out over several years.

Experimental

Materials and Equipment

Lanthanon chlorides (99.9% pure), mostly in the hydrated form were obtained from Thikol/Ventron Division of Alpha Products and the radioisotopes used in the study were supplied by Amersham Corporation. Only reagent chemicals were used for making solutions needed for the study. Doubly distilled water was employed for making solutions. Polyethylene ware was chosen for handling fluoride solutions and their mixtures with lanthanons.

The equipment used for the study are the following: Harshaw model $3 \text{ in}^+ \times 3$ in NaI(Tl) well crystal γ -ray spectrometer, Giger-Muller counter, Orion ion analyser meter model 407, Orion expandable and digital ion analyser model E 920 (for more recent work on stability constants) and their fluoride ion electrode model 96.09, Yellow Springs Instrument Co. Inc. (YSI) model 32 conductance meter and their model 3403 conductivity cell, a Burnell model AB wrist-action shaker and a Fisher Scientific model 137 Versa Bath.

Solubility Measurements

The detailed procedures for the measurement of solubilities of the lanthanon trifluorides $(LnF_3 \cdot 0.5H_2O)$ by the conductometric, potentiometric and radiometric methods have been reported elsewhere.⁸⁻¹³ Lanthanon trifluorides were precipitated by mixing hot solutions of the respective chlorides and sodium fluoride. Precipitated fluorides were washed several times with doubly distilled water to remove the absorbed ions and then dried in the oven at 110 °C. Small portions of the purified and dried precipitate (fluoride semi-hydrates) were agitated with doubly distilled water in four set of graduate cylinders made of polyethylene, intermittantly with the shaker for more than 48 h to prepare saturated solutions. Attainment of saturation condition at 25 °C was tested with repeated measurement of the conductance of solutions. The conductance of saturated solutions of the fluoride as a function of temperature, ranging from 20 to 55 °C, was measured by agitating the mixtures in constant-temperature bath for a minimum of 7 h. The conductance of doubly distilled water and the pH of the saturated solutions were also measured at each temperature. The total solubility of LnF_3 was measured using equations described in previous publications.⁸⁻¹³

The free fluoride ion concentration in saturated solutions of LnF_3 was also measured potentiometrically using the Orion ion analyser meter. An Orion standard (0.100 mol dm⁻³ NaF) was diluted with doubly distilled water to prepare the working standards (10⁻³-10⁻⁴ mol dm⁻³) for calibration of the instrument. The pH and ionic strength of the standards were very similar to those of the samples. The pH of the fluoride solutions, in general, ranged from 5.0 to 6.0. No other electrolytes were added to the system.

Radiometric procedure was employed only to such cases where a radioisotope of moderate half-life was available. In this method the solutions of lanthanon chlorides of

† 1 in = 2.54×10^{-2} m.

2684

known concentration was mixed with appropriate amount (*ca.* 500 μ Ci) of the respective radioisotope and the radioactive fluoride was precipitated as discussed before. After the precipitates had been washed and dried, small portions were agitated with water in four polyethylene bottles until saturation was attained. The specific radioactivity (cpm mmol⁻¹) of the original stock solution and of a solid standard, after digestion with concentrated H₂SO₄ and dilution with doubly distilled water, was determined by counting either γ or β radiation. The specific radioactivity of the stock solution and of the solid standard agreed well within experimental errors. After filtration and centrifugation radioactivity of 2 cm³ of the clear filtrate from each sample was measured under identical geometry and then compared with the specific activity of the labelled standard to determine the total concentration of lanthanon.¹³

Measurement of the Stability Constants of Lanthanon Fluoride Complexes

Stability constants for the monofluoride complexes were measured, in the past, using an Fe^{II}/Fe^{III} electrode,¹⁴ solvent extraction using radioisotopes^{15,16} and potentiometric titration using an LaF₃ electrode.⁷ Hefter *et al.*¹⁷ used a simple potentiometric method for the measurement of the stability constants of fluoride complexes of a few monovalent and divalent metals. Since there is no evidence for the formation of trifluoride complexes of lanthanons¹⁵ we attempted to measure the stability constants β_1 and β_2 for the mono-and di-fluoride complexes of lanthanons using a simplified potentiometric technique.

Unsaturated solution mixtures in 0.5 mol dm⁻³ NH_4NO_3 (I = 0.5 mol dm⁻³) were prepared by mixing various amounts of lanthanon and a constant amount of F⁻ to obtain a final concentration of 5×10^{-5} mol dm⁻³ F⁻ and $(1.0-1.5) \times 10^{-3}$ mol dm⁻³ Ln³⁺. Sodium fluoride standards of appropriate concentration were also prepared in the same medium. The concentration of free fluoride ion and the pH of each mixture were measured at room temperature, 25 ± 0.5 °C to compute the stability constant, β_1 of the monofluoride complex. In early experiments the Orion ion analyser meter was used for measurement of the concentration of the free fluoride. One of the problems we experienced in using the meter is to know when the specific fluoride-ion electrode reached equilibrium with fluoride ion in solution. It takes quite some time to reach this equilibrium and record a constant reading on the meter. The other problem was the inability to measure from the instrument the linearity or slope of the calibration curve. We used only one standard for our measurements with the meter. We recently acquired an expandable and digital Orion ion analyser E 920 which uses two standards for calibration and lights a ready signal when the electrode- F^- ion equilibrium is reached. Furthermore, it also provides the slope of the calibration curve. We have therefore, used the new instrument also to measure the stability constants, β_1 and β_2 of the mono- and di-fluoride complexes, respectively, of lanthanons.

For the measurement of β_2 for LnF⁺₂, unsaturated solution mixtures containing 5×10^{-5} mol dm⁻³ Ln³⁺ and varying amounts of F⁻ ($< 5 \times 10^{-4}$ mol dm⁻³) were prepared in 0.5 mol dm⁻³ NH₄NO₃ (I = 0.5 mol dm⁻³). After mixing the solutions thoroughly, the concentration of the free fluoride ion and pH of each solution were measured.

Measurement of the Solubilities as a Function of pH

Buffer solutions of the same ionic strength but with pH ranging from 1 to 8 were prepared. Each of these solutions was saturated with the desired LnF_3 and the free fluoride ion concentration was measured by the ion analyser meter. Stoichiometrically one-third of this concentration represents the solubility of the lanthanon trifluoride in each buffer solution.

Solution Chemistry of Lanthanon Trifluoride-Water

Results and Discussion

Solubilities and Solubility Products

The total solubility of lanthanon trifluoride without any allowance being made for the hydrolysis and/or complexation of lanthanide and fluoride ions are presented in table 1. The major processes that involve complex formation of Ln^{3+} and F^- and the hydrolysis of the former are according to Vasile'v and Kojlovski⁵ the following:

$$Ln^{3+} + F^{-} \rightleftharpoons LnF^{2+}; \beta_1 = (LnF^{2+})/(Ln^{3+})(F^{-})$$
 (1)

$$\mathbf{F}^- + \mathbf{H}^+ \rightleftharpoons \mathbf{HF}; \ K_{\mathbf{HF}} = (\mathbf{HF})/(\mathbf{H}^+)(\mathbf{F}^-) \tag{2}$$

$$Ln^{3+} + H_2O \rightleftharpoons Ln(OH)^{2+} + H^+; K_H = (Ln(OH)^{2+})(H^+)/(Ln^{3+})$$
 (3)

Mean activity coefficients are omitted in these equations as their values in dilute solutions ($< 10^{-3} \text{ mol dm}^{-3}$) are close to unity.

Menon *et al.*¹³ have shown that the concentration of the free metal ions and of free fluoride ions can be computed from the measurements of either the total concentration of the metal (radiometric and conductometric) or the concentration of free fluoride ion (potentiometric) using the reported values of β_1 , $K_{\rm H}$ and $K_{\rm HF}$ and the measured pH of the saturated solutions. In this work we have used our measured values of β_1 and the reported values of $K_{\rm H}^{18}$ and $K_{\rm HF}^{12}$ to compute the values for the concentration of free lanthanide ion or the fluoride at 25 °C from the appropriate solubility data. The thermodynamic solubility product was then computed using the relation:

$$K_{\rm so} = ({\rm Ln^+})_{\rm F} ({\rm F^-})_{\rm F}^3 \gamma_{\pm}^4 \tag{4}$$

where γ_{+} is the mean activity coefficient of the electrolyte. The negative logarithm of the solubility products (pK_{so}) so obtained from three different types of measurements are listed in table 1, and the literature values of pK_{sp} are also included for comparison. It appears that most of the literature values of pK_{sp} are based on the stoichiometric concentrations without any correction for complexation and hydrolysis. Although the contribution from the hydrolysis of Ln^+ to its total concentration is minimal (ca. 1%), that from complexation is significant (> 10%). Although there is significant difference between stoichiometric and thermodynamic solubility products for a particular LnF₃, there is only slight difference in their pK_{sp} values. In most cases the literature cites only the p K_{sp} values, but these values differ in some cases by as much as three units.^{2.4} The disagreement among pK_{sp} values may be attributed to the difference in the aging of the precipitate² or the method of preparation of the fluoride.¹⁹ We have studied the effect of aging of the precipitate in the mother liquor, pH and nature of the precipitant on the solubility of DyF_3 . The results are shown in table 2. It is obvious from this table that all of these variables do affect the pK_{sp} values. We have used 10 min aging time and NaF as precipitant in most cases. The pH of the saturated solutions varied from 5 to 6.

Selected values of pK_{sp} from literature and from our own work that do not differ by more than one unit (one order of magnitude in K_{sp}) were averaged to obtain reasonably accurate values for this parameter. The selected values for pK_{sp} , their average values, the respective values for K_{sp} , the concentration of free lanthanide ion and the estimated activity coefficients used for computation are shown in table 3. The general trend in the variation of solubilities of LnF_3 in aqueous solution at 25 °C as a function of atomic number is depicted in fig. 1. Our solubility values and those computed from the average pK_{sp} values show three maxima when plotted against the atomic number of lanthanons. No such data exist in literature for the whole lanthanide series for comparison. However, the data reported by Nikolaev *et al.*²⁰ for the solubilities of the fluorides from EuF_3 to LuF_3 also shows a maximum at Er.

In fig. 2, the variation of pK_{sp} values for LnF₃ are plotted as a function of the atomic

lanthanon	total solubility ^a		
trifluoride	$/10^{-5}$ mol dm ⁻³	pK _{so} ^a	p <i>K</i> _{so} ^b
LaF.	7.37 ± 0.24 (13) ^c	15.3	14.9 (4) ^c
3	7.61 ± 0.28 (13) ^P	15.3	$24.0(26)^{P}$
	7.05 ± 0.68 (13) ^R	15.4	$18.7(5)^{R}$
CeF.	4.58 ± 0.61 (12) ^c	16.1	19.2 (3) ^P
3	4.57 ± 0.55 (12) ^P	16.1	$17.1 (4)^{P}$
	3.14 ± 0.53 (12) ^R	16.7	$19.1(5)^{R}$
PrF ₂	$3.01 \pm 0.31^{\circ}$	16.7	18.9 (3) ^P
5	$2.09 + 0.17^{P}$	17.4	17.0 (4) ^P
			20.2 (3) ^T
NdF	$8.14 \pm 0.68 (13)^{\circ}$	15.2	17.08 (22) ^P
5	$11.13 \pm 0.72 (13)^{P}$	14.9	18.6 (3) ^P
	$1.59 \pm 0.09 (13)^{R}$	17.9	$20.3(5)^{R}$
SmF ₃	4.82 ± 0.72 (24) ^c	16.1	17.9 (3) ^P
Ŭ	4.76 ± 0.60 (24) ^P	16.0	19.3 (3) ^T
	$1.69 \pm 0.32 (24)^{R}$	17.8	16.0 (4) ^P
EuF_3	26.90 ± 2.4 (8) ^c	13.7	$17.2(3)^{P}$
-	34.00 ± 2.90 (8) ^P	13.1	$21.9(5)^{R}$
	$7.39 \pm 0.85 \ (8)^{R}$	15.6	$15.4(4)^{P}$
GdF_3	$2.96 \pm 0.45 (24)^{\circ}$	17.2	$16.8(3)^{P}$
-	$2.14 \pm 0.31 (24)^{P}$	17.3	18.1 (3) ^T
	$1.92 \pm 0.40 (24)^{R}$	17.6	15.3 (4) ^P
TbF3	5.87±0.15 (9) ^c	15.9	16.7 (3) ^P
	$4.17 \pm 0.17 (9)^{P}$	16.3	18.0 (3) ^T
	$3.59 \pm 0.52 (9)^{R}$	16.6	14.9 (4) ^P
DyF_3	$9.03 \pm 0.46^{\circ}$	15.3	16.3 (3) ^P
	8.66 ± 0.88^{P}	15.1	14.6 (4) ^P
			17.6 (3)т
HoF_3	$20.8 \pm 1.4^{\circ}$	13.9	15.8 (3) ^P
	15.90 ± 1.60^{P}	14.1	14.6 (4) ^P
			17.2 (3) ^T
ErF ₃	$13.1 \pm 1.4 (11)^{\circ}$	14.7	15.5 (3) ^р
	$11.10 \pm 2.90 \ (11)^{P}$	14.6	14.5 (4) ^P
	$1.98 \pm 0.20 (11)^{R}$	17.6	18.0 (5) ^R
TmF ₃	4.23±0.66 (10) [℃]	16.4	15.8 (3) ^P
	$4.53 \pm 0.41 \ (10)^{P}$	16.1	14.6 (4) ^P
	1.49 ± 0.04 (10) ^R	18.0	17.1 (5) ^T
YbF ₃	$8.55 \pm 0.62^{\circ}$	15.3	$15.0(3)^{P}$
	6.85 ± 0.54^{P}	15.4	$14.6 (4)^{P}$
	8.95 ± 0.62^{R}	15.2	16.3 (3) ^T
LuF ₃	$27.7 \pm 1.7^{\circ}$	13.6	15.0 (3) ^P
	37.5 ± 3.2^{P}	12.9	$14.6 (4)^{P}$
			16.4 (3) ^T

Table 1. Solubilities and solubility products (pK_{so}) of lanthanon trifluorides in aqueous solutions at 25 °C

C, Conductometric; P, potentiometric; R, radiometric; T, thermochemical. "This work. "Previous work.

number of lanthanons. Two of these curves also show three minima corresponding to lanthanons that exhibit the maximum solubilities. The pK_{sp} values reported by Vasile'v and Kozlovski⁵ also show an increase in pK_{sp} values from La to Eu and a drop to Er. Fig. 3 depicts the variation of pK_{sp} values of Ln(OH)₃ and of oxidation potentials for Ln/Ln³⁺ systems [taken from ref. (18)] as a function of the atomic number of

2687

Solution Chemistry of Lanthanon Trifluoride–Water

aging time		solubility			solubility	
/min	pН	/10 ⁻⁵ mol dm ⁻³	pK_{sp}^{b}	pН	/10 ⁻⁵ mol dm ⁻³	pK _{sp} ^b
	NaF	as precipitant		HF as precipitant		
10	4.8	8.66	14.96	4.18	2.78	16.79
				5.30	4.13	16.10
30	c	10.90	14.57	3.97	2.98	16.75
				5.27	5.13	15.73
60		20.0	13.42	4.18	1.57	17.78
				5.26	2.20	17.27
90		37.4	12.55	3.92	1.65	17.76
				5.25	4.10	16.21
120	_	28.4	13.00	d	2.49	17.06
150		24.3	13.25	_	2.18	17.28
180		29.8	12.92	_	2.41	17.11

Table 2. Effect of aging, pH and nature of precipitant on the solubility and pK_{sp} of dysprosium trifluoride^{*a*}

^a Concentration of fluoride ion was measured by potentiometric method. ^b Stoichiometric value for K_{sp} was computed. ^cpH of these samples is *ca*. 5. ^dpH of these samples is *ca*. 4.

lanthanon fluorides	selected values of pK_{sp}	average value of pK_{sp}	activity coefficient	$10^{17}K_{\rm sp}$	$[Ln^{3+}]_{\rm F}^{}/10^{-5} \text{ mol } dm^{-3}$
LaF ₃	15.3, 15.3, 15.4, 14.9	15.2	0.931	63.10	7.47
CeF	16.1, 16.1, 16.7, 17.1	16.5	0.953	3.16	3.45
PrF,	16.7, 17.4, 17.0	17.0	0.958	1.00	2.58
NdĔ	17.8, 17.9	17.9	0.939	0.13	1.56
SmF	16.1, 16.0, 16.0	16.0	0.944	10.00	4.65
EuF	15.6, 15.4	15.5	0.917	31.60	6.38
GdF	17.2, 17.3, 17.6, 16.8	17.2	0.958	0.63	2.30
TbF	15.9, 16.3, 16.6, 16.7,	16.1	0.945	7.94	4.38
0	14.9				
DyF.	15.3, 15.1, 16.3, 14.6	15.3	0.918	50.1	7.15
HoF	13.9, 14.1, 14.6	14.2	0.914	631.0	13.53
ErF.°	14.7, 14.6, 15.5, 14.5	14.8	0.928	158.5	9.43
Tmể	16.4, 16.1, 15.8	16.1	0.948	7.94	4.37
YbF。	15.3, 15.4, 15.2, 15.0,	15.3	0.935	50.1	7.02
- 3	14.6, 16.3				
LuF。	13.6, 15.0, 14.6	14.4	0.919	398.0	11.99
3					

Table 3. Averages of selected values of pK_{sp} from literature and from this work^a

^a The pK_{sp} values from the literature and from our work that do not differ by more than one unit were averaged. The selected values are shown in the table.

lanthanons. These graphs also do not follow a pattern of gradual increase or decrease in the respective quantities with increase in atomic number.

Thermodynamic Functions for the Dissolution of LnF₃ in Water at 25 °C

The only enthalpies of dissolution of lanthanon trifluorides available in literature seem to be those reported by Afanas'ev *et al.*^{21, 22} Owing to the low solubility of LnF_3 in water they used a solvent with composition, $HCl \cdot 5.05H_2O \cdot 0.02H_3BO_3$ to measure enthalpies of solution of eight lanthanon trifluorides at 50 °C with the aid of a microcalorimeter.



Fig. 1. General trend in the solubilities of LnF_3 in aqueous solution at 25 °C as a function of their atomic number. \bigcirc , Our average values from conductometric and potentiometric measurements; \bigcirc , average values from selected literature and our data; \triangle , reported by Nikolaev *et al.*²⁰



Fig. 2. General trend in the variation of pK_{sp} values of LnF_3 in aqueous solution at 25 °C as a function of atomic number of lanthanons. \bigcirc , Our values from conductometric and potentiometric measurements; \bigcirc , average values from selected literature and our data; \triangle , reported by Vasil'ev.⁵

We have used the temperature dependence of the K_{so} to measure the standard enthalpy change for the dissolution process. Such temperature-dependent graphs of K_{so} have been reported in previous publications.^{8-10, 12, 13}. The enthalpy changes were measured from the slopes of these straight-line graphs using the van't Hoff equation. The K_{so} values at 25 °C measured from these graphs were used to compute the standard free energy



Fig. 3. General trend in the variation of pK_{sp} values of Ln(OH)₃ and of oxidation potentials for Ln/Ln³⁺ system in aqueous solution as a function of atomic number (\bigcirc) oxidation potentials, ($\textcircled{\bullet}$) pK_{sp} of Ln(OH)₃ (data taken from Morss¹⁸).

lanthanon fluorides	$\Delta H^{\circ}/\mathrm{kJ} \mathrm{mol}^{-1a}$	$\Delta G^{\circ}/\mathrm{kJ} \mathrm{mol}^{-1a}$	$\Delta S^{\circ}/J \mathrm{K}^{-1} \mathrm{mol}^{-1a}$
LaF ₃	59.7 ± 2.9	89.9 ± 4.7	$-(92.4\pm7.3)$
CeF,	53.0 ± 17.4	91.7 ± 0.1	$-(129.7\pm58.3)$
PrF、	54.2 ± 2.1	97.2 ± 1.7	$-(145.0\pm2.0)$
NdĔ	43.4 ± 3.1	90.7 ± 5.3	$-(141.5\pm8.8)$
SmF ₃	51.0 ± 1.8	91.3 ± 1.0	$-(135.3\pm7.0)$
EuF	39.8 ± 4.0	86.9 ± 8.0	$-(157.0\pm16.0)$
GdF ₃	50.8 ± 8.0	97.6 ± 2.3	$-(157.0\pm19.0)$
TbF	27.4 ± 0.5	93.8 ± 4.7	$-(222.8\pm16.0)$
DyF ₃	56.1 <u>+</u> 9.9	85.1 ± 0.3	$-(97.8\pm34.1)$
HoF ₃	36.4 <u>+</u> 2.8	78.2 ± 1.4	$-(140.1 \pm 14.2)$
ErF ₃	34.2 ± 3.5	99.6 <u>+</u> 18.2	$-(217.3\pm 62.0)$
TmF ₃	14.7 <u>+</u> 0.7	102.3 ± 10.1	$-(294.2 \pm 34.1)$
YbF ₃	135.7 <u>+</u> 2.3	86.5 ± 1.0	$+(165.2\pm11.1)$
LuF ₃	59.8 ± 4.0	73.0 ± 1.4	$-(44.4 \pm 18.0)$

Table 4. Values for the thermodynamic functions for the dissolution of lanthanon trifluorides inwater at 25 °C

^a These are averages of the values obtained from conductometric and potentiometric measurements.

change and these values, in turn, were used to calculate the standard entropy change for the dissolution of the fluoride. The average values obtained from the conductometric and potentiometric data for the above three functions are listed in table 4. The enthalpy and free-energy changes are both positive for all the systems, but the entropy changes, except for YbF₃, are all negative. The enthalpy change for YbF₃ system is also very high when compared with the rest. Krestove and Egorva²³ have reported negative entropy

changes for the dissolution of all lanthanon trifluorides and attribute the negative entropy change to the structural changes of water in the region of long-range hydration of the ions. It appears that the hydration of the lanthanide ions play an important role in the solution properties of lanthanon fluoride-water systems.

Stability Constants for the Mono- and Di-fluoride Complexes of Lanthanons

The stability constant, β_1 , for the monofluoride complex was computed using the expression:²⁴

$$\beta_1 = \frac{[Ln^{F^{+}}]}{[Ln^{3+}][F^{-}]} = \frac{([F^{-}]_{tot.} - [F^{-}] - \delta_1[H^{+}][F^{-}] - 2\delta_2[H^{+}][F^{-}]^2)}{[Ln^{3+}][F^{-}]}$$
(5)

where $[Ln^{3+}]$ and $[F^{-}]$ are the concentration of free lanthanide and free fluoride ions, respectively, and δ_1 and δ_2 are the association constants ($\delta_1 = 1160$, $\delta_2 = 4.8 \times 10^4$)¹² for the formation of HF and HF₂⁻. The concentration of Ln³⁺ was obtained by subtracting $[F^{-}]_{complex.}$ from $[Ln^{3+}]_{tot.}$. The method is based on the fact that when the lanthanide ion is taken in large excess over that of fluoride ion, the only possible fluoride complex is LnF^{2+} in the mixture. The value for β_1 reported in this work is the average of six measurements using an ion analyser meter and/or a digital ion analyser.

On the assumption that Ln^{3+} forms only the mono- and di-fluoride complexes we have derived the following equation for the computation of β_2 , from the analytical data:²⁵

$$\beta_2 = \frac{\bar{n} - (1 - \bar{n})\beta_1[F^-]}{(1 - \bar{n})[F^-]^2}$$
(6)

where β_1 is the stability constant for the monofluoride complex, [F⁻] the measured concentration of free fluoride, \bar{n} the average number of fluoride ions that complex with one lanthanide ion. The value of \bar{n} is given by the following equation:²⁵

$$\bar{n} = ([F^{-}]_{\text{tot.}} - [F^{-}] - \delta_1 [H^{+}] [F^{-}] - 2\delta_2 [H^{+}] [F^{-}]^2) / [Ln^{3+}]_{\text{tot.}}.$$
(7)

Experimentally measured values of β_1 and other quantities were used to compute β_2 analytically with the use of eqn (6) and (7).

Eqn (6) may be converted into a linear form, to determine β_1 and β_2 simultaneously, as follows: $\bar{n} = (2 - \bar{n})[F^{-1}]$

$$\frac{\bar{n}}{[\mathbf{F}^{-}](1-\bar{n})} = \beta_1 + \beta_2 \frac{(2-\bar{n})[\mathbf{F}^{-}]}{(1-\bar{n})}.$$
(8)

The intercept and the slope of the plot of the term on the left against $(2 - \bar{n})[F^-]/(1 - \bar{n})$ were used to determine the values of β_1 and β_2 simultaneously by a linear-regression method. The stability constants for the mono- and di-fluoride complexes of lanthanons measured in this work at an ionic strength of 0.5 mol dm^{-3} along with the literature values are presented in table 5. Becker and Bilal⁷ and also Gmelin Handbuch list the stability constants for the monofluoride complex at different ionic strengths reported by various authors. In general, the value for β_1 tends to increase with decrease in ionic strength. We feel the values we obtained with our digital ion analyser are more precise than the ones we measured with ion analyser meter. In some cases there are differences between the previously reported values and ours. Our values for β_2 are, in general, not as precise as those for β_1 , as indicated by the error limits. Errors associated with the results are standard deviations from the mean of 8-10 individual measurements. Our values are much higher than those reported in literature for a few lanthanons at an ionic strength of 0.5 mol dm^{-3, ^{7, 16, 24} We have also included in parentheses the values obtained} for the complexes of a few lanthanides by the linear regression method using eqn (8). Corresponding r values are also given. The results with r values < 0.7 were omitted. Previous authors have used a pH of 3.6 and a higher concentration of Ln³⁺ and/or F⁻ ions in their experiments. It is important that the measurement of free fluoride ion

Solution Chemistry of Lanthanon Trifluoride-Water

			0	β_2		
lanthanon	method ^a	this work	previous work	this work $(\times 10^{-6})$	previous work $(\times 10^{-6})$	
La	A B C	453±29	$427 \pm 17 (13) 485 \pm 10 (16)$	13.5 ± 1.4^{b}	$15.40 \pm 3.1 (13)$ 0.15 (6)	
Ce	D A B C	790 <u>+</u> 44	$600 \pm 100 (7)$ 997 ± 98 (12)	3.7±1.6	0.10 ± 0.04 (12) 0.91 (6)	
Pr	E A B	912 ± 12 637 ± 67	1288 (6) 	7.5 ± 2.1 3.7 ± 0.8		
Nd	A B D	618±51 	$ \begin{array}{r} 724 \\ 670 \pm 100 \\ 77) \end{array} $	4.1±0.8 	25.10±2.9 (13)	
Sm	A B	1416±41	1076 ± 14 (24)	9.0 <u>+</u> 3.7	1.10 ± 1.1 (24)	
Eu	A D C	1172±54 (1025,	$r = 0.91)^c$ 2455 (6) 2512 (6)	1.9±0.6 (2. 	38, $r = 0.91)^c$	
Gd	A B C D E	1638±61 	$ \begin{array}{c} 1215 \pm 70 (24) \\ 2692 (6) \\ 2344 (6) \\ 2344 (6) \end{array} $	3.6±1.1 	1.4±1.2 (24)	
Tb	A D	1720 ± 50 (2378,	r = 0.72) 2320 ± 50 (7)	4.6 ± 1.7 (3.	38, $r = 0.72$) 0.13 ± 0.04 (7)	
Dy	A E	2390±79 (2004, 	r = 0.85) 3802 (6)	2.7 ± 1.1 (3.	.75+0.85)	
Но	A B	2028±74 (1911, 1269±41	, <i>r</i> = 0.97)	6.4 ± 1.0 (6. 4.3 ± 1.5	6, r = 0.97)	
Er	A D E	2452±42 (2406, 	r = 0.92) $1770 \pm 50 (7)$ 3467 (6)	10.8±2.7 (1)	1.0, r = 0.92)	
Tm	Α	1784±35 (1766,	r = 0.99	8.7 ± 0.9 (8.	7, r = 0.99	
Yb	A B E	$2031 \pm 53 (2752)$ 1900 ± 72	r = 0.97) 4074 (6)	8.9 ± 1.2 (7. 5.7 ± 3.0	(8, r = 0.97)	
Lu	A D E	2122±58 (2022) —	r = 0.92) 1730 ± 50 (7) 2951 (6)	4.5±1.5 (4. 	6, <i>r</i> = 0.92)	

Table 5. Stability constants for the mono- and di-fluoride complexes of lanthanons in aqueous solutions of $I = 0.5 \text{ mol dm}^{-3}$ at 25 °C

^a Method (A) potentiometric F⁻ ion concentration measurement using an expandable and digital Orion ion analyser and F^- ion-selective electrode, (B) potentiometric F^- ion concentration measurement using an Orion ion analyser meter, (C) solvent extraction using radioisotopes, (D) potentiometric titration using LnF_3 electrode, (E) potentiometric titration using Fe^{II}/Fe^{III} electrode. ^b These are analytical results obtained using eqn (6). ^c These are results obtained by a linear-regression method using eqn (8).



Fig. 4. pH dependence of the solubility of LnF_3 (potentiometric measurement). \bigcirc , LaF_3 ; \bigcirc , TmF_3 ; \triangle , TbF_3 .

concentration be made in unsaturated solution. The measured pH of each of our mixtures was in the range 4.5-5.0.

pH Dependence of the Solubility of Lanthanon Trifluorides

Fig. 4 shows the solubility *versus* pH of a few lanthanon trifluorides in various buffer solutions of ionic strength equal to 0.5 mol dm⁻³. The solubilities of all lanthanon trifluorides in buffered solutions were measured by the potentiometric method. In all cases the solubility was found to reach a minimum value at a pH of *ca.* 4. Menon⁹ has shown that the effect of complexation of F^- with H⁺ and Ln⁺ on solubility will be minimum at this pH so that the fluoride will be least soluble at this pH.

Conclusions

The solubilities and pK_{sp} values of lanthanon trifluorides do not follow a pattern of gradual increase or decrease with the atomic number of lanthanons. The solubilities and the averages of selected pK_{sp} values from literature and from our own work, that do not differ by more than unit, show three maxima when plotted against the atomic number of lanthanons. The wide difference in the reported pK_{sp} values may be attributed to the difference in the aging of precipitate, techniques used for the measurement and also in the evaluation methods. The solubilities of all lanthanon trifluorides in buffered solutions of constant ionic strength (0.5 mol dm⁻³) show a minimum at a pH between 3 and 4. Standard enthalpy and free energy changes for the dissolution of the fluorides in water are both positive while the entropy change, except for YbF₃, are negative. Although the stability constant for the monofluoride complexes can be measurement.

The financial support provided by the U.S. Department of Energy through their grant no. DE-FG09-84SR14014 for this work is gratefully acknowledged. Acknowledgement

2693

Solution Chemistry of Lanthanon Trifluoride–Water

is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society for support of initial phases of this research through their grant no. 11218-83. The authors are also thankful to numerous undergraduate chemistry majors who contributed to this work at different times.

References

- 1 IUPAC Solubility Data Project Combined Newsletter (Pergamon Press Oxford, February 1980).
- 2 J. Burgess and J. Kiljowski, Adv. Inorg. Chem., 1981, 24, 57.
- 3 J. J. R. Frausto da Dilva and M. M. Queimado, Rev. Port. Quim., 1973, 15, 29.
- 4 G. N. Koroleva, S. A. Gava, N. S. Poluektov, A. I. Kirillov and M. E. Kornelli, *Dokl. Akad. Nauk* SSSR., 1976, 228, 1384.
- 5 V. P. Vasil'ev and E. V. Kozlovskii, Russ. J. Inorg. Chem. (Engl. Transl.), 1977, 22, 472.
- 6 Gmelin Handbuch der Anorganischen Chemie (Springer-Verlag, Berlin, 8th edn, 1976), no. 39, part C3, p. 123.
- 7 P. Becker and B. A. Bilal, J. Solution Chem., 1985, 14, 4067.
- 8 M. P. Menon, J. Radioanal. Chem., 1981, 63, 283.
- 9 M. P. Menon, J. Chem. Eng. Data, 1982, 27, 81.
- 10 M. P. Menon, Int. J. Appl. Radiat. Isotop., 1982, 33, 1375.
- 11 M. P. Menon, J. Radioanal. Nucl. Chem. Lett., 1985, 96, 311.
- 12 M. P. Menon, J. James and J. D. Jackson, J. Radioanal. Nucl. Chem., 1986, 102, 419.
- 13 M. P. Menon, J. James and J. D. Jackson, Lanthanide and Actinide Res., 1987, 2, 49.
- 14 J. B. Walker and G. R. Choppin, Thermodynamic Parameters of Fluoride Complexes of the Lanthanides in the Lanthanide/Actinide Chemistry, Adv. Chem. Ser. 71 (ACS, Washington D.C., 1967), p. 127.
- 15 B. A. Bilal and J. Kob, J. Inorg. Nucl. Chem., 1980, 42, 629.
- 16 A. Aziz and S. J. Lyle, J. Inorg. Nucl. Chem., 1970, 32, 1925.
- 17 G. T. Hefter, C. B. Chan and N. H. Tioh, Anal. Chem., 1984, 56, 749.
- 18 L. R. Morss, Yttrium, Lanthanum and Lanthanide Elements in Standard Potentials in Aqueous Solution, ed. A. J. Bard, R. Parsons and J. Jordon (Marcel Dekker, New York, 1985), p. 587.
- 19 A. I. Popov and G. E. Krundson, J. Am. Chem. Soc., 1954, 76, 3921.
- 20 N. S. Nikolaev, Sh. A. Abdurakhmanov and Kh. Sh. Dzhuraev, Russ. J. Inorg. Chem., 1974, 19, 618.
- 21 Yu. A. Afans'ev, E. I. Khanaev and M. G. Kotov, Radiokhimiya (Engl. Transl.), 1975, 17, 203.
- 22 T. P. Storozhenko, E. I. Khanaev and Yu. A. Afans'ev, Russ. J. Phys. Chem., 1975, 49, 1241.
- 23 G. A. Krestov and I. V. Egorova, Radiokhimiya (Engl. Transl.), 1970, 12, 903.
- 24 B. A. Bilal and P. Becker, J. Inorg. Nucl. Chem., 1979, 41, 1607.
- 25 M. P. Menon, J. James and T. L. Hill, Int. J. Appl. Radiat. Isotop., 1988, 39, 949.
- 26 J. L. Weaver and W. G. Purdy, Anal. Chim. Acta, 1959, 20, 376.

Paper 8/04465A; Received 4th November, 1988