

## Hydrophilic Complexes of the Actinides. III.

### Lactates of $\text{Am}^{3+}$ , $\text{Eu}^{3+}$ , $\text{U}^{4+}$ and $\text{UO}_2^{2+}$

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$\text{Am}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{U}^{4+}$ , and  $\text{UO}_2^{2+}$  complexation by lactate ion in a 1 M  $\text{NaClO}_4$  medium at 25 °C were studied through liquid–liquid distribution and potentiometric titration measurements. Three extractants, tributyl phosphate (TBP), bis(2-ethyl-hexyl)phosphoric acid (HDEHP), and 2-thenoyltrifluoroacetone (HTTA), were employed.

Formation constants,  $\beta_n$ , of  $\text{Am}(\text{Lac})_n^{3-n}$  and  $\text{Eu}(\text{Lac})_n^{3-n}$ ,  $n=1-4$ , and related thermodynamic constants,  $\Delta H_n$  and  $\Delta S_n$ , were derived through distribution measurements. Formation constants for  $\text{U}(\text{Lac})_n^{4-n}$ ,  $n=1-6$ , and  $\text{UO}_2(\text{Lac})_n^{2-n}$ ,  $n=1-3$ , were obtained from potentiometric titrations. No polymeric U(IV) or U(VI) species were obtained at  $\text{pH}<1.7$  for U(IV) and  $\text{pH}<3.6$  for U(VI) at uranium concentrations in the range of 5 to 20 mM.

The results are compared with twoparametric models for stepwise complexation.

Alternatives for safe and economic treatment of actinide containing materials rest on a detailed knowledge of the chemical and physical properties of the actinides. The aqueous behaviour is of special interest because this is the main medium for actinide separation and recovery processes as well as for transporting of such nuclides from a waste repository to man.

The ligand chosen in this study is lactic acid. Lactic acid may serve as a representative of the great variety of carboxylic acids occurring in natural compounds *i.e.* fulvic and human acids. Furthermore lactic acid is used as a complexing agent in some separation processes, one of them

recently developed and studied in our laboratory.<sup>1,2</sup>

The aim of this work is to determine the lactate formation constants for tri-, tetra- and hexavalent actinides. For this purpose we have selected  $\text{U}^{4+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  as a representative for the heavier trivalent actinides. The experimental techniques chosen were liquid–liquid distribution in the case of  $\text{Am}^{3+}$  and  $\text{Eu}^{3+}$  and potentiometric titration for  $\text{U}^{4+}$  and  $\text{UO}_2^{2+}$ . Here we report the formation and related thermodynamic constants obtained for the  $\text{M}(\text{Lac})_n$  complexes in a perchlorate medium, including the stability of the anionic species  $\text{Am}(\text{Lac})_4^-$ ,  $\text{Eu}(\text{Lac})_4^-$ ,  $\text{U}(\text{Lac})_5^-$ ,  $\text{U}(\text{Lac})_6^{2-}$  and  $\text{UO}_2(\text{Lac})_3^-$ .

Lactate complexation of the actinides have been compiled and reviewed.<sup>3,4</sup> Tetravalent uranium seems not to have been studied previously and thermodynamic data for the lactates of trivalent actinides were lacking. Furthermore, the statement that mixed lactate and acidic organophosphorous complexes are formed is questionable.<sup>5</sup> In a preliminary study we could not find any evidence for such mixed complexes.<sup>6</sup>

## EXPERIMENTAL

**Chemicals.** Uranyl perchlorate was prepared from uranium metal (Merck, Darmstadt, *nuclear grade*) by dissolution into perchloric acid. In addition uranyl perchlorate was made by conversion of uranyl nitrate (British Drug House). The uranium concentration was determined by gravimetry and by X-ray fluorescence. The excess acid was determined by Gran titration. Lactic acid (BDH, *AnalaR*) was prepared as a 2.3 M stock solution after hydrolyzing the anhydrides

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by heating diluted acid at 70 to 80 °C for 2 to 3 d. The total acidity was determined by alkali titration and the complete conversion of the condensation product back into the acid was proved by the appearance of one single titration curve.<sup>7</sup> Radioactive isotope (<sup>14</sup>C) labelled lactic acid with a specific activity of 7.4 GBq/ml was purchased from the Radiochemical Centre in Amersham and was used as received. HDEHP (Farbenfabriken Bayer AG) was contacted with equal volumes of 6 M HNO<sub>3</sub> followed by three washes with water and finally 1 M NaClO<sub>4</sub> and analyzed by acidity titration. TBP (Fluka) was pre-extracted with 1 M NaOH and 1 M NaClO<sub>4</sub>. HTTA (Merck, *p.a.*) was used after recrystallization. Heptane served as organic diluent.

**Radioisotopes.** <sup>152</sup>Eu and <sup>241</sup>Am were obtained from the Radiochemical Centre in Amersham and were prepared as 0.1 M HClO<sub>4</sub> stock solutions of about 10<sup>5</sup> Bq/ml.

**Analysis.** The nuclides <sup>152</sup>Eu and <sup>241</sup>Am were analyzed through gamma spectroscopy using a 71 cm<sup>3</sup> Ge(Li) detector connected to an Intertechnique 4096 multichannel analyzer (IN45) or, after purity check, by a NaI(Tl) well type (3"×3") Intertechnique (CG4000) gamma counter. Uranium was analyzed by spectrophotometry (Beckman DB), 260 nm for UO<sub>2</sub><sup>2+</sup> and 650 nm for U(IV). Finally, the <sup>14</sup>C labelled lactic acid was measured by liquid scintillation counting using a Packard Tricarb 2425 spectrometer.

**Reduction of U(VI) to U(IV).** Electrolytic reduction was carried out in a closed glass cell equipped with a mercury cathode and a platinum anode. The anode compartment was separated from the bulk with a dense fritted glass diaphragm as described earlier.<sup>8,9</sup> 15 ml of the uranium (0.005–0.02 M) perchlorate solution in 1 M NaClO<sub>4</sub> was de-aired with argon gas before electrolysis at about 10–30 mA. The progress of reduction was followed on line by coulometry and by measuring the increasing concentration of U(IV) spectrophotometrically at 650 nm. During the electrolysis the solution was pumped through a 1 cm cuvette of 0.7 ml volume positioned in a spectrophotometer. When the absorption of U(IV) at 650 nm reached a constant level corresponding to 100 % reduction the electrolysis was stopped and all solution in the loop (*ca.* 3 ml) was brought back into the cell and the anode compartment was removed. In some initial experiments it was observed that monitoring the U(IV) by redox potential measurements, using a Pt or Au metal electrode against an Ag/AgCl reference electrode, was not sufficiently reliable.

**Liquid-liquid distribution experiments.** Batch experiments were carried out at a constant

temperature, ±0.1 °C, in a glass apparatus. 15 ml of both phases plus 10 μl of radioisotope stock solution were equilibrated by mixing with a magnetic stirrer. Equilibrium was obtained after a mixing time of 10 to 30 min depending on the extraction system. After allowing the phases to separate, samples of 1 ml were taken from both phases for radioactivity assay. In case of faulty material balance the experimental data were refused.

**Potentiometric titration experiments.** 20 ml of an aqueous perchlorate solution containing a known concentration of uranyl perchlorate was kept under argon atmosphere in a closed glass cell thermostated at 25±0.1 °C. If U(IV) was to be investigated the solution was reduced electrolytically as described above before titrating with lactate. The titration was performed with lactate buffers (*e.g.* 0.25 M HLac+0.25 M NaLac+0.75 M NaClO<sub>4</sub>) and the resulting hydrogen concentration was measured by a glass electrode calibrated at known acidities as described previously.<sup>8</sup> Reference titrations of the perchlorate solutions in absence of uranium were made separately.

## LIQUID-LIQUID DISTRIBUTION MEASUREMENTS

**Method.** The method of liquid-liquid distribution for studying metal complex chemistry is based on the measurement of the distribution, *D* of a metal, *M*, between two immiscible liquid phases according to eqn. (1);

$$D = [M]_{\text{org}}/[M] \quad (1)$$

where no index refers to the aqueous phase. Introduction of a complexing ligand, *L*, into the aqueous phase results in the formation of metal complexes, ML<sub>*n*</sub>, which we initially may assume are both unextractable and unhydrolyzed. Neglecting aqueous metal complexation with the extractant, eqn. (1) is transformed into eqn. (2),

$$D/D^{\circ} = [M] / \sum_{n=0}^n [ML_n] = 1 / (1 + \beta_1[L] + \beta_2[L]^2 + \dots) \quad (2)$$

where *D*<sup>°</sup> is the distribution value at zero concentration of the complexing ligand and β<sub>*n*</sub> is the gross complex formation constant for the formation of ML<sub>*n*</sub> from *M* and *L*.

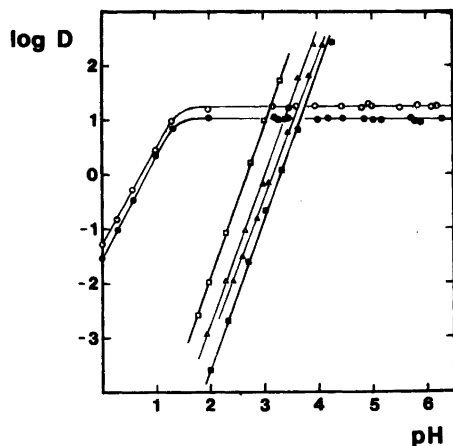


Fig. 1. The distribution,  $\log D$ , of Am and Eu between an organic phase and 1 M (Na,H)ClO<sub>4</sub> as a function of pH at 25 °C. The initial composition of the organic phases were; 100 % TBP (○,●), 5·10<sup>-4</sup> M HDEHP in n-heptane (□,■) and 0.5 M HTTA in toluene (△,▲). Unfilled symbols denote Eu and filled Am.

In principle the actual extraction mechanism need not to be known. However, it is a requirement that the extraction mechanism is unchanged during the experiment.

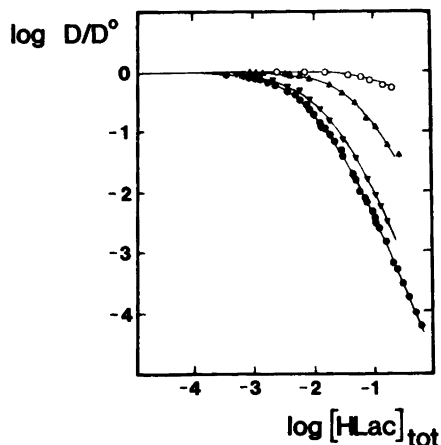
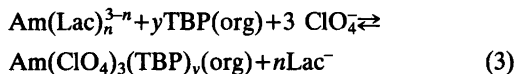


Fig. 2. The influence of lactic acid on the normalized distribution,  $\log D/D^{\circ}$ , of Am(III) between undiluted TBP and 1 M Na(ClO<sub>4</sub>, Lac) at 25 °C and different pH.  $D^{\circ}$  is the distribution in absence of lactic acid. (○)=pH 2, (▲)=pH 3, (▼)=pH 4, (●)=pH 5 and pH 6.

In this study three extraction reagents were used, TBP, HTTA and HDEHP. In Fig. 1  $\log D^{\circ}$  for Eu(III) and Am(III) as a function of pH for these three extraction systems is described. A more detailed description of these systems with respect to mechanisms, side reactions, and usefulness in complex chemistry studies was given in Part II of this series.<sup>10</sup>

**Lactate-complexation: TBP.** The distribution of Am between 1 M NaClO<sub>4</sub> and 100 % TBP decreased upon addition of lactic acid (HLac in 1 M NaClO<sub>4</sub>). The relation between  $\log (D/D^{\circ})$  and the logarithm of the total initial concentration of lactic acid is presented in Fig. 2. The slope  $\delta \log (D/D^{\circ})/\delta \log [\text{HLac}]_{\text{tot}}$  decreases from 0 to -3 when the concentration of lactic acid increases.  $[\text{HLac}]_{\text{tot}}$  refers to the total amount of lactic acid and lactate in the organic and aqueous phase.

At  $D=D^{\circ}$  the organic phase is dominated by the  $M(\text{ClO}_4)_3(\text{TBP})_y$  species, while the aqueous phase mainly contains uncomplexed  $M^{3+}$ .<sup>10</sup> Appreciable hydrolysis does not occur until  $\text{pH} > 6$ .<sup>11</sup> With increasing  $[\text{Lac}^-]$   $M^{3+}$  becomes increasingly complexed by  $\text{Lac}^-$  in the aqueous phase, forming  $M(\text{Lac})_n^{3-n}$  species, according to eqn. (2). When the aqueous phase is dominated by  $M(\text{Lac})_3$ , eqn. (2) yields  $\log (D/D^{\circ}) = -3 \log [\text{Lac}^-]$  corresponding to the slope -3 in Fig. 2. Thus the shape of the extraction curves agree with an extraction mechanism according to relation (3).



where  $\text{Am}(\text{Lac})_n^{3-n}$  denotes the average aqueous Am species. At  $\text{pH} \leq \text{p}K_a$  HLac is only partly dissociated. Thus the  $D/D^{\circ}$ -curves indicate less complexation.

In order to calculate the free ligand concentration,  $[\text{Lac}^-]$ , one must take into account that TBP extract a fraction of the HLac. Hence it was necessary to determine the distribution coefficient  $k_d$  of HLac. Eqn. (4) gives the relation between  $D_{\text{HLac}}$  and  $k_d$ ;

$$\begin{aligned} D_{\text{HLac}} &= \frac{[\text{HLac}]_{\text{org}}}{[\text{HLac}] + [\text{Lac}^-]} = \\ \frac{k_d[\text{HLac}]}{[\text{HLac}](K_a[\text{H}^+]^{-1} + 1)} &= \frac{k_d}{K_a[\text{H}^+]^{-1} + 1} \quad (4) \end{aligned}$$

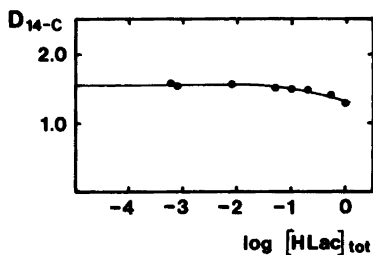


Fig. 3. The distribution of  $^{14}\text{C}$ -lactic acid,  $D_{14-c}$ , between undiluted TBP and 1 M  $\text{NaClO}_4$  as a function of the total lactic acid concentration at pH 2 and 25 °C.

where  $K_a = [\text{H}^+][\text{Lac}^-]/[\text{HLac}]$  and  $k_d = [\text{HLac}]_{\text{org}}/[\text{HLac}]$ .

The distribution of HLac as a function of the total concentration of HLac and of pH is shown in Figs. 3 and 4. At high HLac or  $\text{HClO}_4$  concentrations there is a decrease in  $D_{\text{HLac}}$  which is most probably related to the consumption of free TBP by the extraction of HLac and  $\text{HClO}_4$  respectively. Any dimerization of HLac in the organic phase is negligible due to the invariance of  $D_{\text{HLac}}$  with HLac concentration, Fig. 3. Using eqn. (4) and values of  $D_{\text{HLac}}$  for  $\text{pH} > 2$  and  $[\text{HLac}]_{\text{total}} < 0.1$  M we calculated  $k_d = 1.60 \pm 0.04$  and  $\text{p}K_a = 3.63 \pm 0.02$  (literature value  $\text{p}K_a = 3.63 \pm 0.03$ ).<sup>12</sup>

Recalculating the data of Fig. 2 into  $\log D/D^\circ = f(\log[\text{Lac}^-])$  using eqn. (4) the curves, obtained at different pH, coincide into one single curve with a limiting slope of  $-3$  at increasing

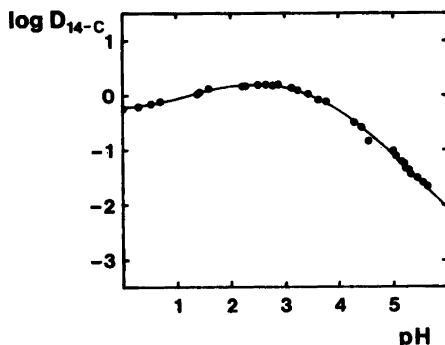
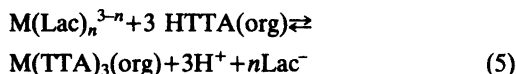


Fig. 4. The distribution of  $^{14}\text{C}$ -lactic acid,  $D_{14-c}$ , between undiluted TBP and 1 M  $(\text{Na},\text{H})\text{ClO}_4$  as a function of pH. Total lactic acid concentration  $10^{-3}$  to  $10^{-1}$  M.

lactate concentration, which proves that relation (3) is valid.

The overall complex formation constants were derived by minimizing the weighted error square sum  $\sum (D_{\text{exp}} - D_{\text{calc}})^2$ .  $\beta_1$  and  $\beta_2$  were close to those calculated below from the HDEHP system, Table 1.  $\beta_3$  deviates somewhat due to increased ionic strength because the perchlorate concentration has to be kept constant as it participates in the extraction mechanism.

**HTTA.** The distribution of Am(III) and Eu(III) between 1 M  $(\text{Na},\text{H})\text{ClO}_4$  and 0.5 M HTTA in toluene was investigated at different lactate concentrations. The extraction of trivalent metals,  $\text{M}^{3+}$ , in this system is assumed to proceed according to relation (5)



in analogy with the extraction mechanism in absence of lactate.<sup>10</sup> Alkali titration analysis indicated no extraction of HLac which allows a simple calculation of the lactate concentration from the extent of dissociation.

Fig. 5 shows  $\log D/D^\circ$  for Am(III) and Eu(III) as a function of  $\log[\text{Lac}^-]$  at constant acidity ( $\text{pH} = 3.6$ ). The stronger complexation of Eu

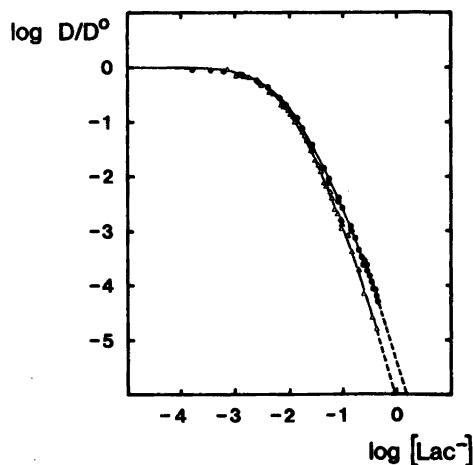


Fig. 5. The influence on the distribution coefficient,  $\log D/D^\circ$ , of Am(III) and Eu(III) on the lactate concentration at 25 °C. Organic phase: 0.5 M HTTA in toluene. Aqueous phase: 1 M  $(\text{Na},\text{H})\text{ClO}_4$ ,  $\text{pH} = 3.60$ . (●)=Am and (Δ)=Eu.

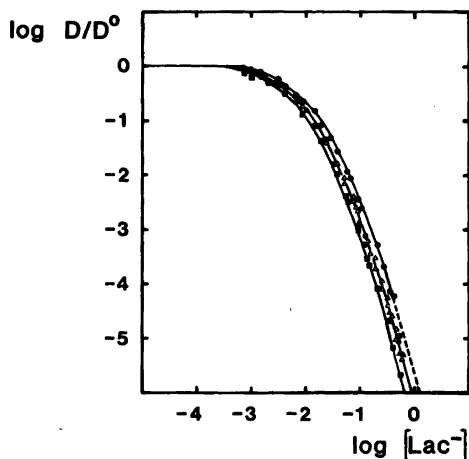


Fig. 6. The effect of temperature on the distribution,  $\log D/D^\circ$ , of Am as a function of the lactate concentration.  $5 \cdot 10^{-4}$  M HDEHP in n-heptane and 1 M (Na,H)(ClO<sub>4</sub>,Lac) at pH 4. (●)=45 °C, (△)=25 °C, (■)=5 °C.

compared to Am appears as a larger decrease in  $\log D/D^\circ$  with increasing lactate concentration. The figure also indicates that an anionic lactate specie,  $\text{Eu}(\text{Lac})_4^-$ , is formed at the highest lactate concentrations because the limiting slope is  $< -3$ .

The stability and kinetics of the HTTA–Am system is dependent upon extractant concentration and pH.<sup>10</sup> The chosen combinations of HTTA concentration and pH minimize the sensitivity towards impurities and sorption of Am and results in acceptable reproducibility.

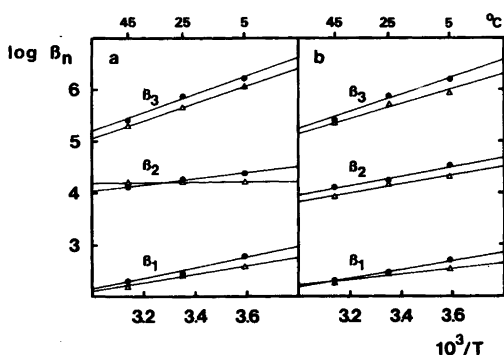
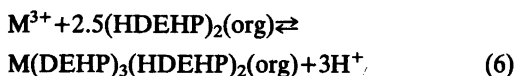


Fig. 7. The relationships between the lactate formation constants,  $\beta_n$ ,  $n=1-3$ , and the inverted temperature,  $1/T$ , in the range 5–45 °C. (△)=Am and (●)=Eu. a)=experimental  $\beta_n$ , b) theoretical  $\beta_n$  according to Mihailov's model.<sup>35</sup>

**HDEHP.** Trivalent metals are extracted by HDEHP in aliphatic diluents according to the apparent extraction mechanism;<sup>10</sup>



Just as in the previous case no correction for extraction of lactic acid was made. The maximum impact on the extraction system of the lactic acid extraction is a decrease in free HDEHP concentration ( $\leq 0.5\%$ ), which corresponds to a less than 2% decrease in the distribution of Am or Eu; the loss of HLac to the organic phase is insignificant ( $\leq 10^{-5}\%$ ). These estimates were made from measurements of the distribution of HLac at high HDEHP concentrations (0.2 M HDEHP).

For the above reasons, and because HDEHP allowed better reproducibility in a broader pH and extractant range than HTTA and TBP, we expanded the HDEHP measurements with a temperature study. The relations between  $\log D/D^\circ$  and  $\log [\text{Lac}^-]$  were obtained at 5 °C, 25 °C and 45 °C at pH 4 and  $5 \cdot 10^{-4}$  M HDEHP in n-heptane, Fig. 6. Although the temperature dependence was weak there was a perceptible drop in  $\log D/D^\circ$  with decreasing temperature. The stability constants  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  for the formation of Am(III) and Eu(III) lactates were calculated at each temperature and for  $[\text{Lac}^-] \leq 0.3$  M using a least squares regression analysis programme. The effect of temperature on the formation constants is shown in Fig. 7 where  $\log \beta_n$  is plotted as a function of the inverse absolute temperature.

The thermodynamic constants,  $\Delta H$  and  $\Delta S$ , were calculated for each complex formation step. In addition, the formation constants for the anionic species  $\text{Am}(\text{Lac})_4^-$  and  $\text{Eu}(\text{Lac})_4^-$  were graphically estimated at 25 °C from the distribution data at  $[\text{Lac}^-] \geq 0.3$  M which indicate a limiting slope of  $-4$ , Fig. 6. Table 2 gives a summary of the constants obtained for the Am and Eu lactates.

## POTENTIOMETRIC TITRATION EXPERIMENTS

**Method.** The method of potentiometric titration for calculating stability constants is based on

Table 1. Comparison of formation constants for Am and Eu lactate complexes obtained by different solvent extraction systems and from literature.

Solvent extraction system (1 M NaClO <sub>4</sub> , 25 °C)	Literature (numbers refer to the reference list)											
	100 % TBP pH 2-6	5 × 10 <sup>-4</sup> M HDEHP in n-heptane pH 4.00	0.5 M HTTA in toluene pH 3.60	20 <sup>a</sup>	28 <sup>b</sup>	29 <sup>c</sup>	30 <sup>d</sup>	31 <sup>e</sup>	32 <sup>f</sup>	33 <sup>g</sup>	19 <sup>h</sup>	18 <sup>i</sup>
Am												
log β <sub>1</sub>	2.48 ± 0.09	2.43 ± 0.09	2.35 ± 0.09	2.52	2.57	—	2.77	—	—	—	—	—
log β <sub>2</sub>	4.34 ± 0.44	4.23 ± 0.27	4.37 ± 0.46	4.77	4.21	—	4.64	—	—	—	—	—
log β <sub>3</sub>	5.32 ± 0.56	5.65 ± 0.15	5.30 ± 0.69	5.98	—	5.71 ± 0.03	—	—	—	—	—	—
log β <sub>4</sub>	—	6.0 ± 0.2	—	—	—	—	—	—	—	—	—	—
Eu												
log β <sub>1</sub>	—	2.46 ± 0.09	2.48 ± 0.13	—	2.62	—	—	2.55	2.949	2.48	2.53	2.95
log β <sub>2</sub>	—	4.28 ± 0.25	4.29 ± 0.66	—	4.22	—	—	4.67	5.18	4.56	4.60	4.40
log β <sub>3</sub>	—	5.76 ± 0.10	5.80 ± 0.48	—	—	—	—	5.55	6.43	5.83	5.82	5.47
log β <sub>4</sub>	—	6.5 ± 0.2	6.3 ± 0.3	—	—	—	—	6.06	—	—	—	—

<sup>a</sup> 1 M NaClO<sub>4</sub>, 25 °C; solvent extraction (HDEHP). <sup>b</sup> 1.5 M KCl, 10 °C; electrophoresis. <sup>c</sup> 0.1 M NaClO<sub>4</sub>, 20 °C; solvent extraction (HTTA). <sup>d</sup> 2 M NaClO<sub>4</sub>, 25 °C; ion exchange. <sup>e</sup> 0.2 M NaClO<sub>4</sub>, 25 °C; potentiometric titration. <sup>f</sup> 0.1 M NaClO<sub>4</sub>, 20 °C; potentiometric titration. <sup>g</sup> 2 M NaClO<sub>4</sub>, 25 °C, solvent extraction (HDEHP). <sup>h</sup> 2 M NaClO<sub>4</sub>, 25 °C; potentiometric titration. <sup>i</sup> 1 M NaCl, 25 °C; solvent extraction (HDEHP).

Table 2. Formation and thermodynamic constants for Am(III), Eu(III) and U(VI) lactates, in 1 M NaClO<sub>4</sub>, 25 °C. The constants are derived from HDEHP solvent extraction (Am, Eu) and potentiometric (1-20 mM U) experiments.

	log β <sub>1</sub>	ΔH <sub>β1</sub> kJ mol <sup>-1</sup>	ΔS <sub>β1</sub> J mol <sup>-1</sup> K <sup>-1</sup>	log β <sub>2</sub>	ΔH <sub>β2</sub> kJ mol <sup>-1</sup>	ΔS <sub>β2</sub> J mol <sup>-1</sup> K <sup>-1</sup>	log β <sub>3</sub>	ΔH <sub>β3</sub> kJ mol <sup>-1</sup>	ΔS <sub>β3</sub> J mol <sup>-1</sup> K <sup>-1</sup>	log β <sub>4</sub>
Am <sup>3+</sup>	2.43 ± 0.09	-16 ± 3	-6 ± 9	4.23 ± 0.27	-2 ± 1	80 ± 8	5.65 ± 0.15	-32 ± 3	0 ± 9	6.0 ± 0.2
Eu <sup>3+</sup>	2.46 ± 0.09	-19 ± 2	-16 ± 6	4.28 ± 0.25	-10 ± 2	50 ± 4	5.87 ± 0.10	-33 ± 6	2 ± 15	6.5 ± 0.2
Eu <sup>3+</sup> (a)	2.54 ± 0.01	-8 ± 1	-22 ± 3	4.59 ± 0.02	-5 ± 3	71 ± 13	5.94 ± 0.05	-23 ± 9	36 ± 32	—
UO <sub>2</sub> <sup>2+</sup>	2.68 ± 0.03	—	—	4.47 ± 0.06	—	—	5.64 ± 0.03	—	—	—
UO <sub>2</sub> <sup>2+</sup> (b)	2.81 ± 0.06	—	—	4.56 ± 0.14	—	—	5.46 ± 0.17	—	—	—
UO <sub>2</sub> <sup>2+</sup> (c)	2.43 ± 0.02	—	—	4.49 ± 0.08	—	—	6.35 ± 0.16	—	—	—
UO <sub>2</sub> <sup>2+</sup> (d)	2.77	—	—	4.40	—	—	5.73	—	—	—
UO <sub>2</sub> <sup>2+</sup> (e)	3.36 ± 0.05	—	—	5.6 ± 0.3	—	—	7.6 ± 1	—	—	—

<sup>a</sup> 2 M NaClO<sub>4</sub>, calorimetry and potentiometric titration, Ref. 23. <sup>b</sup> 0.1 M NaClO<sub>4</sub>, <0.5 mM UO<sub>2</sub><sup>2+</sup>, solvent extraction, 20 °C, Ref. 24. <sup>c</sup> 1 M NaClO<sub>4</sub>, 0.5-5 mM UO<sub>2</sub><sup>2+</sup>, spectrophotometry, 20 °C, Ref. 25. <sup>d</sup> 1 M NaClO<sub>4</sub>, 25 mM UO<sub>2</sub><sup>2+</sup>, potentiometric titration, 25 °C, Ref. 26. <sup>e</sup> 1 M NaClO<sub>4</sub>, 10 mM UO<sub>2</sub><sup>2+</sup>, potentiometric titration, 31 °C, Ref. 27.

the determination of the mean ligand number  $\bar{n}$  as a function of the free ligand concentration,  $L$ , followed by a mathematical analysis of this function.<sup>13,14</sup>

The lactate titrations were made by adding a buffer solution of HLac + NaLac to a uranium solution containing HClO<sub>4</sub> (all solutions were adjusted with NaClO<sub>4</sub> to give unit ionic strength). Using EMF measurements the hydrogen ion concentration was calculated and [Lac<sup>-</sup>] and  $\bar{n}$  could be derived using eqns. (7) through (10). The equations are valid for any  $h$ ,  $c_H$ , and hydrolytic state of the metal.

$$[\text{Lac}^-] = c_L + h - c_H - \bar{n}c_M \quad (7)$$

$$\bar{n} = \frac{[\text{Lac}]_{\text{tot}} - [\text{Lac}^-]}{[\text{M}]_{\text{tot}}} = \frac{(h + K_a)(h - c_H + c_L) - K_a(c_L + c_{\text{HL}})}{h c_M} \quad (8)$$

$$K_a = \frac{h'(c_L + h')}{c_{\text{HL}} - h'}; h' \approx h \approx K_a \quad (9)$$

$$K_a = \frac{[\text{Lac}^-]h}{c_{\text{HL}} + c_H - h}; h \gg K_a \quad (10)$$

where the molar concentrations at each point are denoted by;

$h$  = the hydrogen ion concentration

$h'$  = the hydrogen ion concentration when  $c_M=0$  and  $c_H=0$

$c_H$  = the initial acidity added to the uranium solution

$c_M$  = the uranium concentration

$c_{\text{HL}}$  = the stoichiometric HLac concentration originated from the buffer solution

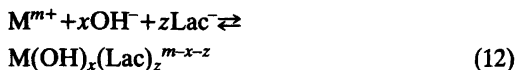
$c_L$  = the stoichiometric NaLac concentration originated from the buffer solution

The value of  $K_a$  in eqn. (10) was calculated by an iterative procedure starting with  $K_a = 2.2 \cdot 10^{-4}$ . When  $K_a$  became constant the values of  $\bar{n}$  and [Lac<sup>-</sup>] were derived. In the UO<sub>2</sub><sup>2+</sup> experiments, however, the initial pH was high enough so that  $K_a$  obtained from eqn. (9) could be used.

The  $\bar{n}$  values obtained can be used to derive the formation constants  $\beta_{xz}$  according to eqn. (11)

$$\bar{n} = \frac{\sum_{x=0}^z \sum_{z=0}^x z \beta_{xz} [\text{OH}]^x [\text{Lac}^-]^z}{1 + \sum_{x=0}^z \sum_{z=1}^z \beta_{xz} [\text{OH}]^x [\text{Lac}^-]^z} \quad (11)$$

where  $\beta_{xz}$  denotes the stability constant of the mixed complex according to eqn. (12)



**Uranium (VI).** UO<sub>2</sub><sup>2+</sup> perchlorate solutions, containing 1.3 mM up to 21 mM of uranium, were titrated with a lactate buffer solution (0.256 M HLac + 0.250 M NaLac + 0.75 M NaClO<sub>4</sub>). The calculated values of  $\bar{n}$  are presented as a function of the lactate concentration in Fig. 8. Independent on the metal concentration the calculated  $\bar{n}$  values fall on one curve indicating that no polynuclear uranium species are formed. Titrations were also performed with a lactate buffer of higher relative content of lactic acid (0.508 M HLac + 0.125 M NaLac + 0.875 M NaClO<sub>4</sub>), giving the same results as above.

The average ligand number  $\bar{n}$  reaches almost 3 indicating that the anion UO<sub>2</sub>(Lac)<sub>3</sub><sup>-</sup> is formed. Furthermore, since all experiments were made in the acidity range from pH=2.3 to pH=3.6 we can neglect hydrolysis of the metal ion. The stability constants derived from the formation functions according to eqns. (11) and (12) are gathered in Table 2 together with constants obtained by other investigators. Our data are in good agreement with literature data obtained by various techniques (potentiometric titration, solvent extraction, and spectrophotometry).

**Uranium (IV).** After testing the potentiometric technique on hexavalent uranium we continued with titrations of electrolytically reduced solu-

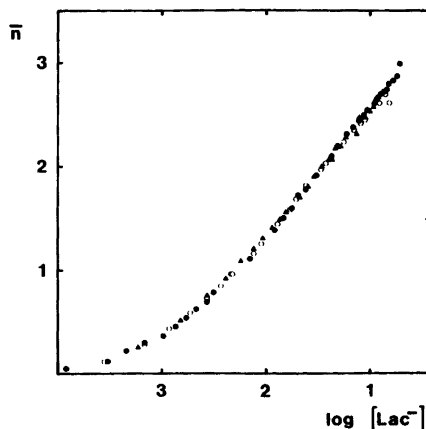


Fig. 8. Average ligand number,  $\bar{n}$ , as a function of the lactate concentration for UO<sub>2</sub><sup>2+</sup> at 25 °C. Potentiometric titrations performed at (▲)=6 mM, (○)=12 mM and (●)=21 mM uranium.

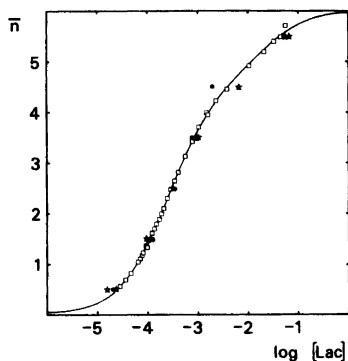
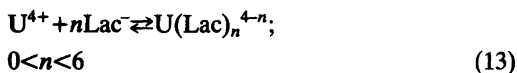


Fig. 9. Average ligand  $\bar{n}$  as a function of the lactate concentration for U(IV) at 25 °C. Potentiometric titrations carried out at various uranium concentrations; Buffer ratios  $\delta = [\text{HLac}]/[\text{NaLac}]$ . (●)=4.8 mM,  $\delta=4$ , (☆)=10.7 mM,  $\delta=4$ , (★)=14 mM,  $\delta=1$  and (□)=19.1 mM,  $\delta=1$ . pH varied between 1–1.7.

tions. 5–20 mM U(IV) in acidic 1 M (Na,H)ClO<sub>4</sub> were titrated with lactate buffer solutions ( $\delta x$  M HLac +  $x$  M NaLac + (1- $x$ ) M NaClO<sub>4</sub>, where  $\delta; x = 1; 0.250, 4; 0.125$  and  $10; 0.100$ ). The calculated  $\bar{n}$  values increase smoothly from  $\bar{n}=0$  up to almost  $\bar{n}=6$  with rising lactate concentration, Fig. 9. It was found that data, obtained at different uranium concentrations and acidity in the range from pH 1 to pH 1.7, coincide into one curve. This behaviour indicates, firstly that no polynuclear U(IV) species are formed, secondly that the hydrolysis of U(IV) is suppressed, and thirdly that anionic complexes U(Lac)<sub>5</sub><sup>-</sup> and U(Lac)<sub>6</sub><sup>2-</sup> are formed. Formation constants  $\beta_n$  according to relation (13)



were calculated with a graphical method, as described by Rossotti and Rossotti, and refined by computer calculations.<sup>14</sup> The results are presented in Table 3.

Table 3. U(IV)-lactate formation constants obtained by potentiometric titration in 1 M NaClO<sub>4</sub> at 25 °C. The constants  $k_n(\text{U}(\text{Lac})_{n-1}^{4-(n-1)} + \text{Lac}^- \rightleftharpoons \text{U}(\text{Lac})_n^{4-n})$  and  $\beta_n(\text{U}^{4+} + n\text{Lac}^- \rightleftharpoons \text{U}(\text{Lac})_n^{4-n})$  are derived for  $n=1$  through 6.

	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$
$\log \beta_n$	4.4±0.05	8.3±0.1	11.8±0.1	15.1±0.1	17.5±0.2	19.0±0.2
$\log k_n$	4.4±0.05	3.9±0.05	3.5±0.05	3.3±0.05	2.4±0.05	1.5±0.05

Estimates on the influence of U(IV) hydrolysis on the experiments were made using the following set of hydrolysis data for U(IV) in 1 M NaClO<sub>4</sub>;  $\log^* \beta_1 = -1.6$ ,  $\log^* \beta_2 = -4.5$  and  $\log^* \beta_3 = -8.4$ .<sup>15,16,17</sup> It was concluded that hydrolysis was negligible (<5 % at pH 1.7) in comparison with the lactate complexation.

A few experiments were carried out at extremely low pH (pH~0.6) but the uncertainties in  $\bar{n}$  became very large because of the low accuracy in determining small pH changes with the glass electrode at such high acidities.

## DISCUSSION

*Solvent extraction systems.* It is crucial for the interpretation of the distribution data that the extraction mechanism and the distribution coefficients,  $k_d$ , of the hydrophilic ligand and the hydrophobic extractant are unchanged upon addition of complexing ligand. Reactions that may interfere are formation of extractable metal lactate complexes as well as reactions between the extractant and the hydrophilic ligand or electrolyte constituents. The use of several extraction reagents, with different extraction mechanisms, makes it possible to discover such interferences by checking the systems against each other. In this work we used three extraction agents: a neutral and a monoacidic organophosphorous reagent, TBP and HDEHP, respectively and a betadiketone, HTTA. The agreement between the formation constants obtained for the three systems, *c.f.* Table 1, supports the conclusion that the extraction mechanisms are unchanged and that no significant disturbing reactions occur.

As was stated in Part II of this series, HTTA is less advantageous due to poor reproducibility under certain conditions.<sup>10</sup> TBP is generally very useful but the extraction of the acid HLac was a small though not negligible complication in this work. Another drawback of the TBP system is



the participation of the ionic media in the metal extraction. In order to simplify the interpretation of the TBP data, we have chosen to keep the perchlorate concentration constant. Thus there will be an increase in ionic strength with increasing ligand concentration. Hence the limiting slope  $\delta \log(D/D^0)/\delta \log[\text{Lac}^-]$  in the lactate system will not fall below  $-3$  as it does with HDEHP and HTTA. However, this problem is negligible for moderate lactate concentrations ( $[\text{Lac}^-] \leq 0.1 \text{ M}$ ). The good reproducibility combined with negligible disturbing reactions made the HDEHP system the most suitable for our study. Thus we consider the formation constants obtained from this system as the most reliable ones, and use them for comparing with literature data, Table 2.

The results are of interest for the TALSPEAK separation process in which actinides and lanthanides are separated by the use of HDEHP, lactic acid, and DTPA (diethylenetriaminepentaacetic acid). Kosyakov and Yering have suggested that actinides, are extracted in the form of mixed lactate-HDEHP complexes.<sup>5</sup> It is our opinion that this is not the case even under the technical conditions of the TALSPEAK process because there is no indication of mixed complexes in our experiments.<sup>6</sup> Our findings agree with a recent study of Danesi, Cianetti and Horwitz.<sup>18</sup>

In this work the liquid-liquid distribution technique has been applied for determining  $\Delta H$  and  $\Delta S$  of complex formation reactions. Compared to the traditional calorimetric method, within error limits, it seems to give the same results, *c.f.* Eu in Table 2.

**Formation constants.** The existence of anionic Am lactates have not been reported before, but some observations have been made on Eu by potentiometric titrations.<sup>19,31</sup> Hence a value of  $\beta_4$  for Eu has been stated and it is in fair agreement with our value, Table 1.

The stability of the U(IV) lactate complexes should be expected to be the intermediary of that of Th(IV) and Pu(IV) following the order of ionic radii. This seems also to be the case although a comparison of the lactate stabilities is hampered by the scarcity of literature information. Only one value,  $\log \beta_4 = 16.18$ , for Pu(IV) has been reported and the information on Th(IV) is limited to the first four constants.<sup>21,22</sup> However, in analogy with the behaviour of U(IV) we expect anionic Th(Lac)<sub>5</sub><sup>-</sup> and Th(Lac)<sub>6</sub><sup>2-</sup> to be formed at

(sufficiently) high lactate concentration. The original work on Th(IV) was carried out at a too low lactate concentration to allow observation of anionic species,  $[\text{Lac}^-] \leq 0.01 \text{ M}$ . Predicted values of the formation constants  $\beta_5$  and  $\beta_6$  have been calculated below according to van Panthaleon's relation, Table 4.

**Comparison with statistical models.** Because of the limited data on chemically analogue elements we have compared our set of lactate formation constants with two twoparametric models. Although such mathematical models are of limited applicability they may be used for analysis of regularities in the stepwise complexation constants. The models applied are derived by Van Panthaleon van Eck and Mihailov.<sup>34,35</sup> Van Panthaleon's model is a purely empirical eqn. (14);

$$\log \beta_n = n(\log k_1 - \lambda(n-1)) \quad (14)$$

where  $k_1$  is the first stepwise constant and  $\lambda$  is a constant characteristic of the system. Mihailov's model is based on statistical thermodynamics. This implies *e.g.* that the forces between the ligand and the metal ion are unaffected by the degree of complexation and that the coordination sites of the metal ion are equivalent, eqn. (15);

$$\beta_n = A \cdot a^n / n! \quad 1 < n < N \quad (15)$$

where  $A$  and  $a$  are constants and  $N$  is the coordination number.

Van Panthaleon's model gives a good agreement with all metal lactates, Table 4, which indicates that the complexation proceeds in a regular manner.

Mihailov's model, however, does not fit equally well. It gives a good description of the first three constants for Am, Eu and U(VI) and for the first four constants for U(IV) while the formation constants for the anionic species, except  $\text{UO}_2(\text{Lac})_3^-$ , becomes substantially overestimated, Table 4. A reason for the failure to describe the anionic species might be due to violation of the model assumptions. Firstly, the equality of the coordination sites may change upon the formation of higher complexes. Secondly, and more likely, the forces between the ligand and the metal may be affected by the extent of complexation. This is reasonable because of the high degree of electrostatic forces in actinide

Table 4. Twoparametric description of the metal-lactate stability constants. I: according to Mihailov's model  $\beta_n = A \cdot d^n / n!$  where  $n$  is the number of ligands,  $A$  and  $a$  are constants.<sup>35</sup> II: according to the van Panthaleon van Eck's model  $\log \beta_n = n(\log k_1 - (n-1)\lambda)$  where  $k_1$  and  $\lambda$  are constants.<sup>34</sup> III: Experimentally derived constants from this work at 1 M NaClO<sub>4</sub> and 25 °C.

Metal ion	log A	log a	$\lambda$	log $\beta_1$	log $\beta_2$	log $\beta_3$	log $\beta_4$	log $\beta_5$	log $\beta_6$
Am <sup>3+</sup>	I	0.42±0.04	2.02±0.05		4.16±0.08	5.70±0.16	7.1±0.3		
	II			2.44±0.04	4.24	5.43	5.97		
	III			2.43±0.09	4.23±0.27	5.65±0.15	6.0±0.2		
Eu <sup>3+</sup>	I	0.36±0.05	2.10±0.04		4.26±0.07	5.88±0.12	7.4±0.3		
	II			2.46±0.04	4.34	5.64	6.36		
	III			2.46±0.09	4.28±0.25	5.87±0.10	6.5±0.2		
UO <sub>2</sub> <sup>2+</sup>	I	0.81±0.02	1.90±0.01		4.31±0.03	5.73±0.05			
	II			2.71±0.02	4.55	5.61			
	III			2.68±0.03	4.47±0.06	5.64±0.03			
U <sup>4+</sup>	I	0.35±0.02	4.05±0.03		8.15±0.04	11.72±0.08	15.17±0.13	18.52±0.15	21.79±0.15
	II			4.40±0.02	8.30	11.70	14.60	17.0	18.9
	III			4.4±0.05	8.3±0.1	11.8±0.1	15.1±0.1	17.5±0.2	19.0±0.2
Th <sup>4+</sup>	I	0.85±0.02	3.45±0.02		7.45±0.05	10.42±0.07	13.27±0.10	16.02	18.69
	II			4.30±0.02	7.76	10.65	12.88	14.45	15.36
	III <sup>a</sup>			4.21±0.02	7.78±0.03	10.54±0.06	12.90±0.08		

<sup>a</sup> 20 °C, Ref. 22.

complexes which counteracts formation of anionic species. The  $\text{UO}_2(\text{Lac})_3^-$  is an exception because of the high effective charge of the uranyl ion ( $\geq +3.3$ ).<sup>36</sup>

An advantage of Mihailov's model is that it can be used to estimate the thermodynamic quantities  $\Delta H$  and  $\Delta S$  since the constants  $A$  and  $a$  can often be approximated with linear functions of the temperature.<sup>37</sup> Applying Mihailov's model on our Am and Eu data gives reasonable agreement between experimental and calculated  $\beta_n$  at different temperatures, Fig. 7. However, there is some discrepancy for the  $\beta_2$  values for Am indicating that its temperature dependency is poorly determined.

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## REFERENCES

- Svantesson, I., Hagström, I., Persson, G. and Liljenzin, J. O. *Radiochem. Radioanal. Lett.* 37 (1979) 215.
- Svantesson, I. and Lundqvist, R. *Proc. 12ème Journées des Actinides*, IPN, Orsay, France 24–25 May 1982, p. 65.
- Perrin, D. O. *Stability Constants of Metal-Ion Complexes, Part B*, IUPAC Chem. Data Ser. No. 22, Pergamon, Oxford 1979.
- Degischer, G. and Choppin, G. R. *Gmelin Handbuch der Anorganischen Chemie, Transurane D1* (1975) 129.
- Kosyakov, V. N. and Yering, E. A. *J. Radioanal. Chem.* 56 (1980) 93.
- Lundqvist, R., Lu, J. F. and Svantesson, I. *Proc. Actinides-81*, Asilomar, California, Sept. 10–15, 1981, LBL-124441, p. 284.
- Fetzer, W. R. and Jones, R. L. *Anal. Chem.* 24 (1952) 835.
- Lundqvist, R. *Acta Chem. Scand. A* 28 (1974) 243.
- Lundqvist, R. and Rydberg, J. *Acta Chem. Scand. A* 28 (1974) 399.
- Lundqvist, R., Lu, J. F. and Svantesson, I. *Acta Chem. Scand. A* 37 (1983) 743.
- Lundqvist, R. *Acta Chem. Scand. A* 36 (1982) 741.
- Bottari, E. and Vicedomini, M. *Gazz. Chim. Ital.* 101 (1971) 860.
- Beck, M. T. *Chemistry of Complex Equilibria*, Van Nostrand, Budapest 1978.
- Rossotti, F. J. C. and Rossotti, H. *Determination of Stability Constants*, McGraw Hill, New York 1961.
- Allard, B., Kipatsi, H. and Liljenzin, J. O. *J. Inorg. Nucl. Chem.* 42 (1980) 1015.
- Högfeldt, E. *Stability Constants for Metal-Ion Complexes, Part A, Inorganic Ligands*, IUPAC Chem. Data Ser. No. 21, Pergamon, Oxford 1982.
- Sillén, L. G. and Martell, A. E. *Stability Constants of Metal Ion Complexes*, Spec. Publ. Nos. 17 and 25, The Chemical Society, London 1964 and 1971.
- Danesi, P. R., Cianetti, C. and Horwitz, E. *P. Sep. Science Techn.* 17 (1982) 507.
- Choppin, G. R. and Choppoorian, J. A. *J. Inorg. Nucl. Chem.* 22 (1961) 97.
- Aziz, A. and Lyle, S. J. *J. Inorg. Nucl. Chem.* 33 (1971) 3407.
- Nebel, D. *Z. Phys. Chem. (Leipzig)* 233 (1966) 62.
- Magon, L., Bismondo, A., Maresca, L., Tomat, G. and Portanova, R. *J. Inorg. Nucl. Chem.* 35 (1973) 4237.
- Choppin, G. R. and Friedman, G. H. *Inorg. Chem.* 5 (1966) 1599.
- Stary, J. and Balek, W. *J. Inorg. Nucl. Chem.* 29 (1967) 241.
- Miyake, C. and Nürnberg, H. W. *J. Inorg. Nucl. Chem.* 29 (1967) 2411.
- Thun, H., Guns, W. and Verbeek, F. *Anal. Chim. Acta* 37 (1967) 333.
- Crutchfield, C. A., Jr., McNabb, W. M. and Hazel, J. F. *J. Inorg. Nucl. Chem.* 24 (1962) 291.
- Sakanoue, M. and Nakatani, M. *Bull. Chem. Soc. Jpn.* 45 (1972) 3429.
- Ermakov, V. A. and Stary, I. *Radiokhimiya* 9 (1967) 197.
- Lebedev, I. A. and Yakolev, G. W. *Radiokhimiya* 3 (1961) 455.
- Deelstra, H. and Verbeek, F. *Anal. Chim. Acta* 31 (1964) 251.
- Powell, J. E., Karraker, R. H., Kolat, R. S. and Farrell, J. L. In Vorres, K. S., Ed., *Rare Earth Research II*, Gordon and Branch, New York 1964, p. 513.

33. Aziz, A., Lyle, S. J. and Newberry, J. E. *J. Inorg. Nucl. Chem.* 33 (1971) 1757.
34. Van Panthaleon van Eck, C. L. *Recueil* 72 (1953) 529.
35. Mihailov, M. H. *J. Inorg. Nucl. Chem.* 36 (1974) 107.
36. Choppin, G. R. *Radiochim. Acta* 32 (1983) 43.
37. Strezov, A., Milailov, M. H., Mihailova, V. T. and Taskaeva, M. I. *Proc. Thermodynamics of Nuclear Materials 1979*, Vol. II, p. 75., IAEA, Vienna 1980.

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