Solvent Extraction Studies of Lanthanide Acetylacetonates. Part III. Complexes formed by Tb, Ho, Tm and Lu*

Yngve Albinsson

Department of Nuclear Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

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The complex formation of the heavier trivalent lanthanides (Ln) $_{65}$Tb, $_{67}$Ho, $_{69}$Tm and $_{71}$Lu with acetylacetone (HAa) has been studied at 25 ± 0.1 °C by the liquid–liquid extraction technique in the system 0.02–3.5 M HAa in benzene/1.0 M Na(H)ClO$_4$ using trace amounts of radioactive lanthanides. The stepwise formation constants, $K_n = [\mathrm{LnAa}_n][\mathrm{LnAa}_{n-1}]^{-1}[\mathrm{Aa}^-]^{-1}$ ($n = 2$ to 4), the distribution constant of the neutral complex LnAa$_3$ between the phases (P_3), and the self-adduct formation of LnAa$_3$ · HAa in the organic phase (K_{add1}) have been evaluated.

To obtain the necessary data for a precise evaluation of the lower formation constants, distribution values as low as 0.0001 had to be measured with high accuracy in the pH range 3–9. To make this possible the investigation was made by the recently developed AKUFVE–LISOL technique. A survey of the results on all the lanthanides studied in this series is also given.

Solvent (or liquid–liquid) extraction is a well-known method for determining metal complexation. The extraction of the metal is often described by an "extraction curve", where the distribution ratio D of the metal is plotted as a function of pH or ligand concentration. The gathering of the data needed is conventionally achieved by a "test-tube technique", which, however, often gives scattered data.[2] To provide a continous solvent extraction technique, Rydberg and coworkers in the 1960s developed the AKUFVE instrument.[3] In this investigation the AKUFVE, coupled to a recently developed detector system called LISOL (Liquid scintillation on line)[4] has been used.

With the AKUFVE–LISOL equipment it has been possible to measure the weak complexation of the lanthanides Pm,[1] La, Nd, Sm and Eu[2] and the actinide Am[5] with acetylacetone; this has been reported before in this series. In this paper the extraction of Tb, Ho, Tm and Lu in the system 0.02–3.5 M acetylacetone (HAa) in benzene/1 M Na(H)ClO$_4$ will be reported. Also, a survey on all the lanthanides investigated in this series will be made.

AKUFVE–LISOL

In our continuous studies of fission product, lanthanide (Ln) and actinide (An) complexation with acetylacetone the AKUFVE technique was used in order to achieve good accuracy and to speed up the collection of data. Several on-line measurement techniques have been used with the AKUFVE, but all of them have suffered from the facts that it was possible to detect only γ-radiation and that sorption limited the detection range, especially at high pH values.[2] Further, the complexation of the lanthanides with HAa takes place in the pH range 3–9, where these metals become hydrolyzed, leading to increased sorption on the walls of the flow system, with consequent radionuclide losses to the container walls and memory effects in the detector system. Most of these difficulties are overcome by the LISOL detector system used in this paper. The principle of the AKUFVE–LISOL technique and its performance is given in Part II of this series;[2] see also Fig. 1.

Experimental

Chemicals. Acetylacetone of analytical grade (Merck p.a.) was used. It was purified by fractional distillation, the fraction at 139 °C being collected. The HAa was kept in

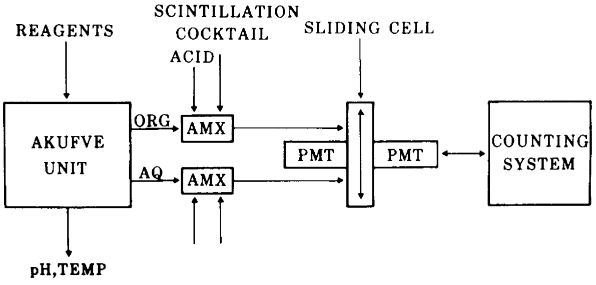

Fig. 1. Schematic picture of the AKUFVE–LISOL system. The AKUFVE consists of a mixing vessel, a continuous flow centrifugal separator and connecting pipework. Samples of the pure aqueous and organic phases are withdrawn from the liquids circulating in the AKUFVE system. These samples are mixed with acid to suppress sorption and a liquid-scintillation cocktail (AMX). The radioactivity is measured by a photomultiplier counting (PMT) system by a sliding cell mechanism that alternately measures the mixtures coming from the two AMXs.

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* For Parts I and II, see Refs. 1 and 2.

dark bottles to avoid any degradation; it was stored no longer than two weeks prior to use. Different concentrations of HAa were prepared by dilution with benzene that had been washed three times with doubly distilled water. The aqueous phase was made up using $NaClO_4$ (Merck p.a.) analytically free from carbonate.

Radiotracers of Tb, Ho, Tm and Lu were prepared by neutron activation of pure lanthanide oxides (>99.999% by Ventron, F.R.G.) at the Institutt for Energiteknikk in Norway. The irradiated oxides were dissolved in warm concentrated perchloric acid, filtered and diluted with doubly distilled water to give 1.0 M $HClO_4$. Gamma spectrometry with a HPGe detector showed no detectable amounts of other radioactivity in the solutions than the desired one. The following radionuclides were used; ^{160}Tb $t_{1/2} = 72$ d, ^{166}Ho $t_{1/2} = 27$ h, ^{170}Tm $t_{1/2} = 128$ d, ^{177}Lu $t_{1/2} = 7$ d.

A non-gelling liquid-scintillation cocktail made for heavily buffered aqueous solutions (FLOW-SCINT III from Radiomatic Instruments and Chemicals Co., U.S.A.) was used in the LISOL system (Fig. 1).

Distribution measurements. All experiments were made in the AKUFVE under nitrogen flow to maintain an "inert" atmosphere. Nitrogen gas was bubbled through both solvents before entering the mixer in the AKUFVE to avoid substantial losses of solvent. The liquid evaporating from the AKUFVE system under these conditions is mainly benzene (from the AKUFVE centrifuge), amounting to about 4 ml h^{-1}. To keep the composition of the organic phase constant a peristaltic pump was used that continuously added benzene to compensate for the evaporation losses.

Two different original concentrations of HAa in benzene (1.0 and 3.0 M) were used in the experiments carried out to evaluate the formation constants. The pH was adjusted by adding 4 M NaOH into the mixing vessel of the AKUFVE. This gives a deviation in the ionic strength at the highest measured pH values (maximum 10%), which, however, should be neglectable in the evaluation of the formation constants. The results, corrected for quenching (see below), are presented in Fig. 2. The distribution ratio D is defined as the total concentration of all metal species in the

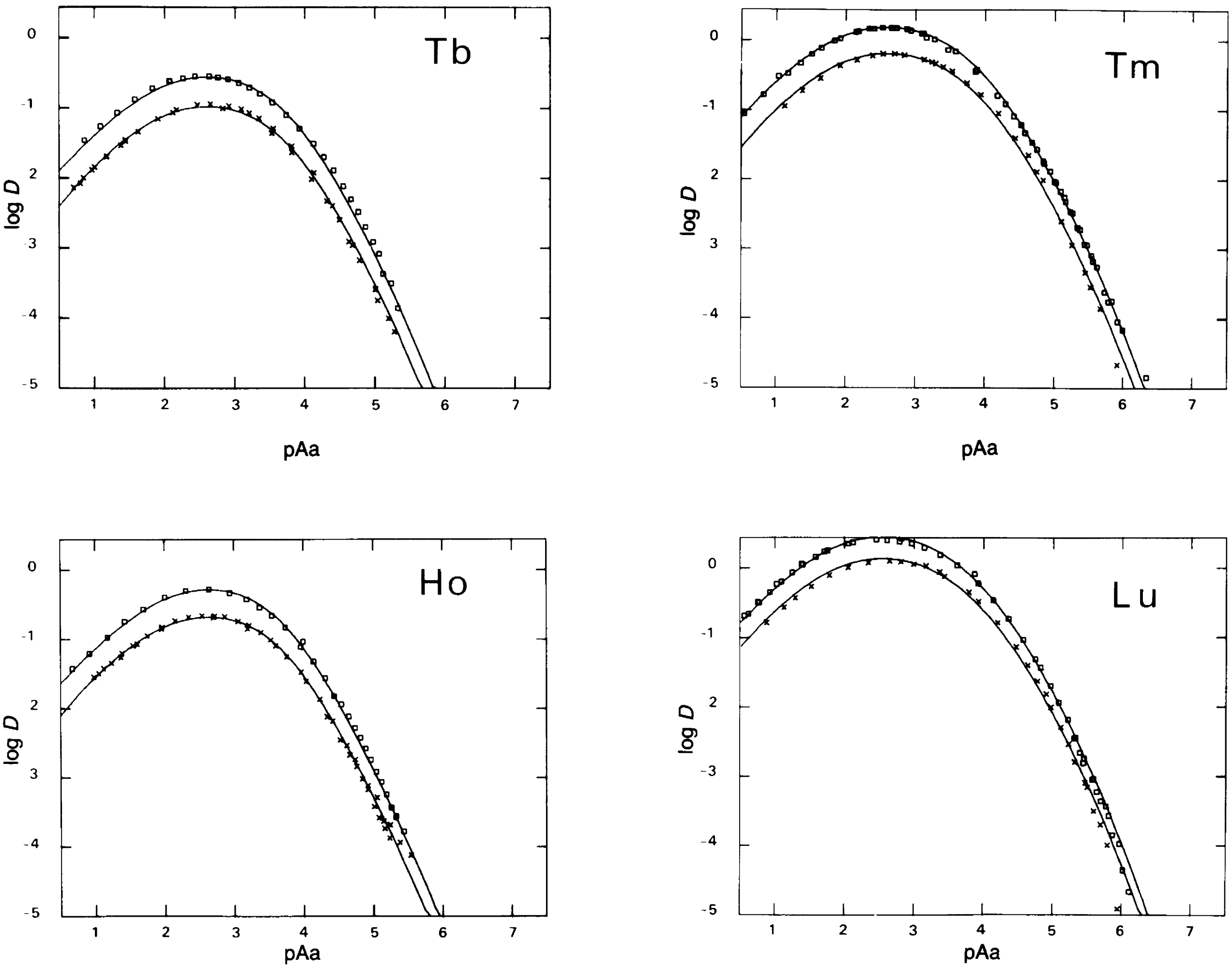

Fig. 2. Distribution ratio (D) of tracer Ln(III) (Tb, Ho, Tm and Lu) between 1 M $Na(H)ClO_4$ and C_6H_6 containing (×) 1 M $[HAa]^{\circ}_{org}$ and (□) 3 M $[HAa]^{\circ}_{org}$ as a function of pAa = $-\log[Aa^-]$. The curves are calculated with the experimentally obtained constants β_n, P_3 and K_{add1}.

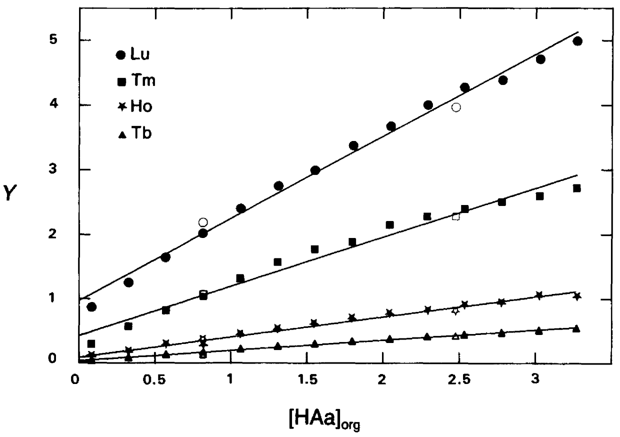

Fig. 3. The extraction of the lanthanides at constant pAa but varying concentration of $[HAa]_{org}$ using the function $Y([HAa]_{org})$, eqn. (8). Open symbols are values calculated from the extraction curves in Fig. 2. The distribution constant P_3 is obtained from the intercept, and the adduct formation constant, K_{add1}, from the slope.

organic phase divided by the total concentration of all metal species in the aqueous phase, see eqn. (3) below. pAa = $-\log[Aa^-]$ is obtained from eqn. (7) below.

To measure the adduct formation with HAa, one experiment was made starting with 1 M $NaClO_4$/0.02 M HAa in benzene at equal phase volumes and then increasing the concentration of HAa by adding equal volumes of pure HAa and 1.0 M $NaClO_4$. The results, corrected for quenching, are presented in the form of the Y-function in Fig. 3.

The pH was measured by a flow-through glass reference electrode (A1205DO3 2195-100 LKB, Sweden). The KCl solution in the electrode was replaced with $NaClO_4$ to avoid precipitation in the electrode membrane.[6] The electrode was placed in a side flow of the centrifuge exit aqueous phase. The temperature was in all experiments kept at 25 ± 0.1 °C by a thermostat system.

The scintillation detector was a modified version of a Flow-One detector (Radiometric Instruments and Chemical Co., Tampa U.S.A.), in which the detector cell was replaced by a specially constructed sample changer.[4]

The experimental conditions are further described in Ref. 7.

Quenching. When using liquid scintillation as a detection technique for β-emitting radionuclides, as in our experiments, quenching becomes a problem. The quenching is mostly due to the presence of HAa:[8] consequently it will depend on the pAa (or pH) value and the original concentration of HAa. Quenching may cause losses of counting efficiency up to 20 % with ^{166}Ho [$E_{max}(\beta) = 1.9$ MeV] and up to 50 % with ^{177}Lu [$E_{max}(\beta) = 0.5$ MeV] in 3 M HAa in benzene. To correct for this effect, calibration measurements were made, holding all other parameters as in the main experiment. In this experiment the radioactive Ln is fed through the sorption suppression liquid (i.e. 2 M $HClO_4$, Fig. 1), the same amount to each phase, while no activity is added to the AKUFVE. A plot of F_{HAa} [eqn. (1)], where R_{org} and R_{aq} are the measured radio-

$$F_{HAa} = R_{org}/R_{aq} \qquad (1)$$

activities in the respective phases corrected for background radioactivity, as a function of $[Aa^-]$ at given original concentration of HAa in the organic phase ($[HAa]^\circ_{org}$), see Fig. 4, can be best approximated by a straight line [eqn. (2)]

$$F_{HAa} = a + b[Aa^-] \qquad (2)$$

for each $[HAa]^\circ_{org}$. $[Aa^-]$ is obtained from eqn. (7) below.

For the experiments in which HAa was varied but the pAa was kept constant, the correction factors were obtained by making an experiment under exactly the same conditions as in the main experiment (including pAa and $[HAa]_{org}$), but with the radioactive Ln fed through the sorption surpression liquid, and with no radioactivity added to the AKUFVE flows. In Fig. 5 F_{HAa} has been plotted against $[HAa]_{org}$ for the lanthanides used.

F_{HAa} also takes into account differences in volumes between the two spiral cells in the detector. All data in Figs. 2 and 3 are D_{corr}-values.

The extraction curve

From the considerations in Parts I and II of this series,[1,2] the conclusion can be drawn that only acetylacetone complexes are of any importance in our system. The model for Ln(III) extraction will then be given by eqn. (3) (leaving out water of hydration):

$$D=\frac{P_3\beta_3[Aa^-]^3(1+K_{add1}[HAa]_{org}+K_{add2}[HAa]^2_{org}+\ldots)}{1+\beta_1[Aa^-]+\beta_2[Aa^-]^2+\beta_3[Aa^-]^3+\beta_4[Aa^-]^4} \qquad (3)$$

where

$$\beta_n = [LnAa_n][Ln^{3+}]^{-1}[Aa^-]^{-n} \qquad (4)$$

$$P_3 = [LnAa_3]_{org}[LnAa_3]^{-1} \qquad (5)$$

and

$$K_{addi} = [LnAa_3(HAa)_i]_{org}[LnAa_3]^{-1}_{org}[HAa]^{-i}_{org} \qquad (6)$$

The $[Aa^-]$ value is calculated from eqn. (7)[1,9]

$$[Aa^-] = K_a[H^+]^{-1}[HAa]^\circ_{org}(1 + K_d + K_a[H^+]^{-1})^{-1} \qquad (7)$$

where $K_a = 1.0\times10^{-9}$ and $K_d = 4.4$ in 1 M $NaClO_4$,[10] and $[HAa]^\circ_{org}$ is the original concentration of HAa in the organic phase. No index refers to the aqueous phase.

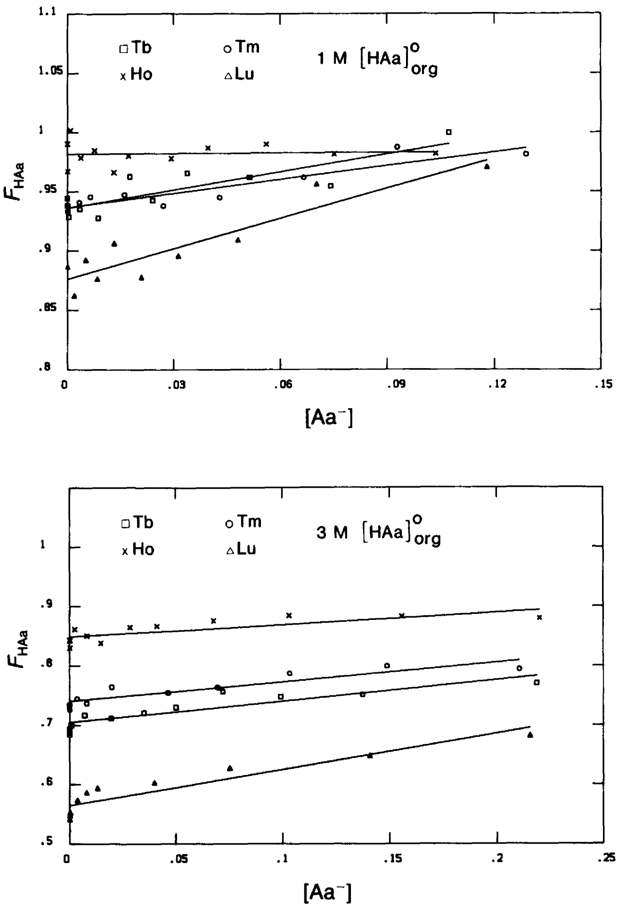

Fig. 4. The upper figure shows the correction factor F_{HAa} for quenching of the radioactivities from ^{160}Tb, ^{166}Ho, ^{170}Tm and ^{177}Lu in the aqueous and organic phases as a function of [Aa$^-$] at 1 M original concentration of HAa in the organic phase. The lower figure shows the same for 3 M $[\mathrm{HAa}]^{\circ}_{\mathrm{org}}$. Points are experimental values, lines are the calculated correction functions, $F_{\mathrm{HAa}} = a + b[\mathrm{Aa}^-]$.

Treatment of data

The experimental data with 1.0 and 3.0 M $[\mathrm{HAa}]^{\circ}_{\mathrm{org}}$ (Fig. 2) were corrected for quenching and then fitted by a least-squares method (Simplex) to calculate the formation constants according to the procedure described in Part II of this series.[2] The final minimized error square sum ($S_{\min} = X^2/k$)[11] was 1.0 ± 0.3, indicating that the mathematical model and the weights are consistent with the experimental data.[12,13] The errors given for the formation constants are the change in that constant that doubles the $S_{\min}$ value.

The distribution and adduct formation constants can be obtained in two ways, based on eqn. (8), which is derived from eqn. (3):

$$Y = D\beta_3^{-1} \Sigma\, \beta_n[\mathrm{Aa}^-]^{n-3} = P_3(1 + K_{\mathrm{add1}}[\mathrm{HAa}]_{\mathrm{org}} + K_{\mathrm{add2}}[\mathrm{HAa}]^2_{\mathrm{org}} + \dots) \qquad (8)$$

From the data in Fig. 2 and using the β_n values derived according to the previous paragraph, Y may be calculated using the left-hand side of eqn. (8). The two curves (for each Ln) in Fig. 2 yield two points in Fig. 3. The other way to calculate the parameters is to measure D_{Ln} as a function of $[\mathrm{HAa}]_{\mathrm{org}}$ at approximately constant pAa.[2] This yields the filled points in Fig. 3. Both sets of Y values should follow the right-hand relation of eqn. (8). The points seem to fit a straight line. From these lines, the parameters P_3 and K_{add1} are obtained.

Results

Using the experimental technique and data treatment described above, the complexation of Tb, Ho, Tm and Lu with acetylacetone has been investigated, yielding the formation constants β_2, β_3 and β_4, the distribution constant P_3 and the first adduct formation constant K_{add1}. The values are listed in Table 1, together with β_1 values from Grenthe *et al.*[14] These values are used to calculate the "theoretical" curves in Fig. 2. The distribution curves go smoothly through the experimental points, and no interfering reactions from, e.g. hydrolysis, can be detected. Also, the influence of polynuclear species can be excluded, because within the concentration range 3×10^{-4} to 5×10^{-5} M Ln no change in the extraction curves could be observed.

Discussion

The complex formation of the lanthanides Pm (Part I[1]), La, Nd, Sm and Eu (Part II[2]) and Tb, Ho, Tm and Lu (this paper) with HAa in 1 M $\mathrm{NaClO_4}$ has been studied by the AKUFVE–LISOL technique and the stepwise formation constants calculated. Some of the first three formation constants have been reported earlier by other researchers,[14,16–20] but only one group[21,22] has reported a fourth formation constant, besides us.[1,2,23] Although we can estimate a K_1 value, within ± 0.3 log units, we have not been able to determine it with satisfactory accuracy, because of experimental limitations which would have required reliable measurements of D values as low as 10^{-6}, which is practically impossible in our opinion. Therefore we have taken the most accurate K_1 values available in the literature (measured potentiometrically), converted them to 1.0 M ionic strength,[1,15] and used them in our final D versus pAa plots.

In Fig. 6 the K_n values have been plotted against atomic number. Each K_n value increases with increasing atomic number, as expected due to the lanthanide contraction, which increases the metal charge density and thus also the strength of the electrostatic bond to the Aa$^-$ oxygen atoms. The increase in formation constant with increasing Ln atomic number has been observed with many complexing ligands.[24] Often in such plots a break around Gd is observed; in $_{64}$Gd, the 4f electron shell is half-filled. We can also see such a break in Fig. 6, but only as a slight indication, perhaps being more prominent for the first com-

Table 1. Complex formation constants for terbium, holmium, tulium and luthetium with acetylacetone at 25 °C in 1.0 M $NaClO_4$ [eqn. (4)].

Ln	log β_1[a]	log β_2	log β_3	log β_4	log P_3[b]	log K_{add1}[c]
Tb	(5.93)	10.00±0.12	13.34±0.06	15.26±0.11	−1.42	0.62
Ho	(5.96)	9.93±0.11	13.30±0.05	15.23±0.08	−1.04	0.54
Tm	(6.00)	10.43±0.08	13.82±0.05	15.66±0.08	−0.35	0.25
Lu	(6.14)	10.58±0.12	13.81±0.07	15.60±0.13	−0.05	0.12

[a]The β_1 values are taken from Ref. 14 corrected for ionic strength.[1,15] [b]The distribution constant for $LnAa_3$ (hydrated) is defined by eqn. (5). [c]The adduct formation constant, K_{add1}, refers to pure benzene (water saturated), see eqn. (6).

Table 2. Stepwise formation constants for $LnAa_n$ complexes from (a) this series of papers, $I = 1.0$, (b) Refs. (21) and (22), solvent extraction, $I = 0.1$, (c) Ref. 14, potential titration, $I = 0.1$, and (d) Ref. 17, potential titration, $I = 2$, converted to 1 M ionic strength.[1,15]

	log K_2				log K_3			log K_4	
	This paper	Refs. 21,22	Ref. 14	Ref. 17	This paper	Refs. 21,22	Ref. 14	This paper	Refs. 21,22
$_{57}La$	2.74	3.50	3.36	3.62	2.56	1.94	2.41	1.11	1.67
$_{60}Nd$	3.66	4.30	4.01	–	2.99	3.17	3.11	1.71	1.71
$_{61}Pm$	3.90	–	–	–	3.03	–	–	1.84	–
$_{62}Sm$	3.80	4.29	4.37	4.57	3.29	2.93	2.81	1.72	1.75
$_{63}Eu$	4.01	–	4.39	4.47	3.33	–	3.20	1.85	–
$_{65}Tb$	4.07	–	4.52	–	3.34	–	3.32	1.92	–
$_{67}Ho$	3.97	–	4.59	–	3.38	–	3.31	1.93	–
$_{69}Tm$	4.43	4.65	4.67	4.89	3.39	3.13	3.39	1.84	1.70
$_{71}Lu$	4.44	4.58	4.68	4.95	3.23	3.31	3.54	1.79	1.47

plexation steps; see e.g. the two dashed lines through the K_1 data which meet at $Z = 64$. It should be observed that K_2, K_3 and K_4 are independently measured values, not products (log β_n). No tetrade effect (or double–double) break can be seen (cf. e.g. Ref. 24).

A comparison of the log K_2 values obtained in this investigation using solvent extraction (at $I = 1$) and those obtained with potentiometric titration (Table 2) reveals a difference of about 0.5 in log value (lower in our investigation). For this there is no explanation at the moment. The K_2 values given by Nakamura and Suzuki,[21,22] measured by the solvent extraction technique, are uncertain, since they often depend on a few measured points at low distribution values.

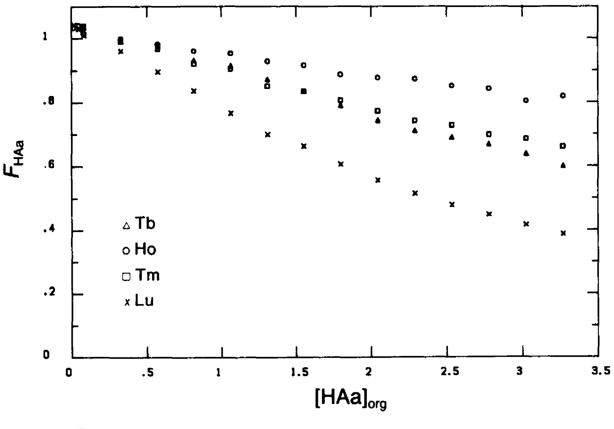

Fig. 5. Quenching ratios, F_{HAa}, at approximately constant $[Aa^-]$ ($-\log[Aa^-] = 2.75 \pm 0.07$) as a function of $[HAa]_{org}$ for Tb, Ho, Tm and Lu.

The value of log K_3 obtained in this investigation is in fair agreement with those measured by Grenthe *et al.*, with a mean deviation of less than 0.1 in log value. For the values given by Nakamura and Suzuki for K_3 the agreement improves with increasing Ln atomic number (within 0.6–0.2 in log value); this can be explained by the increased accuracy of the Nakamura–Suzuki data.

Also, for K_4 there is good agreement between our values and those obtained by Nakamura and Suzuki, except for La (deviation 0.6 in log value).

The maximum distribution of Ln(III) in the Ln(III)–HAa C_6H_6/1 M $NaClO_4$ system, log $D_{max}(Ln)$, is low. The $D_{max}(Ln)$ value increases with atomic number Z, being −1.4 for $_{57}La$ and +0.1 for $_{71}Lu$ in 1 M $[HAa]^{\circ}_{org}$; at 3 M $[HAa]^{\circ}_{org}$ the values go from −0.7 to +0.4. These low distribution ratios can be explained by the strong hydration of the $LnAa_3$ complex, which does not give up its water of hydration even on transfer from the aqueous to the organic phase, thus all the time being strongly hydrophilic. Studies on solid $LnAa_3$ dissolved in benzene show several molecules of water attached to the metal complex.[1] The increase

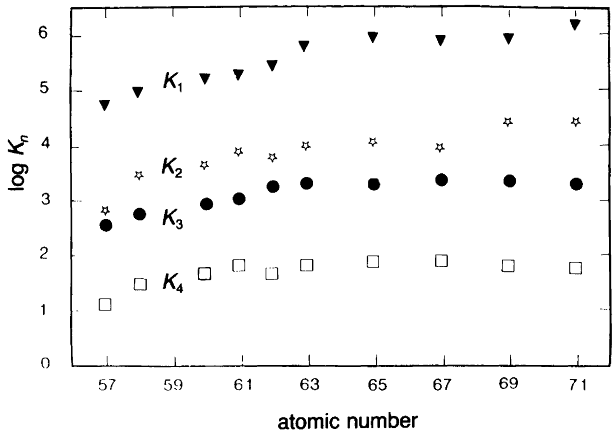

Fig. 6. Stepwise formation constants, K_n, for $LnAa_n^{3-n}$ complexes in 1.0 M $Na(H)ClO_4$ at 25 °C as a function of Z. The K_1 values are taken from Ref. 14. Experiments yielding the Ce(III) values will be published separately.

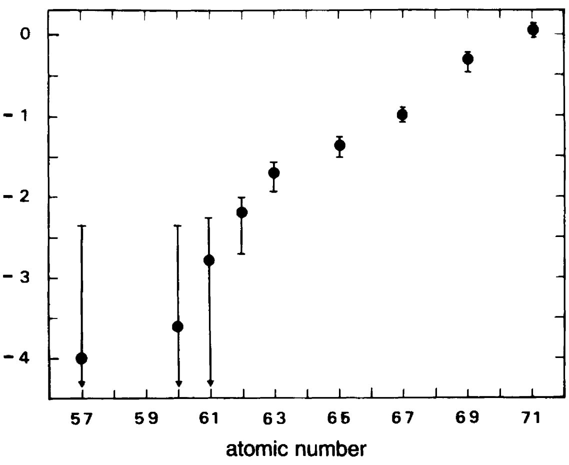

Fig. 7. The distribution constant, P_3, for $LnAa_3$ between benzene and 1.0 M $Na(H)ClO_4$ at 25 °C as a function of Z. The errors are obtained using 90 % confidence limits.

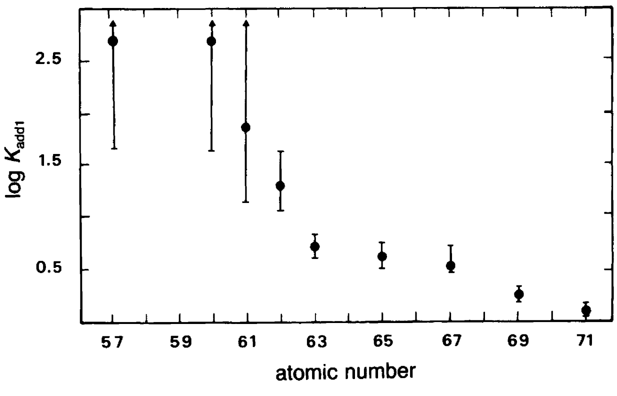

Fig. 8. The self-adduct formation constants, K_{add1}, for the reaction $LnAa_3(org) + HAa(org) \rightleftharpoons LnAa_3 \cdot HAa(org)$ in benzene, as a function of Z. The errors are obtained using 90 % confidence limits.

in $D_{max}(Ln)$ with Z could then be explained by a decreasing hydration of the complex with increasing Z, e.g. perhaps being $LaAa_3(H_2O)_3$ for $_{57}La$ and $LuAa_3(H_2O)_2$ for $_{71}Lu$. The successive increase in $D_{max}(Ln)$ from Z 57 to 71 requires a dynamic view of the number of hydrate waters on the molecule.

A comparison of the distribution ratios log $D_{max}(Ln)$ with those obtained by Suzuki *et al.*[21,22] reveals a difference of about 0.2 in log values (higher in this investigation) at 0.2 M $[HAa]^{\circ}_{org}$. This can be explained by the variation in ionic strength, 1.0 M (ours) and 0.1 M (Suzuki *et al.*), respectively. Allard *et al.*[25] found the difference in D_{max} for $ZnAa_2$ in the benzene/$NaClO_4$ system at ionic strengths 0.1 and 1.0, respectively, to be about 0.2 log units. This is in accordance with our findings on the $LnAa_3$ complex. La, however, differs in the opposite direction.

With the support of the extraction data in this series (Parts I and II and this paper) and the literature survey in Part I concerning the adduct formation of $LnAa_3$, it is concluded that in the organic phase at least two complexes exist, $LnAa_3$ and the self-adduct $LnAa_3HAa$; also, for the lower lanthanides (especially for La) a second self-adduct, $LnAa_3(HAa)_2$, may possibly exist.

Assuming the adduct to be in the keto-form, $LnAa_3 \cdot HAa$ would occupy 8 coordination positions and $LnAa_3(HAa)_2$ 10 coordination positions. For the hydration of Ln(III), the coordination number is assumed to decrease from 9 for $_{57}La$ to 8 for $_{71}Lu$. With the exception of structural difficulties accompanying an $LnAa_3(HAa)_2$ complex, our results are otherwise in accordance with the picture of a decreasing coordination number as Z increases.

Although P_3K_{add1} can be determined exactly, the values of the distribution constants, P_3, and the adduct formation constants, K_{add1}, are difficult to calculate with high precision, at least for the lower lanthanides, because P_3 is very low and imprecise, and the K_{add} value depends on the P_3 value. Thus the values in Figs. 7 and 8 must be taken with some care. A decreasing adduct formation constant K_{add1} with Z has been observed by Nakamura and Suzuki[26] for the $LnAa_3phen$ (phen = 1,10-phenanthroline) system, in agreement with our findings.

From the distribution of the uncharged complex (P_3) in Fig. 7 it can be seen that there may be a break at around $_{63}Eu$. This is more strongly indicated in the adduct formation constant K_{add1} (Fig. 8). It may be explained by a change in the coordination number from 9 to 8 around atomic number 63,[27-29] thus decreasing the ability of the $LnAa_3$ complex to add an HAa molecule.

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