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EQUILIBRIUM CONSTANTS FOR AQUEOUS FLUORO COMPLEXES OF SCANDIUM, YTTRIUM, AMERICIUM(III) AND CURIUM(III) BY EXTRACTION INTO DI-2-ETHYLHEXYL PHOSPHORIC ACID

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Abstract—From studies of the extraction of yttrium, americium(III) and curium(III) from aqueous fluoride, $[F^-]$, into di-2-ethylhexyl phosphoric acid, H_2D_2, it has been deduced that for $[F^-] = (0{\cdot}1-4{\cdot}0)\times 10^{-3}\,ml^{-1}$ and pH = 3·60 substances other than $M(HD_2)_3$ contribute appreciably to the metal, M, ion distribution. From known equilibrium constants for aqueous fluoro metal complexes of yttrium it was concluded that, under the prevailing experimental conditions, a substance of the form $YF_3\,.\,3H_xD_x$ (where x is an unknown integer) also extracts. A method was thus evolved whereby distribution data alone were made to yield equilibrium constants for the stepwise formation of the first three complexes for americium(III) $[\beta_1 = 2{\cdot}46\times 10^3, \beta_2 = 1{\cdot}28\times 10^6, \beta_3 = 1{\cdot}0\times 10^9]$ and curium-(III) $[\beta_1 = 2{\cdot}21\times 10^3, \beta_2 = 1{\cdot}50\times 10^6, \beta_3 = 1{\cdot}2\times 10^9]$ at $\mu = 0{\cdot}500$ ($NaClO_4$). For $[F^-] = (0{\cdot}2–220)\times 10^{-5}\,ml^{-1}$ and pH 2·50 scandium extracts overwhelmingly as $Sc(HD_2)_3$ and $\beta_1-\beta_4$ are obtained in good agreement with published values. Tests, which throw light on the nature and number of the principle metal species which extract, are described.

LIQUID–liquid extraction studies using di-2-ethyl-hexyl phosphoric acid (HDEHP) have been carried out in an attempt to determine step-wise equilibrium constants for interactions between lanthanoid(III) and fluoride ions in aqueous solution. In the work reported previously[1], evidence was obtained for the existence of two complex ions, $LnF^{2+}_{aq.}$ and $LnF^{+}_{2aq.}$ over a range of fluoride ion concentrations. Equilibrium constants for formation of the first complex cation were in good agreement with reported values; in general however, independent data are not available for higher complex formation. Extension of the measurements to solutions containing higher fluoride concentrations showed that the extraction behaviour of the metal under such conditions was more complicated than had hitherto been assumed. Accordingly, partition studies with HDEHP, now reported, were carried out to obtain sufficient information on the nature of the species extracted to enable equilibrium constants for the first three complex fluorides in the aqueous phase to be calculated. Results from the partition of scandium and yttrium for which equilibrium constants are available from other sources[2–4] were used in this study to devise a method for the calculation of constants for the complexes of americium(III) and curium(III).

EXPERIMENTAL

Radionuclides

Scandium-46 of high specific activity and carrier-free yttrium-91 were obtained from The Radio chemical Centre, Amersham, England. Americium-241 and curium-244 have been described pre-

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1. S. J. Lyle and S. J. Naqvi, *J. inorg. nucl. Chem.* **28**, 2993 (1966); *ibid.* **29**, 2441 (1967).
2. J. W. Kury, A. D. Paul, L. G. Hepler and R. E. Connick, *J. Am. chem. Soc.* **81**, 4185 (1959).
3. A. D. Paul, L. S. Gallo and J. B. Van Camp, *J. phys. Chem.* **65**, 441 (1961).
4. A. Aziz and S. J. Lyle, Unpublished work, this laboratory (1968).

viously[5]. All these isotopes were counted in solution; scandium and americium in a well-type Na(Tl)I scintillation counter, yttrium by Geiger–Muller counter and curium by the liquid scintillation method[5].

Equilibrations

Distribution ratios were determined using HDEHP and reagent grade chemicals as described in earlier publications[1]. Unless otherwise stated aqueous solutions had a pH = 3·60.

In some measurements (see Tables 6 and 7 and Fig. 1) the pH was varied from 3·60 to 4·58. In these experiments the initial pH was obtained by careful addition of the minimum quantity of dilute sodium hydroxide to the appropriate mixture of stock solutions originally at pH 3·60. The pH was checked after equilibration and if within 0·03 pH units of that of the pre-equilibrated solution this final value was used to compute the ligand concentration; if the change was greater than 0·03 units the sample was discarded because of the possibility of interference from accidental contamination during or immediately after equilibration.

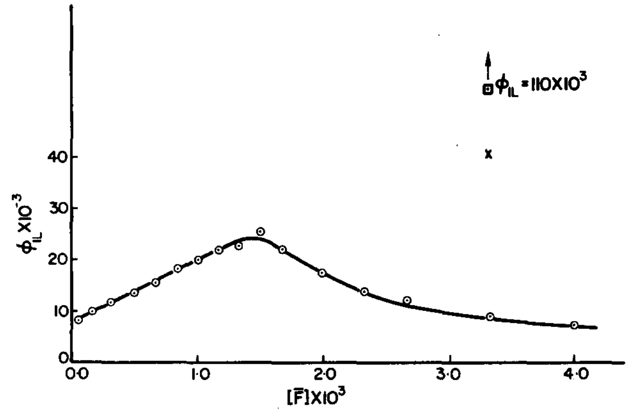

Fig. 1. ϕ_{1L} plotted ⊙ as a function of [F$^-$] for yttrium distribution from aqueous [F$^-$] at μ = 0·500 (NaClO$_4$), and pH 3·60 into 0·01% w/v HDEHP in toluene. X and ⊡ represent ϕ_{1L} from similar solutions at [F$^-$] = 3·32 × 10^{-3} ml^{-1} and pH 3·83 and 3·97 respectively. The full curve represents ϕ_{1L} calculated from Equations (9) or (10) taking K = 1·92 (see text). The temperature was 25°C.

RESULTS AND DISCUSSION

Distribution ratios, ϕ_L, for scandium, yttrium, americium(III) and curium(III) between HDEHP (H_2D_2) in toluene and aqueous fluoride solutions at constant ionic strength were used to calculate ϕ_{1L} as a function of fluoride ion concentration, [F$^-$]. [$\phi_{1L} = (k_0/\phi_L - 1)/[F^-]$ where k_0 and ϕ_L are metal ion partition ratios between equal volumes of the phases in the absence and presence of fluoride ion respectively]. If only $M(HD_2)_3$ extracts into the toluene ϕ_{1L} should be a steadily increasing function of increasing [F$^-$] in the aqueous phase as was observed for indium(III)[6]. ϕ_{1L} is plotted against [F$^-$] for yttrium in Fig. 1. Curves of similar shape are obtained for americium(III) and curium(III) but not for scandium. Other less detailed measurements with lanthanum, cerium(III), europium(III), gadolinium and actinium not reported here[4] behave like yttrium. Independent

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5. A. Aziz, S. J. Lyle and S. J. Naqvi, *J. inorg. nucl. Chem.* **30**, 1013 (1968).
6. A. Aziz and S. J. Lyle, *J. inorg. nucl. Chem.* **30**, 3223 (1968).

potentiometric studies[3,4] have provided reliable data for overall equilibrium constants, β_j, for yttrium interaction with $[F^-]$. Accordingly the yttrium system was used in the attempt to find a method whereby equilibrium constants can be computed from the partition data alone. This approach may be justified on the grounds (1) that existing potentiometric methods are not applicable to a study of americium and curium and (2) that it should provide information concerning the nature of the extraction process.

The yttrium–fluoride system

From Fig. 1 values for β_1 and β_2 can be obtained directly from the intercept and slope, respectively, of the curve as was done for previously reported[1] measurements over limited and sufficiently low fluoride concentration ranges. β_1 and β_2 thus obtained are in good agreement with values got by independent methods of measurement (Table 1). The decrease in ϕ_{1L} at higher fluoride concentrations could conceivably be due to precipitation or surface adsorption of metal fluoride; careful material balance checks on both phases however appear to rule out this possibility. It may therefore be concluded that $[F^-]$ interaction with the metal ion gives rise to a fluoro metal complex which is readily solvated and thus extracted by HDEHP. In view of the shape of the $\phi_{1L}-[F^-]$ curve at low $[F^-]$ and the suspected low degree of solvation of MF_3 by water it seems reasonable to conclude that YF_3 is solvated by the HDEHP. To ascertain qualitatively whether one or more species were undergoing phase transfer, experiments similar to those devised by Martin and Gillies[7] were employed with the results presented in Fig. 2. In these experiments the yttrium activity per unit volume of phase is obtained and plotted for distributions carried out over a range

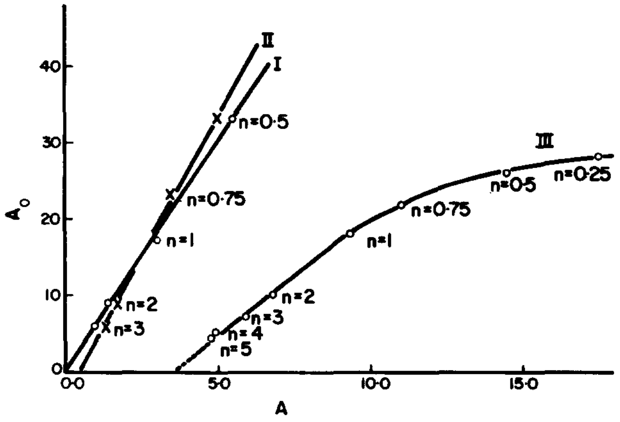

Fig. 2. The effect of changing organic:aqueous phase ratio, *n*, on the distribution of yttrium from aqueous solutions of three different compositions into 0·01% w/v HDEHP in toluene. Curve I, $[F^-]$ absent; curve II, $[F^-] = 9{\cdot}97\times10^{-4}\,ml^{-1}$ and for curve III, $[F^-] = 3{\cdot}32\times10^{-3}\,ml^{-1}$. $\mu = 0{\cdot}500$ ($NaClO_4$) at 25°C. A_0 and A represent the relative concentrations of yttrium in the organic phase to that in the aqueous phase.

[7] F. S. Martin and G. M. Gillies, *A.E.R.E. Rep. No.* C/R816 (1951).

Table 1. Equilibrium constants, β_j, for metal(III)-fluoride complexes in aqueous solution at an ionic strength, $\mu = 0{\cdot}500$ ($NaClO_4$) and 25°C

Metal ion	Method	μ	β_1	β_2	β_3	β_4	Reference
Sc^{3+}	dis*	0·5	$(1{\cdot}47 \pm 0{\cdot}11)10^{6}$	$(2{\cdot}77 \pm 0{\cdot}07)10^{11}$	$(2{\cdot}91 \pm 0{\cdot}14)10^{15}$	$(3{\cdot}06 \pm 0{\cdot}12)10^{18}$	p.w.
	Pot	0·5	$1{\cdot}51 \times 10^{6}$	$2{\cdot}82 \times 10^{11}$	$3{\cdot}31 \times 10^{15}$	$2{\cdot}34 \times 10^{18}$	[2]
Y^{3+}	dis	0·5	$(7{\cdot}70 \pm 0{\cdot}21)10^{3}$	$(12{\cdot}8 \pm 0{\cdot}3)10^{6}$	$20{\cdot}0 \times 10^{9}$		p.w.
	Pot	0·5	$8{\cdot}51 \times 10^{3}$	$13{\cdot}6 \times 10^{6}$	$21{\cdot}8 \times 10^{9}$	$\sim 176 \times 10^{12}$	[3]
	Pot	0·5	$(8{\cdot}20 \pm 0{\cdot}21)10^{3}$	$(13{\cdot}8 \pm 0{\cdot}6)10^{6}$	$(19{\cdot}5 \pm 0{\cdot}8)10^{9}$		[4]
Am^{3+}	dis	0·5	$(2{\cdot}46 \pm 0{\cdot}07)10^{3}$	$(1{\cdot}28 \pm 0{\cdot}09)10^{6}$	$1{\cdot}0 \times 10^{9}$		p.w.
Cm^{3+}	dis	0·5	$(2{\cdot}21 \pm 0{\cdot}07)10^{3}$	$(1{\cdot}50 \pm 0{\cdot}09)10^{6}$	$1{\cdot}2 \times 10^{9}$		p.w.

dis = liquid–liquid distribution; Pot = Potentiometric; p.w. = present work.

of organic to aqueous phase volumes; the composition of the phases is held constant except for the distributing metal ion which should be at as low concentration as possible. Curve I is a straight line passing through the origin so it can be concluded that only one species extracts and one species exists in the aqueous phase; it may be deduced from curve II for $[\mathrm{F}^-] = 9{\cdot}97 \times 10^{-4}\,\mathrm{ml}^{-1}$ that one species extracts predominantly but that the aqueous phase contains non-extracting components. Curve III for $[\mathrm{F}^-] = 3{\cdot}32 \times 10^{-3}\,\mathrm{ml}^{-1}$ provides evidence, since it is non-linear, for the extraction of more than one species into the toluene. Distribution studies for equal volumes of phases for which the HDEHP concentration in toluene is varied show that ϕ_L retains a cubic dependence on HDEHP even at the high $[\mathrm{F}^-]$ (Table 2). It was also observed that at constant HDEHP in the toluene phase and at a constant and large ($3{\cdot}32 \times 10^{-3}\,\mathrm{ml}^{-1}$ concentration of F^-] at which the second partitioning species might be expected to swamp any contribution from $\mathrm{Y(HD_2)_3}$, ϕ_L is independent of hydrogen ion over the pH range (3·4–4·0) where measurements (ϕ_L) were possible.

Table 2. Distribution ratio, ϕ_L, for yttrium between HDEHP in toluene and an aqueous phase $\mu = 0{\cdot}500$ ($\mathrm{NaClO_4}$) in the absence and presence of $[\mathrm{F}^-]$

Exp. No.	HDEHP % w/v x 10^2	$[\mathrm{F}^-] = 0$ ϕ_L	$[\mathrm{F}^-] = 0$ ϕ_L^*	$[\mathrm{F}^-] = 9{\cdot}97 \times 10^{-4}\,\mathrm{ml}^{-1}$ ϕ_L	$[\mathrm{F}^-] = 9{\cdot}97 \times 10^{-4}\,\mathrm{ml}^{-1}$ ϕ_L^*	$[\mathrm{F}^-] = 3{\cdot}32 \times 10^{-3}\,\mathrm{ml}^{-1}$ ϕ_L	$[\mathrm{F}^-] = 3{\cdot}32 \times 10^{-3}\,\mathrm{ml}^{-1}$ ϕ_L^*
1	2·50			35·41	35·46	24·10	24·05
2	1·25	92·54	9·54	4·44	4·43	3·02	3·01
3	1·00	47·38		2·27		1·54	
4	0·75	20·00	19·98	0·96	0·96	0·65	0·65
5	0·50	5·91	5·92				

*Calculated from the data for experiment 3 and assuming ϕ_L is proportional to $[\mathrm{HDEHP}]^3$.

It is proposed on the basis of the evidence presented above that $\mathrm{YF_3}$ solvated by HDEHP and $\mathrm{Y(HD_2)_3}$ extract into the toluene at and beyond the fluoride concentrations at which ϕ_{1L} attains a maximum (Fig. 1). The reactions giving rise to extractible species are then of the form

$$M^{3+} + 3\mathrm{H_2D_2} \rightleftharpoons M(\mathrm{HD_2})_3 + 3\mathrm{H}^+ \tag{1}$$

and

$$M\mathrm{F_3} + 3\mathrm{H}_x\mathrm{D}_x \rightleftharpoons M\mathrm{F_3}\,.\,3\mathrm{H}_x\mathrm{D}_x \tag{2}$$

where x is an unknown integer (probably 1 or 2) and M^{3+} the metal ion, e.g. yttrium.

If it is assumed that at equilibrium $M(\mathrm{HD_2})_3$ and $M\mathrm{F_3}\,.\,3\mathrm{H}_x\mathrm{D}_x$ concentrations in the aqueous phase can be neglected, i.e. their distribution coefficients are large, the overall distribution ratio, ϕ_L, for the metal ion is given by

$$\phi_L = \frac{[M(\mathrm{HD_2})_3]_{\mathrm{org.}} + [M\mathrm{F_3}\,.\,3\mathrm{H}_x\mathrm{D}_x]_{\mathrm{org.}}}{[M^{3+}] + [M\mathrm{F}^{2+}] + [M\mathrm{F_2}^{+}] + [M\mathrm{F_3}] + \ldots}. \tag{3}$$

(Aqueous phase concentrations are distinguishable by the absence of a subscript).

By limiting the discussion to three fluoro complexes in the aqueous phase

$$\phi_L = \frac{K'[H_2D_2]^3_{\text{org.}}[M^{3+}] + K''\beta_3[H_xD_x]^3_{\text{org.}}[M^{3+}][F^-]^3}{[M^{3+}]+\beta_1[M^{3+}][F^-]+\beta_2[M^{3+}][F^-]^2+\beta_3[M^{3+}][F^-]^3} \tag{4}$$

$$\text{where } K' = \frac{[M(HD_2)_3]_{\text{org.}}[H^+]^3}{[M^{3+}][H_2D_2]^3_{\text{org.}}} \text{ and } K'' = \frac{[MF_3 \,.\, 3H_xD_x]_{\text{org.}}}{[MF_3][H_xD_x]^3_{\text{org.}}}$$

from Equations (1) and (2) respectively.

In the absence of fluoride the distribution ratio, k_0, is given by $k_0 = K'[H_2D_2]^3_{\text{org.}}[H^+]^{-3}$ so that Equation (4) becomes

$$\phi_L = \frac{k_0 + K''\beta_3[H_xD_x]^3[F^-]^3}{1+\beta_1[F^-]+\beta_2[F^-]^2+\beta_3[F^-]^3}. \tag{5}$$

Since H_2D_2 is kept at a constant concentration in the toluene we can write $K''[H_xD_x]^3 = \text{constant} = K$ and

$$\phi_{1L} = \beta_1+\beta_2[F^-]+\beta_3[F^-]^2 - \frac{K\beta_3}{\phi_L}[F^-]^2 \tag{6}$$

or

$$\phi_{1L} = \phi^*_{1L} - \frac{K\beta_3}{\phi_L}[F^-]^2 \tag{7}$$

Rearranging Equation (7)

$$(\phi^*_{1L} - \phi_{1L})\phi_L/[F^-]^2 = K\beta_3 \tag{8}$$

If β_1, β_2 and β_3 are known, ϕ^*_{1L} and hence the l.h.s. of Equation (8) can be evaluated numerically; this has been done over a fluoride concentration range of (2–4) × 10^{-3} ml^{-1} with the results set out in Table 3.

Table 3. Test of Equation (8) using yttrium distribution data

$[F^-] \times 10^3$	1·993	2·325	2·658	3·322	3·986
$K\beta_3 \times 10^{10}$*	3·20	3·54	3·50	3·68	3·86
K	1·60	1·77	1·75	1·84	1·93

*Calculated from Equation (8) taking $\beta_1 = 8{\cdot}00 \times 10^3$, $\beta_2 = 13{\cdot}0 \times 10^6$ and $\beta_3 = 2{\cdot}0 \times 10^{10}$.

It is seen that K is a constant at least for the present practical purposes (see later).

In order to obtain β_3 values from partition data alone Equation (5) is rearranged so that

$$\frac{1}{\phi_L} = \left(\frac{1+\beta_1[F^-]+\beta_2[F^-]^2}{[F^-]^3}\right)\frac{1}{K\beta_3+\dfrac{k_0}{[F^-]^3}} + \frac{1}{K+\dfrac{k_0}{\beta_3[F^-]^3}}. \tag{9}$$

Under conditions where $K\beta_3 \gg k_0/[F^-]^3$, i.e. where extraction of $M(HD_2)_3$ is negligible compared to $MF_3 . 3H_xD_x$ Equation (9) reduces to

$$\frac{1}{\phi_L} = \left(\frac{1+\beta_1[F^-]+\beta_2[F^-]^2}{[F^-]^3}\right)\frac{1}{K\beta_3}+\frac{1}{K}. \qquad (10)$$

A plot of $1/\phi_L$ against $(1+\beta_1[F^-]+\beta_2[F^-]^2)/[F^-]^3$ gives a straight line for yttrium over the fluoride range $(2\text{–}4)\times 10^{-3}\,\text{ml}^{-1}$ (Fig. 3). ($\beta_1 = 7{\cdot}70\times 10^3$ and $\beta_2 = 12{\cdot}8\times 10^6$ are taken from Fig. 1 at sufficiently low fluoride concentrations). The ratio of the intercept with the vertical axis to the slope of the curve (Fig. 3) gives $\beta_3 = 2{\cdot}0\times 10^{10}$ in good agreement with values from other sources (Table 1).

A departure was observed for points (Fig. 3) corresponding to $[F^-]$ greater than $5\times 10^{-3}\,\text{ml}^{-1}$; this could be explained by the formation of additional extractible fluoro complexes.

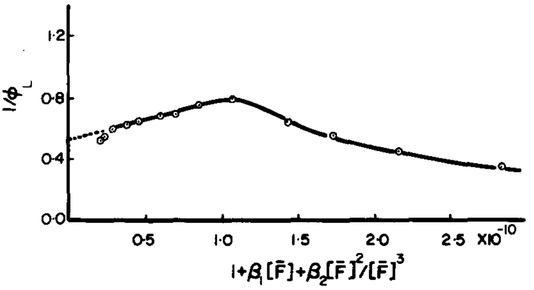

Fig. 3. Experimentally based points, ⊙, plotted for yttrium from the same data as that used in Fig. 1. The full line corresponds to $1/\phi_L$ calculated from Equations (9) or (10).

It should be noted that the function $(1+\beta_1[F^-]+\beta_2[F^-]^2)/[F^-]^3$ converges with increasing $[F^-]$ so that the two points falling below the extrapolated (broken) line in Fig. 3 represent values at widely differing $[F^-]$ from each other and the nearest point on the curve. At $[F^-]$ lower than 2×10^{-3} mole l.$^{-1}$ the distribution of $Y(HD_2)_3$ becomes significant and Equation (10) is no longer adequate (see Fig. 3). K obtained from Fig. 3 enables ϕ_L to be calculated from the β values using Equation (9) over the range $(0{\cdot}8-2{\cdot}0)\times 10^{-3}$ $M[F^-]$ where $k_0/[F^-]^3$ cannot be ignored. Values for ϕ_L thus calculated fit the curve in Fig. 3 confirming the method of treatment at low and moderately high $[F^-]$ up to 4×10^{-3} M. ϕ_L thus obtained from Equations (9) or (10) give ϕ_{1L} values in good agreement with those obtained experimentally (Fig. 1).

It may be concluded that by means of a careful analysis, partition data of the form obtained for yttrium (Fig. 1) can yield satisfactory values for the first three overall stability constants without recourse to results from other experimental methods; ϕ_{1L} at low $[F^-]$ gives β_1 and β_2 as reported previously and Equation (10), β_3 at higher $[F^-]$. However, it should be noted from Table 3 that K is not strictly constant, but appears to increase slightly with increasing $[F^-]$. Thus application of Equation (6) to calculate ϕ_{1L} from a mean value for K and accepted values for β does not lead to satisfactory agreement with experimentally based ϕ_{1L} at $[F^-]$

Table 4. HDEHP extraction data in the presence of $[F^-]$ at $\mu = 0{\cdot}500$ ($NaClO_4$) and 25°C

*Scandium**										
$\phi_{1L} \times 10^{-8}$	0·0218	0·0270	0·0350	0·0400	0·0460	0·0615	0·0768			
$[F^-] = 10^4$	0·0224	0·0448	0·0672	0·0892	0·1120	0·1680	0·2240			
$\phi_{1L} \times 10^{-8}$	0·1084	0·2737	0·4519	0·7580	1·396	2·163	3·169			
$[F^-] \times 10^4$	0·3361	0·5601	0·7841	1·120	1·680	2·240	3·361			
$\phi_{1L} \times 10^{-8}$	9·480	19·80	59·13	94·13	173·1	292·1	402·4			
$[F^-] \times 10^4$	5·601	7·841	11·20	13·44	16·80	20·16	22·40			
Americium(III)										
$\phi_{1L} \times 10^{-3}$	2·563	2·787	2·889	3·107	3·428	3·579	3·734	4·038		
$[F^-] \times 10^4$	1·661	2·685	3·322	4·982	6·644	8·305	9·966	11·63		
$\phi_{1L} \times 10^{-3}$	4·767	4·203	3·414	2·956	2·628	2·410	2·044	1·709	1·302	1·194
$[F^-] \times 10^4$	13·29	16·61	19·93	21·59	23·25	24·92	26·58	29·90	33·22	36·54
Curium(III)										
$\phi_{1L} \times 10^{-3}$	2·494	2·854	2·970	3·015	3·269	3·422	3·733	3·807		
$[F^-] \times 10^4$	2·658	3·322	4·982	5·980	6·644	8·305	9·966	10·63		
$\phi_{1L} \times 10^{-3}$	3·949	4·106	3·742	2·994	1·786	1·492	1·230	1·043		
$[F^-] \times 10^4$	11·63	13·29	16·61	19·93	26·58	29·90	33·22	36·54		

*Distributions were carried out at pH = 2·50 and with variable HDEHP [(1·3–125) 10^{-3}% (w/v)] in toluene.

Table 5. Distribution ratios*, k_0, for trivalent metal ions between 0·075% w/v HDEHP and 0·5 M $NaClO_4$ at pH 3·60 and 25°C

Metal ion	Sc^{3+}	In^{3+}	y^{3+}	Gd^{3+}	Eu^{3+}	Am^{3+}	Cm^{3+}	La^{3+}	Ac^{3+}
k_0	6×10^{10}	3×10^7	2×10^4	4×10^2	2×10^2	10	10	9×10^{-1}	7×10^{-2}

*'Normalised' to the common HDEHP concentration quoted and rounded up to one significant figure.

greater than $10 \times 10^{-4} M$. The large discrepancies arise because the third and fourth terms on the r.h.s. of Equation (6) dominate numerically and a small variation in K produces a large resultant effect. The assumptions made are therefore not strictly valid, but as concluded above they appear sufficient to permit calculation of reasonable (having regard to the present stage of development) equilibrium constants.

Americium(III) *and curium*(III) *fluoride systems*

Partition of americium(III) and curium(III) between HDEHP in toluene and aqueous fluoride solutions was studied over a $[F^-]$ range of $(1\text{–}40) \times 10^{-4}$ ml^{-1} and the results (Table 4) treated as outlined at the beginning of the previous paragraph. Equilibrium constants thus obtained are recorded in Table 1. Results suitable for comparison have to the best of our knowledge not been published.

The scandium-fluoride system

Scandium was found to behave like indium(III)[6]; from partition measurements (Table 4) and the use of the relation

$$\phi_{1L}^* = \beta_1 + \beta_2[F^-] + \beta_3[F^-]^2 + \beta_4[F^-]^3 + \ldots\ldots$$

values for β_1–β_4 in good agreement with those obtained otherwise (Table 1) have been calculated.

Extraction of the various metal ions by HDEHP

At the higher end of the $[F^-]$ range used in the measurements described, the overall distribution ratio, ϕ_L, is the sum of contributions from $M(HD_2)_3$ and HDEHP solvated fluoro-metal complexes, mainly MF_3. The first is dependent on the third power whereas the second is independent of $[H^+]$ assuming the behaviour of yttrium to be typical. It is seen from the data collected in Table 5 that scandium and indium have by far the largest k_0 values at the pH common to all the ions of the elements listed; the fraction of each of these metals extracted as $MF_3 . 3H_xD_x$ is negligible compared to that extracted as $M(HD_2)_3$ although $M_{aq.}^{3+}$ diminishes rapidly in concentration as $[F^-]$ increases. Evidently under the conditions of measurement the contributions from the former source are con-

Table 6. pH dependence of americium(III) distributing between 0·075% w/v HDEHP in toluene and an aqueous phase containing $[F^-] = 3{\cdot}32 \times 10^{-3}$ ml^{-1} at $\mu = 0{\cdot}500$ and 25°C

pH	k_0	ϕ_L	$\phi_{1L} \times 10^{-3}$	$\phi_{1L}^* \times 10^{-3}$
3·60	11·33	2·13	1·302	18·07
3·86	68·33	2·50	7·920	
4·02	179·0	3·07	16·30	
4·50	5661	96·46	17·37	
4·58	9872	190·4	15·31	

ϕ_{1L}^* is calculated on the basis of the β values in Table 1.

siderable in the extraction of yttrium, americium and curium. However, from Equations (3) and (4) an increase in pH should result in an increase in ϕ_{1L} for a given high [F$^-$]; ϕ_{1L} should tend to a limiting value, ϕ^*_{1L}. This has been found for yttrium (Fig. 1) and americium (Table 6).

It may be noted that k_0 values were computed from the relatively much smaller k_0 at pH = 3·60; the lower than expected ϕ_{1L} at pH 4·58 (Table 6) is thereby readily accounted for from the expected error in k_0.

Table 7. pH dependence of americium(III) distributing between 0·075% w/v HDEHP in toluene and an aqueous phase containing [F$^-$] = 8·305 × 10^{-4} M at μ = 0·500 and 25°C

pH	k_0	ϕ_L	$\phi_{1L} \times 10^{-3}$
3·60	11·33	2·852	3·579
3·86	68·33	17·20	3·560
4·12	410·0	102·6	3·610
4·48*	182·4	48·34	3·340

*Distributions were measured for 0·025% w/v HDEHP and the appropriate k_0 calculated to obtain ϕ_{1L}.

A test of the effect of pH on ϕ_{1L} at low [F$^-$] was also carried out for americium. The results recorded in Table 7 confirm that $AmF_3 . 3H_xD_x$ contributes to a negligible extent to ϕ_L at [F$^-$] = 8·305 × 10^{-4} ml^{-1}. The constancy of ϕ_{1L} is consistent with the model from which β_3 is calculated and the test provides a useful check on the data from which β_1 and β_2 are obtained.

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