THE DISTRIBUTION OF POSITIVELY CHARGED CERIUM (III) AND GADOLINIUM COMPLEXES BETWEEN A CATION-EXCHANGER AND AN AQUEOUS PHASE

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(Received 15 April 1967)

Abstract—Using the method reported previously the distribution of positively charged cationic complexes partitioning into a cation-exchanger has been studied and compared with distributions for the "free" metal ions. Cerium (III) partition from α -hydroxy-isobutyrate (at $\mu = 1$), fluoride and sulphate systems and gadolinium from oxalate, fluoride and sulphate solutions (all at $\mu = 0.5$) have been examined. The results confirm the earlier observations on the partition of monobutyrate, fluoride and oxalate complex cations with [LnF]²⁺ showing by far the greatest tendency to enter the exchanger. The monosulphate complex ion of cerium (III) did not appear to exchange while the corresponding gadolinium complex exchanged slightly. Equilibrium constants for step-wise complex formation in the aqueous phase are computed and compared where possible with reported values.

IN A PREVIOUS paper⁽¹⁾ a method was described for the study of the distribution of series of cations, M^{3+} , $MA^{(3-n)+}$, $MA_2^{(3-2n)+}$... between an aqueous solution and a cation-exchanger. (A^{n-} is a ligand.) Some data were reported for europium (III) interacting with α -hydroxy-isobutyrate, fluoride and oxalate. The measurements have been extended to cerium (III) with α -hydroxy-isobutyrate, fluoride and sulphate and to gadolinium with oxalate, fluoride and sulphate in order to substantiate the observations reported previously. Distribution ratios for the cations at different degrees of complexation and equilibrium constants for metal ion-ligand interaction in the aqueous phase have been obtained. Results are reported and discussed here together with further observations on the calculation of equilibrium constants from cation-exchange distribution data.

EXPERIMENTAL

Apart from the comments below, the substances used and the methods employed have been described in the previous paper.⁽¹⁾

Radioactive tracers

"Carrier free" cerium-144/praesodymium-144 and gadolinium of high specific activity were used in the distribution measurements. The isotopes mass 144 were counted (in equilibrium) in an annular type Geiger-Muller liquid counter and the gadolinium in a well-type Na(Tl)I crystal scintillation counter. The gadolinium concentration in the solutions equilibrated was about 3×10^{-8} M.

The sodium perchlorate was prepared from AR perchloric acid and sodium hydroxide. The sulphate solution was prepared from AR sulphuric acid in a similar way.

For some of the measurements ion-exchange resin taken from the batch used previously was washed with distilled water and re-dried. This was done in order to avoid possible side effects arising from the dissolution of break-down products resulting from long-storage of the resin.⁽¹⁾

⁽¹⁾ S. J. LYLE and S. J. NAQVI, J. inorg. nucl. Chem. 28, 2993 (1966).

⁽²⁾ S. J. LYLE and A. R. SANI, Analytica chim. Acta 33, 619 (1965).

A pK value of 1.08 taken from the literature⁽³⁾ was checked and found to be satisfactory for computing sulphate and monohydrogen sulphate concentrations from pH measurements with our electrode system. The study using α -hydroxy-isobutyrate was carried out at $\mu = 1.000$ and the required pK = 3.52 was determined experimentally.

Water doubly distilled from glass was used throughout in the work.

Much of the numerical computation was carried out with the aid of a suitably programmed Elliott 803 computer.

EXPERIMENTAL DATA AND ITS TREATMENT

In the previous study⁽¹⁾ of europium evidence was produced to show that only $Eu(H \cdot Y_2)_3$ extracted into the toluene phase from aqueous solutions containing α -hydroxy-isobutyrate, fluoride or oxalate at appropriate concentration levels. (H₂Y₂ is the dimeric form of di-(2-ethylhexyl)phosphoric acid.) Partition of cerium (III) between H₂Y₂ in toluene and constant and representative sulphate and hydrogen ion concentrations in the aqueous phase gave distribution ratios (Table 1)

Table 1.—The distribution ratio, $\phi_{\rm L}$, for cerium (III) between di(2-ethylhexyl)phosphoric acid (H₂Y₂) in toluene and an aqueous phase pH 3.60, $\mu = 0.500$ (NaClO₄) containing 8.40×10^{-2} M l^{-1} sulphate ion

Exp.	${ m H_{2}Y_{2}}$ %(v/v) $ imes$ 10 ²	$\phi_{\mathbf{L}}$	ϕ_{L} cal.*
1	0.5000	0.2220	
2	1.000	1.768	1.776
3	1.500	5.980	5.994
4	2.000	14.19	14.21

* On the basis of data from Exp. 1 assuming $\phi_{\mathbf{L}}$ is proportional to $(\mathbf{H}_2\mathbf{Y}_2)^{(3)}$.

in compliance with the extraction of $Ce(HY_2)_3$ only. In the work described here it is assumed that any lanthanide (III) ion, Ln^{3+} , would only extract as $Ln(HY_2)_3$ into toluene from aqueous solutions under similar conditions and containing one of the ligands previously listed.

In Tables 2 and 3 data obtained by the ion-exchange and liquid-liquid distribution methods are recorded for cerium (III) and gadolinium sulphate systems. The values of ϕ_{1L} and ϕ_{1R} plotted against corresponding sulphate concentrations give curves to which straight lines are readily fitted over the whole ligand ranges examined. (The notation used throughout is that of the previous paper⁽¹⁾.) Least squares treatment of each set of data separately in the manner used to calculate equilibrium constants from europium oxalate data gave the results presented in Table 4. It was assumed in calculating β_1 and β_2 from the ion-exchange data that distribution of the ion, $[LnSO_4]^+$ could be neglected. While ϕ_{1L} and ϕ_{1R} were sensibly coincident for cerium over the entire ligand range a divergence occurred with gadolinium at higher sulphate concentrations and l_1' (Table 3) and hence l_1 (Table 5) were calculated as described previously⁽¹⁾ for europium with α -hydroxy-isobutyrate.

In the study of the fluoride systems large differences were observed between ϕ_{1L} and ϕ_{1R} at each ligand value (Tables 6 and 7). A good deal of spread was obtained in ϕ_{1L} for gadolinium which however rises more steeply with increasing fluoride

⁽³⁾ S. FRONAEUS, Acta chem. scand. 4, 72 (1950).

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No.	$\begin{array}{c} [\mathrm{A}^{2-}] \times 10^{2} \\ (\mathrm{mole/l}) \end{array}$	$\phi_{1R} \times 10^{-2}$ (l/mole)	$\phi_{1L} imes 10^{-2}$ (l/mole)
1	0.4080	0.8700	
2	1.224	1.022	0.9412
3	1.632	1.007	0.9910
4	2.040		1.029
. 5	2.448	1.058	1.017
6	2.856	1.078	—
7 -	3.264	1.068	0.9870
.8	3.672		1.142
9	4.080	1.160	1.164
10	4.896	1.249	1.302
			1.330
11	5.712	1.268	1.436
12	6.528	1.373	1.417
13	7.344		1-386
14	7.752		1.498
15	8.160	1.400	1.510
16	8.568		1.610
17	8.976	1.513	1.532
18	9.792		1.421

Table 2.—Cation-exchange and liquid-liquid partition data for the cerium (III)-sulphate system at $\mu = 0.5$

 ϕ_{1L} were obtained using approx. 0.075% (v/v) H₂Y₂ having $k_0 = 20.46 \pm 0.31$ (4 values) and ϕ_{1R} using 0.1000 g of exchanger for which $l_0 = 7499 \pm 59$ (6 values).

No.	[A ²⁻] × 10 ² (mole/l)	$\phi_{1B} \times 10^{-3}$ (l/mole)	$\phi_{1L} imes 10^{-2}$ (l/mole)	$\begin{bmatrix} \phi_{1L} - \phi_{1R} \\ \hline 1 + \phi_{1R}(A^{-}) \end{bmatrix}$ (1/mole)
1	0.8160	0.8430		·
2	1.224		0.9607	<u> </u>
3	1.632	0.9001	0.9630	—
4	2.448	1.005	1.070	
5 -	2.856		1.113	
6	3.264	1.047		
7	3.672		1.119	
8	4.080	1.055	1.129	
9	4.896	1.130	1.186	
10	5.712	1.187	1.424	3.05
11	6-528	1.268	1.507	2.58
12	7.344	1.321	1.529	1.94
13	8.160	1.359	1.579	1.82
			1.542	1.51
14	8.976	1.397	1.745	2.58
15	9.792	1.499		

Table 3.—Cation-exchange and liquid-liquid partition data for the gadolinium-sulphate system at $\mu=0.5$

 $\phi_{1\text{L}}$ were obtained using approx. 0.025% (v/v) H_2Y_2 with $k_0 = 17.42 \pm 0.15$ (10 values) and $\phi_{1\text{R}}$ using 0.1000 g of exchange resin for which $l_0 = 4616 \pm 60$ (6 values).

			TAI	BLE 4.—COL	LECTED VALUES FOR THE	EQUILLERIUM CONSTANTS			
Metal				Ionic					
ion	Ligand	Method	Temp. (°C)	strength	β1	βa	β_3	β.	Ref.
Ce ³⁺	C4H703-	i. ex.	25	1.0	228	0.92×10^4	1	1	p.w.
	1				[230]	$[0.9 imes 10^4]$	$[5 imes 10^4]$	\sim [4 \times 10 ⁶]	4
		dis.	24-25	1.0	(235)	$0.85 imes10^4$	$7 imes 10^4$	$\sim 7 imes 10^5$	p.w.
		pot.	25	0.5	234	$1.02 imes10^4$	1	1	(2) (2)
	F-	dis.	24-25	0-5	$(1\cdot41\pm0\cdot08) imes10^{3}$	(9.07 \pm 0.78) $ imes$ 10 5	1	[p.w.
		red.	25	0.S	$1.29 imes 10^{3}$	I	1	1	(8)
	SO4 ³⁻	i. ex.	25	0-5-0-6	88.5 ± 1.8	(6.85 \pm 0.37) $ imes$ 10 ⁸	1	1	p.w.
		dis.	24-25	0-2-0-6	87·3 土 4·4	$(7.56 \pm 0.74) \times 10^{3}$!	ļ	p.w.
		i. ex.	25	0.5	60		I	[(6)
		i. ex.	25	0-5	56	$8.0 imes10^{2}$	1	1	(10)
Gd ³⁺	н-	dis.	24-25	0.5	$(2\cdot 67\pm 0\cdot 27) imes 10^{3}$	(5.17 \pm 0.32) $ imes$ 10 ⁶	I	1	p.w.
		red.	25	0.5	2.34×10^{3}		1		(8)
	SO4 ²⁻	dis.	24-25	0-5-0-6	$80{\cdot}1\pm 3{\cdot}7$	$(9.88\pm0.70) imes10^{2}$		1	p.w.
		i. ex.	25	0-5-0-6	79.9 ± 1.3	$(6.96 \pm 0.22) imes 10^{3}$	1	I	p.w.
	C,042-	i. ex.	25	0.5	$(5.96\pm0.47) imes10^{4}$	$(4.83 \pm 0.29) imes 10^8$	1	!	p.w.
		dis.	24-25	0.5	$(5.75 \pm 0.42) imes 10^4$	$(4.50 \pm 0.28) imes 10^{6}$	I	[p.w.
For th	le data quote	d the ionic	strength wa	s maintained	I constant with sodium I	perchlorate. $C_4H_7O_{3}^- = \alpha$	c-hydroxy-isobu	tyrate; C ₂ O ₄ ²⁻	= oxalate;
i. ex. = ic	n-exchange;	dis. = liqu	id-liquid dist	ribution; pc	ot. = potentiometric; red	. = redox; p.w. = present	t work. Errors	where quoted as	re standard
errors of 1	he means rou	inded upwa	rds to give th	e number of	significant figures recorde	ed. Values for β_3 and β_4 in	square bracket	s were calculate	d assuming
the β_1 and	β_{s} and that	only "free"	cerium (III)	exchanged.					

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Metal	.,			•	11 1		, s
IOI	Ligand	10	l_1	12	10/11	1/18	ket.
లి	C4H,Os-	958·8 ± 7·5	13.3 ± 0.4	****	$72\cdot 1 \pm 2\cdot 2$	I	p.w.
Eu	C4H,03-	4154 土 17	291 ± 11	I	$14\cdot 3 \pm 0\cdot 6$	1	Ē
ථ	- Ľ	6017 ± 92	$(33\cdot 8 \pm 3\cdot 3) imes 10^{2}$	677 ± 371	1.78 ± 0.18	5.0 ± 2.8	p.w.
			$[(37\cdot 8 \pm 2\cdot 4) imes 10^{2}]$		$[1.59 \pm 0.11]$	[ſ
Eu	- Ч	4154 ± 17	828 ± 36	174 ± 36	5.02 ± 0.22	4.8 ± 1.0	Ξ
			$[996 \pm 22]$	1	$[4 \cdot 17 \pm 0 \cdot 10]$	1	
Gd	Ļ	4269 ± 26	$(19.5 \pm 2.8) imes 10^{3}$	321 ± 116	2.19 ± 0.32	6.1 ± 2.4	p.w.
			$[(25.0 \pm 2.6) imes 10^{3}]$	I	$[1.71 \pm 0.18]$	I	ſ
	SO4 ³	4616 ± 60	130 ± 15	I	35·6 土 4·0	1	p.w.
$l_0, l_1 \text{ and } l_2$ resin/metal in 1 in the previous	are the distributic I ml of solution. J : calculations the Values within sou	on ratios for the "free It should be noted tha discussion and concluant brackets were ob	" metal ion, $MA^{(3-n)+}$ and M . It the values for Eu are 150 timusions reached then are in no obtained assuming only MF^{3+} ($A^{(3-2n)+}$ in that orde hes those recorded in the vay altered. C_4H_1 distributes. Standar	r; the distribution ra Table 5, Ref. 1; alt O_3^- is the α -hydrox d errors of the mean:	ttio is defined as n hough this factor y-isobutyrate lig s are quoted.	tetal in 1 g of was omitted and. p.w. =
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The distribution of positively charged cerium (III)

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No.	[A [−]] × 10 ⁴ (mole/l)	$\phi_{1 m R} imes 10^{-3}$ (l/mole)	$\phi_{1 extsf{L}} imes 10^{-3}$ (l/mole)	$\frac{\phi_{1\text{L}} - \phi_{1\text{R}}}{1 + \phi_{1\text{R}}[\text{A}^-]}$ (l/mole)
1	1.993		1.474	·
2	2.657	0.6184	1.525	7.79
3	3.322	(0.6990)	1.834	9-21
4	3.986	0.7792	1.767	7.54
5	4.650	(0.7924)	1.689	6.55
6	5.315	0.8053	1.938	7.93
7	6.643	0.7707	2.023	8.28
8	7.972	0.6512	2.190	10.1
9	9.304	0.6925	2.479	10.9
10	10-63	0.7611	2.535	9.81
11	11.96	0.7095	(2.549)	9.95
12	13-29	0.8141	2.556	8.37
13	14.62	0.8253	(2.748)	8.71
14	15.94	0.7742	(2.935)	9.67
15	16.96	(0.8263)	3.081	9.40
16	17-27	0.8425	(3.028)	8-91
17	18.60	· · · · ·	2.836	

Table 6.—Cation-exchange and liquid-liquid extraction data for the cerium (III)-fluoride system at $\mu = 0.5$

In experiments 1 to 5, ϕ_{1L} were obtained using 0.025% (v/v) H_2Y_2 with $k_0 = 0.7827 \pm 0.0087$ (6 values) and in the remainder approx. 0.04% H_2Y_2 for which $k_0 = 3.768 \pm 0.091$ (6 values) was used. ϕ_{1R} were obtained using 0.2000 g of resin; l_0 was 6017 \pm 92 (7 values). Data in parenthesis were got by interpolation.

No.	[A ⁻] × 10 ⁴ (mole/l)	$\phi_{1R} imes 10^{-3}$ (l/mole)	$\phi_{1L} imes 10^{-3}$ (l/mole)	$rac{\phi_{1 extsf{L}}-\phi_{1 extsf{R}}}{1+\phi_{1 extsf{R}}[extsf{A}^{-}]} imes10^{-2}$ (l/mole)
1	2.657	2.066	3.786	1.110
2	3.986	2.133	4.822	1.45
3	5.315	2.275	5.325	1.38
4	6.643	2.343	6.042	1.45
5	6.772	(2.339)	6.418	1.58
6	7.972	2.294	(7.133)	1.71
7	9.300	2.420	(7.933)	1.70
8	10.63	2.372	8.001	1.60
9	10.76	(2.383)	8.704	1.77
10	11.96	2.495	8.420	1.49
11	12.08	(2.482)	8.733	1.56

Table 7.—Cation-exchange and liquid-liquid partition data for the gadolinium-fluoride system at $\mu=0.5$

 ϕ_{1L} were obtained using approx. 0.025% (v/v) H₂Y₂ having $k_0 = 21.12 \pm 0.33$ (7 values) and ϕ_{1R} using 0.1000 g of resin for which $l_0 = 4269 \pm 26$ (10 values). Data in parenthesis were got by interpolation.

concentration than does the corresponding function for either cerium (III) or europium (III); the validity of this observation is supported by subsequent additional independent measurements in the laboratory.⁽⁴⁾ Equilibrium constants were again calculated from the liquid-liquid distribution data on the assumption that only LnF²⁺ and LnF₂⁺ need be considered. l_1' and l_2' were computed as described for europium. l_1' was also computed on the assumption that $(\phi_{1L} - \phi_{1R})/(1 + \phi_{1R}A^-)$ was constant over the range of measurements. For corresponding oxalate concentrations differences between ϕ_{1L} and ϕ_{1R} are not significant (Table 8) for gadolinium. Each set of ϕ_1

	System at $\mu = 0.5$				
No.	$\begin{array}{c} [\mathrm{A^{2-}}]\times10^4\\ (\mathrm{mole/l}) \end{array}$	$\phi_{1R} imes 10^{-4}$ (l/mole)	$\phi_{1L} imes 10^{-4}$ (l/mole)		
1	0.2452	6.721	7.353		
2	0.4904	7.732	8.012		
3	0.6183		9.413		
4	0.8290	11.14	9.533		
5	1.031		9.367		
6	1.237	12.26	10.72		
7	1.443	13.06	11.99		
8	1.716		12.77		
9	1.962	14.55	14·39		
10	2.102	16.52			
11	2.267	16.70	16.86		
12	2.473	17.98	17-26		

 TABLE 8.—CATION-EXCHANGE AND LIQUID-LIQUID

 PARTITION DATA FOR THE GADOLINIUM-OXALATE

 ϕ_{1L} were obtained using approx. 0.02% H₂Y₂ for which $k_0 = 13.79 \pm 0.55$ (4 values) and ϕ_{1R} using 0.1000 g of cation-exchanger for which $l_0 = 3669 \pm 26$.

plotted against $[A^{2-}]$ is well represented by a straight line, the slope and intercept of which gave the β_1 and β_2 values recorded in Table 4.

The data obtained for cerium (III) with α -hydroxy-isobutyrate show that $\phi_{1L} - \phi_{1R}$ diverges as the ligand concentration increases. Further, ϕ_{1L} rises steeply with increasing [A⁻] at the higher end of the ligand range. Owing to the paucity of experimental data in the lowest ligand region precise extrapolation of ϕ_{1L} to [A⁻] = 0 is not readily accomplished. An estimate of $\beta_1 = 235$ was therefore made. Considerable weight was given to the work of STAGG *et al.*⁽⁵⁾ in choosing this value, but since the ionic strength used in their measurement is different, consideration was also given to unpublished potentiometric measurements made in this laboratory.⁽⁶⁾ This value for β_1 was then fed into the relation:

$$\phi_{1 ext{L}} = eta_1 + eta_2 [ext{A}^-] + eta_3 [ext{A}^-]^2 + eta_4 [ext{A}^-]^3 + \dots$$

and best fitting β_n values calculated by iteration (Table 4).

From both sets of ϕ_1 data (Table 9) the function $(\phi_{1L} - \phi_{1R})/(1 + \phi_{1R}[A^-])$ was calculated and found to be roughly constant where $\phi_{1L} - \phi_{1R}$ is reasonably large;

⁽⁶⁾ S. J. LYLE and D. RAMASWAMY. Unpublished work, Londonderry Laboratory for Radiochemistry, Durham University, England (1960).

⁽⁴⁾ A. Aziz. Unpublished work, this laboratory.

⁽⁵⁾ W. R. STAGG and J. E. POWELL, Inorg. Chem. 3, 242 (1964).

			$\phi_{1L} - \phi_{1R}$	*	Δf	
$[A^-] \times 10^2$ (mole/l)	$\phi_{1R} imes 10^{-3}$ (l/mole)	$\phi_{1L} imes 10^{-3}$ (l/mole)	$\frac{1+\phi_{1R}[A^-]}{(l/mole)}$	$f imes 10^{-5}$ (l²/mole²)	$\frac{\overline{\Delta\phi_{1R}}}{(l/mole)}$	$g \times 10^{-6}$ (l ³ /mole ³)
1.000	_	0.3587				
1.020	0.3251	(0.3603)		0.6592	232.2	2.833
2.000	(0.4053)	0.4509				
2.103	0.4138	(0.4651)	_	0.8723	236-2	3.742
3.000	(0.5226)	0.5859	_	_		
3.102	0.5354	(0.5978)		1.144	231.1	4.820
4.653	0.7578	(0.7939)		1.646	227.7	6.834
5.180	(0.8366)	0.8619				—
5.687	0.9132	(1.024)		2.000	228.6	8.252
6.000	(0.9512)	1.127				_
6.865	1.056	(1.293)	3.22	2.387	235.8	9.877
7.000	(1.084)	1.319	3.06			—
8.985	1.525	(2.080)	4.02	3-396	228.4	13.83
9.000	(1.527)	2.084	4.04	_		
10.04	1.820	(2.583)	4.172	4.027	225.0	16 ·88
10.57	2.061	(2.838)	3.56	4.615	228.1	18.71
12.00	(2.630)	3.521	2.81	_		
12.68	2.905	(4.185)	3.47	6.555	228.6	26.49
13.00	(3.047)	4.403	3.42	<u> </u>		
13.50	(3.275)	4.630	3.06	—		_
14.27	3.625	(5.196)	3.03	8.173	227.8	32.93
14.50	(3.850)	5.364	2.71	—		
15.53	4.697	(5.959)	1.75	10.61	227.8	42.69
17.00		7.187	—			

Table 9.—Cation-exchange and liquid-liquid partition data for the cerium (III)- α -hydroxy-isobutyrate system at $\mu = 1$

 ϕ_{1L} were obtained using approx. 0.125% (v/v) H₂Y₂ having $k_0 = 122.0 \pm 1.9$ (7 values) and ϕ_{1R} using 0.5000 g of exchanger for which $l_0 = 958.8 \pm 7.5$ (7 values). $\phi_{1R}^{\circ} = 230$ and $f^{\circ} = 4.50 \times 10^4$ were used in the calculations. ϕ_{1L} and ϕ_{1R} in parenthesis were obtained by interpolation.

the mean was therefore equated with l_1' . As for the corresponding europium system the ion-exchange data was treated by the method of FRONAEUS.⁽⁷⁾ A value of 230 was taken for ϕ_{1R}° in the calculations. A plot of $\Delta f/[A^-]$ against $\Delta \phi_{1R}/[A^-]$ is linear; the slope of the line according to this treatment may be equated with β_1 . The function g (Equation (7), Ref. 1) was calculated and found to be linear in ϕ_{1R} (Fig. 1).

DISCUSSION

The equilibrium constants obtained as described above from the experimental data along with relevant published values are recorded in Table 4. In general, agreement between the new and, where available, previously published constants is good. However, the β_1 values for cerium (III) sulphate are somewhat higher than reported^(9,10) values (around 60 1 M⁻¹); the reason is not obvious since ion-exchange methods were also used. It is noteworthy that the β_1 values are quite similar for gadolinium and

- (9) R. E. CONNICK and S. W. MEYER, J. Am. chem. Soc. 73, 1176 (1953).
- ⁽¹⁰⁾ L. A. BLATZ, J. phys. Chem. 66, 160 (1962).

⁽⁷⁾ S. FRONAEUS, Acta chem. scand. 5, 859 (1951).

⁽⁸⁾ J. W. KURY, Z. Z. HUGUS, JR. and W. M. LATIMER, UCRL-3678 (1957); *idem. J. phys. Chem.* 61, 1021 (1957).



FIG. 1.—The function g (Equation (7), Ref. 1) plotted against ϕ_{1R} for the ion-exchange distribution data for cerium in the presence of α -hydroxy-isobutyrate (Table 9).

cerium; such constancy in β_1 for lanthanide (III) sulphate systems has been observed previously^(11,12) under different experimental conditions. The β_1 appear to be rather sensitive to changes in ionic strength and if β_2 are affected similarly it is possible that the change in ionic strength with change in ligand concentration necessitated by the nature of the ion-exchange method adds to the overall uncertainty in the recorded values.

Published data for fluoride complex ion formation are sparse, but the β_1 values obtained by KURY *et al.*⁽⁸⁾ are in reasonably good agreement with the values found from the present work. The constants obtained for gadolinium with oxalate are slightly lower but not far removed from those reported for europium.

The higher ionic strength was chosen for the study with α -hydroxy-isobutyrate to allow a larger ligand concentration range to be investigated. Appreciable evidence has

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accumulated pointing to the existence of complex ions up to $[LnA_4]^-$ for $A^- =$ glycollate⁽¹³⁻¹⁶⁾ lactate^(15,16) and α -hydroxy-isobutyrate.⁽¹⁵⁻¹⁷⁾ In the present work, the liquid-liquid distribution data clearly shows the presence of a fourth complex ion. It is therefore of some interest to examine the ion-exchange data over the same ligand concentration range by the method of FRONAEUS⁽³⁾ to find out whether it predicts the same degree of complex formation. A calculation of the function g and its plot against ϕ_{1R} should give a non-linear curve; Figure 1 shows the plot to be linear. It is perhaps not surprising that this test proves so insensitive for the detection of a fourth complex since the intercept at $\phi_{1R} = 0$ frequently provides an unsatisfactory means of arriving at a numerical value for β_3 . If the ion-exchange data are treated in the same manner as those from the liquid extraction measurements the presence of a fourth complex is indicated (Table 4). $\Delta f/[A^-]$ plotted against $\Delta \phi_{1R}/[A^-]$ for the ion-exchange data gives a straight line slope 228 ± 2 (by least squares) which is in good agreement (as it should be) with the mean $\Delta f/\Delta \phi_{1R}$ (230 ± 1) from Table 9. The first six points in the plot of the former may be taken to represent the common situation where the range of data is insufficient to merit the use of such a plot. Agreement is satisfactory if the mean (232 \pm 2) of the corresponding six values for $\Delta f/\Delta \phi_{1R}$ are compared with β_1 from the slope of the curve for the complete data.

Distribution ratios for "free" and partly complexed ions

Distribution ratios, l_j , calculated from the appropriate β_j and l_j' are recorded in Table 5 along with the experimentally measured l_0 values for the ion-exchange systems. In treating the fluoride data l_j have been calculated assuming on the one hand that only LnF^{2+} , and on the other that both LnF^{2+} and LnF_2^+ exchange. The accompanying standard errors would suggest that the fit is slightly better if it is assumed that only LnF^{2+} exchanges (Table 5). The values obtained previously for europium are included for comparison; they have been recalculated since through an oversight a factor of 150 was omitted before. (This omission does not affect any of the comparisons or conclusions made previously.⁽¹⁾) Although the same resin was used in all the measurements its exchange capacity per unit weight varies somewhat because of reprocessing (see the experimental section) and because in the course of time the stored resin was found to have taken up some moisture. The ratios of adjacent l are therefore best used for comparison.

In general the observed distribution trends support and supplement those obtained with europium. Fluoride systems show the greatest tendency for partially complexed cations to distribute. The CeF²⁺ and GdF²⁺ ions have l_1 more than a half of the appropriate l_0 irrespective of the method of computation whereas EuF²⁺ appears to distribute to a significantly lesser extent. More recent measurements made independently in the laboratory⁽⁴⁾ on all three systems confirm this result. It is clear that the cation-exchange behaviour of these metal ions in the presence of fluoride is "anomalous" when compared with other ligand systems; ϕ_{1R} is almost independent of fluoride over appreciable ligand concentration ranges. "Anomalous" behaviour is not however

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confined to lanthanide systems; ϕ_{1R} has been found⁽¹⁸⁾ to be a decreasing function of increasing hydrogen fluoride (formal) concentration for neptunium (IV) in 4 M perchloric acid.

Unlike the monooxalate complex of gadolinium, the monosulphate would appear to distribute to some extent in spite of the ion charge reduction of two whereas distribution of the corresponding cerium (III) complex ion was not observed. Ignoring the presence of a possible effect due to differences in ionic strength the mono- α hydroxy-isobutyrate complex of cerium also shows less tendency to distribute relative to "free" cerium (III) than does the corresponding europium complex cation. Although a wide ligand range was used in the cerium measurements and complexes up to and including $[CeA_4]^-$ are present in the aqueous solution there is no evidence from the present study for distribution of a ligand containing cation other than [CeA]²⁺.

Recently BRUCHER et al.⁽¹⁹⁾ have reported the results of diffusion and elution studies dealing with the behaviour of tracer lanthanide (III) ions in ammonium lactate solution. They found that above a certain ligand concentration (about 0.1 M) the main exchange process can be represented by:

$$\overline{\mathrm{LnA}^{2+}} + 2\mathrm{NH}_{4}^{+} \rightleftharpoons \mathrm{MA}^{2+} + \overline{2\mathrm{NH}_{4}^{+}},$$

where a bar is used to indicate the resin phase. Table 10 gives computed ratios of l_0 to l_1 and of $[LnA]^{2+}$ to Ln^{3+} aq. at different α -hydroxy-isobutyrate concentrations.

	AND $\mu = 0.5$ (for Eu)					
Metal		[LnA] ²⁺ /	[Ln ³⁺] at			
ion	l_0 / l_1	0.01 M[A-]	0·1 M[A ⁻]	0·5[A~]		
Ce(III)	72	2.4	24	120		
Eu(III)	14	5.2	52	260		

Making the reasonable assumption that lactate behaves in the same way as its homologue it is seen that the experimental results obtained in the present and previous⁽¹⁾ work are essentially consistent with their conclusion.

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