

11. Kinell, P. O. and Strandberg, B. *Acta Chem. Scand.* **13** (1959) 1607.
12. Morgan, H. W. J. *Inorg. Nucl. Chem.* **16** (1960) 368.
13. Chamberlain, M. M. and Bailer, J. C. *J. Am. Chem. Soc.* **81** (1959) 6412.

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## On the Stability of the Acetate and Glycolate Complexes of Trivalent Curium

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In a previous communication<sup>1</sup> the stability constants of the acetate and glycolate complexes of trivalent europium and americium were reported. In this work the corresponding complexes of trivalent curium have been studied. No quantitative reports of the stability constants of these complexes have been delivered so far. Qualitative studies of the cation exchange behaviour of curium in glycolate solutions have been published by Stewart<sup>2</sup>. In this investigation the curium acetate and glycolate complexes were studied by using the cation-exchange method developed by Fronaus<sup>1, p. 1696</sup>. All stability constants refer to a 0.50 M sodium perchlorate medium and a temperature of 20.0°C.

**Experimental. Chemicals used.** A stock solution of trivalent curium was prepared by dissolving a curium sample obtained from A. E. R. E. Harwell in a solution of the composition:  $C_{\text{NaClO}_4} = 500 \text{ mM}$ ,  $C_{\text{HClO}_4} = 2.00 \text{ mM}$ . The curium sample consisted of 92.3 % <sup>244</sup>Cm, 7.6 % <sup>242</sup>Cm and 0.14 % <sup>238</sup>Pu. Dibutylphosphate, DBP, (Albright & Wilson Ltd) was purified according to Dyrssen *et al.*<sup>3</sup> A 0.1 M stock solution in hexane was prepared from the purified product. All other chemicals were the same as used before.<sup>1, p. 1697</sup> Stock solutions of the various chemicals were prepared and analysed as described before.<sup>1, p. 1697</sup>

**Procedure.** 0.100 ml of a curium(III)-stock solution was added to 5.00 ml of buffer solutions S of the composition:  $C_{\text{A}} \text{ mM NaA}$ ,  $C_{\text{HA}} = C_{\text{NaA}} \text{ mM HA}$ ,  $I = 0.50 \text{ M}$ . Each of these solutions was then equilibrated with 150 mg ion-exchanger (Dowex 50 W  $\times$  8, 50–100 mesh, in the sodium form) in a thermostat at

20.0°C. After equilibrium had been attained, 4.00 ml of the aqueous phase was extracted with an equal volume of 0.1 M DBP in hexane. In all cases more than 99 % of the curium was extracted into the organic phase. The curium concentration was then determined by measuring the  $\alpha$ -activity of the DBP-phase. The procedure for preparing solid samples for the activity determinations has been described before<sup>4, p. 1063</sup>. All activity measurements were made using an  $\alpha$ -scintillation counter. From the activity of the solutions before and after addition of ion exchanger the distribution coefficients  $\varphi$  were calculated. The concentration free ligand was obtained in the same way as described before<sup>1, p. 1697</sup>. For each ligand, series with varying  $C_{\text{A}}$  were performed at four different values of  $C_{\text{M}}$  (1.4, 2.7, 3.8,  $7.4 \times 10^{-9} \text{ M}$ ) and each series was repeated several times. The average  $\varphi$ -values with their corresponding standard deviations have been tabulated in Table 1. The reproducibility of the measurements was much lower than for the corresponding americium systems. The low accuracy was most pronounced for low values of  $\varphi$  and the useful  $C_{\text{A}}$ -range was therefore smaller than for the corresponding americium systems. It was not possible to detect any variation in the measured  $\varphi$ -values with the value of  $C_{\text{M}}$ . The ion-exchanger is thus monofunctional for the loads used here.

**Calculation of stability constants.** From the corresponding values of the distribution coefficient  $\varphi$  and the concentration free ligand A, the stability constants were computed by using the least-square procedure "Letagrop"<sup>5</sup>. Two different weighing procedures were used. In the first procedure the individual weights were based on the measured  $\sigma_{\varphi}$ -values and in the second one on a constant percentual error in  $\varphi$ .

Approximately the same result was obtained by the two methods (*cf.* Table 2). In the first attempt five constants  $l_0$ ,  $l_1'$ ,  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  were determined. The result for the glycolate system is given in Table 2. Both  $l_1'$  and  $\beta_3$  turned out to be negative and as negative values of  $l_1'$  and  $\beta_3$  have no physical meaning, only three parameters were used to describe the experimental material. These three constants ( $l_0$ ,  $\beta_1$  and  $\beta_2$ ) obtained by using weighing procedure 1 and 2 are also given in Table 2. The final constants are for the acetate system:

$l_0 = 2.37 \pm 0.07 \text{ l.g}^{-1}$ ;  $\beta_1 = 114 \pm 9 \text{ M}^{-1}$ ;  
 $\beta_2 = 1240 \pm 240 \text{ M}^{-2}$ ;

and for the glycolate system:

$l_0 = 2.39 \pm 0.07 \text{ l.g}^{-1}$ ;  $\beta_1 = 700 \pm 60 \text{ M}^{-1}$ ;  
 $\beta_2 = (5.6 \pm 0.6) \times 10^4 \text{ M}^{-2}$ .

Table 1. Corresponding values of  $\varphi$  and A for the curium acetate and glycolate systems. The  $\varphi$ -values are tabulated with their corresponding standard deviations.

The Cm <sup>3+</sup> -acetate system			The Cm <sup>3+</sup> -glycolate system		
A (mM)	$\varphi \pm \sigma$ (l.g <sup>-1</sup> ) $\varphi$	$\frac{\varphi - \varphi_{\text{calc}}}{\varphi} \times 100$	A (mM)	$\varphi \pm \sigma$ (l.g <sup>-1</sup> ) $\varphi$	$\frac{\varphi - \varphi_{\text{calc}}}{\varphi} \times 100$
0	2.42 $\pm$ 0.12	4.2	0	2.42 $\pm$ 0.12	4.5
5.00	1.42 $\pm$ 0.09	-2.1	1.50	1.05 $\pm$ 0.08	-1.6
10.00	1.02 $\pm$ 0.08	2.7	3.00	0.65 $\pm$ 0.03	2.2
15.00	0.81 $\pm$ 0.06	-2.3	5.00	0.42 $\pm$ 0.02	-3.8
20.00	0.63 $\pm$ 0.03	-0.6	7.00	0.29 $\pm$ 0.02	-3.8
25.00	0.52 $\pm$ 0.03	-1.9	10.00	0.17 $\pm$ 0.01	1.5
30.00	0.44 $\pm$ 0.02	-2.2	14.50	0.106 $\pm$ 0.005	-1.1
40.00	0.32 $\pm$ 0.02	-0.5	19.00	0.068 $\pm$ 0.003	2.4
50.00	0.24 $\pm$ 0.02	3.2	29.00	0.035 $\pm$ 0.002	0.4

Table 2. The parameters  $l_0$ ,  $l_1'$ ,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  with their corresponding standard deviations. The values refer to the Cm<sup>3+</sup>-glycolate system. In methods 1 and 2 individual weights have been used and in method three the weights are based on a constant percentual error in  $\varphi$ .

Method	$l_0$ (l.g <sup>-1</sup> )	$l_1'$ (M <sup>-1</sup> )	$\beta_1$ (M <sup>-1</sup> )	$\beta_2 \times 10^{-4}$ (M <sup>-2</sup> )	$\beta_3 \times 10^{-5}$ (M <sup>-3</sup> )
1	2.39 $\pm$ 0.09	-7 $\pm$ 6	670 $\pm$ 58	5.6 $\pm$ 1.0	-6.6 $\pm$ 2.0
2	2.40 $\pm$ 0.07	0	697 $\pm$ 49	5.6 $\pm$ 0.7	0
3	2.38 $\pm$ 0.07	0	696 $\pm$ 50	5.55 $\pm$ 0.4	0

The percentual deviation  $(\varphi - \varphi_{\text{calc}})/\varphi \times 100$  for the different  $\varphi$ -values is given in Table 1, columns three and six.

**Discussion.** The stability constants  $\beta_1$  for the curium acetate and glycolate complexes are somewhat larger than the  $\beta_1$ -values for the corresponding americium complexes and much larger than those for the gadolinium acetate and glycolate systems. The difference in stability between the lanthanide complex and its corresponding actinide complex is as before <sup>1,p.1709</sup> most pronounced for the glycolate systems. In the rare earth series there is a decrease in stability of the first acetate and glycolate complex from europium to gadolinium. The corresponding decrease does not occur from americium to curium. The decrease in stability from europium to gadolinium has been described as a ligand field effect <sup>6,7</sup> in the rare earth series. However, the fact that there is no corresponding decrease in  $\beta_1$  from ameri-

cium to curium makes this explanation less probable.

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1. Grenthe, I. *Acta Chem. Scand.* **16** (1962) 1695.
2. Stewart, D. C. *Proc. Intern. Conf. Peaceful Uses Atomic Energy*, Geneva 1955, Vol. 7, p. 321.
3. Dyrssen, D. and Liem Djiet Hay, *Acta Chem. Scand.* **14** (1960) 1091.
4. Åhrland, S., Grenthe, I. and Norén, B. *Ibid* **14** (1960) 1059.
5. Sillén, L. G. *Ibid* **16** (1962) 159.
6. Staveley, L. A. K. and Randall, T. *Discussions Faraday Soc.* **26** (1958) 157.
7. Rossotti, F. J. C. *Ibid* **26** (1958) 190.

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