

## On the Complex Chemistry of the Tervalent Rare-Earth Ions

### IV. Ion-Exchange Studies of the Gadolinium Acetate and Glycolate Systems

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The gadolinium acetate and glycolate systems have been investigated by means of both cation and anion exchangers. The measurements have been performed at 20°C using the radioactive isotope  $^{153}\text{Gd}$ . For the investigation with cation exchanger solutions with the constant ionic strength  $I = 1.0$  M have been used ( $\text{NaClO}_4$  was added). The solutions used for the investigation with the anionic exchanger had varying ionic strength.

The complexity constants obtained for both the acetate system and the glycolate system by means of the cation-exchange method are in good agreement with the constants obtained potentiometrically (pages 1444 and 1446). Anionic complexes, however, could not be proved by the cation-exchange method.

The investigation of the glycolate system by means of an anion exchanger confirms the existence of anionic glycolate complexes. The maximum point of the  $\varphi$ -curve (Fig. 3) indicates that  $\bar{n} = 3$  in a water solution having  $[\text{AcOH}^-] \approx 100$  mM, which is quite in accordance with the potentiometric measurements. The ligand numbers computed from data obtained by the anion exchange method are in good agreement with the ligand numbers obtained potentiometrically in the whole region investigated. Attempts have also been made to compute the stability constants.

According to the measurements with the anion exchanger no anionic complexes should be formed in the gadolinium acetate system for  $[\text{Ac}^-] < 800$  mM (Fig. 3). However, the low  $\varphi$ -values may also be caused by steric effects which depress the sorption of the acetate complexes into the exchanger below measurable values.

In the Parts I, II, and III (Sonesson <sup>1-3</sup>) we have given an account of our investigations of the complex formation in acetate and glycolate solutions of some rare earths. The complexity constants have been computed from the hydrogen-ion concentration of the complex solutions. It is not

possible in investigations of this kind to eliminate completely the errors caused by the variation of the activity factors when the perchlorate ions of the initial solution are replaced by acetate or glycolate ions. The constants computed from data obtained at high ligand concentrations are especially uncertain. Therefore it is necessary to check the results obtained potentiometrically by new investigations, which are independent of the potentiometric measurements.

The erbium acetate system and the neodymium glycolate system have been examined extinctionmetrically as well as potentiometrically. The accordance between the complexity constants obtained potentiometrically and those obtained extinctionmetrically is good, but the constants obtained by the latter method must be considered as relatively uncertain. Therefore investigations by means of ion exchangers have also been performed.

Fronæus <sup>4</sup> has used a cation exchanger for an examination of the cerium acetate system. For the first three complexity constants the accordance between the values obtained by the cation-exchange method and those obtained by the potentiometric method was very good. The present author has used the method given by Fronæus for the examination of the acetate and the glycolate systems of gadolinium.

The formation of anionic complexes in solutions containing cerium and acetate ions has also been examined by Fronæus <sup>5</sup> by means of anion exchange. According to the potentiometric measurements the ligand number exceeds three when  $[Ac^-] > 500$  mM. In the examination with the anion exchanger anionic complexes could not be proved, although  $[Ac^-]$  was increased to about 1 000 mM. Now both the acetate and the glycolate systems of gadolinium have been examined by means of an anion exchanger.

#### A. INVESTIGATION BY MEANS OF A CATION EXCHANGER

##### Theoretical

The method employed in the present investigation has been developed by Fronæus <sup>4</sup>.

The same notations as in the previous Parts I, II and III have been used as much as possible, but in some cases the definitions of the symbols have been altered in some respects.

$C'_M, C'_A$  = the total concentrations of the rare earth and the ligand, respectively, in the solution before the exchanger is added.

$C_M$  = the total concentration of the rare earth in the solution at equilibrium with the exchanger.

$[M^{3+}], [A^-]$  = the concentration of free central ion and free ligand, respectively, in the solution at equilibrium.

Then, as earlier, we have

$$C_M = [M^{3+}] \left( 1 + \sum_{j=1}^N \beta_j \cdot [A^-]^j \right) = [M^{3+}] \cdot X \quad (1)$$

In addition the following notations are introduced:

$[M^{3+}]_R$ ,  $[MA^{2+}]_R$ , etc. = the concentrations in the resin phase at equilibrium with the solution. The concentrations are expressed in moles per gram of the air-dried resin.

$\beta_{jR}$  = the complexity constants for the complexes  $MA_{jR}^{3-j}$  in the resin.

$C_{MR}$  =  $[M^{3+}]_R + [MA^{2+}]_R + [MA_2^+]_R = [M^{3+}]_R(1 + \beta_{1R} \cdot [A^-]_R + \beta_{2R} \cdot [A^-]_R^2)$  (2)

$\bar{n}_R$  = the ligand number in the resin. For the cation exchanger we have

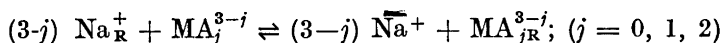
$$\bar{n}_R = ([MA^{2+}]_R + 2 [MA_2^+]_R) \cdot C_{MR}^{-1} \quad (3)$$

$m$  = the weight in grams of the air-dried resin.

$v$  = the volume of the solution before the resin is added.

$v \cdot \delta$  = the volume at equilibrium with the resin.  $\delta$  is a factor caused by the swelling of the resin.

The following equilibrium is obtained between a cation exchanger in the sodium form and a solution containing rare-earth ions  $M^{3+}$  and complex ions  $MA_j^{3-j}$ :



If we apply the law of mass action to this exchange equilibrium, we get

$$\frac{[MA_{jR}^{3-j}]_R}{[MA_j^{3-j}]} = k_j \frac{[Na_R^+]^{3-j}}{[Na^+]^{3-j}} = l_j; \quad (j = 0, 1, 2) \quad (4)$$

In the cation-exchange investigations described in this paper the total concentration of the rare earth is very low ( $C_M \leq 3.0$  mM,  $C_{MR} < 0.07$  mmole·g<sup>-1</sup>). Therefore both  $[Na^+]$  and  $[Na^+]_R$  have been approximately constant. The load  $C_{MR}$  has been very low compared with the total exchange capacity ( $\approx 3.85$  mequiv. g<sup>-1</sup>) and the ionic strength of both the exchanger and the water phase has been nearly constant. In the calculations all values have been referred to a constant value of  $C_{MR}$  and then both  $k_j$  and  $l_j$  may be considered approximately constant.

If we denote by  $\varphi$  the distribution of the rare earth between the resin phase and the solution, then

$$\varphi = \frac{C_{MR}}{C_M} = l_0 \frac{1 + l'_1 \cdot [A^-] + l'_2 \cdot [A^-]^2}{X} \quad (5)$$

$$l_0 = \frac{[M^{3+}]_R}{[M^{3+}]} \quad ; \quad l'_j = \beta_j \frac{l_j}{l_0} \quad (j = 1, 2) \quad (6)$$

To facilitate the calculations Fronæus introduced two new parameters

$$\varphi_1 = \frac{l_0 \cdot \varphi^{-1} - 1}{[A^-]} \quad (7)$$

$$f = \frac{l_0 \cdot \varphi^{-1}[(\beta_1 - l'_1) [A^-] - 1] + 1}{[A^-]^2} \quad (8)$$

It can be shown by combining eqns. (5), (7) and (8) that

$$f = \beta_1 \cdot \varphi_1 - X_2 + l'_2 \cdot l_o \cdot \varphi^{-1} \quad (9)$$

After having introduced the value of  $\varphi$  from eqn. (5) into eqns. (7) and (8), we get

$$\lim_{[A^-] \rightarrow 0} \varphi_1 = \varphi_1^\circ = \beta_1 - l'_1 \quad (10)$$

$$\lim_{[A^-] \rightarrow 0} f = f^\circ = \beta_1 \cdot \varphi_1^\circ - (\beta_2 - l'_2) \quad (11)$$

From eqns. (9), (10) and (11) it can be deduced that

$$\left. \begin{aligned} \Delta f \cdot [A^-]^{-1} &= \beta_1 \cdot \Delta \varphi_1 [A^-]^{-1} - \beta_3 - X_4 [A^-] + l'_2 \varphi_1 \\ \Delta f &= f - f^\circ \text{ and } \Delta \varphi_1 = \varphi_1 - \varphi_1^\circ \end{aligned} \right\} \quad (12)$$

The last two terms of (12) vary with  $[A^-]$ . At low values of  $[A^-]$ , however, they are only correction terms and we can calculate an approximate value of  $\beta_1$  by plotting  $\Delta f \cdot [A^-]^{-1}$  as a function of  $\Delta \varphi_1 \cdot [A^-]^{-1}$ .

Now  $\beta_1$  being known, an approximate value of  $\beta_2 - l'_2$  can be calculated by means of eqn. (11). Then a new parameter  $g$  is introduced

$$g = \frac{f - \beta_1 \varphi_1 + l_o \cdot \varphi^{-1} (\beta_2 - l'_2)}{[A^-]} = \beta_2 \varphi_1 - \beta_3 - X_4 \cdot [A^-] \quad (13)$$

At so low  $[A^-]$  that  $X_4$  can be neglected,  $g$  is a linear function of  $\varphi_1$ . The slope of the line gives  $\beta_2$ , and the intercept an approximate value of  $\beta_3$ .

$X_2$  can be computed according to eqn. (9), but we must know  $l'_2$ . As  $l'_2$  seems to be very small compared with  $\beta_2$ , we get only a very rough value of  $l'_2$  from  $\beta_2$  and  $\beta_2 - l'_2$ . Another way of computing  $l'_2$  is shown by Frønaeus<sup>4, p. 20</sup>. With the assumption that  $\beta_{1R}^2 \cdot \beta_{2R}^{-1}$  has about the same value as  $\beta_1^2 \cdot \beta_2^{-1}$  it can be deduced that

$$\frac{\beta_1^2}{\beta_2} = \frac{(l'_1)^2}{l'_2} \quad (14)$$

For the glycolate system eqn. (12) could not be used for the computation of  $\beta_1$ , as  $\Delta \varphi_1 \cdot [A^-]^{-1}$  and  $\Delta f \cdot [A^-]^{-1}$  are approximately constant. However, if only four complexes are formed, eqn. (12) can be written

$$\beta_1 = \frac{\Delta f}{\Delta \varphi_1} + \beta_3 \cdot \frac{[A^-]}{\Delta \varphi_1} + \beta_4 \cdot [A^-] \cdot \frac{[A^-]}{\Delta \varphi_1} - l'_2 \varphi_1 \cdot \frac{[A^-]}{\Delta \varphi_1} \quad (15)$$

The first term,  $\Delta f \cdot \Delta \varphi_1^{-1}$ , dominates. Then, an approximate value of  $\beta_1$  can be calculated if rough values of  $\beta_3$ ,  $\beta_4$  and  $l'_2$  are known.

All the equations above have been deduced on the assumption that only mononuclear complexes are formed both in the solution and in the resin. The

potentiometric measurements on the  $\text{Gd}^{3+}$ — $\text{Ac}^-$ -system reported in Part I showed a slight tendency for formation of polynuclear complexes. However, the tendency is so slight that it may be neglected in the present investigation, as both  $C_M$  and  $C_{MR}$  are very low.

### Experimental

*Chemicals used.* A known amount of radioactive  $\text{Gd}_2\text{O}_3$  (from A.E.R.E., Harwell, England) was dissolved in perchloric acid. After the addition of a known amount of inactive gadolinium perchlorate, the solution was evaporated to remove the excess perchloric acid.

The concentration of the stock solution of radioactive gadolinium perchlorate was calculated from the known amounts of radioactive and inactive materials. The stock solution contained  $\text{NaClO}_4$  to make the ionic strength 1.0 M.

The cation exchanger was Dowex 50 converted into the sodium form and air-dried. The same batch was used for all of the measurements. The exchange capacity was 3.85 mequiv.  $\text{g}^{-1}$ .

The value of the factor  $\delta$  was determined by shaking a solution with a known concentration of  $\text{NaClO}_4$  and a known amount of the resin until equilibrium was reached. Then the value of  $\delta$  was given by the ratio between the initial and the equilibrium sodium-ion concentrations, which were determined by means of a cation-exchanger column in the hydrogen state.  $\delta$  was determined to be 0.985.

Other chemicals were of analytical grade as in Parts I, II, and III.

*The apparatus.* The total gadolinium concentration of the solutions was determined by measurement of the gamma activity of  $^{153}\text{Gd}$ . A scintillation detector type P-20 from Tracerlab was used. The scintillation tube was immersed to a fixed depth in the centre of a lead shielding. A glass cup containing 10 ml of the solution to be measured was placed in a fixed place in the lead shielding. A satisfactory reproducibility of the geometry was assured. A solution of radioactive  $\text{Gd}(\text{ClO}_4)_3$  was diluted with varying amounts of 1 M  $\text{NaClO}_4$  and the solutions were counted. It was found that the relation between the cpm and the gadolinium concentration was linear within the limits of the statistical errors ( $\sim 1\%$ ).

### The gadolinium acetate system

The complex solutions to be measured were prepared by mixing two solutions,  $S_1$  and  $S_2$ , in varying proportions.

$$S_1 = \begin{cases} C_M^\circ \text{ mM Gd}(\text{ClO}_4)_3 \\ C_H^\circ \text{ mM HClO}_4 \\ 1000 \text{ mM NaClO}_4 \end{cases} \quad \text{and } S_2 = \begin{cases} C_{\text{HA}}^\circ \text{ mM HAc} \\ C_A^\circ \text{ mM NaAc} \\ (1000 - C_A^\circ) \text{ mM NaClO}_4 \end{cases}$$

Four  $S_1$  solutions were used with  $C_M^\circ = 0.566, 1.010, 2.020$  and  $3.010$  mM, respectively. All solutions had  $C_H^\circ \approx 0.03$  mM. At this pH the hydrolysis of the gadolinium ions can be neglected, as shown in Part I.

One buffer solution had  $C_{\text{HA}}^\circ = C_A^\circ = 500$  mM, and the other  $C_{\text{HA}}^\circ = C_A^\circ = 1000$  mM.

A fixed volume ( $v$  liters) of the complex solution was shaken (about 20 h) in a thermostat at  $20^\circ\text{C}$  with a fixed amount ( $m$  gram) of the dried resin. The value of  $v \cdot m^{-1}$  was kept at  $0.025 \text{ l} \cdot \text{g}^{-1}$ . After exchange equilibrium was reached, the resin phase was separated from the solution. The equilibrium concentration  $C_M$  was computed by comparing the radioactivity of 10 ml of the complex solution with the radioactivity of 10 ml of solution  $S_1$ .

Table 1. Cation-exchange measurements on the acetate system.

$C'_A \cdot \delta^{-1}$ mM	$C'_M$ mM	$C_{MR} \times 10^3$ mmole. g <sup>-1</sup>	$\varphi \times 10^3$ l.g <sup>-1</sup>	$C'_M$ mM	$C_{MR} \times 10^3$ mmole. g <sup>-1</sup>	$\varphi \times 10^3$ l.g <sup>-1</sup>	$C'_M$ mM	$C_{MR} \times 10^3$ mmole. g <sup>-1</sup>	$\varphi \times 10^3$ l.g <sup>-1</sup>	$C'_M$ mM	$C_{MR} \times 10^3$ mmole. g <sup>-1</sup>	$\varphi \times 10^3$ l.g <sup>-1</sup>
0	0.566	13.1	320	1.010	23.4	314	2.020	46.6	293	3.010	69.1	277
8.32	0.557	12.4	207	0.995	22.2	204	1.985	44.1	191			
16.00	0.557	12.0	148	0.995	21.2	143	1.990	42.1	134			
22.60	0.541	11.1	114.5	0.965	19.8	112	1.930	39.2	107.5			
32.75	0.548	10.5	81.0	0.975	18.4	79.8	1.955	37.0	76.6			
49.1	0.511	8.65	51.5	0.910	15.3	50.4	1.825	30.4	49.1			
67.7	0.528	7.65	34.0	0.945	13.5	33.0	1.885	27.0	32.9			
101.5	0.453	4.78	18.0	0.810	8.55	18.1	1.615	16.9	17.8	2.410	26.0	18.6
135.3				0.875	6.50	10.4	1.750	13.5	11.0	2.610	19.6	10.6
169.2				0.675	3.72	7.0	1.345	7.70	7.3	2.005	11.25	7.2
217.5				0.795	2.80	4.0	1.585	6.00	4.4	2.365	11.15	5.5

The results for the four series are shown in Table 1.  $C_{MR}$ , the total equilibrium concentration of gadolinium in the resin phase, has been calculated according to the equation

$$C_{MR} = v \cdot m^{-1}(C'_M - \delta \cdot C_M) \quad (16)$$

As  $\varphi$  varies, with  $C_{MR}$ , all  $\varphi$ -values used in the calculations must be referred to a constant value of  $C_{MR}$ . The relation between  $\varphi$  and  $C_{MR}$  at a constant value of  $C'_A \cdot \delta^{-1}$  proves to be practically linear. Then  $\varphi$  in Table 2 has been determined by graphic interpolation for  $C_{MR} = 10 \times 10^{-3}$  mmole  $\cdot$  g<sup>-1</sup>.

$[A^-]$ , the equilibrium concentration of the free ligand in the solution, must be known before the functions  $\varphi_1$  and  $f$  can be computed. We know the total concentration  $C'_A$  before the resin is added and must, when computing  $[A^-]$ , correct for:

- 1) ligand ions bound in the complexes  $MA_j^{3-j}$  in the solution (correction term:  $a_1 = \bar{n} \cdot C_M$ ),
- 2) ligand ions bound in the complexes  $MA_{2R}^{2+}$  and  $MA_{2R}^+$  in the resin phase (correction term:  $a_2 = \bar{n}_R \cdot C_{MR} \cdot m \cdot v^{-1} \cdot \delta^{-1}$ ),
- 3) ligand ions produced by the protolysis of the acid HA (the correction term  $a_3$  can be neglected in this investigation of the acetate system as the starting pH of the solutions to be measured is about 4.5),
- 4) ligand ions produced when hydrogen ions replace sodium ions in the resin (as the acetate buffers have pH  $\approx$  4.8, this correction term,  $a_4$ , can be neglected in the investigation of the acetate system).

Then we have

$$[A^-] + \bar{n} \cdot C_M + \bar{n}_R \cdot C_{MR} \cdot m \cdot v^{-1} \cdot \delta^{-1} = C'_A \cdot \delta^{-1} + a_3 + a_4 \quad (17)$$

As both  $C_M$  and  $C_{MR}$  are low, the terms  $a_1$  and  $a_2$  are small compared with  $[A^-]$ . Then it may be allowed as a first approximation to consider  $[A^-] = C'_A \cdot \delta^{-1}$ .

However, as we have already examined the gadolinium system potentiometrically (Part I), we can use the potentiometrically obtained values of  $\bar{n}$  for the computation of  $\bar{n} \cdot C_M$ .

In the second correction term  $\bar{n}_R$  can be computed according to Frønaes<sup>6</sup> by means of the formula

$$\bar{n} - \bar{n}_R = - \frac{[A^-]}{\varphi} \left( \frac{\partial \varphi}{\partial [A^-]} \right) C_{MR} \approx - \frac{C'_A}{\varphi} \left( \frac{\partial \varphi}{\partial C'_A} \right) C_{MR} \quad (18)$$

The second approximate expression has been used for the computation of  $\bar{n}_R$ .

Table 2. The cation-exchange measurements on the acetate system. The corresponding values of  $\varphi$ ,  $[A^-]$  and the functions formed from these quantities are valid for the constant load on the resin of  $C_{MR} = 10 \times 10^{-3}$  mmole-g<sup>-1</sup>. (4), (18), etc. refer to the equations with these numbers

$C'_A \cdot \delta^{-1}$ mM	$\varphi \times 10^3$ l.g <sup>-1</sup>	(4) $C_M$ mM	$\bar{n}_{pot}$	(18) $\bar{n}_R$	(17) $[A^-]$ mM	(7) $\varphi_1$ M <sup>-1</sup>	$\Delta\varphi_1$ $[A^-]$ M <sup>-2</sup>	(8) $f$ M <sup>-2</sup>	$\frac{\Delta f}{[A^-]} 10^{-2}$ M <sup>-3</sup>	(13) $g \times 10^{-3}$ M <sup>-3</sup>	$X_3 \times 10^{-3}$ M <sup>-3</sup>
0	323	0.0310	0	0	0	58.9		2 530			$\sim 9$
8.32	208	0.0480	0.45	0.08	8.27	66.9	965	2 975	540	77.4	
16.00	148	0.0675	0.75	0.11	15.90	74.4	975	3 410	555	89.6	
22.60	114.5	0.0875	0.94	0.12	22.45	81.1	990	3 790	560	98.9	
32.75	81.0	0.1235	1.17	0.15	32.55	91.8	1 010	4 400	575	113.3	
49.1	51.2	0.1955	1.43	0.22	48.8	108.8	1 025	5 385	585	136.5	10.4
67.7	33.5	0.299	1.65	0.24	67.1	129	1 045	6 545	600	163	11.0
101.5	18.1	0.552	1.91	0.25	100.3	168	1 085	8 805	625	215.5	11.2
135.3	11.0	0.909	2.12	0.34	133.1	213	1 155	11 400	670	275.5	11.9
169.2	7.2	1.39	2.27	0.4	166	264	1 235	14 330	710	343.5	12.9
217.5	5	2.0	2.43	0.8	212	300	1 135	16 540	660	410	

$\varphi_1^\circ$  and  $f^\circ$  in Table 2 have been determined by graphic extrapolations of  $\varphi_1$  and  $f$ , respectively, to  $[A^-] = 0$ . The extrapolations could be performed with rather great accuracy.

As seen in Fig. 1,  $\Delta f \cdot [A^-]^{-1}$  is approximately a linear function of  $\Delta\varphi_1 \cdot [A^-]^{-1}$ . The slope of the line gives  $\beta_1 = (66 \pm 3) \text{ M}^{-1}$ .

According to eqn. (11) we obtain  $\beta_2 - l'_2 \approx 1\,350$ . Then  $g$  is computed by means of eqn. (13). The slope of the line in Fig. 2 gives  $\beta_2 = 1\,347$  and the intercept gives  $\beta_3 \sim 9\,000$ . Then  $X_3$  is computed from the expression  $X_3 = \beta_2 \cdot \varphi_1 - g$ . The extrapolation of  $X_3$  to  $[A^-] = 0$  gives also  $\beta_3 \sim 9\,000$ .

$X_3$  seems to increase somewhat with increasing values of  $[A^-]$ , which should indicate the formation of a fourth complex. However  $g$  is a quite linear function of  $\varphi_1$  in whole the region, indicating that  $X_4$  is negligible. Therefore, the formation of anionic complexes is very uncertain.

The accordance is good between the complexity constants obtained by the potentiometric method and those obtained by the cation-exchange method.

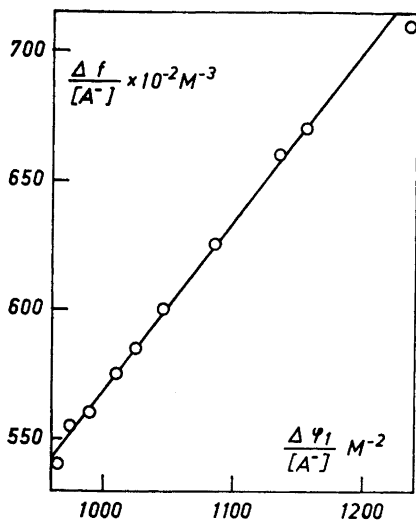


Fig. 1. The cation-exchange measurements on the acetate system.  $\Delta f \cdot [A^-]^{-1}$  is represented as a function of  $\Delta \varphi_1 \cdot [A^-]^{-1}$  for acetate-ion concentrations between 8 and 218 mM. The slope of the line gives  $\beta_1$ .

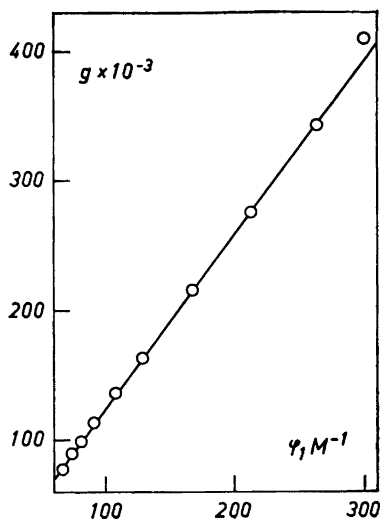


Fig. 2. The cation-exchange measurements on the acetate system.  $g$  is represented as a function of  $\varphi_1$  for acetate concentrations between 8 and 218 mM. The slope of the line gives  $\beta_2$  and the intercept for  $\varphi_1 = 0$  gives  $-\beta_3$ .

Potentiometric measurements.  $I = 2.0$  M. Cation-exchange measurements.  $I = 1.0$  M

$$\begin{aligned} \beta_1 &: 69 \pm 2 \\ \beta_2 &: 1\,320 \pm 150 \\ \beta_3 &: 5\,200 \pm 1\,000 \\ \beta_4 &: \sim 5\,000 \end{aligned}$$

$$\begin{aligned} &66 \pm 3 \quad M^{-1} \\ &1\,350 \pm 250 \quad M^{-2} \\ &9\,000 \pm 3\,000 \quad M^{-3} \\ &- - - \quad M^{-4} \end{aligned}$$

### The gadolinium glycolate system

The complex solutions were obtained by mixing the solutions  $S_3$  and  $S_4$  in varying proportions:

$$S_3 = \begin{cases} C_M^\circ \text{ mM Gd}(\text{ClO}_4)_3 \\ C_H^\circ \text{ mM HClO}_4 \\ 1\,000 \text{ mM NaClO}_4 \end{cases} \quad \text{and} \quad S_4 = \begin{cases} C_{HA}^\circ \text{ mM HA}c\text{OH} \\ C_A^\circ \text{ mM Na}Ac\text{OH} \\ (1\,000 - C_A^\circ) \text{ mM NaClO}_4 \end{cases}$$

The measurements were performed with three  $S_3$  solutions having  $C_M^\circ = 0.550, 1.000$  and  $2.000$  mM and  $C_H^\circ = 0.03$  mM. The buffer solution  $S_4$  had  $C_{HA}^\circ = C_A^\circ = 300$  mM.

The investigation was performed exactly in the same way as for the acetate system.

The results of the measurements on the glycolate system are shown in Table 3. For the calculation of  $[A^-]$  at equilibrium eqn. (17) was used. The potentiometrically obtained values of  $\bar{n}$  were used in the computation of the



Table 3. The cation-exchange measurements on the glycolate system.

$C_M^0 \rightarrow$	0.550 mM		1.000 mM		2.000 mM		$C_{MR} = 10 \times 10^{-3}$ mM				
$C_A' \cdot \delta^{-1}$ mM	$C_{MR} \times 10^3$ mmole · $g^{-1}$	$\varphi \times 10^3$ $l \cdot g^{-1}$	$C_{MR} \times 10^3$ mmole · $g^{-1}$	$\varphi \times 10^3$ $l \cdot g^{-1}$	$C_{MR} \times 10^3$ mmole · $g^{-1}$	$\varphi \times 10^3$ $l \cdot g^{-1}$	$\varphi \times 10^3$ $l \cdot g^{-1}$	(4) $C_M$ mM	$\bar{n}_{pot}$	(18) $\bar{n}_R$	(17) [A <sup>-</sup> ] mM
0	12.75	322					323	0.0310			0
1.213	12.30	216	22.3	215			216	0.0465	0.35	0.02	1.380
2.815	11.75	151.5	21.4	152.5			151	0.0660	0.66	0.06	2.97
4.995	10.90	102.5	19.9	106			102	0.0980	0.96	0.08	5.10
7.14	10.05	73.1	18.4	75.3			73.0	0.1370	1.18	0.12	7.17
9.83	9.00	52.7	16.7	54.9			53.0	0.189	1.40	0.25	9.70
14.51	7.50	32.7	13.80	33.9			33.2	0.301	1.66	0.30	14.15
20.30	5.75	20.0	10.80	21.4	22.5	22.9	21.0	0.475	1.90	0.40	19.50
29.60	3.85	11.1	7.35	11.9	15.95	13.5	12.4	0.805	2.13	0.55	27.90
40.6			4.90	7.2	10.35	7.7	7.7	1.30	2.33	0.75	37.5
50.8			3.15	4.4	7.05	5.0	5.5	1.82	2.46	0.9	46.2
60.9			2.25	3.1	5.05	3.6	4.3	2.33	2.60	1.0	54.7
71.0			1.60	2.3	3.90	2.8					

correction term  $a_1$ . An approximate value of  $\bar{n}_R$  has been determined according to eqn. (18). For the glycolate system  $a_3$  and  $a_4$  cannot be neglected for the lowest values of  $C_A'$ . For the ionic strength  $I = 1.0$  M the acid constant of glycolic acid is  $2.4 \times 10^{-4}$  M (cf. Fronæus<sup>7, p.67</sup>). Using this value we get  $a_3 = 0.16$  mM for  $[A^-] = 1.4$  mM and  $a_3 = 0.20$  mM for  $[A^-] = 28$  mM. The correction term  $a_4$  has been computed on the assumption that  $[H^+]_R \cdot [H^+]^{-1} \approx [Na^+]_R \cdot [Na^+]^{-1}$ . Then we get  $a_4 \approx 0.03$  mM.

$\beta_1$  for the glycolate system has been computed by means of eqn. (15) instead of eqn. (12) as both  $\Delta f \cdot [A^-]^{-1}$  and  $\Delta \varphi_1 \cdot [A^-]^{-1}$  are approximately constant. For  $\beta_3$  and  $\beta_4$  the potentiometrically obtained constants have been used. A probable value of  $l'_2$  has been calculated by means of eqn. (14) in the following way. We know that  $\varphi_1^\circ = \beta_1 - l'_1 = 322$  M<sup>-1</sup>. In most cases  $l'_1$  is about 10 % of  $\beta_1$ . Then we have assumed that  $l'_1 \approx 30$  M<sup>-1</sup> and  $\beta_1 \approx 350$  M<sup>-1</sup>. As  $f^\circ = \beta_1 \cdot \varphi_1^\circ - (\beta_2 - l'_2) = 82\,500$  we can write  $\beta_2 \approx \beta_2 - l'_2 \approx 30\,000$  M<sup>-2</sup> (in most cases  $l'_2 \ll \beta_2$ ). This value of  $\beta_2$  is in good accordance with the potentiometric value. Then eqn. (14) gives  $l'_2 \approx 200$  M<sup>-2</sup>.

As seen in Table 4 the  $\beta_1$ -values calculated by means of eqn. (15) are very close to 350. It should be emphasized that  $l'_2$  has only a slight influence on  $\beta_1$ . Therefore the values of  $\beta_1$  calculated from eqn. (15) are practically independent of the value of  $l'_1$  assumed above.

$\beta_1 = 350$  M<sup>-1</sup> gives  $\beta_2 - l'_2 = 29.5 \times 10^3$  M<sup>-2</sup>. Then  $\beta_2$  can be determined by means of eqn. (13). The function  $g(\varphi_1)$  seems to be linear over the whole region and therefore  $X_4$  must be negligible for  $[A^-] < 55$  mM. The slope of

Table 4. The cation-exchange measurements on the glycolate system. The values of  $[A^-]$ ,  $\varphi$  and the various functions are valid for  $C_{MR} = 10 \times 10^{-3}$  mmole.g $^{-1}$ . In calculating  $\beta_1$  the potentiometric obtained values  $\beta_3 = 62 \times 10^4$  and  $\beta_4 = 26 \times 10^5$  have been used.

$[A^-]$ mM	$\varphi \times 10^3$ l.g $^{-1}$	$\varphi_1$ M $^{-1}$	$f \times 10^{-2}$ M $^{-2}$	$\beta_1$ from eqn. (15)	(13) $g \times 10^{-4}$ M $^{-3}$
0	323	322	825		
1.40	216	353	915		
3.00	150	385	1 030	$325 + 31 + 0 - 4 = 352$	1 060
5.00	103.5	424	1 165	$333 + 32 + 1 - 4 = 362$	1 205
7.00	75.5	468	1 300	$325 + 31 + 1 - 5 = 352$	1 320
10.00	51.2	531	1 500	$323 + 31 + 1 - 5 = 350$	1 505
14.00	33.5	617	1 775	$322 + 31 + 2 - 6 = 349$	1 755
20.0	20.3	746	2 190	$322 + 31 + 3 - 7 = 349$	2 135
28.0	12.3	902	2 700	$323 + 31 + 4 - 9 = 349$	2 605
38.0	7.5	1 107	3 360	$323 + 31 + 5 - 11 = 348$	3 210
46.0	5.5	1 255	3 840	$323 + 32 + 6 - 12 = 349$	3 645
55.0	4.2	1 380	4 265	$325 + 34 + 7 - 14 = 352$	4 025

the line gives  $\beta_2 = 29.5 \times 10^3$  M $^{-2}$ , and the intercept for  $\varphi_1 = 0$  gives  $\beta_3 \approx 70 \times 10^4$  M $^{-3}$ .

The values of  $\beta_1$ ,  $\beta_2$  and  $\beta_3$  obtained in this investigation are in good accordance with those obtained potentiometrically.

Potentiometric measurements.  $I = 2.0$  M. Cation-exchange measurements.  $I = 1.0$  M.

$\beta_1$ : $300 \pm 15$	$350 \pm 20$	M $^{-1}$
$\beta_2$ : $(27 \pm 4) \times 10^3$	$(30 \pm 4) \times 10^3$	M $^{-2}$
$\beta_3$ : $(62 \pm 8) \times 10^4$	$(70 \pm 20) \times 10^4$	M $^{-3}$
$\beta_4$ : $(26 \pm 5) \times 10^5$	— — —	M $^{-4}$

## B. INVESTIGATION BY MEANS OF AN ANION EXCHANGER

### Theoretical

Fronæus<sup>5</sup> has given a theory for the equilibrium distribution of the central ion  $M^{3+}$  between a solution containing a complexing ligand  $A^-$  and an anion exchanger saturated with  $A^-$ .

In the anion-exchange investigation the ionic strength of the outer solution is not kept constant by addition of sodium perchlorate as perchlorate ions would displace ligand ions in the resin. Then the activity coefficients will vary when the buffer solution is added.

For the distribution of the ions  $M^{3+}$  and  $A^-$  between the resin and the solution, we have according to the Donnan equation

$$[M^{3+}]_R \cdot [A^-]_R^3 = K \cdot [M^{3+}] \cdot [A^-]^3 \quad (19)$$

The factor  $K$  includes the activity coefficients of the two ion species in both phases.

For the load on the exchanger we have the equation

$$C_{MR} = [M^{3+}]_R \left( 1 + \sum_{j=1}^N \beta_{jR} \cdot [A^-]_R^j \right) = [M^{3+}]_R \cdot X([A^-]_R) \quad (20)$$

Then we get according to eqn. (19)

$$\varphi = \frac{C_{MR}}{C_M} = K \frac{X([A^-]_R)}{[A^-]_R^3} \cdot \frac{[A^-]^3}{X([A^-])} = l_3 \cdot \frac{\alpha_3}{\alpha_{3R}} \quad (21)$$

with  $l_3 = K \cdot \beta_{3R} \cdot \beta_3^{-1}$

Here  $l_3$  is the Nernst distribution coefficient for the third uncharged complex and can be assumed to be approximately constant.  $\alpha_3$  and  $\alpha_{3R}$  denote the fractions  $[MA_3] \cdot C_M^{-1}$  and  $[MA_3]_R \cdot C_{MR}^{-1}$ , respectively.

As shown by Fronæus<sup>5</sup> the function  $\varphi([A^-])$  shows a maximum for a ligand concentration in the outer solution corresponding to  $\bar{n} = 3$ .

Then, if anionic complexes are formed,  $\varphi$  will to begin with increase with increasing  $[A^-]$ . After the maximum point has been reached at  $\bar{n} = 3$ ,  $\varphi$  will decrease with increasing values of  $[A^-]$ .

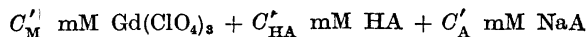
If anionic complexes are not formed,  $\varphi$  ought to increase uniformly for increasing  $[A^-]$ .

However, the possibility must be taken into consideration that a part of  $C_{MR}$  is due to gadolinium ions or complexes adsorbed on the surface of the resin particles. This has been discussed by Fronæus<sup>8</sup>. In addition to the quaternary ammonium groups the anion exchanger possibly contains amine groups, which might form complexes with the central ion  $M^{3+}$  and, most likely to a lesser extent, with the complexes  $MA_j^{3-j}$ . Then the presumed amine complexes ought to be found preferably on the surface of the resin. The contribution of the surface adsorption to  $\varphi$  is denoted by  $\Delta\varphi^s$ . As  $[M^{3+}]$  decreases when  $[A^-]$  increases, this surface adsorption ought to decrease with increasing  $[A^-]$  — that is,  $\Delta\varphi^s$  decreases when  $[A^-]$  increases.

## Experimental

*Chemicals used.* Dowex 1 × 4, an anion-exchanger containing fixed quaternary ammonium groups, was used. It was converted to the acetate or the glycolate form and air-dried. The swelling factor  $\delta$  was determined to be 0.96.

*Method of investigation.* The complex solutions had the initial composition



The gadolinium perchlorate contained<sup>1</sup> the radioactive isotope  $^{153}\text{Gd}$ .  $C'$  was kept constant in a series (0.0730 mM and 0.0630 mM in the investigations of the acetate and the glycolate systems, respectively).

The quotient  $C'_{HA} : C'_A$  was 2.0 for the acetate buffer and 1.0 for the glycolate buffer. The pH of the initial solution of  $\text{Gd}(\text{ClO}_4)_3$  was about 4.5.

The complex solution ( $v$  liters) together with  $m$  grams of air-dried exchanger was shaken during 20 h in a thermostat at 20°C. The value of  $v \cdot m^{-1}$  was always  $0.025 \text{ l} \cdot \text{g}^{-1}$ .

As the measurements of the equilibrium concentration  $C_M$  of the water phase showed that the sorption was very slight at all concentrations of acetate and glycolate ions,  $C_{MR}$  could not be calculated indirectly by means of eqn. (16) from the difference  $C'_M - \delta \times C_M$ . For this reason  $C_{MR}$  was determined directly by eluting the resin, which had been carefully separated from the solution, with  $v_1$  liters of 2 M  $\text{HClO}_4$  in small portions. After having determined the gadolinium concentration  $C''_M$  of this solution, it was possible to calculate  $C_{MR}$  from the relation  $C_{MR} = v_1 \cdot m^{-1} \cdot C''_M$ . Here  $v_1 \cdot m^{-1}$  had the value  $0.042 \text{ l} \cdot \text{g}^{-1}$ . However, a certain amount of radioactive solution adhered to the particles of the separated resin, which could not be washed before the elution. Thus the  $C_{MR}$ -value included a quantity  $C_{MR}^a$  caused by this adherent solution. As  $v \cdot m^{-1}$  had the same value for all the complex solutions and as the experiments were performed in quite the same manner, we have  $C_{MR}^a \approx k \cdot C_M$ , where  $k$  is a constant. The  $C_{MR}^a$  contributes to  $\varphi$  in the term  $\Delta\varphi^a = C_{MR}^a \cdot C_M^{-1}$  — that is, all  $\varphi$ -values differ from the true  $\varphi$ -values by the constant term  $\Delta\varphi^a = k$ .

*The gadolinium acetate system.* The data from the measurements on the  $\text{Gd}^{3+} - \text{Ac}^-$ -system are collected in Table 5 a. Curve *a* in Fig. 3 shows  $\varphi$  plotted against  $[\text{Ac}^-]$ . In the calculation of  $[\text{Ac}^-]$  it is supposed that the perchlorate ions in the initial solution are nearly completely replaced by an equivalent amount of acetate ions from the resin.

According to the potentiometric measurements anionic complexes are formed in the  $\text{Gd}^{3+} - \text{Ac}^-$ -system and the ligand number  $\bar{n} = 3$  is reached at  $[\text{Ac}^-] \approx 500 \text{ mM}$ . However, the function  $\varphi([\text{Ac}^-])$  does not show any maximum at this acetate concentration. For  $100 \text{ mM} < [\text{Ac}^-] < 800 \text{ mM}$ ,  $\varphi$  has a very low value and is approximately constant. At low  $[\text{Ac}^-]$ ,  $\varphi$  is somewhat higher,

Table 5. The anion-exchange measurements on the acetate and glycolate systems.

a. The acetate system $C'_M = 73.0 \times 10^{-3} \text{ mM}$				b. The glycolate system $C'_M = 63.0 \times 10^{-3} \text{ mM}$			
$[\text{A}^-]$ mM	$C_M \times 10^3$ mM	$C_{MR} \times 10^4$ mmole · $\text{g}^{-1}$	$\varphi \times 10^3$ $\text{l} \cdot \text{g}^{-1}$	$[\text{A}^-]$ mM	$C_M \times 10^3$ mM	$C_{MR} \times 10^4$ mmole · $\text{g}^{-1}$	$\varphi \times 10^3$ $\text{l} \cdot \text{g}^{-1}$
0.2	72.0	1.05	1.45	0.2	63.0	1.00	1.60
11.7	71.5	1.23	1.70	12.5	60.0	1.52	2.50
104	75.0	0.44	0.59	26	57.5	2.08	3.60
208	75.0	0.39	0.51	45	58.0	2.19	3.80
347	76.0	0.38	0.50	64	57.5	2.22	3.85
485	74.5	0.38	0.52	128	56.0	2.25	4.00
625	74.0	0.39	0.52	174	57.0	2.13	3.75
830	73.5	0.48	0.65	243	58.0	2.10	3.60
				347	58.0	1.85	3.20
				555	61.0	1.48	2.40

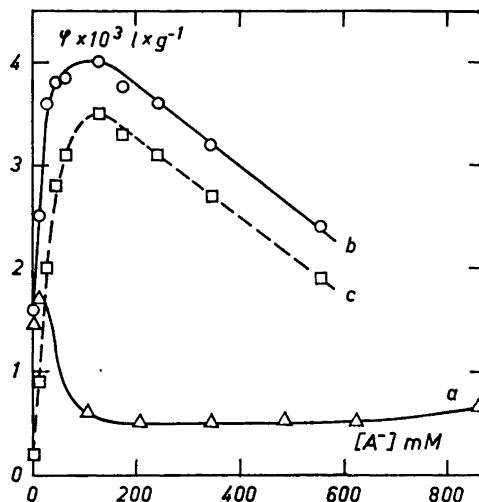


Fig. 3. The anion-exchange measurements on the acetate and the glycolate systems. Curve *a* represents the function  $\varphi([Ac^-])$  and curve *b* the function  $\varphi([AcOH^-])$ . Curve *c* is the function  $\varphi_c([AcOH^-])$ , where  $\varphi_c$  means the  $\varphi$ -values of the glycolate system reduced by the  $\varphi$ -values of the acetate system.

certainly depending on the surface adsorption, which increases for decreasing  $[Ac^-]$ .

Then, according to these measurements anionic gadolinium acetate complexes cannot be formed by appreciable amounts in the resin phase. However, this does not necessarily mean that anionic complexes are not formed in the water phase.

*The gadolinium glycolate system.* The results from the measurement on the  $Gd^{3+}-AcOH^-$ -system are collected in Table 5 b. As shown in Fig. 3 (curve *b*) the function  $\varphi([AcOH^-])$  has a distinct maximum for  $[AcOH^-] \approx 100$  mM. This agrees with the potentiometric measurements as  $\bar{n}_{pot} = 3$  for  $[AcOH^-] \approx 100$  mM. Thus it is very probable that anionic glycolate complexes are formed both in the resin phase and in the water phase.

We may assume that the  $\varphi$ -values of the acetate system are due to surface adsorption and to solution adherent to the resin particles — that is,  $\varphi_{Ac} \approx \Delta\varphi_{Ac}^s + \Delta\varphi_{Ac}^a$ . We may also assume that these two  $\Delta\varphi$ -values have about the same values for the acetate and the glycolate systems. Then the true  $\varphi$ -values for the glycolate system should be  $\varphi_c = \varphi - \varphi_{Ac}$ . Curve *c* in Fig. 3 shows  $\varphi_c$  as a function of  $[AcOH^-]$ .

If we take the logarithm of eqn. (21), derivate  $\ln\varphi$  with respect to  $\ln[A^-]$  and introduce the ligand numbers  $\bar{n}_R$  and  $\bar{n}$  according to the definitions ( $\bar{n} = d\ln X/d\ln[A^-]$ ), we get

$$\frac{d\ln\varphi}{d\ln[A^-]} = \frac{d\ln[A^-]_R}{d\ln[A^-]} (\bar{n}_R - 3) - (\bar{n} - 3) \quad (22)$$

In this investigation we may consider  $[A^-]_R$  as constant. Then we get

$$\frac{d\ln\varphi}{d\ln[A^-]} = 3 - \bar{n} \quad (23)$$

Table 6. The anion-exchange measurements on the gadolinium glycolate system. The function  $\frac{1}{k} \cdot X$  is computed according to eqn. (24) and the functions  $\frac{1}{k} \cdot X_n$  according to eqn. (8) in paper II.

[A <sup>-</sup> ] mM	$\varphi_c \times 10^3$ $l \cdot g^{-1}$	(23) $\bar{n}$	$\bar{n}_{pot}$	$\frac{[A^-]^3}{\varphi_c} = \frac{1}{k} \cdot X$ $M^3 \cdot g \cdot l^{-1}$	$\frac{1}{k} \cdot X_1$ $M^2 \cdot g \cdot l^{-1}$	$\frac{1}{k} \cdot X_2$ $M \cdot g \cdot l^{-1}$	$\frac{1}{k} \cdot X_3$ $g \cdot l^{-1}$	$\frac{1}{k} \cdot X_4$ $M^{-1} \cdot g \cdot l^{-1}$
0	0	—	—	—	0.10	4.0	200	~500
0.2	0.1	—	0.1	$0.1 \cdot 10^{-6}$	—	—	—	—
12.5	0.9	1.5	1.6	0.0022	0.18	6.5	200	—
26	2.0	2.3	2.1	0.0088	0.34	9.2	200	—
45	2.8	2.6	2.5	0.032	0.72	13.8	220	—
64	3.1	2.7	2.7	0.085	1.32	19.0	230	—
128	3.5	3.0	3.1	0.60	4.7	36	250	400
174	3.3	3.2	3.3	1.60	9.2	52	270	400
243	3.1	3.3	3.5	4.6	19.0	78	300	400
347	2.7	3.6	3.7	15.5	45	130	360	500
555	1.9	4.0	3.9	90	162	290	510	600

The values of  $\bar{n}$  in Table 6 are calculated from the corrected  $\varphi_c$ -values by means of this equation. The accordance with the ligand numbers obtained potentiometrically is good.

Attempts have also been made to calculate approximate values of the complexity constants from the anion-exchange measurements. The  $\varphi_c$ -values have been used. Eqn. (21) can be transformed to

$$\frac{[A^-]^3}{\varphi} = \frac{1}{k} \cdot X = \frac{1}{k} + \frac{\beta_1}{k} [A^-] + \frac{\beta_2}{k} [A^-]^2 + \dots \quad (24)$$

where

$$k = l_3 \cdot \beta_3 \cdot \alpha_{3R}^{-1}$$

$\alpha_{3R}$  is assumed to be constant as the ligand concentration of the resin is approximately constant.

Theoretically, the value of  $1/k$  and the complexity constants can be calculated by means of the  $X/k$ -functions by extrapolation to  $[A^-] = 0$ .

However, the  $X$ -function decreases so rapidly with decreasing  $[A^-]$  that it is impossible to obtain even an approximate value of  $1/k$  (cf. Table 6), but for the  $X_n/k$ -functions we have obtained the following approximate values for  $[A^-] = 0$ :

$$\frac{\beta_1}{k} = 0.10; \quad \frac{\beta_2}{k} = 4.0; \quad \frac{\beta_3}{k} = 200; \quad \frac{\beta_4}{k} = 500$$

As we have no value of  $1/k$  we can compute only the stability constants  $b_n = \beta_{n+1} \cdot \beta_n^{-1}$ . Thus  $b_2 = 40$ ,  $b_3 = 50$ ,  $b_4 = 2.5$ . These values are of the same order of magnitude as the potentiometrically obtained values  $b_2 = 90$ ,  $b_3 = 20$ ,  $b_4 = 4$ , but there are considerable differences between the two

sets of constants. One of the reasons may be that the potentiometric measurements are performed at the constant ionic strength 2.0 M whereas the anion-exchange experiments have been performed with solutions having an ionic strength increasing from about 0.01 M for the lowest value of  $[A^-]$  (12.5 mM) to about 0.5 M for the highest value of  $[A^-]$ . In this region the activity coefficients are, of course, not constant. On the whole the stability constants obtained from the anion-exchange measurements are very uncertain. The cause of the too low value of  $b_2$  may be a too high value of  $\beta_1 \cdot k^{-1}$ , because we have used the same value of  $\Delta\varphi^s$  for the glycolate system as for the acetate system. If especially non-complex gadolinium ions are adsorbed on the surface of the resin,  $\Delta\varphi^s$  ought to decrease more rapidly for the glycolate system than for the acetate system.

### DISCUSSION

The investigations by use of the cation exchanger confirm the potentiometrically obtained values for the first three complexity constants for both the acetate and the glycolate system. It is true that the constants obtained for the glycolate system by the cation-exchange method are not quite independent of those obtained potentiometrically, but the potentiometric influence is so slight that it falls for the most part within the limits of the maximum random errors.

The question whether anionic complexes are formed can be answered definitely only for the glycolate system. The  $\varphi$ -curve obtained in the anion-exchange investigation of this system shows a rather pronounced maximum for  $[AcOH^-] \approx 100$  mM, and, according to the potentiometric measurements, we should have  $\bar{n} \approx 3$  for just this concentration of free glycolate ions. We may then conclude that anionic glycolate complexes are formed.

The  $\varphi$ -function obtained for the acetate system by means of the anion exchanger has an aspect quite different from that of the  $\varphi$ -curve of the glycolate system. We must conclude that anionic acetate complexes are not formed in the resin phase (*cf.* Fronæus<sup>5</sup>), but this does not necessarily mean that anionic complexes are not formed in the water phase. The low  $\varphi$ -values at the maximum point for the glycolate system indicates that it is very difficult for the complexes to be formed in the anionic resin phase. There may be a steric hindrance reducing the tendency to form complexes. This may be the reason why the considerably weaker acetate complexes cannot be formed in the resin phase. The relation between the heights of  $\varphi_{\max}$  of systems of equal type should, according to Fronæus<sup>5, p.3</sup>, give a qualitative measure of the difference in strength of the anionic complexes. However, it is also possible that the potentiometric measurements have given too high values for the complexity at high ligand concentrations, so that anionic complexes are not really formed to a measurable extent at the concentrations used in the anion-exchange measurements.

As seen in Fig. 3 the  $\varphi$ -values of the acetate system increase slightly at high ligand concentrations. This is probably due to the presence of a non-exchange electrolyte in the resin. Calculations show that this ought to increase the  $\varphi$ -values appreciably when  $[A^-] > 0.7$  M. As  $[A^-]_R \approx 3$  M for  $[A^-] = 0$ ,

the increase in  $[A^-]_R$  ought to be  $\sim 5\%$  at  $[A^-] \approx 0.7\text{ M}$  (cf. Fronæus<sup>8</sup>, p.1181). The presence of a non-exchange electrolyte probably does not influence the calculations for the glycolate system at lower ligand concentrations.

The sorption of the complex ions in the cation exchanger is very low compared with that of the non-complex gadolinium ions. For the acetate system we get  $l'_1 = (7 \pm 3)\text{ M}^{-1}$  and  $l'_2 \approx 15\text{ M}^{-2}$  (according to eqn. (14)). Eqns. (6) and (4) give for the distribution of the non-complex gadolinium ions and the acetate complexes between the resin phase and the water phase  $l_0 = 0.323\text{ l} \cdot \text{g}^{-1}$ ,  $l_1 = 0.035\text{ l} \cdot \text{g}^{-1}$  and  $l_2 = 0.0035\text{ l} \cdot \text{g}^{-1}$ . For the glycolate system the corresponding values are  $l_0 = 0.323\text{ l} \cdot \text{g}^{-1}$ ,  $l_1 = 0.025\text{ l} \cdot \text{g}^{-1}$  and  $l_2 = 0.002\text{ l} \cdot \text{g}^{-1}$ . This shows that the equilibrium concentration of  $\text{Gd}(\text{AcOH})_2^+$  is only about twice as high in the resin phase as in the water phase. Then, when  $\text{Gd}(\text{AcOH})_2^+$  is transformed to higher complexes, the absolute decrease of  $\varphi$  will be rather small (relatively however, the decrease may be large). Therefore the random errors will seriously affect the determination of  $\beta_3$  and the higher complexity constants, and this is probably the reason why the existence of the anionic glycolate complexes could not be detected by the cation-exchange method.

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#### REFERENCES

1. Sonesson, A. *Acta Chem. Scand.* **12** (1958) 165.
2. Sonesson, A. *Acta Chem. Scand.* **12** (1958) 1937.
3. Sonesson, A. *Acta Chem. Scand.* **13** (1959) 998.
4. Fronæus, S. *Svensk Kem. Tidskr.* **65** (1953) 19.
5. Fronæus, S. *Svensk Kem. Tidskr.* **65** (1953) 1.
6. Fronæus, S. *Svensk Kem. Tidskr.* **64** (1952) 64.
7. Fronæus, S. *Komplexsystem hos koppar* (Diss.) Lund 1948.
8. Fronæus, S. *Acta Chem. Scand.* **8** (1954) 1174.

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