

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

### VI. A Study of the Complex Formation between Gadolinium and Glycolate Ions in an Anion Exchanger

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The complex formation between gadolinium and glycolate ions in an anion exchanger phase has been studied at 20°C, a resin with quarternary ammonium groups (Dowex 1 × 4) being used. The glycolate concentration of the resin was varied widely by exchange for perchlorate ions. The amount of water of the resin phase was determined and the ionic strength of the resin phase was calculated formally. The ionic strength of the water phase was approximately constant, 0.21 M.

The glycolate concentration of the two phases was determined by oxidation with potassium permanganate in a solution made alkaline by sodium carbonate.

It was found that the ligand number of the resin phase could not be calculated in the whole concentration range as the ionic strength probably varied too widely, owing to the dependence of the swelling upon the glycolate load on the exchanger.

Approximate values of  $K \cdot \beta_{nR}$ , where  $K$  is a constant, were determined, but it was not possible to compute  $K$ . The values of  $K \cdot \beta_{nR}$  ( $n = 1, 2, 3, 4$ ) are of the same order of magnitude as the potentiometrically obtained complexity constants for a water solution. It seems probable that only the first anionic complex is formed in the resin phase.

Complexity constants of the gadolinium-glycolate system are also reported for solutions with the ionic strengths 0.21 M and 3.0 M.

The method of calculation given by Fronæus *et al.*<sup>1</sup> has been used. As to the notations and the equations used for the calculations, the reader is referred to the previous papers<sup>1,2</sup>.

In this investigation the ionic strength of the water phase was kept approximately constant ( $I = 0.21$  M). Therefore the complexity constants for the water phase may be considered as approximately constant.

For the distribution of a trivalent ion species,  $M^{3+}$ , between a water phase and a resin phase, both containing the ligand  $A^-$ , we have the Donnan equilibrium

$$f_{MR} \cdot [M^{3+}]_R \cdot f_{AR}^3 \cdot [A^-]_R^3 = K_a \cdot f_{ML} \cdot [M^{3+}]_L \cdot f_{AL}^3 \cdot [A^-]_L^3 \quad (1)$$

Here we mean by  $f$  the activity coefficient, by  $K_a$  the thermodynamic equilibrium constant, and by the indices R and L the resin phase and the water phase, respectively.

For the distribution of the uncharged third complex  $MA_3$  between the two phases, we have

$$[MA_3]_R = l_3 \cdot [MA_3]_L \quad (2)$$

where  $l_3$  is the distribution coefficient for the third complex.

It is now easily seen from eqns. (1) and (2) that

$$K_a = l_3 \cdot \frac{f_{3R}}{f_{3L}} \cdot \frac{\beta_{3L}^{(a)}}{\beta_{3R}^{(a)}} \quad (3 a)$$

Here,  $f_3$  is the activity coefficient for the third, uncharged complex, and we may assume that  $f_{3R} \approx f_{3L} \approx 1$ .  $\beta_3^{(a)}$  is the thermodynamic complexity constant, and  $\beta_3$ , the concentration complexity constant for the third complex.

In the following we use a concentration constant  $K$ , defined

$$K = l_3 \cdot \frac{\beta_{3L}}{\beta_{3R}} \quad (3 b)$$

Thus 
$$K = K_a \cdot (f_{ML} \cdot f_{AL}^3) \cdot (f_{MR} \cdot f_{AR}^3)^{-1} \quad (3 c)$$

According to Fronæus<sup>1</sup>, (cf. IV eqn 21) we have for a trivalent ion

$$K \cdot X([A]_R) = \varphi \cdot X([A]_L) \cdot \frac{[A]_R^3}{[A]_L^3} \quad (4)$$

where 
$$X([A]_R) = 1 + \sum_{n=1}^N \beta_{nR} \cdot [A]_R \quad (4 a)$$

The function  $X([A]_L)$  is formed in the corresponding way.

If corresponding values of  $K \cdot X_R$  and  $[A]_R$  are known\*, it ought to be possible to calculate  $K \cdot \beta_{nR}$  and perhaps also  $\bar{K}$ .

If the activity coefficients for the two phases are constant under the experimental conditions, the ligand number,  $\bar{n}_R$ , of the resin phase can be obtained according to Fronæus<sup>1</sup>:

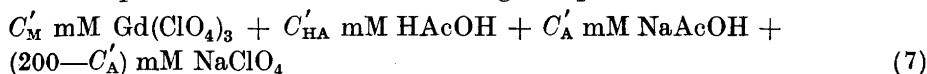
$$\bar{n}_R = 3 + \frac{d \ln \varphi}{d \ln [A]_R} + (\bar{n} - 3) \cdot \frac{d \ln [A]_L}{d \ln [A]_R} \quad (5)$$

Thus, to be able to compute  $\bar{n}_R$  and  $\beta_{nR}$ , we must know  $\varphi = C_{MR} \cdot C_{ML}^{-1}$  (i.e., the distribution of gadolinium ions between the resin phase and the water phase),  $[A]_L$  and  $[A]_R$  (i.e., the concentration of free glycolate ions in both the phases),  $\bar{n}_L$  and  $X([A]_L)$  (i.e., the complexity constants for the outer solution). Also, we must know the volume of the inner solution to be able to express  $\beta_{nR}$  in the usual way ( $M^{-n}$ ).

\*  $X_R$  and  $X_L$  are used as abbreviations for  $X([A]_R)$  and  $X([A]_L)$ , respectively.

## MEASUREMENTS

The complex solutions had the starting composition



$\text{AcOH}^-$  is the glycolate ion. The ratio  $C'_{\text{HA}}/C'_A$  was 0.49.  $C'_M$  was kept constant at 0.0975 mM. The gadolinium perchlorate contained the radioactive isotope  $^{153}\text{Gd}$ . The pH of the starting solution of  $\text{Gd}(\text{ClO}_4)_3$  was about 4.5. The initial ionic strength of the solutions was always 0.20 M.

The anion-exchanger Dowex 1  $\times$  4 was used for this investigation. It was converted in the glycolate form and air-dried. The glycolate amount was found to be 3.05 mequiv. per gram air-dried resin.

15 ml of the complex solution was shaken with 1 g of the air-dried, glycolate-saturated exchanger for 20 h in a thermostat at 20°C.

The distribution  $\varphi = C_{\text{MR}} \cdot C_{\text{ML}}^{-1}$  was determined by means of the radioactive isotope in the way described before (Sonesson<sup>2</sup>). The exchanger was carefully separated from the outer solution (solution A) by means of a small glass-filter funnel. The exchanger was then eluted with regard to both gadolinium ions and glycolate ions by means of 20 ml 2 M  $\text{NaClO}_4$  in small portions, and the "resin solution" (solution B, diluted to 25 ml) was obtained.

However, a certain amount of solution A adhered to the funnel and to the particles of the resin and could not be removed before the elution. An approximate value of the volume of the adhering solution was obtained in the following way. In special measurements with  $C'_M = 0$ , the resin was separated from the solution in exactly the same way as before. The resin and the funnel was washed rapidly with cold water. Then both the outer solution A and the wash water was analysed. After having determined the total concentration of  $\text{HAcOH} + \text{NaAcOH}$  and the amount of  $\text{HAcOH}$ , we could calculate the amount of  $\text{NaAcOH}$  in both the solutions. The sodium glycolate in the wash solution ought to have come from solution A adsorbed to the funnel and the resin. Calculations showed that 0.20–0.25 ml of solution A was adsorbed\*. Therefore in the calculations of  $C_{\text{MR}}$  and  $[\text{AcOH}^-]_{\text{R}}$  corrections have been made for 0.20 ml outer solution adsorbed. This correction term is perhaps too high. A part of the glycolate now assumed to be adsorbed may have been present in the resin phase as non-exchange electrolyte according to the Donnan equilibrium.

It was found that the resin was radioactive after it had been eluted with 20 ml 2 M  $\text{NaClO}_4$ . Thus, it still contained gadolinium ions, possibly as hydrolytic products precipitated in the resin during the elution. It is also possible that  $\text{Gd}(\text{AcOH})_3$  has been precipitated in the resin phase, as the glycolate is rather slightly soluble. Therefore, the resin was eluted a second time, now with 2 ml warm 2 M  $\text{HClO}_4$  in small portions. After this elution the resin showed very low activity. The solution was diluted to 25 ml and analysed on both gadolinium and glycolate ions. When the total value of  $C_{\text{MR}}$  was to be cal-

\* In separate measurements it was found that about 30 % of the solution assumed adsorbed should adhere to the resin and the rest to the funnel.

culated the gadolinium content of this last solution had to be taken into consideration. The content of glycolate ions was, however, always so low that it could be neglected.

The total concentration of glycolic acid + sodium glycolate, *i.e.*,  $C_{\text{HA}} + C_{\text{NaA}}$ , was determined through oxidation by potassium permanganate in solutions made alkaline by sodium carbonate. To a known volume of the glycolate solution was added sodium carbonate solution and a known amount of potassium permanganate so large that the glycolate was quantitatively oxidized to carbon dioxide when the permanganate was reduced to manganese dioxide\*. The solution was warmed in a glass flask fitted with a condenser (all in glass) for 30 min. on a boiling water bath. Then the solution was acidified with sulphuric acid and a known amount of sodium oxalate was added to a slight excess. Finally the excess of oxalate was back-titrated with permanganate.

This method of determining the glycolate proved, however, somewhat uncertain, because permanganate ions have a tendency to decompose spontaneously in alkaline solutions. Therefore, we had to use two different values for the permanganate titer, one "alkaline titer" for the permanganate heated in alkaline solution, and another "acid titer" for the permanganate added for the back-titration in acid solution.

The degree of decomposition seemed to depend on the purity of the permanganate solution, on the way in which the analysis was performed, and on the nature of the glass wall of the flask in which the solution was heated. Therefore, the stock solution of permanganate was boiled and filtered several times before it was used. All analyses were performed in exactly the same way using only two sets of flasks and condensers, for which it was checked that the same degree of decomposition occurred.

The "acid titer" of the permanganate solution was determined in the usual manner by means of sodium oxalate. The "alkaline titer" was determined by oxidizing a known amount of glycolic acid in the way described above. Several determinations were performed with varying amounts of glycolic acid. With few exceptions the values obtained for the "alkaline titer" deviated less than 0.3 % from the mean value. The "alkaline titer" was about 2.5 % lower than the "acid titer".

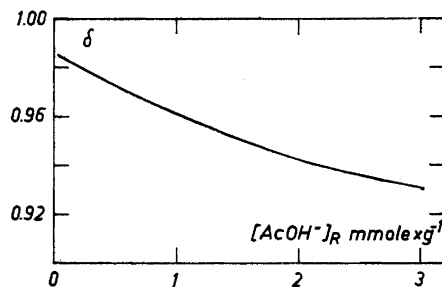
For every solution the determination of the total concentration  $C_{\text{HA}} + C_{\text{NaA}}$  was performed at least twice. The uncertainty of  $C_{\text{HA}} + C_{\text{NaA}}$  was estimated at  $\pm 3$  %.

After having determined  $C_{\text{HA}}$  by titration with sodium hydroxide, we could compute  $C_{\text{NaA}}$ , *i.e.*, the concentration of free glycolate ions,  $[\text{AcOH}^-]$ . Correction terms depending on the protolyze of glycolic acid and of the complex formation between gadolinium and glycolate ions could be neglected. The random errors of  $[\text{AcOH}^-]$  were estimated at  $\pm 4$  %.

To be able to express  $[\text{AcOH}^-]_{\text{R}}$  in mole per liter, we must determine the volume of the water in the resin phase. This was done by determining the water content of the air-dried resin and by measuring the swelling of the air-

\* As it was found in the literature that calcium ions catalyse the reaction, calcium nitrate was added in small amounts. Any significant effect of this was, however, not observed.

Fig. 1. The variation of the swelling factor  $\delta$  with the concentration of glycolate ions in the resin phase. The total amount of water was  $[15(1-\delta) + 0.13]$  g per g air-dried resin in the glycolate form.



dried resin in buffer solutions with  $C'_M = 0$ . In the latter case the concentration of sodium ions was determined firstly with no resin present ( $[Na^+]'$ ), and secondly when equilibrium was reached between 1 g air-dried resin and 15 ml buffer solution ( $[Na^+]''$ )\*. The ratio  $[Na^+]'/[Na^+]'' = \delta$  is called the swelling factor. The value of  $\delta$  was determined for different values of  $C'_A$  (ionic strength always 0.20 M). The variation of  $\delta$  with  $[AcOH^-]_R$  is shown in Fig. 1. The volume of water absorbed by the resin was 15 (1- $\delta$ ) ml per gram air-dried resin.

The glycolate-saturated resin contained in the air-dried state 0.13 g water per g resin. It was determined as the loss of weight when the resin was slowly heated to 100°C.

Thus per g air-dried and glycolate-saturated resin there was taken up totally  $[15(1-\delta) + 0.13]$  g water. All this water cannot be considered as free solvent in the resin phase, as a part of it is surely bound in hydrated ions. Since the amount of absorbed water increases strongly with increasing  $[AcOH^-]_R$ , it is probable that the absorbed water is to a rather large extent bound by the glycolate ions. It is, however, impossible to estimate through the measurements done, to what extent the absorbed water shall be counted as free solvent. Nor have any investigations of this problem been found in the literature.

Table I. The complexity constants  $\beta_n$  and the stability constants  $b_n = \beta_n \cdot \beta_{n-1}^{-1}$  ( $b_1 = \beta_1$ ) for the gadolinium glycolate system at different values of the ionic strength. The constants at the ionic strength 1.0 M have been determined by measurements with a cation exchanger. In the other cases potentiometric measurements have been performed. The temperature has always been 20°C.

| Ionic strength | $\beta_1$       | $\beta_2$          | $\beta_3$          | $\beta_4$           | $\beta_5$          | $\beta_6$         | $b_1$ | $b_2$ | $b_3$ | $b_4$ | $b_5$ | $b_6$ |
|----------------|-----------------|--------------------|--------------------|---------------------|--------------------|-------------------|-------|-------|-------|-------|-------|-------|
|                | M <sup>-1</sup> | M <sup>-2</sup>    | M <sup>-3</sup>    | M <sup>-4</sup>     | M <sup>-5</sup>    | M <sup>-6</sup>   |       |       |       |       |       |       |
| 0.21 M         | 540             | 61·10 <sup>3</sup> | 20·10 <sup>5</sup> | 130·10 <sup>5</sup> | 10·10 <sup>6</sup> | —                 | 540   | 115   | 33    | 6.5   | 0.8   | —     |
| 1.0 M          | 350             | 30·10 <sup>3</sup> | 7·10 <sup>5</sup>  | —                   | —                  | —                 | 350   | 85    | 23    | —     | —     | —     |
| 2.0 M          | 300             | 27·10 <sup>3</sup> | 6·10 <sup>5</sup>  | 26·10 <sup>5</sup>  | 1·10 <sup>6</sup>  | —                 | 300   | 90    | 23    | 4     | 0.4   | —     |
| 3.0 M          | 390             | 40·10 <sup>3</sup> | 13·10 <sup>5</sup> | 65·10 <sup>5</sup>  | 6·10 <sup>6</sup>  | 4·10 <sup>6</sup> | 390   | 105   | 33    | 5     | 0.9   | 0.7   |

\* The concentration of sodium ions was determined by means of a cation exchanger column in the hydrogen state. In this way the total concentration of sodium salts and glycolic acid was obtained. Then the concentration of glycolic acid was determined separately and the concentration of sodium ions could be computed.

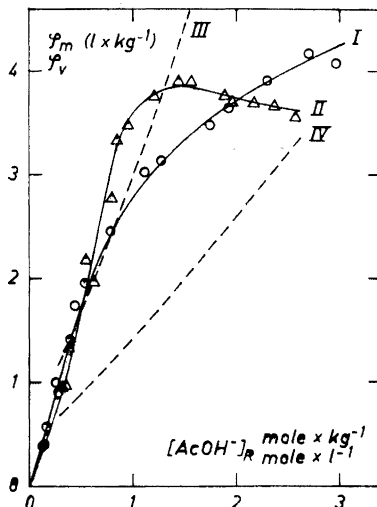


Fig. 2. The variation of the distribution  $\varphi = C_{MR} \cdot C_{MI}^{-1}$ , with the glycolate concentration of the resin phase,  $[\text{AcOH}^-]_R$ . Curve I (symbol  $\circ$ ) shows  $\varphi_m$  and is obtained when  $[\text{AcOH}^-]_R$  is expressed in moles per kg resin. Curve II (symbol  $\Delta$ ) shows  $\varphi_v$  when  $[\text{AcOH}^-]_R$  is expressed in moles per liter water in the resin phase. The figures show the values obtained experimentally. Curves III and IV have been calculated, both with  $[\text{AcOH}^-]_R$  expressed in moles per liter. Curve III has been obtained with the values of  $K \cdot \beta_{nR}$  given in Table 4 and therefore it should be valid for the ionic strength 6 to 8 M. For the calculation of curve IV, the values of  $\beta_n$  obtained potentiometrically at the ionic strength 3 M have been used. It has also been assumed that  $K = 1$ .

To be able to compute  $K \cdot X_R$  by means of eqn. (4), we must know the  $X_I$ -function for the water phase. This function and the complexity constants were determined by a potentiometric investigation in the way described in part III (Sonesson<sup>3</sup>). Sodium perchlorate was added to give the ionic strength 0.21 M as this was a mean value of the ionic strength of the water phase in the experiments with the anion exchanger ( $\delta = 0.95$ ). The complexity constants at the ionic strength 3.0 M were also determined potentiometrically, as it was probable that in our measurements with the anion exchanger the ionic strength of the resin phase was about 3 M at high values of  $[\text{AcOH}^-]_R$ . In Table 1 the values of the complexity constants obtained at different values of the ionic strength have been collected (Sonesson<sup>2,3</sup>).

#### DISCUSSION OF THE RESULTS

The experimentally obtained values of  $\varphi$ ,  $[\text{AcOH}^-]_R$  and  $[\text{AcOH}^-]_L$  are shown in Table 2. The glycolate concentration of the resin phase is given both in moles per kg resin and in moles per liter inner solution. The function  $\varphi([\text{AcOH}^-]_R)$  is shown in Fig. 2.

To be able to calculate  $\bar{n}_R$  according to eqn. (5),  $\log \varphi$  is plotted as a function of  $\log [\text{AcOH}^-]_R$ . Curve I in Fig. 3 is obtained if  $[\text{AcOH}^-]_R$  is expressed in moles per kg (*i.e.*  $\varphi = \varphi_m$ ), and curve II if  $[\text{AcOH}^-]_R$  is given in moles per liter (*i.e.*

Table 2. The experimentally obtained values of  $\varphi$  and the concentrations of free glycolate ions in the water phase and in the resin phase ( $[\text{AcOH}^-]_{\text{L}}$  and  $[\text{AcOH}^-]_{\text{R}}$ , respectively). The starting concentration of gadolinium ( $C_{\text{M}}$ ) was 0.0975 mM.  $\varphi_{\text{m}}$  and  $\varphi_{\text{v}}$  are the  $\varphi$ -values when  $[\text{AcOH}^-]_{\text{R}}$  is expressed in moles per kilogram resin and in moles per liter solvent, respectively.  $I_{\text{R}}$  is the calculated ionic strength of the resin phase.

| $[\text{AcOH}^-]_{\text{L}}$<br>M | $[\text{AcOH}^-]_{\text{R}}$<br>mole · kg <sup>-1</sup> | $\varphi_{\text{m}}$<br>l · kg <sup>-1</sup> | g H <sub>2</sub> O<br>per g resin | $[\text{AcOH}^-]_{\text{R}}$<br>M | $\varphi_{\text{v}}$ | $I_{\text{R}}$<br>M |
|-----------------------------------|---|--|-----------------------------------|-----------------------------------|----------------------|---------------------|
| 0.183                             | 0.13  | 0.38   | 0.40                              | 0.325                             | 0.95                 | 7.6                 |
| 0.182                             | 0.15  | 0.40   | 0.415                             | 0.360                             | 0.96                 | 7.3                 |
| 0.194                             | 0.17  | 0.57   | 0.43                              | 0.395                             | 1.32                 | 7.1                 |
| 0.201                             | 0.25  | 1.00   | 0.46                              | 0.545                             | 2.17                 | 6.6                 |
| 0.200                             | 0.29  | 0.90   | 0.46                              | 0.630                             | 1.96                 | 6.6                 |
| 0.204                             | 0.40  | 1.40   | 0.505                             | 0.795                             | 2.77                 | 6.0                 |
| 0.201                             | 0.44  | 1.73   | 0.52                              | 0.845                             | 3.33                 | 5.9                 |
| 0.203                             | 0.54  | 1.96   | 0.565                             | 0.955                             | 3.47                 | 5.4                 |
| 0.206                             | 0.79  | 2.45   | 0.655                             | 1.205                             | 3.74                 | 4.7                 |
| 0.208                             | 1.12  | 3.02   | 0.775                             | 1.445                             | 3.90                 | 3.9                 |
| 0.208                             | 1.26  | 3.13   | 0.805                             | 1.565                             | 3.89                 | 3.8                 |
| 0.210                             | 1.75  | 3.47   | 0.925                             | 1.89                              | 3.75                 | 3.3                 |
| 0.211                             | 1.93  | 3.64   | 0.985                             | 1.96                              | 3.70                 | 3.1                 |
| 0.212                             | 2.30  | 3.91   | 1.06                              | 2.17                              | 3.69                 | 2.9                 |
| 0.215                             | 2.70  | 4.17   | 1.14                              | 2.37                              | 3.66                 | 2.7                 |
| 0.216                             | 2.97  | 4.08   | 1.15                              | 2.58                              | 3.55                 | 2.65                |

$\varphi = \varphi_{\text{v}}$ ). The last term of eqn. (5), *i.e.*  $(\bar{n}-3) \cdot d \ln [A]_{\text{L}}/d \ln [A]_{\text{R}}$ , is only a small correction term, as  $[\text{AcOH}^-]_{\text{L}}$  varies only slightly with  $[\text{AcOH}^-]_{\text{R}}$  except at the lowest values of  $[\text{AcOH}^-]_{\text{R}}$  (Table 2). The ligand number of the water phase is about 3.6 at  $[\text{AcOH}^-]_{\text{L}} = 0.2$  M. Thus  $(\bar{n}-3) \cdot d \ln [A]_{\text{L}}/d \ln [A]_{\text{R}}$  does not exceed 0.1 (for  $[\text{AcOH}^-]_{\text{R}} > 0.5$  M it is lower than 0.05), irrespective of the way in which  $[\text{AcOH}^-]_{\text{R}}$  is expressed.

The ligand number  $\bar{n}_{\text{R}}$  obtained from curve II in Fig. 3 will, to begin with, increase with increasing  $[\text{AcOH}^-]_{\text{R}}$ , as seen in Table 3. From a maximum

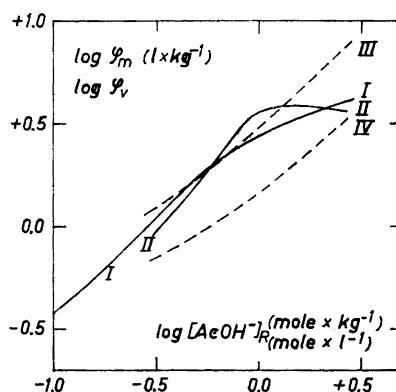


Fig. 3. Curves showing  $\log \varphi$  as a function of  $\log [\text{AcOH}^-]_{\text{R}}$ . The curves correspond to the curves with the same number in Fig. 2.

value of about 4.3 at  $[\text{AcOH}^-]_{\text{R}} \approx 0.5 \text{ M}$ , it decreases to about 3.0 for  $[\text{AcOH}^-]_{\text{R}} \geq 1.5 \text{ M}$ . Also, curve I gives a decrease of  $\bar{n}_{\text{R}}$ , though the decrease is not so pronounced (from 4.1 at 0.3 M to 3.4 at 3 M).

It can, however, not be correct that  $\bar{n}_{\text{R}}$  decreases when  $[\text{AcOH}^-]_{\text{R}}$  increases. One of the possible reasons why incorrect values of  $\bar{n}_{\text{R}}$  are obtained, may be the variation of the volume and thereby also the ionic strength of the resin solution. If all the water absorbed is considered as solvent, the ionic strength varies as shown in Table 2. As seen in Table 1 the complexity constants increase, especially the last ones, when the ionic strength increases from 2 M to 3 M, and it is likely that the  $\beta_n$ -values are still higher at higher values of the ionic strength. As the highest values of the ionic strength in the resin phase are reached at the lowest values of  $[\text{AcOH}^-]_{\text{R}}$ , it is evident that  $\varphi = l_3 \cdot a_3 / a_{3\text{R}}$  (Fronäus<sup>1</sup>) must increase more slowly with  $[\text{AcOH}^-]_{\text{R}}$  than if the ionic strength had been constant. Therefore, applying eqn. (5), we must obtain too low values of  $\bar{n}_{\text{R}}$ . Another reason for the incorrect values of  $\bar{n}_{\text{R}}$  may be a variation of  $K$  with the ionic strength.

In calculating  $K \cdot X_{\text{R}}$  according to eqn. (4) we have taken the values  $\varphi_{\text{v}}$  and  $[\text{A}]_{\text{R}}$  from the curves in Fig. 2. The values of  $K \cdot X_{\text{R}}$  are given in Table 3. The values in brackets are obtained by extrapolations of the corresponding curves and are therefore very uncertain.

It was not possible to obtain a value of  $K$  by extrapolation of  $K \cdot X_{\text{R}}$  to  $[\text{A}]_{\text{R}} = 0$ . The values of  $K \cdot \beta_{n\text{R}}$  have been calculated by extrapolations of

Table 3. Computation of the  $K \cdot X([\text{A}]_{\text{R}})$ -function from the experimentally obtained values of the glycolate concentrations  $[\text{AcOH}^-]_{\text{R}}$  and  $[\text{AcOH}^-]_{\text{L}}$ , and of the distribution  $\varphi_{\text{v}}$  (with  $[\text{AcOH}^-]_{\text{R}}$  expressed in moles per liter). The  $X([\text{A}]_{\text{L}})$ -function, i.e. the  $X([\text{A}])$ -function for the glycolate concentrations in the water phase given in the  $[\text{AcOH}^-]_{\text{L}}$ -column at the ionic strength 0.21 M, has been obtained potentiometrically.

The ligand number  $\bar{n}_{\text{R}}$  has been calculated according to eqn. (5) from curve I in Figure 3.  $I_{\text{R}}$  is the ionic strength of the resin phase.

| $[\text{AcOH}^-]_{\text{R}}$<br>M | $I_{\text{R}}$<br>M | $\varphi_{\text{v}}$ | $[\text{AcOH}^-]_{\text{L}}$<br>M | $\bar{n}_{\text{R}}$ | $\varphi_{\text{v}} \frac{[\text{A}]_{\text{R}}^3}{[\text{A}]_{\text{L}}^3}$ | $X([\text{A}]_{\text{L}})$<br>$\cdot 10^{-3}$<br>$I = 0.21 \text{ M}$ | $K \cdot X([\text{A}]_{\text{R}})$<br>$\cdot 10^{-5}$ |
|-----------------------------------|---------------------|----------------------|-----------------------------------|----------------------|--|---|---|
| 0                                 |                     |                      |                                   |                      |  |   |   |
| 0.10                              | 8.5                 | (0.30)               |                                   | 4.1                  |  |   | (0.03)  |
| 0.20                              | 8.1                 | (0.60)               |                                   | 4.1                  |  |   | (0.32)  |
| 0.30                              | 7.7                 | 0.90                 | (0.17)                            | 4.1                  | 5.0  | 23.8  | 1.19  |
| 0.40                              | 7.3                 | 1.25                 | 0.19                              | 4.2                  | 11.7   | 35.5  | 4.15  |
| 0.50                              | 7.0                 | 1.65                 | 0.197                             | 4.3                  | 27.0   | 40.0  | 10.8  |
| 0.60                              | 6.6                 | 2.05                 | 0.200                             | 4.3                  | 55.4   | 42.1  | 23.3  |
| 0.80                              | 6.0                 | 2.95                 | 0.203                             | 4.1                  | 180  | 44.4  | 80.0  |
| 1.00                              | 5.3                 | 3.60                 | 0.204                             | 3.6                  | 424  | 45.0  | 191   |
| 1.20                              | 4.7                 | 3.75                 | 0.206                             | 3.2                  | 742  | 46.8  | 347   |
| 1.50                              | 3.8                 | 3.85                 | 0.208                             | 3.0                  | 1 445  | 48.5  | 701   |
| 1.70                              | 3.5                 | 3.80                 | 0.209                             | 3.0                  | 2 045  | 49.3  | 1 008   |
| 2.00                              | 3.0                 | 3.75                 | 0.211                             | 3.0                  | 3 200  | 51.0  | 1 630   |
| 2.20                              | 2.8                 | 3.70                 | 0.213                             | 3.0                  | 4 080  | 52.7  | 2 150   |
| 2.50                              | 2.6                 | 3.65                 | 0.215                             | 3.0                  | 5 740  | 54.5  | 3 130   |
| 2.70                              | 2.5                 | 3.60                 | 0.216                             | 3.0                  | 7 030  | 55.2  | 3 880   |



$K \cdot X_{nR}$  to  $[A]_R = 0$  (Table 4) \*. They must, however, be considered rather approximate (especially  $K \cdot \beta_{1R}$ ) as the extrapolations were very difficult. The values obtained may be considered valid at the ionic strength 6 to 8 M, i.e. the ionic strength at low glycolate concentrations.

From the values of  $K \cdot \beta_{3R} = 1 \times 10^6 \text{ M}^{-3}$  and  $\beta_{3L} = 2 \times 10^6 \text{ M}^{-3}$  we can calculate a value of  $l_3$ . Eqn. (3 b) gives us  $l_3 = 0.5 \pm 0.2$ .

The stability constants  $b_n = \beta_n \cdot \beta_{n-1}^{-1}$  ( $b_1 = \beta_1$ ) calculated from the values of  $K \cdot \beta_{nR}$  in Table 4, have the following values

$$b_{2R} \geq 100; \quad b_{3R} \sim 10; \quad b_{4R} \sim 15$$

These stability constants are of the same order of magnitude as those in Table 1, but the increase of  $b_{3R}$  to  $b_{2R}$  seems to be somewhat greater than the increase of  $b_3$  to  $b_2$  shown in the table. Therefore, we may expect that  $b_{1R} = \beta_{1R}$  is somewhat greater than  $b_1 = \beta_1$ . Thus, as we have obtained  $K \cdot \beta_{1R} \leq 1 \times 10^3$ , it seems probable that  $K \approx 1$ . This value of  $K$  should be valid for the ionic strength 6 to 8 M. It is not possible to calculate a value of  $K$  at lower ionic strength, but it seems more probable that  $K$  increases than decreases for

Table 4. Calculation of the values of  $K \cdot \beta_{nR}$  by extrapolations of the  $K \cdot X_{nR}$ -functions to  $[\text{AcOH}^-]_R = 0$ . The  $X([A])$ -function in the last but one column has been obtained potentiometrically at the ionic strength 3 M for the glycolate concentrations given in the first column. The  $X([A])$ -function in the last column has been calculated with the potentiometrically obtained complexity constants under the assumption that only the four first complexes are formed.

The following values of  $K \cdot \beta_{nR}$  were obtained:  $K \cdot \beta_{1R} \leq 1 \times 10^3 \text{ M}^{-1}$ ;  $K \cdot \beta_{2R} \approx 1 \times 10^5 \text{ M}^{-2}$ ;  $K \cdot \beta_{3R} = 1 \times 10^6 \text{ M}^{-3}$ ;  $K \cdot \beta_{4R} \approx 10 \text{ to } 20 \times 10^6 \text{ M}^{-4}$ ;  $K \cdot \beta_{5R} < 10 \times 10^6 \text{ M}^{-5}$ .

| $[\text{AcOH}^-]_R$<br>M | $K \cdot X([A]_R)$<br>$\cdot 10^{-4}$ | $K \cdot X_{1R}$<br>$\times 10^{-4}$<br>M <sup>-1</sup> | $K \cdot X_{2R}$<br>$\times 10^{-5}$<br>M <sup>-2</sup> | $K \cdot X_{3R}$<br>$\times 10^{-6}$<br>M <sup>-3</sup> | $K \cdot X_{4R}$<br>$\times 10^{-6}$<br>M <sup>-4</sup> | $I_R$<br>M | $X([A]) \times 10^{-4}$<br>$I = 3 \text{ M}$ | $X([A]) \times 10^{-4}$<br>$I = 3 \text{ M}$<br>$\beta_1 \cdot \beta_4$ |
|--------------------------|---------------------------------------|---|---|---|---|------------|--|---|
| 0                        |                                       | $\leq 0.1$  | 1   | 1   | 10-20   |            |  |   |
| 0.10                     | (0.3)                                 | 3   | 3   | 2   | 10  | 8.5        | 0.25   | 0.24  |
| 0.20                     | (3.2)                                 | 16  | 8   | 3.5   | 13  | 8.1        | 2.54   |   |
| 0.30                     | 11.9                                  | 40  | 13.5  | 4.2   | 11  | 7.7        | 11.4   | 9.1   |
| 0.40                     | 41.5                                  | 104   | 26  | 6.5   | 14  | 7.3        | 35.0   |   |
| 0.50                     | 108                                   | 216   | 43  | 8.5   | 15  | 7.0        | 87   | 58  |
| 0.60                     | 233                                   | 390   | 65  | 10.5  | 16  | 6.6        | 188  |   |
| 0.80                     | 800                                   | 1 000   | 125   | 15.5  | 18  | 6.0        | 663  |   |
| 1.00                     | 1 910                                 | 1 910   | 190   | 19  | 18  | 5.3        | 1 830  | 780   |
| 1.20                     | 3 470                                 | 2 890   | 240   | 20  | 16  | 4.7        | 4 380  |   |
| 1.50                     | 7 010                                 | 4 670   | 310   | 21  | 13  | 3.8        | 12 900                                       | 3 800   |
| 1.70                     | 10 080                                | 5 930   | 350   | 21  | 12  | 3.5        | 24 200                                       | 6 100   |
| 2.00                     | 16 300                                | 8 150   | 410   | 20  | 10  | 3.0        | 61 700                                       | 11 500  |
| 2.20                     | 21 500                                | 9 760   | 445   | 20  | 8.5   | 2.8        | 92 900                                       | 16 600  |
| 2.50                     | 31 300                                | 12 500  | 500   | 20  | 7.5   | 2.6        | 184 000                                      | 27 500  |
| 2.70                     | 38 800                                | 14 400  | 535   | 19.5  | 7   | 2.5        | 319 000                                      | 37 700  |

\* The values of  $K \cdot \beta_{1R}$  and  $K \cdot \beta_{2R}$  have been obtained by extrapolations of  $\log K \cdot X_{1R}$  and  $\log K \cdot X_{2R}$  to  $[A]_R = 0$ .

decreasing ionic strength (*cf.* the variation of  $\beta_3$  in Table 1;  $l_3$  may be assumed constant).

A comparison of  $K \cdot X_R$  with the potentiometrically obtained values of  $X([A])$  for  $I = 3$  M (Table 4) shows that the two sets of values agree rather well for  $[\text{AcOH}^-]_R < 1000$  mM. However, at higher values of  $[\text{AcOH}^-]_R$ , when the ionic strength of the resin phase probably is rather near 3 M,  $K \cdot X_R$  is lower than  $X([A])$ , and the difference between the two functions increases for increasing values of  $[\text{AcOH}^-]_R$ . At high glycolate concentrations the values of  $K \cdot X_R$  correspond better to an  $X([A])$ -function calculated by means of the potentiometrically obtained complexity constants, if it is assumed that only the first four complexes can be formed in the resin phase (the last column in Table 4). It cannot be decided from the  $K \cdot X_{4R}$ -function in Table 4 if a fifth complex is formed, but if the estimated value of  $K$  is correct, the coincidence at high glycolate concentrations between the  $K \cdot X_R$ -function and the  $X$ -function in the last column of Table 4, must indicate that the complex formation in the resin phase is chiefly completed when the fourth complex has been formed. It is true that for lower glycolate concentrations the  $K \cdot X_R$ -function is considerably higher than the calculated  $X$ -function but this may depend on the fact that in this concentration range the ionic strength of the resin phase is considerably higher than 3 M.

The values of  $\varphi$  shown by curve III in Fig. 2 have been calculated assuming that only four complexes are formed in the resin phase with the values of  $K \cdot \beta_{nR}$  given in Table 4 ( $K \cdot \beta_{4R} = 15 \times 10^6 \text{ M}^{-4}$ ). Thus, curve III should show the function  $\varphi([\text{AcOH}^-]_R)$  if the ionic strength of the resin phase had been constantly 6 to 8 M. Curve IV shows the same function for the case that the ionic strength of the resin phase had been 3 M constantly, assuming that the complexity constants are the same in a resin phase as in a water phase of the same ionic strength, and that the constant  $K$  has a value of about 1. Curve II shows the function obtained experimentally when  $[\text{AcOH}^-]_R$  is given in moles per liter.

At low values of  $[\text{AcOH}^-]_R$  the coincidence between curve III and curve II is rather good. At higher concentrations, when the ionic strength becomes lower than 4 M, curve II approaches towards curve IV. Thus it seems probable that at least at this ionic strength the values of  $K \cdot \beta_{nR}$  are about the same as the  $\beta_n$ -values for a water phase of the ionic strength 3 M.

I wish to express my sincere thanks to Professor Sture Fronæus for the valuable aid he has given me in different respects.

Further I wish to thank Fil. mag. Lennart Månsson for his valuable assistance in the measurements.

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Received September 19, 1960.