

## Multicomponent Polyanions

### V. A Potentiometric and Polarimetric Study of Borate-Mannitol Equilibria in 3.0 M Na(ClO<sub>4</sub>) Medium

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Equilibria between H<sup>+</sup>, B(OH)<sub>3</sub>, and D-mannitol (C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>) have been studied in 3.0 M Na(ClO<sub>4</sub>) medium at 25°C by means of potentiometric (glass electrode) and polarimetric measurements. The pH-range 2–9 has been covered. All data could be explained with the ternary complexes (H)<sub>-1</sub>(B(OH)<sub>3</sub>)(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sup>-</sup>, (H)<sub>-1</sub>(B(OH)<sub>3</sub>)(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sub>2</sub><sup>-</sup>, (H)<sub>-2</sub>(B(OH)<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sup>2-</sup>, and (H)<sub>-2</sub>(B(OH)<sub>3</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sub>2</sub><sup>2-</sup> and a binary uncharged complex (B(OH)<sub>3</sub>)(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>). The existence of the last complex has been established mainly from polarimetric measurements.

Data have been analysed using the least squares computer program LETAGROPVRID. "Best" equilibrium constants obtained from the potentiometric and polarimetric measurements are collected in Tables 2 and 3, respectively. "Best" molar rotations are given in Table 4.

Complex formation between borate ions and mannitol has long been known. Most frequently proposed complexes are (B(OH)<sub>4</sub>)(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sup>-</sup> and (B(OH)<sub>4</sub>)(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sub>2</sub><sup>-</sup>. For the experimental methods used and equilibrium constants obtained in these previous investigations we refer to Stability Constants<sup>1</sup> (covered up to the end of 1968). The investigations can be divided into two groups, one assuming solely (B(OH)<sub>4</sub>)(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sup>-</sup> and another both (B(OH)<sub>4</sub>)(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sup>-</sup> and (B(OH)<sub>4</sub>)(C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>)<sub>2</sub><sup>-</sup>.

In a recent investigation Knoeck and Taylor<sup>2</sup> have shown that both a 1 : 1 and 1 : 2 borate-mannitol complex exist together. They have also discussed and reevaluated data of previous workers and thereby obtained results consistent with their own.

Although the existence of 1 : 1 and 1 : 2 borate-mannitol complexes, both with the charge -1, seems to be well established there are no thorough investigations covering wide concentration ranges and consequently the models proposed are restricted to rather narrow concentration ranges. Furthermore, the existence of possible uncharged and/or polynuclear complexes has not yet been thoroughly tested.

The need for a thorough study of the borate-mannitol equilibria has been expressed (so *e.g.* in a critical review by Magnusson<sup>3</sup>). In order to undertake a complicated equilibrium study such as the borate-mannitol system presents, it is necessary to take the following general points into special consideration:

(i) that the system must be considered as a three component system with equilibria  $pA + qB + rC \rightleftharpoons A_p B_q C_r$ , where A, B, and C stand for  $H^+$ ,  $B(OH)_3$ , and mannitol, respectively;

(ii) that the binary equilibria must be determined in separate experiments before one can obtain the ternary complexes;

(iii) that data must be collected over as wide concentration ranges as possible; and

(iv) that the experimental data can be adequately mathematically analysed. Graphical methods and hand calculations are of little use and it is necessary to use least squares computer methods. It is important that the finally proposed model can be tested directly against the measured quantities to assess how well or how poorly the proposed model fits the data.

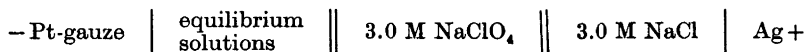
The aim of the present study is to collect suitable data and try to analyse them in order to obtain a more exact equilibrium model of the system. We will thereby use experimental and computational methods especially suited for treating complicated three component equilibria.<sup>15</sup>

## EXPERIMENTAL

The present study has been carried out in close connection with Parts II<sup>4</sup> and III<sup>5</sup> in this series.

*Chemicals and analyses.* Solutions of  $NaClO_4$ ,  $HClO_4$ , and  $NaOH$  were prepared and analysed as described by Sjöberg<sup>6</sup> and D-mannitol as in Part II.<sup>4</sup> Boric acid solutions were prepared by dissolving known amount of recrystallized  $B(OH)_3$  (Merck *p.a.*).

*Coulometric  $OH^-$ -addition.* In titrations with low B concentrations (10 and 20 mM),  $OH^-$  was added by using a coulometer with the following cell-arrangement:

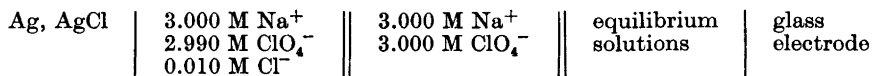


cathode reaction:  $H^+ + e^- \rightleftharpoons 1/2 H_2(g)$

anode reaction:  $Ag(s) + Cl^- \rightleftharpoons AgCl(s) + e^-$

The coulometer used was either a Metrohm type E 211 or a Leeds and Northrup coulometric analyzer (catalogue No. 7960).

*Methods and apparatus in the emf measurements* were essentially the same as described earlier.<sup>6,7</sup> The measurements were carried out as a series of potentiometric titrations in 3.0 M  $Na(ClO_4)$  medium. In every titration the total boron concentration,  $B$ , and the total mannitol concentration,  $C$ , were kept constant. The free hydrogen ion concentration,  $h$ , was varied by addition of  $OH^-$  or  $H^+$ . The equilibrium concentration of  $H^+ = h$  was determined by measuring emf of the cell



Assuming the activity coefficients to be constant the following expression is valid for the measured emf:

$$E = E_0 + 59.157 \log h + E_j \quad (1)$$



where  $E_0$  is a constant and  $E_j$  the liquid junction potential.  $E_0$  was determined in every titration in the acid range where complex formation with  $H^+$  can be neglected.

For the liquid junction potential we have used  $E_j = -16.3 h + 8.0 K_w h^{-1}$  (mV), where  $K_w = 6.17 \times 10^{-16} M^2$  (the ionic product of water in 3.0 M  $NaClO_4$ ).<sup>8</sup> From  $h$ , calculated by using eqn. (1), and from  $H$ , the excess concentration of hydrogen ions over the zero level  $B(OH)_3$ , mannitol and  $H_2O$  one can calculate  $Z$ , the average number of  $H^+$  bound per  $B$ , using the relation:

$$Z = \frac{H - h + K_w h^{-1}}{B} \quad (2)$$

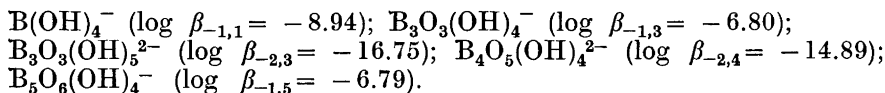
*Methods and apparatus in the polarimetric measurements* were the same as described in Part II in this series.<sup>4</sup> The angle of optical rotation,  $\alpha$ , was measured at points with known  $H$ ,  $B$ , and  $C$ , at the five wavelengths:  $\lambda_1 = Na$  589 nm,  $\lambda_2 = Hg$  578 nm,  $\lambda_3 = Hg$  546 nm,  $\lambda_4 = Hg$  436 nm, and  $\lambda_5 = Hg$  365 nm. We had no difficulties in obtaining stable  $\alpha$ -values at these wavelengths.

*Data treatment.* The mathematical analysis of data was made using the least squares program LETAGROPVRID.<sup>9</sup> For the emf data the version ETITR<sup>10</sup> and for the polarimetric data the version SPEFO<sup>11</sup> have been used. On treating the emf and the polarimetric data the error squares sums  $U = \sum (Z_{calc} - Z)^2$  and  $U = \sum (\alpha_{calc} - \alpha)^2$  have been minimized, respectively. The standard deviations are defined and calculated according to Sillén.<sup>12,13</sup> The computation has been performed both on CD 3600 (Uppsala) and on CD 3200 (Umeå) computers.

## DATA, CALCULATIONS AND RESULTS

*Emf data.* Data  $Z(\log h)_{BC}$  have been collected covering the concentrations  $10 \text{ mM} \leq B \leq 400 \text{ mM}$ ,  $2.5 \text{ mM} \leq C \leq 360 \text{ mM}$ ;  $-\log h$  has been varied from  $\approx 1.5$  to 9.0. All experimental data used in the calculations are collected in Table 1.

Accurate equilibrium data for  $H^+ - B(OH)_3$  (25°C and 3.0 M  $Na(ClO_4)$ ) has already been presented by Ingri.<sup>14</sup> He reports the following species and formation constants:



Note that the values of the constants given by Ingri are calculated with  $OH^-$  as component and they have been recalculated with  $H^+$  as component using the ionic product of water in 3.0 M  $Na(ClO_4)$  medium ( $\log K_w = -14.21$ ).<sup>8</sup>

We have assumed these species and constants to be correct and in the search for complexes no attempts were made to introduce new species or to refine the constants.

The LETAGROP calculations were started with data for low  $B$ -values ( $B = 10$  and  $20 \text{ mM}$ ;  $2.5 \leq C \leq 320 \text{ mM}$ ) and gave clear indications for simultaneous existence of the two complexes  $A_{-1}B C$  and  $A_{-1}B C_2$  (see Table 2). The complex  $A_p B_q C_r$  will often be referred to as the  $(p, q, r)$  species or complex.

We then extended the data range to include higher total concentration of  $B$  and tested this model. However, in this case it was impossible to explain the data solely with the complexes  $(-1, 1, 1)$  and  $(-1, 1, 2)$ . We found deviations which indicated the possibility of complexes, polynuclear in boron. In order to find the composition of these additional complexes we made a  $pqr$ -analysis<sup>16</sup>

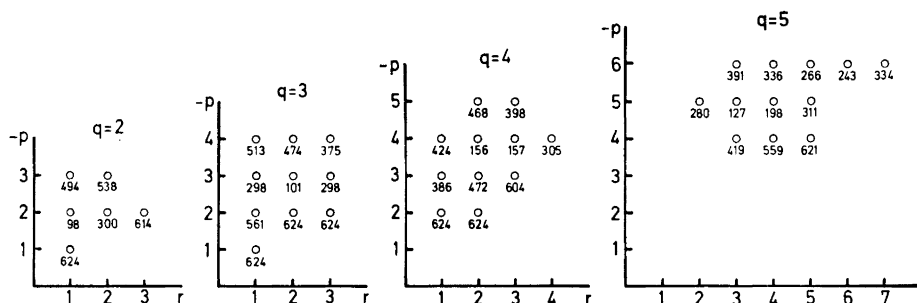


Fig. 1. Results of a  $pqr$ -analysis using data with  $B=200$  and  $400$  mM. Lowest error squares sums are plotted as a function of various  $pr$ -sets for  $q=2, 3, 4$ , and  $5$ .

using data for  $B=200$  and  $400$  mM. The result of the analysis is given in Fig. 1. We see that the lowest error squares sums are obtained for  $(-2,2,1)$ ,  $(-3,3,2)$ ,  $(-4,4,2)$ ,  $(-4,4,3)$ , and  $(-5,5,3)$ . However, the magnitude of the sums are approximately the same and it is impossible to distinguish between them. We may however notice that in all these "possible" complexes  $p/q = -1$  and  $q/r$  always are greater than one.

In the next step in our calculations the data range was extended to include  $B=50, 100, 200$ , and  $400$  mM and the  $pqr$ -search was continued. It was then found that of the possible complexes,  $(-2,2,1)$  gave the lowest error squares sum and the other complexes could be more or less excluded.

However, the residuals obtained in the calculations still showed systematic deviations especially at high total boron-mannitol concentrations. The deviations appeared both in the acidic and the alkaline regions. These observations would indicate the existence of both an uncharged  $B(OH)_3$ -mannitol complex and an additional three component complex polynuclear in boron.

In order to test the possibility of an uncharged complex we made a series of polarimetric measurements in acidic  $B(OH)_3$ -mannitol solutions, with  $Z=0$ . We thereby found an optical activity, much higher than would be expected due to the mannitol alone. An equilibrium analysis of a set of optical data (see below) indicated the existence of an uncharged complex  $(0,1,1)$  with  $\log \beta_{0,1,1} = -0.14$ .

By introducing this  $(0,1,1)$  complex together with the polynuclear  $(-2,2,2)$  complex into a LETAGROP calculation the observed systematic deviations disappeared and we could obtain a good explanation of all data assuming the complexes  $(0,1,1)$ ,  $(-1,1,1)$ ,  $(-1,1,2)$ ,  $(-2,2,1)$ , and  $(-2,2,2)$ . "Best" constants and standard deviations obtained in the calculations are collected in Table 2.

*Polarimetric data.* The only one of the three components possessing optical activity is mannitol. The molar rotation of mannitol at the wavelengths 589, 578, 546, 436, and 365 nm had earlier been determined (see Part II in this series <sup>4</sup>) and the values are given in Table 4.

Table 2. Results from LETAGROP calculations on potentiometric data, minimizing  $U = \sum (Z_{\text{calc}} - Z)^2$ . In all the calculations the binary  $\text{H}^+ - \text{B}(\text{OH})_3$  species were given the values found by Ingri. However, in calculations No. 6  $\log \beta_{-1,1,0}$  was varied. In the calculations 4, 5, and 6 the complex (0,1,1) with  $\log \beta = -0.14$  (found from polarimetric data) was added.

No.	B (mM)	$U \times 10^4$	$\sigma(Z)$	$\log(\beta_{-1,1,0} \pm 3\sigma)$	$\log(\beta_{-1,1,1} \pm 3\sigma)$	$\log(\beta_{-1,1,2} \pm 3\sigma)$	$\log(\beta_{-2,2,1} \pm 3\sigma)$	$\log(\beta_{-2,2,2} \pm 3\sigma)$
1	$10 \leq B \leq 20$ (132 points)	133	0.0101	-8.94	-5.92 ± 0.02	-4.17 ± 0.02	-	-
2	$10 \leq B \leq 400$ (293 points)	961	0.0182	-8.94	-5.84 ± 0.03	-4.21 ± 0.03	-	-
3	»	329	0.0107	-8.94	-5.91 ± 0.02	-4.18 ± 0.02	-13.50 ± 0.07	-
4	»	300	0.0102	-8.94	-5.91 ± 0.02	-4.11 ± 0.02	-13.45 ± 0.07	-
5	»	114	0.0063	-8.94	-6.00 ± 0.02	-4.10 ± 0.01	-13.53 ± 0.05	-10.79 ± 0.08
6	»	102	0.0060	-8.92 ± 0.01	-6.01 ± 0.02	-4.10 ± 0.01	-13.61 ± 0.08	-10.76 ± 0.07

Table 3. Results from LETAGROP calculations on polarimetric data minimizing  $U = \sum(\alpha_{\text{calc}} - \alpha)^2$ . In calculations 2 and 3 the binary species were given the values found by Ingri. When no  $3\sigma$  is given, the formation constant has not been varied.

No.	Z	$U \times 10^2$	$\sigma(\alpha)^\circ$	$\log(\beta_{0,1,1} \pm 3\sigma)$	$\log(\beta_{-1,1,1} \pm 3\sigma)$	$\log(\beta_{-1,1,2})$	$\log(\beta_{-2,2,1} \pm 3\sigma)$	$\log(\beta_{-2,2,2} \pm 3\sigma)$
1	Z=0 (21 solutions)	0.11	0.003	-0.14 ± 0.03	-	-	-	-
2	-1 ≤ Z ≤ 0 (86 solutions)	9.1	0.018	-0.14	-6.00	-4.10	-13.53	-10.79
3	3	6.9	0.013	-0.14	-5.78 ± 0.13	-4.10	-13.09 ± 0.11	-10.78 ± 0.22

Table 4. Molar rotations  $\phi(\lambda) \pm \sigma$  of the optically active species, results from LETAGROP calculations. The molar rotations of mannitol were obtained in a separate determination and (0,1,1) in calculation No. 1. The molar rotations of (-1,1,1), (-1,1,2), (-2,2,1), and (-2,2,2) were obtained in calculation No. 3. The corresponding formation constants are given in Table 3.

$\lambda$ (nm)	$\phi_{0,1,1} \pm \sigma$ (deg dm <sup>-1</sup> M <sup>-1</sup> )	$\phi_{0,1,1} \pm \sigma$ (deg dm <sup>-1</sup> M <sup>-1</sup> )	$\phi_{-1,1,1} \pm \sigma$ (deg dm <sup>-1</sup> M <sup>-1</sup> )	$\phi_{-1,1,2} \pm \sigma$ (deg dm <sup>-1</sup> M <sup>-1</sup> )	$\phi_{-2,2,1} \pm \sigma$ (deg dm <sup>-1</sup> M <sup>-1</sup> )	$\phi_{-2,2,2} \pm \sigma$ (deg dm <sup>-1</sup> M <sup>-1</sup> )
589	-0.109 ± 0.003	6.43 ± 0.02	6.02 ± 0.11	4.71 ± 0.03	5.37 ± 0.08	7.81 ± 0.19
578	-0.119 ± 0.003	6.71 ± 0.02	6.25 ± 0.10	4.90 ± 0.03	5.60 ± 0.07	8.15 ± 0.17
546	-0.142 ± 0.003	7.58 ± 0.02	6.96 ± 0.11	5.50 ± 0.03	6.36 ± 0.08	9.35 ± 0.20
436	-0.329 ± 0.004	12.42 ± 0.04	11.31 ± 0.19	8.54 ± 0.05	10.52 ± 0.13	15.20 ± 0.33
365	-0.750 ± 0.007	18.58 ± 0.05	16.69 ± 0.26	11.71 ± 0.07	16.96 ± 0.19	22.65 ± 0.46

In order to test the possibility of the existence of uncharged complexes ( $p=0$ ) the present optical data collecting was started with a series of measurements on acidic  $B(OH)_3$ -mannitol solutions ( $40 \leq B \leq 400$  and  $40 \leq C \leq 400$  mM) with  $Z=0$ . The data clearly indicated that at least one uncharged complex must be formed and in a LETAGROP calculation we found that the complex (0,1,1) with  $\log \beta = -0.14$  could well explain the data ( $\sigma(\alpha) = 0.003^\circ$ ). Calculations assuming the complex (0,2,2) could not explain data ( $\sigma(\alpha) = 0.015^\circ$ ).

The polarimetric measurements were then extended to the more alkaline region ( $-1 \leq Z \leq 0$ ), and the following  $B(C)$  concentrations (in mM) were studied: 50 (50,100,400); 200 (100,200,400); 400 (100, 200, 400). The B-concentrations were intentionally kept rather high in the hope of obtaining a distinct answer to the question of which was the predominant three component complex polynuclear in boron. The analysis of these data was started by testing the emf models where only one complex polynuclear in boron is present together with (-1,1,1), (-1,1,2), and (0,1,1). We found that none of these emf models could explain the optical data. However, a combination of the two polynuclear complexes (-2,2,1) and (-2,2,2) gave an acceptable explanation of the data (see Table 3).

In a final calculation the formation constants of (-1,1,1), (-2,2,2), and (-2,2,1) were varied together with the molar rotations for the optical active species. The "best" values of equilibrium constants and molar rotations obtained are collected in Table 3 and 4, respectively.

### CONCLUSIONS

The present investigation has strongly established the existence of the complexes (0,1,1), (-1,1,1), and (-1,1,2). The data also clearly indicate that polynuclear (in boron) three component complexes must be formed and that these polynuclear complexes most certainly have the  $p/q$  ratio -1.

Since the mononuclear complexes (-1,1,1) and (-1,1,2) also have this ratio it was found very difficult, especially from emf data, to make a choice between different models containing polynuclear complexes with this ratio. However, in this situation the polarimetric data have been of great value. It was possible to discard a great number of possibilities and it was found that the most probable polynuclear complexes are (-2,2,1) and (-2,2,2). Another great advantage with the polarimetric data was that it became possible to detect the uncharged complex (0,1,1) and to determine its formation constant. From emf data alone, this determination would certainly have been impossible.

Strengths and concentrations of species in the present system in the pH-range 3-9 are well illustrated at some B, C concentrations by the distribution diagrams given in Fig. 2, a-c. When the B to C ratio is 1 and  $B=20$  mM (see Fig. 2a) the main ternary complex is (-1,1,1) but there are also small amounts of the complexes (-2,2,2), (-1,1,2), and (-2,2,1) present. At the same  $B=20$  mM but with great mannitol excess  $C=160$  mM (see Fig. 2b), the (-1,1,2) complex is quite predominating. One may, however, note that about 20 % of B is bound in the complex (0,1,1) in the acid range. For rather high total concentrations of B and C and with a small mannitol excess, as



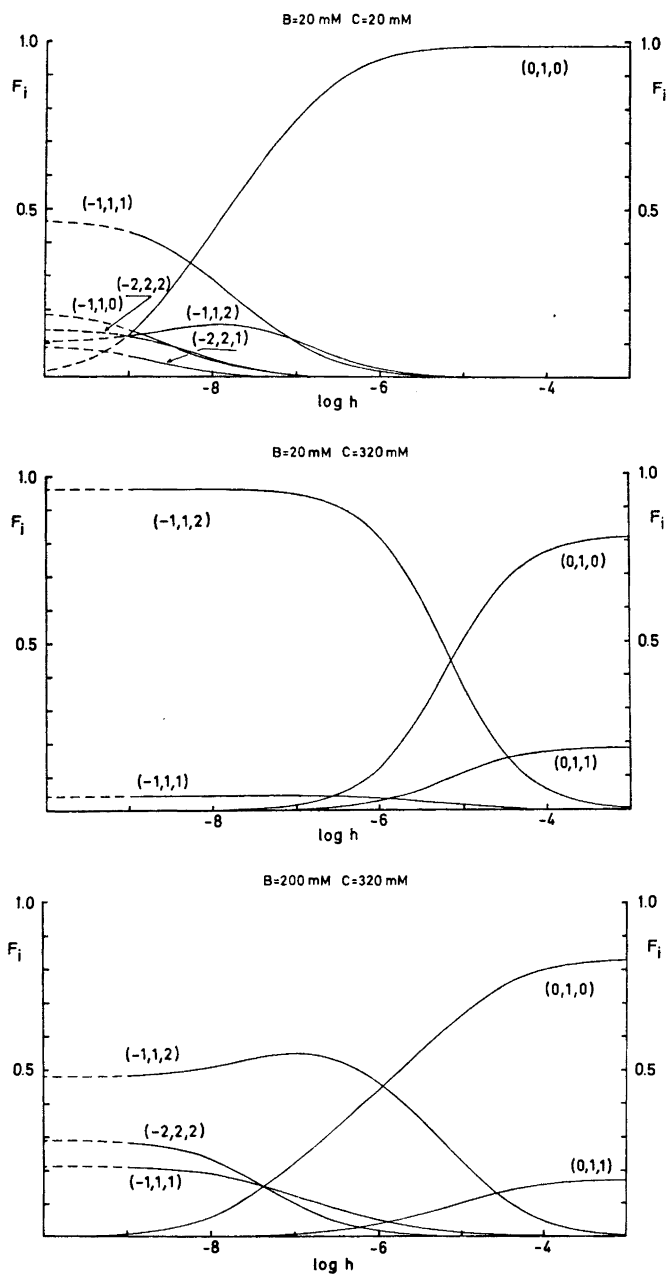


Fig. 2. Distribution diagrams  $F_i(\log h)_{BC}$ . The quantity  $F_i$  is defined as the ratio between boron in a species to total boron. The computer program HALTAFALL<sup>16</sup> was used for the calculation with the constants in Table 2, calculation No. 5.

illustrated in Fig. 2c, the  $(-1,1,2)$ ,  $(-2,2,2)$ , and  $(-1,1,1)$  complexes are all present in considerable amounts.

In Part III of this series<sup>5</sup> we have made a potentiometric study of germanate-mannitol equilibria in 0.5 M Na(Cl) medium. In this system the three ternary complexes  $(-1,1,1)$ ,  $(-1,1,2)$ , and  $(-2,2,2)$  were found with  $\log \beta_{-1,1,1} = -6.46$ ,  $\log \beta_{-1,1,2} = -3.94$ , and  $\log \beta_{-2,2,2} = -10.68$ . Complexes with these compositions have also been found as main species in the present investigation. The equilibria in the two systems thus show many similarities and the reason that the complexes  $(0,1,1)$  and  $(-2,2,1)$  were not found in the germanate-mannitol system may simply be that only low total concentrations of germanium was studied because of the low solubility of  $\text{Ge}(\text{OH})_4$ .

A comparison of the formation constants for species with the same  $pqr$ -values in the two systems shows that they are of the same magnitude. A direct comparison cannot, however, be made since the ionic media were not the same in the two investigations.

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