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Moreover, the  $\tan \alpha - \Delta\nu$  correlation can be used to determine the structure of complexes by comparing the data for a series of complexes with known and unknown structures: a correlation should be observed if the complexes are of the same type.

## SUMMARY

The dissociation constants of *NN*-di-(2-hydroxyethyl)-glycine ( $\text{DG1}^-$ ) and iminodiacetic acid ( $\text{IMDA}^{2-}$ ) and the stability constants of the equimolar complexes formed by neodymium with these ligands in aqueous methanol solutions with different alcohol concentrations have been determined by potentiometric titration. For these complexes, as for the complexes with gluconic acid ( $\text{GH}_4^-$ ), glycine ( $\text{G1}^-$ ), acetylacetone ( $\text{Acac}^-$ ), and phenanthroline ( $\text{Phen}^0$ ), a linear relationship is observed between  $\lg K_1$  and the mole fraction of methanol ( $n_x$ ). The values of  $\tan \alpha$  (the slope of the straight lines) and  $\Delta\nu$  (the long-wave displacement of the bands in the absorption spectra of the complexes relative to the aquo-ion) for all these complexes have been compared. For ligands of the same type ( $\text{GH}_4^-$ ,  $\text{Acac}^-$ ,  $\text{IMDA}^{2-}$ , and  $\text{G1}^-$ ), a correlation is observed between the values of  $\tan \alpha$  and  $\Delta\nu$ . The deviation of  $\text{DG1}$  from the  $\tan \alpha - \Delta\nu$  correlation straight line is attributed to the fact that in the complex of neodymium with this ligand there is an increase in the number of rings as a result of coordination with the oxygen atom of the undissociated alcohol group; the deviation of  $\text{Phen}^0$  is attributed to the decrease in the charge of this ligand.

## REFERENCES

1. H. Irving and H. Rossotti, *Acta Chem. Scand.*, **10**, 72 (1956).
2. E. D. Romanenko and N. A. Kostromina, *Zhur. Neorg. Khim.*, **13**, 1840 (1968) [*Russ. J. Inorg. Chem.*, 958 (1968)].
3. N. A. Kostromina, *Zhur. Neorg. Khim.*, **13**, in the press (1968).
4. V. A. Smirnova and E. D. Romanenko, *Zhur. Neorg. Khim.*, in the press.
5. H. Irving and H. Rossotti, *J. Chem. Soc.*, 2904 (1954).
6. S. Chaberek and A. Martell, *J. Amer. Chem. Soc.*, **74**, 5052 (1952).
7. N. A. Kostromina, T. V. Ternovaya, E. D. Romanenko, and K. B. Yatsimirskii, *Zhur. Teor. Eksper. Khim.*, **2**, 673 (1966).
8. A. K. Babko, "Fiziko-khimicheskii Analiz Kompleksnykh Soedinenii v Rastvorakh" (The Physicochemical Analysis of Complex Compounds in Solution), *Izd. Akad. Nauk SSSR*, Kiev, 1955.
9. T. V. Ternovaya, N. A. Kostromina, and E. D. Romanenko, *Ukrain. Khim. Zhur.*, **33**, 651 (1967).
10. L. Van Uitert and W. Fernelius, *J. Amer. Chem. Soc.*, **76**, 375 (1954).
11. F. Basolo and R. Murman, *J. Amer. Chem. Soc.*, **74**, 5243 (1952).
12. N. Li, White and E. Doody, *J. Amer. Chem. Soc.*, **76**, 6219 (1954).
13. R. Přibil, "Kompleksy v Chemické Analýze" (Translated into Russian), *Inostr. Lit.*, Moscow, 1960.
14. N. A. Kostromina, *Ukrain. Khim. Zhur.*, **26**, 3 (1960).
15. A. N. Grigor'ev, N. D. Mitrofanova, and L. I. Martynenko, *Zhur. Neorg. Khim.*, **10**, 1409 (1965); **11**, 213 (1966) [*Russ. J. Inorg. Chem.*, 766 (1965); 116 (1966)].
16. K. B. Yatsimirskii and N. K. Davidenko, *Zhur. Strukt. Khim.*, **7**, 700 (1966).

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## Cationic Hydroxo-complexes of Germanium(IV) in Solutions with Ionic Strength 0-1

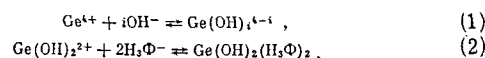
V. A. Nazarenko and G. V. Flyantikova

A review<sup>1</sup> on the state of germanium(IV) in solutions pointed out the contradictory nature of the opinions held regarding the existence of germanium cations in weakly acidic medium. In papers<sup>2,3</sup> published later, this contradiction was not resolved, apparently because of the unreliability of the method used (electrodialysis). The formation constants for hydroxo-complexes of germanium, recently determined<sup>4</sup> by the extraction distribution method, characterize quantitatively the ranges of existence of germanium(IV) cations and confirm that these actually exist in weakly acidic media. The constants were calculated for solutions with an ionic strength  $I = 8$  and high chloride concentration, so that they are unsuitable for calculations aimed at establishing the chemistry of the reactions of germanium, which usually take place in solutions with lower ionic strength. We therefore continued our studies in order to establish the ranges of existence of cationic hydroxo-complexes of germanium in solutions with low ionic strength and the simultaneous prevention of the formation of mixed hydroxoacido-complexes.

## PROCEDURE

The formation constants of the hydroxo-complexes of germanium were determined spectrophotometrically with the coloured competing ligand 2,3,7-trihydroxy-9-*o*-hydroxyphenyl-6-fluorone (salicylfluorone), which, like other trihydroxyfluorones, reacts with germanium to form a sparingly soluble complex with composition  $\text{GeL}_2$ ;<sup>5</sup> dilute solutions of this complex, stabilised with gelatin, remain transparent and obey Beer's law over a wide range of concentrations. The chemistry of the reaction of germanium with trihydroxyfluorones was studied<sup>6</sup>, the known hydrolysis constants for germanium cations<sup>4</sup> in solutions with an ionic strength equal to 8 being used. It was established that the complex-forming germanium ion is the  $\text{Ge}(\text{OH})_2^+$  cation, and the coordinating ion the singly-charged trihydroxyfluorone anion. It was also established that the chemistry of the reactions of germanium with trihydroxyfluorones is the same in solutions with ionic strengths in the range 0.1-8.

The reactions of germanium with hydroxide ions and salicylfluorone ( $\text{H}_4\Phi$ ) can be represented



corresponding to the cumulative formation constant for the hydroxo-complexes

$$\beta_i = \frac{[Ge(OH)_i]^{4-i}}{[Ge^{4+}][OH^-]^i} \quad (3)$$

and the solubility product of the salicylfluoronato-com-pound

$$SP = [Ge(OH)_2^{2+}][H_2\Phi^-]^2 \quad (4)$$

The equilibrium concentration of germanium not combined in the salicylfluoronato-complex can be written:

$$c_{Ge} - c_c = [Ge^{4+}](1 + \sum \beta_i [OH^-]^i), \quad (5)$$

from which

$$[Ge^{4+}] = \frac{c_{Ge} - c_c}{1 + \sum \beta_i [OH^-]^i} \quad (6)$$

and

$$\beta_2 = \frac{[Ge(OH)_2^{2+}](1 + \sum \beta_i [OH^-]^i)}{(c_{Ge} - c_c)[OH^-]^2}, \quad (7)$$

where  $c_{Ge}$  and  $c_c$  are the total concentrations of germanium and the salicylfluoronato-complex respectively. The concentration of the complex is found spectrophotometrically from the equation

$$c_c = \frac{D c_{c_0}}{D_M},$$

where  $D$  and  $D_M$  are the optical densities of the solution at the given pH and when the germanium is completely bound in the complex<sup>7</sup>.

In acidic and weakly acidic solutions, trihydroxyfluorones are present as onium cations, un-ionised molecules, and singly-charged anions. The quantity of more extensively ionised species can be neglected because of the low values of the ionisation constants of the trihydroxyfluorones. Thus the equilibrium concentration of salicylfluorone not combined in the complex can be represented

$$c_L - 2c_c = [H_2\Phi^-] + [H_2\Phi] + [H_2\Phi^-], \quad (8)$$

or

$$c_L - 2c_c = [H_2\Phi^-] \left( 1 + \frac{[H^+]^2}{K_0 K_1} + \frac{[H^+]}{K_1} \right), \quad (9)$$

where  $c_L$  is the total concentration of salicylfluorone, from which we have

$$[H_2\Phi^-] = \frac{(c_L - 2c_c) K_0 K_1}{[H^+]^2 + K_0 [H^+] + K_0 K_1} \quad (10)$$

and

$$SP = \frac{[Ge(OH)_2^{2+}](c_L - 2c_c)^2 (K_0 K_1)^2}{([H^+]^2 + K_0 [H^+] + K_0 K_1)^2} \quad (11)$$

Dividing Eqn. (7) by Eqn. (11) and transforming, we obtain

$$\frac{\beta_2}{SP} \frac{[OH^-]^2 (c_{Ge} - c_c) (c_L - 2c_c)^2 (K_0 K_1)^2}{([H^+]^2 + K_0 [H^+] + K_0 K_1)^2} = 1 + \sum \beta_i [OH^-]^i. \quad (12)$$

If we denote the second term in the left-hand side of this equation by the symbol  $S$ , we have

$$\frac{\beta_2}{SP} S = 1 + \sum \beta_i [OH^-]^i. \quad (13)$$

The subsequent transformations are carried out by the method of Fomin and Maiorova<sup>8</sup>. Differentiation of Eqn. (13) with respect to  $[OH^-]$  gives

$$\frac{\beta_2}{SP} \frac{dS}{d[OH^-]} = \sum i \beta_i [OH^-]^{i-1}. \quad (14)$$

Dividing (14) by (13), with allowance for the fact that

$$\frac{\sum i \beta_i [OH^-]^i}{1 + \sum \beta_i [OH^-]^i} = \bar{n},$$

where  $\bar{n}$  is Bjerrum's formation function<sup>9</sup>, we obtain

$$\frac{d \ln S}{d[OH^-]} = \frac{\bar{n}}{[OH^-]}. \quad (15)$$

The quantity  $\bar{n}/[OH^-]$  is determined as the slope of the tangent at a given point on the curve which gives the dependence of  $\ln S$  on  $[OH^-]$ . The values of the constants  $\beta_i$  are found graphically from the familiar equations<sup>8</sup>

$$\begin{aligned} \lim_{[OH^-] \rightarrow 0} G_1 &= \lim_{[OH^-] \rightarrow 0} \frac{\bar{n}}{[OH^-]} = \beta_1, \\ \lim_{[OH^-] \rightarrow 0} G_2 &= \lim_{[OH^-] \rightarrow 0} \frac{G_1 - \beta_1}{[OH^-]} = 2\beta_2 - \beta_1^2, \\ \lim_{[OH^-] \rightarrow 0} G_3 &= \lim_{[OH^-] \rightarrow 0} \frac{G_2 - (2\beta_2 - \beta_1^2)}{[OH^-]} = 3\beta_3 - 3\beta_1\beta_2 + \beta_1^3, \\ \lim_{[OH^-] \rightarrow 0} G_4 &= \lim_{[OH^-] \rightarrow 0} \frac{G_3 - (3\beta_3 - 3\beta_1\beta_2 + \beta_1^3)}{[OH^-]} = 4\beta_4 - 4\beta_1\beta_2 + 4\beta_1^2\beta_2 - 2\beta_2^2 - \beta_1^4. \end{aligned}$$

## EXPERIMENTAL

The starting materials used were: a 0.01 M aqueous solution of highly pure germanium dioxide containing not more than  $1 \times 10^{-5}\%$  individual impurities; a  $5 \times 10^{-4}$  M ethanol solution, 0.0025 M with respect to HCl, of salicylfluorone prepared by the published method<sup>10</sup> and purified as the sulphate by precipitation from a mixture of ethanol and sulphuric acid; 2.5 M solutions of "chemically pure" grades nitric acid and potassium nitrate; 2% urea solution; and 1% gelatin solution.

The experiments were made in nitric acid, since it does not form complexes with germanium<sup>11-13</sup>. The ionic strength in each series of experiments was kept constant using potassium nitrate. The pH of the solution was varied by means of nitric acid. Urea was used to remove traces of nitrous acid which is formed in solution and which decomposes the salicylfluorone. Perchloric acid and perchlorates were found to be unsuitable for producing the required medium, since perchlorate solutions of the trihydroxyfluoronato-complexes of germanium rapidly become turbid, making the spectrophotometric measurements impossible.

**Procedure.** A series of solutions of germanium dioxide in 25 ml graduated flasks was treated with the required quantity of potassium nitrate and nitric acid solutions, the mixtures were diluted with water to about 18 ml, 1 ml urea solution and 1 ml gelatin solution were added, the solutions were mixed, 1 ml salicylfluorone solution was added, the mixtures were diluted with water to the mark, and left until equilibrium had been established (18 h).

The optical density was measured on an SF-4A spectrophotometer in a 10 mm cell at 515 nm relative to solutions with the same composition but containing no germanium. The pH of the solutions was then measured on an LPU-01 potentiometer with glass electrode. The temperature was kept at  $25^\circ \pm 0.5^\circ C$ . The value of  $D_M$  for each series was obtained by measuring the optical density of solutions with the same germanium concentration but with a tenfold excess of salicylfluorone and pH 1.8-2.1.

## RESULTS AND DISCUSSION

The values of the optical density ( $D$ ) of solutions of the salicylfluoronato-complex of germanium at various pH and ionic strengths of 0.1, 0.3, 0.5, and 1.0 are given in Table 1, together with the values of  $c_c$  and  $\ln S$  calculated from these results. The values of the ionisation constants of salicylfluorone for an ionic strength of 0.1 were taken from published data<sup>14</sup> and the values for the other ionic strengths were determined experimentally (Table 2).

Graphical differentiation of the curve giving the dependence of  $\ln S$  on  $[\text{OH}^-]$  gives the function  $G_1 = f([\text{OH}^-])$ , and extrapolation of the latter to  $[\text{OH}^-] \rightarrow 0$  gives the first formation constant  $\beta_1$  (Fig. 1). Graphical extrapolation gives

Table 1. Data used to calculate the formation constants of hydroxo-complexes of germanium.  $c_{\text{GeO}_2} = 1 \times 10^{-5}$  M,  $c_L = 2 \times 10^{-5}$  M, ethanol 4%, gelatin 0.04%,  $t = 25^\circ \pm 0.5^\circ \text{C}$ .

pH	$I=0.1; D_{\text{max}}=0.740$			$I=0.3; D_{\text{max}}=0.690$			$I=0.5; D_{\text{max}}=0.700$			$I=1.0; D_{\text{max}}=0.720$		
	$D$	$10^6 c_c$	$\ln S$	$D$	$10^6 c_c$	$\ln S$	$D$	$10^6 c_c$	$\ln S$	$D$	$10^6 c_c$	$\ln S$
1.05	—	—	—	—	—	—	—	—	—	0.440	6.11	-129.2
1.15	—	—	—	—	—	—	—	—	—	0.456	6.33	-128.0
1.20	0.418	5.65	-128.0	0.420	6.09	-127.8	0.428	6.11	-127.5	—	—	—
1.25	0.435	5.88	-127.3	0.440	6.38	-127.3	0.444	6.34	-127.0	0.472	6.56	-126.8
1.30	0.445	6.02	-126.7	0.457	6.62	-126.8	0.460	6.57	-126.5	—	—	—
1.35	0.455	6.15	-126.1	0.468	6.80	-126.3	0.474	6.77	-126.0	0.490	6.81	-125.6
1.40	0.464	6.27	-125.5	0.479	6.94	-125.8	0.486	6.94	-125.5	—	—	—
1.45	0.472	6.38	-124.9	0.488	7.07	-125.2	0.500	7.14	-125.0	0.512	7.11	-124.5
1.50	—	—	—	0.498	7.22	-124.7	0.510	7.28	-124.4	0.525	7.29	-124.0
1.55	0.487	6.58	-123.7	0.506	7.33	-124.1	—	—	—	—	—	—
1.60	—	—	—	0.514	7.45	-123.5	0.532	7.60	-123.4	0.548	7.61	-123.0
1.70	0.505	6.82	-121.9	—	—	—	—	—	—	—	—	—
1.85	0.520	7.00	-121.0	—	—	—	—	—	—	—	—	—

Table 2.

$I$	$K_0$	$K_1$
0.1	$2.6 \cdot 10^{-4}$	$8.6 \cdot 10^{-7}$
0.3	$2.32 \cdot 10^{-4}$	$1.16 \cdot 10^{-6}$
0.5	$2.19 \cdot 10^{-4}$	$1.43 \cdot 10^{-6}$
1.0	$1.82 \cdot 10^{-4}$	$2.11 \cdot 10^{-6}$

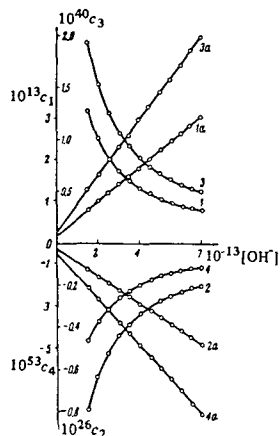


Figure 1. Determination of the formation constants  $\beta_i$  for hydroxo-complexes of germanium at  $I = 0.1$ .

1) and 1a)  $\beta_1$ ; 2) and 2a)  $\beta_2$ ; 3) and 3a)  $\beta_3$ ; 4) and 4a)  $\beta_4$ .

approximate results, however. In our example the  $G_i = f_i([\text{OH}^-])$  curves satisfy formulae of the type

$$G_i([\text{OH}^-]) = \frac{1}{a_i + b_i[\text{OH}^-]}$$

and

$$\frac{1}{G_i([\text{OH}^-])} = a_i + b_i[\text{OH}^-],$$

where  $a_i = 1/\beta_i$ .

For  $I = 0.1$ , extrapolation of these straight lines by the method of least squares gave the expressions:

$$\frac{1}{G_1([\text{OH}^-])} = 0.066 \times 10^{-13} + 0.165[\text{OH}^-],$$

$$\frac{1}{G_2([\text{OH}^-])} = -0.027 \times 10^{-26} - 0.066 \times 10^{-13}[\text{OH}^-],$$

$$\frac{1}{G_3([\text{OH}^-])} = 0.111 \times 10^{-40} + 0.270 \cdot 10^{-27}[\text{OH}^-]$$

$$\frac{1}{G_4([\text{OH}^-])} = -0.046 \times 10^{-53} - 0.111 \times 10^{-40}[\text{OH}^-],$$

Table 3. Cumulative formation constants ( $\beta$ ), hydrolysis constants ( $K_h$ ) and basic dissociation constants  $K_b$  for the complexes  $[\text{Ge}(\text{OH})_i]^{4-i}$ ;  $t = 25^\circ \text{C}$ ,  $K_w = 1 \times 10^{-14}$ .

Constant	Ionic strength of solution			
	0.1	0.3	0.5	1.0
$\beta_1$	$1.52 \cdot 10^{14}$	$2.15 \cdot 10^{14}$	$2.85 \cdot 10^{14}$	$6.54 \cdot 10^{14}$
$\beta_2$	$9.63 \cdot 10^{27}$	$1.85 \cdot 10^{28}$	$3.15 \cdot 10^{28}$	$1.85 \cdot 10^{29}$
$\beta_3$	$3.29 \cdot 10^{41}$	$8.00 \cdot 10^{41}$	$1.70 \cdot 10^{42}$	$2.96 \cdot 10^{43}$
$\beta_4$	$6.41 \cdot 10^{54}$	$1.70 \cdot 10^{55}$	$0.43 \cdot 10^{56}$	$2.95 \cdot 10^{57}$
$K_{h1}$	1.52	2.15	2.85	6.54
$K_{h2}$	0.64	0.86	1.11	2.83
$K_{h3}$	0.34	0.43	0.54	1.60
$K_{h4}$	0.20	0.21	0.25	0.99
$K_{b1}$	$5.0 \cdot 10^{-14}$	$4.7 \cdot 10^{-14}$	$4.0 \cdot 10^{-14}$	$1.0 \cdot 10^{-14}$
$K_{b2}$	$3.0 \cdot 10^{-14}$	$2.3 \cdot 10^{-14}$	$1.8 \cdot 10^{-14}$	$6.2 \cdot 10^{-15}$
$K_{b3}$	$1.5 \cdot 10^{-14}$	$1.1 \cdot 10^{-14}$	$9.0 \cdot 10^{-15}$	$3.5 \cdot 10^{-15}$
$K_{b4}$	$6.0 \cdot 10^{-15}$	$4.6 \cdot 10^{-15}$	$3.5 \cdot 10^{-15}$	$1.5 \cdot 10^{-15}$

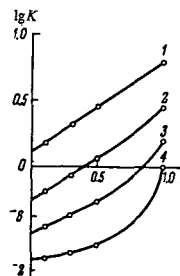


Figure 2. Dependence of the hydrolysis constants of germanium cations on  $I$ .

1)  $K_{h1}$ ; 2)  $K_{h2}$ ; 3)  $K_{h3}$ ; 4)  $K_{h4}$ .

from which the values of  $\beta_i$  were obtained. The values of  $\beta_i$  for solutions with other ionic strengths were calculated analogously. All these results are given in Table 3, which also gives the consecutive hydrolysis constants of the germanium cations and the basic dissociation constant of its

hydroxide, calculated from the values obtained for  $\beta_i$ . In the calculations we used the value  $K_w = 1 \times 10^{-14}$  at  $25^\circ\text{C}$ .<sup>15</sup>

The dependence of the logarithms of the hydrolysis constants on the ionic strength (Fig. 2) shows that for the first constant the dependence is linear as far as  $I = 1$  and is given by the straight-line equation

$$\lg K' = 0.113 + 0.694 I.$$

For the second, third, and fourth hydrolysis constants, the linear dependence is observed only as far as  $I = 0.5$ . The hydrolysis constants extrapolated to  $I = 0$  have the following values:

$$K_{1h}^0 = 1.30; K_{2h}^0 = 0.55; K_{3h}^0 = 0.30; \text{ and } K_{4h}^0 = 0.19.$$

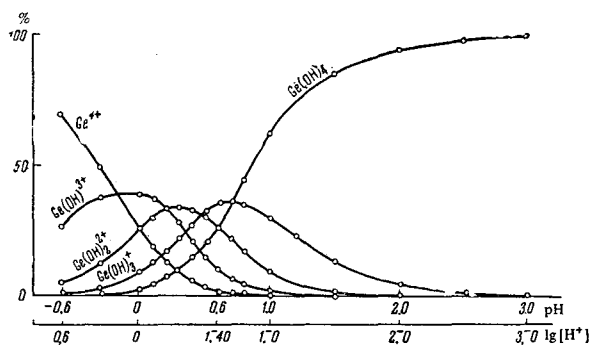


Figure 3. pH dependence of the distribution of hydroxo-complexes of germanium.

The values of the hydrolysis constants for  $I = 0.1$  were used to calculate the dependence of the distribution of the various forms of germanium cations on the hydrogen ion concentration (Fig. 3). The calculation shows that in solutions with  $I = 0.1$  and a concentration of  $1 \times 10^{-5}$  M  $\text{GeO}_2$ , at which polymerisation does not take place<sup>16,17</sup>, a decrease in pH from 3 to 1 leads to an increase in the quantity of cationic forms from 0.5% to 40% of the total germanium content. If we also make allowance for the low value of the acidic dissociation constants of metagermanic acid  $K_1 = 1.86 \times 10^{-9}$  at  $25^\circ\text{C}$  and  $I = 0$ ,<sup>18</sup> it becomes evident that in the range  $2 < \text{pH} < 7$ , molecular forms of  $\text{GeO}_2$  predominate in the solution, as stated by Babko and Gridchina<sup>3</sup>. On the other hand, calculation shows that in the pH range 1–3 the quantity of cationic forms is greater than the quantity of anionic forms, as we previously found<sup>19</sup>, if simultaneous processes leading to the formation of acido-complexes of germanium do not take place in the solution.

## SUMMARY

Complex formation by germanium with hydroxide ions in solutions with ionic strengths in the range  $0.1-1.0$  at  $25^\circ \pm 0.5^\circ$  has been studied by a spectrophotometric method; a coloured competing ligand in nitrate medium was used, which prevents the formation of acido-complexes. The cumulative formation constants for the complexes  $\text{Ge}(\text{OH})_i^{4-i}$  have been calculated and used to calculate the hydrolysis constants of  $\text{Ge}^{4+}$  and the basic dissociation constants of

$\text{Ge}(\text{OH})_4$ . The thermodynamic hydrolysis constants of the germanium cations have been determined by extrapolation of the hydrolysis constants to  $I = 0$ :

$$K_{1h}^0 = 1.30, K_{2h}^0 = 0.55, K_{3h}^0 = 0.30, \text{ and } K_{4h}^0 = 0.19.$$

## REFERENCES

1. V.A. Nazarenko and A.M. Andrianov, Uspekhi Khim., 34, 1313 (1965) [Russ. Chem. Rev., 547 (1965)].
2. N.S. Fortunatov and L.E. Slobtsov, Ukrain. Khim. Zhur., 30, 1279 (1964).
3. A.K. Babko and G.I. Gridchina, Zhur. Neorg. Khim., 11, 1973 (1966) [Russ. J. Inorg. Chem., 1053 (1966)].
4. A.M. Andrianov and V.A. Nazarenko, Zhur. Neorg. Khim., 11, 1527 (1966) [Russ. J. Inorg. Chem., 816 (1966)].
5. V.A. Nazarenko and N.V. Lebedeva, Zavod. Lab., 25, 899 (1959).
6. V.A. Nazarenko, G.V. Flyantikova, and A.M. Andrianov, Zhur. Neorg. Khim., 12, 3072 (1967) [Russ. J. Inorg. Chem., 1625 (1967)].
7. V.A. Nazarenko, N.V. Lebedeva, E.A. Biryuk, and M.B. Shustova, Zhur. Neorg. Khim., 7, 2731 (1962) [Russ. J. Inorg. Chem., 1423 (1967)].
8. V.V. Pomin and E.P. Maiorova, Zhur. Neorg. Khim., 1, 1703 (1956).
9. J. Bjerrum, "Metal Ammine Formation in Aqueous Solution" (Translated into Russian), Moscow, 1961, p. 29.
10. V.A. Nazarenko, N.V. Lebedeva, M.B. Shustova, and E.A. Biryuk, in Collected Papers, "Metody Polucheniya Reaktivov i Preparatov" (Methods of Preparing Reagents and Materials), Izd. IREA, Moscow, 1963, p. 21.
11. G. Brauer and H. Müller, Z. anorg. Chem., 287, 71 (1956).
12. R.L. Myuller, T.P. Markova, and S.M. Repinskii, Vestnik Leningrad. Univ., Ser. Fiz. Khim., No. 16, 106 (1959).
13. M.C. Cretella and H.C. Gatos, J. Electrochem. Soc., 105, 487 (1958).
14. V.A. Nazarenko and E.A. Biryuk, in Collected Papers, "Sovremennye Metody Analiza" (Modern Methods of Analysis), Izd. Nauka, Moscow, 1965, p. 157.
15. "Spravochnik Khimika" (Chemist's Handbook), Izd. Khimiya, Moscow-Leningrad, 1964, p. 109.
16. Lourijsen-Teyssedre, Bull. Soc. chim. France, 1118 (1955).
17. N. Ingri and G. Schorsch, Acta Chem. Scand., 17, 580 (1963).
18. P.J. Antikainen, Suomen Kem., 30, B123 (1957).
19. V.A. Nazarenko, G.V. Flyantikova, and N.V. Lebedeva, Ukrain. Khim. Zhur., 28, 266 (1962).

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## The Dehydration of Sulphatoquo-complexes of Cerium(IV)

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Infrared spectroscopic study of the genetic series of  $\text{Ce}^{\text{IV}}$  sulphatoquo-complexes from the bis(sulphato)- to the hexakis(sulphato)-compounds indicates that they have a bridged structure and that they contain extensively deformed water molecules in the inner sphere<sup>1</sup>. The  $\nu_{\text{OH}}$  absorption band of the stretching vibrations of the water molecules in these compounds lies at about  $3200 \text{ cm}^{-1}$ , indicating a considerable decrease in the strength of their O-H