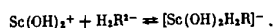


was found that in the range pH 4.9–5.6 the complex-forming ion is $\text{Sc}(\text{OH})_2^+$, this replacing one hydrogen atom in the Pyrocatechol Violet molecule (Fig. 1).

The complex formation equation can be written:



Experimental results on the mechanism of complex formation allow S to be expressed in the fundamental equation of the method²:

$$S = \frac{(c_0 - c_c)(c_L - c_c)[\text{OH}^-]^2}{\left[1 + \frac{[\text{H}^+]}{K_1 L}\right] c_c}$$

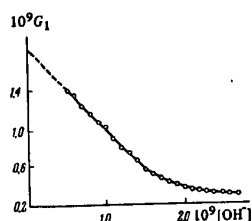


Figure 3. Determination of β_1 .

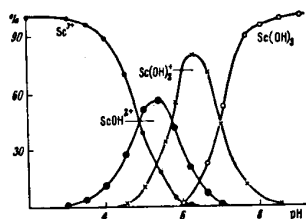


Figure 4. Distribution of the hydroxo-complexes of scandium with pH.

Table 2. Hydrolysis constants of scandium ions.

K_1	K_2	K_3	pK_1	pK_2	pK_3	t	References
$1.81 \cdot 10^{-5}$	—	—	4.74	—	—	0.1	1, 2
$1.17 \cdot 10^{-5}$	—	—	4.93	—	—	1.0	1, 2
$8 \cdot 10^{-6}$	$8 \cdot 10^{-7}$	—	5.10	6.10	—	0.1	3
$8 \cdot 10^{-6}$	$8 \cdot 10^{-6}$	—	5.10	5.10	—	1.0	3
$1.82 \cdot 10^{-5}$	—	—	4.74	—	—	0.1	4
$7.76 \cdot 10^{-6}$	—	—	5.11	—	—	1.0	5
—	—	$1.26 \cdot 10^{-9}$	—	—	9.90	0.1	6
$1.26 \cdot 10^{-3}$	$1.65 \cdot 10^{-6}$	$2.6 \cdot 10^{-7}$	4.90	5.78	6.58	0.1	our work

and $\ln S$ to be calculated as a function of pH (Table 1). Graphical differentiation of the curve of the variation of $\ln S$ with $[\text{OH}^-]$ (Fig. 2) gives the function $G_1 = G_1([\text{OH}^-])$, which was extrapolated in the range $[\text{OH}^-] = 0.6 \times 10^{-9} - 1.5 \times 10^{-9}$ (Fig. 3) by the method of least squares. The values thus obtained were $\beta_1 = 1.843 \times 10^9$ and $K_1 = 1.256 \times 10^{-5}$. Values of β_2 and β_3 were obtained by extrapolating the functions $G_2 = G_2([\text{OH}^-])$ and $G_3 = G_3([\text{OH}^-])$, which were treated similarly².

The values of the constants which were obtained are:

$$\beta_2 = 4.485 \times 10^{17}, K_2 = 1.65 \times 10^{-6}$$

$$\beta_3 = 1.7 \times 10^{25}, K_3 = 2.6 \times 10^{-7}$$

By using these values we calculated the distribution of different hydroxo-complexes of scandium according to pH (Fig. 4).

Table 2 gives the hydrolysis constants of scandium ions published in the literature and determined by us.

SUMMARY

The cumulative stability constants of the hydroxo-complexes of scandium $\beta_1 = 1.84 \times 10^9$; $\beta_2 = 4.49 \times 10^{17}$; $\beta_3 = 1.7 \times 10^{25}$, and the consecutive constants of the mononuclear hydrolysis of its ions: $K_1 = 1.26 \times 10^{-5}$, $K_2 = 1.65 \times 10^{-6}$, and $K_3 = 2.6 \times 10^{-7}$ have been determined spectrophotometrically by the competing-ligand method, using Pyrocatechol Violet.

REFERENCES

- M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, 100, 85 (1953).
- M. Kilpatrick and L. Pokras, *J. Electrochem. Soc.*, 101, 39 (1954).
- G. Biedermann, M. Kilpatrick, L. Pokras, and L.G. Sillén, *Acta. Chem. Scand.*, 10, 1327 (1956).
- V.N. Kumok and V.V. Serebrennikov, *Zhur. Neorg. Khim.*, 10, 2019 (1965) [*Russ. J. Inorg. Chem.*, 1099 (1965)].
- B.J. Aveston, *J. Chem. Soc.*, 1599 (1966).
- I.V. Zaglyadimova, Thesis, Gor'kii, 1966.
- V.A. Nazarenko and E.A. Biryuk, in *Collected Papers "Sovremennye Metody Analiza" (Contemporary Methods of Analysis)*, Izd. Nauka, Moscow, 1965, p. 157.
- V.A. Nazarenko, V.P. Antonovich, and E.M. Nevskaya, *Zhur. Neorg. Khim.*, 13, 854 (1968) [*Russ. J. Inorg. Chem.*, 450 (1968)].
- S.P. Onosova and G.K. Kuntsevich, *Zhur. Anal. Khim.*, 20, 802 (1965).
- D.I. Ryabchikov, S.B. Savvin, and Yu.M. Dedkov, *Zhur. Anal. Khim.*, 19, 1210 (1964).
- O. Ryba, J. Cifka, M. Malat, and V. Suk, *Coll. Czech. Chem. Comm.*, 21, 349 (1956).

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Stability Constants of the Chloro-complexes of Tellurium

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Complex formation by tellurium(IV) with chloride ions has been insufficiently studied. Ion exchange studies¹ have disclosed three complexes in hydrochloric acid solutions: TeCl_3^+ up to an HCl concentration of 0.8 M, TeCl_4 in ~ 1 M HCl, and TeCl_5^+ at HCl concentrations greater than 0.8 M. The authors found that hydrolysis products occur

only at HCl concentrations less than 0.007 M. Investigation of the tellurium electrode in hydrochloric acid solutions² indicated that an ionic chloro-complex of tellurium with formula TeCl_5^{2-} is stable in 2.5 M and more concentrated HCl, and it was suggested that hydrolysis does not take place at this acidity. The composition of the tellurium(IV) complex extracted from 3 M HCl by a solution of tributyl phosphate in n-hexane³ corresponds to the formula $\text{TeCl}_4 \cdot 3\text{TBP}$. The constants for the extraction of the complex were calculated on the assumption that 3 M HCl contains the singly-charged cation TeO_2H^+ , but this does not agree with the other data cited^{1,2}. It has also been established⁴ that the Te:Cl ratio in the chloro-complexes extracted depends on the concentration of hydrochloric acid in the aqueous solutions and on the extracting agent. There are no published data on the stability of chloro-complexes of tellurium.

We studied complex formation by tellurium(IV) with chloride ions using an extraction distribution method. To cover the extraction of tellurium over as wide a chloride ion concentration range as possible, the ionic strength in the aqueous phase was kept equal to 7 (HCl + LiCl, HCl + HClO_4). A 3:7 mixture of n-hexanol and benzene was used as extracting agent.

A hydrochloric acid solution of the radioactive tellurium isotope ^{127}Te was employed and the experimental procedure was the same as that used in the determination of the stability constants of the bromo-complexes of tellurium⁵. As in that work⁵, the calculation was by the method of Fomin and Maiorova⁶. The $G_i = f([\text{Cl}^-])$ curves were extrapolated by the method of least squares after smoothing by means of the equation

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

Table 1. Dependence of the distribution constant of tellurium on the hydrogen ion concentration. $I = 7$ (HCl + LiCl); $t = 25^\circ\text{C}$; [Hex] = 2.403 M.

$[\text{H}^+]_{\text{equil. M}}$	$K_d \text{ Te}$
6.53	6.30
5.65	5.15
4.70	4.71
3.73	3.66
2.79	2.37

Preliminary recording of the light-absorption curves for the aqueous solutions and the extracts showed that at a constant ionic strength of 7 and constant chloride ion concentration of 7 g-ion litre⁻¹, the position of the absorption maxima remains unchanged with change in the concentration of hydrogen ions both in the aqueous phase and in the extract. This indicates that the composition of the chloro-complex of tellurium extracted remains constant. The composition of this complex was determined graphically from the dependence of the distribution constant K_d of tellurium on the concentration of hydrogen ions and hexanol. It was found that the complex contains one hydrogen ion and one molecule of hexanol, so that the formula of the compound extracted can be written $\text{HTeCl}_4 \cdot \text{Hex}$. The results of the experiments are given in Tables 1 and 2. The fact that the dependence of $\lg K_d$ for tellurium on $\lg [\text{H}^+]$ is linear indicates that hydrolysis does not take place under the conditions of the experiment.

The composition of the hydrochloric and perchloric acid solvates was determined from the dependence of their distribution constants on the concentration of hexanol in its mixtures with benzene. The results (Table 2) show that hydrochloric and perchloric acids are extracted from solutions with an ionic strength of 7 in the form of the compounds $\text{HCl} \cdot \text{Hex}$ and $\text{HClO}_4 \cdot \text{Hex}$.

Table 2. Dependence of the distribution constant of tellurium and the distribution constants of HCl and HClO_4 on the concentration of n-hexanol in its mixtures with benzene. $I = 7$ (HCl + HClO_4); $t = 25^\circ\text{C}$.

Hexanol concn., M	$K_d \text{ Te}$	$K_d \text{ HCl}$	$K_d \text{ HClO}_4$
4.005	10.10	0.173	0.212
3.204	8.52	0.128	0.182
2.403	6.10	0.094	0.123
1.602	3.52	0.060	0.079
0.801	0.97	0.021	0.028

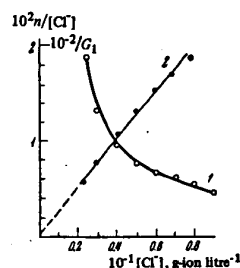
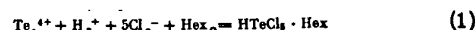


Figure 1. Graph of the function $G_i([\text{Cl}^-])$ before (1) and after (2) smoothing, for the determination of β_1 .

The equation for the formation of the compound extracted can be written



and the equilibrium constant for the formation of the complex is

$$K = \frac{[\text{HTeCl}_4 \cdot \text{Hex}]_o}{[\text{Te}^{4+}]_a [\text{H}^+]_a [\text{Cl}^-]_a^5 [\text{Hex}]_o} \quad (2)$$

The distribution constant for tellurium between the phases is

$$K_d = \frac{[\text{HTeCl}_4 \cdot \text{Hex}]_o}{c_a} \quad (3)$$

where c_a is the concentration of all forms of tellurium in the aqueous phase

$$c_a = [\text{Te}^{4+}] \left(1 + \sum \beta_i [\text{Cl}^-]^i \right) \quad (4)$$

Appropriate substitution and transformation of Eqn. (2) gives the equation

$$\frac{K [\text{H}^+]_a [\text{Cl}^-]_a^5 [\text{Hex}]_o}{K_d} = 1 + \sum \beta_i [\text{Cl}^-]^i \quad (5)$$

If we introduce the symbol

$$\frac{[\text{H}^+]_a [\text{Cl}^-]_a^5 [\text{Hex}]_o}{K_d} = S$$

we can write Eqn. (5) in the form

$$KS = 1 + \sum \beta_i [Cl^-]^i \quad (6)$$

By taking logarithms and transforming in accordance with the published method⁶, we obtain

$$\frac{d \ln S}{d [Cl^-]} = \frac{\bar{n}}{[Cl^-]} \quad (7)$$

This equation forms the basis for the graphical differentiation of the curve $\ln S = f([Cl^-])$.

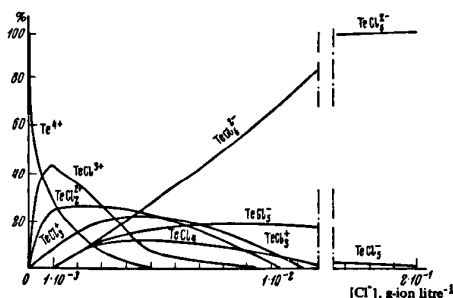


Figure 2. Dependence of the distribution of the complexes $TeCl_4^{2-}$ on $[Cl^-]$.

Table 3. Dependence of the distribution constant of tellurium on the Cl⁻ concentration. $[Hex]_a = 0.05 M$, $[H^+]_a = 6.9 M$, $[Hex]_o = 1.53 M$, $[H^+]_o = 0.7 M$; $I = 7$.

$[Cl^-]$, g-ion litre ⁻¹	$K_d Te$	$-\ln S$	$[Cl^-]$, g-ion litre ⁻¹	$K_d Te$	$-\ln S$
0.025	0.23	14.6020	0.100	0.82	8.9605
0.050	0.47	11.8533	0.150	0.93	7.0506
0.075	0.69	10.2115	0.200	1.00	5.6789

Differentiation of this curve gives the value of the ratio $\bar{n}/[Cl^-]$, and extrapolation of this to zero value of $[Cl^-]$ gives the value of β_1 . Construction of the subsequent auxiliary functions gave the other stability constants of the chloro-complexes.

The dependence of K_d for tellurium on the chloride ion concentration is shown in Table 3. The dependence of $\bar{n}/[Cl^-]$ on $[Cl^-]$ is shown in Fig. 1. Calculation gave the following values for the constants:

$$\begin{aligned} \beta_1 &= 1.75 \times 10^3; & \beta_3 &= 1.02 \times 10^6; \\ \beta_2 &= 2.19 \times 10^2; & \beta_4 &= 1.53 \times 10^{10}; \\ \beta_5 &= 5.75 \times 10^{12}; & \beta_6 &= 1.99 \times 10^{14}. \end{aligned}$$

The probable relative error in the determination of these constants with a reliability $\alpha = 0.95$ is $\pm 12\%$.

The dependence of the distribution of the chloro-complexes of tellurium(IV) on the concentration of chloride ions at a total ionic strength of 7 is shown in Fig. 2.

SUMMARY

The stability constants of chloro-complexes of tellurium(IV) $\beta_1 - \beta_6$ have been determined by the distribution method involving extraction of the complex by a mixture of n-hexanol and benzene from solutions with an ionic strength

of 7. The composition of the tellurium complex extracted is $HTeCl_5 \cdot Hex$, and the composition of the hydrochloric and perchloric acid solvates is $HA \cdot Hex$.

REFERENCES

- R. Ripan and M. Marc, *Studii si Cercetari Chim. (Fil. Cluj)*, **14**, 41 (1963).
- V. S. Yakovleva and E. A. Andreev, *Uch. Zap. Leningrad. Ped. Inst.*, **160**, 181 (1959).
- A. V. Belyaev and B. V. Pitsyn, *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, No. 3, 144 (1965).
- B. Z. Ioffa, Wang Wan-hsing, and I. Ridvan, *Radiokhimiya*, **8**, 14 (1966).
- G. G. Shitareva and V. A. Nazarenko, *Zhur. Neorg. Khim.*, **12**, 999 (1967) [*Russ. J. Inorg. Chem.*, 527 (1967)].
- V. V. Fomin and E. P. Maiorova, *Zhur. Neorg. Khim.*, **1**, 1703 (1956).

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Double Salt of Lithium and Sodium Carbonates Formed in Aqueous Solutions

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The region of crystallisation of pure lithium carbonate from solutions containing lithium and sodium carbonates can be found by polythermal study of the $Li_2CO_3 - Na_2CO_3 - H_2O$ system. We observed the compound $Li_2CO_3 \cdot Na_2CO_3$ in this system at 100°C and identified it by various methods. The present work seeks to find the conditions of formation of this salt at various temperatures.

$Li_2CO_3 \cdot Na_2CO_3$ was first isolated by Eitel and Skaliks in 1929² from a melt. Later the $Li_2CO_3 - Na_2CO_3$ system was studied by several authors³ but continues to attract investigators owing to discrepancies in the published results (see, for example, Refs. 4-8).

In recent years further information has appeared on the properties of molten mixtures of lithium and sodium carbonates: density, electrical conductivity⁹, surface tension¹⁰, and viscosity¹¹ at various temperatures have been measured. The first three properties have also been investigated in the temperature range 500-900°C for the eutectic composition (Li_2CO_3 53.30, Na_2CO_3 46.70 mole %)¹².

We isolated the double salt from aqueous solution at 100°C in the very narrow concentration interval from 26.8 to 31.8% Na_2CO_3 .¹ At 50°C the system is eutonic, but on introducing the salt into the solution it continues to exist in a metastable state at that temperature. Various investigators have been unable to detect the formation of complex phases between lithium and sodium carbonates at 25°C;¹³⁻¹⁵ only Kindyakov and Kurtova¹⁶ reported the formation of solid solutions at 25° and 75°C.

We have studied the $Li_2CO_3 - Na_2CO_3 - H_2O$ system between 25° and 200°C by the method of invariant points, observing microscopically the appearance and disappearance of new phases and then bringing these phases into equilibrium with the solution by the isothermal method.