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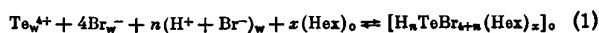
BROMO-COMPLEXES OF TELLURIUM(IV)

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The formation of simple bromo-complexes of tellurium(IV) and of bromotellurates(IV) of inorganic and organic bases is used for the separation and determination of tellurium itself and of other elements^{1,2}. Moreover, published information on the state of tellurium in acid solution³⁻⁶, including that of hydrobromic acid, is very incomplete. Information characterising the formation conditions, region of existence, and stability of the individual bromo-complexes is completely absent, as is the composition of the complexes which are extracted by organic solvents.

We give here our determinations of the formation constants for the bromo-complexes of tellurium(IV). Since one of these complexes is extracted by organic solvents — higher alcohols, ketones, esters — the method of distribution and extraction of the tellurium complex with n-hexanol, which has a very low solubility in water and solutions of acids, was used.

Assuming that during the extraction the complex forms a solvate with the hexanol, the reaction for its formation can be written in the general form:



with the equilibrium constant:

$$K = \frac{[\text{H}_n\text{TeBr}_{4+n}(\text{Hex})_x]_o}{[\text{Te}^{4+}]_w [\text{Br}^-]_w^{4+n} [\text{H}^+]_w^n [\text{Hex}]_o^x} \quad (2)$$

where n can be between 0 and 2.

At constant ionic strength the hydration of the ions is constant and need not be considered.

The partition coefficient for the tellurium complex being extracted is

$$K_p = \frac{[\text{H}_n\text{TeBr}_{4+n}(\text{Hex})_x]_o}{c_w} \quad (3)$$

where c_w is the equilibrium concentration of all the types of tellurium species in the aqueous phase; using the formation constants for the bromo-complexes

$$\beta_i = \frac{[\text{TeBr}_i]^{4-i}}{[\text{Te}^{4+}][\text{Br}^-]^i} \quad (4)$$

it can be expressed by the sum:

$$c_w = [\text{Te}^{4+}](1 + \sum \beta_i [\text{Br}^-]^i) \quad (5)$$

From Eqns. (2), (3), and (5):

$$K_p = \frac{K[\text{Br}^-]_w^{4+n} [\text{H}^+]_w^n [\text{Hex}]_o^x}{1 + \sum \beta_i [\text{Br}^-]^i} \quad (6)$$

Eqn. (6) was used to find the composition of the complex being extracted and the formation constants of all the complexes formed in the $\text{Te}^{4+}-\text{Br}^--\text{H}_2\text{O}$ system.

After taking logarithms of Eqn. (6) and taking $[\text{Hex}]$ or $[\text{H}^+]_w$ as variable, we obtain equations of straight lines:

$$\log K_p = x \log [\text{Hex}]_o + \log a, \quad (7)$$

$$\log K_p = n \log [\text{H}^+]_w + \log a_1, \quad (8)$$

with the aid of which we can find the composition of the complex



The formation constants of the complexes were calculated by the method of Fomin and Malorova⁷ with graphical differentiation after Chmutov and Ermishin⁸ and by the Fronaues method^{9,10}. On transforming the equation⁶ and writing:

$$\frac{[\text{H}^+]_w^n [\text{Br}^-]_w^{4+n} [\text{Hex}]_o^x}{K_p} = S$$

we obtain:

$$1 + \sum \beta_i [\text{Br}^-]^i = K_p S \quad (9)$$

Differentiating this equation w.r.t. $[\text{Br}^-]$ and dividing by the same equation (9) gives:

$$\frac{\sum \beta_i [\text{Br}^-]^{i-1}}{1 + \sum \beta_i [\text{Br}^-]^i} = \frac{d \ln S}{d [\text{Br}^-]} \quad (10)$$

Since:

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

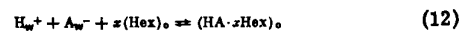
then:

$$\frac{\bar{n}}{[\text{Br}^-]} = \frac{d \ln S}{d [\text{Br}^-]} \quad (11)$$

where $\bar{n}/[\text{Br}^-]$ is the slope of the tangent drawn to any given point of the curve $\ln S = f([\text{Br}^-])$.

All these conclusions are correct and the determination of the constant is possible when hydrolysis, the formation of hydroxo-complexes, and the polymerisation of the simple or complex species of tellurium do not occur in this system and the formation of solvates of the extractant with acids does not lead to a significant change in the equilibrium concentrations of hydrogen ions and bromide ions in the aqueous phase and extractant in the organic phase.

In the extraction of acid by hexanol the equilibrium



is set up. From the equation for the equilibrium constant of this reaction and the expression for the distribution coefficient of the acid HA between the phases, we obtain:

$$K_{p\text{HA}} = \frac{K[\text{H}^+]_w [\text{A}^-]_w [\text{Hex}]_o^x}{[\text{HA}]_w} \quad (13)$$

By taking logarithms of this equation, and $[\text{Hex}]_o$ as variable, we obtain the equation of a straight line:

$$\log K_{p\text{HA}} = x \log [\text{Hex}]_o + \log a_2, \quad (14)$$

similar to Eqn. (7), from which we can find the composition of the solvate extracted and calculate the equilibrium constant of the reaction for the formation of the complex of HBr with hexanol:

$$K = \frac{[\text{HA} \cdot x\text{Hex}]_o}{[\text{H}^+]_w [\text{A}^-]_w [\text{Hex}]_o^x} \quad (15)$$

EXPERIMENTAL

Materials and Methods

n-Hexanol (b.p. 157–157.5°), benzene (80°), and hydrobromic acid were purified by distillation. Sodium bromide

was freed from chlorides after Karyakin¹¹ and then re-crystallised from water. "Chemically pure" grade perchloric acid and "analytical reagent" grade sodium perchlorate were used without additional purification.

The tellurium was used in the form of TeO₂ labelled with the isotope ¹²⁷Te in 3 M HBr. The distribution of tellurium was studied radiometrically and the activity of the phases was measured on a "Floks" PS-10 000 apparatus.

The extraction was by solutions of hexanol in benzene in graduated test-tubes, dia. 12 mm and 35 ml volume with mechanical shaking for 1 h, sufficient to establish equilibrium, this being confirmed by determining the successive partition coefficients of tellurium in extraction and back-extraction. The initial volume of the phases was 10 ml. The acid concentration in the aqueous phase was found by titration with 0.2–0.5 N NaOH and Methyl Orange, the acid in the organic phase by difference, with allowance for the change in the volume of the phases. The titre of the NaOH solution was found with potassium hydrogen tartrate, the titre of the acids with sodium oxalate.

The bromide ion concentration was determined by a Fajans titration with eosin indicator. The hexanol in the aqueous phase was determined photometrically with vanadium oxinate¹².

To find accurately the change in the volume of the phases during extraction, experiments were made with 50:50 ml volumes and the hydrogen ion concentration in the aqueous phase and hexanol concentration in the organic phase were varied. The results were used to compile a graph for subsequent use.

The ionic strength of the solutions was kept constant at 3 with sodium bromide or perchlorate. The temperature was 25° ± 1°. The experimental results given in the tables are the mean of two independent measurements.

RESULTS AND DISCUSSION

The extraction of HBr and HClO₄ were studied with variation of hexanol concentration in the organic phase from 0.801 to 4.006 M. Tables 1 and 2 give the results of the experiments, treatment of which showed that solvates HA.2Hex are formed in the extraction of HBr and HClO₄. The equilibrium constant calculated with allowance for this for the complex formation by HBr is 0.003 for concentrations of hexanol in the organic phase varying from 2.4 to 4.0 M (30–50%).

TABLE 1. Distribution of hydrobromic acid and tellurium between the phases as a function of change in concentration of hexanol in the organic phase.
 $I = 3(\text{HBr} + \text{NaBr})$.

Initial concentration of hexanol in the organic phase, M	Decrease in volume of aqueous phase, ml	Equilibrium concentration of HBr in aqueous phase, M	Equilibrium concentration of HBr in organic phase, M	Concentration of hexanol in aqueous phase, M	Partition coefficient of HBr	Equilibrium concentration of HBr	Partition coefficient of Te
4.006	0.20	2.018	0.218	0.022	0.108	0.0028	6.38
3.204	0.10	2.021	0.157	0.018	0.077	0.0031	3.43
2.403	0.08	2.023	0.092	0.018	0.045	0.0031	1.47
1.602	0.04	2.025	0.065	0.015	0.031	0.0042	0.46
0.801	0.02	2.006	0.037	0.013	0.018	0.0120	0.037

TABLE 2. Dependence of the partition coefficient of perchloric acid on the hexanol concentration in the organic phase.

Equilibrium concentration of HClO ₄ in aqueous phase, M	Equilibrium concentration of HClO ₄ in organic phase, M	Initial concentration of hexanol, M	Partition coefficient of HClO ₄
2.010	0.364	4.005	0.181
2.050	0.262	3.204	0.128
2.040	0.184	2.403	0.090
2.070	0.085	1.602	0.041

Dependence of the partition coefficient of tellurium on its concentration was found by experiments with solutions of tellurium in hydrobromic acid of various concentrations. As Table 3 shows, for each series of experiments at constant HBr concentration and variable tellurium the partition coefficient of the latter remains constant. This shows the absence of polymerisation in the tellurium concentration range studied (2×10^{-5} – 4×10^{-4} M).

The dependence of the partition coefficient of tellurium on the hexanol concentration in the organic phase is also shown in Table 1. Treatment of the experimental results by Eqns. (6) and (7) shows that three hexanol molecules enter into the composition of the bromo-complex of tellurium which is extracted.

Table 4 shows the dependence of the partition coefficient of tellurium on the hydrogen ion concentration. Fig. 1 gives the results of treating the experimental results by Eqns. (6) and (8), and shows that the tellurium complex extracted is a dibasic acid.

Summarising the results obtained, the equation for the formation of the complex extracted, Eqn. (1), can be re-written:



TABLE 3. Dependence of K_p for tellurium on its concentration, $I = 3(\text{HBr} + \text{NaBr})$, 100% hexanol.

[H ⁺], M	10 ⁴ [Te], M		K _p for Te	10 ⁴ [Te], M		K _p for Te	10 ⁴ [Te], M		K _p for Te		
	10 ⁴ [Te], M	K _p for Te		10 ⁴ [Te], M	K _p for Te		10 ⁴ [Te], M	K _p for Te			
0.3	0.017	0.03	1.2	0.5	2.40	0.6	0.5	0.29	2.4	1.0	11.6
	0.035	0.03		2.0	2.40		1.0	0.28		2.0	11.8
	0.10	0.03		3.0	2.30		1.5	0.28		4.0	13.0

TABLE 4. Dependence of K_p for tellurium on [H⁺], $I = 3(\text{HBr} + \text{NaBr})$, [Hex]_{init} = 2.4 M.

Decrease in volume of aqueous phase, ml	[H ⁺] _{equil} in aqueous phase, M	[H ⁺] _{equil} in organic phase, M	[Hex] _{equil} in aqueous phase, M	K _p for Te
0.016	0.380	0.020	0.008	0.021
0.024	0.580	0.021	0.011	0.065
0.032	0.775	0.027	0.012	0.158
0.040	0.970	0.034	0.014	0.290
0.048	1.162	0.043	0.017	0.474
0.056	1.357	0.050	0.017	0.660
0.072	1.740	0.071	0.017	0.960
0.088	2.110	0.108	0.021	1.440
0.104	2.50	0.125	0.026	1.930

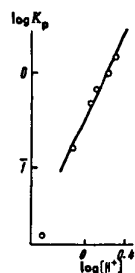


Fig. 1. Variation of the partition coefficient of tellurium with the hydrogen ion concentration.

The graphical dependence of $\log K_p$ on $[H^+]$ at $[H^+] > 1$ is linear, indicating the absence of hydrolysis of the tellurium ions in this region.

The dependence of the partition coefficient of tellurium on the Br^- concentration is shown in Table 5. The dependence of $\ln S$ on $[Br^-]$ — Eqns. (6), (9), (10), and (11) — is given in Fig. 2 and that of $\bar{n}/[Br^-]$ on $[Br^-]$ in Fig. 3.

Extrapolation of the dependence of $\bar{n}/[Br^-] = f([Br^-])$ to zero Br^- concentration allows the first constant β to be found, and construction of the auxiliary functions $G_i = f([Br^-])$, the remaining formation constants.

TABLE 5. Dependence of K_p for tellurium on the Br^- concentration. $[H^+] = 3.0 \pm 0.04$ (HBr + $HClO_4$); $[Hex]_{equil} = 1.9$ M in organic phase, 0.040 M in aqueous; $[H^+]_{equil}$ in organic phase = 0.22 M; decrease in volume of aqueous phase = 0.15 ml.

Test No.	[HBr] in aqueous phase, M	K_p for tellurium	$\ln S$	Test No.	[HBr] in aqueous phase, M	K_p for tellurium	$\ln S$
1	0.196	0.028	3.9236	6	1.183	1.230	4.9190
2	0.393	0.208	0.08947	7	1.381	1.300	5.7912
3	0.591	0.560	1.5456	8	1.781	1.520	7.1585
4	0.790	0.964	2.7418	9	2.171	1.690	8.2407
5	0.985	1.170	3.8704	10	2.560	2.105	9.0056

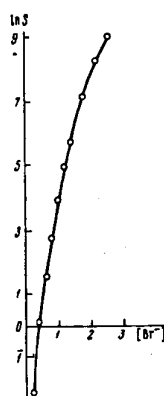


Fig. 2. Dependence of $\ln S$ on $[Br^-]$.

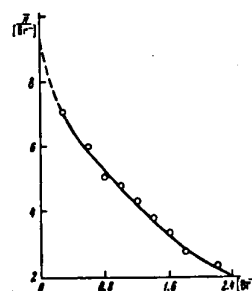


Fig. 3. Graph of the function $G_i = f([Br^-])$; determination of β_i .

The dependence $G = f([Br^-])$ is expressed by the equation $y = 1/(a + bx)$. On putting $Z = 1/y$, the equation is converted into an equation of a straight line:

$$Z = a + bx.$$

By comparing a series of equations with different values of Z and x we can find by the method of least squares a value of a , the intercept on the ordinate cut off by the straight line at $x = 0$; $1/a$ is the value of the function at $[Br^-] = 0$.

In this way we calculated all six formation constants for the bromo-complexes of tellurium:

$$\beta_1 = 9.4; \beta_2 = 38.2; \beta_3 = 90.8, \\ \beta_4 = 141.4; \beta_5 = 160.5; \beta_6 = 134.3.$$

When these values are substituted in Eqn. (11) instead of the β_i , the calculated values of $\bar{n}/[Br^-]$ completely agree with their values on the graph (Table 6).

The formation constants for the bromo-complexes of tellurium which we have calculated by the Fronaesus method from the same experimental results are given in Table 6. Putting

$$1 + \sum \beta_i [Br^-]^i = X([Br^-])$$

we find

$$\int_0^{\bar{n}} \frac{\bar{n}}{[Br^-]} d[Br^-] = \ln X([Br^-]).$$

Table 7 gives the auxiliary functions necessary for calculating the constants by this method and Fig. 4 shows the graphical dependence of the auxiliary functions on $[Br^-]$. By this method we succeeded in determining only the first four formation constants, which agreed satisfactorily with the constants calculated by Fomin and Maiorova's method:

$$\beta_1 = 9.0; \beta_2 = 38.0; \beta_3 = 90.0; \beta_4 = 140.0.$$

TABLE 6. Comparison of the experimental and calculated values of $\bar{n}/[Br^-]$.

[Br ⁻], M	$\frac{\bar{n}}{[Br^-]}$	
	calculated	found graphically
0.2	7.68	7.7
0.4	6.62	6.65
0.5	6.18	6.0
0.7	5.34	5.45
1.0	4.40	4.6

TABLE 7. Calculated auxiliary functions for the determination of the formation constants by the Fronaeus method.

[Br ⁻], M	X(Br ⁻)	Y(Br ⁻)	Z(Br ⁻)	U(Br ⁻)	V(Br ⁻)
0.1	2.42	14.5	47.5	95	100
0.2	5.40	22.	68.0	125	175
0.3	11.32	34.1	83.3	151	200
0.4	21.95	52.0	107.5	161.4	177
0.5	42.55	83.4	147.0	242	304
0.6	81.83	134.4	208.8	284	323
0.7	143.0	203.1	276	340	357
0.8	241.9	301.7	364	407	397

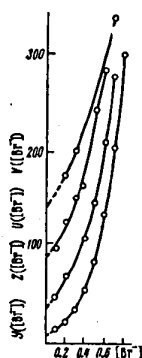


Fig.4. Determination of β_i by the Fronaeus method.

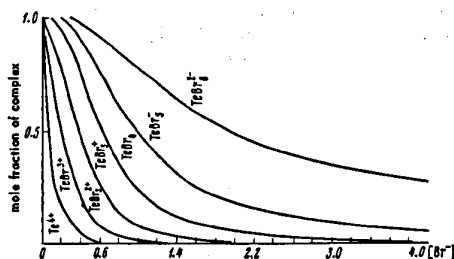


Fig.5. Distribution of the TeBr_i^{4-i} complexes as a function of $[\text{Br}^-]$ in mole fractions.

The consecutive formation constants calculated from the first values of the cumulative constants are:

$$k_1 = 9.40; k_2 = 4.06; k_3 = 2.38; \\ k_4 = 1.56; k_5 = 1.14; k_6 = 0.84.$$

Fig. 5 shows graphically the distribution of the individual bromo-complexes of tellurium in mole fractions as a function of the Br^- concentration in the solution.

SUMMARY

Complex formation in the $\text{Te}^{4+}-\text{Br}^--\text{H}_2\text{O}$ system at high hydrogen ion concentrations has been studied by extraction of the complex with solutions of n-hexanol in benzene.

The distribution of HBr and HClO_4 between water and hexanol at $I = 3$ has been observed and the formation of the solvates $\text{HBr} \cdot 2\text{Hex}$ and $\text{HClO}_4 \cdot 2\text{Hex}$ established. The tellurium complex which is extracted has the composition $\text{H}_2\text{TeBr}_6 \cdot 3\text{Hex}$.

The formation constants for the bromo-complexes of tellurium have been calculated:

$$\beta_1 = 9.4; \beta_2 = 38.2; \beta_3 = 90.8; \\ \beta_4 = 141.4; \beta_5 = 160.5; \beta_6 = 134.3.$$

1. A.I. Busev and N.L. Babenko, *Zhur. Anal. Khim.*, **18**, 972 (1963).
2. D.P. Shcherbov, "Fluorimetriya v Khimicheskoy Analize Mineral'nogo Syr'ya" (Fluorimetry in the Chemical Analysis of Mineral Raw Materials), Nedra, Moscow, 1965, p.180.
3. R. Ripan and M. Marc, *Studii si Cercetari Chim. (Fil. Cluj)*, **14**, 41 (1963).
4. V.M. Tarayan and Zh.M. Arstamyanyan, *Izv. Akad. Nauk Armyan SSR, Khim. Nauki*, **17**, 623 (1964).
5. M.W. Hanson, W.C. Bradburg, and I.K. Carlton, *Analyt. Chem.*, **29**, 490 (1957).
6. B.Z. Iofa, Wang Wan-hsing, and M. Ridvan, *Radiokhimiya*, **8**, 14 (1966).
7. V.V. Fomin and E.P. Maierova, *Zhur. Neorg. Khim.*, **1**, 1703 (1956).
8. K.V. Chmutov and V.E. Ermishin, *Zhur. Fiz. Khim.*, **29**, 930 (1955).
9. S. Fronaeus, *Acta Chem. Scand.*, **4**, 72 (1950).
10. S. Fronaeus, *Acta Chem. Scand.*, **5**, 139 (1951).
11. Yu.V. Karyakin, "Chistye Khimicheskie Reaktivy" (Pure Chemical Reagents), Moscow, 1947, p.358.
12. M. Stiller, *Analyt. Chim. Acta*, **25**, 85 (1961).

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EXTRACTION OF ZIRCONIUM AND HAFNIUM BY TRIBUTYL PHOSPHATE FROM SOLUTIONS OF NITRIC AND PERCHLORIC ACID MIXTURES

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It has previously been established¹⁻³ that in the extraction of zirconium and hafnium by tributyl phosphate (TBP) from nitric acid-hydrochloric acid and nitric acid-perchloric acid mixtures with constant ionic strengths the partition coefficient passes through a maximum. The sharpest maximum is found for extractions from nitric-perchloric acid mixtures. The increase in partition coefficient is due to the formation of mixed chloronitrate- and nitratoperchlorato-complexes. We have also noted that this behaviour may be governed by a number of other factors, such as change in free TBP concentration, change in the activity coefficients of the extractable compounds, and also change