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Nitrato-complexes of Tellurium(IV) in Solution

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The consecutive stability constants of the tellurium nitrato-complexes $Te(NO_3)_n^{4-n}$ have been determined by ion exchange at ionic strength $I \geqslant 3$ and temperature 20 °C: $\beta_1 = 0.52$, $\beta_2 = 0.35$, $\beta_3 = 0.29$, $\beta_4 = 0.27$, $\beta_5 = 0.23$, $\beta_6 = 0.15$.

We found earlier[1] that the non-hydrolysed cations Te^{4+} predominate in 3 *N* $HClO_4$. The present paper describes an ion-exchange study of complex formation by Te^{4+} with nitrate ions in $HClO_4$ + HNO_3 mixtures with a total acid concentration of 3 M (I = 3.0); the ionic strength in solutions with a higher HNO_3 concentration is not constant. The initial solution of tellurous acid was made by dissolving TeO_2 in perchloric acid. The tellurium concentration in the test solutions was 2×10^{-4} g-ion litre^{-1}, which ruled out the formation of polynuclear compounds[1].

The test solutions (20 ml) were added to either cation-exchange resin KU-2† in the H^+ form or anion-exchange resin AV-17# in the NO_3^--form (1.0 g), shaken together until equilibrium was reached and then the tellurium concentration determined photometrically with tin(II) chloride. The results are given in the Table and show that as the NO_3^--concentration is raised absorption of tellurium by the cation-exchange resin falls and that by the anion-exchange resin increases. The variation of $1/K_d$ (where K_d is the distribution coefficient of tellurium on the cation-exchange resin) with the NO_3^- concentration is non-linear, showing the formation of several complexes.

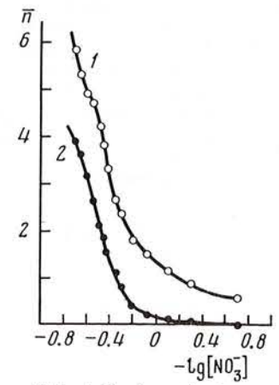
The absorption of tellurium by the anion-exchange resin reaches a maximum at c_{HNO_3} and remains constant, showing the formation of anionic complexes with maximum charges. The charge was found by determining the ion-exchange capacity of the anion-exchange resin for the test ion and a standard ion with a known charge (Cl^-) under dynamic conditions. To do this, 0.1 M HCl was passed through a column containing the anion-exchange resin in the NO_3^- form (3 g) until absorption of the chloride ions stopped; the ion-exchange capacity for Cl^- is 5.5 mg-equiv. litre^{-1}. Then a nitric acid (5 *N* HNO_3) solution of tellurium was passed through the same column until its absorption stopped; the ion-exchange capacity for tellurium is 2.8 mg-atom g^{-1}. The charge was calculated thus:

$$Z = \frac{5.5}{2.8} = 1.96 .$$

†KU-2 is a monofunctional, strongly acid cation-exchange resin with $-SO_3H$ active groups, prepared by treating a swollen styrene–divinylbenzene copolymer with chlorosulphonic acid, then saponifying the sulphonyl chloride (Ed. of Translation).

#AV-17 is a strongly basic anion-exchange resin containing quaternary nitrogen-groups. It is based on styrene and trimethylamine (Ed. of Translation).

The results show that under conditions of maximum absorption by the anion-exchange resin the complex $Te(NO_3)_6^{2-}$ predominates.



Formation curves of the tellurium nitrato-complexes: *1*) from experimental results; *2*) third approximation.

The stability constants of the tellurium nitrato-complexes were determined by a method[2] which allowed the cation- and anion-exchange results to be used to find the variation of the formation function $\bar{n}$ (the mean number of ligands attached to the central ion) with the concentration of the free ions of the ligand under conditions when only the non-complexed cation of the metal is absorbed by the cation-exchange resin and only the anionic complex with the highest charge is absorbed by the anion-exchange resin.

In calculating $\bar{n}$ it is necessary to find the relative fraction of all the cationic (γ_+) and anionic (γ_-) species at various ligand concentrations:

$$\gamma_+ = \frac{(100-[M]_+)\cdot c_0}{(100-c_0)\cdot[M]_+}; \quad \gamma_- = \frac{(100-[M]_-)\cdot c_0}{(100-c_0)\cdot[M]_-},$$

where c_0 is the concentration of the test element in the solutions in equilibrium with the ion-exchange resins in the absence of the ligand (for cationic exchange) or at maximum absorption (for anionic exchange), $[M]_+$ and $[M]_-$ are the total concentrations of the test element in solutions in equilibrium respectively with the cation- and anion-exchange resins in the presence of the ligand.

$\bar{n}$ was calculated by the formula

$$\bar{n} = \frac{q_+(\gamma_+ - 1) + q_-\gamma_-}{Z_A}$$

where q_+ is the charge of the central ion (+4), q_- the charge of the anionic complex under conditions of greatest absorption by the anion-exchange resin (−2), and Z_A the charge of the ligand (−1).

The results of the calculations carried out with the results from the first experiments are given in the Table and Figure (curve *1*). The Table shows that the sum of the fractions of the cationic and anionic species exceeds unity, indicating appreciable absorption by the anion-exchange resin of other tellurium complexes in addition to $Te(NO_3)_6^{2-}$.§ Futhermore, curve *1* in the Figure is not symmetric, which does not

§Absorption of cationic complexes is improbable owing to the high concentration of hydrogen ions.

permit the stability constants of the complexes to be calculated from the experimental results.

We calculated the constants by successive approximations. Initially from curve *1* we found the approximate values of the stability constants, numerically equal to $1/[NO_3^-]$, for which $\bar{n}$ equals 0.5, 1.5, 2.5, 3.5, 4.5, or 5.5. Then the constants obtained were used to calculate the fractions of cationic and anionic species for various values of $c_{NO_3^-}$ and constructed a new relation $\bar{n} = f(c_{NO_3^-})$. The curve obtained was treated by Bjerrum's method[3], new values found for the stability constants, and the calculation of γ_+, γ_-, and $\bar{n}$ repeated for different NO_3^- concentrations. The second and third approximations gave the almost coincident results given in the Table and Figure (curve *2*). Mathematical treatment of curve *2* by Bjerrum's method gave the following results:

$$\left(\frac{1}{[NO_3^-]}\right)_{\bar{n}=\frac{N}{2}=3} = 0.28; \quad \frac{d\bar{n}}{dp\,[NO_3]} = 8.43; \quad \Delta = 3.66; \quad x = 0.79 .$$

The stability constants were calculated by the formula[3]:

$$\beta_n = \frac{N-n+1}{n}\cdot 0.28\cdot x^{N+1-2n} .$$

In the present instance, N = 6. As a result of the calculation we obtained the following consecutive stability constants of the tellurium nitrato-complexes¶: $\beta_1 = 0.52$, $\beta_2 = 0.35$, $\beta_3 = 0.29$, $\beta_4 = 0.27$, $\beta_5 = 0.23$, $\beta_6 = 0.15$.

Calculation of the formation function $\bar{n}$ as a concentration of NO_3^- ions is varied for the Te^{4+}–NO_3^- system: $q_+ = +4$; $q_- = -2$; $c_{Te} = 2 \times 10^{-4}$ g-atom litre^{-1}; $I \geqslant 3$, $[H^+] \geqslant 3$ g-ion litre^{-1}.

c_{HNO_3}, M	lg $[NO_3^-]$	Absorption, %		γ_+	γ_-	$\bar{n}$	First approximation			Third approximation		
		KU-2	AV-17				γ_+	γ_-	$\bar{n}$	γ_+	γ_-	$\bar{n}$
0	–	50.0	1	1.00	0	0	1.00	0	0	1.00	0	0
0.2	0.699	48.0	12.0	0.92	0.12	0.56	1.00	0	0	1.00	0	0
0.5	0.301	47.0	20.0	0.89	0.21	0.86	0.99	0	0.04	0.99	0	0.03
0.8	0.093	46.5	27.0	0.87	0.31	1.14	0.96	0.01	0.18	0.98	0	0.08
1.2	−0.079	45.0	33.0	0.83	0.42	1.52	0.89	0.04	0.52	0.96	0.01	0.18
1.6	−0.204	44.0	36.0	0.79	0.48	1.80	0.78	0.08	1.04	0.91	0.03	0.42
2.0	−0.301	42.0	42.0	0.72	0.62	2.36	0.68	0.15	1.43	0.83	0.07	0.82
2.2	−0.342	40.0	44.0	0.67	0.67	2.66	0.62	0.19	1.90	0.78	0.10	1.08
2.6	−0.415	35.5	47.0	0.55	0.75	3.30	0.52	0.26	2.44	0.69	0.14	1.52
2.8	−0.447	32.0	50.0	0.47	0.85	3.82	0.47	0.30	2.72	0.63	0.18	1.85
3.0	−0.477	29.0	52.0	0.41	0.92	4.20	0.43	0.33	2.94	0.58	0.21	2.10
3.5	−0.544	24.0	53.7	0.32	0.98	4.70	0.33	0.43	3.54	0.50	0.29	2.58
4.0	−0.602	22.0	54.0	0.28	1.00	4.88	0.27	0.51	3.94	0.40	0.37	3.14
4.5	−0.653	15.0	54.0	0.18	1.00	5.28	0.21	0.57	4.30	0.33	0.45	3.58
5.0	−0.699	4.0	54.0	0.04	1.00	5.84	0.17	0.63	4.58	0.28	0.51	3.90

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¶ The constants β_4, β_5, and β_6 are approximate, since they were calculated from experimental results obtained at variable ionic strength.

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Complex Formation by Molybdenum(V) with Diphenylthiophosphinic Acid [Diphenylphosphinothionic and Diphenylphosphinothiolic Acids]

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Features of complex formation by molybdenum(V) with diphenylthiophosphinic acid (DTPH) have been studied by EPR. When DTPH reacts with molybdenum(V) oxide all the theoretically possible complexes of oxomolybdenum(V)† with the composition of the equatorial plane $[S_xO_y]$ ($x + y = 4$; DTPH is unidentate). Use of the oxide, which contains the coordinatively unsaturated centre MoO^{3+}, allows complexes to be obtained, containing, the bidentate DTP-ions, as is shown by the presence in the EPR spectra of an additional hyperfine structure (AHFS) from the ^{31}P phosphorus atoms.

The available published information about complex formation by molybdenum(V) with diphenylphosphinic acid (DTPH) is limited and contradictory. Thus in Yunusov's studies[1,2] of the interaction of $MoOCl_3$ with DTPH oxomolybdenum(V) complexes with the composition of the equatorial plane $[S_xO_y]$ ($x + y = 4$, x, $y \neq 0$) could not be observed. From this it was concluded that sulphur and oxygen atoms are incompatible in the first coordination sphere of oxomolybdenum. However, complexes $[MoOCl_2(DTP).L]$, where DTP is bidentate and L is an out-of-plane ligand, were obtained by the interaction of solutions of $MoCl_5$ and DTPH and identified by EPR.[3]

Parameters of the EPR spectra of oxomolybdenum complexes with DTPH.

Complex No.	g_0	g_0 (расч)	$*a^{Mo}$	$*a^{P}$	$g_{\parallel}$	$g_{\perp}$	Immediate environment
1	1.911	–	5015		1.889	1.992	O_4
2	1.922	1.926	4856		1.906	1.930	SO_3
3	1.937	1.943					*trans*-S_2O_2
4	1.943						*cis*-S_2O_2
5	1.960	1.960					S_3O
6	1.975	–					S_4
7	1.947	1.943	3980	3502			S_2O_2
8	1.963	1.960		3264			S_3O

*The values of the HFS and AHFS constants are given in Å m^{-1}.

The present paper describes an attempt to obtain compounds by the interaction of DTPH with specimens of pure and partly reduced molybdenum(V) oxide (which excludes the presence of foreign ions in the reaction medium) to study complex formation by oxomolybdenum(V) with DTPN.

†Incorrectly termed oxomolybdenum(III) or MoO(III) throughout the Russian paper (Ed.of Translation).