formation of pyrocatecholato-complexes of vanadium takes place with the liberation of two hydrogen ions, that is with the replacement of the protons of both hydroxyl groups in the pyrocatechol molecule.

Thus the ternary antipyrine pyrocatecholato-complexes of vanadium are the products of the attachment of the antipyrinium ion to the binary pyrocatecholato-complexes of vanadium existing in aqueous solutions under the corresponding conditions. The effect of complex-forming ions on the formation of the extractable ternary compounds in this system is similar to their action on the pyrocatecholato-complexes of vanadium. This indicates that the compounds formed are identical, that is they are inner-complex compounds.

REFERENCES

1. V. Patrovsky, Chem. listy, 48, 622 (1953).
2. C. G. Nestler and M. Noble, Z. analyt. Chem., 167, 81 (1959).
3. P. Blanquet, Chim. analyt., 41, 359 (1959).
4. F. Z. Dzhabarov and S. V. Gorbachev, Zhur. Neorg. Khim., 9, 2399 (1964) [Russ. J. Inorg. Chem., No. 10 (1964)].
5. K. Schiller and E. Thilo, Z. anorg. allgem. Chem., 310, 261 (1961).
6. A. K. Babko, "Fiziko-khimicheskii Analiz Kompleksnykh Soedinenii v Rastvorakh" (The Physicochemical Analysis of Complex Compounds in Solution), Kiev, 1955.
7. I. V. Pyatnitskii, Uspekhi Khim., 32, 93 (1963) [Russ. Chem. Rev., No. 1 (1963)].
8. S. Ya. Shnaiderman and G. I. Khrustalev, Zhur. Obshch. Khim., 29, 20 (1959).
9. N. P. Komar', Trudy Nauch.-Issled. Inst. Khim. Khar'kov. Gos. Univ., 12, 61 (1954).
10. H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions" (Translated into Russian), Inostr. Lit., Moscow, 1952.

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Reaction of Tantalum Hydroxide with Ethylenediaminetetra-acetic Acid

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The reaction of tantalum hydroxide with ethylenediaminetetra-acetic acid (EDTA) in aqueous solutions in the pH range 1.0-6.0 has been studied. It has been shown that the reaction of tantalum hydroxide with EDTA takes place according to the equation:

$$Ta(OH)_5 + H_4Y \rightleftharpoons [Ta(OH)_2Y]^- + 3H_2O + H^+.$$

The concentration instability constant of the complexonato-compound of tantalum K_{instab}, characterising this reaction at an ionic strength $I = 1.08$ (K_2SO_4) and 20°C, is $10^{-33.6}$.

The mechanism of the dissolution and establishment of equilibria for sparingly soluble hydroxides, for example those of niobium and tantalum, is complicated by the marked tendency of the ions of these metals to undergo hydrolysis and form hydrolytic polymers. Complex formation generally takes place with displacement of OH^- ions from the coordination sphere of the metal hydroxide by ligand ions, decomposition of the polymeric forms, and the formation of monomeric complexes. Thus the complex compounds of tantalum (or niobium) can be regarded as complex ternary compounds of various types[1].

The state of tantalum (or niobium) in solutions and the processes of complex formation are being intensively studied: quantitative characteristics have been obtained for complex formation by these elements with hydrogen peroxide and sulphuric, oxalic, and tartaric acids[2-5].

The aim of the present work was to study the reaction of tantalum hydroxide with ethylenediaminetetra-acetic acid (EDTA).

There is very little published information on the reaction of tantalum (or niobium) with EDTA. The reaction of niobium hydroxide with EDTA has been studied[6]. The composition and the values of the conditional and concentration instability constants of the complexonato-compound of niobium were given.

It has been shown[7] that the optimal conditions for the formation of the complexonato-compound of tantalum are pH 3.0–3.5 and an excess of EDTA corresponding to a molar ratio of ~ 200.

Since niobium and tantalum react with EDTA to form complexes with M : Y = 1 : 1,[7-9] and since the complexonato-compound of tantalum is polarographically inactive, the composition and stability of the complex were determined by the polarographic displacement method, described in detail earlier[7,10].

The equilibrium for a two-metal system in EDTA solution is determined by the equation[11]:

$$A_1 = B_1 + \frac{c_2/c_1}{\frac{K_2}{K_1}\frac{1-B_1}{B_1}} + \frac{K_1}{c_1}\frac{B_1}{1-B_1} \qquad (1)$$

which gives the dependence of the yield of the complex of one metal ($B_1 = c_{MY}/c_{M_1}$) on the relative concentration of EDTA ($A_1 = c_Y/c_1$) in the presence of the second metal.

In Eqn. (1), c_1 and c_2 are the original concentrations of the first and second metals, and K_1 and K_2 the conditional instability constants of the complexonato-compounds of the first and second metals. It follows from the equation that

$$\frac{K_2}{K_1} = \left[\frac{c_2/c_1}{A_1 - B_1 - \frac{K_1}{c_1}\frac{B_1}{1-B_1}} - 1\right]\frac{B_1}{1-B_1}. \qquad (2)$$

Having determined the yield of the complexonato-compound of the first polarographically active metal (B_1) in the presence of the second metal at different relative concentrations of EDTA (A) or at different acidities of the solution, we can calculate the ratio of the instability constants of the complexonato-compounds of the second and first metals, and if one of the constants is known we can determine the other.

As polarographically active element, whose complexonato-compound is reduced at a dropping mercury electrode, we used niobium.

Procedure. The original niobium and tantalum solutions were prepared by dissolving their pentoxides in an HF + H_2SO_4 acid mixture followed by removal of the fluoride ion and transfer of the solution to a graduated flask with sulphuric acid (1 : 1).

Solutions of the complexonato-compounds of niobium and tantalum were prepared by adding the original metal solutions with stirring to an alkaline solution of EDTA. The pH of the solutions was brought to a value in the range 1–6 (KOH and H_2SO_4) and the solutions were heated to

boiling, cooled, and transferred to a graduated vessel with water.

The polarographic study of niobium was carried out at a polarisation potential difference between −0.4 V and +1.0 V (sat.cal.et.). Oxygen was removed by passing nitrogen through the solution for 2–3 min.

The results of the polarographic measurements were used to determine the yield of the complexonato-compound of niobium, given by the ratio of the concentration of niobium combined in the complex to the original niobium concentration, and equal to the ratio of the heights of the waves $B = c_{MY}/c_M = I/I_{max}$.[6]

Table 1. Determination of the yield of the complexonato-compound of niobium as a function of the EDTA concentration in the presence of tantalum. $c_{Nb_2O_5} = 0.75 \times 10^{-4}$ M, $c_{Ta_2O_5} = 0.72 \times 10^{-4}$ M, pH 3.5.

EDTA concn., M	$A_1 = c_Y/c_{Nb}$	Wave height I for niobium,* mm	$B_1 = I/I_{max}$	$\frac{K_{Ta}}{K_{Nb}} = \left[\frac{\frac{c_{Ta}}{c_{Nb}}}{A_1 - B_1 - \frac{K_{Nb}}{c_{Nb}}\frac{B_1}{1-B_1}} - 1\right]\frac{B_1}{1-B_1}$
$1.5 \cdot 10^{-4}$	2	5.0	0.29	2.16
$2.25 \cdot 10^{-4}$	3	6.5	0.37	1.49
$3.0 \cdot 10^{-4}$	4	3.5	0.50	4.47
$3.75 \cdot 10^{-4}$	5	9.5	0.54	5.90
$4.50 \cdot 10^{-4}$	6	10.0	0.58	1.46
$5.25 \cdot 10^{-4}$	7	10.5	0.62	4.95
$3.75 \cdot 10^{-3}$	50	17.0	0.99	—
$7.50 \cdot 10^{-3}$	100	17.0	0.99	—
			mean	3.6±1.7

* Mean results from three series of experiments.

The dependence of the yield of the complexonato-compound of niobium on the EDTA concentration is shown in Table 1 and Fig. 1. The concentrations of niobium and tantalum were constant, and the pH of the solutions was 3.5.

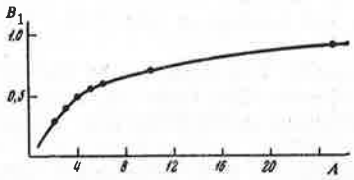

Figure 1. Dependence of the yield of the complexonato-compound of niobium on the concentration of EDTA in solution in the presence of tantalum. Niobium concentration 0.75×10^{-4} M, tantalum concentration 0.72×10^{-4} M.

Formula (2) was used to calculate the ratio of the conditional instability constants of the complexonato-compounds of tantalum and niobium; the mean value found for pH 3.5 was 3.6 ± 1.7.

The mean value of the conditional constant for the complexonato-compound of niobium at pH 3.5 is 2.85×10^{-4},[6,7] so that the conditional instability constant of the complexonato-compound of tantalum at pH 3.5 is $K_{Ta} = 3.6 \times 2.85 \times 10^{-4} = 1.03 \times 10^{-3}$.

The values of the conditional instability constants of the complexonato-compound of tantalum at various pH values were calculated by means of Eqn. (1) from the experimentally observed dependence of the yield of the complexonato-compound of niobium in the presence of tantalum on the pH of the medium. The values of the conditional instability constants of the complexonato-compound of tantalum at various pH values are given in Table 2.

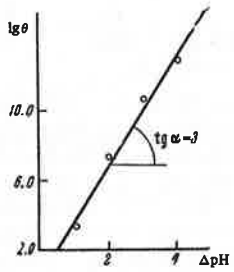

Figure 2. Plot of $\lg K_{Ta''}\Phi'/K_{Ta'}\Phi'' = \lg \theta$ vs. ΔpH.

The conditional instability constant (K) is related to the concentration instability constant (K_{instab}) by the equation:

$$K = K_{instab}\,\Phi \cdot F \qquad (3)$$

where $\Phi = f(H)$ is the hydrogen function of the anion, and $F = f(OH) = \xi(H)$ the hydrogen function of the metal[6,12].

Table 2. Determination of the conditional instability constant for the tantalum compound at pH values in the range 1–6. $c_{Nb_2O_5} = 2.46 \times 10^{-4}$ M, $c_{Ta_2O_5} = 1.4 \times 10^{-4}$ M.

pH	EDTA concn., M	$B = \frac{I}{I_{max}}$	Conditional constant for tantalum, K_{Ta}	$-\lg K_{Ta}$	$\lg \Phi$	$\lg \theta$	n
1.0	$6.0 \cdot 10^{-4}$	0.40	$1.36 \cdot 10^{-3}$	2.87	17.68	—	—
2.0	$4.2 \cdot 10^{-4}$	0.85	$3.9 \cdot 10^{-4}$	3.41	13.65	3.49	3.3
3.0	$5.0 \cdot 10^{-3}$	0.95	$6.0 \cdot 10^{-4}$	3.29	10.64	7.60	3.0
3.5	$5.0 \cdot 10^{-3}$	0.90	$1.0 \cdot 10^{-3}$	3.00	9.54	8.50	3.3
4.0	$5.0 \cdot 10^{-3}$	0.70	$3.5 \cdot 10^{-3}$	1.16	7.94	10.78	3.4
5.0	$5.0 \cdot 10^{-3}$	0.20	$0.87 \cdot 10^{-1}$	1.06	6.45	13.04	3.2

To determine the concentration instability constant it is necessary to know the values of Φ and F. The values of Φ for EDTA have been calculated and published[12]. The hydrogen functions F for tantalum can be calculated if the consecutive dissociation constants of tantalum hydroxide and the form of the dissociated hydroxide reacting with EDTA are known. Tantalum hydroxide dissociates according to the scheme:

$$Ta[OH]_5 \rightleftharpoons [Ta(OH)_4]^+ \rightleftharpoons [Ta(OH)_3]^{2+} \rightleftharpoons [Ta(OH)_2]^{3+} \rightleftharpoons [Ta(OH)]^{4+} \rightleftharpoons Ta^{5+}$$

with the formation of cations of several types.

For each of the forms of dissociation of tantalum hydroxide, the dependence of the hydrogen function F on the

concentration of hydrogen ions is given by the following equations[6,12]:

$$F_0 = \frac{c_{\text{Ta init}}}{[\text{Ta(OH)}_5]} = 1 + \frac{\text{H}K_{\alpha_1}}{K_w} + \frac{\text{H}^2K_{\alpha_1}K_{\alpha_2}}{K_w^2} + \frac{\text{H}^3K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}}{K_w^3} + \frac{\text{H}^4K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}}{K_w^4} + \frac{\text{H}^5K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}K_{\alpha_5}}{K_w^5}$$

$$F_1 = \frac{c_{\text{Ta init}}}{[\text{Ta(OH)}_4^+]} = \frac{K_w}{\text{H}K_{\alpha_1}} + 1 + \frac{\text{H}K_{\alpha_2}}{K_w} + \frac{\text{H}^2K_{\alpha_2}K_{\alpha_3}}{K_w^2} + \frac{\text{H}^3K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}}{K_w^3} + \frac{\text{H}^4K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}}{K_w^4} = F_0\frac{K_w}{\text{H}K_{\alpha}}$$

$$F_2 = \frac{c_{\text{Ta init}}}{[\text{Ta(OH)}_3^{2+}]} = \frac{K_w^2}{\text{H}^2K_{\alpha_1}K_{\alpha_2}} + \frac{K_w}{\text{H}K_{\alpha_3}} + 1 + \frac{\text{H}K_{\alpha_3}}{K_w} + \frac{\text{H}^2K_{\alpha_3}K_{\alpha_4}}{K_w^2} + \frac{\text{H}^3K_{\alpha_3}K_{\alpha_4}K_{\alpha_5}}{K_w^3} = F_0\frac{K_w^2}{\text{H}^2K_{\alpha_1}K_{\alpha_2}}$$

$$F_3 = \frac{c_{\text{Ta init}}}{[\text{Ta(OH)}_2^{3+}]} = \frac{K_w^3}{\text{H}^3K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}} + \frac{K_w^2}{\text{H}^2K_{\alpha_3}K_{\alpha_4}} + \frac{K_w}{\text{H}K_{\alpha_4}} + 1 + \frac{\text{H}K_{\alpha_4}}{K_w} + \frac{\text{H}^2K_{\alpha_4}K_{\alpha_5}}{K_w^2} = F_0\frac{K_w^3}{\text{H}^3K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}}$$

$$F_4 = \frac{c_{\text{Ta init}}}{[\text{Ta(OH)}^{4+}]} = \frac{K_w^4}{\text{H}^4K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}K_{\alpha_5}} + \frac{K_w^3}{\text{H}^3K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}} + \frac{K_w^2}{\text{H}^2K_{\alpha_3}K_{\alpha_4}} + \frac{K_w}{\text{H}K_{\alpha_4}} + 1 + \frac{\text{H}K_{\alpha_5}}{K_w} = F_0\frac{K_w^4}{\text{H}^4K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}}$$

$$F_5 = \frac{c_{\text{Ta init}}}{[\text{Ta}^{5+}]} = \frac{K_w^5}{\text{H}^5K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}K_{\alpha_5}} + \frac{K_w^4}{\text{H}^4K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}K_{\alpha_5}} + \frac{K_w^3}{\text{H}^3K_{\alpha_3}K_{\alpha_4}K_{\alpha_5}} + \frac{K_w^2}{\text{H}^2K_{\alpha_4}K_{\alpha_5}} + \frac{K_w}{\text{H}K_{\alpha_5}} + 1 = F_0\frac{K_w^5}{\text{H}^5K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}K_{\alpha_4}K_{\alpha_5}}$$

where K_W is the ionic product of water, and K_α the dissociation constants of tantalum hydroxide[13]:

$$K_{\alpha_1} = \frac{[\text{Ta(OH)}_4^+][\text{OH}^-]}{[\text{Ta(OH)}_5]} = 1.1\cdot10^{-13}$$

$$K_{\alpha_2} = \frac{[\text{Ta(OH)}_3^{2+}][\text{OH}^-]}{[\text{Ta(OH)}_4^+]} = 2.0\cdot10^{-18}$$

$$K_{\alpha_3} = \frac{[\text{Ta(OH)}_2^{3+}][\text{OH}^-]}{[\text{Ta(OH)}_3^{2+}]} = 4.0\cdot10^{-23}$$

$$K_{\alpha_4} = \frac{[\text{Ta(OH)}^{4+}][\text{OH}^-]}{[\text{Ta(OH)}_2^{3+}]} = 2.5\cdot10^{-27}$$

$$K_{\alpha_5} = \frac{[\text{Ta}^{5+}][\text{OH}^-]}{[\text{Ta(OH)}^{4+}]} = 2.5\cdot10^{-30}$$

In the pH range 2–6, F_0 has a value close to 1, so that $F_i = \text{const}/\text{H}^n$, and since the conditional instability constant $K = f(\text{pH})$, the ratio of the conditional constants for two different values of the concentrations H' and H'' is equal to:

$$\frac{K_{\text{Ta}}''}{K_{\text{Ta}}'} = \frac{\Phi''F''}{\Phi'F'} \quad \text{or} \quad \frac{K_{\text{Ta}}''\Phi'}{K_{\text{Ta}}'\Phi''} = \theta = \frac{F''}{F'} = \left(\frac{H'}{H''}\right)^n. \qquad (4)$$

By taking logarithms of the last expression, we obtain

$$\lg\theta = \lg\frac{K_{\text{Ta}}''\Phi'}{K_{\text{Ta}}\Phi''} = n(\text{pH}'' - \text{pH}'); \quad n = \frac{\lg\theta}{\Delta\text{pH}}. \qquad (5)$$

Substitution of the values of Φ and the conditional instability constants of the complexonato-compound of tantalum (Table 2) at different pH values in Eqn. (5) makes it possible to plot the dependence of lg θ on ΔpH, and this can be used to determine n—the number of hydroxide groups removed during the dissociation of tantalum hydroxide—that is to determine the form of dissociated tantalum hydroxide reacting with EDTA.

Table 2 gives the data used to calculate θ, and Fig. 2 gives the dependence of lg θ on Δ(pH). This is given by a straight line with slope tan α = 3.0, indicating that the reaction of EDTA with tantalum hydroxide takes place according to the equations:

$$\text{Ta(OH)}_5 \rightleftharpoons [\text{Ta(OH)}_2]^{3+} + 3\text{OH}^-$$

$$[\text{Ta(OH)}_2]^{3+} + \text{Y}^{4-} \rightleftharpoons [\text{Ta(OH)}_2\text{Y}]^-$$

Table 3. Calculation of the concentration instability constant of the complexonato-compound of tantalum.

pH	lg F	lg Φ	pK	pK_{instab}
1.0	14.0	17.1	2.87	33.97
2.0	17.0	13.6	3.41	34.01
3.0	20.0	10.6	3.29	33.89
3.5	21.5	9.5	3.0	34.0
4.0	23.0	8.5	1.16	32.66
5.0	26.0	6.5	1.06	33.56
				Mean. 33.6

The known composition of the complex made it possible to calculate the hydrogen function of the metal $F_{\text{Ta}} = K_W^3/H^3K_{\alpha_1}K_{\alpha_2}K_{\alpha_3}$ and the value of the concentration instability constant $K_{\text{instab}}^{\text{Ta}} = K/\Phi F$ for each value of the pH of the solution (Table 3).

REFERENCES

1. I. M. Gibalo and I. P. Alimarin, "Sovremennye Metody Khimicheskogo i Spektral'nogo Analiza Materialov" (Modern Methods for the Chemical and Spectroscopic Analysis of Materials), Metallurgizdat, Moscow, 1967.
2. E. A. Mazurenko and B. I. Nabivanets, Ukrain. Khim. Zhur., 33, 98 (1967).
3. A. K. Babko and B. I. Nabivanets, "Problemy Sovremennoi Khimii Koordinatsionnykh Soedinenii" (Problems of the Modern Chemistry of Coordination Compounds), Izd. Leningrad. Gos. Univ., Leningrad, 1968, p. 111.
4. I. P. Alimarin, I. M. Gibalo, and Ch'in Ch'uang-jung, Vestnik Moskov. Gos. Univ., 4, 34 (1962).
5. I. V. Pyatnitskii and E. S. Sereda, Ukrain. Khim. Zhur., 33, 408 (1967).
6. G. A. Volkova and V. G. Sochevanov, Zhur. Neorg. Khim., 12, 433 (1967) [Russ. J. Inorg. Chem., No. 2 (1967)].
7. G. A. Volkova, Candidate's Thesis, Moscow, 1968.
8. V. Patrovsky, Coll. Czech. Chem. Commun., 29, 5 (1964).
9. V. V. Lukachina, Candidate's Thesis, Kiev, 1962.
10. V. G. Sochevanov and G. A. Volkova, Zhur. Neorg. Khim., 14, 118 (1969).
11. M. M. Sochevanova and V. G. Sochevanov, Zavod. Lab., No. 9, 1058 (1965).
12. V. G. Sochevanov, Zavod. Lab., No. 5, 531 (1963).
13. A. K. Babko, V. V. Lukachina, and B. I. Nabivanets, Zhur. Neorg. Khim., 8, 1839 (1963) [Russ. J. Inorg. Chem., No. 8 (1963)].

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