

DETERMINATION OF THE COMPOSITION AND INSTABILITY CONSTANTS OF OXALATE COMPLEXES OF NIOBIUM AND TANTALUM BY THE SOLUBILITY METHOD

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In the previously published investigation [1], using the method of solubility, we established the maximum number of oxalate groups bonded to the Nb(Ta) atom. The application of this method, using more accurate instruments, made it possible to determine the composition of the inner sphere of the oxalate complexes of Nb and Ta, their instability constants, and to establish the presence of polynuclear complex compounds. In a determination of the composition of the oxalate complexes, we compared two equilibrium systems: 1) a saturated solution of oxalic acid + $\text{HClO}_4 + \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$; 2) a saturated solution of oxalic acid + HClO_4 + oxalotantallic or oxaloniobic acids + $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

The normality with respect to perchloric acid for both systems ($\text{N}_{\text{HClO}_4(1)}$ and $\text{N}_{\text{HClO}_4(2)}$) is known from the data on the compilation of the systems.

The dependence of the pH of system (1) on N_{HClO_4} was determined experimentally. When the pH of systems (1) and (2) are equal, the following equation is correct:

TABLE 1. Verification of the Presumed Composition of the Binuclear Complex of Niobium According to the Balance of Hydrogen Ions

CNb , mole/dm ³	N_{HClO_4} graphic, g-ion/dm ³	N_{HClO_4} according to the compilation of system (2), g-ion/dm ³	H_1 in the presence of a binuclear complex	H_2 in the presence of a binuclear complex	pH of system (2)	$\Delta \text{N} = \text{N}_{\text{HClO}_4 \text{ graphic}} - \text{N}_{\text{HClO}_4}$ according to the compilation of system (2), g-ion/dm ³	Summary concentration of extrasphere hydrogen ions, g-ion/dm ³
0.0752	0.130	0	2.43	2.86	0.510	0.1300	$0.0752 \cdot 0.5 \cdot 1 + 0.0752 \cdot 0.5$ $\times 0.85 \cdot 3 + 0.0752 \cdot 0.5 \cdot 0.14$ $\times 1 = 0.1400$
0.0753	0.700	0.5743	2.35	2.58	0.155	0.1257	$0.0753 \cdot 0.5 \cdot 1 + 0.0753 \cdot 0.5$ $\times 0.58 \cdot 3 + 0.0753 \cdot 0.5 \cdot 0.42$ $\times 1 = 0.1187$
0.0750	1.245	1.1599	2.12	2.24	-0.070	0.0851	$0.075 \cdot 0.5 \cdot 1 + 0.075 \cdot 0.5$ $\times 0.24 \cdot 3 + 0.075 \cdot 0.5 \cdot 0.76$ $\times 1 = 0.0930$
0.0735	1.547	1.4746	1.99	1.99	-0.175	0.0724	$0.0735 \cdot 0.5 \cdot 1 + 0.0735 \cdot 0.5$ $\times 0.99 \cdot 1 + 0.0735 \cdot 0.5 \cdot 0.01$ $\times 1 = 0.0735$
0.0746	2.025	1.9598	1.85	1.72	-0.300	0.0652	$0.0746 \cdot 0.5 \cdot 1 + 0.0746 \cdot 0.5$ $\times 0.72 \cdot 1 + 0.0746 \cdot 0.5 \cdot 0.28$ $\times 1 = 0.0746$

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TABLE 2. Verification of the Proposed Composition of Mononuclear Complexes of Niobium and Tantalum According to the Balance of Hydrogen Ions

Number of $C_2O_4^{2-}$ groups per metal atom \bar{n}	Concentration of metal, mole/dm ³	pH of system (2)	$NHClO_4$ graphic, g-ion/dm ³	$NHClO_4$ according to compilation of system (2), g-ion/dm ³	Content of complexes, %	Presumed composition of complex	$\Delta N = NHClO_4 \text{ graphic} - NHClO_4$ according to compilation of system (2), g-ion/dm ³	Summary concentration of extrasphere hydrogen ions, g-ion/dm ³
Niobium								
2.90	0.021	0.56	0.0565	0	90.0 10.0	$H_3[NbO(C_2O_4)_3]$ $H[NbO(C_2O_4)_2]$	0.0565	$0.021 \cdot 0.9.3$ $+ 0.021 \cdot 0.1$ $\times 1 = 0.0567$
2.82	0.021	0.38	0.310	0.2563	82.0 18.0	$H_3[NbO(C_2O_4)_3]$ $H[NbO(C_2O_4)_2]$	0.0540	0.0554
2.60	0.021	0.165	0.688	0.6446	60.0 40.0	$H_3[NbO(C_2O_4)_3]$ $H[NbO(C_2O_4)_2]$	0.0440	0.0431
2.14	0.021	-0.105	1.316	1.2890	14.0 86.0	$H_3[NbO(C_2O_4)_3]$ $H[NbO(C_2O_4)_2]$	0.0270	0.0269
1.80	0.0209	-0.28	1.932	1.9120	80.0 20.0	$H[NbO(C_2O_4)_2]$ $H[NbO_2C_2O_4]$	0.0200	0.0209
1.74	0.0209	-0.30	2.072	2.0510	74.0 26.0	$H[NbO(C_2O_4)_2]$ $H[NbO_2C_2O_4]$	0.0210	0.0209
Tantalum								
2.87	0.0116	0.585	0.031	0	87.0 23.0	$H_3[TaO(C_2O_4)_3]$ $H[TaO(C_2O_4)_2]$	0.0310	0.0317
2.58	0.0116	0.260	0.505	0.4790	58.0 42.0	$H_3[TaO(C_2O_4)_3]$ $H[TaO(C_2O_4)_2]$	0.0260	0.0251
2.30	0.0116	0.115	0.790	0.7699	30.0 70.0	$H_3[TaO(C_2O_4)_3]$ $H[TaO(C_2O_4)_2]$	0.0200	0.0184

$$N_{HClO_4(1)} = N_{HClO_4(2)} + X \cdot C_{Me} \cdot (\bar{n} - 2) + Y \cdot C_{Me} \cdot [1 - (\bar{n} - 2)], \quad (1)$$

where \bar{n} is the average number of oxalate groups, bonded to the Nb(Ta) atom; $(\bar{n} - 2)$ is the fraction of complex ions with three oxalate groups; $[1 - (\bar{n} - 2)]$ is the fraction of complex ions with two oxalate groups; C_{Me} is the concentration of Nb or Ta (mole/dm³); X is the number of hydrogen ions in the outer sphere of the complex with three oxalate groups; Y is the number of hydrogen ions in the outer sphere of the complex with two oxalate groups. The value of \bar{n} was determined in the same way as before [1].

Let us note $N_{HClO_4(1)} - N_{HClO_4(2)} = \Delta N$, and let us rewrite Eq. (1) in the following form:

$$X \cdot C_{Me} \cdot (\bar{n} - 2) + Y \cdot C_{Me} \cdot [1 - (\bar{n} - 2)] = \Delta N. \quad (2)$$

After compiling and simultaneously solving two equations of the type of (2) (at two close values of the pH), we find the number of hydrogen ions in the outer sphere of complexes with two and three oxalate groups. However, it is more convenient, after setting the values of X and Y (0, 1, 2, 3), to verify the identity of the left- and right-hand portions of Eq. (2). We find the composition of the inner sphere of the complexes according to the known values of X , Y , and \bar{n} .

EXPERIMENTAL METHOD AND DISCUSSION OF RESULTS

Reagents and Instruments. The initial highly concentrated solutions of oxalonitric and oxalotantalonic acids were produced by dissolving well-washed niobium and tantalum hydroxides in the calculated amounts of chemically pure oxalic acid. The perchloric acid used was cp grade. The pH values of the solution were measured with a glass electrode with an LPU-0.1 tube potentiometer. The dependence of the pH of system 1 on the normality with respect to perchloric acid is presented in Fig. 1. Here, and in the subsequent experiments, the time of mixing of the solution and bottom phase was no less than 2 h.

TABLE 3. Data of a Calculation of the Instability Constants of Mono-nuclear Complexes of Niobium and Tantalum

Function of formation \bar{n}	Density of solution, g/cm ³	Concentration of metal, mole /1000 g H ₂ O	a_{H^+} , activity of hydrogen ions	HClO ₄ according to compilation of system, mole/1000 g H ₂ O	Ionic strength of solution	γ'	γ''	γ'''	Concentration of C ₂ O ₄ ²⁻ , g-ion /1000 g H ₂ O	pK _{inst}
Niobium										
2.90	1.0445	0.022	0.2754	0	0.285	0.7129	0.2582	0.0475	1.775 · 10 ⁻⁶	6.12
2.82	1.052	0.022	0.4169	0.2687	0.520	0.6933	0.2310	0.0369	7.725 · 10 ⁻⁷	6.24
2.60	1.069	0.0225	0.6839	0.6916	0.900	0.7000	0.2401	0.0404	2.479 · 10 ⁻⁷	6.16
Tantalum										
2.87	1.041	0.012	0.2600	0.0	0.229	0.7240	0.2747	0.0546	1.931 · 10 ⁻⁶	5.98
2.71	1.053	0.012	0.4121	0.2874	0.481	0.6947	0.2329	0.0377	7.933 · 10 ⁻⁶	5.86
2.58	1.061	0.012	0.5495	0.5093	0.686	0.6926	0.2303	0.0367	4.176 · 10 ⁻⁷	5.88

The distribution of metals between the solid and liquid phases was monitored using the radioactive isotopes (⁹⁵Nb, ¹⁸²Ta). Only traces of the metal were detected in all the experiments in the solid phase. It was shown earlier that with the systems selected, two-hour mixing is sufficient to reach equilibrium solubility [1]. A graph of the dependence of the equilibrium concentration of oxalic acid on the pH of the solution is depicted in Fig. 2. Figures 3 and 4 present graphs of the dependence of \bar{n} (the Bjerrum function) on the summary equilibrium concentration of oxalate ions (for Nb at various molar concentrations of the metal). The graphs were constructed according to the results of a measurement of the solubility of oxalic acid in system 2 and according to the data of Fig. 2. The maximum number of C₂O₄²⁻ groups added by niobium and tantalum atoms under these conditions is equal to three. We were unable to establish the presence of oxalate complexes of Nb and Ta with $\bar{n} < 1$ (at C_{Nb} > 0.02 and C_{Ta} > 0.01 mole/dm³), since with the increase in the perchloric acid concentration necessary for this (>2 mole/dm³), the porous diaphragm of the electrolytic bridge of the electrode system is tightly packed with the relatively insoluble salt KClO₄, and the rate of the flow of potassium chloride changes. As a result of this, the error in the measurement of the pH value increases.

Figure 3 shows that the composition of oxalate complexes depends not only on the equilibrium concentration of the metal in solution. Thus, at the same value $\left[\sum_{i=0}^{i=2} H_i C_2 O_4^{i-2}\right] = 0.9$ mole/dm³, the function of formation as a function of the niobium concentration has the following values: 2.4 (C_{Nb} = 0.08 mole/dm³) and 2.9 (C_{Nb} = 0.01 mole/dm³). The dependence of the function of formation (\bar{n}) on the metal concentration is evidence of the existence of polynuclear complexes in solution. The composition of the polynuclear complexes and their contents can be determined according to the data of Fig. 3, if we assume that at a given metal concentration the relative content of the polynuclear form and the composition of the polynuclear complex remain almost unchanged within the entire interval of variation of $\left[\sum_{i=0}^{i=2} H_i C_2 O_4^{i-2}\right]$. At point A (Fig. 3), the average number of C₂O₄²⁻ groups per niobium atom is the same and equal to two for both concentrations of the metal. The following expression is correct for this case:

$$2 = X \cdot Y + (1 - X) \cdot 2, \quad (3)$$

where X is the fraction of niobium bound in the polynuclear complex; (1 - X) is the fraction of niobium bound in a mononuclear complex; the factor 2 next to (1 - X) is the value of the function of formation at the point A for mononuclear complexes; Y is the number of oxalate groups per niobium atom in the polynuclear complex.

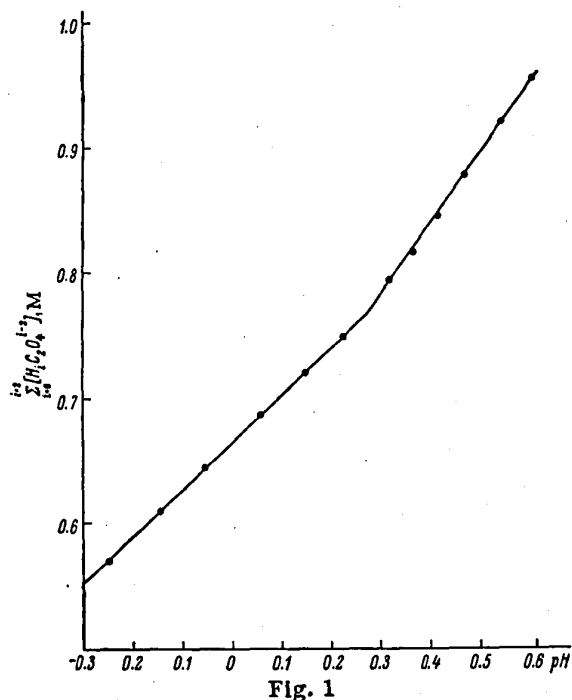


Fig. 1

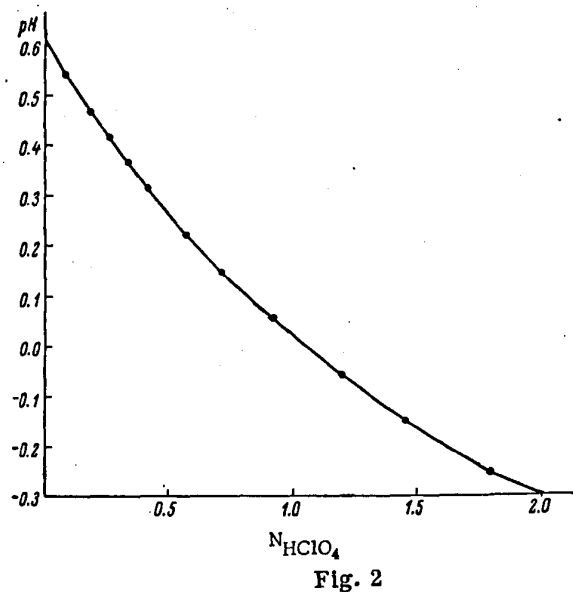


Fig. 2

Fig. 1. Curve of pH versus $NHClO_4$ for system (1).

Fig. 2. Dependence of the equilibrium concentration of oxalic acid in a saturated solution of it on the pH at $t = 20 \pm 0.1^\circ C$.

From formula (3) it is evident that in the polynuclear complex, each metal atom corresponds to two oxalate groups ($Y=2$). At a given niobium concentration (0.075 mole/dm^3), 50% of the metal exists in the polynuclear form ($X=0.5$).

The composition of the polynuclear oxalate complex corresponding to the formula $H_2[Nb_2O_2(C_2O_4)_4]$ seems more probable to us. This hypothesis on the composition is confirmed by the data of Table 1. Table 1 compares the actual acidification of system 2 by the extrasphere hydrogen ions of the oxalate complexes with the calculated acidification. In the calculation we proceeded on the basis of the presumed composition of the binuclear complex, as well as the premise that the complex acids are strong. $NHClO_4$ graphic in Table 1 represents the number of g-eq of $HClO_4$ that would be required to create an acidity in system 1 equal to the actual acidity of system 2. The coefficients 1 and 3 (Table 1) represent the number of hydrogen ions in the outer sphere of the complexes. The summary concentration of the extrasphere hydrogen ions was determined on the assumption that mononuclear complexes of niobium have the following composition: $H_3[NbO \cdot (C_2O_4)_3]$, $H[NbO(C_2O_4)_2]$, and $H[NbO_2C_2O_4]$.

The data of Table 2 confirm the hypothesis on the composition of mononuclear complexes. The values of \bar{n} and the pH in Tables 1 and 2 present the arithmetic mean of the data of three parallel experiments. In Table 2 it is shown that when the pH value is varied in the system (2) there is not only a dissociation of the complexes of niobium and tantalum, but also a change in the composition of the inner sphere (an increase in the number of oxygen atoms).

Using the data of Table 2 and the data of a measurement of the acidity of the solutions, we can calculate the values of the equilibrium constant of the dissociation of the oxalate complex:

$$[MeO(C_2O_4)_3]^{3-} \rightleftharpoons [MeO(C_2O_4)_2]^{-} + [C_2O_4]^{2-} \quad (4)$$

$$k_3 = \frac{[MeO(C_2O_4)_2] \cdot [C_2O_4^{2-}]}{[MeO(C_2O_4)_3^{3-}]} \cdot \frac{f' \cdot f''}{f'''}$$

where k_3 is the particular instability constant of the oxalate complex with three oxalate groups; f' , f'' , and f''' are the activity coefficients of singly, doubly, and triply charged ions; Me represents niobium or tantalum.

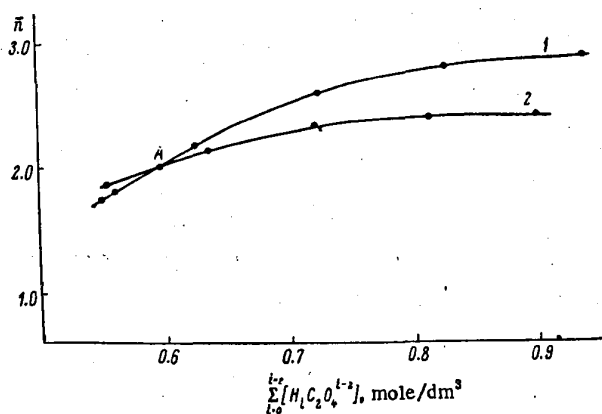


Fig. 3

Fig. 3. Dependence of the composition of the oxalate complexes of niobium on the equilibrium concentration of oxalic acid. 1) Niobium concentration 0.02 mole/dm³; 2) niobium concentration 0.075 mole/dm³.

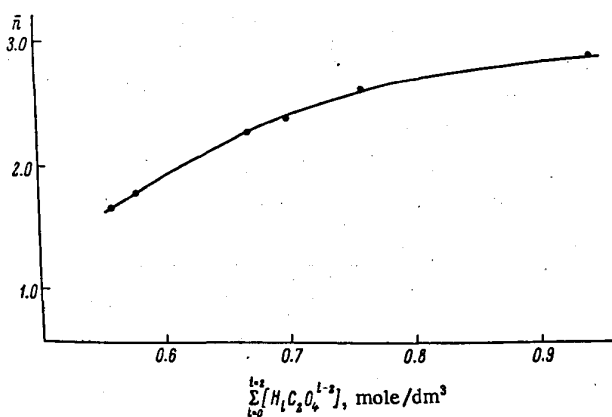


Fig. 4

Fig. 4. Dependence of the composition of oxalate complexes of tantalum on the equilibrium concentration of oxalic acid at $C_{Ta} = 0.01$ mole/dm³.

For such a calculation it is necessary to know the equilibrium concentration of oxalate ions and the activity coefficients. From the equation of balance of oxalate ions, let us find the equilibrium concentration

$$[C_2O_4^{2-}] = \frac{\left[\sum_{i=0}^{i=2} H_i C_2 O_4^{i-2} \right]}{\frac{[a_{H+}]^2 \cdot f''}{K_1 \cdot K_2} + \frac{[a_{H+}] \cdot f''}{K_2 \cdot f'} + 1}, \quad (5)$$

where $\left[\sum_{i=0}^{i=2} H_i C_2 O_4^{i-2} \right]$ is the summary equilibrium concentration of oxalate ions (determined graphically);

K_1 and K_2 are the thermodynamic dissociation constants of oxalic acid (taken from [2]); f' and f'' are the activity coefficients.

We find the activity coefficients and the ionic strength of the solution by solving the following equation by the method of successive approximations:

$$2\mu = C_{ClO_4^-} + C_{H^+} + 9 \cdot C_{[MeO(C_2O_4)_2]^{2-}} + 4 \cdot C_{[MeO(C_2O_4)_3]^{3-}} + \frac{\left[\sum_{i=0}^{i=2} H_i C_2 O_4^{i-2} \right]}{\frac{[a_{H+}]^2 \cdot f''}{K_1 \cdot K_2} + \frac{[a_{H+}] \cdot f''}{K_2 \cdot f'} + 1} \cdot \left[\frac{[a_{H+}] \cdot f''}{K_2 \cdot f'} + 4 \right]. \quad (6)$$

Equation (6) represents the equation of the ionic strength as applied to the case under consideration.

In solving Eq. (6), let us set the value of the ionic strength (μ) and calculate the activity coefficients according to the Davies formula [3]. The values of the activity coefficients at which Eq. (6) is converted to an identity will be considered constant, and we shall use them in the calculation of the instability constants according to formula (4).

Yatsimirskii has shown [4] that the Davies formula is correct up to a value of the ionic strength of ~ 1.3 . The use of this formula in the calculation of the instability constants introduces an error no greater than ± 0.1 pK. The numbers of lines in Table 3 correspond to the numbers of lines in Table 2.

As can be seen from Table 3, oxalate complexes of niobium are somewhat more stable than the analogous complexes of tantalum (for Nb $k_3 = 6.17 \pm 0.4$, for Ta $k_3 = 5.91 \pm 0.05$).

These data confirm the purely qualitative considerations in the literature concerning the stability of niobium and tantalum oxalates [5].

No calculation of the instability constants of complexes of niobium and tantalum containing two oxalate groups were performed, since at $\bar{n} \leq 2$, the value of the ionic strength in system 2 is greater than 2. Moreover,

the transition of the complex with two oxalate groups into the complex with one oxalate group is associated with a change in the number of oxygen atoms (possibly OH^- groups) in the inner sphere.

Therefore k_2 , calculated according to formula (4), will not be the particular instability constant of complexes with two oxalate groups.

Data on the composition of the oxalate complexes of niobium agree with the analogous data of the work of Nevzorov and Songina [6]. In the work it was noted that oxalate complexes of niobium with two and three oxalate groups exist in the interval of $\text{pH} = 0.5-5$.

As can be seen from Table 2, niobium complexes of the indicated composition can exist in solution up to pH value equal to 0.1. At $\text{pH} = 5$, the oxalate complexes of niobium and tantalum are unstable.

In our work [7] it was established by an electromigration method that at $\text{pH} 3.3$ and a 20-fold excess of oxalate ions with respect to niobium, after five days 25% of the niobium was in the hydrolyzed form. After the pH was lowered to 1.8, the hydrolyzed form was not detected even after 11 days of exposure of the solution (Fig. 4, [7]).

CONCLUSIONS

1. As a result of the dissolution of niobium and tantalum hydroxides in a saturated solution of oxalic acid, complex oxalonibic and oxalotantallic acids of the following compositions are formed: $\text{H}_3[\text{NbO}(\text{C}_2\text{O}_4)_3]$; $\text{H}[\text{NbO}(\text{C}_2\text{O}_4)_2]$; $\text{H}[\text{NbO}_2\text{C}_2\text{O}_4]$; $\text{H}_3[\text{TaO}(\text{C}_2\text{O}_4)_3]$; $\text{H}[\text{TaO}(\text{C}_2\text{O}_4)_2]$; $\text{H}[\text{TaO}_2\text{C}_2\text{O}_4]$.
2. The predominance of one form of the complex acid or another in solution under these conditions is determined by the pH of the solution.
3. The stepwise instability constant of the oxalate complex of tantalum with three oxalate groups ($\text{pK}_3 = 5.91 \pm 0.05$) and the analogous constant of the oxalate complex of niobium ($\text{pK}_3 = 6.17 \pm 0.04$) were determined.
4. The existence in solution of a binuclear oxalate complex of niobium at $C_{\text{Nb}} = 0.075$ mole/ dm^3 of the composition: $\text{H}_2[\text{Nb}_2\text{O}_2(\text{C}_2\text{O}_4)_4]$ was established.
5. Mononuclear oxalonibic and oxalotantallic acids are stable within the range of pH from 0.3 to 1.8.

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