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THE STATE OF NIOBIUM IN OXALIC ACID SOLUTIONS

A. N. Nevzorov and O. A. Songina

There is lack of agreement about the composition of the oxalato-compounds of niobium in solution. Russ[1] isolated from solution the alkali metal oxalatoniobates with general formula $Nb_2O_5 \cdot 3MO \cdot 6C_2O_3 \cdot nH_2O$, and hydrogen oxalatoniobate $H_5[Nb(C_2O_4)_5]$[1,2] and later, compounds with $Nb : C_2O_4^{2-} = 1 : 3$ were isolated by others[3-6]. However, Vlasov and Lapitskii[7,8] found niobium to be present in oxalic acid solution as the complex $[NbO_2(C_2O_4)]^-$. Gibalo and Ch'in[9] suggest that in the pH range 1.3–5 the solution contains the complex $H[NbO(C_2O_4)_2]$. Babko and Lukachina[10] obtained solutions with molar ratio $C_2O_4^{2-} : Nb < 1$.

We have studied the composition and properties of the oxalato-compounds of niobium under various conditions, using the methods of potentiometry with a mercury(I) oxalate electrode[11], spectrophotometry, dialysis, and potentiometric titration.

EXPERIMENTAL

The measurement of the potentials and the preparation of $Hg_2C_2O_4$ paste have been described earlier[11]. The measurements were at constant ionic strength $I = 0.5$ and a temperature of $25° \pm 0.1°C$ on an R-307 potentiometer with 195/3 galvanometer. The pH of the solutions was measured with an LPU-0.1 pH-meter.

The solutions were prepared from a 0.094 M solution of potassium metaniobate containing the radioactive isotope ^{95}Nb, and a potassium oxalate solution with pH 7. The acidity was controlled by adding nitric or perchloric acids. The ionic strength was kept constant by adding KNO_3 or $NaClO_4$ respectively. The quantity of potassium metaniobate solution taken was the same in all experiments. In the absence of residue, the concentration of niobium in these solutions should have been 0.0094 M. The distribution of niobium between the residues and the solutions was followed by measuring the radioactivity. In all the experiments, freshly prepared potassium metaniobate solution was used.

Dependence of the Potential of the Mercury(I) Oxalate Electrode on the $C_2O_4^{2-}$ Concentration at $I = 0.5$

The dependence of the potential of the mercury(I) oxalate electrode on the oxalate ion concentration[11] can be written in the general form

$$E = a - b \log [C_2O_4^{2-}] , \qquad (1)$$

where E is the potential relative to the reference electrode, and a and b are constants for the given conditions.

In order to be able to use expression (1) for any pH value, we determined the dissociation constants of oxalic acid under the conditions of the experiment, that is, at $I = 0.5$. For this purpose we prepared a series of standard solutions with $K_2C_2O_4$ concentrations in the range 0.0005 to 0.05 M, and different pH values. From the total concentration of potassium oxalate, the pH of the solution, and the quantity of nitric acid required to establish a given pH value, it is possible to determine the formation function of oxalic acid[12]. The formation curve for oxalic acid at $I = 0.5$ is shown in Fig. 1. The values of K_1 and K_2 calculated from these data are 9.25×10^{-2} and 2.3×10^{-4} respectively.

To observe the dependence of the potential of the mercury(I) oxalate electrode on the concentration of oxalate ions, we measured the potentials of the standard solutions relative to a saturated calomel electrode. These results, and the values found for the dissociation constants of oxalic acid, were used to construct the plot of E against $-\lg[C_2O_4^{2-}]$ (Fig. 2). This plot is linear in the pH range 1–6. The values of the constants in expression (1) are $a = 0.2025$ and $b = 0.031$. For solutions with pH 0.5 (Fig. 2), it is necessary to take other values for the constants: $a = 0.182$ and $b = 0.0325$. Unstable results are obtained in more acidic solutions.
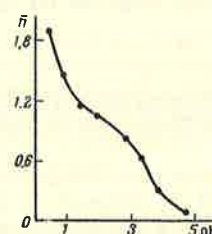

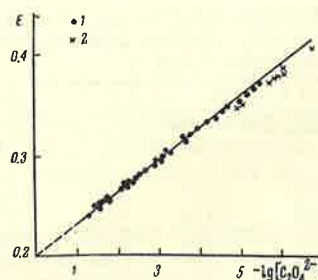Fig. 1. Formation curve for the $C_2O_4^{2-}$–HNO_3 system at $I = 0.5$.

Fig. 2. Dependence of the potential of the mercury(I) oxalate electrode on the $C_2O_4^{2-}$ concentration. $I = 0.5$; 1) pH 1–6; 2) pH 0.5.

The results obtained allow the total concentration of oxalic acid and its dissociation products to be obtained from the measured potential of the solutions, according to the formula:

$$\log \Sigma c_{ox} = -\frac{E - 0.2025}{0.031} + \log(1 + \beta_1[H^-] + \beta_2[H^+]^2) , \qquad (2)$$

where

$$\Sigma c_{ox} = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}] ,$$
$$\beta_1 = \frac{1}{K_1} = 4.35 \times 10^9; \qquad \beta_2 = \frac{1}{K_1 \cdot K_2} = 4.7 \times 10^4 .$$

Determination of the Composition of the Oxalato-Complex of Niobium by the Potentiometric Method

Results for the study of the reaction of solutions of potassium metaniobate and potassium oxalate at various pH are given in Table 1. Different quantities of potassium oxalate were taken for a given pH, in order to determine the formation function both when there was complete dissolution of niobium and also in the presence of hydroxide precipitate. The solutions were kept at 25°C for 24 h. Equilibrium between the precipitate and solution was established in 4–6 h after mixing.

The formation function of the oxalato-compounds of niobium was calculated[12] from the difference between the total concentration of oxalate ions in the solution and the concentration of oxalic acid, calculated from formula (2). The total concentration of oxalate ion was determined by titration with potassium permanganate.

The formation function of the oxalato-complex of niobium changes from 3 to 2 with change in pH from 4 to 0.5 (Table 1). It does the same in the presence of hydroxide precipitate, that is, when the quantity of potassium oxalate taken was less than that required for the complete dissolution of niobium.

Spectrophotometric Measurements and Determination of the Relative Dialysis Coefficient of Niobium

We did not detect the mono-oxalato-compound of niobium in solution (Table 1), although its absorption spectrum has been reported[7]. We therefore measured the optical

density of our solutions relative to water (Fig. 3) and relative to "blanks" (Fig. 4). The "blanks" had the same components as the solution being studied, except that niobium was absent. NaClO$_4$ was used as an inert electrolyte. since solutions containing NO$_3^-$ absorb in the ultraviolet range. Curves 3 and 4 give the absorption spectra under conditions in which, according to the data in Table 2, the solution contains complexes with Nb : C$_2$O$_4^{2-}$ ratios of 1 : 2 and 1 : 3 respectively.

The spectra of the oxalato-compounds of niobium, relative to that of water, are slightly distorted owing to the absorption of light by oxalic acid (curve 1 in Fig. 3). Their spectra, relative to those of "blanks", have a maximum at 270 nm and differ from one another in the magnitude of the absorptivity (Fig. 4).

In the absence of an inert electrolyte, niobium is retained in solution at an overall Nb : C$_2$O$_4^{2-}$ ratio of 1 : 1 and 1 : 0.5. The optical spectra of these solutions agree
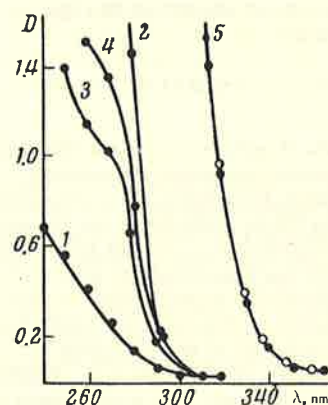
Fig.3. Light-absorption spectra of solutions, relative to water.
1) 0.01 M H$_2$C$_2$O$_4$; 2) 0.01 M KNbO$_3$;
3) 0.0094 M Nb + 0.03 M K$_2$C$_2$O$_4$, pH 0.5, $I = 0.5$; 4) 0.0094 M Nb + 0.03 M K$_2$C$_2$O$_4$, pH 2.6, $I = 0.5$; 5) 0.0094 M Nb + 0.01 M K$_2$C$_2$O$_4$ (●) and 0.0094 M Nb + 0.005 M K$_2$C$_2$O$_4$ (o), pH 2.6, $I = 0.05$.

TABLE 1. Reaction of KNbO$_3$ and K$_2$C$_2$O$_4$ solutions at $I = 0.5$. Niobium concentration in all experiments 0.0094 M.

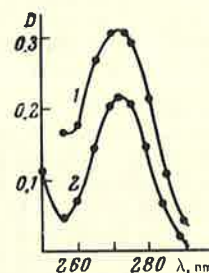| pH	Total oxalate ion concentration, M	Final niobium concentration, M	E, relative to sat. cal. el.	Concn. of oxalic acid, calc. from Eqn.(2), M	$\bar{n}$
3.93	0.0060	0.00133	0.2918	0.0020	3.0
4.08	0.0400	0.0093	0.2669	0.0112	3.1
2.90	0.0067	0.00183	0.3139	0.00158	2.8
2.90	0.0300	0.0094	0.3045	0.00274	2.9
2.60	0.0071	0.0022	0.3300	0.00094	2.8
2.60	0.0404	0.0094	0.2954	0.0122	3.0
2.00	0.0072	0.00242	0.3456	0.00115	2.5
2.00	0.0300	0.0094	0.3248	0.00556	2.5
1.00	0.0200	0.00797	0.3703	0.00366	2.05
1.05	0.0313	0.0094	0.3517	0.01344	1.9
0.50	0.0195	0.0082	0.3910	0.00226	2.1
0.50	0.0310	0.0094	0.3337	0.01414	1.9

Fig.4. Light-absorption spectra of solutions, relative to blank specimen.
1) 0.0047 M Nb + 0.015 M K$_2$C$_2$O$_4$, pH 2.6; 2) 0.0047 M Nb + 0.015 M K$_2$C$_2$O$_4$, pH 0.5.

TABLE 2. Determination of the relative dialysis coefficient of niobium. Niobium concentration 0.0094 M.

Expt. No.	Total oxalate ion concentration, M	pH	D_{Nb}	Characteristics of solution
1	0.01	2.55	0.045	$I < 0.05$ (without inert electrolyte)
2	0.03	3.50	0.34	$I = 0.5$ (electrolyte KNO_3)
3	0.03	2.60	0.32	ditto
4	0.03	1.00	0.36	»
5	0.03	0.50	0.37	»

with one another (curve 5 in Fig. 3) and with the light-absorption curve given by Vlasov and Lapitskii[7]. We have assumed that unstable polymeric compounds are formed under these conditions, and have carried out experiments to determine the relative dialysis coefficient.

The procedure and calculations were the same as those described by Babko and Gridchina[13]. The iodide ion was used as reference ion. The results are given in Table 2.

The relative dialysis coefficient of niobium in solutions containing compounds with Nb : $C_2O_4^{2-}$ ratios of 1 : 3 and 1 : 2 (experiments 2–5) remains almost constant, indicating that the dimensions of the molecules remain unchanged. However, in the solution with equal molar concentrations of oxalate ion and niobium (experiment 1), the relative dialysis coefficient is much smaller than that for experiments 2–5, indicating unambiguously that there is polymerisation of niobium in this solution.

Potentiometric Titration of Oxalate Solutions of Niobium

For the potentiometric titration, we took 50 ml of a solution containing 9.2×10^{-3} M niobium and 0.0298 M oxalate ion, and used 0.5 N NaOH solution in the titration. The titration curves for the oxalato-complex of niobium and the blanks are given in Fig. 5. The moles of hydrogen combined with one mole of oxalate ion at a pH of 1 and 3, calculated from curve 2, are 1.45 and 0.85 respectively. These values show satisfactory agreement with the 1.5 and 0.82 calculated from the dissociation constants of oxalic acid.
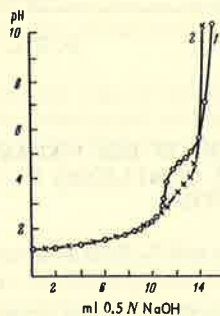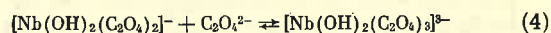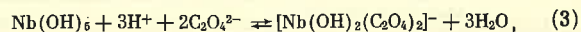

Fig.5. Potentiometric titration of oxalic acid solutions.
1) 0.0092 M Nb + 0.03 M $K_2C_2O_4$, pH 1, $I = 0.5$; 2) 0.03 M $K_2C_2O_4$, pH 1, $I = 0.5$.

At pH 1, the formation function of niobium oxalate is equal to 2 (Table 1). With allowance for this, we used curve 1 in Fig. 5 to calculate the quantity of alkali used up in the hydrolysis of the oxalato-complex of niobium. Three moles of alkali are used up for every mole of niobium combined in the complex at pH 1. The same value is obtained for an original solution with pH 3, in which the 1 : 3 complex predominates (Table 1).

A precipitate of niobium hydroxide begins to form during the titration at pH 3.5, and the precipitation of niobium is complete at pH 7. In some experiments it was established that, in agreement with the results of potentiometric titration, the formation of one mole of the oxalato-complex of niobium from the freshly-precipitated hydroxide requires three moles of hydrogen ion. Thus the formation of the oxalato-compounds of niobium can be represented by the following scheme:

$$Nb(OH)_5 + 3H^+ + 2C_2O_4^{2-} \rightleftharpoons [Nb(OH)_2(C_2O_4)_2]^- + 3H_2O, \quad (3)$$

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

Determination of the Equilibrium Constants for the Formation of the Oxalato-Complexes of Niobium

The equilibrium constant of reaction (3) can be determined[13] when the solubility of niobium hydroxide in the absence of complex-forming reagents is known. However, the published solubility data[14–16] are contradictory. Our attempt to determine the solubility of niobium hydroxide in solutions of HNO_3 and $HClO_4$ at pH 6–0.5 and $I = 0.5$ did not give a definite result. The activity in the final solutions varied in the range 0–20 counts min^{-1} for a specific activity of 20 000 counts min^{-1} for 1×10^{-3} mole niobium. The fluctuation in the results is apparently due to the marked tendency of niobium hydroxide to become colloidal[17,18].

If we regard the reactions involved in the formation of the oxalato-compounds as heterogeneous reactions[16] and carry out the experiments in such a way that niobium hydroxide precipitate is present in equilibrium with the solution, the equilibrium constants for reactions (3) and (4) can be written in the form:

$$K_1 = \frac{[Nb(OH)_2(C_2O_4)_2]^-}{[H^+]^3[C_2O_4^{2-}]^2} \quad (5)$$

$$K_1 \cdot K_2 = \frac{[Nb(OH)_2(C_2O_4)_3]^{3-}}{[H^+]^3[C_2O_4^{2-}]^3} \quad (6)$$

where K_2 is the consecutive stability constant.

In the presence of niobium hydroxide precipitate in solutions with $I = 0.5$, the greater part of the niobium is present as $[Nb(OH)_2(C_2O_4)_2]^-$ at pH ≤ 1, and as $[Nb(OH)_2 \cdot (C_2O_4)_3]^{3-}$ at pH ≥ 3 (Table 1). From a knowledge of the niobium concentration, the total oxalate ion concentration, the pH of the solution, and the dissociation constants of oxalic acid, it is possible to calculate approximately K_1 and K_1K_2 (Table 3).

The dissolution of niobium hydroxide is possibly a more complex process than indicated by Eqns. (3) and (4). We were unable, however, to detect any compounds apart from bis(oxalato)niobate and tris(oxalato)niobate, either in the solutions or in the precipitates in equilibrium with them. Presumably, therefore, Eqns. (3) and (4) and the

TABLE 3. Determination of the equilibrium constants for reactions (3) and (4) at $I = 0.5$.

pH	Niobium concentration × 10^3, M	Total oxalate ion concentration × 10^2, M	K_1	$K_1 K_2$
0.45	8.05	1.95	$0.87 \cdot 10^{12}$	
0.55	3.35	0.816	$1.74 \cdot 10^{12}$	
0.79	1.88	0.475	$1.74 \cdot 10^{12}$	
0.79	3.05	0.75	$1.39 \cdot 10^{12}$	
0.79	4.19	1.05	$0.84 \cdot 10^{12}$	
4.23	3.46	1.74		$0.97 \cdot 10^{17}$
4.29	6.23	2.88		$0.88 \cdot 10^{17}$
4.70	0.22	0.615		$1.26 \cdot 10^{17}$
4.88	0.94	1.60		$1.45 \cdot 10^{17}$
5.02	4.26	4.80		$2.10 \cdot 10^{17}$
5.04	1.43	2.76		$1.70 \cdot 10^{17}$
		Mean	$1.3 \cdot 10^{12}$	$1.4 \cdot 10^{17}$

TABLE 4. Comparison of the calculated and experimentally observed values.

pH	$10^2 \Sigma C_2O_4^{2-}$, M	$[C_2O_4^{2-}]$ found potentiometrically, M	$[C_2O_4^{2-}]$ calculated, M	Nb concentration found radiometrically, × 10^3, M	Calculated Nb concentration × 10^3, M	Calculated $[Nb(OH)_2(C_2O_4)_2]^-$ concentration × 10^3, M	Calculated $[Nb(OH)_2(C_2O_4)_3]^{3-}$ concentration × 10^3, M
0.45	1.95	$3.90 \cdot 10^{-7}$	$3.70 \cdot 10^{-7}$	8.05	8.26	7.95	0.316
0.55	0.816	$2.60 \cdot 10^{-7}$	$3.25 \cdot 10^{-7}$	3.35	3.19	3.08	0.107
0.79	1.05		$8.41 \cdot 10^{-7}$	4.20	4.27	3.92	0.210
1.02	0.815	$1.69 \cdot 10^{-6}$	$1.62 \cdot 10^{-6}$	3.35	3.47	2.96	0.516
2.85	1.83	$2.70 \cdot 10^{-4}$	$2.35 \cdot 10^{-4}$	5.30	5.31	0.20	5.11
4.23	1.74	$3.80 \cdot 10^{-3}$	$5.06 \cdot 10^{-3}$	3.46	3.71	0.0068	3.70
5.04	3.70	$2.80 \cdot 10^{-2}$	$2.85 \cdot 10^{-2}$	2.50	2.45	0.0008	2.45
5.02	4.80		$3.32 \cdot 10^{-2}$	4.40	4.46	0.0012	4.46

corresponding equilibrium constants (Table 3) correspond to the final stage of the dissolution of niobium hydroxide in the presence of oxalate ion.

To verify the values found for the equilibrium constants of reactions (3) and (4), we calculated the equilibrium concentrations of oxalate ion and the concentrations of niobium in solutions with different pH values. The solutions were in equilibrium with hydroxide precipitates.

Using the data in Table 1, expressions (5) and (6), and the dissociation constants of oxalic acid, we can readily set up the equation

$$3K_1 \cdot K_2 [H^+]^3 [C_2O_4^{2-}]^3 + 2K_1 [H^+]^3 [C_2O_4^{2-}]^2 + B[C_2O_4^{2-}] - \Sigma C_2O_4^{2-} = 0, (7)$$

where $B = 1 + \beta_1 [H^+] + \beta_2 [H^+]^2$, $\Sigma C_2O_4^{2-}$ is the total concentration of oxalate ion, determined by titration, and $[C_2O_4^{2-}]$ the equilibrium concentration of oxalate ion.

Expressions (5)–(7) can be used to calculate the equilibrium concentrations of oxalate ion and the concentrations of bis(oxalato)niobate and tris(oxalato)niobate from $\Sigma C_2O_4^{2-}$ and the hydrogen ion concentration. The calculated results and the experimentally observed values are given in Table 4. The satisfactory agreement between the calculated and experimental values confirms the correctness of the reactions which we have assumed to be involved in the formation of oxalato-compounds of niobium by the dissolution of niobium hydroxide in the pH range 0.5–5.

SUMMARY

Two stable complexes $[Nb(OH)_2(C_2O_4)_2]^-$ and $[Nb(OH)_2.(C_2O_4)_3]^{3-}$ are formed in oxalic acid solutions of niobium. The absorption spectrum of the complexes has $\lambda_{max} = 270$ nm.

In the absence of inert electrolytes, unstable polymeric compounds with $C_2O_4^{2-} : Nb \leqslant 1$ may be formed in solution.

Suggestions about the reactions involved in the formation and hydrolysis of the oxalato-compounds have been examined. The equilibrium constants of the reactions involved in the formation of the complexes $[Nb(OH)_2.(C_2O_4)_2]^-$ and $[Nb(OH)_2(C_2O_4)_3]^{3-}$, for solutions in equilibrium with hydroxide precipitates, have been calculated and the results verified experimentally; the values are 1.3×10^{12} and 1.4×10^{17} respectively.

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DETERMINATION OF THE FORMATION FUNCTIONS OF COMPLEXES IN THE UO_2^{2+}–$C_2O_4^{2-}$ SYSTEM

A.V.Stepanov and T.P.Makarova

There are defects in the methods of studying complex formation which are based on the measurement of an overall physical property of a solution:

$$y = \sum_0^N x_n c_n; \quad \varepsilon = \frac{y}{c_M} = \sum_0^N x_n \beta_n [A]^n \Big/ \sum_0^N \beta_n [A]^n . \quad (1)$$