

## Mathematical Modeling and Analysis of Equilibria in Solutions of Nb(V)

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**Abstract**—The processes of Nb(V) polycondensation in solutions of different alkalinity and acidity with a total Nb(V) concentration of  $2.0 \times 10^{-4}$ – $0.5 \times 10^{-4}$  mol/l ( $\mu = 1.0$  KCl) were refined using pH measurements, spectrophotometry, and mathematical modeling. It was demonstrated that, along with the hexaniobate ions, the dodecaniobate  $H_xNb_{12}O_{36}^{(12-x)-}$  ( $x = 2$ – $9$ ) ions can form in acidified solutions, while the tetra- and mononiobate ions can form in strongly alkaline solutions.

It is known that the state of niobium in alkaline and acidified solutions is characterized by a diversity of anionic forms differing in both the extent of polymerization and the degree of protonation. Apparently, the qualitative and quantitative compositions of the ionic niobium(V) forms are controlled by many factors, among which the pH value, the Nb(V) concentration, and the temperature should be mentioned first. Hexaniobate anions  $H_xNb_6O_{19}^{(8-x)-}$  ( $x = 0$ – $3$ ) are the most typical Nb(V) forms in solutions. However, the character of the processes occurring upon the acidification and alkalization of the niobate solutions, as well as the effect of the niobium(V) concentration on the extent of polymerization of the anionic forms still remains to be studied. The authors of [1] explored the polycondensation processes in the niobate solutions by the cryoscopic and potentiometric methods to suggest that the freshly prepared solutions of potassium hexaniobate “evolve” with time owing to the polycondensation into the  $Nb_{12}O_{36}^{12-}$  and  $H_2Nb_{12}O_{36}^{10-}$  ions through the dimerization of  $H_2Nb_6O_{19}^{6-}$  and  $H_3Nb_6O_{19}^{5-}$ , respectively. These dodecaniobate anions convert into various protonated  $H_xNb_{12}O_{36}^{(12-x)-}$  ( $x = 4$ – $6$ ) forms upon the acidification of a solution of potassium niobate. Although the existence of dodecaniobate anions was predicted by other authors as well [2, 3], the stability of the anionic dodecaniobate forms in solutions and the probability of their formation have not been assessed so far. It is customarily thought that the dodecaniobate anions depolymerize to hexaniobate anions upon the alkalization, while the latter decompose into the tetrameric  $[Nb_4O_{16}^{12-}, Nb_4O_{12}(OH)_4^{8-}]$  and monomeric forms in strongly alkaline solutions [4]. However, the lack of detailed information on the dodeca-, tetra-, and

mononiobate anions allows their existence in aqueous solutions to be considered as unproved.

The interpretation of the data used for putting forward one or another model for the polycondensation processes in niobate solutions is ambiguous, contradictory, and needs refinement. In this work, the pH-potentiometric and spectrophotometric data were used to study the state of Nb(V) ions in diluted aqueous solutions by mathematical modeling of interactions with the object of calculating the formation constants and extinction coefficients for the isopolyniobate ions.

The final goal of studying the equilibria by mathematical modeling is to determine the stoichiometry of the chemical forms coexisting in solution and to calculate the corresponding equilibrium constants. The problem is solved through the analysis and mathematical processing of the experimental correlations of the type “properties of solution–composition of solution.” To arrive at the quantitative result, one should find out the functional relationship between the measured physicochemical property (properties) of a solution and its analytical composition in the explicit or implicit form. Mathematically, this relationship is modeled by the following equations.

(1) Material balance equations, which represent, in essence, a mathematical model describing the experimental pH-metric curve. This model reveals the relationship between the equilibrium constants, initial concentrations, and equilibrium composition. The corresponding vector is a solution to the set of nonlinear equations of the form

$$f_i = c_i - \sum_{j=1}^s \xi_{ji} k_j \prod_{k=1}^s x_k^{\xi_{jk}} = 0,$$

where account is taken of the mass action law and  $i$  is the number of components involved in the complexation ( $i = 1, 2, 3 \dots n$ );  $c_i$  is the overall concentration of

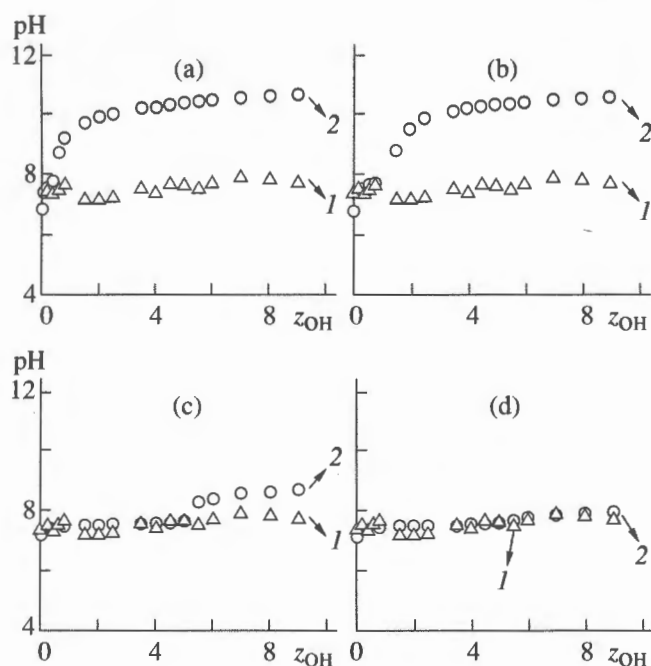


Fig. 1. Plots of pH against  $z_{\text{OH}}$  for the Nb(V)-OH-H<sub>2</sub>O system according to (1) pH measurements and (2) mathematical modeling for models (a) 1, (b) 3, (c) 4, and (d) 5.

the  $i$ th component;  $x_k$  is the equilibrium concentration of the  $k$ th component;  $\xi_{ji}$  is the stoichiometric coefficient corresponding to the  $i$ th component in the  $j$ th complex; and  $k_j$  is the formation constant of the  $j$ th complex.

(2) Equations linking measured property and the equilibrium concentrations of chemical forms:

$$A_v = \sum_{j=1}^s \epsilon_{vj} x_j,$$

where  $A_v$  is the optical density of solution at wavelength  $v$  and  $\epsilon_{vj}$  is the extinction coefficient of the  $j$ th complex at wavelength  $v$ .

The mathematical model allows the elaboration of a procedure for comparing the experimental data on the system of interest with the *a priori* postulated reaction scheme. Such a comparison makes it possible to determine how much the original hypothesis for the number and type of reactions (represented by the matrix of stoichiometric composition) fits the experimental data and to refine and determine the unknown equilibrium constants. The problem of mathematical modeling of the interactions in chemical systems represents an extremum problem in circumstances where the lack of an explicitly formulated functional relationship between the optimized index and the controlled parameter introduces uncertainty and where the output parameters of the object cannot be measured with the required accuracy. Such problems cannot be solved without invoking the search optimization methods. The optimum values of the

parameters must provide the smallest deviations of the calculated equilibrium properties from the experimental values of the corresponding parameters. The optimization criterion for these parameters may be chosen in various ways. The sum of the squares of differences between the calculated and experimental pH values; i.e., the

$$F = \sum_i (\text{pH}_i^{\text{theor}} - \text{pH}_i^{\text{exp}})^2,$$

functional, and the sum of squares of the differences between the calculated and experimental optical densities

$$F = \sum_v \sum_j (A_{jv}^{\text{theor}} - A_{jv}^{\text{exp}})^2$$

were chosen as a performance criterion for the model used in this work. A search for the function minimum was carried out by the deformed polyhedron method.

It often turns out that the modeling reveals several sets of constants fitting measurements equally well. Though being of nearly the same quality, such sets of equilibrium constants may sizably differ from one another, while the experimental data used do not allow different solutions to be discriminated. The uncertainty arises, first, if one checks several, rather than one, hypotheses, so that ambiguity in the constants is embodied in the physicochemical formulation of a problem; second, the functional relationship between the convergence criterion and the controlling parameters of a mathematical model chosen cannot be written in an explicit form, so that one cannot distinguish between the global and local minima during the course of a search for the function minimum. In our opinion, the problem of parameter determination becomes practically less ambiguous if one processes different experimental relationships obtained without changing the type of experiment.

For this purpose, the pH-metric and spectrophotometric data were invoked to carry out mathematical modeling of interactions with the aim of unambiguously revealing the state of niobium(V) ions in aqueous solutions and determining the corresponding formation constants for a series of solutions with a constant concentration of niobium ions [ $c_{\text{Nb(V)}} = 2.0 \times 10^{-4}$ ,  $1.0 \times 10^{-4}$ , and  $0.5 \times 10^{-4}$  mol/l,  $\mu = 1.0$  KCl] and various basicities  $z_{\text{OH}}$  ( $z_{\text{OH}} = c_{\text{OH}^-} / c_{\text{Nb(V)}}$ ) and for a series of solutions with a constant concentration of the Nb(V) ions [ $c_{\text{Nb(V)}} = 2.0 \times 10^{-4}$  mol/l,  $\mu = 1.0$  KCl] and various acidities  $z_{\text{H}}$  ( $z_{\text{H}} = c_{\text{H}^+} / c_{\text{Nb(V)}}$ ). The basicity was changed from 0 to 10 by introducing a KOH solution. The acidity was changed from 0 to 1 by introducing an HCl solution. The series were allowed to stand over a month to attain equilibrium state.

The electronic absorption spectra of the solutions were measured on a Specord UV-VIS spectrophotometer in the UV region ( $54000\text{--}32000\text{ cm}^{-1}$ ) in 1-cm thick quartz cells with the use of the absorbance and trans-

**Table 1.** Stoichiometry matrix, formation constants, and total concentrations for the equilibrium Nb(V)–OH<sup>–</sup>–H<sub>2</sub>O system

Particles	Components		Formation constants
	H <sub>2</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>10–</sup> (A)	OH <sup>–</sup> (B)	
H <sub>2</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>10–</sup>	1	0	$k_1$
OH <sup>–</sup>	0	1	$k_2$
HNb <sub>12</sub> O <sub>36</sub> <sup>11–</sup>	1	1	$k_3$
Nb <sub>12</sub> O <sub>36</sub> <sup>12–</sup>	1	2	$k_4$
H <sub>3</sub> Nb <sub>6</sub> O <sub>19</sub> <sup>5–</sup>	0.5	0	$k_5$
H <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> <sup>6–</sup>	0.5	1	$k_6$
HNb <sub>6</sub> O <sub>19</sub> <sup>7–</sup>	0.5	2	$k_7$
Nb <sub>6</sub> O <sub>19</sub> <sup>8–</sup>	0.5	3	$k_8$
Nb <sub>4</sub> O <sub>12</sub> (OH) <sub>4</sub> <sup>8–</sup>	1/3	14/3	$k_9$
Nb <sub>4</sub> O <sub>14</sub> (OH) <sub>2</sub> <sup>10–</sup>	1/3	20/3	$k_{10}$
Nb <sub>4</sub> O <sub>16</sub> <sup>12–</sup>	1/3	26/3	$k_{11}$
NbO <sub>2</sub> (OH) <sub>4</sub> <sup>3–</sup>	1/12	26/12	$k_{12}$
NbO <sub>6</sub> <sup>7–</sup>	1/12	74/12	$k_{13}$

Note:  $c_A/12 = \sum_{j=0}^2 [H_i Nb_{12} O_{36}] + 1/2 \sum_{j=0}^3 [H_i Nb_6 O_{19}] + 1/3 \sum_{i=0}^2 [Nb_4 O_{(16-2j)} (OH)_{2j}] + 1/12 \times \sum_{i=0}^1 [NbO_{(6-4i)} (OH)_{4j}] =$   
 $[A] + \sum_{j=3}^4 k_i [A] [B]^{i-2} + 0.5 \sum_{j=5}^8 k_i [A]^{0.5} [B]^{j-5} + 1/3 \sum_{j=9}^{11} k_i [A]^{1/3} [B]^{(j+5(j-8))} + 1/12 k_{12} [A]^{1/12} [B]^{26/12} +$   
 $1/12 k_{13} [A]^{1/12} [B]^{74/12}.$   
 $c_B = [OH] + \sum_{i=0}^1 (2-i) [H_i Nb_{12} O_{36}] + \sum_{i=0}^3 (3-j) [H_i Nb_6 O_{19}] + \sum_{i=0}^2 (26-6j) / 3 [Nb_4 O_{16-2j} (OH)_{2j}] + 26/12 [NbO_2 (OH)_4] +$   
 $74/12 [NbO_6] - 10^{-7} = [B] + \sum_{i=3}^4 k_j (i-2) [A] [B]^{j-2} + \sum_{j=5}^8 k_j (j-5) [A]^{0.5} [B]^{j-5} + \sum_{j=9}^{11} k_j (j+5(j-8)) [A]^{1/3} [B]^{(j+5(j-8))} +$   
 $26/12 k_{12} [A]^{1/12} [B]^{26/12} + 74/12 k_{13} [A]^{1/12} [B]^{74/12} - 10^{-7}.$

**Table 2.** Modeling of the Nb(V)–OH<sup>–</sup>–H<sub>2</sub>O system according to the data of pH and spectrophotometric measurements

No.	Model	$F_{\min}$			
		data of pH measurements*			spectrophotometric data
		1	2	3	
1	HNb <sub>12</sub> O <sub>36</sub> <sup>11–</sup> , Nb <sub>12</sub> O <sub>36</sub> <sup>12–</sup> , H <sub>3</sub> Nb <sub>6</sub> O <sub>19</sub> <sup>5–</sup> , H <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> <sup>6–</sup>	108.95	149.23	119.2	327.4
2	Model 1 + HNb <sub>6</sub> O <sub>19</sub> <sup>7–</sup> + Nb <sub>6</sub> O <sub>19</sub> <sup>8–</sup>	94.32	121.20	89.17	156.9
3	H <sub>3</sub> Nb <sub>6</sub> O <sub>19</sub> <sup>5–</sup> , H <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> <sup>6–</sup> + HNb <sub>6</sub> O <sub>19</sub> <sup>7–</sup> , Nb <sub>6</sub> O <sub>19</sub> <sup>8–</sup>	74.27	114.76	82.56	155.6
4	Model 3 + Nb <sub>4</sub> O <sub>16</sub> <sup>12–</sup>	2.90	0.66	4.5	74.9
5	Model 4 + NbO <sub>6</sub> <sup>7–</sup>	0.57	0.35	0.24	1.09

\*  $c_{Nb(V)}^{\text{tot}} = 0.5 \times 10^{-4}$  (1),  $1.0 \times 10^{-4}$  (2),  $2.0 \times 10^{-4}$  mol/l (3).

**Table 3.** Stoichiometry matrix, formation constants, and total concentrations for the equilibrium Nb(V)–H<sup>+</sup>–H<sub>2</sub>O system ( $c_{\text{Nb(V)}}^{\text{tot}} = 2 \times 10^{-4}$  mol/l)

Particles	Components		Formation constants
	H <sub>3</sub> Nb <sub>6</sub> O <sub>19</sub> <sup>5-</sup> (A)	H <sup>+</sup> (B)	
H <sub>3</sub> Nb <sub>6</sub> O <sub>19</sub> <sup>5-</sup>	1	0	$k_1$
H <sup>+</sup>	0	1	$k_2$
H <sub>2</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>10-</sup>	2	0	$k_3$
H <sub>3</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>9-</sup>	2	1	$k_4$
H <sub>4</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>8-</sup>	2	2	$k_5$
H <sub>5</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>7-</sup>	2	3	$k_6$
H <sub>6</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>6-</sup>	2	4	$k_7$
H <sub>7</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>5-</sup>	2	5	$k_8$
H <sub>8</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>4-</sup>	2	6	$k_9$
H <sub>9</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>3-</sup>	2	7	$k_{10}$
H <sub>10</sub> Nb <sub>12</sub> O <sub>36</sub> <sup>2-</sup>	2	8	$k_{11}$

Note:  $c_A/6 = [\text{H}_3\text{Nb}_6\text{O}_{19}] + \sum_{i=2}^{10} [\text{H}_i\text{Nb}_{12}\text{O}_{36}] = [\text{A}] + 2 \sum_{i=3}^{11} k_i [\text{A}]^2 [\text{B}]^{i-3}$ .

$$c_B = [\text{H}] + \sum_{i=0}^8 i [\text{H}_i\text{Nb}_{12}\text{O}_{36}] - 10^{-7} = [\text{B}] + \sum_{i=0}^8 j k_{j+3} \times [\text{A}]^2 [\text{B}]^i - 10^{-7}.$$

mittance scales 0–100% relative to water. The pH values were monitored by a universal EV-34 pH meter. All measurements were made at a temperature of  $25 \pm 0.1^\circ\text{C}$ .

## RESULTS AND DISCUSSION

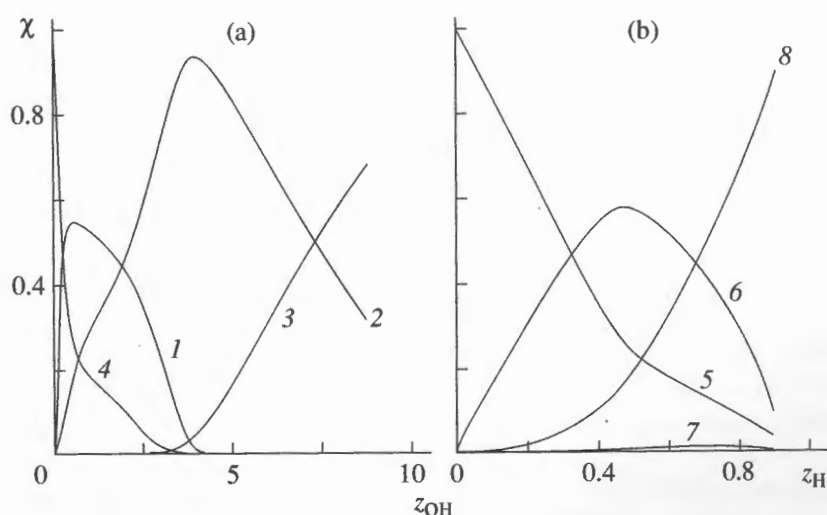
We invoked the literature data and our previous data [3] to formulate the hypothesis for the interaction processes occurring in the Nb(V) solutions of various basicities. The hypothesis was based on the following positions, whose validity was checked in the course of mathematical modeling:

(1) the protonated hexaniobate ions H<sub>3</sub>Nb<sub>6</sub>O<sub>19</sub><sup>5-</sup> and H<sub>2</sub>Nb<sub>6</sub>O<sub>19</sub><sup>6-</sup> and their dimers Nb<sub>12</sub>O<sub>36</sub><sup>12-</sup> and H<sub>2</sub>Nb<sub>12</sub>O<sub>36</sub><sup>10-</sup> can be present in solutions at low  $z_{\text{OH}}$  values. These species can form upon a deep hydrolysis that is favored by the low Nb(V) concentration in solutions ( $2.5 \times 10^{-4}$ – $5 \times 10^{-5}$  mol/l) and upon holding the latter for a month to initiate polycondensation. For this reason, the H<sub>2</sub>Nb<sub>12</sub>O<sub>36</sub><sup>10-</sup> particle was chosen as a starting component in the formation of the stoichiometry matrix for the system of interest (Table 1), under the assumption that the hexaniobate ions H<sub>3</sub>Nb<sub>6</sub>O<sub>19</sub><sup>5-</sup> are present in the solution in small amounts;

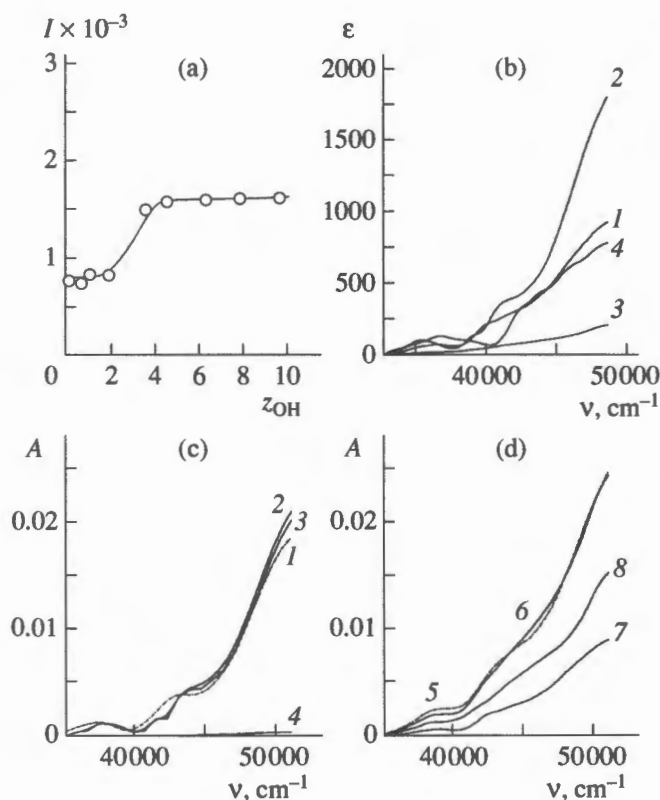
(2) upon gradual alkalization, the dodecaniobate anions can depolymerize to hexaniobate anions that, in turn, can convert from the more protonated into the less protonated forms, down to Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup>;

(3) upon further increase in alkalinity, either the hexaniobate anions decompose to tetra- and mononiobates or, otherwise, the free OH<sup>-</sup> ions are accumulated.

The results of modeling are demonstrated in Table 2 and Fig. 1. With the initial system corresponding to model 1, the value of objective function ( $F_{\text{min}}$ ) allowing for the discrepancy between the experimental and calculated data was found to be large (Fig. 1a). Whereas

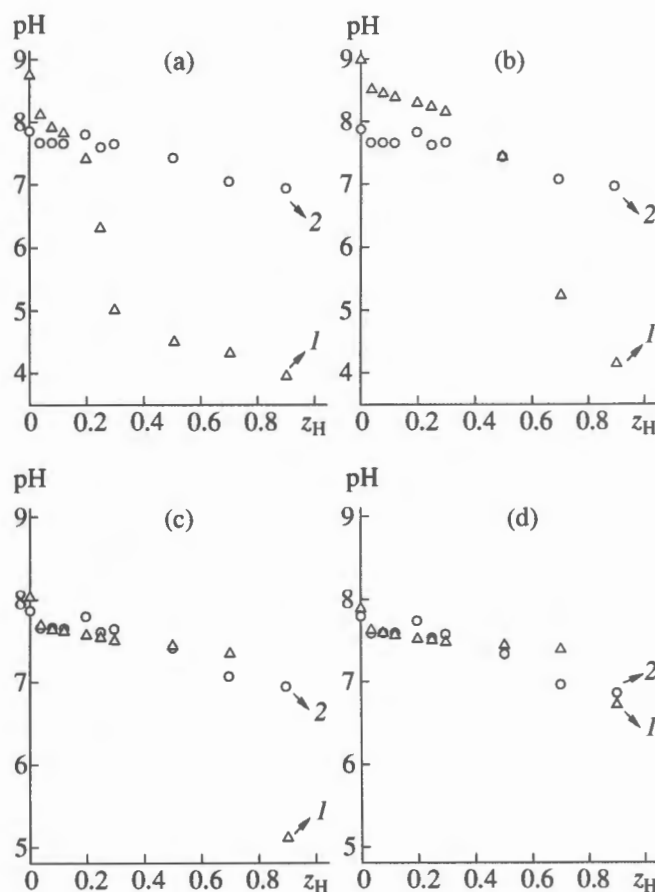


**Fig. 2.** Distribution curves for the (1) Nb<sub>6</sub>O<sub>19</sub><sup>8-</sup>, (2) Nb<sub>4</sub>O<sub>16</sub><sup>12-</sup>, (3) NbO<sub>6</sub><sup>7-</sup>, (4, 5) H<sub>2</sub>Nb<sub>12</sub>O<sub>36</sub><sup>10-</sup>, (6) H<sub>7</sub>Nb<sub>12</sub>O<sub>36</sub><sup>5-</sup>, (7) H<sub>9</sub>Nb<sub>12</sub>O<sub>36</sub><sup>3-</sup>, and (8) H<sub>10</sub>Nb<sub>12</sub>O<sub>36</sub><sup>2-</sup> niobate ions vs. (a) alkalinity and (b) acidity of a medium.



**Fig. 3.** (a) Integrated intensity of the electronic absorption spectrum of the Nb(V)-OH-H<sub>2</sub>O system as a function of  $z_{OH}$ ; (b) frequency-dependent extinction coefficients of the (1)  $Nb_6O_{19}^{8-}$ , (2)  $Nb_4O_{16}^{12-}$ , (3)  $NbO_6^{7-}$ , and (4)  $H_2Nb_{12}O_{36}^{10-}$  niobate ions; and (c, d) (1, 5) experimental absorption spectrum of the Nb(V)-OH-H<sub>2</sub>O system and the spectra calculated for (2, 6) model 5 and the (3)  $Nb_6O_{19}^{8-}$ , (4)  $H_2Nb_{12}O_{36}^{10-}$ , (7)  $Nb_4O_{16}^{12-}$ , and (8)  $NbO_6^{7-}$  ions at  $z_{OH}$  = (c) 0.2 and (d) 10.

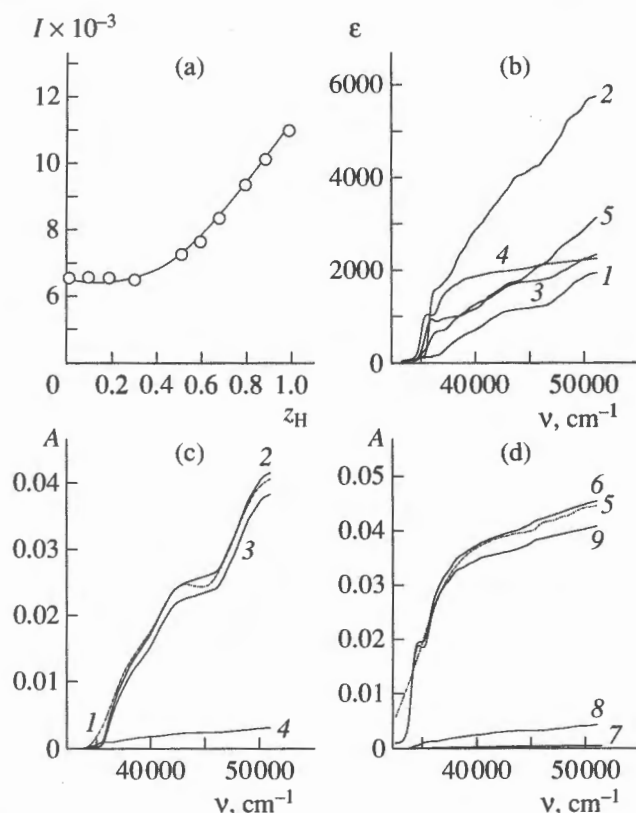
model 3 satisfactorily describes the system below  $z_{OH} = 1.5$  (Fig. 1b; the experimental and calculated data virtually coincide), there is a jump in the pH curve at high  $z_{OH}$  values because of an appearance of the free OH<sup>-</sup> ions in the system. To reduce the value of the objective function, one has to include the particles whose formation requires many OH<sup>-</sup> groups. Whereas the objective function decreases only slightly upon adding  $HNb_6O_{19}^{7-}$  and  $Nb_6O_{19}^{8-}$ , the addition of  $Nb_4O_{16}^{12-}$  results in a sharp decrease in  $F_{min}$ . However, the discrepancy between the experimental and calculated data in the  $z_{OH} > 5$  region is still appreciable (Fig. 1c). Probably, the decomposition in strongly alkaline solutions proceeds deeper and gives monomeric anionic forms. The experimental and calculated data virtually coincide upon an addition of the  $NbO_6^{7-}$  particles to the model (Fig. 1d, Table 2).



**Fig. 4.** Plots of pH against  $z_H$  for the Nb(V)-H<sup>+</sup>-H<sub>2</sub>O system according to (1) pH measurements and (2) mathematical modeling for models (a) 1, (b) 3, (c) 5, and (d) 7.

Therefore, among the systems examined, model 5, composed of the  $H_2Nb_{12}O_{36}^{10-}$ ,  $H_3Nb_6O_{19}^{5-}$ ,  $H_2Nb_6O_{19}^{6-}$ ,  $HNb_6O_{19}^{7-}$ ,  $Nb_6O_{19}^{8-}$ ,  $Nb_4O_{16}^{12-}$ , and  $NbO_6^{7-}$  forms, has the smallest objective function. The fact that the calculated and experimental data satisfactorily coincide (the discrepancy between them is within the error of pH measurements,  $\epsilon = 0.046$ ) indicates that this model adequately describes the solution equilibria between different forms of niobate anions. The extent of accumulation of the  $H_3Nb_6O_{19}^{5-}$ ,  $H_2Nb_6O_{19}^{6-}$ ,  $HNb_6O_{19}^{7-}$  particles is small, and one may believe that these anionic forms virtually do not form under the experimental conditions chosen. An analysis of the resulting distribution curves for the series with different concentrations of Nb(V) ions showed that the dimerization of the hexaniobate ions depends on the concentration. Whereas the amount of dodecaniobate ions at  $c_{Nb(V)} = 2.0 \times$





**Fig. 5.** (a) Integrated intensity of the electronic absorption spectrum of the Nb(V)-H<sup>+</sup>-H<sub>2</sub>O system as a function of  $z_{\text{H}}$ ; (b) frequency-dependent extinction coefficients of the (1)  $\text{H}_2\text{Nb}_{12}\text{O}_{36}^{10-}$ , (2)  $\text{H}_7\text{Nb}_{12}\text{O}_{36}^{5-}$ , (3)  $\text{H}_9\text{Nb}_{12}\text{O}_{36}^{3-}$ , and (4)  $\text{H}_{10}\text{Nb}_{12}\text{O}_{36}^{2-}$  dodecaniobate ions; and (c, d) (1, 5) experimental absorption spectrum of the Nb(V)-H<sup>+</sup>-H<sub>2</sub>O system and the spectra calculated for (2, 6) model 7 and the (3)  $\text{H}_2\text{Nb}_{12}\text{O}_{36}^{10-}$ , (4, 7)  $\text{H}_7\text{Nb}_{12}\text{O}_{36}^{5-}$ , (8)  $\text{H}_9\text{Nb}_{12}\text{O}_{36}^{3-}$ , and (9)  $\text{H}_{10}\text{Nb}_{12}\text{O}_{36}^{2-}$  ions at  $z_{\text{H}}$  = (c) 0.08 and (d) 1.0.

$10^{-4}$  mol/l exceeds 90%, it is no greater than 30% at  $c_{\text{Nb(V)}} = 0.5 \times 10^{-4}$  mol/l at the same point. The  $z_{\text{OH}}$ -dependent distribution of the forms is shown in Fig. 2a.

The spectrophotometric studies of the Nb(V)-OH<sup>-</sup>-H<sub>2</sub>O system showed that the absorption intensity ( $I$ ) increases with alkalinity in a highly nonmonotonic fashion (Fig. 3a). Two domains of  $z_{\text{OH}}$  values, where the integrated intensity remains virtually unchanged, can be clearly recognized in the curve: 0–1.5 and 3–10. A sharp rise in intensity at  $z_{\text{OH}} = 2.0$  and 3.0 occurs in the region where the destruction of the dodeca- and hexaniobate anions occurs with the formation of the tetranio- bate anions. To confirm the equilibrium model obtained by the mathematical modeling of the results of pH measurements, PC simulation of the spectroscopic data was carried out to calculate the extinction coefficients for the relevant forms. The  $F_{\text{min}}$  values at differ-

ent modeling steps are shown in Table 2. Model 5 and the resulting formation constants ( $k_8 = 8.4 \times 10^{17}$ ,  $k_{11} = 1.2 \times 10^5$ , and  $k_{13} = 6.36 \times 10^{35}$ ) provide satisfactory description of the spectrophotometric data in the whole range of the  $z_{\text{OH}}$  values studied (Figs. 3c, 3d). The extinction coefficients of niobate ions as functions of a wavelength are shown in Fig. 3b.

To obtain unambiguous data on the polycondensation processes occurring in solutions of Nb(V), a series of Nb(V)-H<sup>+</sup>-H<sub>2</sub>O solutions was studied by pH measurements and spectrophotometry, and the results were used for the mathematical modeling and a search for the equilibrium model. The stoichiometry matrix and the material balance equations are given in Table 3. The mathematical modeling steps and the corresponding objective functions are presented in Table 4 and Fig. 4. The calculated pH and optical density values become progressively closer to the experimental data as the more and more protonated forms of the dodecaniobate anions are successively included into the model. A model including the  $\text{H}_2\text{Nb}_{12}\text{O}_{36}^{10-}$ ,  $\text{H}_5\text{Nb}_{12}\text{O}_{36}^{7-}$ ,  $\text{H}_6\text{Nb}_{12}\text{O}_{36}^{6-}$ ,  $\text{H}_7\text{Nb}_{12}\text{O}_{36}^{5-}$ ,  $\text{H}_8\text{Nb}_{12}\text{O}_{36}^{4-}$ ,  $\text{H}_9\text{Nb}_{12}\text{O}_{36}^{3-}$ , and  $\text{H}_{10}\text{Nb}_{12}\text{O}_{36}^{2-}$  particles provides good convergence of the experimental and calculated data (Table 4, Figs. 4d, 5c, 5d). The amounts of the formed  $\text{H}_5\text{Nb}_{12}\text{O}_{36}^{7-}$ ,  $\text{H}_6\text{Nb}_{12}\text{O}_{36}^{6-}$ , and  $\text{H}_8\text{Nb}_{12}\text{O}_{36}^{4-}$  ions are very small. The fact that the particle distribution in the system of interest (Fig. 2) agrees well with the results of calculation of the particle distribution in alkaline solutions provides further proof that the model chosen adequately describes the real process. The extinction coefficients of the dodecaniobate ions are presented in Fig. 5b. The mathematical modeling yields the following optimized equilibrium constants for the Nb(V)-H<sup>+</sup>-H<sub>2</sub>O system:  $k_3 = 2.86 \times 10^{23}$ ,  $k_8 = 1.06 \times 10^{61}$ ,  $k_{10} = 6.85 \times 10^{66}$ , and  $k_{11} = 1.09 \times 10^{78}$ .

The study of the polycondensation processes in solutions of Nb(V) by pH measurements, spectrophotometry, and mathematical modeling has shown that the dodecaniobate  $\text{H}_2\text{Nb}_{12}\text{O}_{36}^{10-}$  ions, the dimers of the  $\text{H}_3\text{Nb}_6\text{O}_{19}^{5-}$  ions, are present in solutions at low concentration of the Nb(V) ions and  $z_{\text{OH}}$ ,  $z_{\text{H}} = 0$ . The results of mathematical modeling of a series with different concentrations of the Nb(V) ions give evidence that the dimerization of the hexaniobate ions depends on the Nb(V) concentration. The acidification of solutions gives rise to the more protonated forms of dodecaniobate anions, among which  $\text{H}_7\text{Nb}_{12}\text{O}_{36}^{5-}$  and  $\text{H}_{10}\text{Nb}_{12}\text{O}_{36}^{2-}$  are the most stable. The dodecaniobate ions rapidly convert into hexaniobate ions upon the introduction of even small amounts of alkali. The dodecaniobate and hexaniobate ions decompose into the tet-

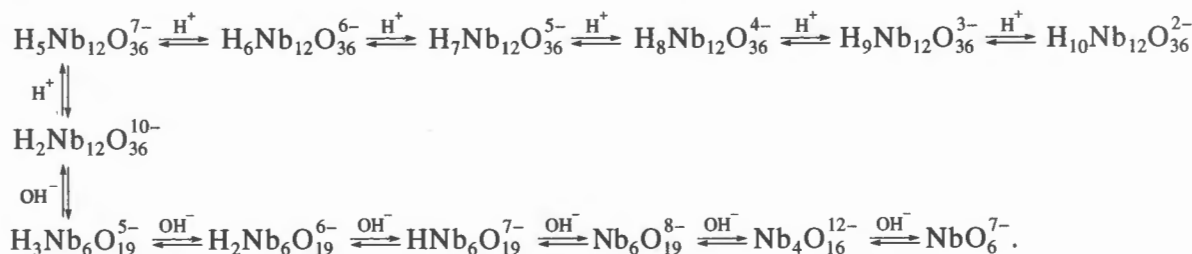
**Table 4.** Modeling of the Nb(V)-H<sup>+</sup>-H<sub>2</sub>O system according to the data of pH and spectrophotometric measurements ( $c_{\text{Nb(V)}}^{\text{tot}} = 2 \times 10^{-4}$  mol/l)

No.	Model	$F_{\text{min}}$	
		data of pH measurements	spectrophotometric data
1	$\text{H}_2\text{Nb}_{12}\text{O}_{36}^{10-}$ , $\text{H}_3\text{Nb}_{12}\text{O}_{36}^{9-}$ , $\text{H}_4\text{Nb}_{12}\text{O}_{36}^{8-}$ , $\text{H}_5\text{Nb}_{12}\text{O}_{36}^{7-}$	55.01	764.8
2	Model 1 + $\text{H}_6\text{Nb}_{12}\text{O}_{36}^{6-}$	21.60	522.4
3	Model 2 + $\text{H}_7\text{Nb}_{12}\text{O}_{36}^{5-}$	11.08	198.43
4	$\text{H}_2\text{Nb}_{12}\text{O}_{36}^{10-}$ , $\text{H}_5\text{Nb}_{12}\text{O}_{36}^{7-}$ , $\text{H}_6\text{Nb}_{12}\text{O}_{36}^{6-}$ , $\text{H}_7\text{Nb}_{12}\text{O}_{36}^{5-}$	10.91	147.22
5	Model 4 + $\text{H}_8\text{Nb}_{12}\text{O}_{36}^{4-}$	8.53	54.9
6	Model 5 + $\text{H}_9\text{Nb}_{12}\text{O}_{36}^{3-}$	2.9	29.8
7	Model 6 + $\text{H}_{10}\text{Nb}_{12}\text{O}_{36}^{2-}$	0.46	2.61

rameric and monomeric forms in strongly alkaline solutions.

The study presented in this work allows the follow-

ing scheme to be suggested for the polycondensation processes occurring in an aqueous solution of Nb(V) after establishing equilibrium:



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