donor groups, the changes in the infrared spectrum of $Cu_2A.5H_2O$ on dehydration would be similar to those for $K_2[CuA].3H_2O$ and $Ca[CuA].4H_2O$.   In the latter the A^{4-} ion is sexidentate[7] with respect to the copper atom, and water is not present directly in the Cu^{2+} coordination sphere, so that unsaturation of the Cu^{2+} coordination sphere apparently does not arise when these compounds are dehydrated.

An interesting feature is that the dehydration of the complexonato-compounds of copper which we studied is not accompanied by a change in the values of the ν^{C-N} and ν^{C-H} frequencies. These frequencies have the same values for hydrated and anhydrous specimens of the given complexonato-compounds (Table 3).   The nature of the ν^{C-N} frequency, however, is different for the hydrated and anhydrous specimens of Cu_2A and the salts $K_2[CuA]$ and $Ca[CuA]$.   Thus in the spectrum of Cu_2A the ν^{C-N} band at 1090 cm^{-1} is not split, whereas the spectra of $K_2[CuA]$ and $Ca[CuA]$ show two bands ($\nu^{C-N} = 1110$ cm^{-1} and 1090 cm^{-1}). The splitting of the ν^{C-N} bands into two components can be regarded as a result of the interaction of two C−N bonds. This interaction is probable in so far as the compounds $K_2[CuA]$ and $Ca[CuA]$, containing sexidentate EDTA, have a five-membered ethylenediamine ring including both C−N bonds. On the other hand, the presence of only one narrow ν^{C-N} band in the infrared spectra of the Cu_2A specimens can be taken as an indication that there is no interaction between two C−N bonds.   This may be due to the fact that in the Cu_2A molecule the EDTA functions as two independent terdentate groups (two aceto-groups and a nitrogen atom), each of which forms the coordination sphere of one copper atom.   Thus these facts lead to the conclusion that the positions of the two copper atoms are equivalent in anhydrous and hydrated Cu_2A.

The spectra of the aqueous solutions of all the complexonato-compounds of copper which we studied (Nos. 4 and 5 in Table 3 and Fig. 3) are identical; they show none of the characteristic features associated with the ν^{C-O} splitting and displacement resulting from the formation of hydrogen bonds (hydrated $K_2[CuA]$ and $Ca[CuA]$) or from covalent Cu−O bonds (anhydrous Cu_2A).   Complete hydration apparently takes place in solution and all the bonds between the copper ion and EDTA oxygen are replaced by bonds with the oxygen of water molecules.   The bands due to the ν^{C-N} stretching vibrations cannot be observed directly in the spectra of the dissolved complexonato-compounds of copper, owing to superimposition of the bands due to the ν^{D-O} stretching vibrations of the heavy water. The covalent Cu−N bond is not broken when the complexonato-compounds dissolve in water, as indicated by the fact that the frequencies of the ν^{C-H} vibrations in the spectra of the dissolved compounds (curves 4 and 5 in Fig. 3) remain unchanged relative to the spectra of the solid compounds (there is a good correlation between the values of the ν^{C-H} and ν^{C-N} frequencies[16]).

It is difficult, on the basis of the infrared spectra of the dissolved complexonato-compounds, to say whether the structure which we have proposed for solid Cu_2A is preserved in solution or whether the Cu_2A, in which the positions of the copper atoms are equivalent, undergoes rearrangement to $Cu[CuA]$, in which one copper atom is an "outer-sphere" atom and the second coordinates all six donor groups of EDTA.   It may be assumed, however, that in the supersaturated solutions at least, equilibrium is established between these two forms: the tendency of Cu_2A to form supersaturated solutions may in fact be due to the slow rate of conversion of one form of Cu_2A into the other.

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COMPLEX FORMATION BY NIOBIUM HYDROXIDE WITH EDTA

G. A. Volkova and V. G. Sochevanov

Niobium hydroxide is amphoteric.   In the absence of complex-forming substances its solubility is insignificant; for pH in the range 0.0–7.0 the niobium concentration in the solution is 1.4×10^{-5} M.[1]   In the presence of EDTA the amount of niobium in solution rises sharply and solutions stable in time can be obtained at pH from 2 to 5.   As Ferret and Milner[2] and later Kirby and Freiser[3] showed, the solutions of the niobium complexonate are polarographically active.

This paper describes a polarographic investigation of the mechanism of reaction of niobium hydroxide with EDTA and the calculation of the instability constant for this process.

The solution of the niobium complexonate was prepared by adding a sulphuric acid solution of niobium to an alkaline solution of Komplexon III.   The pH of the solution was

brought to 1–6. It was heated to boiling point, cooled, and polarographed with a dropping mercury electrode. Oxygen was removed by purging the solution with nitrogen. The polarographic characteristics of such solutions by ordinary, a.c., and oscillographic polarography showed that:
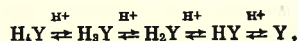
(1) the reduction of the niobium complexonate proceeds in two stages and one electron participates in each stage;

(2) at pH 4 the half-wave potentials are $E_{1/2}$ = -0.76 V, $E_{1/2}$ = -1.2 V (s.c.e.);

(3) the reduction at the first stage is reversible, a diffusion process; that at the second stage is irreversible;

(4) $E_{1/2}$ for the first stage is a function of the pH. $\Delta E/\Delta pH$ = 0.12 V pH^{-1}. This indicates that two hydrogen ions are involved in the reduction of the niobium complexonate. $E_{1/2}$ for the second wave is independent of the pH;

(5) the limiting current of the polarographic wave is independent of the presence in the solution of sulphate ions and of the concentration interval from 0.02 to 0.4 M, but depends on the EDTA concentration in the solution. As the EDTA concentration is raised the current rises and reaches a maximum, as Fig. 1a shows, when there is a fiftyfold excess of EDTA in relation to the niobium;

(6) the limiting current for a fixed excess of EDTA depends on the pH of the solution (Fig. 1b). At pH from 3.0 to 3.5 the limiting current is maximal;

(7) at pH from 2.5 to 3.5 the limiting current is proportional to the concentration of niobium in the solution.

The results show that the polarographic current set up is due to the formation in the solution of niobium complexonate and that the more the complexonate the higher the polarographic current. The equilibrium of the reaction for the formation of niobium complexonate depends both on the EDTA concentration in the solution and on the pH. With sufficient excess of EDTA in the pH range 3.0–3.5 the current is maximal. At a niobium concentration of 3.76×10^{-4} M the current is 1.50 μA and at a niobium concentration of 1.50×10^{-4} M 0.60 μA According to points 5–7 the yield of complexonate,

$$B = \frac{\text{complexonate concentration}}{\text{initial niobium concentration}}$$

at the specified pH has a maximal value, close to unity.

At pH < 3.0 the yield of complexonate falls owing to displacement of the equilibrium of the reaction of deprotonation of EDTA,

$$H_4Y \overset{H+}{\rightleftarrows} H_3Y \overset{H+}{\rightleftarrows} H_2Y \overset{H+}{\rightleftarrows} HY \overset{H+}{\rightleftarrows} Y,$$

to the side of the formation of less dissociated forms of EDTA anions, which, as is known, brings about an increase
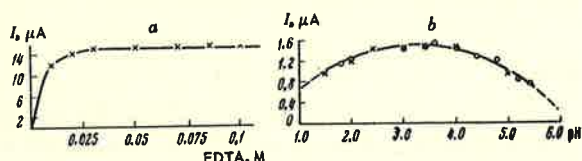
in the hydrogen function $\Phi_{EDTA} = f[H^+]$.[4] At pH > 3.5 the yield of complexonate falls, owing to the displacement of the equilibrium for the dissociation of niobium hydroxide,

$$Nb(OH)_5 \overset{H+}{\rightleftarrows} Nb(OH)_4 \overset{H+}{\rightleftarrows} Nb(OH)_3 \overset{H+}{\rightleftarrows} Nb(OH)_2 \overset{H+}{\rightleftarrows} Nb(OH) \overset{H+}{\rightleftarrows} Nb,$$

towards the side of the compounds richer in hydroxyls, which leads to an increase in the hydrogen function $F = f(OH^-) = \xi(H^+)$[4] as the solution becomes more alkaline.

The polarographic measurements (Fig. 1b) allow the variation of the yield of complex with the pH of the solution to be calculated.

Whereas at pH 3.4 all the niobium is converted into the complexonate, that is, the yield of complex is unity, at other pH it can be considered as the ratio of values of the polarographic currents:

$$B = \frac{I}{I_{max}}.$$

From the results on yields it is easy to calculate the conventional instability constant of the complex[5], which is[6]:

$$K = K_{instab} \cdot \Phi \cdot F = \frac{(A - B) \cdot (1 - B) \cdot c_M}{B} = f(H),$$

where c_M is the total concentration of niobium in the solution, M; $A = c_Y/c_M$; c_Y is the total concentration of EDTA in the solution, M; B the experimental value of the yield, K the conventional instability constant of the niobium complexonate; and K_{instab} the concentration instability constant of the niobium complexonate.

Table 1 gives for various pH the conventional instability constants of niobium complexonate K calculated from the experimental results.

The values of K_{instab} and F in the given equation are unknown. It is possible to calculate the hydrogen functions F if the consecutive dissociation constants of niobium hydroxide and the form of dissociated hydroxide which is capable of reaction with EDTA are known.

It is easy to show that for each of the forms of dissociation of niobium hydroxide the variation of the functions F

TABLE 1. Conventional instability constants for niobium complexonate at solution pH from 1 to 6.

pH	I_{lp}, μA*	$B = \dfrac{I_l}{I_{max}}$	c_Y, M**	c_M, M	K	$\log K$	$\log \Phi$	$\log \theta$	$pH_1 - pH_2$	$\log \theta = n$ $\dfrac{}{\Delta pH}$
1.0	0.430	0.287	$7.95 \cdot 10^{-4}$	$3.76 \cdot 10^{-4}$	$1.7 \cdot 10^{-5}$	-2.767	17.7	—	—	—
2.0	1.180	0.786	$7.2 \cdot 10^{-4}$	$3.76 \cdot 10^{-4}$	$1.15 \cdot 10^{-4}$	-3.939	13.6	2 93	1.0	2.93
3.0	1.460	0.975	$3.82 \cdot 10^{-3}$	$3.76 \cdot 10^{-4}$	$8.8 \cdot 10^{-5}$	-4.056	10.6	5.82	2.0	2.91
4.0	1.443	0.965	$5 \cdot 10^{-3}$	$3.76 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	-2.74	8.5	9.23	3.0	3.07
5.0	0.937	0.625	$5 \cdot 10^{-3}$	$3.76 \cdot 10^{-4}$	$3.0 \cdot 10^{-2}$	-1.523	6.5	12.45	4.0	3.13
6.0	0.150	0.100	$5 \cdot 10^{-3}$	$3.76 \cdot 10^{-4}$	$4.5 \cdot 10^{-1}$	-0.346	4.6	15.52	5.0	3.10

Mean 3.03

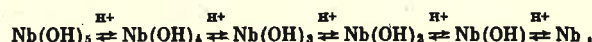| pH	I_{lp}, μA*	$B = \dfrac{I_l}{I_{max}}$	c_Y, M**	c_M, M	K	$\log K$	$\log \Phi$	$\log \theta$	$pH_1 - pH_2$	$\log \theta = n$ $\dfrac{}{\Delta pH}$
1.0	0.245	0.376	$7.46 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$1.15 \cdot 10^{-5}$	-2.60	17.7	--	--	--
2.0	0.525	0.875	$5.51 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$0.6 \cdot 10^{-4}$	-4.22	13.6	2.48	1.0	2.5
3.0	0.585	0.975	$3.6 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	$0.66 \cdot 10^{-4}$	-3.06	10.6	6.64	2.0	3.3
4.0	0.525	0.875	$5 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	$7.1 \cdot 10^{-3}$	-2.15	8.5	9.65	3.0	3.21
5.0	0.300	0.50	$5 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	$4.98 \cdot 10^{-2}$	-1.30	6.5	12.5	4.0	3.0

Mean 3.00

Fig. 1. Variation of the limiting current for the reduction of niobium complexonate with EDTA concentration (a), and solution pH (b) at $c_{Nb} = 3.76 \times 10^{-4}$ M:
a) pH 4.0; b) EDTA concentration 5×10^{-2} M.

* Mean value from the results of three experiments.
** At pH = 1–3 the solubility of EDTA was calculated from published data[7] with allowance for the quantity of EDTA bound in the complex with niobium.

with the hydrogen ion concentration will be expressed by the following equations:

$$F_0 = \frac{c_M}{Nb(OH)_5} = 1 + \frac{H\alpha}{W} + \frac{H_2\alpha_1\alpha_2}{W_2} + \frac{H^3\alpha_1\alpha_2\alpha_3}{W_3} + \frac{H^4\alpha_1\alpha_2\alpha_3\alpha_4}{W_4} + \frac{H^5\alpha_1\alpha_2\alpha_3\alpha_4\alpha_5}{W_5}$$

$$F_1 = \frac{c_M}{Nb(OH)_4} = \frac{W}{H\alpha} + 1 + \frac{H\alpha}{W} + \frac{H^2\alpha_2\alpha_3}{W^2} + \frac{H^3\alpha_2\alpha_3\alpha_4}{W^3} +$$
$$+ \frac{H^4\alpha_2\alpha_3\alpha_4\alpha_5}{W^4} = F_0\frac{W}{H\alpha}$$

$$F_2 = \frac{c_M}{Nb(OH)_3} = \frac{W^2}{H^2\alpha_2\alpha_1} + \frac{W}{H\alpha_2} + 1 + \frac{H^2\alpha_3\alpha_4}{W_2} + \frac{H^3\alpha_3\alpha_4\alpha_5}{W_3} = F_0\frac{W^2}{H^2\alpha_1\alpha_2}$$

$$F_3 = \frac{c_M}{Nb(OH)_2} = \frac{W^3}{H^3\alpha_1\alpha_2\alpha_3} + \frac{W^2}{H^4\alpha_2\alpha_3} + \frac{W}{H\cdot\alpha_3} + 1 + \frac{\alpha_4\cdot H}{W} + \frac{\alpha_4\alpha_5 H^2}{W^2} = F_0\frac{W^3}{H^3\alpha_1\alpha_2\alpha_3}$$

$$F_4 = \frac{c_M}{Nb(OH)} = \frac{W^4}{H^4\alpha_1\alpha_2\alpha_3\alpha_4} + \frac{W^3}{H^3\alpha_2\alpha_3\alpha_4} + \frac{W^3}{H^2\alpha_3\alpha_4} + \frac{W}{H\cdot\alpha_4} +$$
$$+ 1 + \frac{\alpha_5 H}{W} = F_0\frac{W^4}{H^4\alpha_1\alpha_2\alpha_3\alpha_4}$$

$$F_5 = \frac{c_M}{Nb} = \frac{W^5}{H^5\alpha_1\alpha_2\alpha_3\alpha_4\alpha_5} + \frac{W^4}{H^4\alpha_2\alpha_3\alpha_4\alpha_5} + \frac{W^3}{H^3\alpha_3\alpha_4\alpha_5} + \frac{W^2}{\alpha_4\alpha_5 H^2} +$$
$$+ \frac{W}{H\alpha_5} + 1 = F_0\frac{W^5}{H^5\alpha_1\alpha_2\alpha_3\alpha_4\alpha_5}$$

where α_1, α_2, ..., α_5 are the corresponding dissociation constants of the hydroxide and W is the ionic product of water.

Babko and coworkers [1] give the dissociation constants of niobium hydroxide as:

$$\alpha_1 = 2.5\times10^{-15} = \frac{[Nb(OH)_4^+][OH^-]}{[Nb(OH)_5]}$$

$$\alpha_2 = 1.3\times10^{-20} = \frac{[Nb(OH)_3^{2+}][OH^-]}{[Nb(OH)_4^+]}$$

$$\alpha_3 = 6.3\times10^{-26} = \frac{[Nb(OH)_2^{3+}][OH^-]}{[Nb(OH)_3^{2+}]}$$

$$\alpha_4 = 1.6\times10^{-30} = \frac{[Nb(OH)_4^{4+}][OH^-]}{[Nb(OH)_2^{3+}]}$$

$$\alpha_5 = 6.3\times10^{-34} = \frac{[Nb(OH)_4^{4+}][OH^-]}{[Nb^{5+}]}$$

On substituting these quantities in the first equation, for F_0, we find that $F_0 \simeq 1$. This simplifies the calculation of the remaining F quantities, which it is easy to see, are converted into functions of H in various powers. In the general form, $F_i = \text{const}/H$, and since the conventional instability constant $K = f(H)$, for two different concentrations H_1 and H_2 the ratio of constants K_2/K_1 equals $(\Phi_2/\Phi_1) \times (F''/F')$, or

$$\theta = \frac{K_2\Phi_1}{K_1\Phi_2} = \frac{F''}{F'} = \left(\frac{H_1}{H_2}\right)^n.$$

Taking logarithms of the latter expression, we obtain an equation which allows us to find the index n from the experimental results:

$$\log\theta = \log\frac{K_2\Phi_1}{K_1\Phi_2} = n|pH_2 - pH_1|; \quad \frac{\log\theta}{\Delta pH} = n.$$

From the data of Table 1 and Fig. 2, $\tan\alpha = n = 3.0$, from which it follows directly that the reaction of EDTA with niobium hydroxide follows the equations:

$$Nb(OH)_5 = Nb(OH)_2^{3+} + 3OH^-$$
$$Nb(OH)_2^{3+} + Y^{4-} = [Nb(OH)_2Y]^-.$$
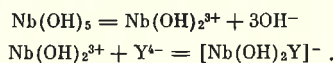
The formation in the solution of the complex $[Nb(OH)_2Y]^-$, in which two hydroxyls are left with weakened bonds, explains why niobium complexonate readily forms the mixed compounds which are now attracting the attention of analysts [8,9]. From the formula for the niobium complexonate
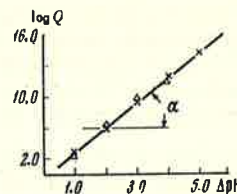

Fig.2. Variation of $\log(K_2\Phi_1/\Phi_2K_1)$ with ΔpH.

TABLE 2. Calculation of the instability constants of niobium complexonate.

pH	1	2	3	4	5	6	pK_{av}
$\log\Phi$·	17.70	13.60	10.60	8.50	6.50	4.60	
$\log F_3$	20.70	23.70	26.70	29.70	32.70	35.70	
$c_M = 3.76\times10^{-4}$ M							
$-\log K$	2.77	3.94	4.06	2.74	1.52	0.35	
pK_{instab}	41.17	41.24	41.36	40.94	40.72	40.65	41.00
$c_M = 1.5\times10^{-4}$ M							
$-\log K$	2.60	4.22	3.06	2.15	1.30		
pK_{instab}	41.00	41.52	40.36	40.35	41.50	·	40.55
						Mean	40.78

and its polarographic characteristics, its reduction at the dropping mercury electrode can be represented as follows:

first stage: $[Nb(OH)_4Y]^- + e + 2H = NbY + 2H_2O$,
second stage: $NbY + e = NbY^-$.
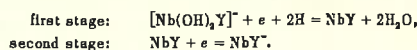
In the first stage the hydroxyl in the complexonate reacts so readily with the hydrogen ions that the reduction is reversible — a departure from the general rule for reductions involving hydrogen ions.

The values obtained for the conventional instability constants enable the concentration instability constant $K_{instab} = K/\Phi F$ to be calculated for each niobium concentration and solution pH (Table 2).

Table 2 shows that the instability constant calculated for two concentrations of niobium in a solution with a pH in the range 1–6, are satisfactorily constant. The mean value of the instability constant for ionic strength $I = 1.08$ is $K_{instab} = 10^{-40.78}$.

It may seem strange that niobium complexonate with such a small instability constant is stable in a comparatively narrow range of pH. However, this is easily explained on considering the exceptionally high tendency of niobium compounds to hydrolyse; this greatly increases the conventional instability constant to values at which complete bonding of the niobium in a complex is possible only when there is a large excess of EDTA in the solution.

SUMMARY

1. A polarographic investigation has shown that the reaction of niobium hydroxide with EDTA takes place with the formation of niobium complexonate $[Nb(OH)_2Y]^-$.

2. The instability constant of niobium complexonate K_{instab} has been calculated. At ionic strength $I = 1.08$ and $20°$, $K_{instab} = 10^{-40.78}$.

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INFLUENCE OF CERTAIN LIGANDS ON EQUILIBRIUM IN THE TITANIUM(IV)–PYROCATECHOL–PICOLINIC ACID SYSTEM

S. Ya. Shnaiderman and E. N. Knyazeva

Pyrocatecholato-complexes of titanium form ternary compounds in the presence of many organic bases[1-5]. These are very similar to inner complexes in their properties, which makes their structure interesting.

This paper describes a spectrophotometric study of complex formation in the titanium(IV)–pyrocatechol–picolinic acid system and the influence of certain ligands on the equilibrium.

EXPERIMENTAL

The initial solutions were 0.356 M titanium tetrachloride in hydrochloric acid, 0.25 M picolinic acid, and 0.6 M pyrocatechol. The ternary complex formed on mixing the initial solutions in definite proportions was extracted by dichloroethane. Different pH were established in the aqueous solutions with sodium hydroxide and hydrochloric acid, and were checked after removal of the dichloroethane layer potentiometrically with a glass electrode. The volumes of the aqueous and organic phases were 10 ml. The optical density of the solutions was measured on an SF-4 spectrophotometer. The optimal condition for the extraction of the compound in the titanium(IV)–pyrocatechol (H_2Bz)–picolinic acid (Pyko) system is pH 1–2. The composition of the ternary complex was found by the equilibrium displacement method[6].

The slope of the logarithmic curves constructed on the basis of the dependence of the optical density of extracts of the ternary complex on the concentrations of pyrocatechol (curve 1, Fig. 1) and picolinic acid (curve 2, Fig. 1), give the ratio $Ti : H_2Bz : Pyko = 1 : 2 : 2$ (Fig. 2a).
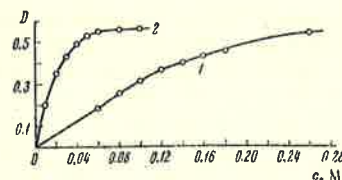

Fig. 1. Variation of the extraction by dichloroethane of the ternary titanium complex with the pyrocatechol and picolinic acid concentrations. [Ti] = 0.85×10^{-4} M; pH 2; λ 400 nm.
1) effect of pyrocatechol [Pyko] = 0.1 M;   2) effect of picolinic acid, [H_2Bz] = 0.24 M.
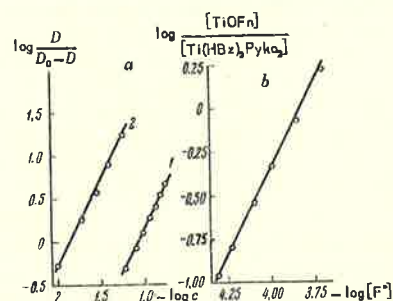

Fig. 2. Calculation of the number of coordinated groups:
a) of pyrocatechol (1) and picolinic acid (2) in the ternary titanium complex; b) of fluorines in the fluoro-complexes of titanium.

These results were confirmed by the isomolar series method[6]. Fig. 3 gives the results of measurements of the optical density of dichloroethane extracts of titanium–pyrocatechol isomolar series at a constant excess concentration of picolinic acid (curve 1) and of pyrocatechol (curve 2). The sharply expressed maxima on the composition–optical density diagrams (Fig. 3) correspond to a stable compound with the component ratios $Ti : H_2Bz = 1 : 2$ and $Ti : Pyko = 1 : 2$.

A ternary complex is also formed in the titanium(IV)–guaiacol (o-methoxyphenol)–picolinic acid system, and the absorption spectrum of an extract of this compound is similar to that of the extract of the ternary compound in the
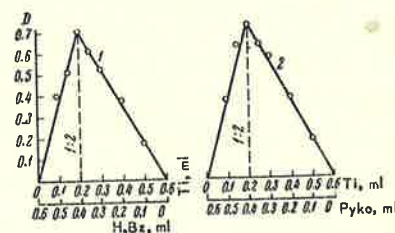

Fig. 3. Isomolar series (dichloroethane extracts) of the systems:
1) Ti–H_2Bz, Σ[Ti] + [H_2Bz] = 0.048 M, [Pyko] = 0.1 M;
2) Ti–Pyko, Σ[Ti] + [Pyko] = 0.0024 M, [H_2Bz] = 0.24 M, pH 2, λ = 400 nm.