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Abstract

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ACETATE COMPLEXES OF TITANIUM

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In colorimetric determinations of titanium with organic reagents, and also in studying interactions in systems consisting of titanium and an organic complexing agent, acetate buffer mixtures are often used. Most investigators do not take into account the possible interaction of titanium salts with acetate ions. Our experiments showed that such interaction often cannot be neglected.

With large excesses of sodium acetate, titanium salts can be retained in solution at pH 6 and higher, whereas hydrochloric-acid solutions of titanium at the same concentrations are hydrolyzed at pH 1–2. In addition, when a large excess of acetate ions is introduced, the coloration is weakened in the colorimetric determination of titanium based on the formation of colored compounds with certain organic reagents. All this can be explained by the existence of acetate complexes of titanium, in which, at pH above 2, titanium is bound practically completely.

We studied the quantitative aspect of the interaction of titanium with acetate ions by precipitating titanium in the presence of large excesses of sodium acetate.

The initial solutions were: a solution of titanium tetrachloride* in $2N$ HCl ($C_{\mathrm{Ti}} = 0.19\ M$); a solution of chemically pure sodium acetate ($C_{\mathrm{NaAc}} = 1\ M$).

The experiments showed that, when alkali was added to a solution of titanium in acetic acid, titanium precipitated irreversibly, which apparently is connected with processes of change in the composition and structure of hydroxides (^{1}). Therefore, the equilibrium pH value at which titanium began to precipitate was determined by us as follows: into several 50 ml flasks one and the same amount of sodium acetate solution was added, and then HCl was added in such an amount as to create a scale of pH values at intervals of 0.1–0.2 units. After this, one and the same volume of titanium salt solution was added to each flask. The pH values of all solutions were measured on an LP-5 pH meter with a glass electrode. In addition, the optical density of the suspension was measured on an FEK N-54 photoelectric colorimeter-nephelometer. The refined value of the pH at the onset of titanium precipitation was determined by extrapolating the obtained pH values to zero optical density. The experiments showed that equilibrium is established 25–30 min after the solutions are mixed. Although titanium still continues to precipitate at this point, the precipitation pH value (found as described above) practically does not change. All experiments were carried out at room temperature (22 ± 0.5°) and at a constant ionic strength value $\mu = 0.5$ (NaCl). The results of determinations of the pH at the onset of precipitation of titanium salts were as follows:

Titanium concentration $\times 10^3$ M	3.82	3.82	3.82	3.82	3.82	5.30	5.20	3.04
Sodium acetate concentration	0.10	0.20	0.30	0.40	0.60	0.37	0.58	0.55
pH at onset of titanium precipitation	2.22	2.35	2.57	3.03	3.93	3.69	4.40	4.55

* A chemically pure titanium tetrachloride solution was distilled over sodium amalgam and subjected twice to fractional distillation.

Using these data, we attempted to determine the composition and strength of titanium acetate complexes. In doing so we proceeded from the assumption that titanium not bound in the complex is present in solution in the form of titanyl ions (for example, (2)), whose concentration at pH values infinitely close to the pH at which precipitation begins is determined by the solubility product of titanyl hydroxide,

$$\mathrm{SP} = a_{\mathrm{TiO}^{2+}} a^2_{\mathrm{OH}^-} = 1 \cdot 10^{-30}. \tag{3}$$

Assuming that complex formation proceeds stepwise, for the complexes TiOAc^+, TiOAc_2, etc., their stability constants can be calculated

$$\beta_1 = \frac{[\mathrm{TiOAc}^+]}{[\mathrm{TiO}^{2+}][\mathrm{Ac}^-]}; \qquad \beta_2 = \frac{[\mathrm{TiOAc}_2]}{[\mathrm{TiO}^{2+}][\mathrm{Ac}^-]^2} \quad \text{etc.}$$

by the method of Leden (4), the essence of which reduces to graphical extrapolation of the functions $\psi_1 = \frac{\Phi - 1}{[\mathrm{Ac}^-]}$; $\psi_2 = \frac{\psi_1 - \beta_1}{[\mathrm{Ac}^-]}$, etc., to a zero value of the concentration of the addend $[\mathrm{Ac}^-]$.

The degree of complexing is $\Phi = \frac{[\mathrm{Ti}_{\mathrm{total}}]}{[\mathrm{TiO}^{2+}]}$, where $[\mathrm{Ti}_{\mathrm{total}}]$ is the initial concentration of titanium.

The equilibrium concentration of titanyl ions can be determined from the equation

$$[\mathrm{TiO}^{2+}] = \frac{\mathrm{SP}}{\gamma_{\mathrm{TiO}^{2+}} \cdot a^2_{\mathrm{OH}^-}} = \frac{\mathrm{SP} \cdot a^2_{\mathrm{H}^+}}{\gamma_{\mathrm{TiO}^{2+}} K_{\mathrm{H_2O}}}.$$

The activity coefficient of the titanyl ion for ionic strength $\mu = 0.5$ was calculated by us as for a divalent ion in general, according to the data of (5). The value obtained was $\gamma_{\mathrm{TiO}^{2+}} = 0.115$. The ionic product of water ($K_{\mathrm{H_2O}}$) at 22° and ionic strength $\mu = 0.5$ is equal to $5.1 \cdot 10^{-15}$ (6).

The concentration of acetate ions was determined from the equation

$$[\mathrm{Ac}^-] = [\mathrm{NaAc}] \frac{K_{\mathrm{HAc}}}{[\mathrm{H}^+] + [K_{\mathrm{HAc}}]}.$$

The numerical values of the functions ψ_1 and ψ_2 are given in Table 1.

The values of the stability constants β_1 and β_2 obtained are as follows:

$$\beta_1 = 7.5 \cdot 10^5; \qquad \beta_2 = 1.8 \cdot 10^8.$$

The instability constants of the acetate complexes will be equal to:

$$K_1 = \frac{[\mathrm{TiO}^{2+}][\mathrm{Ac}^-]}{[\mathrm{TiOAc}^+]} = 1 \cdot 10^{-6}; \qquad K_2 = \frac{[\mathrm{TiOAc}^+][\mathrm{Ac}^-]}{[\mathrm{TiOAc}_2]} = 4 \cdot 10^{-3}.$$

Fig. 1

Table 1

Fig. 2

Figure 1: Fig. 2

Equilibrium conc. of titanyl ions $[TiO^{2+}]$	Conc. of acetate ions (Ac^{-})	Degree of complexing Φ	ψ_1	ψ_2
$1.80 \cdot 10^{-5}$	$2.64 \cdot 10^{-4}$	$2.12 \cdot 10^{2}$	$7.7 \cdot 10^{5}$	$0.7 \cdot 10^{8}$
$6.60 \cdot 10^{-6}$	$7.15 \cdot 10^{-4}$	$5.80 \cdot 10^{2}$	$8.1 \cdot 10^{5}$	$0.8 \cdot 10^{8}$
$2.40 \cdot 10^{-6}$	$1.77 \cdot 10^{-3}$	$1.59 \cdot 10^{3}$	$9.0 \cdot 10^{5}$	$0.8 \cdot 10^{8}$
$2.88 \cdot 10^{-7}$	$6.70 \cdot 10^{-3}$	$1.33 \cdot 10^{4}$	$1.9 \cdot 10^{6}$	$1.8 \cdot 10^{8}$
$4.56 \cdot 10^{-9}$	$7.20 \cdot 10^{-2}$	$8.40 \cdot 10^{5}$	$1.17 \cdot 10^{7}$	$1.52 \cdot 10^{8}$
$1.38 \cdot 10^{-8}$	$2.70 \cdot 10^{-2}$	$3.83 \cdot 10^{5}$	$1.43 \cdot 10^{7}$	$5.3 \cdot 10^{8}$
$5.60 \cdot 10^{-10}$	$1.64 \cdot 10^{-1}$	$0.95 \cdot 10^{7}$	$5.70 \cdot 10^{7}$	$3.5 \cdot 10^{8}$
$2.62 \cdot 10^{-10}$	$1.97 \cdot 10^{-1}$	$1.16 \cdot 10^{7}$	$5.90 \cdot 10^{7}$	$3.0 \cdot 10^{8}$

The results obtained were used by us in explaining certain properties of titanium-phenol complexes. As our experiments showed, under certain conditions (pH 2–4) the interaction of titanium with *o*-polyphenols in the presence of acetate ions proceeds according to the scheme

$$\mathrm{TiOAc}_x + n\mathrm{H_2R} \rightleftarrows \mathrm{TiOR}_n + x\mathrm{HAc} + (2n - x)\,\mathrm{H}^+$$

(charge signs omitted); H_2R is a diatomic phenol. At the same time, at pH 1–2 acetic acid does not cause a change in the color of phenolic

$$\left(K_p = \frac{[\mathrm{TiR_2}][\mathrm{H}^+]^2}{[\mathrm{TiO}^{2+}][\mathrm{H_2R}]^2} = 10^{0.30}\right)^*$$

and peroxide

$$\left(K_p = \frac{[\mathrm{TiO \cdot H_2O_2^{2+}}]}{[\mathrm{TiO}^{2+}][\mathrm{H_2O_2}]} = 10^{4.0}\right) \tag{7}$$

complexes of titanium, although calculation on the basis of the data obtained by us shows that, in this case, a considerable part of the titanium should have been bound in colorless acetate complexes.

Fig. 2

Such a discrepancy can be explained by the fact that, in determining the stability of peroxide and phenolic complexes of titanium, the interaction of the latter with anions of inorganic acids was not taken into account (Cl^-, ClO_4^-, SO_4^{2-}), in whose presence the determinations were carried out (there are, for example, data on the formation of titanium complexes with ClO_4^- ions (2)). To explain what was said above, it is necessary to assume that under these conditions (pH 1-2), at an NaCl concentration equal to $0.5\,M$, the concentration of titanyl ions $[TiO^{2+}] \simeq 10^{-3}[TiOCl_n]$, where $TiOCl_n$ are chloride complexes of unknown composition.

It has been established that titanium salts form colorless complex compounds with acetic acid and its salts. At pH 2-3 the simplest complex $TiOAc^+$ is formed, and at higher pH, $TiOAc_2$. The instability constants calculated by the titanium precipitation method give, for the simplest complex $TiOAc^+$, the value $K_{TiOAc^+} = 1 \cdot 10^{-6}$, and for the more complex one, $K_{TiOAc2} = 4 \cdot 10^{-3}$.

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CITED LITERATURE

1. A. K. Kasimov, *Izv. AN KazSSR, ser. khim.*, **10**, 10 (1956).
2. D. Delafosse, *C. R.*, **240**, 1991 (1955).
3. C. Gharlot, R. Ganguin, *Les méthodes d' analyse de réactions en solution*, Paris, 1951.
4. I. Leden, *Zs. phys. Chem.*, A **188**, 160 (1941).
5. V. A. Kireev, *Course of Physical Chemistry*, Moscow, 1951.
6. *Handbook of Chemistry*, **3**, Moscow, 1952.
7. A. K. Babko, A. I. Volkova, *ZhOKh*, **21**, 1949 (1951).

* According to our investigations.

Note: Figure translations are in progress. See original paper for figures.

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