Talanta 85 (2011) 2339–2343

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Spectrophotometric determination of titanium with *o*-carboxyphenylfluorone in cationic micellar media, and its equilibrium and kinetic studies

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ARTICLE INFO

Article history:
Received 10 June 2011
Received in revised form 19 July 2011
Accepted 19 July 2011
Available online 4 August 2011

Keywords:
Spectrophotometry
Titanium
o-Carboxyphenylfluorone (OCPF)
Equilibrium
Kinetics

ABSTRACT

Spectrophotometric determination of titanium(IV) was accomplished with *o*-carboxyphenylfluorone (OCPF) in the presence of hexadecyltrimethyl ammonium chloride (HTAC) under strongly acidic media. In the determination of titanium(IV), Beer's law was obeyed in the range of 24–340 ng $\mathrm{mL^{-1}}$ with an effective molar absorption coefficient (at 530 nm) and relative standard deviation of 2.24×10^5 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ and 0.64% ($n = 8$), respectively. The severe interference of iron ions was easily eliminated by the addition of ethylenediaminetetraacetic acid (EDTA); the effects of other foreign substances were low. Equilibrium and kinetic studies under analytical conditions were investigated to quantitatively evaluate the reaction mechanism. The obtained orange complex is considered to be $\mathrm{Ti(OCPF)_4}$. Its stability $\log K_f$ and rate constant K_{obs} are 16.88 and $1.65 \times 10^{-2}\ \mathrm{s^{-1}}$, respectively. It is suggested that the color of the complex is related to the species of OCPF in the solution.

1. Introduction

Biological interest in titanium ions has recently arisen due to their increasing industrial and biomedical applications. Since enormous amounts of titanium are included in biomaterials such as anticancer drugs [1], implants [2], and imaging reagents [3], there are abundant opportunities for titanium ions to enter into biochemical pathways in living systems. However, very little is known about the biological chemistry of titanium ions, whereas the poor solubility and bioavailability of titanium(IV) compounds in general indicate that the toxic effects tend to have a local impact in vivo [4]. However, similar to aluminum [5], titanium may cause unexpected problems. Therefore, it is essential to develop a practical analysis of trace amounts of titanium to elucidate their biological role. For the determination of titanium(IV), several methods using various detection systems such as inductively coupled plasma atomic emission spectrometry (ICP-AES) [6], inductively coupled plasma mass spectrometry (ICP-MS) [7], X-ray fluorescence (XRF) [8], chemiluminescence [9], and spectrophotometry [10–12] have been applied. ICP-AES, ICP-MS, and XRF are expensive methods that require skilled operators. Consequently, spectrophotometry has become one of the most widely used detection techniques because of its speed, precision, accuracy, and cost effectiveness.

Phenylfluorone (PF) derivatives that are able to coordinate metals are widely used as powerful chromogenic reagents for various metals and/or biogenic substances [13–15]. Although there are many reports on the analytical application of PF derivatives, there are hardly any described reaction mechanisms between PF derivatives and metals. Here, we report the convenient spectrophotometric determination of titanium(IV) using a characteristically colored reaction with *o*-carboxyphenylfluorone (OCPF) in the presence of a cationic surfactant. This method has advantages of increased sensitivity and selectivity as compared to other methods and is capable of being applied to real biogenic samples without pretreatment. In addition, the reaction mechanisms were investigated and discussed from equilibrium and kinetic viewpoints in a cationic surfactant micellar medium to estimate the determination of titanium(IV).

2. Experimental

2.1. Reagents and apparatus

Stock solution (95.7 mg $\mathrm{L^{-1}}$) of titanium(IV) was prepared by dissolving 9.57 mg of titanium metal (Merck) in 10 mL of HCl (1:1) with warming; after cooling, the solution was diluted to 100 mL with deionized water. Working solutions were prepared daily by the suitable dilution of these stock solutions. A 5.0×10^{-3} mol $\mathrm{L^{-1}}$ solution of synthesized OCPF was prepared in methanol. A buffer solution of pH 0.8 was prepared using 1.0% (w/v) HCl. Aqueous

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doi:10.1016/j.talanta.2011.07.072

hexadecyltrimethyl ammonium chloride (HTAC; Kishida Chemical Co., Ltd.) and polyoxyethylene lauryl ether (Brij35; Kishida Chemical Co., Ltd.) were prepared. Analytical grade chemicals, which were used without further purification, were used throughout. Just before use, pure water was prepared by purifying deionized water with a Milli-Q Labo system.

A Shimadzu spectrophotometer (Model UV-1700) with 1.0 cm matched quartz and glass cells was used for the absorbance measurements. The pH measurements were made with a Horiba (F-11) pH meter.

2.2. Standard procedure for determination of titanium(IV)

The following components were mixed in a 10 mL volumetric flask: a solution containing 0.24–3.6 μg of titanium, 1.0 mL of a 2.0×10^{-2} mol L^{-1} HTAC solution, 1.0 mL of a 1.0% (w/v) HCl buffer solution, and 1.0 mL of a 5.0×10^{-3} mol L^{-1} OCPF solution. The mixture was diluted to 10 mL with water, transferred to a test tube, mixed well, and kept at room temperature for 10 min. The absorbance of the resultant solution was measured at 530 nm against a reagent blank without titanium.

2.3. Equilibrium and kinetic photometric determinations

The equilibrium study was carried out following the procedure of a similar study on a ferrous–bathophenanthroline complex [16]. The composition of the complex between OCPF and titanium(IV) in the presence of HTAC was accurately determined using Job's method of continuous variation and the molar ratio method. The estimation of the pK_{a1} value was determined based on the literature [17]. The absorbance at various pH values was investigated to calculate the stability constant of the colored complex.

In all cases, pseudo-first-order conditions were used with a constantly large excess of OCPF for titanium(IV). In a 10 mL standard flask, 1.0 mL of a 2.0×10^{-2} mol L^{-1} HTAC solution or 1.0% Brij35, 2.0 mL of a buffer solution, appropriate volumes of an OCPF solution, and 1.0 mL of 2.5×10^{-6} mol L^{-1} titanium(IV) standard solution were added in sequence. The stopwatch was then started and the mixture was diluted to the 10 mL mark with water. An aliquot of this reaction mixture was transferred to a cell and its absorbance spectrum was recorded exactly 60 s after the stopwatch started. Absorbance values at 530 nm were acquired from the absorbance spectrum and reflected the subtraction of the spectrum of blank that did not contain titanium(IV). K_{obs}, which indicates the observed pseudo-first-order rate constant, for the reaction in the presence of HTAC was estimated to be reproducible to within ±3%.

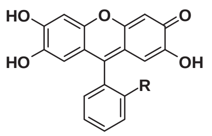
3. Results and discussion

3.1. Optimization of experimental conditions

In preliminary experiments, the effects of the PF derivatives(PF's) for titanium(IV) were studied in strongly acidic media by considering the dissociation of the benzene moiety. As shown in Fig. 1, OCPF was the most sensitive among the PF's tested, which included OCPF, *o*-sulfophenylfluorone (SPF), salicylfluorone (SF), *o*-nitrophenylfluorone (NPF), and *o*-chlorophenylfluorone (CPF).

The analysis of the effect of pH showed that the optimal pH range was from 0.6 to 0.9, which was achieved using 1.0% HCl. After investigating the effects of several acidic media, including HNO_3, H_2SO_4, $HClO_4$, the acid used was determined to have little effect on the absorption.

To stabilize the color development and increase the sensitivity and selectivity, various surfactants were examined including cationic surfactants such as HTAC, hexadecylstearylammonium chloride (HSAC), and zephiramine; anionic surfactants such as sodium dodecylsulfate (SDS); and nonionic surfactants such as Brij35 and poly(*N*-vinylpyrrolidone) (K-15). The presence of cationic surfactants such as a HTAC gave the highest and most constant absorbance, and the absorption maximum was red shifted, as shown in Fig. 2. Color development of the complex was accelerated at HTAC concentrations above 2.0×10^{-3} mol L^{-1}. The optimal OCPF concentration was studied. The maximum constant absorbance was obtained by adding more than a 2.5×10^{-4} mol L^{-1} OCPF solution. Since the rate of the formation of the colored complex depended on the OCPF concentration from the kinetic study mentioned below, we decided to use a 5.0×10^{-4} mol L^{-1} OCPF solution. The colored complex became stable immediately upon combining the reagents, and the absorbance remained stable between 5 min and 24 h. Therefore, a 10 min standing time was selected for all of the measurements before determining the titanium(IV) concentration.



PF's	R	Absorbance[a)]
OCPF	COOH	0.551
SPF	SO_3H	0.484
SF	OH	0.466
NPF	NO_2	0.420
CPF	Cl	0.458

Fig. 1. Structure and reactivity of PF's tested. (a) PF's, 5.0×10^{-4} mol L^{-1}; Ti(IV), 2.5×10^{-6} mol L^{-1}; HTAC, 2.0×10^{-3} mol L^{-1}; pH 0.8.

3.2. Calibration curve, sensitivity, and accuracy

The calibration curve produced using the standard procedure showed a good linear relationship in the concentration range of 24–340 ng mL^{-1} of titanium(IV); the correlation coefficient, *r*, was 0.999. The effective molar absorption coefficient (ε) was 2.24×10^5 dm^3 mol^{-1} cm^{-1}. The relative standard deviation (RSD) of the procedure was below 0.64% ($n = 8$). The sensitivity of the proposed method was 5–50 times that of other reported methods [10–12].

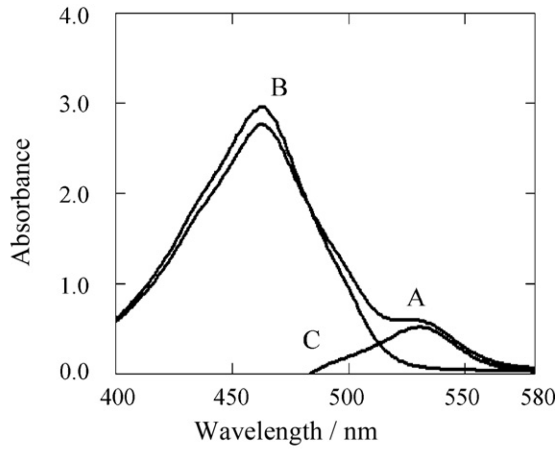


Fig. 2. Absorption spectra. OCPF, 5.0×10^{-4} mol L^{-1}; Ti(IV), 2.5×10^{-6} mol L^{-1}; HTAC, 2.0×10^{-3} mol L^{-1}; pH 0.8. Curve *A*, Ti(IV)–OCPF solution; Curve *B*, OCPF solution; Curve *C*, Curve *A* – Curve *B*.

Table 1
Effect of foreign substances on Ti(IV) determination and selection of masking agents.

Substance (+ masking agent)	Molar ratio (substance/Ti(III))	Absorbance at 530 nm	Recovery, %
None	–	0.551	100.0
K(I)	1000	0.551	100.0
Na(I)	1000	0.551	100.0
Zn(II)	200	0.551	100.0
Cu(II)	200	0.551	100.0
Mg(II)	200	0.551	100.0
Pb(II)	200	0.551	100.0
Al(III)	200	0.551	100.0
Fe(III)	20	0.887	161.0
Fe(III) + EDTA	20	0.551	100.0
Zr(IV)	20	0.595	108.0
Zr(IV) + EDTA	20	0.551	100.0
Bi(III)	5	0.595	108.0
Bi(III) + EDTA	5	0.551	100.0
KH_2PO_4	1000	0.551	100.0
NaF	1000	0.551	100.0
NH_4SCN	1000	0.551	100.0
NaI	1000	0.551	100.0
Glycine	1000	0.551	100.0
Thiourea	1000	0.551	100.0
EDTA	1000	0.551	100.0

Ti(IV) ion, 120 ng mL^{-1}; HTAC, 2.0×10^{-3} mol L^{-1}; pH 0.8; OCPF, 5.0×10^{-4} mol L^{-1}; reference, OCPF solution.

3.3. *Effects of foreign substances and selection of masking agents on titanium(IV)*

The effects of coexisting metal ions on the proposed method were examined using 120 ng mL^{-1} of titanium(IV). The results are summarized in Table 1. Both inorganic cations, which include sodium, potassium, zinc(II), copper(II), nickel(II), lead(II), magnesium(II), and aluminum(III), and anions, which include chloride, phosphate, fluoride, iodide, thiocyanate, acetate, and nitrate, did not noticeably affect the accuracy of the determination, even when present in large excess compared with titanium(IV). However, iron(III), bismuth(III), zirconium(IV), and vanadium(V) showed positive interference when present in a 20- and 5-fold excess. However, the positive interference could be removed by the addition of EDTA as the masking agent. Therefore, the addition of EDTA as a masking agent considerably enhanced the selectivity of the method. Interestingly, the masking effect of EDTA was found to be specific to cationic surfactants such as HTAC.

3.4. *Application*

This method was applied to the recovery test of the human urine, calf serum, and non-pretreated wastewater. The results shown in Table 2 indicate that the recoveries were 99.0–100.9% and that this method can be used for the determination of titanium(IV) in real samples.

Table 2
Recovery tests of titanium spiked in biological and water sample.

Sample	Recovery, %	RSD, %
Urine	99.0	1.5 (n = 4)
Calf serum	100.9	6.0 (n = 4)
Wastewater[a]	100.2	1.3 (n = 4)

Ti(IV) ion, 120 ng mL^{-1}; HTAC, 2.0×10^{-3} mol L^{-1}; pH 0.8; OCPF, 5.0×10^{-4} mol L^{-1}; reference, OCPF solution.

[a] Not pretreated.

3.5. *Composition of the colored complex*

The titanium(IV) to OCPF ratio and OCPF to HTAC ratio determined by Job's method of continuous variation and molar ratio method were 1:4 and 1:1, respectively, as shown in Fig. 3. Interestingly, the formed ternary complex may be expressed as $Ti(OCPF)_4$ coexisting with HTAC.

3.6. *Estimation of pK_{a1} values of OCPF*

OCPF is expected to appear in various pH-dependent forms in aqueous solution. These forms include: (i) univalent cation, (ii) neutral form, (iii) univalent anion, (iv) bivalent anion, etc. The determination of the ionization constant (pK_{a1}) of OCPF coexisting with HTAC was measured by spectrophotometry using the following equations:

$$\mathrm{OCPF}^{+} \leftrightarrows \mathrm{OCPF} + \mathrm{H}^{+} \tag{1}$$

$$K_1 = \frac{[\mathrm{H}^{+}][\mathrm{OCPF}]}{[\mathrm{OCPF}^{+}]} \tag{2}$$

If Eq. (2) is calculated logarithmically, it can be represented by

$$\mathrm{pH} = \mathrm{p}K_{a1} - \log\frac{[\mathrm{OCPF}^{+}]}{[\mathrm{OCPF}]} \tag{3}$$

As is seen in Fig. 4, the absorbance of OCPF and its form are stable at pH values below 1.5. Thus, we predict that the dissociation species is the univalent cationic form, OCPF^{+}, at pH 0.12; its absorbance at 460 nm is indicated by $A_{\mathrm{OCPF}^{+}}$. Assuming that the dissociation species at pH 0.86 is its neutral form, OCPF, its absorbance, similarly, is indicated by A_{OCPF}. The absorbance values between these pH values, which are represented by A, are a mixture of those of OCPF^{+} and OCPF. When the [OCPF^{+}] and [OCPF] in Eq. (3) are replaced with absorbance as per

$$\mathrm{pH} = \mathrm{p}K_{a1} - \log\frac{[A - A_{\mathrm{OCPF}}]}{[A_{\mathrm{OCPF}^{+}} - A]} \tag{4}$$

the pK_{a1} values were obtained from measurement of the spectra of the pH 0.12–0.86 solutions. Due to instrumental uncertainty, each absorbance reading was taken three times. Hence, a pK_{a1} of 0.52 ± 0.05 was determined, as shown in Fig. 5.

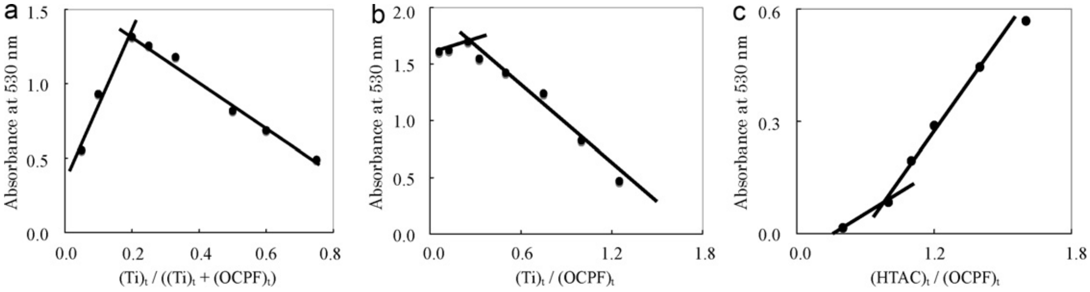


Fig. 3. Composition of the colored complex: (a) Continuous variation method. (b) Molar ratio method. (c) Composition of OCPF and HTAC by the molar ratio method.

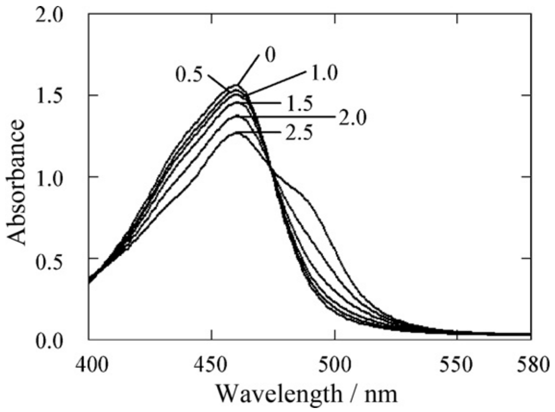


Fig. 4. Absorption spectra of OCPF. The pH values of solutions are given on the peaks. The final concentration is 1.0×10^{-4} mol L^{-1}, the wavelength of the absorption maxima are λ_{max} = 460 nm.

3.7. Stability constant (*Kf*) of the complex

According to the above-mentioned results, we assumed the following equilibrium in analytical conditions:

$$Ti^{4+} + 4OCPF \leftrightarrows TiOCPF_4 + 4H^+$$

$$Kf = \frac{[Ti(OCPF)_4][H^+]^4}{[Ti^{4+}][OCPF]^4} \tag{5}$$

$$(Ti)_t = [Ti^{4+}] + [TiOCPF_4] \tag{6}$$

$$(OCPF)_t = [OCPF^+] + [OCPF] + 4[TiOCPF_4] \tag{7}$$

where $(Ti)_t$ and $(OCPF)_t$ denote the total concentrations of each compound. *Kf* is thus obtained from Eqs. (5)–(7) as follows:

$$Kf = \frac{[Ti(OCPF)_4][H^+]^4\{1+[H^+]/K_a\}^4}{\{(Ti)_t - [Ti(OCPF)_4]\}\{(OCPF)_t - 4[Ti(OCPF)_4]\}^4} \tag{8}$$

When OCPF was added in a four-time excess of titanium(IV), the absorbance at 530 nm was measured after adjusting the ionic strength to 1.5 using sodium chloride at 18 °C. The *Kf* were then calculated from Eq. (8) after measuring the pH. The average log *Kf* of $Ti(OCPF)_4$ was 16.88, as shown in Table 3. Therefore, it was confirmed that $Ti(OCPF)_4$ was primarily formed and is stable under the analytical conditions adopted; there is little, if any, $TiOCPF^{3+}$, $Ti(OCPF)_2{}^{2+}$, and $Ti(OCPF)_3{}^{+}$ present.

Table 3
Stability constant of titanium–OCPF complex.

pH	[TiOCPF$_4$] ($\times 10^{-5}$ mol L^{-1})	*Kf* ($\times 10^{17}$ mol L^{-1})	log *Kf*
0.13	2.30	1.10	17.04
0.18	2.45	2.13	17.32
0.39	2.47	18.70	16.27
Average			16.88

$(Ti)_t = 2.5 \times 10^{-5}$ mol L^{-1}; $(OCPF)_t = 1.0 \times 10^{-5}$ mol L^{-1}; ionic strength, 1.5; temp., 18 °C.

3.8. Kinetics study

The presented kinetic reaction can be written as

$$Ti^{4+} + 4OCPF \leftrightarrows TiOCPF_4 + 4H^+$$

The general differential rate expression is

$$-\frac{d[Ti^{4+}]}{dt} = k[Ti^{4+}][OCPF] \tag{9}$$

where k is the rate constant.

If pseudo-first-order conditions are used with an excess of OCPF in the presence of HTAC, the rate expression takes the form of Eq. (10).

$$-\frac{d[Ti^{4+}]}{dt} = k_{obs}[Ti^{4+}] \tag{10}$$

where K_{obs} is the observed pseudo-first-order rate constant. Eq. (10) permits the pseudo-first-order reaction to be mathematically treated as a true-order reaction. K_{obs} was estimated after exactly 60 s by measuring the absorbance at varying OCPF concentrations. From the results shown in Fig. 6, the rate constants showed a first-order process with a very short half time of 42 s. We can deduce from the slope of the straight line obtained that the second-order rate constant (k) is 5.6×10^{-1} s^{-1}. Furthermore, the reaction rates were considered under the various pH condition by the same procedure. In the result, the rate constants were accelerated by 5 times above a pK_{a1} of 0.5 of OCPF; similarly, the K_{obs} at various pH values, e.g., 1.7×10^{-2} s^{-1} at pH 0.76 and 3.2×10^{-3} s^{-1} at pH 0.13. Consequently, the reaction rate with titanium(IV) were assumed different between [OCPF$^+$] and [OCPF]. The kinetic data obtained in the presence of Brij35 (pK_{a1} = 1.52 ± 0.02) as a nonionic surfactant supplemented and supported the results. This kinetic study indicates the formation rate of complex associates with species of OCPF as well as an equilibrium study.

In summary, OCPF forms $Ti(OCPF)_4$ with titanium(IV) under the analytical conditions used. A potential explanation for the

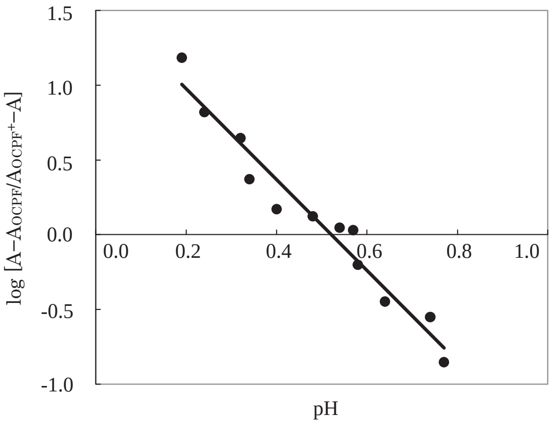


Fig. 5. Determination of the pK_{a1} of OCPF. Ti(IV), 2.5×10^{-6} mol L^{-1}: HTAC, 2.0×10^{-3} mol L^{-1}.

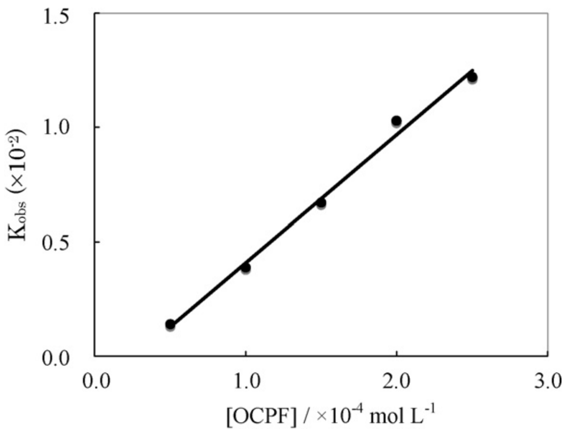
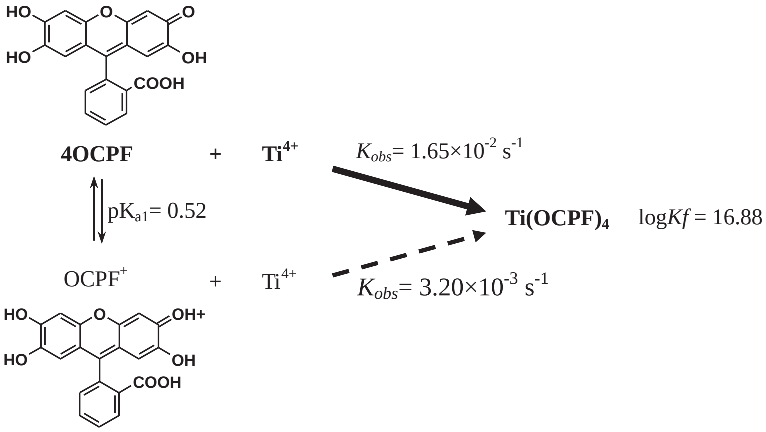


Fig. 6. Observed rate constant, K_{obs}, for the reaction of Ti(IV) with OCPF. Ti(IV), 2.5×10^{-6} mol L^{-1}; HTAC, 2.0×10^{-3} mol L^{-1}; pH 0.8.

formation of Ti(OCPF)$_4$ is shown schematically as follows:



The dissociation of OCPF is normally expected to be fast and, in this case, the stability log *Kf* and rate constant K_{obs} of the complex were spectrophotometrically evaluated as 16.88 and $1.65 \times 10^{-2}\ s^{-1}$, respectively. Thus, the complex binding is related to the species of OCPF present when the pH is buffered.

4. Conclusion

We developed a simple and highly sensitive spectrophotometric method for the determination of titanium(IV) using OCPF as a chromogenic reagent in the presence of HTAC, which is a cationic surfactant. The proposed method has advantages in terms of sensitivity, selectivity, and simplicity compared with other methods. In the determination of titanium(IV) by this method, Beer's law was obeyed in the range of 24–340 ng mL^{-1}, with an effective molar absorption coefficient (at 530 nm) of $2.24 \times 10^5\ dm^3\ mol^{-1}\ cm^{-1}$. This method could be applied to the assay of titanium(IV) in human urine, calf serum, and wastewater; the analytical recoveries were satisfactory. For the purpose of the elucidation of the reaction mechanism under the analytical conditions used, equilibrium and kinetic studies were spectrophotometrically investigated. Since the combining ratio of titanium(IV) and OCPF is one to four in buffered solutions of pH 0.8–1.0, the resultant complex is considered to be Ti(OCPF)$_4$. Following the discussion on the effect of pH on absorbance, the stability constant of the complex was evaluated to be log *Kf* = 16.88. OCPF behaves as a neutral base in the solution and the rate constant of the complex, depending on the concentration of OCPF, was $K_{obs} = 1.65 \times 10^{-2}\ s^{-1}$. After further investigations of the reaction mechanism, i.e., micellar solution effects of HTAC, and a thermodynamic analysis, the proposed method should be used for the determination of trace titanium(IV) in real samples.

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