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Extraction of Titanium(IV)-Pyrocatechol Violet Complex with Tridodecylethylammonium Bromide

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The extraction equilibria and the fundamental conditions for extracting the titanium(IV)–Pyrocatechol Volet complex anion in a form of an ionic associate with tridodecylethylammonium bromide into carbon tetrachloride is described. The absorption maxima of the extracted complex occurs at 586 nm, the molar absorptivity and the distribution ratio being 5.17×10^4 dm^3 mol^{-1} cm^{-1} and 2.82×10^2. The optimum pH range for the extraction is 5.1—6.4. The composition of the complex is estimated to be $Ti(PV)_2(R_3R'N)_2$. The extraction constant would be:

$$K_{ex}=\frac{[Ti(PV)_2(R_3R'N)_2]_o}{[Ti(PV)_2{}^{2-}][R_3R'N^+]^2},$$

log K_{ex} obtained is 13.5. The interference of foreign ions is discussed.

The lipophilic quaternary ammonium salts have played a very important role in the extraction of metal complex anions. Trioctylmethylammonium chloride (Aliquat 336 or Capliquat) has been in common use as an extracting reagent in this field. The chloride of several transition metals,[1] of vanadium,[2] of mercury,[3] thiocyanate of cadmium,[4] 2,2′-dihydroxyazobenzene complex of uranium,[5] chromate,[6] tetrabromopalladate,[7] 4,7-bis(*p*-sulfophenyl)-1,10-phenanthroline complex of iron,[8] dithizone complex of palladium,[9] 8-hydroxy-5-quinolinesulfonic acid complex of zinc,[10] and iodide of 18 elements in geochemical samples[11] were extracted with the foregoing reagent.

Tridodecylethylammonium bromide (TDEABr) synthesized in our laboratory which is more lipophilic than trioctylmethylammonium chloride has been used for extraction of the Pyrocatechol Violet (abbreviated to PV) complexes of copper,[12] tin,[13] aluminium,[14] zirconium,[15] niobium,[16] iron,[17] tungsten,[18] and vanadium.[19] The titanium(IV)–PV complex also can be extracted with TDEABr in carbon tetrachloride. The extraction equilibria and the fundamental conditions for extracting the titanium(IV)–PV complex with TDEABr will be discussed in this paper.

Experimental

Reagent. A 2.50×10^{-3} mol dm^{-3} titanium(IV) solution was prepared by following procedure. A definite amount of titanium oxide was fused with potassium disulfate and the melt was dissolved in 2 mol dm^{-3} sulfuric acid. The solution was diluted by 2 mol dm^{-3} sulfuric acid as required. A5×10^{-4} mol dm^{-3} PV solution was prepared by dissolving the Dotite PV in deionized water without further purification. TDEABr was prepared by the method described in the previous work.[17] A 2×10^{-3} mol dm^{-3} TDEABr solution was prepared by dissolving TDEABr in carbon tetrachloride. A 2 mol dm^{-3} sodium acetate solution was used as a buffer solution. All the other chemicals used were of a guaranteed reagent quality.

Apparatus. A Hitachi 101 spectrophotometer, a Hitachi 200-20 UV-vis. recording spectrophotometer, and a Hitachi Horiba F-7 pH meter were used.

General Procedure. Mix, up to 5 μg of titanium(IV), a definite amount of 1 mol dm^{-3} sulfuric acid, and 2 cm^3 of 5×10^{-4} mol dm^{-3} PV solution in a 100-cm^3 polypropylene beaker. Adjust the pH of the solution to 5.6 by the addition of 2 cm^3 of 2 mol dm^{-3} sodium acetate solution, then dilute to 20 cm^3 with de-ionized water. Transfer the solution into a 35 cm^3 test tube, and extract with 5 cm^3 of 2×10^{-3} mol dm^{-3} TDEABr in carbon tetrachloride for 5 min. Separate the phases and centrifuge the organic phase for 2 min at 3000 min^{-1}. Measure the absorbance of the extract at 586 nm against the reagent blank.

Results and Discussion

Absorption Spectra. The absorption spectra of the titanium(IV)–PV–TDEA complex extracted into carbon tetrachloride and of the titanium(IV)–PV complex anion in an aqueous solution are shown in Fig. 1. The absorption maximum of the complex is slightly shifted toward longer wavelength, and the sensitivity is enhanced a little in an organic phase, as compared with in an aqueous phase.

Effect of pH. The aqueous solution containing titanium(IV) and PV was adjusted to various pH values with the sodium acetate buffer solution, and the extraction was carried out according to the foregoing procedure. As is indicated in Fig. 2, the maximum extraction of the complex is obtained in the pH range 5.1 to 6.4.

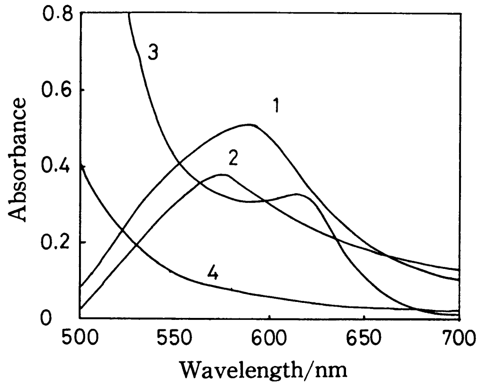

Fig. 1. Absorption spectra of the Ti–PV–TDEA complex in carbon tetrachloride and the Ti–PV complex in aqueous solution.

pH=5.6, V_{aq}=20 cm^3, V_o=5 cm^3, $[TDEABr]_o=2\times10^{-3}$ mol dm^{-3}. 1: Ti–PV–TDEA $[Ti]=2.5\times10^{-6}$ mol dm^{-3}, 2: Ti–PV $[Ti]=1\times10^{-5}$ mol dm^{-3}, 3: PV–EDEA $[PV]=5\times10^{-5}$ mol dm^{-3}, 4: PV $[PV]=1.25\times10^{-4}$ mol dm^{-3}.

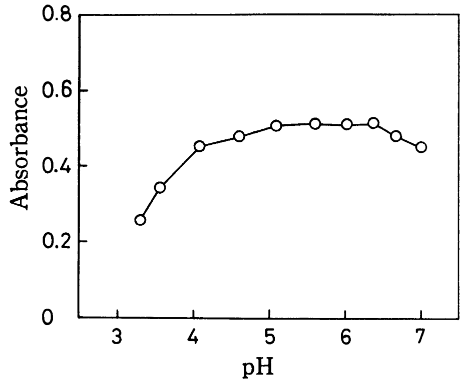

Fig. 2. Effect of pH on the extraction of the Ti–PV–TDEA complex.
[Ti]$=2.5\times10^{-6}$ mol dm^{-3}, [PV]$=5\times10^{-6}$ mol dm^{-3}, [TDEABr]$_0=2\times10^{-3}$ mol dm^{-3}, 586 nm.

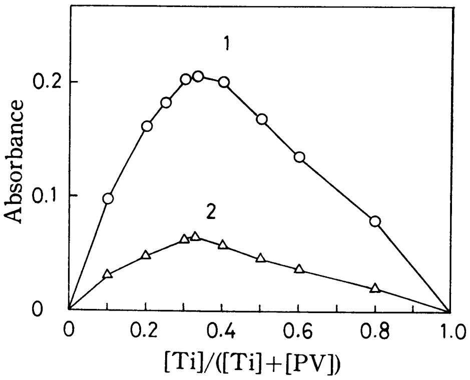

Fig. 3. Continuous variation method applied to the Ti–PV–TDEA and the Ti–PV complexes (Ti: PV).
pH=5.6, [Ti]+[PV]$=2.5\times10^{-5}$ mol dm^{-3}, 1: Ti–PV–TDEA, [TDEABr]$_0=2\times10^{-3}$ mol dm^{-3}, 586 nm, 2: Ti–PV, 572 nm.

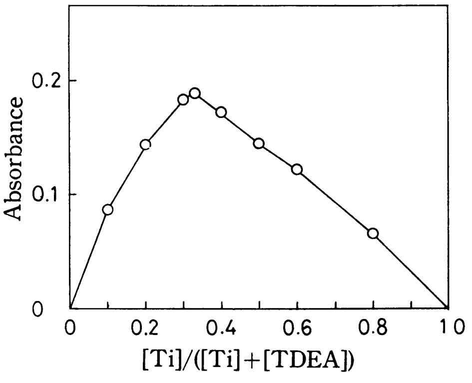

Fig. 4. Continuous variation method applied to the Ti–PV–TDEA complex (Ti: TDEA).
[Ti–PV]+[TDEA]$=5\times10^{-7}$ mol dm^{-3}, pH=5.6, 586 nm.

The absorbance of the extract increase gradually. The PV itself is also readily extracted with TDEABr.

Organic Solvents. Several kinds of organic solvents were tested in order to achieve a quantitative extraction of the complex with TDEABr. The complex is extracted in such solvents as carbon tetrachloride, benzene, toluene, xylene, butyl acetate, isobutyl methyl ketone, and chloroform. There are no serious differences among every solvent on the absorbance of the extract. The stability and the reproducibility of the absorbance, however, are better in the carbon tetrachloride.

Effect of the Reagent Concentration. The extraction of titanium(IV) from the aqueous solutions containing PV in various concentrations was examined. The optimum concentration of PV is in the range 4×10^{-5} mol dm^{-3} to 1×10^{-4} mol dm^{-3}. The concentration of TDEABr in carbon tetrachloride for the quantitative extraction is ranged from 1×10^{-4} mol dm^{-3} to 5×10^{-3} mol dm^{-3}.

Extractability and Molar Absorptivity. An aqueous solution of 20 cm^3 containing 2.40 μg of titanium(IV) and PV was shaken with 5 cm^3 of 5×10^{-3} mol dm^{-3} TDEABr in carbon tetrachloride under the optimum conditions. Extraction was repeated for the remaining aqueous phase after the separation of the extract. The extractability of the titanium(IV) was calculated from the absorbance of the extracts. It was found that 98.6% of the titanium(IV) was extracted by a single extraction. The distribution ratio and the molar absorptivity were 2.82×10^2 and 5.17×10^4 dm^3 mol^{-1} cm^{-1}, respectively. A calibration curve for the determination of the titanium(IV) was made under the optimum conditions. A good linear relationship was obtained over the concentration range from 0.3 μg to 5 μg of titanium(IV) per 5 cm^3 of carbon tetrachloride. The coefficient of the variation in ten measurements was 2.4%.

The Composition of the Complex. The composition of the complex was estimated by the continious-variation method. Figure 3 shows that the mole ratios of titanium(IV) : PV in the titanium(IV)–PV–TDEA complex and in the titanium(IV)–PV complex anion are found either to be 1 : 2. Figure 4 shows the mole ratio of titanium(IV) : TDEA to be 1 : 2. Thus, the composition of the associate complex is estimated to be $Ti(PV)_2(R_3R'N)_2$.

Extraction Constant. When the ionic associate of the titanium(IV)–PV complex anion with TDEA cation is extracted in the organic phase, the equation representing the extraction equilibria will be:

$$Ti(PV)_2{}^{2-} + 2R_3R'N^+ = Ti(PV)_2(R_3R'N)_{2(o)}. \qquad (1)$$

The extraction constant, K_{ex}, is given by:

$$K_{ex} = \frac{[Ti(PV)_2(R_3R'N)_2]_o}{[Ti(PV)_2^{2-}][R_3R'N^+]^2}, \qquad (2)$$

TABLE 1. EXTRACTION CONSTANT FOR $Ti(PV)_2(R_3R'N)_2$ IN CARBON TETRACHLORIDE AT 25 °C
pH=5.6 in an acetate buffer solution (2×10^{-2} mol dm^{-3}), [Ti]$=5\times10^{-6}$ mol dm^{-3}, [PV]$=7.5\times10^{-5}$ mol dm^{-3}, [TDEABr]$_0=5\times10^{-3}$ mol dm^{-3}, $V_{aq}=20$ cm^3, $V_0=10$ cm^3

[Br$^-$]/mol dm^{-3}	log K_{ex}
0.2	13.7
0.4	13.5
0.6	13.5
0.8	13.5
1.0	13.4
	av 13.5

All the concentrations in Table 1 indicate the initial concentrations.

where the subscript 0 denotes the organic phase. The extraction constant, K_{ex}, can be determined by the extraction data of the associate complex from various concentration of bromide in aqueous phase and the extraction constant of TDEABr. Table 1 shows the value of log K_{ex}. The average values of log K_{ex} is 13.5.

Effect of Foreign Ions. The masking reagents such as ethylenediaminetetraacetic acid, 1,2-cyclohexanediamine-*N,N,N′,N′*-tetraacetic acid, diethylenetriaminepentaacetic acid suppress thoroughly the extraction of the titanium(IV)–PV–TDEA complex. 3,6-Dioxaoctane-1,8-diamine-*N,N,N′,N′*-tetraacetic acid (GEDTA) is available as masking reagent in this extraction system, however the absorbance of the extract decreases about twenty percent by the addition of GEDTA. Beryllium, chromium(III), iron(III), bismuth, and thorium are masked by GEDTA, however aluminium, vanadium(V), molybdenum(VI), tungsten(VI), and Uranium(VI) interfere seriously. Iodide, thiocyanate, and perchlorate also interfere seriously, and give a negative error.

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