

## The Extraction of the Tungsten(VI)–Pyrocatechol Violet Complex with Tridodecylethylammonium Bromide

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The extraction equilibria and the fundamental conditions were studied for extracting the tungsten(VI)–Pyrocatechol Violet complex anion in a form of an ionic associate with tridodecylethylammonium salt in carbon tetrachloride. The ternary complex has an absorption maxima at 575 nm in the organic phase. The optimum pH range for the extraction is 4.8–5.6. The distribution ratio and the molar absorptivity are  $3.3 \times 10^2$  and  $4.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  respectively. The composition of the ternary complex is estimated to be  $\text{WO}_2(\text{PV})_2(\text{R}_3\text{R}'\text{N})_2$ . The extraction constant would be:

$$K_{\text{ex}} = \frac{[\text{WO}_2(\text{PV})_2(\text{R}_3\text{R}'\text{N})_2]_0}{[\text{WO}_2(\text{PV})_2^{2-}][\text{R}_3\text{R}'\text{N}^+]^2}$$

It is given by  $\log K_{\text{ex}} = 13.56$ . Many foreign cations can be masked with CyDTA.

The extraction of metal complex anions with quaternary ammonium salts has been successively studied by many workers. Vanadium-4-(2-Pyridylazo)resorcinol,<sup>1)</sup> cobalt-4-(2-thiazolylazo)resorcinol,<sup>2)</sup> iron–Pyrogallol Red,<sup>3)</sup> copper-2-nitroso-1-naphthol-4-sulfonic acid,<sup>4)</sup> and magnesium–Xylidyl Blue I<sup>5)</sup> complexes have been extracted in the form of the ionic associates with zephiramine. Plutonium–Xylenol Orange,<sup>6)</sup> cadmium-8-hydroxyquinoline-5-sulfonic acid,<sup>7)</sup> zinc–thiocyanate,<sup>8)</sup> and chlorides of many metals<sup>9)</sup> have also been extracted with Aliquat 336 (triethylmethylammonium chloride) in the last two years. Besides, the extraction of metal–pyrocatechol violet(PV) complexes with tridodecylethylammonium bromide (TDEABr) has been studied for extracting copper,<sup>10)</sup> tin,<sup>11)</sup> aluminium,<sup>12)</sup> zirconium,<sup>13)</sup> niobium,<sup>14)</sup> and iron.<sup>15)</sup> Tungsten(VI), as well, is known to react with PV to form a complex, and the absorbance is intensified in the presence of the 1-hexadecylpyridinium cation.<sup>6)</sup> Kohara<sup>17)</sup> extracted the tungsten(VI)–PV complex in a form of an ionic associate with zephiramine from a 0.6–0.9 mol dm<sup>-3</sup> hydrochloric acid solution, but the extraction equilibria have not been studied sufficiently. The tungsten(VI)–PV complex has also been extracted with TDEABr in carbon tetrachloride at about pH 5 from a solution containing CyDTA. This extraction system is expected to be selective and sensitive for the spectrophotometric determination of tungsten. In this paper, the extraction equilibria and the fundamental conditions will be discussed for extracting the tungsten(VI)–PV complex with TDEABr.

### Experimental

**Reagent.** A  $2.5 \times 10^{-3} \text{ mol dm}^{-3}$  tungsten(VI) solution was prepared by dissolving a definite amount of sodium tungstate in a 0.1 mol dm<sup>-3</sup> sodium hydroxide solution. The solution was diluted as required. A  $1 \times 10^{-3} \text{ mol dm}^{-3}$  PV solution was prepared by dissolving the Dotite PV in de-ionized water without further purification. TDEABr was prepared by the method described in a previous work.<sup>15)</sup> A  $5 \times 10^{-3} \text{ mol dm}^{-3}$  TDEABr solution was prepared by dissolving TDEABr in purified carbon tetrachloride. A 2 mol dm<sup>-3</sup> 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 employed.

**Standard Procedure.** Up to 20 µg of tungsten(VI), a definite amount of 1 mol dm<sup>-3</sup> sulfuric acid, and 2 cm<sup>3</sup> of a  $1 \times 10^{-3} \text{ mol dm}^{-3}$  PV solution were mixed in a 100-cm<sup>3</sup> polypropylene beaker. The pH of the solution was adjusted to 5 by the addition of 2 cm<sup>3</sup> of a 2 mol dm<sup>-3</sup> sodium acetate solution, after which the solution was diluted to 20 cm<sup>3</sup> with deionized water. The solution was transferred into a 35-cm<sup>3</sup> test tube, and 5 cm<sup>3</sup> of  $5 \times 10^{-3} \text{ mol dm}^{-3}$  TDEABr in carbon tetrachloride were added. The extraction was carried out for 5 min by turning the test tube upside down twice every 5 s. After the phase separation, the organic phase was taken out and centrifuged for 2 min at 3000 min<sup>-1</sup>. The absorbance of the extract at 575 nm was measured against the reagent blank.

### Results and Discussion

**Absorption Spectra.** The absorption spectra of the ternary complex extracted into carbon tetrachloride and of the tungsten(VI)–PV complex anion in an aqueous solution, and also the absorption spectra of the respective blank solutions, are shown in Fig. 1. The ternary complex and the tungsten(IV)–PV complex anion have absorption maxima at 575 nm and 538 nm respectively. As compared with the corresponding absorption maxima of the complex anion, that of the ternary complex is shifted toward wavelengths longer by 37 nm.

**Effect of pH.** The aqueous solution containing tungsten(VI) and PV was adjusted to various pH values with the sodium acetate buffer solution, and the extraction was carried out by the above procedure. The results are shown in Fig. 2. The maximum extraction of the ternary complex is reached in the pH range of 4.8 to 5.6. The extract was stable for at least 1 h. PV itself is readily extracted from an aqueous solution.

**Organic Solvents.** Several kinds of organic solvents were tested in order to achieve a quantitative extraction of the tungsten(VI)–PV complex anion with TDEABr. The ternary complex is extracted in such solvents as carbon tetrachloride, xylene, butyl acetate, and chloroform. The absorbance of the extract was

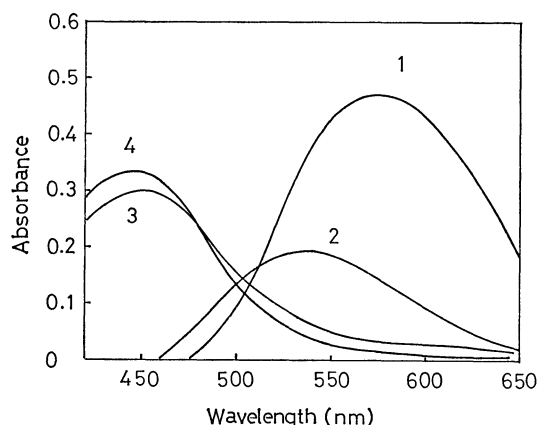


Fig. 1. Absorption spectra of the W-PV-TDEA in carbon tetrachloride and the W-PV complexes in aqueous solution.

pH=5.0,  $V_{aq}=20\text{ cm}^3$ ,  $V_o=5\text{ cm}^3$ ,  $[\text{TDEABr}]_o=5\times 10^{-3}\text{ mol dm}^{-3}$ . (1): W-PV-TDEA in carbon tetrachloride  $[\text{W}]=2.5\times 10^{-6}\text{ mol dm}^{-3}$ , (2): W-PV in aq. soln.  $[\text{W}]=1\times 10^{-5}\text{ mol dm}^{-3}$ , (3): PV-TDEA in carbon tetrachloride  $[\text{PV}]=5\times 10^{-6}\text{ mol dm}^{-3}$ , (4): PV in aq. soln.  $[\text{PV}]=2\times 10^{-5}\text{ mol dm}^{-3}$ .

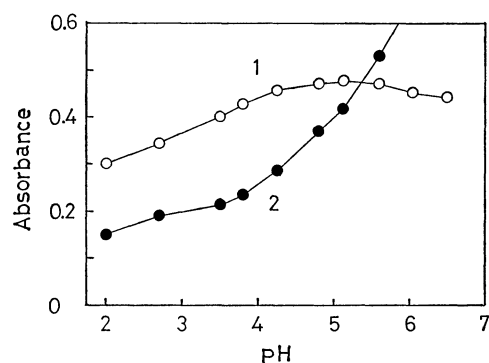


Fig. 2. Effect of pH on the extraction of the W-PV-TDEA complex.

$[\text{W}]=2.5\times 10^{-6}\text{ mol dm}^{-3}$ ,  $[\text{PV}]=1.25\times 10^{-4}\text{ mol dm}^{-3}$ ,  $[\text{TDEABr}]_o=5\times 10^{-3}\text{ mol dm}^{-3}$ , 575 nm. (1): W-PV-TDEA, (2): PV-TDEA.

maximal when carbon tetrachloride was used.

**The Effect of the Reagent Concentration.** The extraction of tungsten(VI) from an aqueous solution containing PV in various concentrations was examined. The optimum concentration range of PV is from  $8\times 10^{-5}\text{ mol dm}^{-3}$  to  $1.5\times 10^{-4}\text{ mol dm}^{-3}$ . The concentration of TDEABr in the organic phase was varied from  $1\times 10^{-4}\text{ mol dm}^{-3}$  to  $5\times 10^{-3}\text{ mol dm}^{-3}$ . The absorbance of the extract was found to be constant in the concentration range from  $9\times 10^{-4}\text{ mol dm}^{-3}$  to  $5\times 10^{-3}\text{ mol dm}^{-3}$ .

**Extractability and Molar Absorptivity.** An aqueous solution of  $20\text{ cm}^3$  containing  $18.4\text{ }\mu\text{g}$  of tungsten(VI) and PV was shaken with  $5\text{ cm}^3$  of  $5\times 10^{-3}\text{ mol dm}^{-3}$  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 tungsten(VI) was calculated from the absorbances of the extracts. It was found

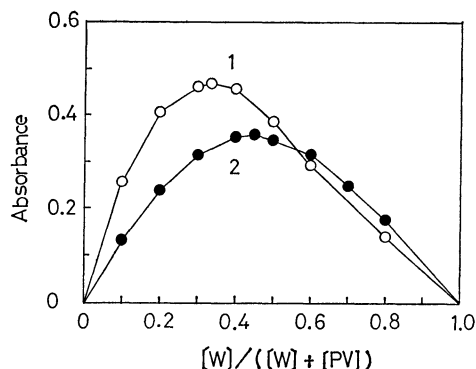


Fig. 3. Continuous variation method applied to the W-PV-TDEA and the W-PV complexes (W:PV). (1): W-PV-TDEA;  $[\text{W}]+[\text{PV}]=5\times 10^{-5}\text{ mol dm}^{-3}$ ,  $[\text{TDEABr}]_o=5\times 10^{-3}\text{ mol dm}^{-3}$ , pH=5.0, 575 nm, (2): W-PV;  $[\text{W}]+[\text{PV}]=2\times 10^{-4}\text{ mol dm}^{-3}$ , pH=5.0, 540 nm

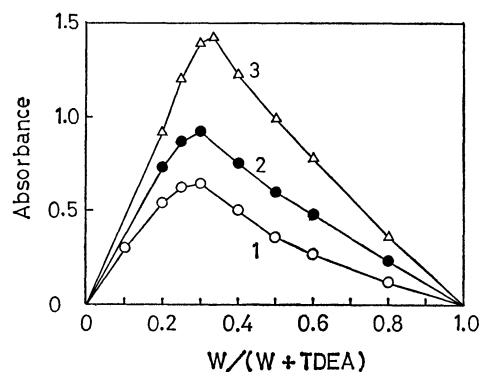
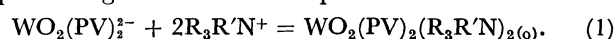


Fig. 4. Continuous variation method applied to the W-PV-TDEA complex (W:TDEA). W-PV+TDEA= $1.5\times 10^{-6}\text{ mol}$ , pH=5.0, (1): 575 nm, (2): 610 nm, (3): 650 nm.

that 98.8% of the tungsten(VI) was extracted by a single extraction. The distribution ratio and the molar absorptivity were  $3.3\times 10^2$  and  $4.7\times 10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ , respectively. A calibration curve for the determination of the tungsten(VI) was made under the optimum conditions. A good linear relationship was obtained over the concentration range from  $1\text{ }\mu\text{g}$  to  $20\text{ }\mu\text{g}$  of tungsten(VI) per  $5\text{ cm}^3$  of carbon tetrachloride. The coefficient of the variation in ten measurements was 2.4%.

**The Composition of the Ternary Complex.** Using the continuous-variation method, the mole ratio of tungsten: PV of the ternary complex and of the tungsten(VI)-PV complex anion were found to be 1:2 and 1:1 respectively, as is shown in Fig. 3. The mole ratio of tungsten: TDEA was found to be 1:2, as is shown in Fig. 4. Thus, the composition of the ternary complex was estimated to be  $\text{WO}_2(\text{PV})_2-(\text{R}_3\text{R}'\text{N})_2$ .

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

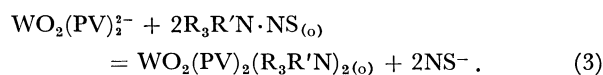


The extraction constant,  $K_{\text{ex}}$ , is given by:

$$K_{\text{ex}} = \frac{[\text{WO}_2(\text{PV})_2(\text{R}_3\text{R}'\text{N})_2]_{\text{o}}}{[\text{WO}_2(\text{PV})_2^{2-}][\text{R}_3\text{R}'\text{N}^+]^2}, \quad (2)$$

where the subscript o denotes the organic phase.

The direct determination of each of the component concentrations in Eq. 1 is a difficult problem, because the pure ternary complex can not easily be prepared. The extraction constant,  $K_{\text{ex}}$ , can, however, be determined by the indirect method, in which the extraction equilibria of the tungsten(VI)-PV complex anion with tridodecylethylammonium 2-naphthalene-sulfonate is employed. The corresponding equilibria are written as follows:



The equilibrium constant for Eq. 3 is:

$$K = \frac{[\text{WO}_2(\text{PV})_2(\text{R}_3\text{R}'\text{N})_{2(\text{o})}][\text{NS}^-]_2}{[\text{WO}_2(\text{PV})_2^{2-}][\text{R}_3\text{R}'\text{N} \cdot \text{NS}]_{\text{o}}^2}, \quad (4)$$

where NS denotes 2-naphthalenesulfonate.

The extraction equilibria of tridodecylethylammonium 2-naphthalenesulfonate may be represented as follows:



The extraction constant for Eq. 5 is:

$$K'_{\text{ex}} = \frac{[\text{R}_3\text{R}'\text{N} \cdot \text{NS}]_{\text{o}}}{[\text{NS}^-][\text{R}_3\text{R}'\text{N}^+]}. \quad (6)$$

Thus,  $K_{\text{ex}}$ , is given by:

$$K_{\text{ex}} = K \times (K'_{\text{ex}})^2. \quad (7)$$

The concentration of the  $\text{WO}_2(\text{PV})_2(\text{R}_3\text{R}'\text{N})_{2(\text{o})}$  species in Eq. 3 was determined spectrophotometrically as a function of  $[\text{NS}^-]$ , and the value of  $K$  was calculated from Eq. 4. The extraction constant,  $K'_{\text{ex}}$ , in Eq. 6 was also determined by the analogous method from the extraction equilibria between  $\text{R}_3\text{R}'\text{N} \cdot \text{NS}$  in  $\text{CCl}_4$  and the PV anion, the extraction constant of which had already been known. Table 1 shows the value of  $\log K_{\text{ex}}$  calculated from Eq. 7. It is given by

TABLE 1. EQUILIBRIUM EXTRACTION DATA FOR  $\text{WO}_2(\text{PV})_2^{2-}$  WITH  $\text{R}_3\text{R}'\text{N}^+$  IN CARBON TETRACHLORIDE AT 25 °C

( $I=0.005$  in an acetate solution and  $\text{Na}_2\text{SO}_4$  solution)  
pH=5.0 in an acetate buffer solution ( $2.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ),  $[\text{W}]=2.5 \times 10^{-6}$  mol  $\text{dm}^{-3}$ ,  $[\text{PV}]=1.25 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ,  $[\text{TDEABr}]_{\text{o}}=5 \times 10^{-3}$  mol  $\text{dm}^{-3}$ ,  $V_{\text{aq}}=20$   $\text{cm}^3$ ,  $V_{\text{o}}=5$   $\text{cm}^3$ .

$[\text{NS}^-]/10^{-3}$ mol $\text{dm}^{-3}$	$\log K_{\text{ex}}$
2.5	13.50
5.0	13.59
7.5	13.56
10	13.59
12.5	13.54
$\log K_{\text{ex}} = 13.56$	

All the concentrations in Table 1 show the initial concentrations.

TABLE 2. EFFECTS OF DIVERSE IONS ON THE DETERMINATION OF TUNGSTEN(VI)

Ions	Amount added mg	Tungsten(VI) found/ $\mu\text{g}$	Error %
—	—	9.2	0
$\text{Be}^{2+}$	0.1	7.9	-14
$\text{Mo(VI)}$	0.1	18.9	+105
$\text{Th}^{4+}$	0.1	10.4	+13
$\text{U(VI)}$	0.1	10.5	+14
$\text{V(V)}$	0.1	11.6	+26
$\text{I}^-$	10	3.8	-59
$\text{SCN}^-$	10	3.0	-67
$\text{ClO}_4^-$	10	0.6	-93
Citrate	10	0.9	-90
EDTA	10	1.0	-89

$\log K_{\text{ex}}=13.56$ .

#### Effect of Foreign Ions.

The effect of foreign ions on the determination of 9.2  $\mu\text{g}$  tungsten(VI) was examined upon the addition of 2  $\text{cm}^3$  of 0.05 mol  $\text{dm}^{-3}$  CyDTA as a masking agent. Portions (0.1 mg) of aluminium, antimony, bismuth, cadmium, cobalt, chromium, copper, gallium, indium, iron, lanthanum, lead, magnesium, manganese, mercury, nickel, tin, and zinc did not interfere, but beryllium, molybdenum, thorium, uranium, and vanadium interfered considerably with the determination of the tungsten(VI). Of the anions tested, 10-mg portions of iodide, thiocyanate, and perchlorate interfered seriously, giving negative errors. Chelating agents, such as EDTA and citrate, also interfered. The main interfering ions are shown in Table 2.

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