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The Extraction of the Vanadium(V)-Pyrocatechol Violet Complex with Tridodecylethylammonium Bromide

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Vanadium(V) can be quantitatively extracted from an aqueous solution into carbon tetrachloride as the ion-association system formed between its Pyrocatechol Violet complex anion and tridodecylethylammonium salt. The optimum pH range for the extraction is around 5. The ternary complex has an absorption maximum at 570 nm in the organic layer. The distribution ratio and the molar absorptivity are 1.78×10^2 and 4.0×10^4 $\text{l mol}^{-1}\text{ cm}^{-1}$ respectively. Omitting the other adducts which may be combined with vanadium, the composition of the ternary complex is estimated to be $V(PV)_2(R_3R'N)_2$. The extraction constant is given by $\log K_{ex}=12.58$. The interference of foreign ions is discussed, too.

The extraction of the ionic associates formed between metal-complex anions with bulky organic cations offers bright prospects of the separation of many metals, because the extraction of the ionic associates usually proceeds rapidly and the miscellaneous metal-complex anions are widely extracted under various conditions. Vanadium can be extracted with 8-hydroxy-5-quinolinesulfonic acid–zephiramine,[1] tiron–diphenylguanidine,[2] *o*-mercaptobenzoic acid–pyridine,[3] Bromopyrogallol red–diphenylguanidine,[4] 3-methylcatechol–dodecyltrimethylammonium,[5] 4-(2-thiazolylazo)resorcinol–trioctylamine,[6] 4-(2-pyridylazo)resorcinol(PAR)–nitron,[7] ascorbic acid–methyltrioctylammonium,[8] thiocyanate–pyridine,[9] ferron–tribenzylamine,[10] Pyrocatechol Violet(PV)–1,10-phenanthroline,[11] PV–diphenylguanidine,[12] pyrocatechol–aniline,[13] thiocyanate-diantipyrylmethane,[14] thiocyanate–N^2-hydroxy-N',N'-diarylbenzamidines,[15] and PAR–zephiramine[16] systems. In the process of investigating the extraction of the metal–PV complex anions with tridodecylethylammonium bromide (TDEABr), we ourselves previously reported on the extraction systems for copper,[17] tin,[18] aluminium,[19] zirconium,[20] niobium,[21] and iron.[22] The vanadium(V)–PV complex also can be extracted with TDEABr in carbon tetrachloride around pH 5. In this paper, the extraction equilibrium and the fundamental conditions will be discussed for extracting the vanadium(V)–PV complex with TDEABr.

Experimental

Reagent. A 2.5×10^{-3} mol/l vanadium(V) solution was prepared by dissolving a definite amount of ammonium vanadate(V) in a 0.25 mol/l surfuric acid solution. The solution was then diluted as required. A 5×10^{-4} mol/l 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.[22] A 5×10^{-3} mol/l TDEABr solution was prepared by dissolving TDEABr in purified carbon tetrachloride. A 2 mol/l sodium acetate solution was used as the 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 5 μg of vanadium(V), a definite amount of 1 mol/l sulfuric acid, and 3 ml of a 5×10^{-4} mol/l PV solution were mixed in a 100-ml polypropylene beaker. The pH of the solution was adjusted to 5 by the addition of 2 ml of a 2 mol/l sodium acetate solution, and then the solution was diluted to 20 ml with de-ionized water. The solution was transferred into a 35-ml test tube, and 5 ml of 5×10^{-3} mol/l TDEABr in carbon tetrachloride was 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 layer was taken out and centrifuged for 2 min at 3000 rpm. The extract was then transferred into an absorption cell, and the absorbance at 570 nm was measured against the reagent blank obtained in the same way.

Results and Discussion

Absorption Spectra. Figure 1 shows the absorption spectra of the ternary complex extracted into carbon tetrachloride, of the vanadium(V)–PV complex anion in an aqueous solution, and also of the respective blank solutions. As is evident from Fig. 1, the ternary complex and the vanadium(V)–PV complex anion have their absorption maxima at 570

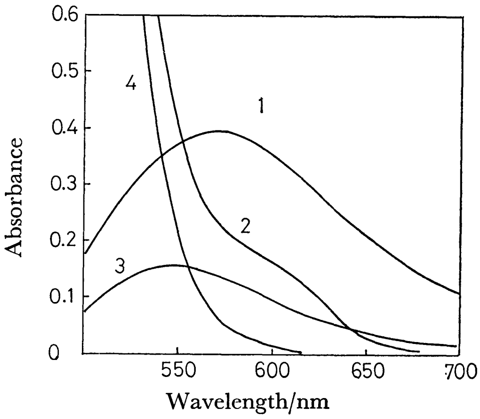

Fig. 1. Absorption spectra of the V–PV–TDEA in carbon tetrachloride and the V–PV complexes in aqueous solution.
pH=5.0, $[\text{TDEABr}]_0=5\times10^{-3}$ mol/l, $V_{aq}=20$ ml, $V_0=5$ ml.
1: V–PV–TDEA in carbon tetrachloride $[V]=2.5\times10^{-6}$ mol/l, 2: V–PV in aq soln $[V]=1\times10^{-5}$ mol/l, 3: PV–TDEA in carbon tetrachloride $[PV]=7.5\times10^{-5}$ mol/l, 4: PV in aq soln $[PV]=3\times10^{-4}$ mol/l.

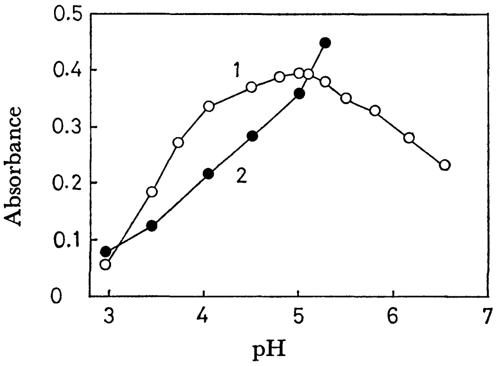

Fig. 2. Effect of pH on the extraction of the V–PV–TDEA complex.
$[V]=2.5\times10^{-6}$ mol/l, $[PV]=7.5\times10^{-5}$ mol/l, $[TDEABr]_o=5\times10^{-3}$ mol/l, 570 nm.
1: V–PV–TDEA, 2: PV–TDEA.

nm and 550 nm respectively. As compared with the corresponding absorption maximum of the complex anion, that of the ternary complex is shifted toward wavelengths longer by 20 nm. The increase in the absorbance at the absorption maximum in the case of the ternary complex over the absorbance of the binary complex is considerable. PV itself is readily extracted from an aqueous solution by TDEABr in carbon tetrachloride.

Effect of pH. Figure 2 shows that the extraction of the ternary complex starts about pH 3, reaches a maximum around pH 5, and thereafter decreases gradually. The extract is stable for at least 30 min.

Organic Solvents. Of the solvents examined, carbon tetrachloride, butyl acetate, chloroform, and benzene are suitable for the quantitative extraction of the ternary complex. The absorbance of the extract is maximal when the carbon tetrachloride is used.

Effect of the Reagent Concentration. The variation in the absorbance was investigated as a function of the PV concentration in an aqueous solution and as a function of the TDEABr concentration in carbon tetrachloride for extracting the ternary complex. The optimum concentration range or PV is from 6×10^{-5} mol/l to 1.25×10^{-4} mol/l. Besides, the concentration range of TDEABr for the quantitative extraction is from 4×10^{-4} mol/l to 5×10^{-3} mol/l.

Extractability and Molar Absorptivity. An aqueous solution of 20 ml containing 6.37 μg of vanadium(V) and 3 ml of 5×10^{-4} mol/l PV was shaken with 5 ml of 5×10^{-3} mol/l TDEABr in carbon tetrachloride under optimum conditions. Extraction was repeated for the remaining aqueous phase after the separation of the extract. The extractability of vanadium(V) was calculated from the absorbances of the extracts. It was found that 97.8% of the vanadium(V) was extracted by one extraction. The distribution ratio and the molar absorptivity were 1.78×10^2 and 4.0×10^4 l mol^{-1} cm^{-1} respectively. A calibration curve for the determination of vanadium(V) was made under optimum conditions. A good linear relationship is obtained over the concentration range from 0.25 μg to 5 μg of vanadium(V) per 5 ml of carbon tetrachloride. The coefficient of variation of ten measurements was 3.9%.

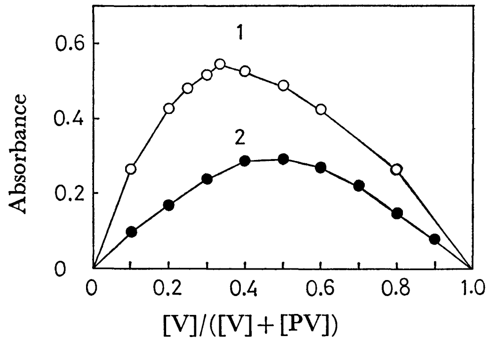

Fig. 3. Continuous variation method applied to the V–PV–TDEA and the V–PV complexes (V:PV).
1: V–PV–TDEA; $[V]+[PV]=1\times10^{-4}$ mol/l, $[TDEABr]_o=5\times10^{-3}$ mol/l pH=5.0, 570 nm. 2: V–PV; $[V]+[PV]=1\times10^{-4}$ mol/l, pH=5.0, 550 nm.

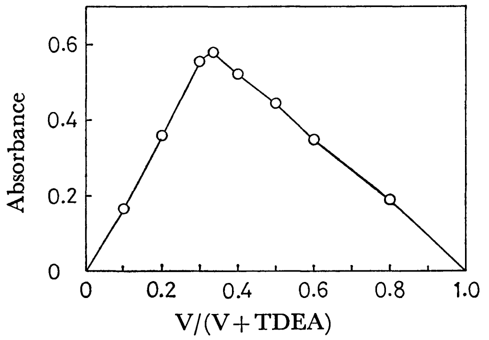

Fig. 4. Continuous variation method applied to the V–PV–TDEA complex (V:TDEA).
V–PV+TDEA=1.5×10^{-6} mol, pH=5.0, 570 nm.

The Composition of the Ternary Complex. The estimate of the composition of the complexes was attempted by means of the continious-variation method. Figure 3 shows that the mole ratios of vanadium(V): PV in the ternary complex and in the vanadium(V)–PV complex anion were found to be 1:2 and 1:1 respectivery. Figure 4 shows the mole ratio of vanadium(V): TDEA to be 1:2. Thus, the composition of the ternary complex is estimated to be $V(PV)_2(R_3R'N)_2$.

Extraction Constant. When the ionic associate of the vanadium(V)–PV complex anion with the TDEA cation is extracted in the organic layer, the extraction equilibrium may be expressed by the following equation:

$$V(PV)_2^{2-} + 2R_3R'N^+ = V(PV)_2(R_3R'N)_{2(o)}, \quad (1)$$

where we omit the other adducts which may be combined with vanadium. The extraction constant, K_{ex}, is given by:

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

where the subscript o denotes the organic layer. An attempted direct determination of each concentration of the components in Eq. 1 was unsuccessful, for the pure ternary complex can not be prepared easily. The equilibrium in Eq. 1 can be represented by the following two steps:

$$V(PV)_2^{2-} + 2R_3R'N\cdot NS_{(o)} = V(PV)_2(R_3R'N)_{2(o)} + 2NS^- \tag{3}$$

$$K = \frac{[V(PV)_2(R_3R'N)_2]_o[NS^-]^2}{[V(PV)_2^{2-}][R_3R'N\cdot NS]_o^2}, \tag{4}$$

where NS denotes 2-naphthalenesulfonic acid.

$$NS^- + R_3R'N^+ = R_3R'N\cdot NS_{(o)} \tag{5}$$

$$K'_{ex} = \frac{[R_3R'N\cdot NS]_o}{[NS^-][R_3R'N^+]}, \tag{6}$$

Thus, K_{ex} is given by

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

The concentration of the $V(PV)_2(R_3R'N)_{2(o)}$ species in Eq. 3 was determined spectrophotometrically as a function of $[NS^-]$, and the value of K was calculated from Eq. 4. The extraction constant, K'_{ex}, of $R_3R'N\cdot NS$ in Eq. 6 was also determined from the extraction equilibrium between $R_3R'N\cdot NS$ in CCl_4 and the PV anion. Table 1 shows the value of $\log K_{ex}$ as calculated from Eq. 7. It is given by $\log K_{ex}=12.58$.

Effect of Foreign Ions. The effect of foreign ions on the determination of 2.55 μg vanadium(V) was examined under optimum conditions. Cadmium, cobalt, chromium, lanthanum, lead, magnesium, manganese, mercury, nickel, and zinc do not interfere when present separately 0.1-mg amounts, but aluminium, beryllium, bismuth, iron, molybdenum, tin, thorium, uranium, and tungsten interfere seriously. Of the anions tested, 10 mg of iodide, thiocyanate, and perchlorate interfere seriously, giving a negative error. Chelating agents such as EDTA and citrate also interfere. Table 2 shows the main interfering ions.

TABLE 1. EQUILIBRIUM EXTRACTION DATA FOR $V(PV)_2^{2-}$ WITH $R_3R'N^+$ IN CARBON TETRACHLORIDE AT 25 °C ($I=0.005$ in NaOAc and Na_2SO_4 solutions) pH = 5.0 in an acetate buffer solution (2×10^{-3} mol/l), $[V]=2.5\times10^{-6}$ mol/l, $[PV]=7.5\times10^{-5}$ mol/l, $[TDEABr]_o=5\times10^{-3}$ mol/l, $V_{aq}=20$ ml, $V_o=5$ ml

$10^3\,[NS^-]$/mol l^{-1}	$\log K_{ex}$
0.5	12.54
1.0	12.56
1.5	12.62
2.0	12.58
2.5	12.59
	$\log K_{ex}=12.58$

All the concentrations in Table 1 show the initial concentrations.

TABLE 2. EFFECTS OF DIVERSE IONS ON THE DETERMINATION OF VANADIUM(V)

Ions	Amount added mg	Vanadium(V) found/μg	Error %
—	—	2.55	0
Al^{3+}	0.1	1.51[a]	−41
Be^{2+}	0.1	3.03[a]	+19
Bi^{3+}	0.1	2.27[a]	−11
Fe^{3+}	0.1	2.86[a]	+12
Mo(VI)	0.1	3.74[a]	+46
Sn^{4+}	0.1	10.4[a]	+309
Th^{4+}	0.1	1.47[a]	−42
U(VI)	0.1	2.83[a]	+11
W(VI)	0.1	4.20[a]	+65
I^-	10	0.59	−77
SCN^-	10	0.40	−84
ClO_4^-	10	0.07	−97
Citrate	10	1.57	−38
EDTA	10	0.09	−96

a) KH_2PO_4 and $Na_2S_2O_3$ solutions were added as masking agents.

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