Spectrophotometric Study on the Extraction of the Ternary Complex Composed of Vanadium(V), 8-Hydroxyquinoline-5-sulfonic Acid and Zephiramine

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The ternary complex composed of vanadium(V),8-hydroxyquinoline-5-sulphonic acid (H_2QS), and zephiramine (Z^+Cl^-) was extracted into chloroform. The absorption maxima of the ternary complex in the organic layer were 375 and 580 nm at pH 2.8 and 375 nm at pH 4.8. The optimum pH range for the extraction was 4.5—5.4. Beer's law held for 1.29—35.6 μg of vanadium(V). The molar absorptivity of the complex was 0.99×10^4 cm^{-1} mol^{-1} l. The composition of the ternary complex was estimated to be $[VO_2{}^+Z^+(QS^{2-}Z^+)_2]_o$ and the extraction equilibrium was given by

$$VO_2{}^+ + 2[(HQS^-Z^+)]_o + Z^+ + 2OH^- \rightleftharpoons [VO_2{}^+Z^+(QS^{2-}Z^+)_2]_o + 2H_2O \quad (1)$$

The logarithm of the equilibrium constant K of this equation was found to be 32.57 ± 0.49.

Oxine, *N*-benzoylphenylhydroxylamine, hydrogen peroxide, and phosphotungstic acid have been used mainly for the determination of trace amounts of vanadium(V). 8-Hydroxyquinoline-5-sulphonic acid (H_2QS), a water-soluble oxine derivative, was also suggested as a chelating agent for vanadium(V).[1] However, details of analytical conditions are lacking. We have extracted ionic association complex of vanadium(V)-H_2QS chelate anion with zephiramine (tetradecyl-dimethyl-benzyl-ammonium chloride) into chloroform. Yellow coloration of the extract obtained from a weakly acidic medium was very stable and the intensity was proportional to the concentration of vanadium(V) in the aqueous layer. A dark green coloration was also obtained by extraction from an acidic medium. However, because of the low sensitivity and instability of coloration, the extraction from a weakly acidic medium is preferable for determination of vanadium(V).

Experimental

Reagent. *Vanadium(V) Standard Solution*: 0.1770 g of guaranteed ammonium metavanadate NH_4VO_3 (Kanto Chemicals Co.) was dissolved in 25 ml of 2 M H_2SO_4 and diluted to 1 liter with water. The solution was standardized by EDTA-titration using a Cu-PAN indicator. The solution was diluted as required.

H_2QS Solution: 1.00×10^{-3} M solution was prepared by dissolving H_2QS (Wako Chemicals Co.) into water.

Zephiramine Solution: 5.00×10^{-3} M solution was prepared by dissolving Dotite zephiramine in water.

Buffer Solutions: A sulphuric acid-acetate buffer solution was prepared by mixing 0.5 M solutions of sulphuric acid and sodium acetate. A borate buffer solution was prepared by mixing 0.1 M solutions of hydrochloric acid and borax.

Chloroform was purified by washing with sulphuric acid, diluted sodium hydroxide and water, followed by distillation.

The other reagents used were all of analytical reagent grade. Resin-deionized water was used.

Apparatus. A Shimadzu QV-50 spectrophotometer with 10-mm cells was used for measurements of absorbance. A Hatachi-Horiba, Model F-5, glass electrode pH meter was used for pH measurements. An Iwaki KM shaker was used.

Procedure. Vanadium(V) (25.5 μg) was dissolved with 6 ml H_2QS solution and 2.5 ml zephiramine solution in a 100 ml separatory funnel. The pH adjustment was performed with 15 ml of the sulphuric acid-acetate buffer solution in the range 4.7—4.9 and then filled up to 50 ml with water. The mixtures with 10 ml of chloroform were shaken for 10 min and left for 5 min to let the layers separate. The chloroform layer was transfered to a beaker containing anhydrous Na_2SO_4 and offered to a optical measurement. The absorbance of the extract at 375 nm was measured against the reagent blank obtained in the same way.

Results and Discussion

Absorption Spectra. Absorption spectra of the aqueous layer are presented in Fig. 1. The vanadium (V)-H_2QS chelate anion in water has an absorption maximum at 365 nm. The ternary complex formed by addition of zephiramine has different absorption maximum depending on pH value, *viz.*, 375 nm at pH 4.8, 395 and 580 nm at pH 2.8. The ionic association complex extracted into chloroform has a yellow coloration at pH 4.8 and dark green coloration at pH 2.8. The absorption maximum of the yellow extract is 375 nm and those of the dark green extract are 375 and 580 nm as shown in Fig. 2. The yellow

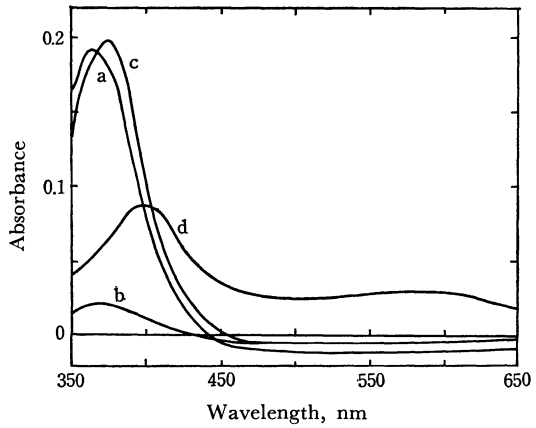

Fig. 1. Absorption spectra of V(V)-QS and V(V)-QS-Z complexes in aqueous layer.
Curve (a) $[V(V)]_w=2.0\times10^{-5}$ M, $[QS]_w=2.4\times10^{-4}$ M, pH 4.8, *vs.* reagent blank, (b) pH 2.8, Curve (c) $[V(V)]_w=2.0\times10^{-5}$ M, $[QS]_w=2.4\times10^{-4}$ M, $[Z]_w=5.0\times10^{-4}$ M, pH 4.8, *vs.* reagent blank, (d) pH 2.8.

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TABLE 1. COMPARISON OF SENSITIVITY OF SOME COMMON SPECTROPHOTOMETRIC METHODS FOR VANADIUM(V)

Reagent	Chemical formula	Molar absorptivity (cm^{-1} mol^{-1} l)	Wavelength (nm)	Reference
Oxine	$VO(OH)Ox_2$	3220 ($CHCl_3$)	540	
		6200 ($CHCl_3$)	365	2
	$C_4H_9NH_3VO_2Ox_2$	7000 (benzene)	380	
N-Benzoylphenyl-hydroxylamine	$VO(OH)(BPA)_2$	4500 (benzene)	530	3
		4650 ($CHCl_3$)	510	4
4-(2-Pyridylazo)-resorcin and zephiramine		43000 ($CHCl_3$)	560	5
8-Hydroxyquinoline-5-sulphonic acid and zephiramine	$VO_2{+}Z(QS^{2-}Z^{+})_2$	9900 ($CHCl_3$)	375	

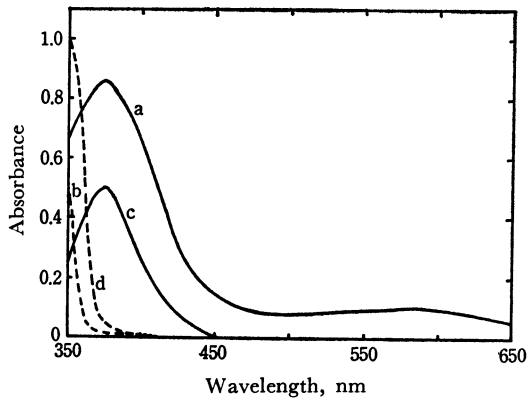

Fig. 2. Absorption spectra of the ternary complex V(V)-QS-Z in chloroform layer.
Curve (a) $[V(V)]_w=2.0\times10^{-5}$ M, $[QS]_w=2.4\times10^{-4}$ M, $[Z]_w=5.0\times10^{-4}$ M, pH 2.8, *vs.* reagent blank, (b) reagent blank *vs.* $CHCl_3$, Curve (c) $[V(V)]_w=1.0\times10^{-5}$ M, $[QS]_w=1.2\times10^{-4}$ M, $[Z]_w=5.0\times10^{-4}$ M, pH 4.8, *vs.* reagent blank, (d) reagent blank *vs.* $CHCl_3$, Volume of aqueous layer $V_w=50$ ml, Volume of organic layer $V_o=10$ ml.

extract was very stable and the absorbance at 375 nm was found to remain unchanged after being left standing for 6 hours, but that at 580 nm decreased in the dark green extract.

Effect of pH. The aqueous layer adjusted to various pH values was treated by the above procedure. It was found that optimum pH range for the extraction was 4.5—5.4; 2.4—2.8 for the dark green extract. In borate buffer solution, no stable and constant absorbance was obtained.

Effect of H_2QS and Zephiramine Concentrations. Concentrations of H_2QS and zephiramine were varied. Absorbance of the extract was found to be constant with concentration range higher than 10-fold of H_2QS and 20—40-fold of zephiramine to vanadium(V).

Effect of Shaking Time. Shaking time was varied from 3 min to 20 min in the above procedure. It was found that the quantitative extraction of vanadium(V) was attained for shaking longer than 5 minutes.

Extractability and Molar Absorptivity. A 50-ml portion of the aqueous layer containing 25.5 μg of vanadium(V) was shaken with 10 ml of chloroform, and the absorbance of the extract was measrued. 25 ml of the separated aqueous layer was then re-extracted with 5 ml of chloroform. Extractability was calculated from the sum of absorbances of the extracts and that of the first extract. It was found that 99.9% of vanadium(V) was extracted by a single extraction, the molar absorptivity of the ternary complex being 0.99×10^4 cm^{-1} mol^{-1} l. The molar absorptivity is larger than that of the corresponding oxine complex as shown in Table 1.

Calibration Curve. Extraction of varying amounts of vanadium(V) was carried out. Beer's law held in the concentration range 1.29—35.6 μg of vanadium(V). Sandell's sensitivity for the absorbance of 0.001 was 0.0051 μg cm^{-2}. The relative standard deviation obtained by 7 measurements was 0.74% for 25.5 μg of vanadium(V).

Composition of Vanadium(V)-H_2QS Complexes. A continuous variation method applied at pH 4.0 indicated that mole ratio of H_2QS to vanadium(V) was 2 : 1. The same result was obtained also by the mole ratio method.

Composition of the Ternary Complex. A continuous variation method of the three-component system[6-9] was applied to the determination of the composition of the ternary complex. The sum of concentrations of vanadium(V), H_2QS, and zephiramine in the aqueous layer was kept to 7.00×10^{-5} M and the extraction was carried out at pH 4.8. As shown in Fig. 3, maximum absorbance was obtained at the concentration ratio of vanadium(V): H_2QS: zephiramine=1.2 : 2.5 : 3.5, namely 1 : 2 : 3. The above result was confirmed by using Affsprung's method.[10] It is known that the group V–OH in 8-hydroxyquinolate is acidic and reacts with amines.[11]

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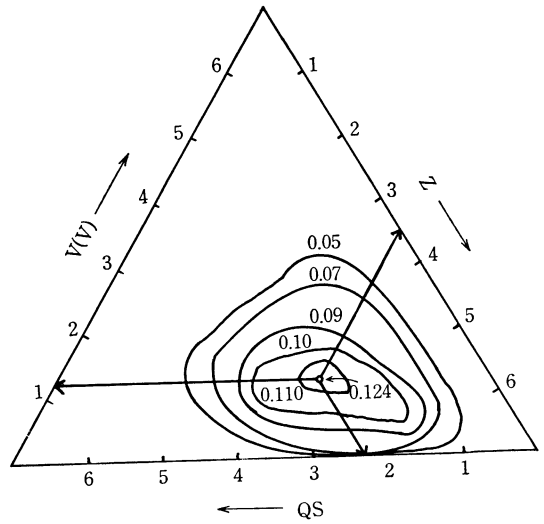

Fig. 3. Continuous variation method applied to three-component system of V(V)-QS-Z complex in organic layer. $V_w=50$ ml, $V_o=10$ ml, $[V(V)]_w+[QS]_w+[Z]_w=7.00\times10^{-5}$ M, pH 4.8, Wavelength: 375 nm, *vs.* $CHCl_3$.

The composition of the ternary complex was therefore estimated to be $[VO_2{}^+Z^+(QS^{2-}Z^+)_2]_o$.

Equilibrium Constant. Extraction of the ternary complex can be given by

$$VO_2{}^+ + 2[(HQS^-Z^+)]_o + Z^+ + 2OH^- \rightleftarrows [VO_2{}^+Z^+(QS^{2-}Z^+)_2]_o + 2H_2O \quad (1)$$

with the equilibrium constant K

$$K=\frac{[VO_2{}^+Z^+(QS^{2-}Z^+)_2]_o}{[VO_2{}^+][(HQS^-Z^+)]_o{}^2[Z^+][OH^-]^2} \quad (2)$$

where subscript o denotes the organic layer. 50 ml of the aqueous layer, containig $*C$ mole of vanadium-(V), $2*C$ mole of H_2QS and $3*C$ mole of zephiramine was equilibrated with 10 ml of chloroform. By measurements of absorbance of the extract, concentration of the ternary complex C_T was calculated from the molar absorptivity. Equation (2) is then given by

$$K=\frac{[C_T]}{\left[*C-\frac{10}{50}C_T\right]\left[\frac{50}{10}\times2*C-2C_T\right]^2[*C][OH^-]^2} \quad (3)$$

The results obtained with various values of concentration of $*C$ are shown in Table 2. The logarithm of the equilibrium constant is 32.57±0.49.

TABLE 2. EQUILIBRIUM CONSTANT OF V(V)-QS-Z TERNARY COMPLEX EXTRACTION SHOWN BY EQUATION (1)—(3)

*C (M)	Absorbance	C_T (M)	pH	log K
1.8×10^{-5}	0.251	2.53×10^{-5}	4.80	32.73
1.2×10^{-5}	0.111	1.12×10^{-5}	4.80	32.28
6.0×10^{-6}	0.025	2.52×10^{-6}	4.81	32.70

Ionic strength $\mu=0.456$, Molar absorptivity $\varepsilon=0.99\times10^4$ $cm^{-1}\,mol^{-1}\,l$, Temp. 18.0°C,
$*C$=Initial amount of V(V) in 50-ml aqueous layer,
$2*C$=Initial amount of H_2QS in 50-ml layer,
$3*C$=Initial amount of Z^+ in 50-ml layer,
C_T=Final amount of the ternary complex in 10-ml $CHCl_3$-extract.