BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (3), 761—762 (1974)

The Extraction and Spectrophotometric Determination of Vanadium(IV) with Tiron[1]

Yoshinobu WAKAMATSU and Makoto OTOMO*

Department of Industrial Chemistry, Hachinohe Technical College, Hachinohe 031
**Department of Synthetic Chemistry, Nagoya Institute of Technology, Showa-ku, Nagoya 466*

(Received August 6, 1973)

Synopsis. The vanadium(IV)-Tiron chelate can be extracted into a mixed solvent of 1:4 isopentyl alcohol-chloroform in the presence of 1,3-diphenylguanidinium salt. Beer's law was obeyed up to 36 μg vanadium per 10 ml of the solvent.

Tiron reacts with vanadium(IV, V) to form water-soluble chelates. Tserkovnitskaya *et al.*[2] studied the complex formation between vanadium(IV) and Tiron in an aqueous solution. On the other hand, Sarma[3] and Nishikawa *et al.*[4] applied the vanadium(V)-Tiron chelate to the visible and ultraviolet spectrophotometric determination of vanadium(V) in an aqueous solution.

The present paper will describe the spectrophotometric determination of vanadium(IV), which is based on the extraction of the vanadium(IV)-Tiron chelate into a mixed solvent of 1:4 isopentyl alcohol–chloroform in the presence of excessive 1,3-diphenylguanidinium-(DPG) salt. The combining ratio of vanadium, Tiron, and DPG in the extracted species has also been determined by a spectrophotometric method.

Experimental

Reagents and Apparatus. A stock solution of vanadium (IV) (about 0.01 M) was prepared by dissolving a reagent grade vanadium(IV) sulfate in distilled water and then standardized against a standard EDTA solution, using Cu-PAN as the indicator.[5] All the other reagents and apparatus used were the same as those reported previously.[6]

Standard Procedure. To a sample solution containing up to 36 μg of vanadium in a 50 ml separatory funnel we added 1.0 ml of a 0.56 M ascorbic acid solution, 4.0 ml of a 0.2 M Tiron solution, and 10.0 ml of a 0.34 M DPG solution which had been adjusted to pH 3.5 with a 0.2 M monochloroacetic acid solution and a 0.2 M sodium acetate solution. The solution was diluted with water to 20.0 ml, allowed to stand for 20 min, and shaken for 10 min with 10.0 ml of a mixed solvent of 1:4 isopentyl alcohol–chloroform. The absorbance of the organic phase was then measured at 585 nm using a reagent blank as the reference.

Results and Discussion

Absorption Spectra. The absorption spectra of the vanadium(IV)-Tiron chelate in an aqueous solution and the ion association complex extracted into the solvent are shown in Fig. 1. The absorption maxima of the vanadium(IV) Tiron chelate and the ion-association complex are found at 565 and 585 nm respectively. Tiron is not extracted into the solvent, not even in the presence of DPG salt at pH 3.5.

The Effect of the pH. The effect of the pH of the aqueous phase on the extraction is shown in Fig. 2.

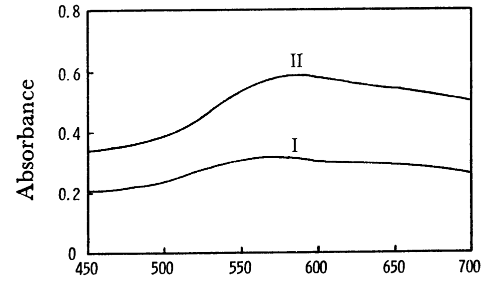

Fig. 1. Absorption spectra of the V(IV)-Tiron chelate in aqueous phase and the association complex in organic phase.
Tiron: 4.0×10^{-2}M, Ascorbic acid: 2.8×10^{-2}M, pH: 3.5, I: V(IV)-Tiron chelate, V(IV); $38._8$ μg, II: association complex, V(IV); $28._5$ μg, DPG; 0.17M.

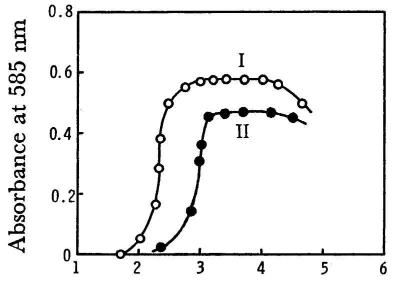

Fig. 2. Effect of pH on the extraction of V(IV)-Tiron-DPG.
V(IV): $28._5$ μg, DPG: 0.17M, Ascorbic acid: 2.8×10^{-2}M, Tiron: I; 4.0×10^{-2}M, II; 5.0×10^{-3}M.

The maximum extraction is reached at pH 2.9—4.1 when the association complex is extracted into the solvent from an aqueous solution containing 4.0×10^{-2} M Tiron. The wavelength of maximum absorption was independent of the pH of the aqueous phase.

The Effect of the Additives. The effect of the Tiron and the DPG concentrations on the extraction was investigated separately by varying the Tiron and the DPG concentrations respectively. It was found that the absorbances of the organic phase were essentially constant provided that the Tiron and the DPG concentrations in the initial aqueous phase were more than 3.0×10^{-2} M and 0.13 M respectively.

Choice of Solvent. The vanadium(IV)-Tiron-DPG association complex can be readily extracted into aliphatic alcohols; its extractability is analogous to those of the corresponding titanium complex.[6] A 1:4 mixed solvent of isopentyl alcohol and chloroform, which proved to give the highest absorbance, was chosen as the solvent.

The Effect of the Standing Time. The formation of the vanadium(IV)-Tiron chelate does not occur instantaneously in an aqueous solution, about 20 min being required to obtain the maximum absorbance. The absorbance of the organic phase remains almost constant for at least 5 hr if the vanadium(IV)-Tiron-DPG association complex is extracted into the solvent after the reaction mixture has been allowed to stand for 20 min.

The Effect of the Shaking Time. It was found that shaking for 5 min sufficed; for safety, though, a shaking time of 10 min was selected. The aqueous phase was colorless after one extraction, indicating that only one extraction is needed for the complete extraction of the association complex.

Calibration Curve. A calibration curve for the determination of vanadium(IV) was prepared under the optimum conditions. A good linear relationship was obtained over the concentration range from 0 to 36 μg of vanadium per 10 ml of the solvent. The molar absorptivity of the extracted species was approximately 1.03×10^4 at 585 nm, 1.4 times as high as that of the vanadium(V)-Tiron chelate at 310 nm.4) The proposed method is comparable in sensitivity to the Methylthymol Blue method.7)

TABLE 1. EFFECT OF METAL IONS
V(IV): 2.8×10^{-5}M ($28._5$ μg), Tiron: 4.0×10^{-2}M, DPG: 0.17M, Ascorbic acid: 2.8×10^{-2}M, pH: 3.5

Metal ion	Amount added (μg)	V(IV) found (μg)
Fe(III)	30	$28._5$
	200	$28._4$
Al(III)	30	$28._3$
	200	$28._8$
Ti(IV)	60	$28._3$
	960	$34._3$
	960	$28._2$ a)
Th(IV)	200	$29._0$
U(VI)	200	$28._9$
W(VI)	30	$28._4$
	200	$29._7$
Mo(VI)	200	$29._7$

a) 2 ml of NaF (0.1M) was added.

The Effect of Diverse Ions. The effect of diverse ions on the determination of vanadium(IV) was examined. The effect of metal ions is summarized in Table 1. Divalent metal ions such as nickel, lead, cadmium, copper, calcium, and magnesium up to at least 200 μg do not interfere with the determination. Molybdenum(VI) and tungsten(VI), when present in large quantities, give positive errors. The interferences from iron(III) and titanium(IV) can be eliminated by the addition of ascorbic acid and sodium fluoride (0.01 M) respectively. Of the anions tested, chloride, sulfate, nitrate, phosphate, fluoride, and tartrate have no effect on the determination even when present in a molar concentration 500 times that of vanadium(IV). Chelating agents such as EDTA and CyDTA, however, interfere seriously.

The Composition of the Extracted Species. The combining ratios of Tiron and DPG to vanadium(IV) in the extracted species were deduced by a spectrophotometric method.6) The number of moles of Tiron in the association complex was determined by plotting log(the distribution ratio of vanadium, D_V) against log (the total concentration of Tiron, $[H_2R]_t$). The pH and the total concentration of DPG were kept constant at 3.5 and 0.17 M respectively. The slope of the straight-line portion indicates that the vanadium: Tiron ratio is 1:2. In the same manner, the number of moles of DPG in the association complex was determined by plotting log D_V against log(the total concentration of DPG, $[DPG]_t$), the pH and the total concentration of Tiron being kept constant. The slope of 6.1 suggests that one vanadium(IV)-Tiron chelate anion associates with six DPG cations to form an extractable neutral species. The pH dependence of the extraction was then examined by plotting log D_V against the pH value of the aqueous phase. The results are shown in Fig. 3. The slope of 4.1, which is calculated by the method of least-squares, indicates that four protons are concerned with the extraction process.

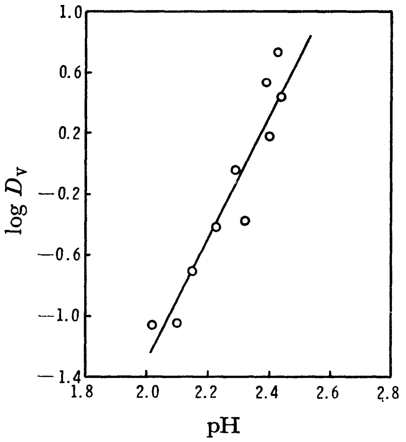

Fig. 3. Relationship between log D_V and pH for the V(IV)-Tiron-DPG system.
V(IV): 2.8×10^{-5}M, Tiron: 4.0×10^{-2}M, DPG: 0.17M, Ascorbic acid: 2.8×10^{-2}M.

From the foregoing observations, it seems natural to express the extraction equilibrium expression in the simplest form:

$$VO^{2+} + 2H_2R^{2-} + 6(DPG)^+ \rightleftarrows VO(R)_2(DPG)_6 + 4H^+$$

$$[VO(R)_2(DPG)_6] \rightleftarrows [VO(R)_2(DPG)_6]_o$$

References

1) Presented at the Tohoku Branch Meeting of the Chemical Society of Japan, Yonezawa, October, 1972.

2) I. A. Tserkovnitskaya and M. F. Grigor'eva, *Ser. Fiz. Khim.*, **3**, 130 (1966); *Chem. Abstr.*, **66**, 16346 (1967).

3) B. Sarma, *J. Sci. Ind. Research India*, **16B**, 569 (1957).

4) S. Nishikawa, Y. Nakagawa, M. Satake, and T. Matsumoto, *Bunseki Kagaku*, **15**, 944 (1966).

5) K. Ueno, "Kireto Tekitei (Chelatometric Titration)" (in Japanese), Nankodo, Tokyo (1960), p. 220.

6) Y. Wakamatsu and M. Otomo, This Bulletin, **45**, 2764 (1972).

7) Y. Wakamatsu and M. Otomo, *Nippon Kagaku Zasshi*, **90**, 595 (1969).