The Solvent Extraction and Spectrophotometric Determination of Vanadium(V) with Thenoyltrifluoroacetone[1]

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In 1963, De and Rahaman[2] reported a method for the rapid extraction of the vanadium(V)-thenoyltrifluoroacetone (TTA) complex using *n*-butyl alcohol. Except for this short communication, however, little work has been reported on this subject.[3-5] However, in the above method, the complex can not be extracted completely because *n*-butyl alcohol has a relatively large solubility in water. In this paper, a detailed study of the extraction of the vanadium(V)-TTA complex will be made, with special reference to the effect of solvents, the absorption spectra, and the composition of the extracted species.

Experimental

Reagents.—All the reagents used were guaranteed reagents.

The standard vanadium(V) solution was prepared by the fusion of 0.9094 g. of vanadium pentoxide with five times as much sodium carbonate for about one hour at about 900°C. This was dissolved in diluted sulfuric acid and diluted to 1 l. The final sulfuric acid concentration was about 6 N. This solution contains 10^{-2} mol./l. of vanadium. A diluted vanadium(V) solution was prepared daily. The organic solvents used for extraction were isoamyl acetate, *n*-butyl acetate, methyl isobutyl ketone, chloroform, benzine, ethyl acetate, carbon tetrachloride, ethylbenzene, toluene, chlorobenzene, cyclohexane, kerosene, xylene, benzene and isopropyl ether.

TTA: Solutions in the above solvents (up to 0.3 M).

Apparatus.—A Hitachi model EPU-2A spectrophotometer, a Hitachi-Horiba model M-3 pH meter (accuracy ±0.05 pH unit), a Toadempa HM-8 pH meter (accuracy ±0.005 pH unit), and an Iwaki KM shaker were used.

Experiments were performed by extracting 50 ml. of an aqueous solution of vanadic acid with 10 ml. of organic solvents containing TTA at 25°C.

Results and Discussion

The Absorption Spectra of the Vanadium(V)-TTA Complex and of the Chelating Agent.—As Fig. 1 shows, TTA is a typical diketone which is in keto-enol equilibrium in an aqueous solution.[6,7] It is the enol form that reacts with numerous metals.[8] Figures 2 and 3 show the various absorption spectra of the chelate extracted in various organic solvents.

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[1] This work was presented at the 11th General Meeting of the Hokkaido District of the Japan Society for Analytical Chemistry, Sapporo, January, 1964.

[2] A. K. De and M. S. Rahaman, *Anal. Chem.*, **35**, 1095 (1963).

[3] G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry," Wiley, New York (1957), p. 159.

[4] T. Takeuchi and M. Suzuki, *Japan Analyst*, **9**, 901, 965 (1960).

[5] E. B. Sandel, "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., New York (1950), p. 605.

[6] E. L. King and W. H. Reas, *J. Am. Chem. Soc.*, **73**, 1806 (1951).

[7] E. H. Cook and E. W. Taft, ibid., **74**, 6103 (1952).

[8] R. W. Taft and E. H. Cook, ibid., **81**, 46 (1959).

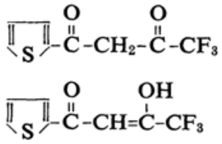

Fig. 1

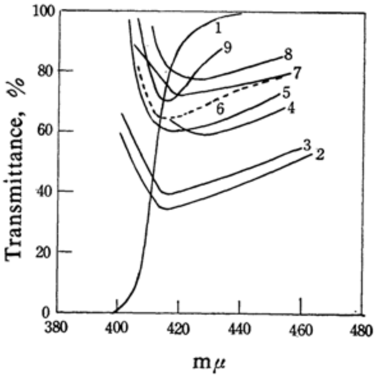

Fig. 2. Absorption spectra of vanadium(V)-TTA complex extracted in aliphatic solvents.

1) 0.1 M TTA isoamyl acetate soln.
2) Isoamyl acetate
3) *n*-Butyl acetate
4) Methyl isobutyl ketone
5) Benzine
6) Ethyl acetate
7) Chloroform
8) Carbon tetrachloride
9) Isopropyl ether

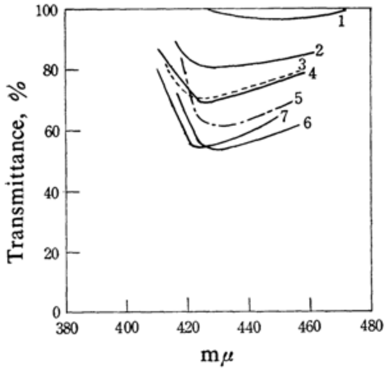

Fig. 3. Absorption spectra of vanadium(V)-TTA complex extracted in aromatic solvents.

1) Xylene, 2) Toluene, 3) Cycrohexane,
4) Chlorobenzene, 5) Benzene,
6) Kerosene, 7) Ethylbenzene

In these experiments, vanadium(V) was extracted for about one hour at pH 3. It was apparent that this complex was extracted more easily in aliphatic solvents, especially isoamyl acetate and *n*-butyl acetate, than in aromatic solvents.

TABLE I. SHIFTS OF THE ABSORPTION MAXIMUM OF THE COMPLEX

	Dielectric constant	Reflactive index	λ_{max} mμ
n-Butyl alcohol	17.1	1.39a)	410
Isoamyl acetate	6.05a)	1.40b)	414.5
Ethyl acetate	6.02	1.37a)	416
Chlorobenzene	5.62	1.52a)	426
Buthyl acetate	5.01a)	1.39a)	416
Chloroform	4.80a)	1.44a)	420
Isopropyl ether	3.88	1.36c)	416
Toluene	2.37	1.48c)	422
Benzene	2.27	1.50d)	430
Ethyl benzene		1.49	424
Carbon tetrachloride	2.22a)	1.46a)	423
Cyclohexane	2.01	1.42a)	424

a) 20°C, b) 21°C, c) 23°C, d) 29°C, other datas are at 25°C.

As is shown in Table I, the blue shifts of λ_{max} and the increment of the absorbance of these chelates were observed in accordance with a decrease in the refractive indices and with an increase in the dielectric constants of organic solvents, with the exception of a few solvents. Within the range of experimental error, the shifts of these chelate bands in organic solvents seem to obey the equation set forth by McRae, which predicts a linear relationship between the frequency shifts in absorption spectra and the expression $(n^2-1)/(2n^2+1)$, and $(D-1)/(D-2)$, where n is the refractive index and D is the dielectric constant of the solvent.[9–12]

The Effect of the Concentration of the Chelating Agent.—The effect of the concentration of the chelating agent on the extraction of the complex was determined by varying the concentration of the chelating agent at a constant vanadium(V) concentration. The changes in the absorbance of the organic phase were measured at 420 mμ since the absorption of the chelating agent was negligible at this point.

As Fig. 4 shows, the absorbance increased up to a maximum value of 0.1 M TTA, beyond which the increase in the chelating agent had no significant effect. Thus, in this experiment, the 0.2 M TTA concentration was used.

The Effect of the Extracting Time.—The effect of the extracting time was determined. About 30 min. were required for the attainment of the extraction equilibrium (Fig. 5).

The Effect of pH.—The effect of pH was determined by controlling the pH with sulfuric acid and sodium hydroxide. The results are as shown in Fig. 6. The chelate was completely extracted over the pH range from 2 to 3.

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[9] H. McConnel, *J. Chem. Phys.*, **20**, 700 (1952).

[10] J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958).

[11] O. Popovych and L. B. Dogers, *J. Am. Chem. Soc.*, **81**, 4469 (1959).

[12] E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957).

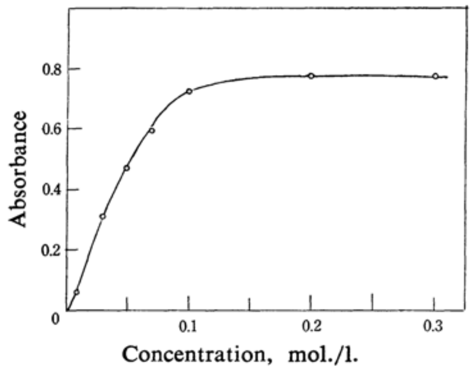

Fig. 4. Effect of the concentration of the chelating agent at pH 2.5 using isoamyl acetate.

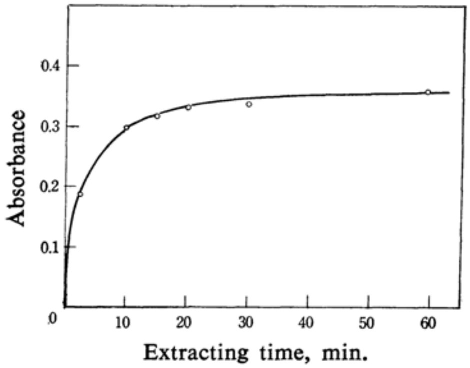

Fig. 5. Effect of the extracting time.

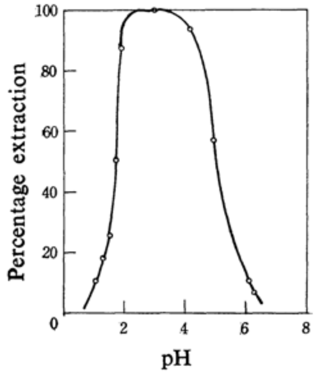

Fig. 6. Effect of pH.

The Determination of the Mole Ratio of Vanadium(V)-TTA Complex.—The determination of the mole ratio of vanadium(V) and TTA of this complex extracted in isoamyl acetate was made by the following two methods.

The Continuous Variation Method.[13]—The sum total of the concentrations of the metal ion and of the chelating agent was held at 10^{-2} mol./l., and the absorbance was plotted against the $[M^{n+}]/([M^{n+}]+[HR])$.

$[M^{n+}]$ and $[HR]$ are the initial concentrations of the vanadium(V) and of the chelating agent respectively. In this method $n=2$ (Fig. 7).

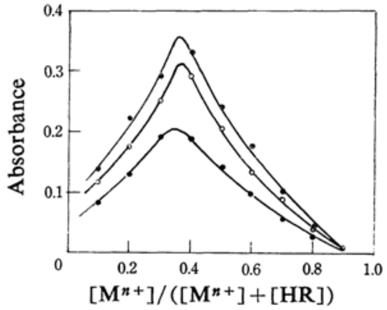

Fig. 7. Cotinueous variation method.

⊙ Determined at 410 mμ
○ Determined at 420 mμ
● Determined at 450 mμ

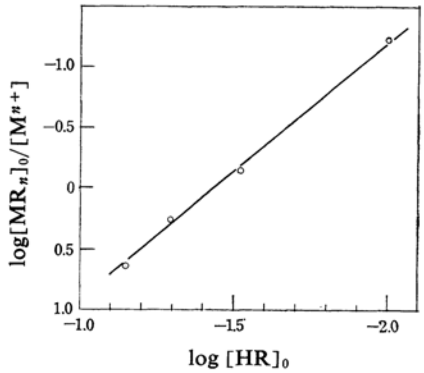

Fig. 8. Slope ratio method.

The Slope Ratio Method.[14]—Provided all intermediate complexes can be neglected,

$$M^{n+}+nR^{-} \rightleftharpoons MR_n$$

$$K_f=[MR_n]/[M^{n+}][R^{-}]^n$$

If the complexation of M^{n+} with a ligand other than R^- is not appreciable, we have:

$$K_f=K_{DR}^n[MR_n]_0[H^+]^n/K_{DX}K_A^n[M^{n+}][HR]_0^n$$

Then, at a constant pH:

$$n\log[HR]_0=C+\log D$$

where $C=-\log K_{DX}K_A^nK_f/K_{DR}^n[H^+]^n$ and D refers to the distribution ratio of M between the aqueous and organic solvent.

From the plots of $\log[HR]_0$ vs. $\log[MR_n]_0/[M^{n+}]$, n was obtained. As Fig. 8 shows, we obtain a slope of $n=2$.

The Calibration Curve and the Effect of Foreign Ions.—Under these conditions, the

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[13] Y. Niimura and N. Itoh, "Chemistry of Complex" (Vol. 11 in the "Zikken Kagaku Kohza" series), Maruzen, Tokyo (1963), p. 311.

[14] H. E. Bent and C. L. French, *J. Am. Chem. Soc.*, **63**, 568 (1941).

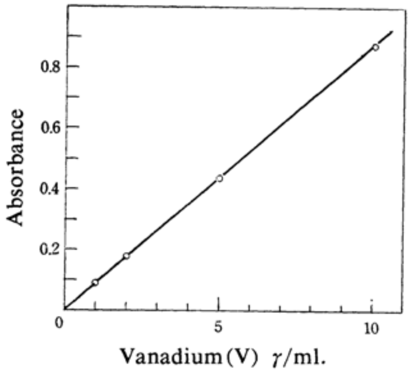

Fig. 9. Calibration curve.
TTA=0.2 mol./l., dissolved in isoamyl acetate, pH 2.5, at 420 mμ.

TABLE II. TOLERANCE LIMIT FOR DIVERSE IONS

Foreign ion	Added as	Tolerance limit p. p. m.
Ti^{4+}	Sulfate	50
Fe^{3+}	$FeSO_4(NH_4)_2SO_4 6H_2O$	10
Al^{3+}	Sulfate	500
Mn^{2+}	Sulfate	500
Zn^{2+}	Sulfate	500
Cu^{2+}	Sulfate	50
Ca^{2+}	Chloride	500
Mg^{2+}	Sulfate	500
Mo^{6+}	$(NH_4)_2MoO_4$	500
Pb^{2+}	$Pb(NO_3)_2$	500

relation between the absorbance and the vanadium(V) concentration was linear up to 10γ/ml. of vanadium(V) in an aqueous solution (Fig. 9). The fading was almost negligible.

Table II shows the effect of several metal ions on this method. Experiments were made in the presence and in the absence of 2×10^{-2} mol./l. of vanadium(V). The tolerance limit indicates the maximum concentration of diverse ions which affects the absorbance of the system by less than ±2%.

Because comparable amounts of Ti^{4+}, Fe^{3+}, Cu^{2+} interfere with the method, these ions should be removed from the sample by the usual methods.

Summary

The extraction of the vanadium(V)-TTA complex has been studied using various organic solvents. The complex has been extracted quantitatively in isoamyl acetate and *n*-butyl acetate. The quantitative extraction has been realized within a range from pH 2 to 3, with the absorption maximum at 410 mμ. The mole ratio of the complex is vanadium(V)-1 : 2-TTA, and Beer's law is applicable in the range from 0 to 10γ/ml. of vanadium(V) at 420 mμ. The solvent effects on the absorption spectra of this complex have also been studied.

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