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Synergistic Extraction of Vanadium(V, IV) with Dithizone

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By employing the synergistic extraction technique, vanadium(V,IV) has been found to form the primary dithizonate in the presence of a synergist. The extraction of the element proceeds according to the following equations.

$$VO_2^+ + H_2dz_{,org} + TBPO_{org} \rightleftharpoons VO_2(Hdz)(TBPO)_{org} + H^+,$$

and

$$VOOH^+ + H_2dz_{,org} + TOPO_{org} \rightleftharpoons VOOH(Hdz)(TOPO)_{org} + H^+,$$

where H_2dz, TBPO, and TOPO denote dithizone, tributylphosphine oxide and trioctylphosphine oxide, respectively, and the subscript org indicates the benzene phase. The resulting adduct $VO_2(Hdz)(TBPO)$ has an absorption maximum at 503 nm and is stable for at least 1 h. However, the red color of VOOH(Hdz)(TOPO) in benzene fades away during the standing time, probably due to the dimerization of the initially extracted monomeric species.

Since the introduction of dithizone(3-mercapto-1,5-diphenylformazan=H_2dz) into the field of analytical chemistry by H. Fischer,[1] extensive studies have been made with the reagent because of its excellent nature as a chelating agent.[2] However, the complexation of vanadium(V,IV) with dithizone has not been reported so far. In the work described below, sufficient evidence for the formation of dithizonatovanadium(V, IV) is given by employing the synergistic extraction technique.

Experimental

Reagent. A stock solution of vanadium(V) (100 μg cm^{-3}) was prepared by dissolving a weighed amount of ammonium metavanadate (NH_4VO_3, Wako Pure Chemicals) in water. Similarly, a stock solution of vanadium(IV) (100 μg cm^{-3}) was prepared by using vanadyl sulfate($VOSO_4$ $3H_2O$, Nakarai Chemicals). Trioctylphosphine oxide (TOPO), tributylphosphine oxide(TBPO), and dithizone were obtained from Wako Pure Chemicals and used without further purification. Benzene and all other reagents used in this work were of guaranteed grade.

Apparatus. The absorbance measurements were conducted with a Hitachi Model 200-10 type spectrophotometer and 1.00 cm glass cells. The pH of the aqueous phase was measured with a Hitachi-Horiba F-7_{ss} type pH meter, and the extraction was carried out by using a Iwaki KM type shaker.

Procedure. The aqueous phase containing 1.96×10^{-5} mol dm^{-3} vanadium(V) or vanadium(IV) was shaken vigorously for 10 min in a separatory funnel with an equal volume of the organic phase(benzene) containing dithizone and a synergist. After the phases were allowed to separate, the vanadium(V) or vanadium(IV) remaining in the aqueous phase was determined spectrophotometrically by using 4-(2-pyridylazo)resorcinol.[3] The pH of the aqueous phase, which was preliminarily adjusted with nitric acid or acetate buffer solution, was measured after the extraction. All experiments were conducted at room temperature.

Results and Discussion

No extraction of vanadium(V and IV) with dithizone(H_2dz) in benzene has been confirmed at any pH range, although vanadyl ion was reported to interfere with the spectrophotometric determination of lead(II).[4,5] In contrast, when the aqueous solution containing vanadium(V) or vanadium(IV) was shaken with a mixture of dithizone and trioctylphosphine oxide (TOPO), the organic phase was observed to change in its color from green to red though the color was not very stable. This phenomenon indicates the possible formation of dithizonatovanadium(V) and vanadium(IV) in the presence of a synergist.

Extraction of Vanadium(V). Although the mechanism was not clear, a stable reddish dithizonatovanadium(V) could be extracted into benzene by using tributylphosphine oxide(TBPO) as a synergist. In this extraction system, HVO_3 was reported to react with dithizone to form $VO_2(Hdz)(TBPO)$ by the present authors.[6] However, this conclusion has become dubious because the formation of $VO_2(Hdz)$-(TBPO) can also be explained by the reactive nature of VO_2^+ toward dithizone.

The effect of the TBPO concentration on the spectrum of the extract is given in Fig. 1. Below 2.0×10^{-3} mol dm^{-3} TBPO, each spectrum agrees with that of dithizone, indicating no formation of the colored

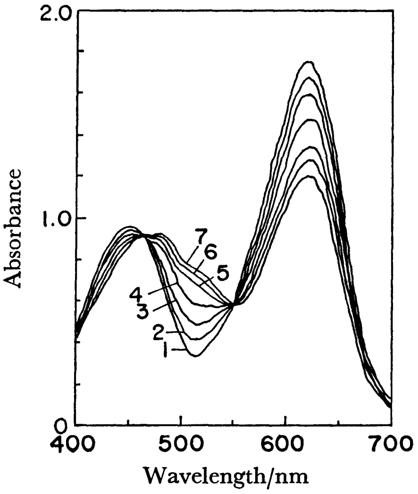


Fig. 1. Effect of TBPO concentration on the absorption spectrum of the organic phase.
H_2dz: 3.9×10^{-5} mol dm^{-3}, pH: 4.10, TBPO(mol dm^{-3}): 1; 2.0×10^{-3}, 2; 6.0×10^{-3}, 3; 1.0×10^{-2}, 4; 2.0×10^{-2}, 5; 4.0×10^{-2}, 6; 6.0×10^{-2}, 7; 1.0×10^{-1}.

vanadium(V) complex. On the other hand, in the higher concentration range of TBPO, the reddish dithizonatovanadium(V) is formed; this has an absorption maximum at 503 nm and is stable for at least 1 h (Fig. 2). The two isosbestic points seen in Fig. 1 suggest that only two kinds of colored species, dithizone and $VO_2(Hdz)(TBPO)$, exist in the organic phase. The shape of the spectrum depends upon the pH of the aqueous phase, as can be seen in Fig. 3, and the existence of two isosbestic points here also supports the above assertion. Therefore, only VO_2(Hdz)(TBPO) is considered to be extracted at any pH region.

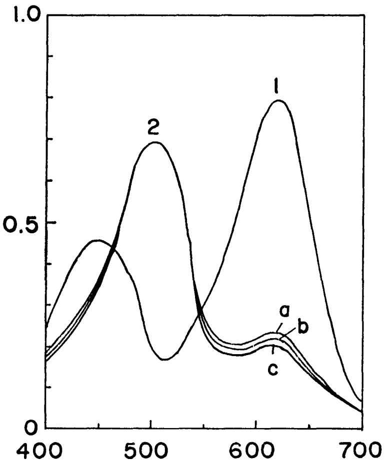


Fig. 2. Absorption spectra of the organic phase.
H_2dz: 1.95×10^{-5} mol dm^{-3}, TBPO: 1.0×10^{-1} mol dm^{-3}, vanadium(V): 1.96×10^{-4} mol dm^{-3}, pH: 4.0, 1: reagent balnk, 2: V(V)–H_2dz–TBPO complex, standing time after the extraction(min): a; 10, b; 30, c; 60.

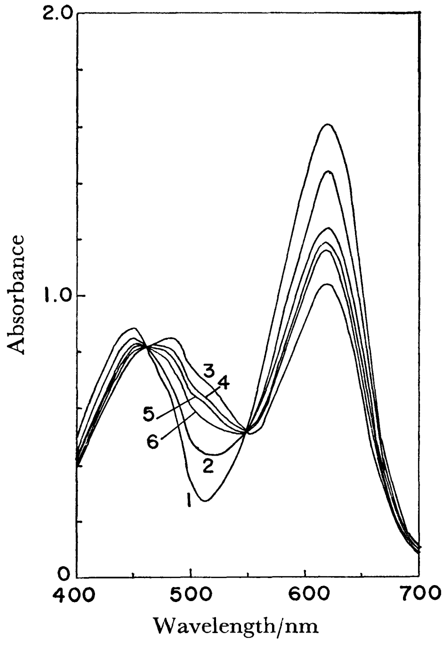


Fig. 3. Effect of pH on the absorption spectrum of the organic phase.
H_2dz: 3.9×10^{-5} mol dm^{-3}, TBPO: 1.0×10^{-1} mol dm^{-3}, pH: 1; 1.16, 2; 2.38, 3; 3.81, 4; 4.43, 5; 4.66, 6; 5.00.

Since the concentration of the polynuclear complex of vanadium(V), $H_iV_{10}O_{28}{}^{i-6}$ can be neglected compared with those of $VO_2{}^+$, HVO_3, and $VO_3{}^-$, according to the previous observation,7) the reactions in the aqueous phase can be written by Eqs. 1 and 2 in all cases.

$$VO_2{}^+ + H_2O \rightleftharpoons HVO_3 + H^+ \tag{1}$$

and

$$HVO_3 \rightleftharpoons VO_3{}^- + H^+. \tag{2}$$

The equilibrium constants for the above reactions are defined by Eqs. 3 and 4.

$$K_1 = \frac{[HVO_3][H^+]}{[VO_2{}^+]} \tag{3}$$

and

$$K_2 = \frac{[VO_3{}^-][H^+]}{[HVO_3]}. \tag{4}$$

The extractions of vanadium(V) with 1-butanol (*n*-BuOH) and trialkylphosphine oxide(TAPO) were ascribed to the formations of $HVO_3(BuOH)_2$ and $HVO_3(TAPO)_2$, respectively.8,9) In both cases BuOH and TAPO can be considered to act as solvating agents, although the detailed scheme of solvation is still unknown. In our previous report, the extraction of vanadium(V) with a mixture of dithizone and TBPO was estimated to proceed according to the reaction: $HVO_3 + H_2dz_{,org} + TBPO_{org} \rightleftharpoons VO_2(Hdz)(TBPO)_{org} + H_2O$, where the subscript org denotes the organic phase.6) And the pH of the maximal extraction of vanadium(V) in the dithizone–TBPO system agreed well with those obtained by alcohol extractions.7,10) At that time, therefore, we concluded that HVO_3 might react with dithizone in this case. However, if we assume HVO_3 to be a reacting species, the extraction of vanadium(V) should be expressed as the OH^- releasing reaction: $VO_2(OH) + H_2dz \rightleftharpoons VO_2(Hdz) + H_2O$; here, HVO_3 seems to act as a base, in contradiction to Eq. 2. And the synergistic extraction of vanadium(V) with a chelating agent has generally been explained by the reactive nature of $VO_2{}^+$ instead of HVO_3.

Moreover, the extraction of 8-quinolinolatovanadium(V) in the presence of alcohol(ROH) was found to proceed according to the reaction: $VO_2{}^+ + 2HQ_{org} + ROH_{org} \rightleftharpoons VOQ_2(OR)_{org} + H^+ + H_2O$.11) Similarly, vanadium(V)/2-thenoyltrifluoroacetone (TTA=Htta)/1-butanol or TOPO systems were explained by the reactions: $VO_2{}^+ + 2Htta_{,org} + BuOH_{org} \rightleftharpoons VO(tta)_2(BuO)_{org} + H^+ + H_2O$ and $VO_2{}^+ + Htta_{,org} + TOPO_{org} \rightleftharpoons VO_2(tta)(TOPO)_{org} + H^+$.7) Consideration of these examples suggests that complexation of vanadium(V) with a chelating agent may start from $VO_2{}^+$ as a Lewis acid.

The extracted species was shown spectrophotometrically to be only one, *e.g.* $VO_2(Hdz)(TBPO)$, which is formed by the reaction:

$$VO_2{}^+ + H_2dz_{,org} + TBPO_{org} \rightleftharpoons VO_2(Hdz)(TBPO)_{org} + H^+ \tag{5}$$

for which the extraction constant is defined as follows:

$$K_{\mathrm{ex}} = \frac{[\mathrm{VO_2(Hdz)(TBPO)}]_{\mathrm{org}}[\mathrm{H^+}]}{[\mathrm{VO_2^+}][\mathrm{H_2dz}]_{\mathrm{org}}[\mathrm{TBPO}]_{\mathrm{org}}}. \tag{6}$$

The distribution ratio of vanadium(V) is written by Eq. 7:

$$D = \frac{[\mathrm{VO_2(Hdz)(TBPO)}]_{\mathrm{org}}}{[\mathrm{VO_2^+}]+[\mathrm{HVO_3}]+[\mathrm{VO_3^-}]}. \tag{7}$$

Combining Eqs. 3, 4, 6, and 7, the following equation can be obtained:

$$\log D = \log\frac{K_{\mathrm{ex}}}{K_1} + \log\,[\mathrm{H_2dz}]_{\mathrm{org}} + \log\,[\mathrm{TBPO}]_{\mathrm{org}} - \log\left(\frac{[\mathrm{H^+}]}{K_1}+1+\frac{K_2}{[\mathrm{H^+}]}\right), \tag{8}$$

where $[\mathrm{H_2dz}]_{\mathrm{org}}$=(total concentration of dithizone)$-[\mathrm{VO_2(Hdz)(TBPO)}]_{\mathrm{org}}$.

A logarithmic plot of D against $[\mathrm{H_2dz}]_{\mathrm{org}}$ is shown in Fig. 4; a straight line having a slope of unity is obtained. Similarly, the plot given in Fig. 5 shows a straight line with a slope of unity. The above results are in good agreement with those expected from Eq. 8. In addition, the pH dependence of $\log D$ also supports Eq. 8 (Fig. 6). By employing the curve-fitting method, K_1 and K_2 were estimated to be 1.9×10^{-4} and 1.3×10^{-4} respectively, K_{ex} being 3.0×10^2.

Extraction of Vanadium(IV). Vanadium(IV) was also found to react with dithizone in the presence of TOPO; the spectra of the resulting reddish complex, along with standing time in the organic phase, are given in Fig. 7. The vanadium(IV)–dithizone–TOPO complex is not very stable, but it is assumed that the complex may be stable during the extraction process and the changes in the spectrum may start after the phase separation. Assuming that the extraction of vanadium(IV) proceeds according to the following reaction:

$$\mathrm{VOOH^+} + \mathrm{H_2dz}_{,\mathrm{org}} + \mathrm{TOPO}_{\mathrm{org}} \rightleftharpoons \mathrm{VOOH(Hdz)(TOPO)}_{\mathrm{org}} + \mathrm{H^+}, \tag{9}$$

the extraction constant may be defined by Eq. 10.

$$K^*_{\mathrm{ex}} = \frac{[\mathrm{VOOH(Hdz)(TOPO)}]_{\mathrm{org}}[\mathrm{H^+}]}{[\mathrm{VOOH^+}][\mathrm{H_2dz}]_{\mathrm{org}}[\mathrm{TOPO}]_{\mathrm{org}}} \tag{10}$$

Neglecting $\mathrm{(VOOH)_2^{2+}}$ compared with $\mathrm{VO^{2+}}$ and $\mathrm{VOOH^+}$, the distribution ratio can be written as follows:

$$D = \frac{[\mathrm{VOOH(Hdz)(TOPO)}]_{\mathrm{org}}}{[\mathrm{VO^{2+}}]+[\mathrm{VOOH^+}]}. \tag{11}$$

Hydrolysis of $\mathrm{VO^{2+}}$ in the aqueous phase can be expressed by Eq. 12 and the equilibrium constant can be written by Eq. 13:

$$\mathrm{VO^{2+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{VOOH^+} + \mathrm{H^+} \tag{12}$$

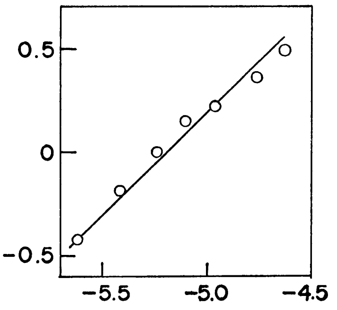


Fig. 4. Effect of dithizone concentration on the extraction of vanadium(V).
TBPO: 1.0×10^{-1} mol dm^{-3}, pH: 4.1.

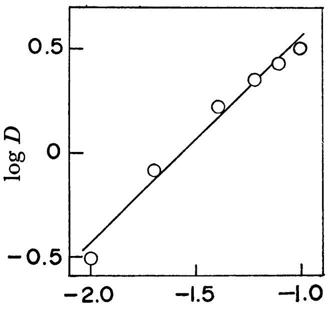


Fig. 5. Effect of TBPO concentration on the extraction of vanadium(V).
$\mathrm{H_2dz}$: 3.9×10^{-5} mol dm^{-3}, pH: 4.1.

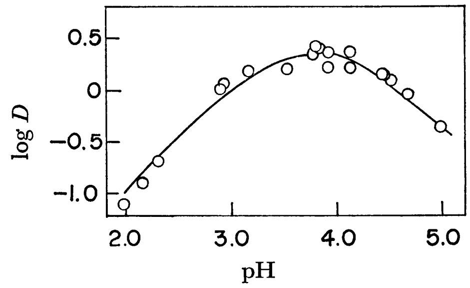


Fig. 6. Effect of pH on the extraction of vanadium(V). $\mathrm{H_2dz}$: 3.9×10^{-5} mol dm^{-3}, TBPO: 1.0×10^{-1} mol dm^{-3}, ○: experimental value, —: the best fitted normalized curve.

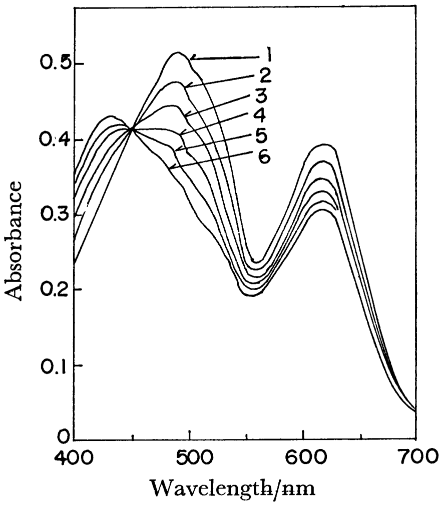


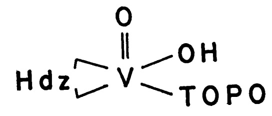
Fig. 7. Absorption spectra of the organic phase.
$\mathrm{H_2dz}$: 3.9×10^{-5} mol dm^{-3}, TOPO: 1.0×10^{-1} mol dm^{-3}, vanadium(IV): 1.96×10^{-4} mol dm^{-3}, pH: 3.96, standing time after the extraction(min): 1; 10, 2; 20, 3; 30, 4; 40, 5; 50, 6; 60.

$$K_h = \frac{[\mathrm{VOOH^+}][\mathrm{H^+}]}{[\mathrm{VO^{2+}}]}. \tag{13}$$

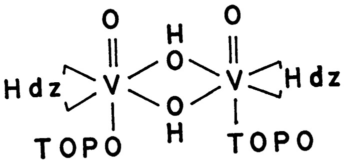
Combining Eqs. 10, 11, and 13, Eq. 14 can be obtained:

$$\log D = \log K^*_{\mathrm{ex}} + \log\,[\mathrm{H_2dz}]_{\mathrm{org}} + \log\,[\mathrm{TOPO}]_{\mathrm{org}} + \mathrm{pH} - \log\left(\frac{[\mathrm{H^+}]}{K_h}+1\right). \tag{14}$$

As is seen in Fig. 8, a logarithmic plot of D against dithizone concentration shows a straight line having a slope of unity in the high concentration region of dithizone. Deviations from the straight line at low dithizone concentration may be due to extraction of vanadium(IV) with TOPO alone. A logarithmic plot of D against TOPO concentration given in Fig. 9 also shows a straight line having a slope of unity regardless of the presence of dithizone. But it should be mentioned that the D value obtained by TOPO alone is negligibly small compared with that given by a mixture of dithizone and TOPO. The above results coincide with those expected from Eq. 14. The pH dependency of $\log D$ given in Fig. 10 fits a curve obtained by calculation using $Y=\mathrm{pH}-\log([\mathrm{H^+}]/K_h+1)$, indicating that the extracted species may contain $\mathrm{VOOH^+}$. This is also valid at low dithizone concentration region, in which the free concentration of dithizone can be calculated by using the equation: $[\mathrm{H_2dz}]_{\mathrm{org}}$=(total concentration of dithizone)−[vanadium(IV)]$_{\mathrm{org}}$. A plot of ($\log D - \log [\mathrm{H_2dz}]_{\mathrm{org}}$) against pH also fits the above curve (Fig. 11). The deviations of some experimental values from the calculated ones above pH 4.6 may be due to the formation of unreactive $(\mathrm{VOOH})_2^{2+}$ in the aqueous phase. From the results given in Figs. 9 and 10, K_h was estimated to be $10^{3.6}$, K^*_{ex} being $10^{2.5\pm0.3}$. As a result, the synergistic extraction of vanadium(IV) with a mixture of dithizone and TOPO proceeds according to Eq. 9. For the composition of the extracted species, VOOH(Hdz)(TOPO), two types of structure can be assumed:



(I)



(II)

where type I is a monomer and presumably extracted initially. The existence of an isosbestic point observed in Fig. 7 shows that VOOH(Hdz)(TOPO) in the organic phase may be converted to another stable complex, *e.g.* type II. That is to say, the instability

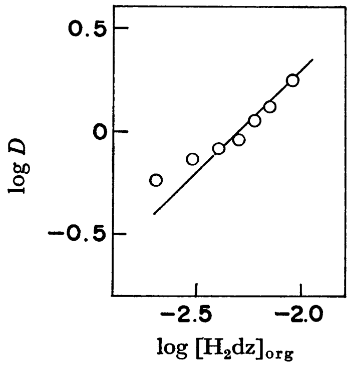


Fig. 8. Effect of dithizone concentration on the extraction of vanadium(IV).
TOPO: 1.0×10^{-2} mol dm^{-3}, pH: 4.0.

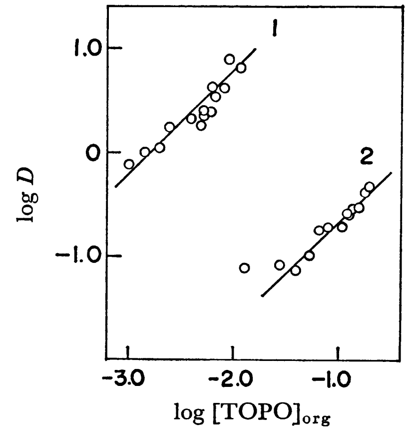


Fig. 9. Effect of TOPO concentration on the extraction of vanadium(IV).
$\mathrm{H_2dz}$: 1; 3.9×10^{-4} mol dm^{-3}, 2; none.

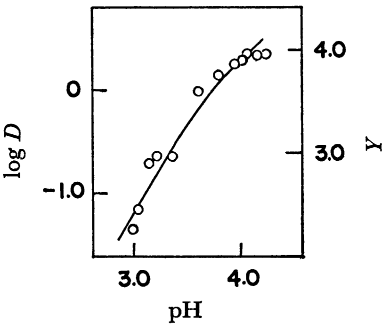


Fig. 10. Effect of pH on the extraction of vanadium (IV).
$\mathrm{H_2dz}$: 1.56×10^{-4} mol dm^{-3}, TOPO: 1.0×10^{-2} mol dm^{-3}, ○: $\log D$ *vs.* pH, —: Y *vs.* pH.

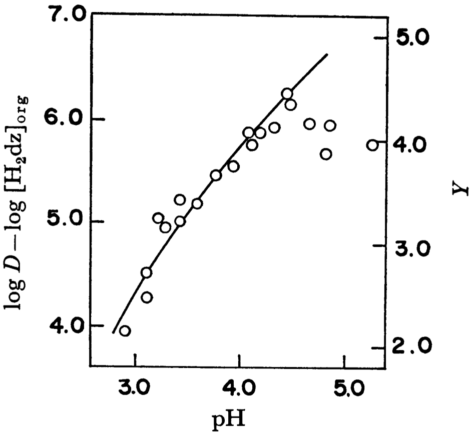


Fig. 11. Effect of pH on the extraction of vanadium (IV).
$\mathrm{H_2dz}$: 3.9×10^{-5} mol dm^{-3}, TOPO: 1.0×10^{-1} mol dm^{-3}, ○: $\log D - \log [\mathrm{H_2dz}]_{\mathrm{org}}$ *vs.* pH, —: Y *vs.* pH.

of VOOH(Hdz)(TOPO) can not simply be attributed to decomposition, as is observed in the cases of dithizonato complexes of manganese(II) and iron(II). It should be mentioned that stable dithizonatovanadium(IV) could be obtained by the extraction with a mixture of dithizone and TBPO. At present, we cannot explain the difference in the stability between TOPO and TBPO complexes.

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