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The Solvent-Extraction Equilibrium of Vanadium(III, IV, V) with Acetylacetone in Nonpolar Solvents

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The extraction of vanadium(III, IV, V) with 0.01—0.1 mol dm^{-3} acetylacetone in such nonpolar organic solvents as heptane, benzene, and chloroform has been investigated at pH 1—7 under a nitrogen atmosphere. The extraction constant, the partition coefficient, and the stability constant for the vanadium(III) and vanadium(IV) chelate were determined. Vanadium(V) was found to have been extracted as the vanadium(IV) chelate with reduction.

Vanadium is present in aqueous solutions in +2, +3, +4, and +5 oxidation states. In the presence of air, the quadrivalent and quinquevalent states are stable. Recently, the extraction equilibrium of vanadium has been investigated by using some chelating agents such as 8-quinolinol for vanadium(V)[1] and dithizone for vanadium(IV, V).[2] On the other hand, the spectrophotometric determination of vanadium using the extraction of vanadium(III) with 50% acetylacetone in chloroform has been previously reported.[3] However, little is known about the extraction equilibrium of vanadium in lower oxidation states, especially of vanadium(III).

In the present paper, the extraction chemistry of vanadium (III, IV, V), which are expected to occur in nature, is systematically studied in acetylacetone-nonpolar organic solvent systems.

Experimental

Reagents. A radioisotope, ^{48}V, was produced from high-purity titanium foils by a (p,n) reaction with 18 MeV protons using a cyclotron of Tohoku University. The titanium targets were dissolved in diluted sulfuric acid, and an excess amount of hydrogen peroxide was added to oxdize the titanium carrier to the quadrivalent state. After the excess of hydrogen peroxide has been removed by heating, carrier-free ^{48}V was extracted with 0.02 M(1 M=1 mol dm^{-3}) diethylammonium diethyldithiocarbamate in carbon tetrachloride at pH 4.5—5, washed with an aqueous solution at pH 4.5, and back-extracted with 10 M nitric acid. This solution was evaporated to dryness and dissolved in concentrated hydrochloric acid. Then the solution was fed into an anion-exchange column (Dowex 1X8, 0.8 cm inner diameter ×10 cm height) and eluted with concentrated hydrochloric acid. The ^{48}V fraction was collected and evaporated to dryness. To the residue, concentrated nitric acid was added, and the mixture was heated to completely decompose organic impurities and then evaporated to dryness. Finally, ^{48}V was dissolved in 0.01 M perchloric acid or sulfuric acid.

A carrier solution of vanadium(V) (ca. 0.02 M) was prepared by dissolving high-purity vanadium(V) oxide (Specpure; Johnson Matthey Chem., Ltd.) in perchloric acid or sulfuric acid. The radioactive vanadium(V) solution (10^{-4}—10^{-2} M) was prepared by mixing an appropriate amount of the vanadium(V) carrier and carrier-free ^{48}V, evaporating the mixture to dryness, dissolving it in 0.5 M perchloric acid, and heating it for about 1 h. To confirm the isotopic equilibrium of vanadium, the radioactive vanadium(V) in a 0.1 M sodium hydroxide solution was also prepared and used for the extraction of vanadium(V). The radioactive vanadium(IV) solution was prepared by reducing the vanadium(V) with sodium hydrogensulfite: to the radioactive vanadium(V) in a sulfuric acid solution, sodium hydrogensulfite (ca. 1 M) was added, and the excess of sulfite was removed by heating.

The 2,4-pentanedione(acetylacetone, Hacac) was washed with a diluted ammonia solution and water and then doubly-distilled through a fractionating column after drying. The tris(acetylacetonato)vanadium(III)[V(acac)$_3$] was prepared by the method of Dilli and Patsalides[4] and used to examine its stability in solutions for air oxidation. The oxobis(acetylacetonato)vanadium(IV)[VO(acac)$_2$] was obtained from Dojindo Laboratories. The chloroform was of a spectroscopic grade and was washed with redistilled water several times before use. The other organic solvents were purified by the usual methods. Unless otherwise stated, the reagents used were of a guaranteed reagent grade.

The ionic strength of an aqueous phase was kept at 0.10 M by the use of perchloric acid and sodium hydroxide. The pH of the aqueous phase was adjusted with 0.01—0.10 M perchloric acid, 0.01 M acetic acid, and 0.01 M sodium hydroxide. All the reagent solutions used for the extraction of vanadium(III) and vanadium(IV) were purged for 30 min with nitrogen which had been purified through a pyrogallol-potassium hydroxide solution just before use.

Apparatus. The γ-activity of ^{48}V was measured with an NaI(Tl) well-type scintillation counter. The electronic spectrum of the vanadium chelate was measured with a doublebeam spectrophotometer. The pH value of the equilibrated aqueous phase was measured with a glass electrode.

Extraction Procedure of Vanadium(III). When vanadium(III) was prepared by the reduction of vanadium(V), the purification of the vanadium(III) formed was found to be inevitable if reliable extraction data were to be obtained. Hence, an organic vanadium(III) solution was prepared and purified as follows, and the distribution ratio of vanadium(III) was determined by the back-extraction technique. A stream of purified nitrogen was passed through an 80-cm^3 extraction vessel with three necks in order to displace the air. An aqueous solution (pH 3—5) containing radioactive vanadium(V) (ca. 1×10^{-4} M) and an organic solvent containing 0.01—0.1 M Hacac were then placed in the vessel, and the mixture was stirred. A small amount of 2 M

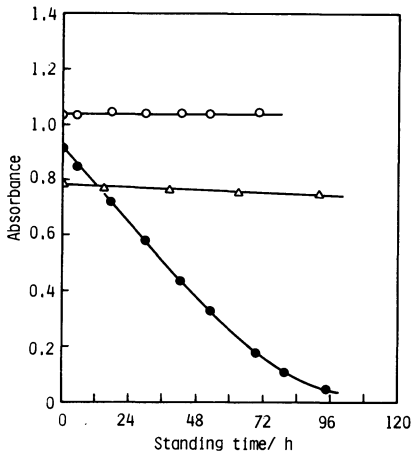

Fig. 1. Stability of $V(acac)_3$ in heptane solutions saturated with nitrogen or air.
○: 1.2×10^{-4} M $V(acac)_3$ at 348 nm under nitrogen atmosphere, ●: 1.1×10^{-4} M $V(acac)_3$ at 348 nm in air, △: 8.9×10^{-5} M $V(acac)_3$ –0.05 M Hacac at 355 nm in air.

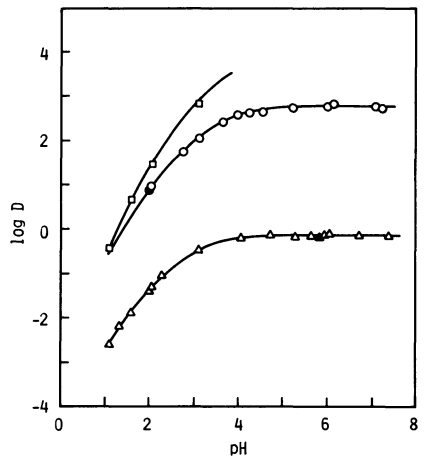

Fig. 2. Extraction of vanadium(III) with 0.10 M Hacac in various organic solvents. The solid lines indicate the computed values.
△: Heptane, ○: benzene, □: chloroform; ●▲: obtained from forward extraction.

sodium dithionite as a reducing agent was added to the contents to make up about a 0.05 M concentration of dithionite. Then the contents were vigorously stirred for 1—3 h. After the mixture had been left to stand, the organic phase was taken out and stirred again with a perchloric acid solution in an appropriate concentraion (0.01—0.1 M) to remove a small amount of the vanadium(IV) complexes from the organic phase. To the purified organic phase containing $V(acac)_3$ we then added an appropriate amount of Hacac, after which the solution was diluted with the organic solvent to adjust it to the desired concentrations of Hacac (0.01—0.1 M) and $V(acac)_3$ (10^{-6}—10^{-5} M). This organic solution (5 cm^3) was shaken with an aqueous solution (5 cm^3) for 1—24 h at pH 1—7 in a stoppered centrifuge tube in which the air had been displaced with nitrogen. After centrifugation, an aliquot was pipetted out from each phase, and the γ-activity was measured. The distribution ratio(D) of vanadium(III) was calculated by the counting rates. The equilibrium pH value was measured immediately after shaking. To confirm the extraction equilibrium, the forward extraction was also performed, and the distribution ratio was measured. Vanadium(III) was back-extracted with 1.0 M perchloric acid from the organic phase. A 0.5-cm^3 portion of the aqueous vanadium(III) solution was added to the centrifuge tube containing the organic (5 cm^3) and the aqueous phase (4.5 cm^3), and the contents were shaken. All the extraction procedures were performed under a nitrogen atmosphere at 25 °C.

Extraction Procedure of Vanadium(IV). An aqueous solution (5 cm^3) containing 1×10^{-5} M radioactive vanadium(IV) was shaken with an organic solution (5 cm^3) containing 0.1 M Hacac for 1—6 h in a centrifuge tube. After centrifugation, an aliquot was pipetted out from each phase, and the γ-activity was measured. In the back-extraction, the organic phase obtained by the forward-extraction was shaken with a fresh aqueous phase. All the extraction procedures were performed under a nitrogen atmosphere at 25 °C.

Extraction Procedure of Vanadium(V). An aqueous solution (5 cm^3) containing 10^{-6}—10^{-4} M radioactive vanadium(V) was shaken with an organic solution (5 cm^3) containing 0.01—0.1 M Hacac for 24 h at 25 °C. The distribution ratio was determined in the same manner as that in vanadium(III, IV). Only the back-extraction was performed under a nitrogen atmosphere.

Theoretical

The extraction equilibrium of a metal ion, M^{n+}, with a chelating agent, HA, can be expressed as follows:

$$M^{n+} + nHA_{org} \rightleftharpoons MA_{n,org} + n\,H^+ \quad (1)$$

$$K_{ex} = \frac{[MA_n]_{org}[H^+]^n}{[M^{n+}][HA]^n_{org}}, \quad (2)$$

where the subscript "org" denotes the organic phase, and K_{ex}, the extraction constant. The distribution ratio of the metal can be written as:

$$D = \frac{[MA_n]_{org}}{[M^{n+}] + \sum_{m=1}^{n} [MA_m{}^{(n-m)+}]}. \quad (3)$$

Equation 3 can be rewritten by using the partition coefficient of the neutral chelate(MA_n), P_M, and the overall stability constant of $MA_m{}^{(n-m)+}$ in the aqueous phase, β_m:

$$D = \frac{P_M\beta_n[A^-]^n}{1 + \sum_{m=1}^{n} \beta_m[A^-]^m} \quad (4)$$

$$= K_{ex}\left(\frac{P_{HA}}{K_{HA}}\right)^n \frac{[A^-]^n}{1 + \sum_{m=1}^{n} \beta_m[A^-]^m}, \quad (5)$$

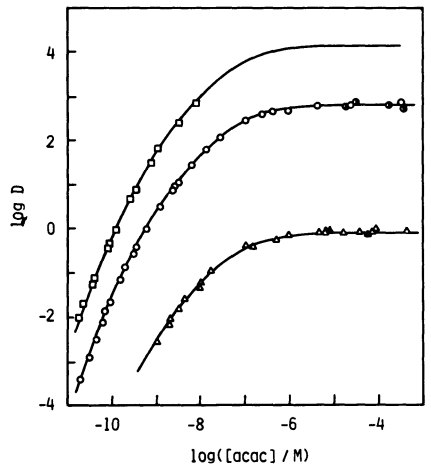

Fig. 3. Distribution ratio of vanadium(III) as a function of acac concentration in the aqueous phase. The solid lines indicate the computed values.
0.01—0.10 M Hacac, 7.5×10^{-7}—6.8×10^{-5} M V(III), pH 1.1—7.4.
△: Heptane, ○: benzene, □: chloroform, ◑▲: successively back-extracted.

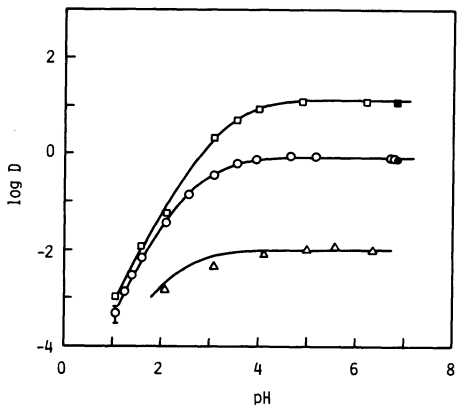

Fig. 4. Extraction of vanadium(IV) with 0.10 M Hacac in various organic solvents. The solid lines indicate the computed values.
△: Heptane, ○: benzene; □: chloroform, ●■: obtained from back extraction.

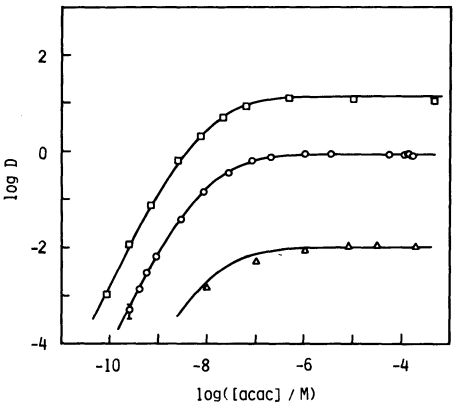

Fig. 5. Distribution ratio of vanadium(IV) as a function of acac concentration in the aqueous phase. The solid lines indicate the computed values.
0.08—0.10 M Hacac, 1.0×10^{-5} M V(IV), pH 1.1—6.9.
△: Heptane, ○: benzene, □: chloroform.

where P_{HA} and K_{HA} denote the partition coefficient and the acid-dissociation constant of HA.

Results and Discussion

Extraction of Vanadium(III). Since vanadium(III) is unstable in the presence of oxygen, the stability of $V(acac)_3$ solutions was examined by using the chelate synthesized in an inert gas atmosphere. Figure 1 shows the absorbance of the chelate in heptane solutions as a function of the standing time. It gradually decomposes in a heptane solution saturated with air until it has completely decomposed after standing for four days. In that solution, the formation of $VO(acac)_2$ due to the oxidation of $V(acac)_3$ was observed from the absorption spectrum. However, the addition of Hacac significantly prevents the oxidation decomposition, even in the presence of air. In addition, the vanadium(III) chelate is quite stable in a heptane solution saturated with nitrogen.

Under a nitrogen atmosphere, the extraction of vanadium(III) with Hacac in an organic solvent was first attempted using an aqueous vanadium(V) solution and a strong reducing agent, such as sodium dithionite or sodium borohydride. However, it was found that the complete conversion of vanadium(V) to vanadium(III) was difficult. Hence, in order to obtain accurate distribution data on vanadium(III), we adopted the back-extraction technique described above. Figure 2 shows the extraction curves of vanadium(III) with 0.10 M Hacac in heptane, benzene, and chloroform. The distribution ratio obtained from the forward extraction is in good agreement with that obtained from the back extraction. This fact means that the extraction equilibrium was completely achieved within the agitation time given in each solvent system; 1—120 min for the heptane system, 2—6 h for the benzene system, and 18—24 h for the chloroform system, at pH 1—2. The solid lines indicate the values calculated using the equilibrium constants determined as below.

Moreover, the detailed extraction of vanadium(III) was performed with a different amount of Hacac in the organic solvent (0.01—0.10 M) at pH 1—7. Figure 3 shows the plots of log D against the logarithm of the equilibrium concentration of the acac anion in the aqueous phase. The equilibrium concentration of acac was calculated by using the following equation:

$$[A^-] = \frac{C_{HA}}{(P_{HA}+1)[H^+]/K_{HA}+1}, \quad (6)$$

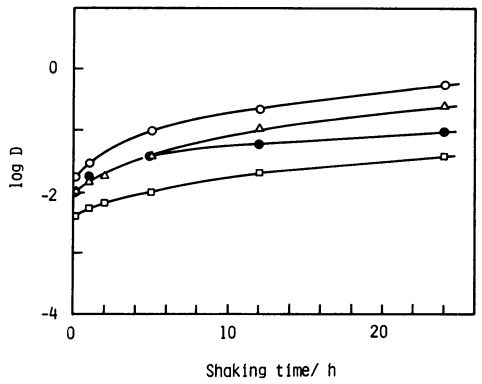

Fig. 6. Effect of shaking time on the extraction of vanadium(V).
1.0×10^{-5} M V(V).
□: 0.10 M Hacac-benzene at pH 2.61, △: 0.10 M Hacac-chloroform at pH 2.61, ○: 0.10 M Hacac-chloroform at pH 4.69, ●: 0.01 M Hacac-chloroform at pH 4.69.

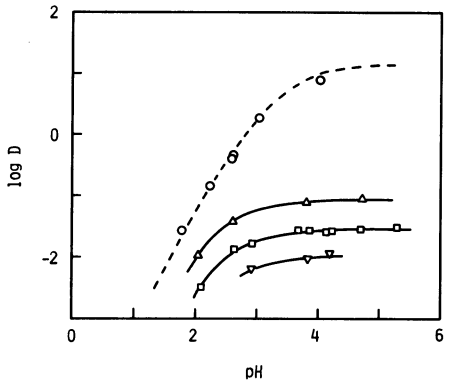

Fig. 7. Extraction and back extraction of vanadium (V) with 0.10 M Hacac in chloroform. The broken line shows the extraction curve of vanadium(IV).
1.0×10^{-5} M V(V).
▽,□,△: Forward extraction at shaking time 5 min, 1 h, 6 h respectively, ○: back extraction at shaking time 1 h.

where C_{HA} denotes the initial concentration of Hacac. The literature values of K_{HA} and P_{HA} were used; i.e., log K_{HA} was −8.82,[5] and log P_{HA} was −0.052 for heptane,[6] 0.736 for benzene,[7] and 1.367 for chloroform.[7] In the low-concentration region of acac, the slope for the plots of log D vs. log [acac] is 3, as is to be expected from the extraction of V(acac)$_3$. The equilibrium constants, P_M and β_m, can be determined according to Eq. 4: the P_M values in the heptane and benzene system were directly determined as the limiting value of the distribution ratio in the high-concentration region of acac. The stability constants, β_1, β_2, and β_3, were determined by the least-square fitting (SALS program, University of Tokyo) on the basis of Eq. 4, using the distribution data in the benzene system. The P_M value in the chloroform system was determined by the least-square fitting using the β_1, β_2, and β_3 values obtained above. The K_{ex} value was calculated as $K_{ex}=P_M\beta_3K_{HA}^3P_{HA}^{-3}$. The equilibrium constants are listed in Table 1. The solid lines in Fig. 3 indicate the values computed using these equilibrium constants, they are in good agreement with the experimental plots.

Extraction of Vanadium(IV). Figure 4 shows the extraction curves of vanadium(IV) with 0.10 M Hacac in heptane, benzene, and chloroform. The distribution ratio of vanadium(IV) did not vary at various agitation times from 1 to 6 h. The distribution ratio obtained from the back-extraction is in good agreement with that obtained from the forward extraction, and the extraction equilibrium is completely achieved. Figure 5 shows the plots of log D against log[acac]. In the low-concentration region of acac, the slope for the plots is 2, as is to be expected from the extraction of VO(acac)$_2$. The P_M value in each solvent system was directly determined as the limiting value of the distribution ratio in the high-concentration region of acac. The stability constants, β_1 and β_2, were determined by the least-square fitting on the basis of Eq. 4, using the distribution data in the benzene system. The K_{ex} value was calculated as $K_{ex}=P_M\beta_2K_{HA}^2P_{HA}^{-2}$. These values are listed in Table 1. The solid lines in Figs. 4 and 5 indicate the values computed using these equilibrium constants; they are in good agreement with the experimental plots.

Extraction of Vanadium(V). The extractability of vanadium(V) was much lower than those of vanadium(III) and vanadium(IV) and the extraction equilibrium could not be achieved. Figure 6 shows that the distribution ratio of vanadium(V) very gradually increases with an increase in the shaking time in both the benzene and chloroform systems. This phenomenon was also observed even at lower vanadium(V) concentrations such as 8.2×10^{-7} M. In such a low-concentration region, polynuclear species of vanadium(V), especially of metavanadates, which are relatively slow equilibrium species, are not formed.[8] Figure 7 shows the plots of log D against the pH at several shaking intervals. The gradual increase in log D is seen at pH 2—5 in the forward-extraction. On the other hand, the distribution ratios in the back-extraction are in agreement with those of vanadium(IV). This result was also obtained in the benzene system under similar extraction and back-extraction conditions. These facts suggest that vanadium(V) is reduced to vanadium(IV) and extracted as stable VO(acac)$_2$. This conclusion is consistent with the previous observation that the vanadium(V)-acetylacetone complex cannot be isolated because of its ready reduction to the quadrivalent state.[3]

Equilibrium Constants of Vanadium(III, IV). The equilibrium constants are summarized in Table 1. No data for vanadium(III) have been reported thus far. It was revealed that not only P_M, β_1, β_2, and β_3 for

Table 1. Equilibrium Constants in the Extraction of V(III) and V(IV) at 25 °C

Chelate	Solvent	$\log K_{ex}$	$\log P_M$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
$V(acac)_3$	Heptane	−0.31	−0.112			
	Benzene	0.23	2.793	10.19	19.18	26.10
	Chloroform	−0.32	4.141			
$VO(acac)_2$	Heptane	−3.42	−1.979			
	Benzene	−3.08	−0.066	8.59	16.10	
	Chloroform	−3.12	1.157			

vanadium(III) are all almost the same as those for iron(III) in a series of first-transition metal(III)-acetylacetone chelates,[9] i.e., the equilibrium constants of iron(III) in the benzene system, log P_M=2.785, log β_1=10.63, log β_2=19.26, and log β_3=26.22. Such similarities are supported by the fact that the ionic radius of vanadium(III), 0.640×10^{-8} cm,[10] is quite close to that of iron(III), 0.645×10^{-8} cm[10]; additionally, the metal-oxygen-bond length in $V(acac)_3$ obtained by the X-ray crystallography, 1.982×10^{-8} cm,[11] is close to that in $Fe(acac)_3$, 1.992×10^{-8} cm.[11] These results suggest that the nature of the coordination bonds in the vanadium(III) chelate is hardly different from that in the iron(III) chelate. Consequently, the agreement of the partition coefficient between the vanadium(III) and the iron(III) chelate may be attributed to the similarity in the polarity of their bonds and in the solute-solvent interactions between the chelate and the organic solvent or water.

The equilibrium constants of $VO(acac)_2$ was compared with those of bis(acetylacetonato) chelates of the first-transition metals(II). It was found that the stability constant of the vanadium(IV) chelate is larger than that of the copper(II) chelate, *i.e.*, log β_1=7.93 and log β_2=14.56,[12] which are largest values among the first-transition metal(II) chelates. On the other hand, the partition coefficient of the vanadium(IV) chelate was considerably smaller than that of the copper(II) chelate; i.e., the log P_M in the benzene system is 0.897.[12] These facts may be attributed to the higher charge of the central metal as +4 as well as to the polarity of the oxo group in the vanadium(IV) chelate.

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