Solvent Extraction of V(III, IV, V) with Acetylacetone

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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.   Thus far the extraction of V(V) has been well investigated by using some chelating agents such as 8-quinolinol, benzoylphenylhydroxylamine, etc.[1], while little is known about the extraction chemistry of V in lower oxidation states.

In this work, the extraction chemistry of V(III, IV, V) which are expected to occur in nature is studied in acetylacetone(Hacac)-nonpolar organic solvent systems.

A radioisotope, V-48, was produced from titanium foil by the (p,n) reaction with 18 MeV protons with a cyclotron of Tohoku University.   Carrier free V-48 was separated from the titanium target by diethyldithiocarbamate extraction and anion exchange chromatography and treated with concentrated nitric acid several times.   A radioactive V(V) solution was prepared by mixing an appropriate amount of the V(V) carrier solution and the carrier free V-48, evaporating to dryness, and dissolving in 0.5 M percholoric acid.   The radioactive V(IV) solution was prepared by reducing the radioactive V(V) with sodium hydrogensulfite.

All reagent solutions to be used for the extraction of V(III) and V(IV) were purged for 30 min with nitrogen purified by passing through a pyrogallol-potassium hydroxide solution.   Ionic strength of an aqueous phase was kept to be 0.10 M with sodium perchlorate.

Extraction procedure of V(III):   In an extraction flask, an aqueous solution containing radioactive V(V) (usually 1×10^{-4} M) and an organic solution containing 0.01-0.10 M Hacac were placed and a small amount of 2 M sodium dithionite as a reducing agent was added to the contents.   Then the contents were vigorously stirred for 1-3 h.   The organic phase was taken out and washed with 0.01-0.10 M perchloric acid to remove V complexes other than V(III).   To the organic solution was added an appropriate amount of Hacac in order to adjust to the desired concentration.   This organic V(III) solution (5 ml) was shaken with an aqueous solution (5 ml) for 1-24 h at pH 1-7.   After centrifugation, an aliquot was pipetted from each phase and the γ-activity was measured with an NaI(Tl) well-type scintillation counter.   The distribution ratio(D) of V(III) was calculated.   The equilibrium pH was measured immediately after shaking.

Extraction procedure of V(IV) and V(V):　An　aqueous　solution　(5 ml)
containing 1×10^{-6} — 1×10^{-5} M radioactive V(IV) or V(V) was shaken for 1-6 h
with an organic solution (5 ml) containing 1×10^{-4} — 1×10^{-1} M Hacac at pH 1-7.
An aliquot was pipetted from each phase and the γ-activity was measured.　All
experiments were performed in nitrogen atmosphere at 25°C.

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

$$M^{n+} + n\ HA_{org} \rightleftharpoons MA_{n,org} + n\ H^+ \tag{1}$$
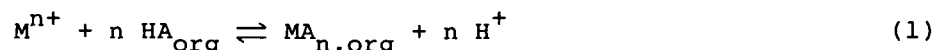
$$K_{ex} = \frac{[MA_n]_{org}[H^+]^n}{[M^{n+}][HA]^n_{org}}, \tag{2}$$

where the subscript org denotes the organic phase and K_{ex}, the extraction
constant.

The distribution ratio of M^{n+} can be written by;

$$D = \frac{[MA_n]_{org}}{[M^{n+}] + \Sigma[MA_m^{n-m}]}. \tag{3}$$

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

$$D = \frac{P_M\beta_n[A^-]^n}{1 + \Sigma\beta_m[A^-]^m} = K_{ex}\left(\frac{P_{HA}}{K_{HA}}\right)^n \frac{[A^-]^n}{1 + \Sigma\beta_m[A^-]^m}, \tag{4}$$

where $[A^-]$ is the chelating anion concentration in the aqueous phase, and P_{HA}
and K_{HA} are the partition coefficient and the acid-dissociation constant of HA
respectively.

Figures 1 and 2 show the plots of log D for V(III) and V(IV) against
logarithm of the equilibrium concentration of acac⁻ anion in the aqueous
phase, which can be calculated by using K_{HA}[2] and P_{HA}.[3]　In the low
concentration region of acac⁻, the slope for the plots of log D vs. log[acac⁻]
is three for V(III) and two for V(IV).　Therefore the respective extracted
species are V(acac)$_3$ and VO(acac)$_2$.　The equilibrium constants, P_M and β_m,
were determined by using a least square fitting (SALS program) on the basis of
the first term of Eq. (4).　The values of V(III) and V(IV) are listed in Table
1.　No data for V(III) have been reported so far.　It is found that not only
P_M but also β_1, β_2 and β_3 for V(III) are almost the same as those for
Fe(III).[4]　The solid lines in Figs. 1 and 2 represent the computed values
using those equilibrium constants obtained and are in good agreement with the
experimental plots.

On the other hand, the extractability of V(V) was much lower than those of V(III) and V(IV), e.g., log D was -1.6 on the extraction of 0.10 M Hacac in benzene at pH 4.0 (shaking time 5 h). The distribution ratio of V(V) very gradually increased with increase in the shaking time. The organic phase obtained from the forward extraction of V(V) was shaken again with an aqueous solution at various pH. The D values in the back extraction were consistent with those of V(IV). These results suggest that V(V) was reduced to V(IV) and extracted as $VO(acac)_2$.

References

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2) Rydberg J., Svensk Kem. Tidskr., 67 (1955) 499.
3) Wakahayashi T., Oki S. and Omori T. and Suzuki N., J. Inorg. Nucl. Chem., 26 (1964) 2255.
4) Imura H., Kodera J. and Suzuki N., 8th Symposium on Solution Chemistry, Kanazawa, 1985, Abstr. p. 72.

Table 1. Equilibrium constants in the extraction of V(III) and V(IV) with acetylacetone at 25°C.

Chelate	Solvent	log K_{ex}	log P_M	log β_1	log β_2	log β_3
$V(acac)_3$	Heptane	-0.31	-0.112			
	Benzen	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			
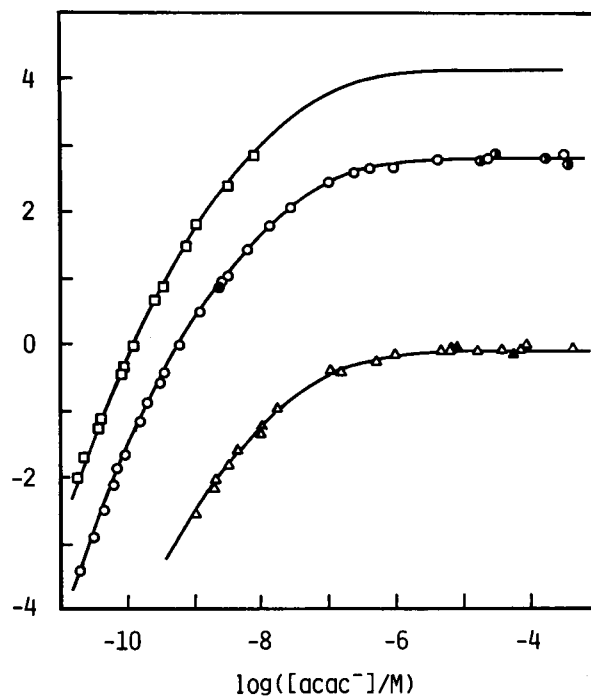
Fig. 1. Extraction of V(III) with Hacac in some organic solvents.
[Hacac]$_{init}$, 1×10^{-2} - 1×10^{-1} M; [V(III)], 1×10^{-6} - 1×10^{-4} M.
pH 1-7.   △ heptane, o benzene, □ chloroform. ▲ ● Extraction
from aqueous to organic phace.
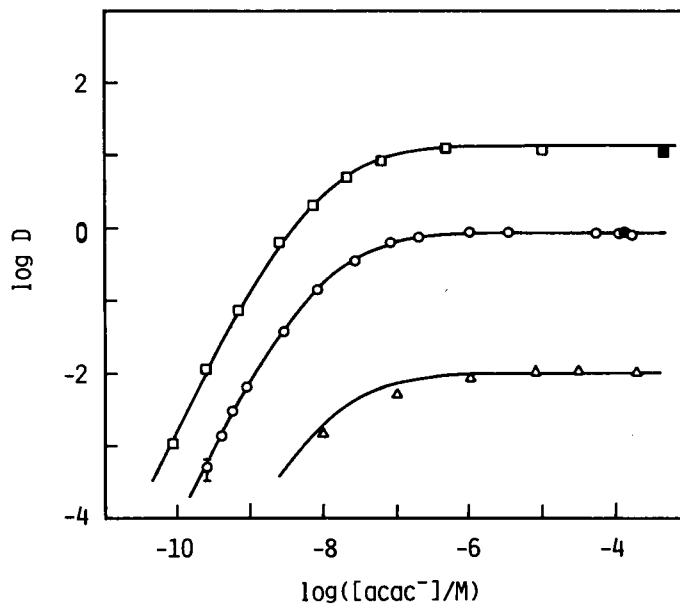
Fig. 2. Extraction of V(IV) with Hacac in some organis solvents.
[Hacac]$_{init}$, 1×10^{-1} M; [V(III)], 1×10^{-5} M.   pH 1-7.
△ heptane, o benzene, □ chloroform. ● ■ Extraction
from organic to aqueous phase.