

# SEPARATION AND PURIFICATION OF VANADIUM AND MOLYBDENUM BY SOLVENT EXTRACTION FOLLOWED BY REDUCTIVE STRIPPING

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The solvent extraction of vanadium and molybdenum by tri-*n*-octylmethylammonium chloride (TOMAC) from neutral solutions was studied and it was found that vanadium was extracted preferentially by an anion exchange mechanism. The pentavalent vanadyl anion in the organic solution was found to be reduced to the form of tetra- or trivalent cations by contact with an aqueous solution containing a reduction agent such as L-ascorbic acid. This enables the vanadium to be stripped selectively by chemical reduction, with the molybdenum remaining in the organic phase. A separation efficiency of  $1.64 \times 10^4$  was obtained for an aqueous solution containing initially equal concentrations of the two metals by single extraction followed by single selective stripping.

## Introduction

Recently, much attention has been paid to rare metals as new industrial materials and solvent extraction is known to be one of the most effective methods for their separation and purification. A solvent extraction process used for rare metals normally consists of three stages: extraction, scrubbing, and stripping. Usually, separation is effected at the extraction stage on the basis of difference in distribution ratio between the metals in the feed solution. When selective stripping of the required metal can be included, it results in a much higher separation efficiency.

In the Purex process for the recovery of plutonium and uranium from waste nuclear fuels, it is known that plutonium is stripped selectively by either chemical<sup>11,16)</sup> or electrochemical<sup>4,5)</sup> reduction from the tetravalent to the trivalent form. The reductive stripping of cerium,<sup>6,17)</sup> europium,<sup>9)</sup> uranium,<sup>7)</sup> and iron<sup>12,15)</sup> have also been reported. Reduction of these metals is very effective in the stripping operation, since their distribution ratio is then considerably reduced in magnitude.

In this work, the separation and purification of vanadium and molybdenum by solvent extraction using tri-*n*-octylmethylammonium chloride (TOMAC,  $R_3R'NCl$ ) as extractant and subsequent selective stripping of vanadium by chemical reduction were investigated. Both metals are contained in waste desulfurization catalyst and also in oil-fired boiler slag. It has been reported previously that vanadium and

molybdenum may be separated from aqueous acidic media by solvent extraction processes using tri-*n*-butyl phosphate (TBP),<sup>8)</sup> di(2-ethylhexyl)phosphoric acid (D2EHPA), and tri-*n*-octylamine (TOA)<sup>3)</sup>. The present separation process differs from these in that extraction is carried out from neutral solutions. The present results may be applied to the previously reported processes above to enhance the separation efficiency.

## 1. Experimental

### 1.1 Reagents

TOMAC (Koei Kagaku Kogyo Co., Ltd.) was purified by the procedure developed for the purification of Aliquat 336<sup>14)</sup> and was diluted with benzene. Aqueous stock solutions of vanadium and molybdenum were prepared by dissolving sodium metavanadate ( $NaVO_3$ ) and sodium molybdate ( $Na_2MoO_4 \cdot 2H_2O$ ) respectively in distilled water. The ionic strength of these solutions was adjusted to the required values with sodium chloride. The pH of the feed solutions was adjusted with either hydrochloric acid or sodium hydroxide solutions using a pH meter (Orion Research model 611). L-ascorbic acid was used as a reduction agent at the stripping stage. The inorganic chemicals and diluent were analytically pure reagent-grade material.

### 1.2 Procedures

Organic and aqueous feed solutions were mixed at volume ratios of 1:1 and shaken for about 2 h for equilibration at 25°C. The two phases were separated and the metal concentration in the aqueous raffinate solution was determined to obtain the extraction percentage, *E*. This was done because a quantitative

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stripping of the metals by single contact with stripping solution was not feasible. It was confirmed in preliminary runs that the organic metal concentrations obtained from the raffinate solution measurement and mass balance were in good agreement with those obtained from repeated contacts with fresh stripping solutions.

Stripping was carried out by shaking equal volumes of the metal-loaded organic solution and aqueous solution together for about 2 h at 25°C. The vanadium and molybdenum concentrations in the aqueous solutions were determined by means of an inductively coupled argon plasma atomic emission spectrophotometer (ICP, Nippon Jarrell-Ash ICAP-575MarkII). The chloride concentration in the organic phases was measured using a Volhard titration method.

## 2. Results and Discussion

### 2.1 Extraction of vanadium and molybdenum by TOMAC

1) Extraction of vanadium Performance of vanadium extraction by TOMAC at various equilibrium pH values are shown in Fig. 1, where  $[V]_f$  and  $[TOMAC]_f = 0.01 \text{ mol} \cdot \text{l}^{-1}$ . Almost all vanadyl ions are extracted at a pH of 6–7, whereas the extraction percentage is reduced to less than 30% at pH > 10. The quantity of chloride ion released from the organic phase and into the aqueous phase during the course of extraction ( $\Delta[Cl^-]$ ) was determined and was compared with the concentration of vanadyl ion extracted into the organic phase ( $[V]$ ). The pH dependence of the ratio  $\Delta[Cl^-]/[V]$  so obtained is also given in Fig. 1. An exchange of chloride anions for vanadyl ions apparently occurs during the extraction, but the ratio of chloride to vanadyl varies with pH. This result may be attributed to the formation of polyvanadate anions in the aqueous solution. Bard *et al.*<sup>2)</sup> and Rossotti *et al.*<sup>10)</sup> have reported that the structure of pentavalent vanadyl ion changes with solution pH as shown in Table 1. If one  $R_3R'N^+$  molecule is assumed to be consumed for each negative electric charge of the vanadyl species during extraction, the resulting ratio values,  $\Delta[Cl^-]/[V]$ , are predicted to vary in magnitude from 0.4 to 2 depending on the aqueous-phase pH value. As shown in Table 1, the observed ratio values appear to be in good agreement with the predicted values, with the exception of the case of pH > 8.5. The vanadyl anions are, therefore, extracted with their structure retained. Thus, an anion exchange extraction mechanism appears to be applicable to the extraction and the following schemes (1) and (2) may be postulated.

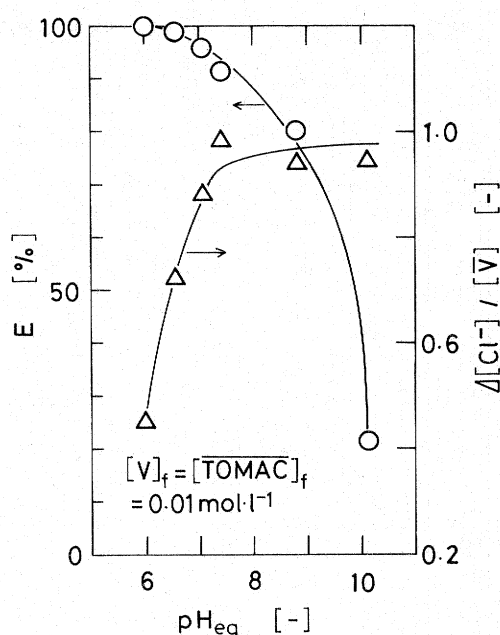
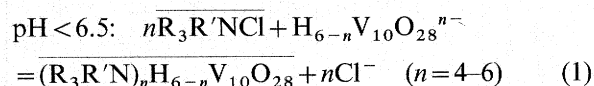
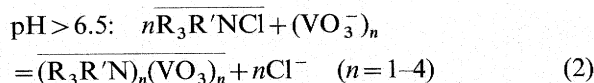


Fig. 1. Effect of equilibrium pH on extraction performance of vanadium and on ratio of chloride released to vanadium extracted

Table 1. Structures of the pentavalent vanadyl and hexavalent molybdate ions and a comparison of the predicted and observed ratio values of chloride ions released and metal ions (M) extracted at various pH.

Solution pH [—]	Structure	Predicted $\Delta[Cl^-]/[M]$ [—]	Observed $\Delta[Cl^-]/[M]$ [—]
2–6.5	$H_2V_{10}O_{28}^{4-}$	0.4	0.4–0.7
	$HV_{10}O_{28}^{5-}$	0.5	
	$V_{10}O_{28}^{6-}$	0.6	
6.5–8.2	$(VO_3^-)_n$ ( $n=1-4$ )	1	0.8–1
8.5–13	$V_2O_7^{4-}$	2	1
1–6	$Mo_7O_{24}^{6-}$	0.86	0.5
	$Mo_8O_{26}^{4-}$	0.5	
pH > 6	$MoO_4^{2-}$	2	1.7–2.7



Sato *et al.* have reported that the pentavalent vanadyl ion is extracted as  $V_2O_7^{4-}$  from sodium hydroxide solution by TOMAC.<sup>13)</sup> But in the present work the observed ratio fails to agree with the predicted value (=2) at pH greater than 8.5. This may be due to the low concentration of vanadium (less than  $10^{-2} \text{ mol} \cdot \text{l}^{-1}$ ) used in the present experimental conditions. The formation of pyrovanadate ion,  $V_2O_7^{4-}$ , actually is reported by Bard *et al.*<sup>2)</sup> to occur at a vanadium concentration level greater than  $10^{-2} \text{ mol} \cdot \text{l}^{-1}$ .

2) Extraction of molybdenum The dependence of

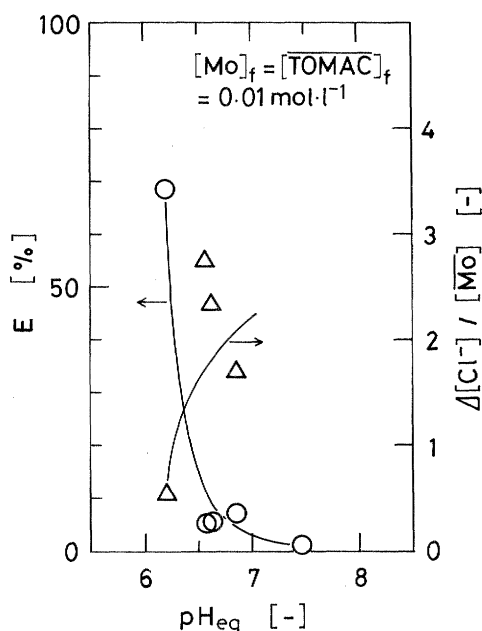
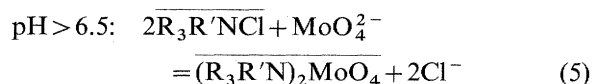
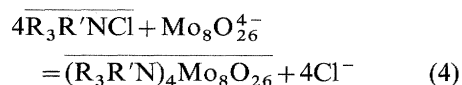
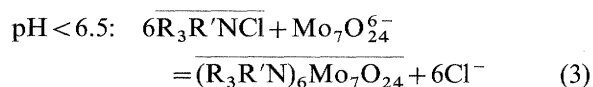


Fig. 2. Effect of equilibrium pH on extraction performance of molybdenum and on ratio of chloride released to molybdenum extracted

extraction performance and of the ratio  $\Delta[\text{Cl}^-]/[\text{Mo}]$  on pH are shown in Fig. 2. The E value decreases as the equilibrium pH increases, and reaches a value of less than 10% at  $\text{pH} > 6.5$ . The structure of the hexavalent molybdate anion is  $\text{MoO}_4^{2-}$  in this pH region, as reported by Bard *et al.*,<sup>2)</sup> and the observed ratio values (1.7–2.7) are in agreement with the predicted value (=2). On the other hand, the E value at  $\text{pH} < 6.5$  is about ten times greater, and the ratio value is reduced to 0.5. If the formation of polymeric species such as  $\text{Mo}_7\text{O}_{24}^{6-}$  and  $\text{Mo}_8\text{O}_{26}^{4-}$  as reported by Aveston *et al.*<sup>1)</sup> is assumed, the present results seem reasonable, since the observed ratio value is very near the predicted value as shown in Table 1. Thus, these polymeric species are the main species extracted at  $\text{pH} < 6.5$ . The extraction equilibria for molybdenum can be described by the following relations.



3) Extraction of vanadium and molybdenum from mixed solutions Figure 3 shows the performance of vanadium and molybdenum extraction from mixed solutions containing equal quantities of each metal ( $0.01 \text{ mol} \cdot \text{l}^{-1}$ ) as a function of the equilibrium pH. The extraction behavior of both metals in solution is

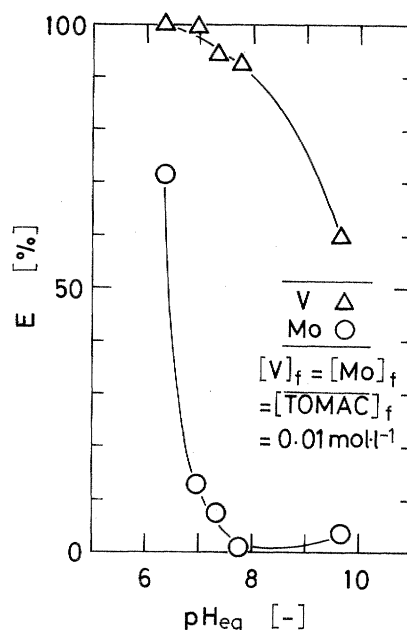


Fig. 3. Relationship between equilibrium pH and extraction performance of vanadium and molybdenum

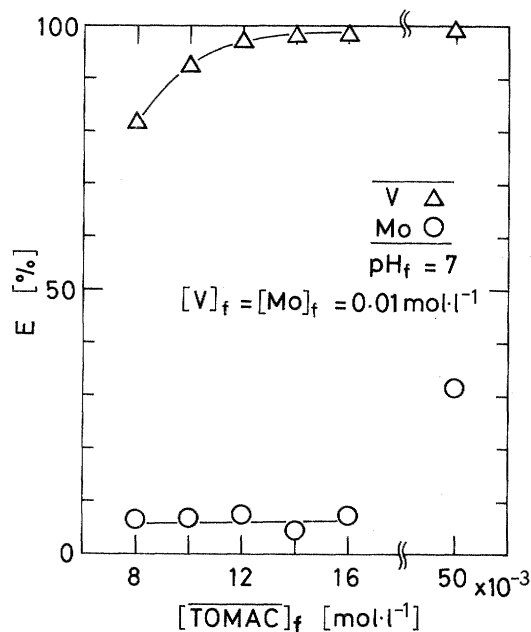


Fig. 4. Effect of TOMAC concentration on extraction performance of vanadium and molybdenum at pH 7

found to be very similar to that found for single-metal extraction, as shown in Figs. 1 and 2. An equilibrium pH of 7 to 8 should be employed for effective separation of the two metals.

The concentration of TOMAC also influences the separation efficiency. As shown in Fig. 4, the extraction of vanadium increases appreciably with TOMAC concentration, whereas the extraction of molybdenum is less affected.

With a TOMAC concentration of  $0.015 \text{ mol} \cdot \text{l}^{-1}$

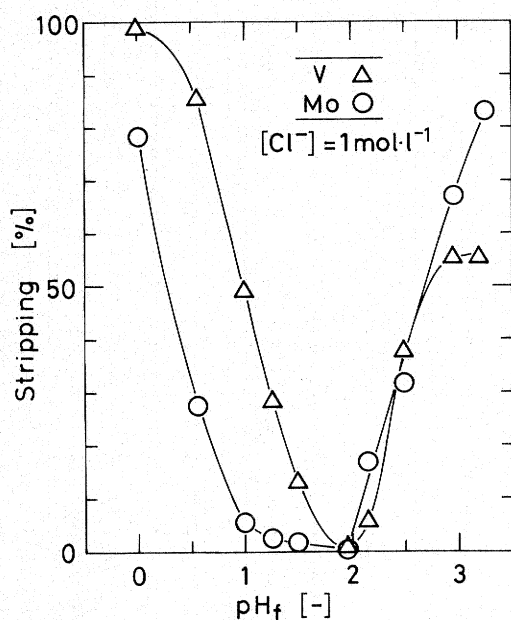


Fig. 5. Effect of stripping solution pH on stripping performance of vanadium and molybdenum

and an input aqueous pH value of 7.0, the resulting equilibrium pH value obtained was ca. 7.4. Under these conditions, the extraction percentages for vanadium and molybdenum were greater than 98% and less than 8%, respectively. Using a feed solution containing  $9.43 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  vanadium and  $1.01 \times 10^{-2} \text{ mol} \cdot \text{l}^{-1}$  molybdenum, the concentration of vanadium in the organic phase was  $9.26 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ , which was more than 12 times greater than that of molybdenum ( $7.59 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ ). More than 92% molybdenum ( $9.37 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ ) remained in the raffinate aqueous solution; in molar terms, its quantity was more than 50 times greater than that of vanadium ( $1.75 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$ ).

## 2.2 Further purification of vanadium by reductive stripping

To improve the separation of the two metals, the scrubbing of molybdenum and/or the selective stripping of vanadium is needed. In this study, the method of selective stripping of vanadium by chemical reduction was investigated.

A series of runs using a stripping solution containing  $1 \text{ mol} \cdot \text{l}^{-1}$  chloride anion at various pH values were carried out. The effect of input pH on stripping performance is shown in Fig. 5. It is seen that the stripping performance shows a minimum value at  $\text{pH}_f = 2$  ( $\text{pH}_{\text{eq}} = \text{ca. } 2.3$ ) and less than 1% of both metals is transferred into the stripping solution. This minimum stripping is likely caused by the very stable structure of the pentavalent vanadyl ion and the hexavalent molybdate ion at this pH in the organic phase. At this pH the effect on the stripping performance of the addition of L-ascorbic acid as a reduction agent was investigated. The results are

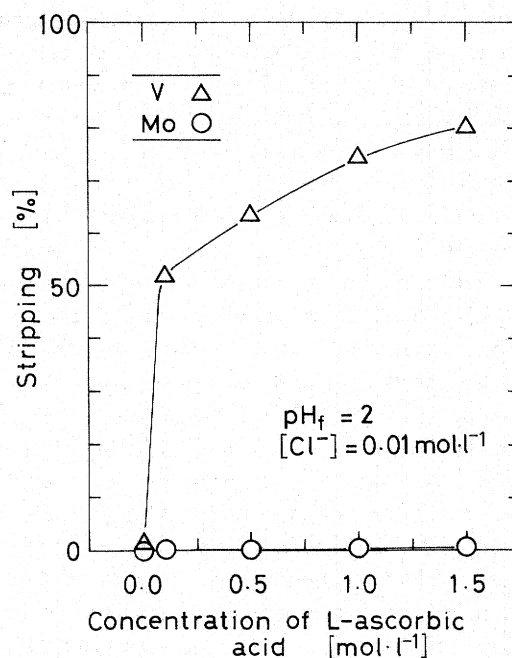


Fig. 6. Effect of addition of L-ascorbic acid on stripping performance of vanadium and molybdenum at pH 2

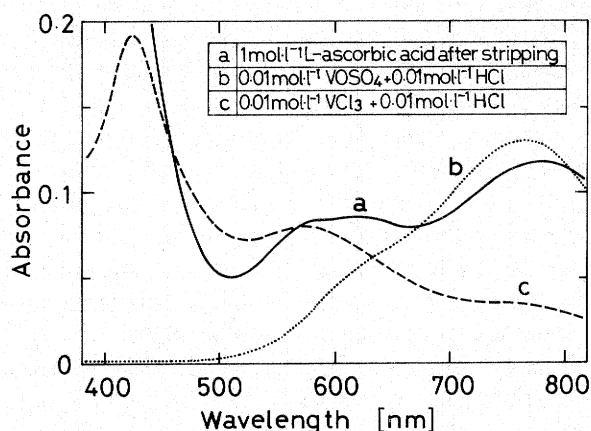


Fig. 7. Visible absorption spectra of aqueous solutions containing vanadyl ions

shown in Fig. 6. The stripping of vanadium was remarkably enhanced, whereas that of molybdenum was insensitive to the addition of the reduction agent. The valency of the vanadium stripped into the aqueous phase was investigated spectroscopically. The visible absorption spectrum of this bluish-green phase is shown in Fig. 7, together with the spectra of tetravalent vanadium (vanadyl sulfate,  $\text{VOSO}_4$ ) and trivalent vanadium (vanadium chloride,  $\text{VCl}_3$ ) at pH 2. The aqueous phase after stripping showed a spectroscopic feature similar to that of a mixture of tetra- and trivalent vanadium. Thus, pentavalent vanadium is likely to be reduced to a mixed state of tetra- and trivalent vanadium by L-ascorbic acid, where the reduced vanadium species exists as cations such as  $\text{VO}^{2+}$  (tetravalent) and  $\text{V}^{3+}$  (trivalent). TOMAC is

basically an anion exchanger and acts as an extractant for anionic species. Consequently, these cationic species are hardly extracted. For molybdenum, the colorless hexavalent molybdate anion in the organic phase was converted to the form of yellowish species by the addition of L-ascorbic acid and still remained in the organic phase. These yellowish species are not characterized exactly, but are likely to be anionic species. The stripping performance remains at an extremely low level, as in the case without a reduction agent. No precipitation was observed in either the aqueous or the organic phases during the stripping operation.

Figure 8 shows the relationship between the stripping solution pH and the stripping performance for both metals for the case of an aqueous solution containing  $1 \text{ mol} \cdot \text{l}^{-1}$  L-ascorbic acid and ca.  $0.01 \text{ mol} \cdot \text{l}^{-1}$  chloride anions (hydrochloric acid and/or sodium chloride being used). The separation efficiency, which is defined as the molar ratio of vanadium to molybdenum, in the resulting stripping solution after stripping is also shown in Fig. 8. The percentage stripping of vanadium increases with decreasing pH, while that for molybdenum shows a minimum value at pHs of 1.8–2. This leads to the appearance of a maximum in the separation efficiency at pH values of 1.8–2. The condition at which vanadium is stripped most efficiently is however not always suitable for separation and purification of vanadium and molybdenum. The effect of the composition of the stripping solution on the stripping performance is shown in Table 2. With  $1 \text{ mol} \cdot \text{l}^{-1}$  L-ascorbic acid solution, the percentage stripping for vanadium reaches 91.3% and a separation efficiency of  $6.47 \times 10^3$  is obtained. On decreasing the concentration of the reduction agent, the stripping performance for both metals decreases. However, the separation efficiency increases up to a value of  $1.64 \times 10^4$  with further decrease in concentration of the reduction agent to  $0.1 \text{ mol} \cdot \text{l}^{-1}$ . Thus, the solution pH and concentration of the reduction agent must be carefully selected to achieve high separation efficiency and/or high percentage recovery.

## Conclusion

The separation and purification of vanadium and molybdenum by solvent extraction and subsequent reductive stripping were studied and the following results were obtained.

1) Vanadium was extracted from neutral solutions preferentially by TOMAC as compared to molybdenum. The resulting vanadium concentration in the organic phase was more than 12 times that of molybdenum.

2) The extracted vanadium was selectively stripped by the chemical reduction method, in which the

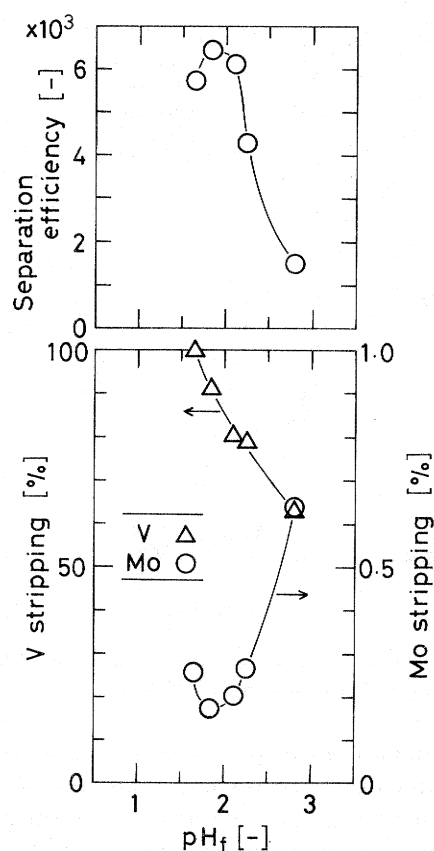


Fig. 8. Effect of stripping solution pH on stripping performance of vanadium and on molybdenum and separation efficiency. Concentrations of L-ascorbic acid and chloride anion are  $1 \text{ mol} \cdot \text{l}^{-1}$  and ca.  $0.01 \text{ mol} \cdot \text{l}^{-1}$ , respectively.

Table 2. Stripping performance of vanadium and molybdenum, and separation efficiency at various conditions. The organic solution used contains  $9.26 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$  vanadium and  $7.59 \times 10^{-4} \text{ mol} \cdot \text{l}^{-1}$  molybdenum. Each stripping solution contains  $0.01 \text{ mol} \cdot \text{l}^{-1}$  hydrochloric acid.

Concentration of L-ascorbic acid [ $\text{mol} \cdot \text{l}^{-1}$ ]	pH <sub>f</sub> [—]	Stripping [%]		Separation efficiency [—]
		V	Mo	
0.1	2.03	64.7	0.048	$1.64 \times 10^4$
0.5	1.91	85.0	0.074	$1.40 \times 10^4$
1.0	1.83	91.3	0.172	$6.47 \times 10^3$

vanadium is changed from a pentavalent anion to tetra- and trivalent cations. The appropriate selection of reduction agent concentration and of solution pH gave high separation efficiency and percentage recovery. The highest separation efficiency obtained by extraction followed by selective stripping was  $1.64 \times 10^4$ .

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#### Nomenclature

$\Delta[\text{Cl}^-]$  = amount of chloride ion moved from organic phase to aqueous phase in the course of extraction [mol·l<sup>-1</sup>]

E = extraction percentage [%]

[ ] = concentration of species in brackets [mol·l<sup>-1</sup>]

#### 〈Subscripts〉

eq = equilibrium value

f = feed or initial value

#### 〈Superscript〉

— = organic phase species

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