

# SOLVENT EXTRACTION PROCESS FOR SEPARATION AND PURIFICATION OF MOLYBDENUM AND VANADIUM BY TRI-*n*-BUTYL PHOSPHATE IN XYLENE

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**Key Words:** Metal Extraction, Scrubbing, Tributyl Phosphate, Mixer Settler, Molybdenum, Vanadium

## Introduction

In the previous work, the extraction equilibrium formulations for single metals such as molybdenum and vanadium from hydrochloric acid by TBP were established.<sup>2)</sup> In the present work, based on the previous work, simultaneous extraction of two metals was carried out in both batch and continuous flow operations with single- and two-stage mixer-settlers. The loaded organic solutions obtained by extraction were then scrubbed with hydrochloric acid to examine the effect of scrubbing on the purification of the solutions.

## 1. Experiments

The extractant solution, TBP in xylene, and procedures for the measurement of batchwise extraction were the same as those described previously.<sup>2)</sup> The aqueous feed solutions contained both molybdenum and vanadium of approximately  $10^{-2}$  mol/l and 3–5 mol/l of hydrochloric acid. In the measurement of molybdenum concentration using an atomic absorption spectrophotometer, the absorption peak was found to be affected by the amounts of co-existing materials such as acid, vanadium and sodium ions. The concentrations were, therefore, determined using calibration graphs that had been obtained with standard solutions containing nearly the same amounts of such interfering materials as the sample solutions.

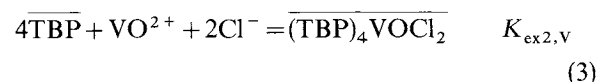
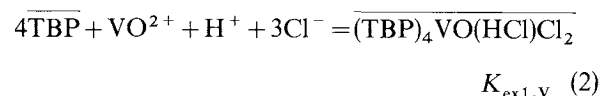
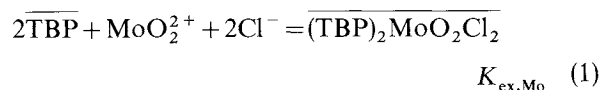
A small mixer-settler battery made of polyvinyl chloride resin was used for continuous operation. This is a miniature-size model of the General Mills unit<sup>1)</sup> and is shown in Fig. 1. It has a rectangular mixer fitted in the base, with a top shrouded turbine that both mixes and pumps the incoming phases. The dispersion exits from the top of the mixer into a rectangular settler. The turbine, 3 cm in diameter, was driven at 1850 rpm. The feed rates of both aqueous

and organic phases were 30 cm<sup>3</sup>/min and the mean residence time was about 4.2 min in the mixer and 6.7 min in the settler. Samples were taken from the outlet for analysis, after about 50 min for single-stage or 100 min for two-stage operation from the start of the feeding of solutions.

## 2. Results

### 1) Extraction equilibria for binary metal extraction

The extraction equilibrium formulations for molybdenum and vanadium have been established as follows, respectively.



The extraction constants under the present experimental conditions are  $K_{\text{ex,Mo}} = 1.50$ ,  $K_{\text{ex1,V}} = 1.41 \times 10^{-5}$  and  $K_{\text{ex2,V}} = 9.19 \times 10^{-5}$ .<sup>2)</sup>

The distribution ratios obtained for the binary metal system are plotted against hydrochloric acid and TBP concentrations in Fig. 2 for comparison with the prediction calculated from Eqs. (1)–(3) and shown

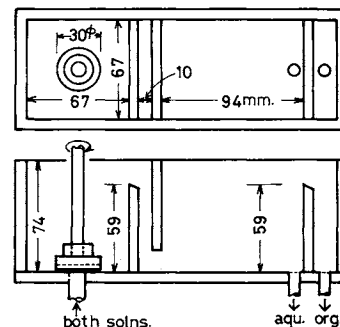


Fig. 1. Miniature-size model of General Mills unit.

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**Table 1.** Effect of single scrubbing of loaded organic solution with HCl. Comparison of observed values with prediction shown in parentheses. Unit of conc.: mol·l<sup>-1</sup>

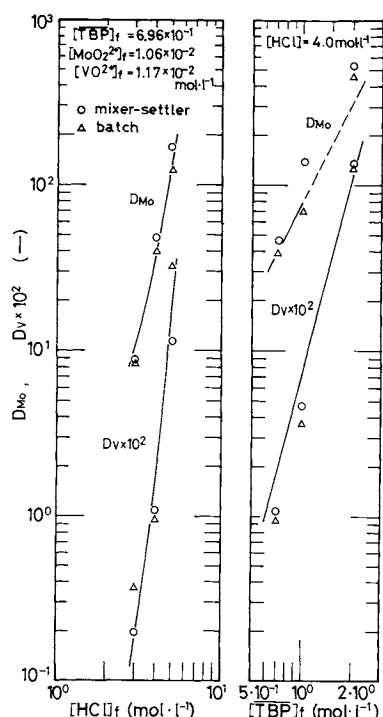
Scrubbing HCl soln.	Feed solution				Scrubbed solution		
	[TBP] <sub>f</sub>	[MoO <sub>2</sub> ]	[VO]	[MoO <sub>2</sub> ]/[VO]	[MoO <sub>2</sub> ]	[VO]	[MoO <sub>2</sub> ]/[VO]
3.0	6.96 × 10 <sup>-1</sup>	9.45 × 10 <sup>-3</sup>	4 × 10 <sup>-5</sup>	2.36 × 10 <sup>2</sup>	8.60 × 10 <sup>-3</sup> (8.65 × 10 <sup>-3</sup> )	Undetectable (1.0 × 10 <sup>-7</sup> )	— (8.65 × 10 <sup>4</sup> )
4.0	6.96 × 10 <sup>-1</sup>	1.03 × 10 <sup>-2</sup>	1.07 × 10 <sup>-4</sup>	9.63 × 10 <sup>1</sup>	1.01 × 10 <sup>-2</sup> (1.02 × 10 <sup>-2</sup> )	Undetectable (2.0 × 10 <sup>-6</sup> )	— (5.10 × 10 <sup>3</sup> )
4.0	6.96 × 10 <sup>-1</sup>	9.77 × 10 <sup>-2</sup>	9.65 × 10 <sup>-4</sup>	1.01 × 10 <sup>2</sup>	9.50 × 10 <sup>-2</sup> (9.53 × 10 <sup>-2</sup> )	1 × 10 <sup>-5</sup> (1.7 × 10 <sup>-5</sup> )	9.5 × 10 <sup>3</sup> (5.61 × 10 <sup>3</sup> )
4.0	9.98 × 10 <sup>-1</sup>	1.02 × 10 <sup>-1</sup>	3.21 × 10 <sup>-3</sup>	3.18 × 10 <sup>1</sup>	9.90 × 10 <sup>-2</sup> (1.01 × 10 <sup>-1</sup> )	6 × 10 <sup>-5</sup> (1.0 × 10 <sup>-4</sup> )	1.6 × 10 <sup>3</sup> (1.01 × 10 <sup>3</sup> )

**Table 2.** Separation of molybdenum and vanadium using two-stage mixer-settlers. Unit of conc.: mol·l<sup>-1</sup>

Aqueous feed concentrations: [VO<sup>2+</sup>]<sub>f</sub> = 1.17 × 10<sup>-2</sup> and [MoO<sub>2</sub><sup>2+</sup>]<sub>f</sub> = 1.06 × 10<sup>-2</sup> mol/l

Values in parentheses: prediction

[HCl] <sub>f</sub>	[TBP] <sub>f</sub>	[MoO <sub>2</sub> ]	[MoO <sub>2</sub> <sup>2+</sup> ]	[VO]	[VO <sup>2+</sup> ]	β
3.0	6.96 × 10 <sup>-1</sup>	1.05 × 10 <sup>-2</sup> (1.05 × 10 <sup>-2</sup> )	2.9 × 10 <sup>-4</sup> (8.28 × 10 <sup>-5</sup> )	3 × 10 <sup>-5</sup> (1.84 × 10 <sup>-5</sup> )	1.15 × 10 <sup>-2</sup> (1.17 × 10 <sup>-2</sup> )	1.4 × 10 <sup>4</sup> (8.06 × 10 <sup>4</sup> )
4.0	6.96 × 10 <sup>-1</sup>	1.06 × 10 <sup>-2</sup> (1.06 × 10 <sup>-2</sup> )	2 × 10 <sup>-5</sup> (7.15 × 10 <sup>-6</sup> )	1.25 × 10 <sup>-4</sup> (1.91 × 10 <sup>-4</sup> )	1.10 × 10 <sup>-2</sup> (1.15 × 10 <sup>-2</sup> )	4.66 × 10 <sup>4</sup> (8.93 × 10 <sup>4</sup> )
5.0	6.96 × 10 <sup>-1</sup>	1.07 × 10 <sup>-2</sup> (1.06 × 10 <sup>-2</sup> )	trace (6.52 × 10 <sup>-7</sup> )	2.50 × 10 <sup>-3</sup> (1.86 × 10 <sup>-3</sup> )	8.14 × 10 <sup>-3</sup> (9.84 × 10 <sup>-3</sup> )	— (8.60 × 10 <sup>4</sup> )
4.0	9.98 × 10 <sup>-1</sup>	1.10 × 10 <sup>-2</sup> (1.06 × 10 <sup>-2</sup> )	1 × 10 <sup>-5</sup> (1.65 × 10 <sup>-5</sup> )	5.2 × 10 <sup>-4</sup> (8.21 × 10 <sup>-4</sup> )	1.04 × 10 <sup>-2</sup> (1.09 × 10 <sup>-2</sup> )	2.20 × 10 <sup>4</sup> (8.53 × 10 <sup>4</sup> )
4.0	1.99 × 10 <sup>0</sup>	1.05 × 10 <sup>-2</sup> (1.06 × 10 <sup>-2</sup> )	trace (1.03 × 10 <sup>-7</sup> )	8.90 × 10 <sup>-3</sup> (8.28 × 10 <sup>-3</sup> )	2.60 × 10 <sup>-3</sup> (3.42 × 10 <sup>-3</sup> )	— (4.25 × 10 <sup>4</sup> )



**Fig. 2.** Comparison of binary-metal extraction obtained in batch and mixer-settler operations with prediction for single-metal extraction shown by solid lines.

by solid lines. No systematic difference is seen between the results of single-metal extraction and those for two metals.

2) **Effect of scrubbing** The effect of scrubbing by acid is shown in **Table 1**. The values in parentheses are predicted values based on Eqs. (1)–(3). The organic feed solutions were obtained by single extraction from aqueous solution containing approximately 10<sup>-2</sup> or 10<sup>-1</sup> mol/l of both metals. The scrub solutions lead to essentially a concentration of 1–8% of the extracted molybdenum being removed and at least 98% of the extracted vanadium, thus causing a great increase in purity.

3) **Continuous-flow operation** The distribution ratios observed in single-stage operation are shown in Fig. 2. No systematic difference is seen between the results obtained in batch and flow operations. This indicates that the conditions of the extraction equilibrium in the mixer and the complete phase separation in the settler have been met satisfactorily. The extraction performance in two-stage operation is shown in **Table 2**. The concentration changes of free (uncomplexed with metals) acid and TBP were at the most 2% and 4.5% of the feed values, respectively. The

mean values of feed and outlet concentrations were adopted in estimating the distribution ratio using Eqs. (1)–(3). The constant values of the ratio enable the outlet concentrations from the 2nd stage to be calculated by the familiar KSB (Kremser, Souder and Brown) equation. The predicted values thus obtained are shown in parentheses in Table 2. For molybdenum, more than 97% of the feed was extracted into the organic phase. For vanadium, the extent of extraction is strongly dependent on the concentration of TBP used, as indicated by Eqs. (2) and (3). It was not easy to determine with accuracy concentrations less than  $10^{-4}$  mol/l for both metals. The limit of detectable concentration was  $10^{-5}$  mol/l. This limitation in the present experiments causes a significant difference between the observed and predicted values of the separation factors.

### Conclusion

The results of extraction of two metals in both batch and flow operations agreed well with prediction using data for single-metal extraction. Scrubbing of loaded organic solution with hydrochloric acid removed 98% of vanadium and only 1–8% of molybdenum, thus increasing greatly the purity of the solution. Continuous flow extraction was successfully

operated, using two-stage mixer-settler batteries, under the conditions of mean residence time of solutions of 4.2 min in the mixer and 6.7 min in the settler. Almost all the molybdenum feed was extracted into organic phase and the separation factor for the two metals increased to the order of  $10^4$ .

### Nomenclature

$D$	= distribution ratio of metal	[—]
$K_{ex}$	= extraction equilibrium constant	[—]
[ ]	= concentration of species in brackets	[mol·l <sup>-1</sup> ]
$\beta$	= $([\overline{\text{MoO}_2}]/[\text{MoO}_2^{2+}])/([\overline{\text{VO}}]/[\text{VO}^{2+}])$ , separation factor	[—]

### <Subscripts>

Mo	= molybdenum
V	= vanadium

### <Superscript>

—	= organic-phase species or organic-phase concentration
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## A SIMPLIFIED METHOD OF ESTIMATING MASS AND HEAT TRANSFER COEFFICIENTS FOR TURBULENT GAS STREAMS IN WETTED-WALL COLUMNS

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**Key Words:** Mass Transfer, Heat Transfer, Absorption, Evaporation, Wetted Wall Column, Turbulent Gas Flow, Simplified Estimation Method

### Introduction

Cylindrical wetted-wall columns are widely employed as equipment for mass or heat transfer between gas and liquid phases. For the rational design of industrial wetted-wall columns, a knowledge of the gas-phase mass or heat transfer coefficient for turbulent gas streams is required. In a previous paper,<sup>8)</sup> a theoretical analysis of mass transfer in turbulent gas

streams in the wetted-wall column was reported and the basic convective-diffusion equation was solved numerically. The solution for the average gas-phase Sherwood number  $Sh_G$  was found to be approximately expressed as a function of the gas-phase Reynolds number  $Re_{Gr}$  based on the gas velocity relative to the liquid surface and the gas-phase Schmidt number  $Sc_G$ , if the column height is sufficiently high and the  $Sc_G$  value is not very large. In another paper,<sup>6)</sup> Hikita *et al.* have shown that the solution for the gas-phase Nusselt number  $Nu_G$  can be

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