

# Extraction and separation of hexavalent molybdenum from acidic sulfate solutions using Alamine 336 as an extractant

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## Abstract

Extraction and separation of hexavalent molybdenum from acidic sulfate solutions using Alamine 336 as an extractant and kerosene as diluent is described. Variation of acid concentration influences the percentage of extraction of hexavalent molybdenum indicating the ion exchange type mechanism. Effect of concentration of Alamine 336 on the extraction of hexavalent molybdenum in the presence of divalent copper and trivalent iron is also presented. The upper limit of concentration of extractant for extraction of hexavalent molybdenum free from divalent copper and trivalent iron is observed with 0.1 mol/L of Alamine 336. However, when the concentration of Alamine 336 is increased to 1.0 mol/L, about 48% of copper is extracted along with molybdenum but without any iron. The method is suitable for the separation of molybdenum from copper and iron contained leach liquor. The optimized experimental parameters such as phase contact time, effect of extractant, metal, loading capacity of extractant and followed by stripping studies with ammonia, hydrogen peroxide, sodium hydroxide, sodium thio-sulfate and thiourea is presented. From the above experimental data we proposed the aqueous mechanism for hexavalent molybdenum extraction processes.

## Keywords

Hexavalent molybdenum · extraction · separation · Alamine 336

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## 1 Introduction

The most important use of the molybdenum atom in living organisms is as a metal hetero-atom at the active site in certain enzymes. In nitrogen fixation in certain bacteria, the nitrogenase enzyme which is involved in the terminal step of reducing molecular nitrogen, usually contains molybdenum in the active site (though replacement of molybdenum with iron or vanadium is known). Molybdenum is alloyed with steel making it stronger and more highly resistant to heat because molybdenum has such a high melting temperature. The alloys are used to make such things as rifle barrels and filaments for light bulbs. The iron and steel industries account for more than 75% of molybdenum consumption [1].

The two largest uses of molybdenum are as in alloy in stainless steels and in alloy steels – these two uses consume about 60% of the molybdenum needs in the United States. Stainless steels include the strength and corrosion-resistant requirements for water distribution systems, food handling equipment, chemical processing equipment, home, hospital, laboratory requirements and it can also be used as a catalyst in some chemical applications [1].

There has been much recent discussion in the farming press about ‘molybdenum toxicity’ and its role in cattle fertility. Despite the discussion, it is unclear how much of a role molybdenum toxicity actually plays in poor fertility. There are two types of molybdenum toxicity. The first, which is well recognized, occurs on high molybdenum pastures (often referred to as ‘teart’ pastures) containing around 20-100 mg of molybdenum per kg. Within a few days of being placed on such pastures, cattle start scouring and develop stary, harsh coats. This can be effectively prevented by high doses of copper, because it has been demonstrated that such levels of molybdenum affect the absorption and metabolism of copper. The second type of molybdenum toxicity, which is the type discussed recently in the press, is more controversial.

Biologically and industrially molybdenum plays the important role and for environment protection we need to recover the title metal from spent matrices or other things. The researchers are continuously developing the separation and recovery of

molybdenum from the solid or other materials by environmentally friendly hydrometallurgical routes.

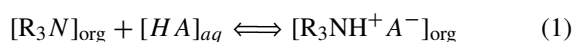
Various organic complexing extractants such as mono (2-ethylhexyl) phosphoric acid [2], alkylated 8-Quinolinol [3],  $\alpha$ -Benzoin oxime [4], Aliquat 336 [5], triphenylphosphine oxide [6], thiophosphinic acids [7], diisododecylamine [8], Cyanex 301 [9], LIX 622 [10] and dibenzo-18-crown-6 [11] were used for extraction and separation of molybdenum. The present paper investigated extraction and separation of molybdenum from the synthetic sulfate solutions using amine based reagent Alamine 336 diluted in kerosene as an extractant.

Alamine 336 is a water insoluble tri-n-octyl/decyl amine which is purifying organic and inorganic species which are capable forming anions using a solvent extraction (SX) process. Alamine 336 contains basic nitrogen atom, it typically can react variety of inorganic and organic acids to form amine salts, which are capable of undergoing ion exchange reactions with a host of other anions. The typical analysis of Alamine 336 was given in Table 1 [12].

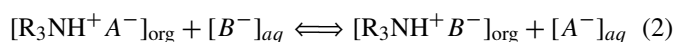
**Tab. 1.** Typical analysis of Alamine 336

Name of the content	
Tertiary amine content	95.0-100.0%
Secondary amine content	≤ 5.0%
Color (APHA)	≤ 500
Clarity	Clear
<i>Chemical &amp; physical properties</i>	
Specific gravity	0.81
Surface tension	53
Pour point (ASTM)	-54°C
Flash point (ASTM)	179°C
Fire point (ASTM)	210°C
Viscosity (CPS) 40°C	23
86°C	11
140°C	06
<i>Solubility</i> (g amine/100g solvent)	11
Acetone	13
Water	≤ 5 ppm
<i>Completely miscible in</i>	
Benzene, Carbon tetrachloride, Chloroform, Cyclohexane, Diisobutyl ketone, Ethanol, #2 Fuel oil, Iso-propanol, Kerosene, n-Butanol, n-Decanol	

*Protonation:*

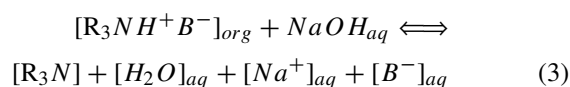


*Exchange:*



The extent to which  $B^-$  will exchange for  $A^-$  is a function of the relative affinity of the two anions for the organic cation and the relative solvation energy of the anions by the aqueous phase.

In separation science particularly when we are using the SX as separation technique we must regenerate the metal (Stripping of the metal) from the complex and reuse the extractant in the industrial phenomena. Amine based extractants can be stripped by a wide variety of salts such as NaCl, NaOH,  $Na_2CO_3$  etc. The type of stripping agent used depends on the overall recovery process, but in general basic stripping agents which reverse the amine protonation reaction, give the best stripping in the fewest stages.



Alamine 336 was used as an extractant to separate and recover the organic and inorganic species from different matrices. SX of transition metals like manganese [13], zinc [14], cobalt [15], cadmium [16], vanadium [17], chromium [18], niobium and tantalum [19] was reported by many researchers. Removal and recovery of mineral acids like hydrochloric and sulphuric acids using Alamine 336 was studied by Sarangi et al [20], Agrawal et al [21] and extraction of various organic acids such as valeric acid [22], picolinic acid [23], lactic acid [24] with Alamine 336 was investigated. In spite of large number of SX studies with Alamine 336 was reported; the systematic extraction and separation of hexavalent molybdenum is scarce.

## 2 Experimental

### 2.1 Apparatus and reagents

Analysis of molybdenum(VI), copper(II) and iron(III) were obtained using inductively coupled plasma optical emission spectrometer (ICP-OES) Perkin Elmer Model Optima 2000 Dr. Stock solutions of  $Na_2MoO_4 \cdot 2H_2O$  (Yakuri Pure Chemicals, Japan),  $CuSO_4 \cdot 5H_2O$  (Yakuri Pure Chemicals, Japan) and  $Fe_2(SO_4)_3$  (Kanto Chemicals, Japan) were prepared in distilled water with addition of concentrated sulphuric acid to prevent hydrolysis of metal ions. The metal solutions used in SX studies were prepared from the stock solution. The commercial grade extractant Alamine 336 was supplied by Cognis Corporation USA and used as it is without purification. All other reagents used were analytical reagent grade.

### 2.2 Extraction and stripping procedure

Extraction and stripping was carried out by shaking equal volumes (30 mL) of aqueous and organic phases ( $A:O$ ) in separating funnels using a mechanical shaker at temperature  $25 \pm 1^\circ C$  for 1800 s, although it was proved that the extraction equilibrium was achieved within 300 s. The concentration of metals (Mo(VI) or Cu(II) or Fe(III)) in aqueous phase was analyzed by ICP-OES and the concentration in the organic phase was obtained by mass balance. These concentrations were used to obtain the distribution ratio 'D' ( $D = [M]_{org} / [M]_{aq}$ , where M = metals such as Mo(VI) or Cu(II) or Fe(III)), the percentage of extraction (%  $E = D \times 100 / (D + 1)$ ) and stripping efficiency 'S' (%  $S =$

$M_{aq}/M_{org} \times 100\%$ ). All the experiments were conducted at room temperature ( $25 \pm 1^\circ\text{C}$ ) and the general agreement with distribution values obtained was within  $\pm 5\%$ .

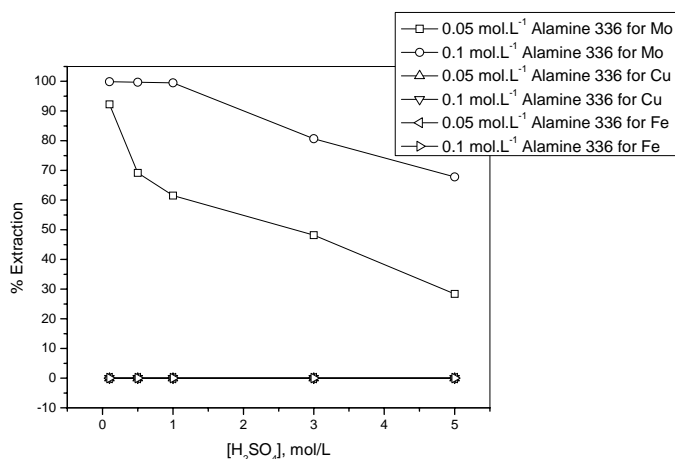
### 3 Results and discussions

#### 3.1 Effect of time

The extraction behavior of molybdenum(VI) (0.1 mol/L) from sulfate (0.1 mol/L) solutions with 0.01 mol/L Alamine 336 in kerosene has been measured at different phase contact times. The percentage extraction of molybdenum was increased with increase in phase contact time up to 300 seconds and further increase in contact time showed a stable behavior. It is found that the equilibrium time for this system is 300 s.

#### 3.2 Effect of acid

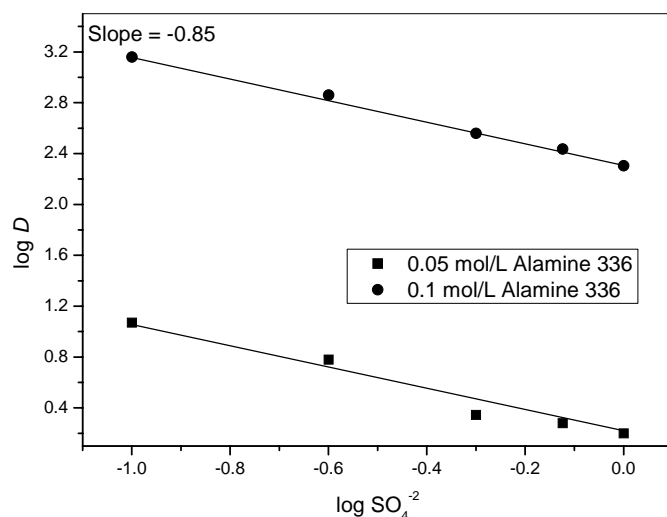
The effect of sulphuric acid on the extraction of molybdenum(VI)/copper(II)/iron(II) was studied in the range of 0.1 mol/L to 5.0 mol/L. Fig. 1 shows that the percentage extraction of molybdenum with 0.05/0.1 mol/L Alamine 336 in kerosene decreased with increasing acid concentration up to 5.0 mol/L. It indicates the present extraction follows ion-exchange mechanism (Fig. 2). On the other hand in the case of copper and iron the percentage extraction is nil.



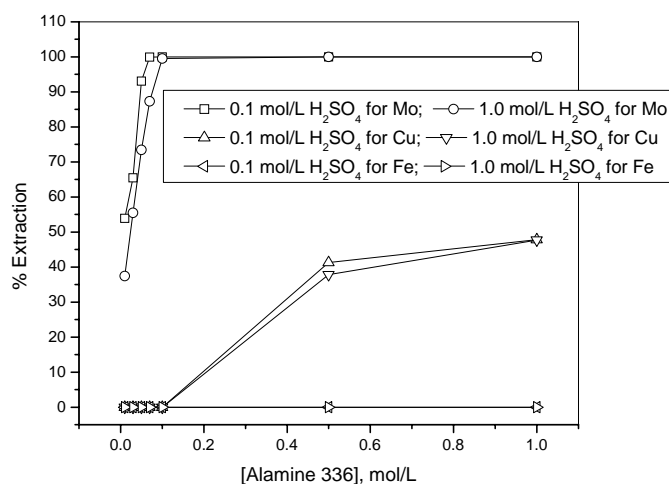
**Fig. 1.** Effect of sulphuric acid on the extraction of molybdenum(VI)/copper(II)/iron(III).

#### 3.3 Effect of Alamine 336

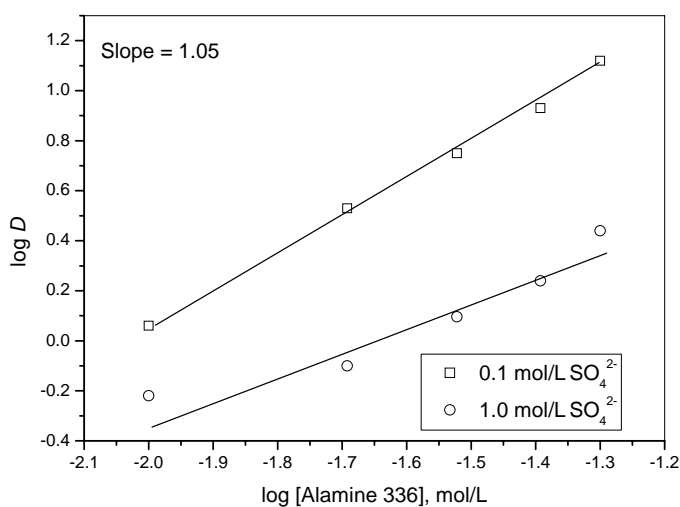
The effect of extractant concentration on the extraction of the 0.1 mol/L molybdenum(VI)/copper(II)/iron(III) and 0.1/1.0 mol/L sulphuric acid, which increased with increasing extractant concentration. The quantitative extraction (100% extraction) achieved with 0.5 mol/L Alamine 336 at 0.1 mol/L sulphuric acid and 1.0 mol/L Alamine 336 at 1.0 mol/L sulphuric acid where as copper was extracted  $\sim 48\%$  using 1.0 mol/L Alamine 336 both times of the acid concentrations. In the case of iron the extraction is nil even with high concentration of Alamine 336 (up to 1 mol/L) (Figs. 3 and 4).



**Fig. 2.** The plot between log sulfate concentration vs. distribution coefficients of molybdenum



**Fig. 3.** Effect of Alamine 336 on the extraction of molybdenum(VI)/copper(II)/iron(III).



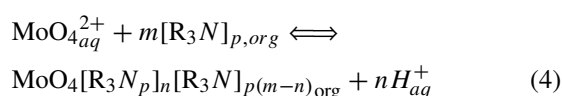
**Fig. 4.** The plot between log extractant concentration vs distribution coefficients of molybdenum

### 3.4 Effect of metal ion concentration

The effect of molybdenum(VI) concentration on the extraction process has been investigated using Alamine 336 (0.05 mol/L) from sulfate solutions (0.1 mol/L). In the above system, the extraction of molybdenum(VI) was found to be independent of metal ion concentration in the aqueous phase ( $D = 12 \pm 0.5$  for 0.05 mol/L Alamine 336). The *log-log* plot (Figure not shown here) of equilibrium organic phase metal concentration against aqueous phase metal concentration is linear with a slope of unity indicating the extraction of mononuclear species into the organic phase.

### 3.5 Aqueous mechanism for hexavalent molybdenum extraction process

The extraction equilibrium of molybdenum(VI) from acidic sulfate solutions with Alamine 336 may be represented as:



where  $K_{ex}$  denotes the equilibrium constant and  $\text{R}_3\text{N}$  refers to the Alamine 336

$$K_{ex} = \frac{[\text{MoO}_4[\text{R}_3\text{N}]_n[\text{R}_3\text{N}]_{p(m-n)}][\text{H}^+]^n}{[\text{MoO}_4^{2+}][(\text{R}_3\text{N})_p]^m} \quad (5)$$

$$K_{ex} = \frac{D[\text{H}^+]^n}{[(\text{R}_3\text{N})_p]^m} \quad (6)$$

where

$$D = \frac{[\text{MoO}_4[\text{R}_3\text{N}]_n[\text{R}_3\text{N}]_{p(m-n)}]}{[\text{MoO}_4^{2+}]} \quad (7)$$

Taking logarithm of Eq. (7) and rearranging

$$\text{Log } D = \log K_{ex} + m \log[(\text{R}_3\text{N})_p] - n \log[\text{H}^+] \quad (8)$$

Analysing the experimental data of distribution ratio ( $D$ ) as a function of acid and extractant concentration at constant value of other parameters allows estimation of the number of extractant molecules associated with the extracted metal complex.

### 3.6 Loading of Alamine 336

Loading of 0.05 mol/L Alamine 336 was determined by contacting 30 mL of organic phase for 30 minutes with the same volume of aqueous phase containing 0.1 mol/L of molybdenum(VI) and  $\text{H}_2\text{SO}_4$ . After equilibrium and phase separation, the aqueous phase was analyzed for molybdenum(VI) content and analysis of loaded organic (L.O) contains 15.5 g/L molybdenum(VI).

### 3.7 Stripping studies

In any commercial extraction process it becomes imperative to back extract the metal from the loaded organic phase. Molybdenum(VI) stripping from L.O (0.05 mol/L Alamine 336) containing 15.5 g/L metal has been studied using various stripping agents such as  $\text{NH}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{NaOH}$ , sodiumthiosulfate and thio-urea and the results are shown in Table 2. The result clearly shows that  $\text{NH}_3/\text{NaOH}$  are better stripping reagents when compared with other base reagents.

**Tab. 2.** Stripping of molybdenum(VI) from loaded organic phase (15.5 g.L<sup>-1</sup> Mo(VI))

Name of the reagent	Number of stages and % stripping				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	4 <sup>th</sup>	5 <sup>th</sup>
14% $\text{NH}_3$	49	51	53	53	53
17% $\text{H}_2\text{O}_2$	19	36	40	40	40
1 mol/L $\text{NaOH}$	50	52	53	53	53
1 mol/L Sodiumthiosulfate	11	13	15	15	15
1 mol/L Thio-urea	< 5	< 5	< 5	< 5	< 5

## 4 Conclusions

The following conclusions are drawn from the present study of extraction/separation of hexavalent molybdenum from sulfate solutions:

- We report in this paper a possible separation of molybdenum(VI), copper(II) and iron(III) from sulfate solutions using Alamine 336 diluted in kerosene.
- Present experimental results conclude good loading of the molybdenum to Alamine 336 and better stripping with 14%  $\text{NH}_3$  and 1.0 mol/L  $\text{NaOH}$ .
- The reported approach can be applied to the separation of molybdenum(VI) from sulfate leach solutions of spent matrices or any other related solutions.

## Acknowledgement

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