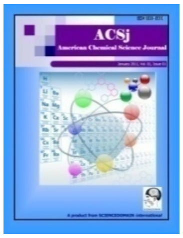

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Effect of Anions, Complexing and Salting - out Agents on the Extraction of Mo (VI) from Acid Media into Chloroform Solution of Bis (4-Acylpyrazolones)

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Authors' contributions

This research work was carried out between the authors in the department of Pure and Industrial Chemistry, University of Port Harcourt. Author BAU designed the project which was carried out by author IAK. As part of her Ph.D research works on Mo (VI) extraction studies. The analysis and interpretation of results were performed by both authors.

Original Research Article

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ABSTRACT

The extraction of Mo (VI) was carried out in the presence of a synergist in the organic phase and also in the presence of the corresponding acids (HCl and H_2SO_4).

The effect of the anions, Cl^-, SO_4^{2-} , Br^- , I^- , SCN^-, PO_4^{3-}, EDTA, Oxalate, acetate and tartarate on the extraction of Mo (VI) into chloroform solutions of 4-adipoylbis (1-phenyl-3methylpyrazolone-5), H_2Adp and 4-sebacoylbis (1- phenyl-3-methylpyrazolone-5), H_2SP were studied. The results showed that the masking effect of the halides on the extraction of Mo (VI) followed the increasingly order $Cl^- < Br^- < I^-$. The trend follows the direction of decrease in electro negativity. Similarly, the extraction of Mo(IV) is increasingly masked with increase in concentration of the complexing agents, decreasing the % extraction from as high as 60% extraction at 10^{-3}M ligand concentration to as low as10% at 1M ligand concentration. The extraction of the metal is greatly enhanced in the presence of their corresponding acid solution by increasing the extraction by as high as 10- 40% and also in the presence of butanol. Under all conditions, H_2SP showed to be a better extract ant than

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H_2Adp:

$$\xrightarrow[\text{Decrease in BuOH Synergism}]{H_2SP >> H_2Adp}$$

Keywords: Anions; complexing agents; salting – out agents; ligands; butanol.

1. INTRODUCTION

Extraction of Mo (VI) in acid media using 4-adipolylbis (1-phenyl-3-methylpyrazolone-5), H_2Adp and 4-sebacoylbis (1-phenyl-3-methyl pyrazolone-5), H_2SP has been achieved and reported [1].

The synthesis and characteristics of metal complexes of 4-adipoyl and 4-sebacoyl derivatives of the β-diketone, bis(1-phenyl-3-methylpyrazone-5) with Mo(VI) has been reported [2]. Studies have shown that these quadridentate ligands are efficient extract ants for metals in acid solution [3-5].

There are few available literatures on the extraction of molybdenum from mineral acids on anionic solutions. However, the use of Cyanex 301 and 302 in the recovery of some 3d metal ions have been reported [6-7] and Menoyo [8]. It was observed that the use of tri-n-butyl phosphate (TBP) was restricted to nitrate and chloride media and the extraction was suppressed by complexing anions such as F^-, SO_4^{2-}, PO_4^{3-} and CO_3^{2-}.

Gupta et al [9] studied the extraction behavior of Ti (IV), V (IV), Cr (III), Fe (III), Mn (II), Co (II), Ni (II), Cu (II) and Zn (II) in Cyanex 923 solution from 1 – 10 mol/l HCl, H_2SO_4 and HNO_3.

Following these reports, this work was carried out to study the effect of some anions, salting–out agents and complexing agents on the extraction of Mo (VI) using 4-adipoylbis (1- phenyl-3-methylpyrazolone-5), H_2Adp and 4-sebacoylbis (1-phenyl-3-methylpyrazolone-5), H_2SP as extract ants. Subsequently, the effect of Cl^- and SO_4^{2-}ions in the presence and absence of their corresponding acid solutions was studied.

2. MATERIALS AND METHODS

Stock solution (100mg/l) of Mo (VI) was prepared by dissolving 0.1288g of ammonium molybdate hydrate $(NH_4)_6Mo_7O_{24}.4H_2O$ in a small volume of conc. HCl in 100ml of 0.001M HCl solution.

The working solution (2mg/l – 20mg/l) were prepared by diluting appropriate volumes of the stock solution with appropriate volumes of water, acid, salting out agent and/or an auxiliary complexing agent in 10ml volumetric flasks.

Reagents used for theses extraction studies were of Merck and BDH analytical grades and were used without further purification.

Fresh solutions of the organic extraction reagents, 4-adipoylbis(1-pheny1-3methylpyrazolones-5) H_2Adp and 4-sebacoylbis (1-phenyl-3methylpyrazolones-5) H_2SPwere prepared as and when required. Appropriate weights of the extract ants were dissolved in $CHCl_3$ to obtain the concentration of the working organic reagent of 0.01M. The standard solution of the extraction reagent H_2Adp was prepared by dissolving 0.4585g of H_2Adp in a small volume of $CHCl_3$ in a 100ml volumetric flask and made up to mark with $CHCl_3$. The concentration of the resultant solution was 0.01M H_2Adp/$CHCl_3$ (stock solution). Working solutions were prepared by diluting appropriate volumes of this stock solution with $CHCl_{3.}$The standard solution of the extraction reagent H_2SP was prepared by dissolving 0.5146g of H_2SP in small volume of $CHCl_3$ in a 100cm^3 volumetric flask and made up to mark with $CHCl_{3.}$ The concentrations of the resultant solutions were prepared by diluting stock solution. Working solutions were prepared by diluting appropriate volumes of this stock solution with $CHCl_{3.}$

Fresh stock solutions of the complexing agents, potassium thiocyanate (KSCN), ammonium bromide (NH_4Br), disodium hydrogen phosphate (Na_2HPO_4), ammonium iodide (NH_4**I**), ammonium oxalate ($(NH_4)_2C_2O_4.H_2O$), ammonium tartrate, sodium acetate, and EDTA, were always prepared when needed. Working solutions were prepared by taking suitable volumes of the stock and diluting with deionized water.

The salting–out agents, Ammonium Chloride (NH_4Cl) and Sodium Sulphate (Na_2SO_4), were prepared as at when needed. The working solutions were prepared by diluting the stock solutions with appropriate volumes of deionized water.

2.1 Extraction Procedures

2.1.1 Extraction in the presence of complexing agents

A 0.2ml volume of the metal ion solution was introduced into 10 extraction bottles. A solution of a complexing agent was added into these bottles. Water was subsequently added to each of the bottles to adjust the volume of the aqueous phase to 1ml so that the final dilution gave solutions with the following range of concentrations of the anions:

Br^- ions : 0.001M - 1M
I^-ions : 0.001M - 1M
SCN^- ions : 0.001M - 1M
Acetate ions : 0.001M - 1M
PO_4^{3-} ions 0.001M - 1M
$C_2O_4^{2-}$ ions: 0.001M - 0.08M
Tartrate ions: 0.001M - 0.08M
EDTA ions: 0.001M - 0.08M

Equal volume (1cm^3) of the 0.01M H_2Adp (or H_2SP) solution was added to each extraction bottle and agitated for 30 minutes. The phases were allowed to settle and separated and the unextracted metal ions in the aqueous phase determined. These processes were also carried out with the $CHCl_3$/BuOH mixture.

2.1.2 Extraction in the presence of salting – out agents

A 0.2ml aliquot of the metal ion solution was pipette into 10 extraction bottles. Into these bottles, solutions of the salting - out agent and mineral acid were added. Water was added to adjust the volume of the aqueous phase to 1cm^3 such that the final dilution gave a concentration range of the salting – out agents as follows:

NH_4Cl	0.001M -	4M
Na_2SO_4	0.001M -	1M

In the presence of the mineral acids, a specific volume (0.1ml) and concentration of the acid having a common anion with the salting out agent in the extraction bottle was used. Hence, each of the extraction bottles contained any of the following combinations: NH_4Cl/HCl and Na_2SO_4/H_2SO_4 with Mo (VI) in the aqueous phase.

2.1.3 Extraction in the presence of a synergist

An equal volume of chloroform solution of the 0.01M H_2Adp (or H_2SP) was agitated with the aqueous solution in the extraction bottles for 30 minutes. The phases were allowed to settle and were separated. The amount of Mo (VI) in the aqueous raffinate was analysed.

Butanol was added as the synergist. The extract ants (H_2Adp and H_2SP) were prepared according to the procedure outlined earlier, using a $CHCl_3$/BuOH mixture in the ratio of 4:1. The resultant solution was a 0.01M standard solution of the extractants. The standard solutions were used for all levels of investigation.

2.1.4 Determination of Mo (VI)

The Mo (VI) ions in the aqueous raffinate were determined using established techniques [10]. The amount of Mo (VI) in the aqueous solution after extraction was determined colorimetrically from of a standard calibration curve using a UV-Vis spectrophotometer at 470nm.

3. RESULTS AND DISCUSSION

3.1 Effect of Salting-out agents

3.1.1 The Effect of chloride and suphate ions

The effect of anions on the extraction of Mo (VI) using H_2Adp and H_2SP is presented in Figs. 1 and 2. In each case, the effect of BuOH as a synergist was also examined.

Fig. 1 shows the effect of chloride ion on the extraction process. The result shows that for both ligands (H_2Adp and H_2SP) there is a synergistic effect of BuOH on the extraction of the metal in the presence of Cl^- ion. The % extraction decreased from 36% to 14% as the Cl^- concentration in the solution increases from 0.001M to 0.8M. In the presence of BuOH, the % extraction rose to 64% and decreased to 46% as the Cl^-concentration increased. A similar result was also obtained with H_2Adp which demonstrates the synergistic effect of BuOH. The result however, shows that H_2SP in $CHCl_3$/BuOH is a better extract ant than H_2Adp for Mo(VI) in the presence of Cl^- ions giving additional extraction of 10-20% at any

Cl^- concentration. The effect of sulphate, (SO_4^{2-}) ion is presented on Fig. 2 or both ligands and it is obvious from the plot that as the concentration of SO_4^{2-} ion increases in solution, the % extraction of Mo (VI) by both ligands decreased. Formation of stable sulphate complex species with Mo (VI) has been attributed as the cause of decrease in extraction. The plot shows that with increase in concentration of SO_4^{2-} ions the sulphato complex species become more stable resulting in further decrease in extraction of Mo (IV). The figure shows that at 10^{-3}M SO_4^{2-} only 60% extraction could be achieved and at 1M SO_4^{2-} the extraction was as low as 10%.

The result obtained shows that BuOH in the organic phase enhances the extraction of Mo (VI) in the presence of SO_4^{2-} ions by both ligands. From the results, it is more obvious that synergism is higher during the extraction with H_2SP and the observed trend is presented as follows:

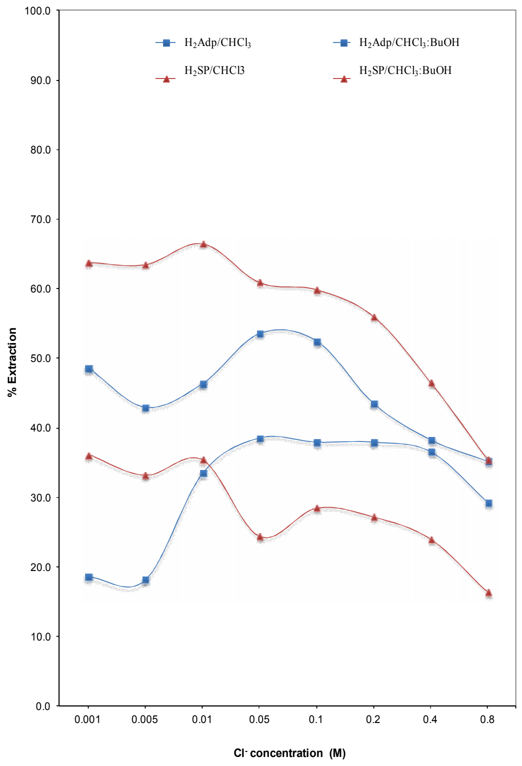

Fig. 1. Variation of % Extraction of Mo(VI) with Cl Concentration for H_2 Adp and H_2SP

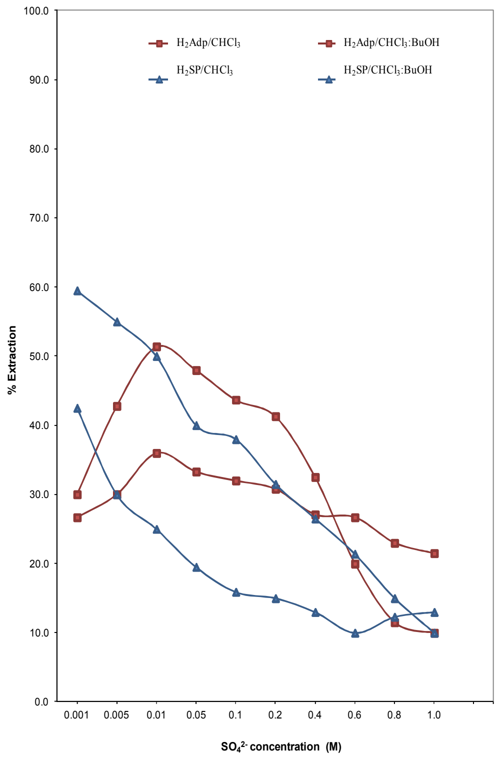

Fig. 2. Variation of % Extraction of Mo(VI) with SO_4^{2-} Concentration for H_2 Adp and H_2SP

The effect of thiocyanide, SCN^- ions is presented in Fig. 3 and it equally shows that increase in SCN^- ion concentration (like those of Cl^- and SO_4^{2-} ions) marks the extraction of Mo (VI) from aqueous medium. It also shows that the masking effect is more pronounced using H_2Adp since not more that 10% extraction could be achieved throughout the SCN^- concentration studies. The % extraction increases significantly when BuOH is introduced into the organic phase. The H_2SP ligand is a better extract ant for Mo (VI) than H_2Adp.

However, synergism is more pronounced with H_2Adp, since % extraction increased from 10% at 0.001 M SCN- concentrations to 56% at the same concentration in the presence of the synergist while that of H_2SP increased from 40% to 62%.

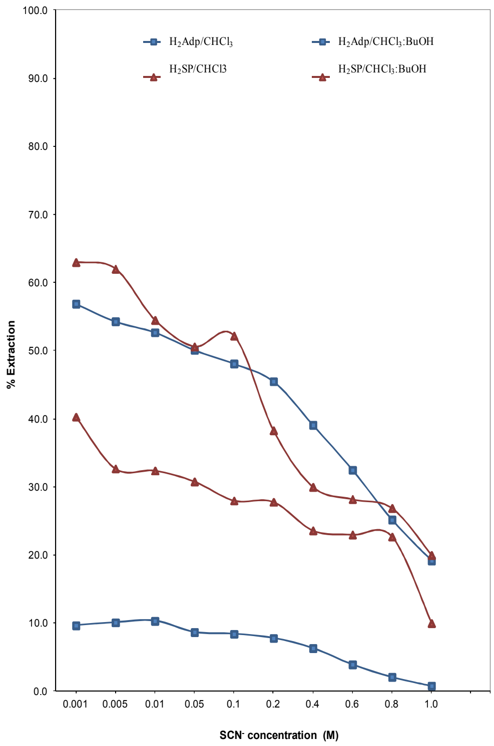

Fig. 3. Variation of % Extraction of Mo(VI) with SCN concentration for H_2Adp and H_2SP

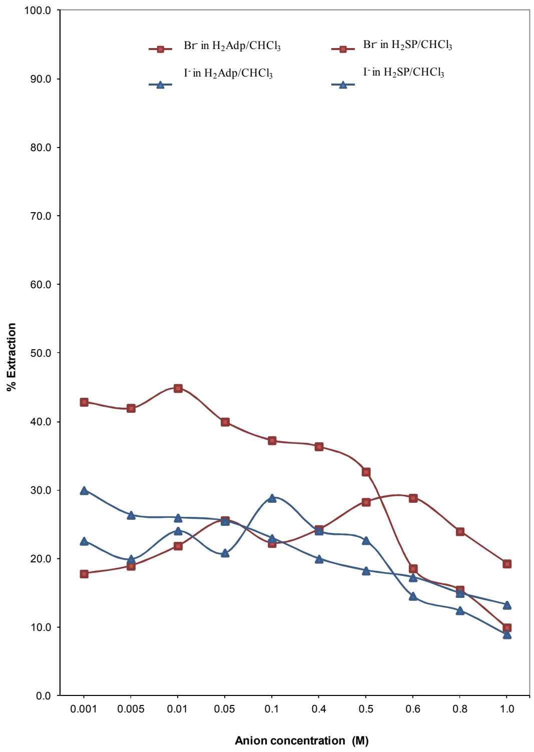

Fig. 4. Variation of % Extraction of Mo(VI) with Br^- and I^- concentration for H_2Adp and H_2SP

3.1.2 The Effect of thiocyanide ions

The results obtained for the other halides (Br^- and I^-) was are presented in Fig.4. To some approximation these results show that the effect of both Br^- and I^- ions is identical because there are slight changes in the % extraction with increase in ligand concentration in solution. However, the effect of Br^- and I^- on extraction with H_2SP is slightly different. Although extraction of not more than 18% was obtained at 0.001M concentration of Br^- with the H_2Adp ligand, a % extraction of 43% at the same anion concentration was obtained with H_2SP. This tends to decrease gradually with increase in Br^- ion concentration which is similar to what was observed with Cl^- ion.

3.2 Effect of Complexing Agents

3.2.1 Effect of acetate and phosphate ions

The effect of acetate and phosphate (PO_4^{3-}) ions are presented in Fig. 5. The result shows that in general, as the concentration of both anions increases, the % extraction tends to decrease gradually. This is in agreement with what was observed in the study with other anions. The % extraction of Mo(VI) with H_2SP in the presence of both anions was found to be relatively higher than the % extraction with H_2Adp.

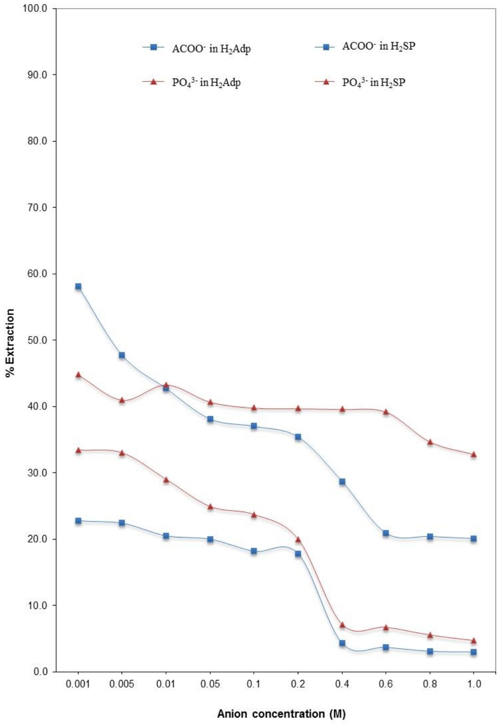

Fig. 5. Variation of % Extraction of Mo(VI) with Acetate and Phosphate concentration for H_2Adp and H_2SP

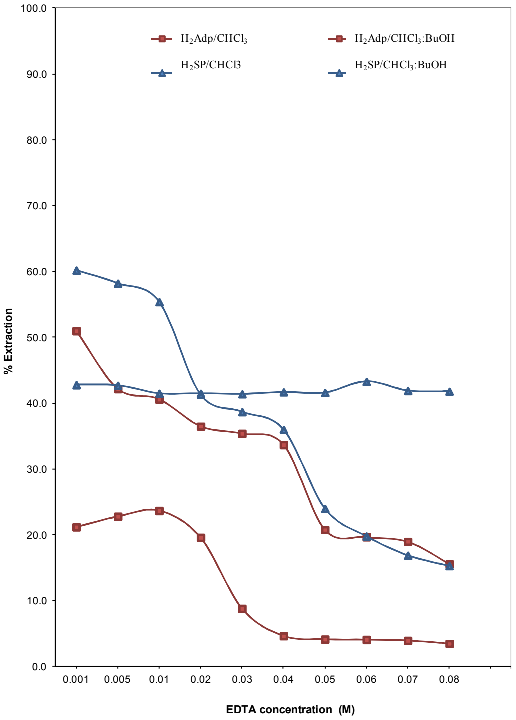

Fig. 6. Variation of % Extraction of Mo(VI) with EDTA concentration for H_2Adp and H_2SP

3.2.2 Effect of EDTA

Presented in Fig. 6 is the effect of EDTA on the extraction of Mo(VI) and the influence of BuOH as a synergist. In all cases, it shows that % extraction decreased at high EDTA concentration particularly when EDTA concentration is greater than 0.001M. Again the effect of BuOH on the extraction is higher in the case of H_2SP although it is more pronounced in the case of H_2Adp.

3.2.3 Effect of oxalate and tartrate

The effect of oxalate on the extraction of Mo (VI) is presented in Fig 7. It shows that extraction is increasingly masked as oxalate ion concentration increases. A similar trend is observed for tart rate ions as presented in Fig 8. The % extraction decreases with increase in tart rate ion concentration and the presence of BuOH enhances the extraction of the metal.

The result shows in general that the extraction of Mo(VI) is increasingly masked with increase in the concentration of complexing agents such as EDTA, oxalate, tart rate, SCN^-, acetate and PO_4^{3-}, as well as the salting - out agents Cl^-, SO_4^{2-}, Br^-, and I^-. Under all conditions however, H_2SP is shown to be a better extract ant than H_2Adp. This is attributed to its longer chain length and decrease in steric interferences due to spatial arrangement of the CH_2 groups.

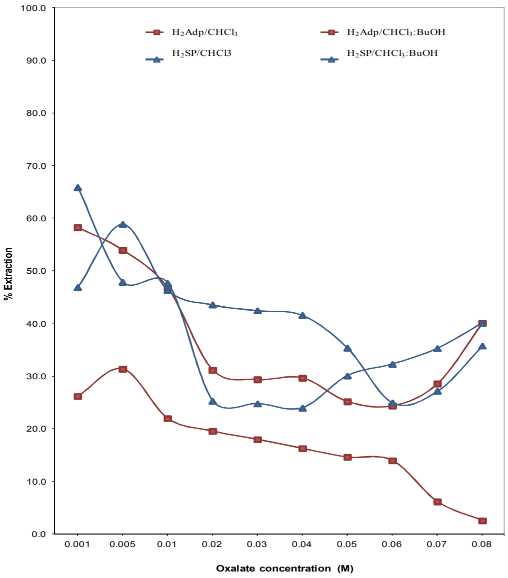

Fig. 7. Variation of % Extraction of Mo(VI) with Oxalate concentration for H_2Adp and H_2SP

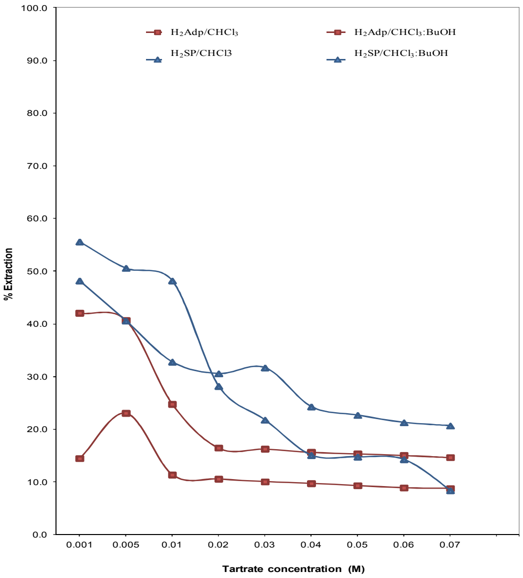

Fig. 8. Variation of % Extraction of Mo(VI) with Tartrate concentration for H_2Adp and H_2SP

3.3 Effect of Anions

The effect of Cl^- ion and SO_4^{2-} ions on the % extraction of the metal from the acid solutions of HCl and H_2SO_4 respectively were studied.

The effects of the Chloride ions on the extraction of Mo (VI) are illustrated in Figs 9 and 10 as plots of the variation of % extraction with anion concentration in solution in the presence and absence of the HCl. The % extraction of Mo (VI) from Cl^- anion solutions is greatly enhanced by the presence of its corresponding acid (HCl) in solution. The effect is more pronounced when BuOH is added to the organic phase. The results obtained show that the salting-out effect of Cl^- ion on the extraction of Mo (VI) resulted in an increase in extraction by 40% with H_2Adp. The results therefore shows that Cl^- ion has a remarkable salting-out effect on the extraction of molybdenum ions.

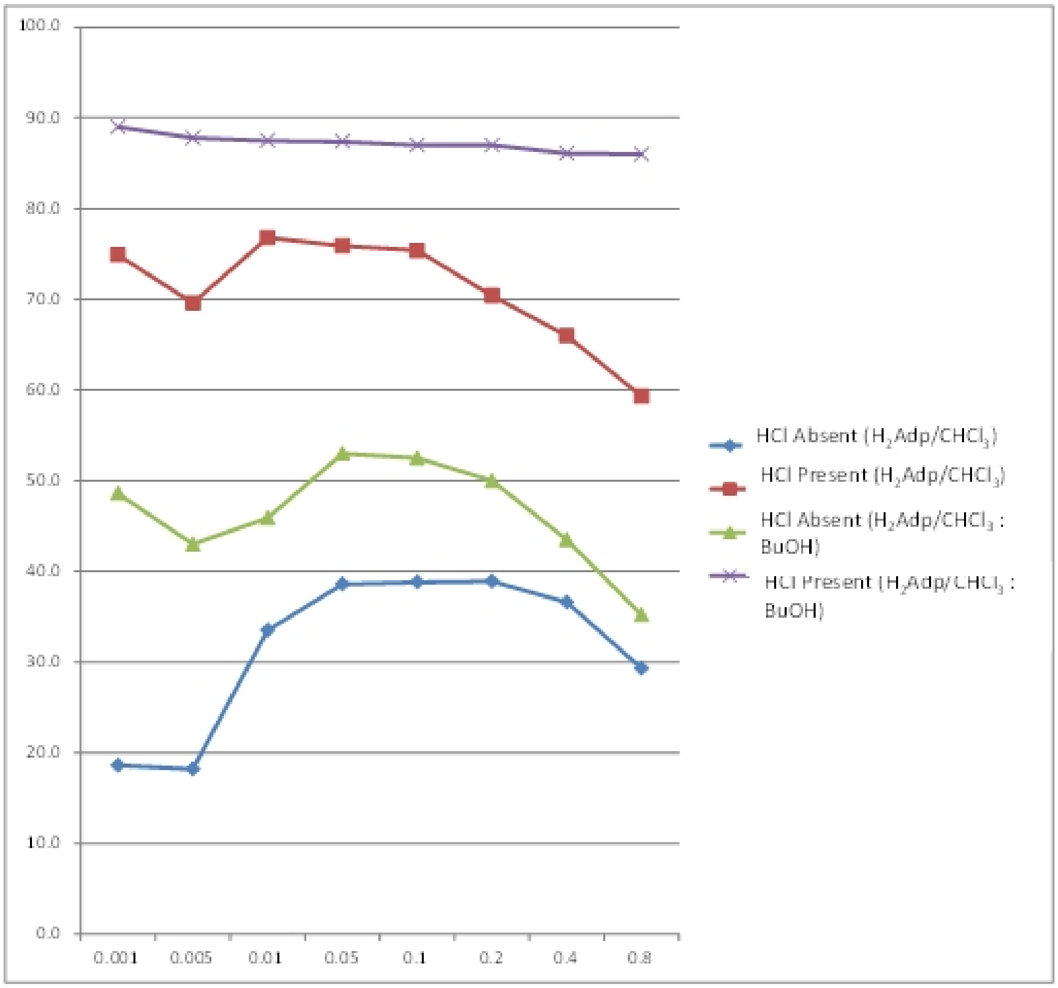

Fig. 9. Variation of % Extraction of Mo(Vi) with Cl- concentration For H_2Adp in $CHCl_3$ and $CHCl_3$: BuOH (in the presence and absence of HCL).

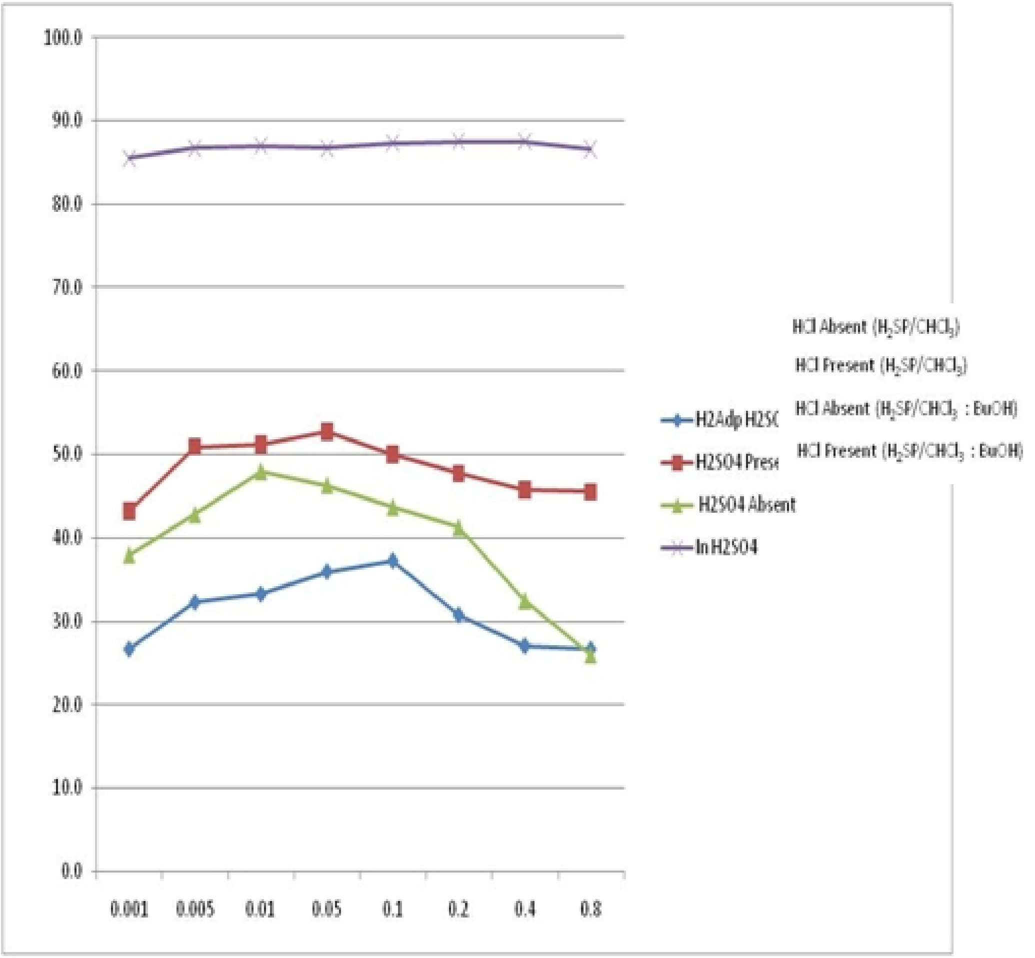

Fig. 10. Variation of % Extraction of Mo(Vi) with Cl- concentration for H_2SP in $CHCl_3$ and $CHCl_3$:BuOH (in the presence and absence of HCl).

Figs. 11 and 12 present the extraction of Mo (VI) from SO_4^{2-}anion solutions which is greatly enhanced by the presence of its corresponding acid, (H_2SO_4) using H_2SP. The addition of BuOH to the organic phase increased the extraction of Mo (VI) from SO_4^{2-} solutions by more than 20%.

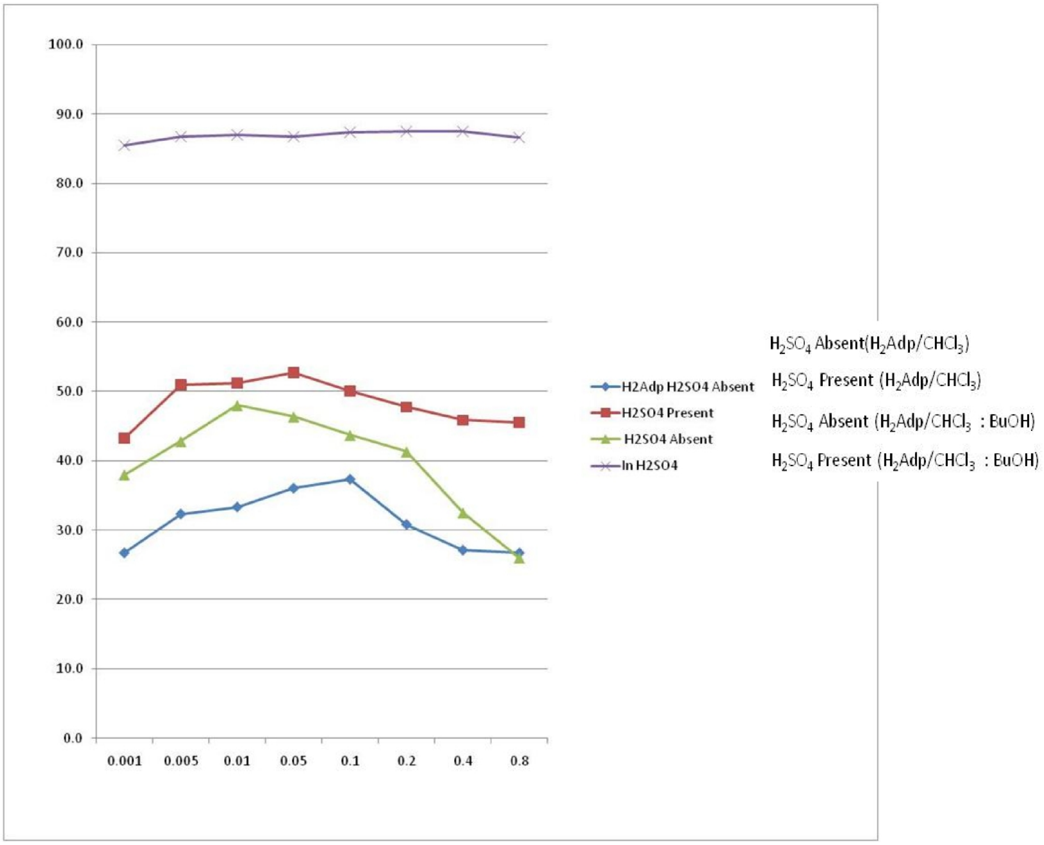

Fig. 11. Variation of % Extraction of Mo(Vi) with SO_4^{2-} concentration for H_2Adpin $CHCl_3$ and $CHCl_3$: BuOH (in the presence and absence of H_2SO_4)

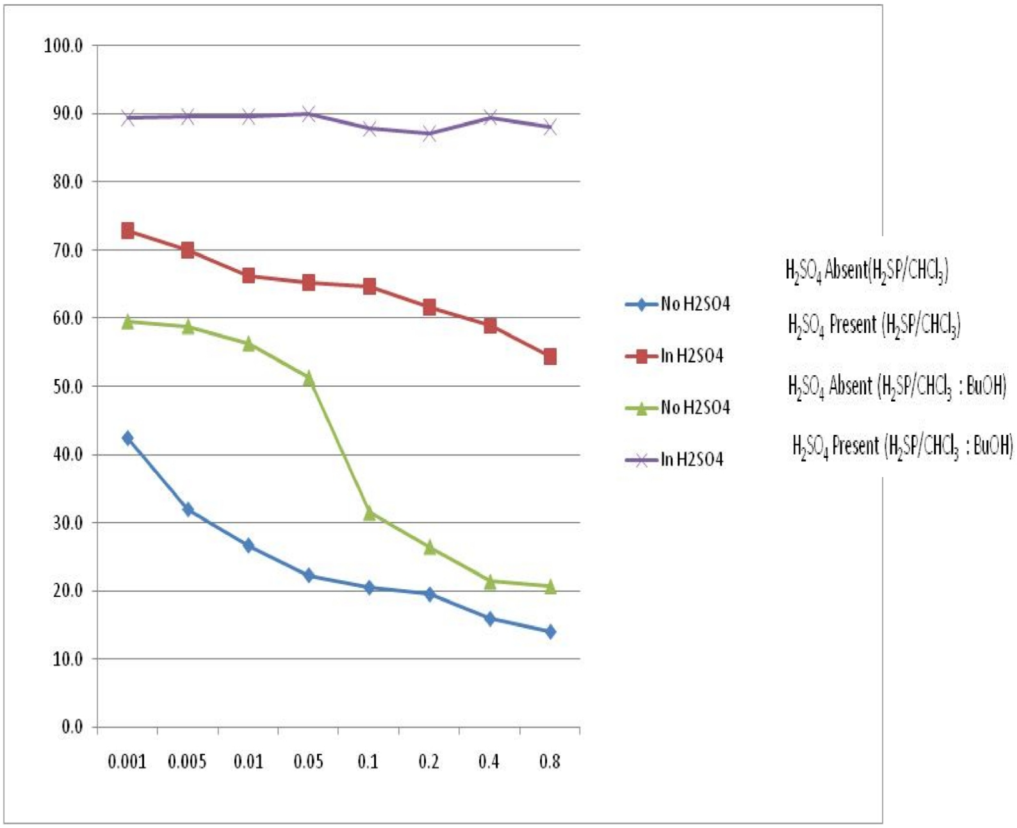

Fig. 12. Variation of % Extraction of Mo(Vi) with SO_4^{2-} concentration for H_2SP in $CHCl_3$ and $CHCl_3$:BuOH (in the presence and absence of H_2SO_4)

4. CONCLUSION

The decrease in metal ion extraction with increase in Cl^- and SO_4^{2-} ion concentration has been attributed to increase in formation of unextractable chloride and sulphate species of the metal at higher concentrations of these anions

A comparison of the masking effects of the halides on the extraction of Mo (VI) follows the following increasing order:

$$Cl^- < Br^- < I^-$$

for both H_2Adp and H_2SP ligands. The trend is consistent with the decrease in electronegativity of the element and increase in ionic radius of the ion.

The effect of complexing agents such as, PO_4^{3-}, acetate, EDTA, oxalate and tartarate on the extraction of Mo (VI) ions appears to be fairly constant for both H_2Adp and H_2SP. The results obtained show that extractions of these metals are increasingly masked as anion concentration increase in the aqueous phase.

COMPETING INTERESTS

Authors have declared that no competing Interests exist.

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