

Anions, Complexing and Salting - Out Agents Effects on the Extraction of Cr (VI) from HCl and H₂SO₄ Acid Media Using 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 Cr (VI) extraction studies. The analysis and interpretation of results were performed by both authors. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/IRJPAC/2015/16790

Editor(s):

(1) Ichiro Imae, Division of Chemistry and Chemical Engineering, Faculty of Engineering, Hiroshima University, Japan.

Reviewers:

(1) Anonymous, India.

(2) Anonymous, India.

Complete Peer review History: <http://www.sciencedomain.org/review-history.php?iid=962&id=7&aid=8793>

Original Research Article

Received 13th February 2015

Accepted 19th March 2015

Published 14th April 2015

ABSTRACT

Extraction of Cr(VI) into chloroform solutions of 4-adipoylbis (1- phenyl-3-methylpyrazolone-5), H₂Adp and 4-sebacoylbis (1- phenyl-3-methylpyrazolone-5), H₂SP were carried out and the effect of the anions, Cl⁻, SO₄²⁻, Br⁻, I⁻, SCN⁻, PO₄²⁻, EDTA, Oxalate acetate and tartarate were studied. The results showed that the masking effect of the halides on the extraction of Cr(VI) followed the order I⁻ < Br⁻ < Cl⁻. This is consistent with the order of increase in electronegativity of the element and decrease in ionic radius of the ions. The effect of complexing agents such as, PO₄²⁻, acetate EDTA, oxalate and tartarate on the extraction of Cr (VI) ions appears to be fairly constant for both H₂Adp and H₂SP. The results obtained show that extractions of these metals are increasingly masked as

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anion concentration increase in the aqueous phase. The extraction of the metal is reduced in the presence of salting-out agent using H₂Adp. Better extractions were obtained when H₂SP was used as the extractant. This shows that H₂SP is a better extractant than H₂Adp for Cr (VI).

Keywords: Complexing agents; extractant; chloroform; salting – out agents; masking agents; butanol.

1. INTRODUCTION

The β diketones, 4-adipoylbis(1-phenyl-3-methylpyrazolone-5), (H₂Adp) and 4-sebacoylbis(1-phenyl-3-methylpyrazolone-5), (H₂SP) were synthesized for the first time and characterized [1]. They have been found to exhibit the ability of effectively trapping toxic metals such as Fe, Cd, Cu, Ni, Mn, U, V and W from water. This is the main reason for their proposed use in organic solutions as [2,3,4]. Studies have shown that 4-acylpyrazolones are efficient extractants forming stable complexes with some group I, II and transition metals [1,5,6,7,8,9]. Liquid –liquid extraction of uranium (VI) and vanadium (V) ions using these chelating agents have been studied and reported [10,11,12].

Several methods have been used for the extraction of Cr (VI). Among these methods are the use of methyl isobutyl ketone (MIBK) [13], triisooctylamine (TIOA) [14] and other methods for the determination of the Cr (VI), [15,16]. The extraction of chromium (VI) in acidic chloride media using tributyl phosphate (TBP) has been reported [17]. The neutral extractant, triphenylphosphin (TPP) has been reported to be an efficient complexing agent for the transport of Cr (VI) from sulphuric acid solutions. The extracted species is the (HTPP) HCr₂O₇ complex [18]. The research is aimed at studying the effect of the anions, complexing and salting-out agents have on the extraction of Cr (VI). The degree of extraction of Cr (VI) in various concentrations of Cl⁻ and SO₄²⁻ in the presence and absence of HCl and H₂SO₄ respectively will be studied.

2. MATERIALS AND METHODS

2.1 Preparation of Stock Solutions

2.1.1 Preparation of chromium stock solution

A stock solution of Cr (VI) was prepared by dissolving 0.0373 g of potassium chromate, (K₂CrO₄) in a small volume of 0.001M HCl in a 100cm³ volumetric flask and made up to mark with the 0.001M HCl solution. The working solutions were prepared by diluting appropriate

volumes of the stock solution with an appropriate volume of water in a 10 cm³ volumetric flasks.

2.1.2 Preparation of organic stock solutions

Fresh solutions of the organic extraction reagents, 4-adipoyl-bis (1-phenyl-3-methylpyrazolones-5) H₂Adp and 4-sebacoyl-bis (1-phenyl-3-methylpyrazolones-5) H₂SP were prepared as and when required. Appropriate weights of the extractants were dissolved in CHCl₃ to obtain the concentration of the working organic reagent of 0.01M. These solutions (H₂Adp and H₂SP) were stable for at least a month.

2.1.2.1 4-adipoylbis(1-phenyl-3-methylpyrazolone-5) H₂Adp

The standard solution of this extraction reagent was prepared by dissolving 0.4585 g of H₂Adp in a small volume of CHCl₃ in a 100 cm³ volumetric flask and made up to mark with CHCl₃. The concentration of the resultant solution was 0.01M H₂Adp/CHCl₃ (stock solution). Working solutions were prepared by diluting appropriate volumes of this stock solution with CHCl₃.

2.1.2.2 4-sebacoylbis(1-phenyl-3-methylpyrazolone-5) H₂SP

The standard solution of this extraction reagent was prepared by dissolving 0.5146 g of H₂SP in small volume of CHCl₃ in a 100 cm³ volumetric flask and made up to mark with CHCl₃. The concentration of the resultant solution was 0.01M H₂SP/CHCl₃ stock solution. Working solutions were prepared by diluting appropriate volumes of this stock solution with CHCl₃.

2.1.3 Preparation of salting – out agents

The salting – out agents were prepared as and when required. The working solutions were prepared by diluting the stock solutions with appropriate volumes of deionized water.

2.1.4 Preparation of solutions of complexing agents

Fresh stock solutions of the complexing agents were always prepared when needed. Working

solutions were prepared by taking suitable volumes of the stock and diluting with deionized water.

2.2 Extraction Procedures

2.2.1 Extraction in the presence of complexing agents

A 0.2 ml 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 -	2M
SCN- ions:	0.001M -	1M
Acetate ions:	0.001M -	1M
PO ₄ ³⁻ ions:	0.001M -	1M
C ₂ O ₄ ²⁻ ions:	0.001M -	0.08M
Tartrate ions:	0.001M -	0.08M
EDTA ions:	0.001M -	0.08M

Equal volume (1 cm³) of the 0.01M H₂Adp (or H₂SP) 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 CHCl₃/BuOH mixture.

2.2.2 Extraction in the presence of salting-out agents

A 0.2 ml aliquot of the metal ion solution was pipetted 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 1cm³ such that the final dilution gave a concentration range of the salting – out agents as follows:

NH ₄ Cl:	0.001M -	4M
Na ₂ SO ₄ :	0.001M -	1M

In the presence of the mineral acids, a specific volume (0.1 ml) 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: NH₄Cl/HCl and Na₂SO₄/H₂SO₄ with Cr(VI) in the aqueous phase.

2.2.3 Extraction in the presence of a synergist

An equal volume of chloroform solution of the 0.01M H₂Adp (or H₂SP) 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 Cr (VI) in the aqueous raffinate was analysed.

Butanol was added as the synergist. The extractants (H₂Adp and H₂SP) were prepared according to the procedure outlined earlier, using a CHCl₃/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.

2.2.4 Determination of Cr (VI)

Chromium (VI) ions present in the aqueous raffinate were determined using diphenylcarbazide (DPC) [19,20]. A 0.5 cm³ volume of the Cr (VI) extraction raffinate was introduced into 5cm³ sample bottles. A 0.5cm³ volume of 10M H₂SO₄ was added followed by 1cm³ of DPC forming a violet complex. The mixture was made up to 5cm³ with deionized water. The absorbance of the complex was obtained at 540nm and the amount of Cr (VI) in the aqueous solution after extraction was determined using the absorbance of the solution from a standard calibration curve.

For each set of results, new calibration curves were obtained at the same time that the chromium ions in the extraction raffinate were analysed.

3. RESULTS AND DISCUSSION

3.1 Effect of the Anions on the Extraction of Cr (VI)

Fig. 1 shows that at concentration of Cl⁻ ions less than 0.01M, the % extraction of Cr (VI) appears to be independent of Cl⁻ ion concentration in the aqueous phase. At this concentration, about 52% of Cr (VI) was extracted using H₂Adp compared to 28% extraction by H₂SP which is an indication that H₂Adp is a better extractant for Cr (VI) in the presence of Cl⁻ ions. When BuOH was added to the organic phase, the % extraction increased tremendously to an average of 90% and 80% for H₂Adp and H₂SP respectively. The result also shows that the extraction of Cr (VI) into BuOH solution of the ligands in chloroform is independent of Cl⁻ ion concentration. The effect

of SO_4^{2-} ion is presented in Fig. 2. For H_2Adp , the % extraction appears to be fairly constant between 60% and 65% but for H_2SP , it is observed that the % extraction tend to increase with increase in SO_4^{2-} concentration. Hence the % extraction increased from 30% at 0.001M SO_4^{2-} to 86% at 1M SO_4^{2-} concentration. It is apparent that SO_4^{2-} ions have a tremendous salting – out effect on the H_2SP complex with Cr (VI) but not with the H_2Adp complex. Addition of BuOH into the organic phase resulted in an increase in the % extraction of Cr (VI) from solutions containing SO_4^{2-} ions by both ligands.

3.1.1 The effect of thiocyanide ions

The effect of SCN^- is presented in Fig. 3. The synergistic effect of BuOH is observed for both ligands. The results obtained show that the % extraction of Cr (VI) by both ligands appears to be fairly constant throughout the range of SCN^- concentrations studied.

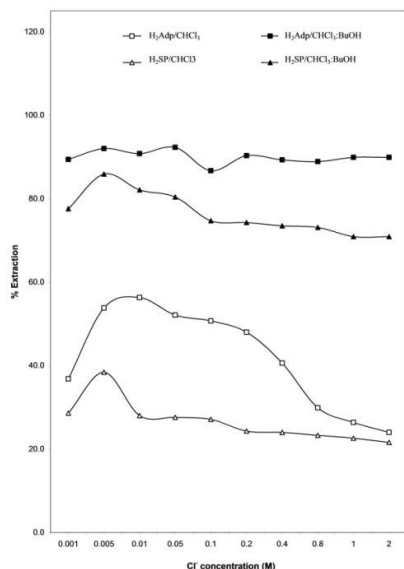


Fig. 1. Variation of % extraction of Cr(VI) with Cl concentration for H_2Adp and H_2SP

3.1.2 The effect of Br^- and I^- ions

The effect of Br^- and I^- ions on the extraction process is presented in Fig. 4. This is similar to what was observed for extraction from Cl^- ion solution presented in Fig. 1. The % extraction appears to be fairly constant throughout the concentrations studied. However, it is pertinent to note that extraction is more efficient by both ligands when the solution contains iodide ions

than when it contains bromide ions. This is an indication that the Br^- ion has a higher masking effect than the iodide ion. At 0.1M concentration of halide ions for instance, 60% extraction of Cr(VI) from Br^- solution by H_2Adp was achieved while 86% extraction from iodide ion solution was obtained. It appears that the smaller ionic radius of Br^- ion may have been responsible for this masking effect since it could more easily interact with the metal ion to form unextractable metal bromo complexes.

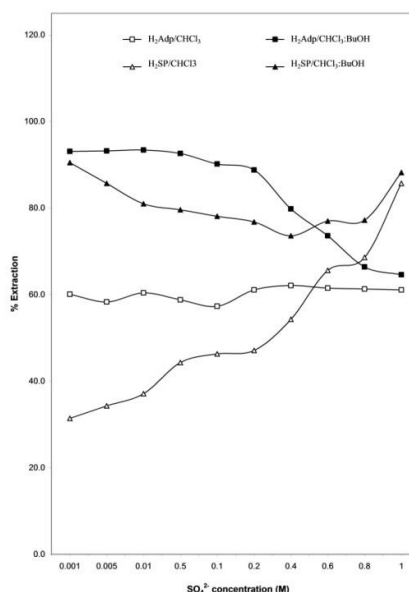
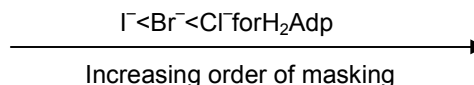


Fig. 2. Variation of % extraction of Cr(VI) with SO_4^{2-} concentration for H_2Adp and H_2SP

A comparison of the three halides studied shows that the masking effect of these halides is in an increasing order as follows:



The trend in this case is consistent with the order of increase in electronegativity of the element and decrease in ionic radius of the ions.

3.2 Effect of Complexing Agent

3.2.1 Effect of phosphate and acetate ions

The effect of PO_4^{2-} ions and acetate ions is illustrated in Fig. 5. Apart from the % extraction of Cr (VI) with H_2Adp from solutions of PO_4^{2-} ion which appears to decrease gradually, increase in both acetate and PO_4^{2-} ion concentrations

appears to cause a decrease in the % extraction of Cr (VI) ions by both ligands. Hence, the masking effects of the anions tend to increase slightly with increase in anion concentration in the aqueous phase for both ligands.

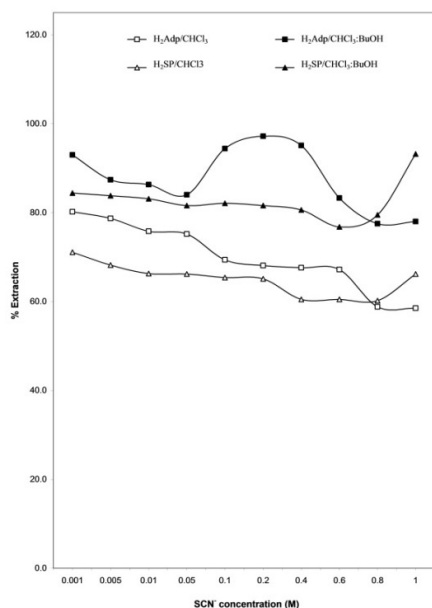


Fig. 3. Variation of % extraction of Cr (VI) with SCN concentration for H₂Adp and H₂Sp

3.2.2 Effect of EDTA

Fig. 6 shows that the % extraction is fairly constant as the concentration of EDTA increases from 0.01M to 1M. Synergism is observed when BuOH is introduced into the organic phase. The effect is more pronounced in the extraction with H₂Adp where the % extraction increased from 30% to 92%.

3.2.3 Effect of oxalate and tartrate

The effect of oxalate ion presented (Fig. 7.) appears to be similar to that of EDTA. The % extraction of Cr (VI) remained fairly constant throughout the concentration range of the complexing agent studied. The only exception however, is the extraction with H₂Adp. Beyond 0.01M oxidation concentration, there appears to be a monotonous decrease in the amount of Cr (VI) extracted even in the presence of BuOH as a synergist.

Fig. 8 shows that the % extraction of Cr (VI) tends to decrease slightly as the concentration of tartarate ion increased. This is observed for both

H₂Adp and H₂SP even with BuOH as a synergist. Fig. 8 shows that synergism of BuOH is more pronounced for extraction with H₂Adp than with H₂SP. This is because with H₂Adp, the % extraction increased from 43% to 86% at 0.001M tartrate ion concentration whereas with H₂SP the increment was from 62% to 78% at the same tartrate ion concentration.

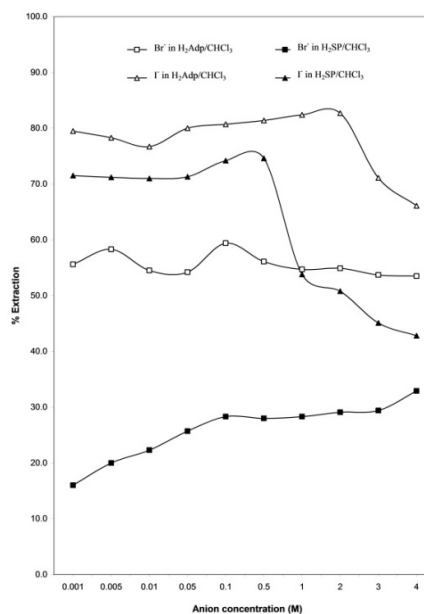


Fig. 4. Variation of % extraction of Cr (VI) with anion concentration for H₂Adp and H₂Sp

3.3 Salting-out Effect of Acid Anions in Acid Solution

The salting-out effect of Cl⁻ and SO₄²⁻ ions on the extraction of Cr (VI) from HCl and H₂SO₄ solutions respectively is depicted in Figs. 9 to 16. Figs. 9 to 12 show the effect of the acidic anions (Cl⁻ and SO₄²⁻) on the % extraction of the metal from its acid solution using H₂Adp. It shows that rather than acting as a salting – out agent, the acid in solution reduces the % extraction of Cr (VI) which is at variance with what was reported for Mo (VI), [21].

The % extraction is reduced by 5% to 20% for both anions in the presence of their respective acids. Even the addition of BuOH did not change the pattern of the extraction process.

The result obtained using H₂SP as extractant is presented in Figs. 13 to 16 showing that both Cl⁻ and SO₄²⁻ anions have some salting-out effect on the extraction of Cr(VI) from the acid species solutions similar to that of Mo(VI). This shows,

that H₂SP is a better extractant than H₂Adp when these anions are used as salting-out agents.

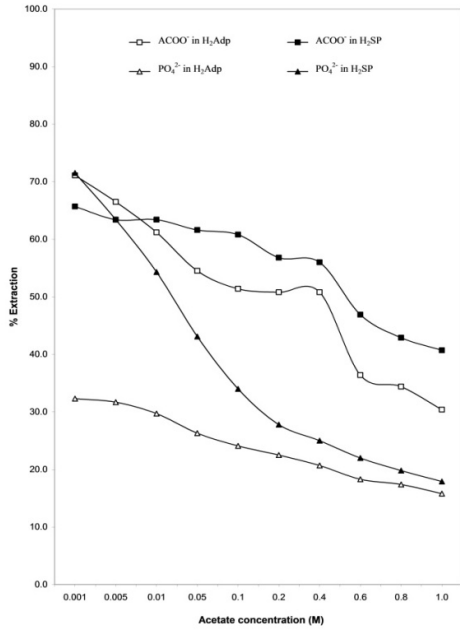


Fig. 5. Variation of % extraction of Cr (VI) with anion concentration for H₂Adp and H₂Sp

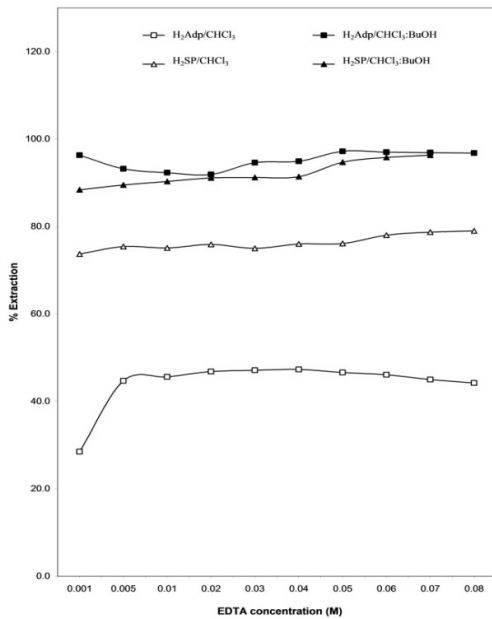


Fig. 6. Variation of % extraction of Cr (VI) with EDTA concentration for H₂Adp and H₂Sp

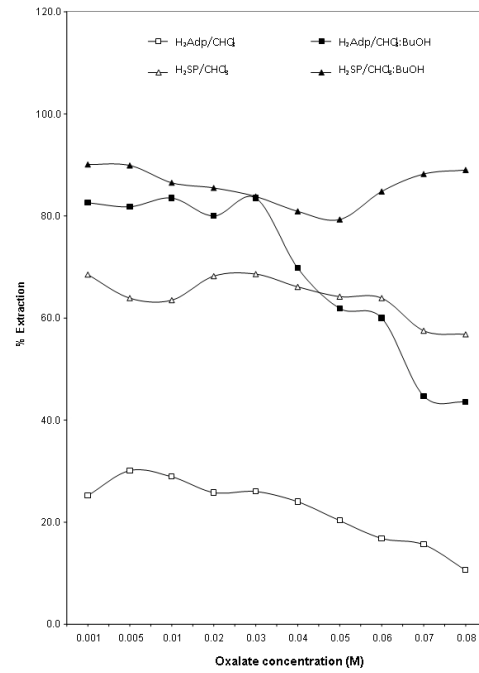


Fig. 7. Variation of % extraction of Cr (VI) with oxalate concentration for H₂Adp and H₂Sp

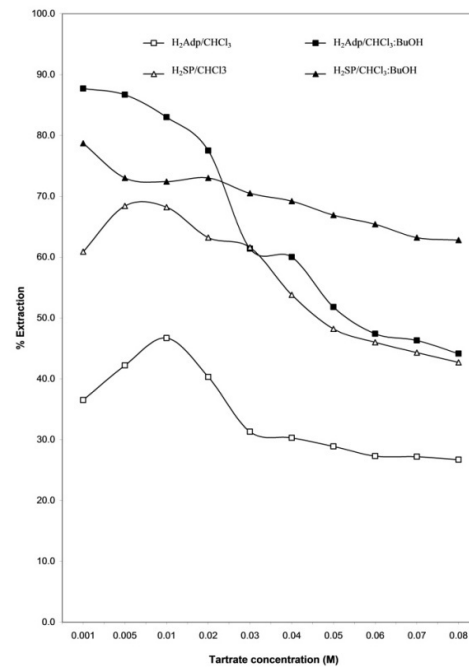


Fig. 8. Variation of % extraction of Cr (VI) with tartrate concentration for H₂Adp and H₂Sp

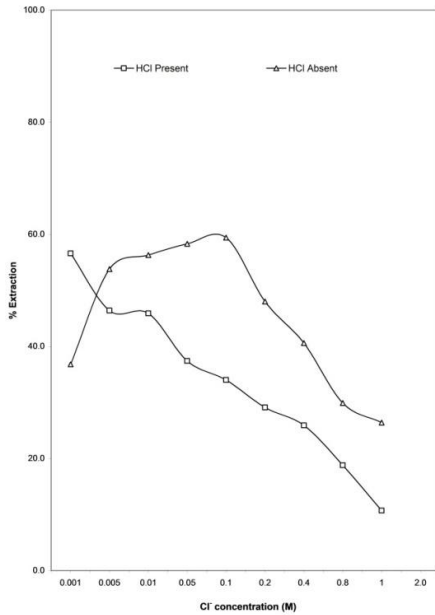


Fig. 9. Variation of % extraction of Cr (VI) with Cl⁻ concentration for H₂Adp in CHCl₃(in the presence and absence of HCl)

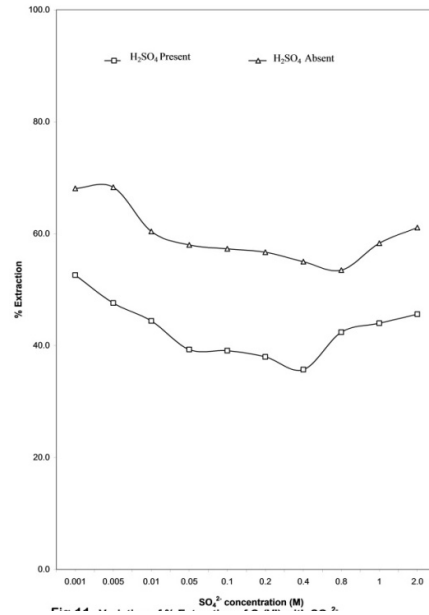


Fig. 11. Variation of % extraction of Cr (VI) with SO₄²⁻ concentration for H₂Adp in CHCl₃:BuOH(in the presence and absence of H₂SO₄)

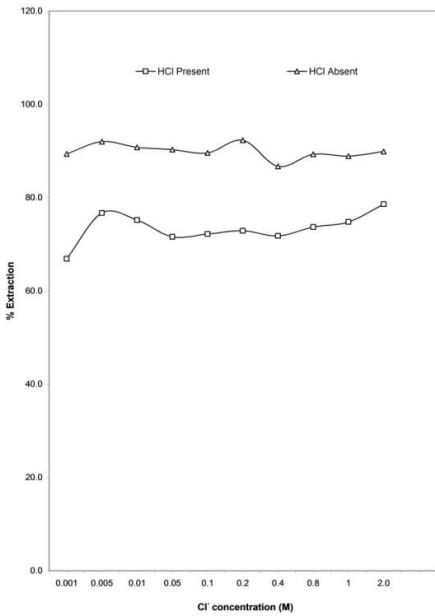


Fig. 10. Variation of % extraction of Cr (VI) with Cl⁻ concentration for H₂Adp in CHCl₃:BuOH(in the presence and absence of HCl)

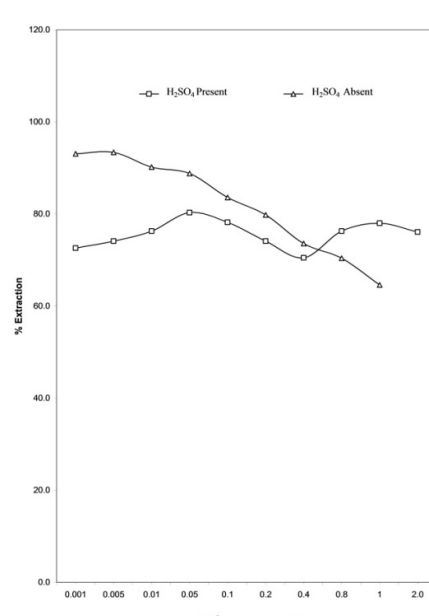


Fig. 12. Variation of % extraction of Cr (VI) with SO₄²⁻ concentration for H₂Adp in CHCl₃:BuOH(in the presence and absence of H₂SO₄)

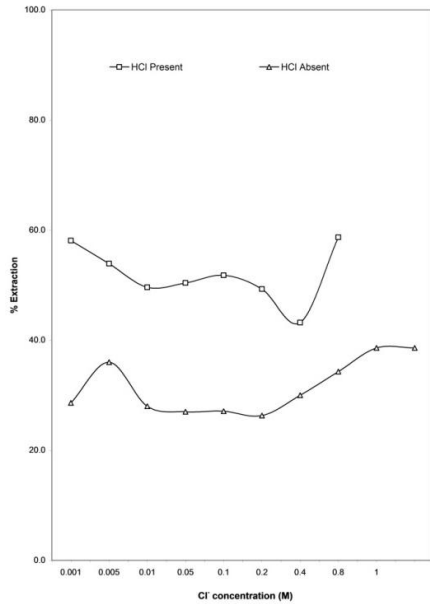


Fig. 13. Variation of % extraction of Cr (VI) with Cl⁻ concentration for H₂Adp in CHCl₃(in the presence and absence of HCl)

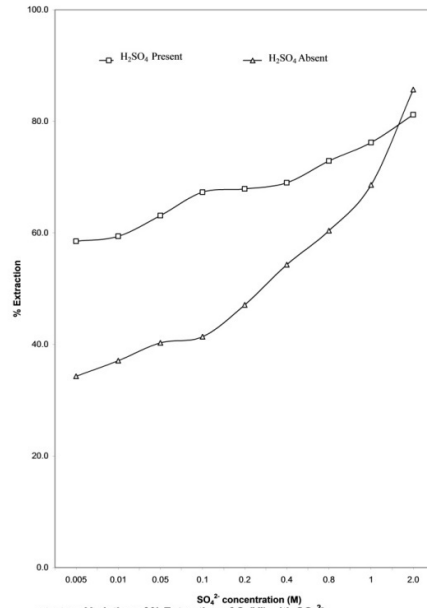


Fig. 15. Variation of % extraction of Cr (VI) with SO₄²⁻ concentration for H₂SP in CHCl₃(in the presence and absence of H₂SO₄)

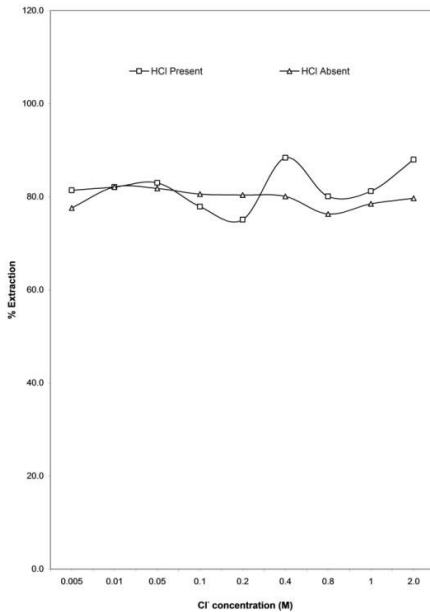


Fig. 14. Variation of % extraction of Cr (VI) with Cl⁻ concentration for H₂SP in CHCl₃:BuOH(in the presence and absence of HCl)

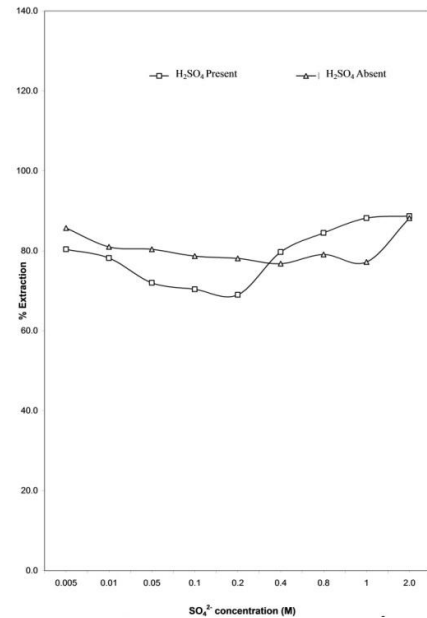


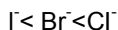
Fig. 16. Variation of % extraction of Cr (VI) with SO₄²⁻ concentration for H₂SP in CHCl₃:BuOH(in the presence and absence of H₂SO₄)

4. CONCLUSION

The decrease in metal ion extraction with increase in Cl⁻ and SO₄²⁻ 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 Cr (VI) follows the following increasing order:



for both H₂Adp and H₂SP 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, PO₄²⁻, acetate EDTA, oxalate and tartarate on the extraction of Cr (VI) ions appears to be fairly constant for both H₂Adp and H₂SP. The results obtained show that extractions of these metals are increasingly masked as anion concentration increase in the aqueous phase. This is consistent with results reported on Mo (VI) [21]. However higher percentages of 88 to 90% were obtained for Cr (VI) extractions using H₂Adp compared to the results obtained for Mo (VI) in H₂Adp (48 to 50%).

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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