

Solvent extraction and separation of Mo(VI) and W(VI) from hydrochloric acid solutions using cyanex-923 as extractant

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A systematic study of solvent extraction of molybdenum(VI) and tungsten(VI) from hydrochloric acid media using neutral phosphine oxide extractant, cyanex-923 in toluene has been performed. These metal ions are quantitatively extracted with cyanex-923 in toluene in the acidic range 5-7 M, and from the organic phase they are stripped with 1.0 M NaOH. The effect of pH, equilibrium period, diluents, diverse ions and stripping agent on the extraction of Mo(VI) and W(VI) has been studied. The extraction reactions proceed by solvation and the probable extracted species in the organic phase were $\text{MoO}_2\text{Cl}_2 \cdot 2\text{Cyanex-923}$ and $\text{WO}_2\text{Cl}_2 \cdot 2\text{Cyanex-923}$. Based on these results a sequential procedure for their separation from each other has been developed.

Keywords: Solvent extraction, Molybdenum(VI), Tungsten(VI), Cyanex-923, Stripping, Separation

Various oxime based extractants such as LIX 84 and LIX-63 have been proposed as suitable reagents for extraction of Mo(VI)¹⁻³. Mohmound *et al.*⁴ have extensively studied the extraction and separation of Mo(VI) and W(VI) with LIX-63 observing good separation characteristics but having some difficulties in recovery of metal from the organic phase. With Alamine-310, the extraction is found to be very poor, while with the mixture of TBP and Cyanex-301, the extraction is quantitative^{5,6}. The effect of pH and temperature on the extraction of W(VI) from NaOH solution by methyl quaternary ammonium chloride has also been studied⁷. Solvent extraction of Mo(VI) and W(VI) with α -benzoin oxime from HCl solution has been investigated by Fan *et al.*⁸. Extraction of Cr(VI), Mo(VI) and W(VI) from sulphate solution is studied using primary amine Primene JM-T⁹. Extraction behaviour of Mo(VI) has been investigated in wide range of concentration (10^{-6} -10 M) of H_2SO_4 , HCl and HNO_3 , using cyanex-301 as extractant in kerosene¹⁰. Extractive spectrophotometric determination of W(VI) using 3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran¹¹ has also been studied. A careful examination of the literature related to the extraction of Mo(VI) and W(VI) reveal the fact that most of the extractant used till date do not give quantitative extraction of the metal and no work has been carried out for the extraction of Mo(VI) and W(VI) using

cyanex-923, which has already proved its potential as extractant for some metal ions. Here, an attempt has been made to investigate the utility of cyanex-923 for the extraction of two metals.

Experimental Procedure

Apparatus and Reagents

The extractant, cyanex-923 supplied by American Cyanamid Company was used without further purification. For preparation of metal solutions a calculated amount of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and/or sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) was dissolved in minimum quantity of sulphuric acid and diluted to desired volume with double distilled water. All other chemical used were of analytical grade. EQUIP-TRONIC model EQ-614 pH meter with combined electrode was used for determination of H^+ ions concentration and ELICO UV-visible SL-27 spectrophotometer with 10 mm cortex quartz cuvettes for absorbance measurements. The amount of Mo(VI) and W(VI) was determined spectrophotometrically by thiocyanate method¹².

Extraction procedure

Initial experiments conducted to ascertain the optimum equilibration time and selection of diluent established the following general procedure for extraction studies.

An aliquot containing 50 μg of Mo(VI) and W(VI) in 10 mL was taken and equilibrated separately with equal volume of cyanex-923 in solvent (toluene) for the required shaking time of 5 and 10 min respectively, after adjusting their aqueous solution to acidity of 5.0 M HCl. The two phases were allowed to separate. The organic phase containing the extracted metal species was then stripped quantitatively with 1.0 M NaOH solutions and it was determined spectrophotometrically at 470 and 403 nm respectively using thiocyanate method. All the experiments were carried out at room temperature.

Results and Discussion

Effect of various diluents and period of equilibration

The extraction of Mo(VI) and W(VI) with cyanex-923 was carried using different aliphatic and aromatic diluents like carbon tetrachloride, chloroform, *n*-hexane, toluene, xylene and cyclohexane (Table 1). Quantitative extraction of Mo(VI) was observed with all the above diluents except chloroform, while quantitative extraction of W(VI) was observed only with toluene and cyclohexane. Toluene was preferred as the diluent for the extraction of Mo (VI) and W(VI) since it provided better phase separation.

Extraction equilibrium was studied for different periods of shaking ranging from 1-10 min. It was observed that 5 min of shaking period was sufficient for quantitative extraction of Mo(VI) with 1.25×10^{-3} M cyanex-923 and 10 min for W(VI) with 5.0×10^{-4} M cyanex-923. However, as time increases the extraction decreases. The equilibrium time required for Mo(VI) is very less (5 min) as compared to diphenyl (dibutyl carbamoyl methyl) phosphine oxide (9 h)¹⁹.

Effect of hydrochloric acid

The effect of HCl concentration on the percentage extraction of Mo(VI) and W(VI) with 0.01 M cyanex-923 in toluene in the acidity range from 1.0-8.0 M is shown in Fig. 1. As the acidity increases the extraction goes on increasing and becomes quantitative in the range 5.0-7.0 M HCl for both the metal ions. Hence all the extractions of Mo(VI) and W(VI) were carried out at 5.0 M HCl. Complete extraction of Mo(VI) and W(VI) is possible with cyanex-923 unlike with alamine-310¹³, methyl isobutyl ketone¹⁴, cupferron (25%)¹⁵ and diethyl dithiocarbamate¹⁶. During the extraction of Mo(VI) with cyanex-923 no masking agents or salting out agent is added as in 5,7-dibromo-8-hydroxyquinoline¹⁷ and 1-phenyl-3-methyl-4-butryl pyrazolone-5¹⁸ respectively.

Effect of stripping agents

The metal loaded organic phase of cyanex-923 was stripped with different strengths of acids like HCl, HNO₃ and H₂SO₄ and bases like NaOH and KOH. The complete recovery of Mo (VI) from metal loaded cyanex-923 was achieved with 1-2 M H₂SO₄, 2.0 M HNO₃, 1-2 M NaOH and KOH solution while

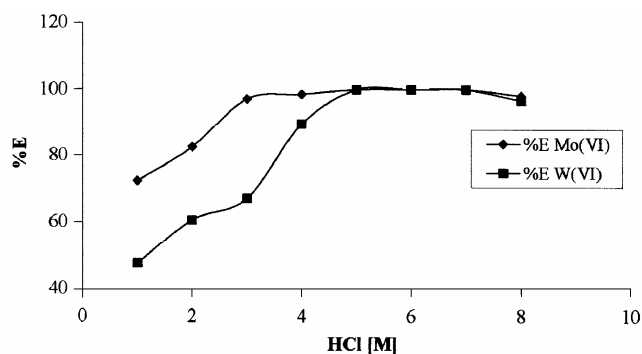


Fig. 1—Effect of hydrochloric acid concentration on percentage extraction of Mo(VI) and W(VI) with cyanex-923 in toluene

Table 1—Effect of diluents on extraction of Mo (VI)/W(VI) with cyanex-923

[Amount of Mo(VI)/W(VI) = 50 μg ; Cyanex-923 = 1.25×10^{-3} M for Mo(VI)/ 5.0×10^{-4} M for W(VI); Acidity of HCl = 5.0 M; Equilibration time = 5 min for Mo(VI) and 10 min for W(VI)]

Diluent	Percentage extraction of Mo(VI)	Distribution ratio (D) of Mo(VI)	Percentage extraction of W(VI)	Distribution ratio (D) of W(VI)
Toluene	99.9	999	99.9	999
Xylene	99.9	999	78.6	3.67
Cyclohexane	99.9	999	99.9	999
Carbon-tetrachloride	99.9	999	85.3	5.80
<i>n</i> -Hexane	99.9	999	86.6	6.46
Chloroform	68.6	2.18	74.6	2.93

complete stripping of W(VI) was observed with 3-4 M H₂SO₄, 1-2 M NaOH and KOH solution. Stripping of W(VI) with cyanex-923 takes place in single step unlike methyl quaternary ammonium chloride⁷, where the stripping takes place in 2 to 5 steps.

Effect of reagent concentration and stoichiometry of extracted species

Extraction of Mo(VI) was carried out by varying the reagent concentration from 1.0×10^{-2} to 5.0×10^{-5} M in toluene and it was found that the extraction increased with increase in the reagent concentration. The extraction of Mo(VI) was quantitative in the range 1.0×10^{-2} - 1.25×10^{-3} M while that of W(VI) in range 1.0×10^{-2} M - 5.0×10^{-4} M. Hence, minimum amount of extractant required for the quantitative extraction of Mo(VI) and W(VI) was 1.25×10^{-3} M and 5.0×10^{-4} M respectively.

In order to determine the stoichiometry and nature of the extracted species, a graph of log D versus log R was plotted (Fig. 2). From the figure it is observed that with increase in the extractant concentration, the distribution ratio goes on increasing. The slope obtained were 1.9 and 2.1 respectively indicating that two molecules of cyanex-923 react with one molecule of molybdenum or tungsten ion. Therefore, the stoichiometry of the extracted species is 1:2. As cyanex-923 is neutral extractant it will extract neutral species from the aqueous phase. The probable nature of the extracted species in the organic phase was found to be MoO₂Cl₂.2Cyanex-923 and WO₂Cl₂.2Cyanex-923 similar to the earlier reported with trioctyl phosphine oxide (TOPO)^{20,21}.

Effect of various diverse ions

Mo(VI) or W(VI) was extracted with cyanex 923 in the presence of large number of foreign ions. The tolerance limit of individual foreign ions was set in such a way that the diverse ion caused interference of $\pm 2.0\%$ in the extraction. It was found that alkali and alkaline metal ions like Na⁺, Li⁺, K⁺, Mg²⁺, Ca²⁺, SO₄²⁻ were highly tolerated (1:30). However, ions/moieties like EDTA, Os⁸⁺, Na-tartarate, W(VI) interfere strongly during the extraction of Mo(VI). Similarly, during the extraction of W(VI) with cyanex 923, alkali metal ions like Na⁺, Li⁺, K⁺, SO₄²⁻ were highly tolerated (1:28). However, EDTA, Mo⁶⁺, Fe³⁺, As³⁺ interfere strongly during extraction. The other metal ions which show intermediate ratio are listed in Table 2.

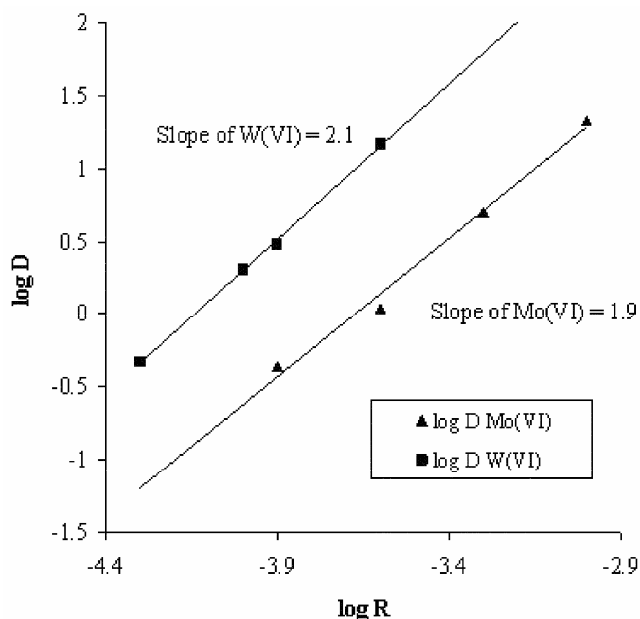


Fig. 2—Effect of reagent concentration on distribution ratio of Mo(VI) and W(VI)

Table 2—Effect of diverse ions on the extraction of Mo (VI) and W (VI) with cyanex-923

[Amount of Mo(VI)/W(VI) = 50 µg; Cyanex-923 = 1.25×10^{-3} M for Mo(VI) and 5.0×10^{-4} M for W(VI); Acidity of HCl = 5.0 M; Equilibration time = 5 min for Mo(VI) and 10 min for W(VI)]

Diverse ions	Mo (VI) Tolerance limit ratio Mo(VI): Diverse ion	Diverse ions	W(VI) Tolerance limit ratio W(VI): Diverse ion
EDTA, Os ⁸⁺ , Na-tartarate, W(VI)	Highly interfering.	EDTA, Mo ⁶⁺ , Fe ³⁺ , As ³⁺	Highly interfering.
Na ⁺ , Li ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , SO ₄ ²⁻	1:30	Na ⁺ , Li ⁺ , K ⁺ , SO ₄ ²⁻	1:28
Al ³⁺ , Be ²⁺ , Ga ³⁺ , In ³⁺ , Ti ³⁺ , SCN ⁻ , NO ₃ ⁻ , Cl ⁻	1:25	Al ³⁺ , Mg ²⁺ , Cd ²⁺ , In ³⁺ , SCN ⁻ , NO ₃ ⁻ , Cl ⁻	1:24
Ag ⁺ , Pd ²⁺ , Pt ⁴⁺ , Rh ³⁺ , Hg ²⁺ , Br ⁻ , I ⁻	1:20	Th ³⁺ , Pd ²⁺ , Pt ⁴⁺ , Hg ²⁺ , Br ⁻ , I ⁻	1:18
V ⁵⁺ , Cr ³⁺ , Mn ²⁺ , Co ²⁺ , Zn ²⁺ , Cs ⁺	1:15	V ⁵⁺ , Cr ³⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Cs ⁺	1:12
Ni ²⁺ , Cu ²⁺ , Pb ²⁺ , Cd ²⁺	1:10	Mn ²⁺ , Co ²⁺ , Ru ³⁺ , Pb ²⁺	1:8

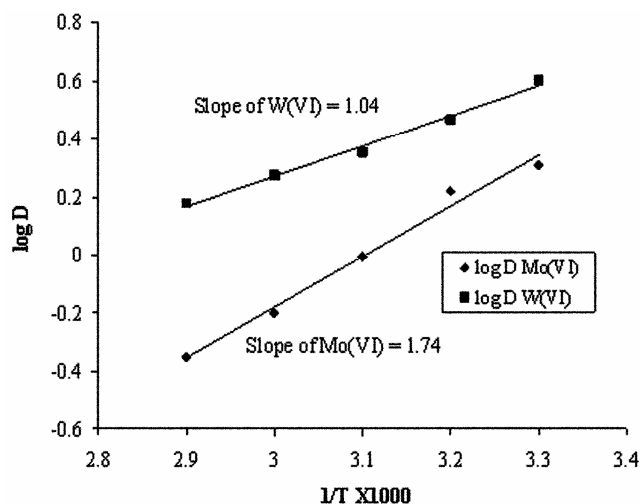


Fig. 3—Effect of temperature on distribution ratio of Mo(VI) and W(VI)

Table 3—Separation of Mo(VI) and W(VI) from multicomponent mixtures from 5 M HCl solution

Sr. No	Mixtures	Amount taken (μg)	Stripping agent	% Recovery
1	Mo(VI)	50	3 M HNO ₃	99.9
	W(VI)	50	1.0 M NaOH	99.7
2	Mo(VI)	50	1 M NaOH	99.9
	Cr(III)	25	Unextracted	99.7
3	Mo(VI)	50	1 M NaOH	99.9
	Ni(II)	25	Unextracted	99.5
4	Fe(III)	50	water	99.2
	Mo(VI)	50	1 M NaOH	99.9
	Cr(III)	25	Unextracted	99.5
5	Fe(III)	50	water	99.3
	Mo(VI)	50	1 M NaOH	99.9
	Ni(II)	25	Unextracted	99.4
6	Mo(VI)	50	3 M HNO ₃	99.9
	W(VI)	50	1.0 M NaOH	99.7
	Ti(IV)	25	Unextracted	99.5

Influence of temperature

Extraction of Mo(VI) and W(VI) with 1.25×10^{-3} M and 5.0×10^{-4} M cyanex-923 in toluene from 1 M HCl solution, was carried out at different temperatures (upto 343 K). From the results it is observed that the distribution ratio decreased with increase in temperature. The Van't Hoff equation is, $\log D = -\Delta H/2.303 RT + C$, where D represent the distribution ratio, ΔH is the enthalpy change for the reaction and C is the constant. The slope obtained from plot of $\log D$ versus $1/T \times 1000$ are 1.74 and 1.04

respectively (Fig. 3). The ΔH values obtained are -33.32 kJ/mol and -19.91 kJ/mol respectively indicating that the reaction is exothermic in nature.

Separation of Mo(VI) and W(VI) from multicomponent mixtures

The proposed method provides mutual separation of Mo(VI) from W(VI) and from other associated metal ions. A mixture of Mo(VI) and W(VI) was first extracted with 1.25×10^{-3} M cyanex-923 in toluene from 5 M HCl solution when Mo(VI) and W(VI) both from the aqueous phase were extracted into the organic phase. Then by using difference in the stripping agent both are separated. Mo(VI) is stripped with 3.0 M HNO₃ while W(VI) is not stripped which was then later on stripped back with 1 M NaOH solution. A mixture of Mo(VI), Fe(III) and Cr(III) was first extracted with 1.25×10^{-3} M cyanex-923 in toluene from 5 M HCl solution. Both Mo(VI) and Fe(III) were extracted in the organic phase, while Cr(III) remained unextracted in the aqueous phase. Iron(III) in the organic phase was stripped back first using water, while Mo(VI) was stripped out using 3 M HNO₃. Similarly Molybdenum(VI) was also separated from ternary mixtures containing Mo(VI)-Ni(II)-Fe(III) and Mo(VI)-W(VI)-Ti(IV) as given in Table 3.

Conclusion

The results obtained show that quantitative-extraction of Mo(VI) and W(VI) is possible with cyanex-923 in toluene in the acidity range 5-7 M HCl. The reagent used is better than many reagents tried earlier. Both the metals can be successfully separated from many other metal ions.

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