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SOLVENT EXTRACTION OF MOLYBDENUM (VI) FROM DILUTED AND CONCENTRATED HYDROCHLORIC ACID SOLUTIONS WITH TRI-N-BUTYL PHOSPHATE

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ABSTRACT

The solvent extraction of Mo (VI) from diluted and concentrated HCl solutions with tri-n-butyl phosphate (TBP) has been studied. The percentage Mo (VI) extraction (E%) reaches maximal levels of 49.60% and 51.20% at pH 1.0 and 4.0 respectively, however, it is much higher (E% = 85.60 –90.80%) in concentrated HCl (2.0 – 7.0M) solutions and decreases with temperature. The mechanism of extraction appears to be through the formation of condensed molybdic acid n($MoO_3.2H_2O$). mTBP at low pH but involves molybdenyl species $MoO_2Cl_{2.}$ $(H_2O)_{2.}$ mTBP in concentrated acid medium and pH 4-6. Electronic and infrared spectra data have been used to deduce the nature of the extracted species.

KEYWORDS: Molybdenum (VI), extraction, TBP, molybdic acid.

INTRODUCTION

Molybdenum has extensive industrial applications and is regarded as one of the vital strategic metals in modern technology. An outstanding application of this element is in the manufacture of anticathode for X-ray tubes. Molybdenum wire is used extensively for the support of tungsten filament, and also as a component of hydrodesulphurization catalyst employed in the petrochemical industry. Due to molybdenum's widespread use this natural resource has become depleted and therefore, its liquid-liquid extraction and purification from ores and very recently wastes which avoids a sole dependence on primary resources that would impact nature by increasing the dispersion of the metal in ecosystems, is regarded to be of utmost importance. (Saberyan et al, 2004; Wernick and Themelis, 1998; Spevack and McIntyre, 1993).

The extraction of molybdenum (VI) from aqueous medium containing hydrochloric, nitric and sulphuric acids using organophosphates or organophosphoric acid has been successfully effected (Kolarik, 1973; Cruywagen and Mckay 1970; Hirai et al, 1995).

Chelating extractants such as 8- hydroxyquinoline and hydroxiquinaldine have also been used to recover molybdenum as cationic complexes from weakly acidic solutions (Trujillo, 1987).

Considerable success has also been recorded in the use of anionic extractants to recover molybdenum either isolatedly or from multimetal solutions (Hirai et al, 1993; Zhang et al, 1997; Cosar and Ziyadangullari, 1998; Chen et al, 2006). Because most of the works we have found in literature have been done at millimolar (10^{-3}M) or lower molybdenum concentration levels due to complexities in the nature of the polymeric or condensed species formed at high concentrations, we have nevertheless carried out this work at high Mo(VI) concentration that simulated typical industrial conditions. In the present study, the recovery of molybdenum (VI) from diluted and concentrated HCl solutions with tri-n-butyl phosphate (TBP) dissolved in n-hexane is presented.

MATERIALS AND METHODS

Materials

The chemicals, MoO_3, HCl, NaOH, TBP and di (2-ethylhexyl) phosphoric acid (D2EHPA) were obtained from the British Drug House Limited (BDH). All the chemicals are of analytical grade except TBP and D2EHPA and were used without further purification.

Preparation of 0.025 M Mo (VI) stock solutions

Molybdenum (VI) oxide (3.60 g, 0.025 mol) and KCl (7.48 g, 0.1 mol) were dissolved in fairly concentrated NaOH and finally made up to the 1-litre mark by adding HCl solution. The adjustment of pH was effected by adding appropriate amounts of NaOH or HCl.

Extraction and Analytical Procedure

Different concentrations of TBP and TBP-D2EHPA mixtures were prepared by mixing appropriate amounts of the extractants with n-hexane. 15 cm^3 portions of TBP or the mixed extractants were equilibrated with 15 cm^3 portions of Mo (VI) solutions (preliminary experiments have shown that variation in Mo(VI) concentration between 0.025 M-0.01M have no significant effect on percentage Mo(VI)extraction) at the appropriate pH and temperature in a separating funnel, swirled manually and later on a mechanical shaker operated at 120 rev/min for 3mins (found optimum for equilibration). The layers were allowed to separate, the lower aqueous layer ran into a conical flask and the upper organic layer removed from the top of the separating funnel to avoid contamination. The amount of molybdenum extracted was determined by spectrophotometry using ultraviolet - visible spectrophotometer.

Biochom 4060 model, which involves measuring the absorbance of the red complex formed between Mo(VI) and thiocyanate ions in isopentyl alcohol at 465 nm. The electronic spectra was recorded on the same instrument while the infrared spectra was recorded on infrared spectrophotometer, Buck scientific model 500.

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RESULTS AND DISCUSSION

Effect of pH

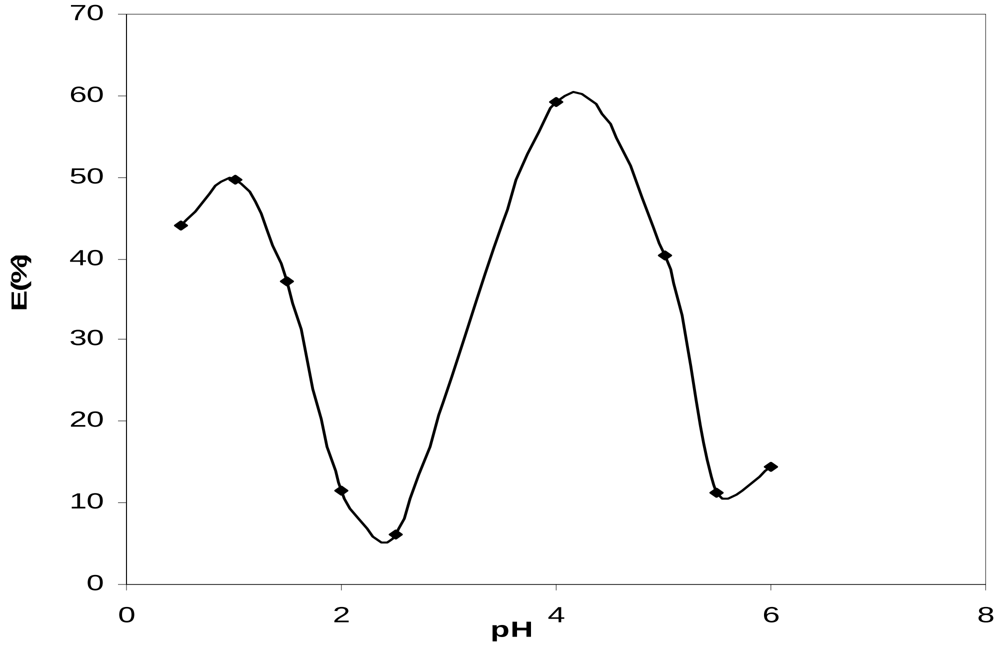

FIG. 1: Effect of pH on Percentage Mo(VI) Extraction from HCl Solution
[Mo(VI)] = 0.025 M; [KCl) = 0.1 M;
[TBP] = 1.098 M

Fig. 1 shows the effect of pH on percentage Mo (VI) extraction.

The observation of different peaks and linear portions on the curve suggest that different Mo (VI) species were involved in the extraction. (Cruywagen and Mckay,1970). The percentage Mo (VI) extraction (E%) reaches maximal levels of 49.60% and 59.20% at pH of 1.0 and 4.0 respectively, and falls subsequently. This could probably be explained by the mechanism below.

The molybdate anion, MoO_4^{4-} is the principal species at alkaline pH (Movsowitz etal, 1997). At pH 5-6, the two competing protonation reactions could be expressed by equations 1& 2.

$$7MoO_4^{2-} + 8H^+ \Leftrightarrow Mo_7O_{24}^{6-} + 4H_2O \qquad (1)$$

$$MoO_4^{2-} + 4H^+ \Leftrightarrow MoO_2^{2+} + 2H_2O \qquad (2)$$

The molybdenyl cation may then combine with Cl^- ion to form extractable neutral chloro complex according to equation 3.

$$MoO_2^{2+} + 2Cl^- \Leftrightarrow MoO_2Cl_2 \qquad (3)$$

Since a low amount of Mo (VI) is extracted at the pH region, it could be infered that the reaction expressed by equation 1 is more(that is MoO_2^{2+} is available in low concentration) favoured than equation 2.

At pH 3.5-4.0, the reactions will probably be

$$MoO_4^{2-} + H^+ \Leftrightarrow HMoO_4^- \qquad (4)$$

$$Mo_7O_{24}^{6-} + 3H^+ + HMoO_4^- \Leftrightarrow Mo_8O_{26}^{4-} + 2H_2O \qquad (5)$$

$$Mo_8O_{26}^{4-} + 20H^+ \Leftrightarrow 8MoO_2^{2+} + 10H_2O \qquad (6)$$

As usual the MoO_2^{2+} ion is the only extractable by TBP. At pH 0.5-1.0, further protonation will occur and might result into the following reactions as expressed by equations 7-9.

$$Mo_8O_{26}^{4-} + 4H^+ \Leftrightarrow H_4Mo_8O_{26} \qquad (7)$$

$$nH_4Mo_8O_{26} \longrightarrow 8(MoO_3.2H_2O)\ n \quad \text{(Condensed molybdic acid)} \qquad (8)$$

$$Mo_8O_{26}^{4-} + 20H^+ \Leftrightarrow 8MoO_2^{2+} + 10H_2O \qquad (9)$$

The MoO_2^{2+} will be converted to the neutral complex as expressed by equation 3. Both the neutral complex and molybdic acid can subsequently be extracted by TBP. Further works were carried out at pH of 1.0 because of the inherent little risk of hydrolysis and a probable less interference from anionic species.

Effect of HCl concentration

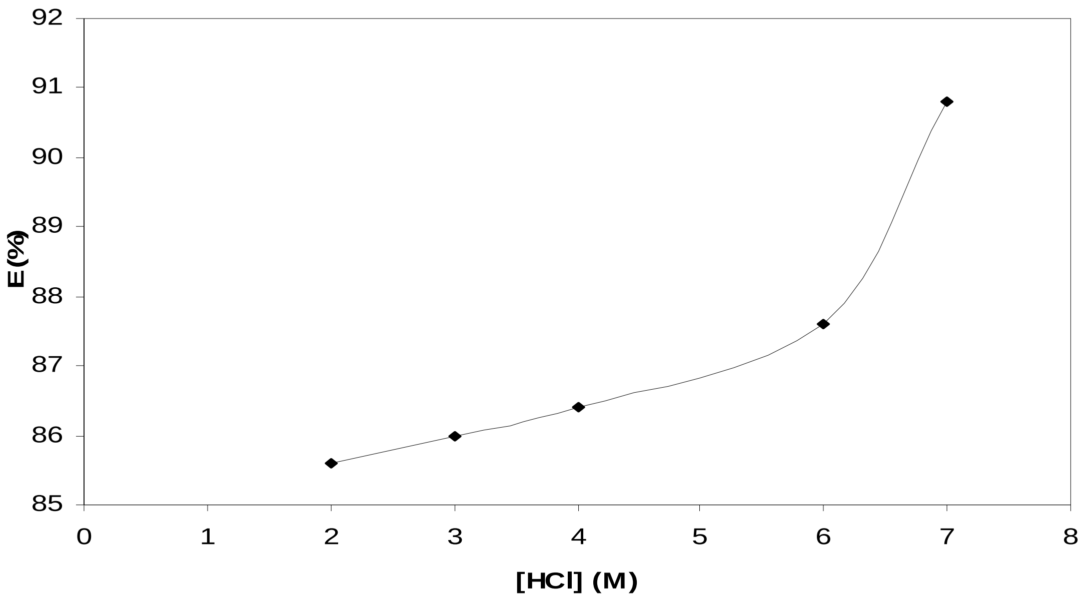

FIG. 2: Effect of HCl Concentration on Percentage Mo(VI) Extraction
[Mo(VI)] = 0.025 M; [KCl) = 0.1 M;
[TBP] = 1.098 M

Fig.2 shows the effect of increase in HCl concentration on the percentage Mo (VI) extraction.

The percentage Mo(VI) extraction (E%) varies from 85.60% for 2.0 M HCl to 90.80% for 7.0 M HCl.

The quantitative extraction observed at 7.0 M HCl might be due to the ease with which MoO_2^{2+} is formed at high acid concentration and the large presence of Cl^- ions required for the formation of an extractable complex. The complex might be further solvated by HCl molecules thereby increasing its extractability.

Effect of TBP concentration

The effect of TBP concentration on percentage molybdenum (VI) extraction is presented in Table 1 and Fig.3.

Table 1: Effect of TBP concentration on percentage Mo(VI) extraction from HCl solutions. pH = 1.0; [Mo(VI)] = 0.025 M; [KCl) = 0.1 M

TBP (%v/v)	[TBP] (M)	D	E (%)
10	0.366	1.232	55.20
15	0.549	1.193	54.50
20	0.732	1.083	52.00
25	0.915	1.016	50.40
30	1.098	0.984	49.60

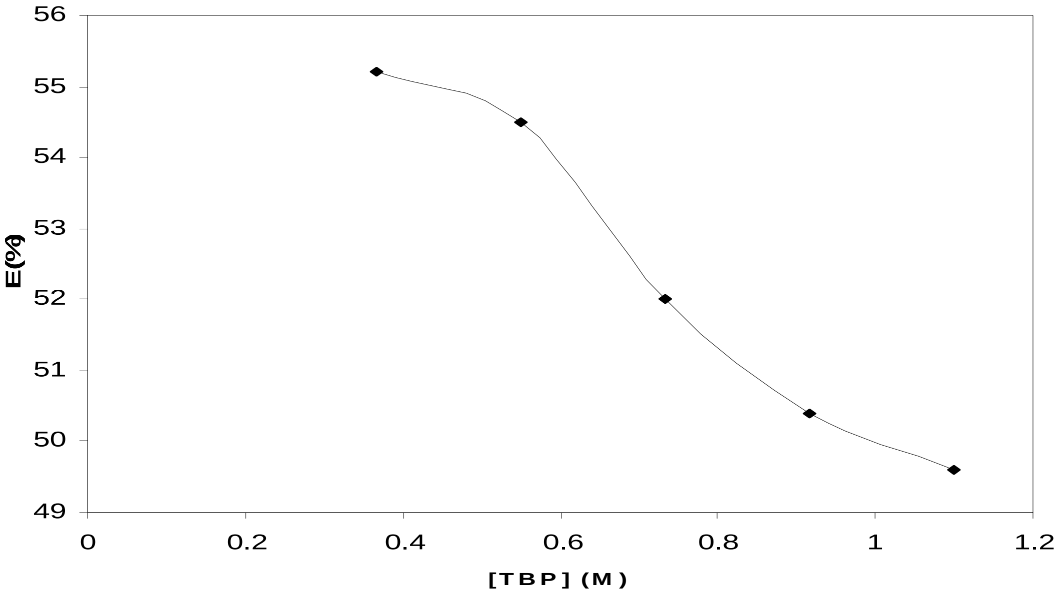

FIG. 3: Effect of TBP Concentration on Percentage Mo(VI) Extraction from HCl Solution
pH = 1.0; [Mo(VI)] = 0.025 M; [KCl) = 0.1 M;

Increase in TBP concentration produces no significant change in percentage Mo (VI) extraction. The E% for Mo varies from 55.20% at 0.366 M TBP to 49.60% at 1.098 M TBP.

If the extraction of Mo (VI) at pH = 1 is assumed to proceed predominantly through molybdic acid formation, the extraction process can be expressed according to equation.10.

$$MoO_3.2H_2O_{(a)} + x\,TBP \Leftrightarrow MoO_3.2H_2O.\,xTBP \qquad (10)$$

$$K_{ex} = \frac{[MoO_3.2H_2O\,.\,xTBP]_o}{[MoO_3.2H_2O]_a[TBP]^x} \qquad (11)$$

$$D = \frac{[MoO_3.2H_2O.x\,TBP]o}{[MoO_3.2H_2O]a} \qquad (12)$$

Substituting (12) into (11) gives

$$K_{ex} = \frac{D}{[TBP]^x}$$

$$\text{Log } D = \log K_{ex} + x \log [TBP] \qquad (13)$$

where D and K_{ex} are distribution coefficient and extraction equilibrium constant respectively.

A plot of log D against log [TBP] (Fig 4) should yield a straight line of the slope x, the number of solvated TBP molecules. The slope determined was – 0.19.This suggests perhaps a non-stoichiometric interaction of Mo(VI) with TBP or the formation of polymeric Mo(VI) species of TBP: Mo less than 1. This could be possible because TBP extracts species by mere solvation. This may be expressed according to equation 14

$$n(MoO_3.2H_2O).mTBP_{(a)} \Leftrightarrow n(MoO_3.2H_2O).mTBP_{(o)} \qquad (14)$$

where n >> m

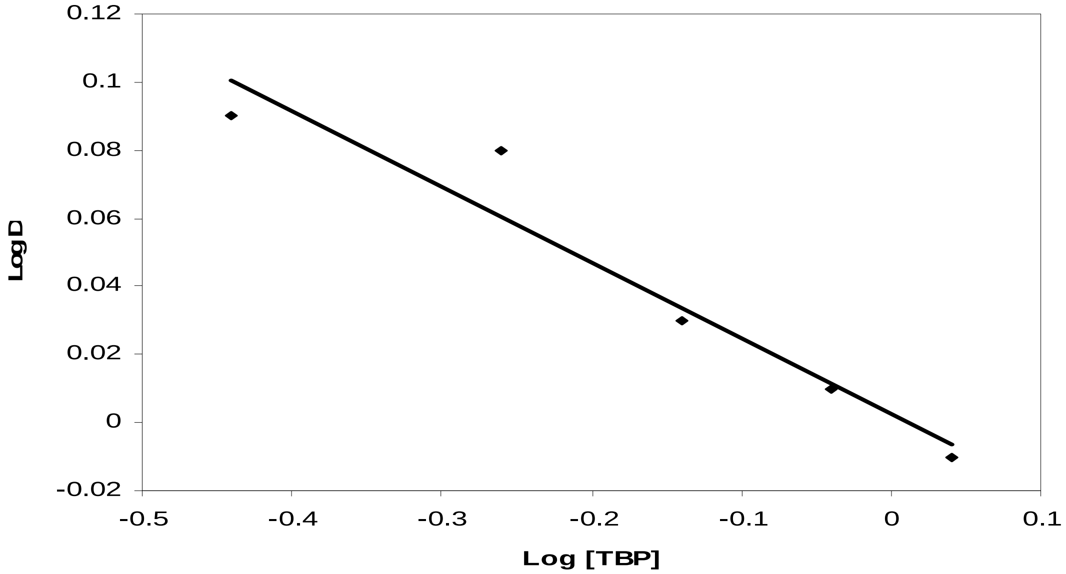

FIG. 4: A Log-Log Plot of Distribution Co-Efficient Against TBP Concentration for Mo (VI)

Effect of addition of D2EHPA to 1.098 M TBP on Mo (VI) Extraction

Fig. 5 illustrates the effect of the addition of D2EHPA to 1.098 M TBP on percentage Mo (VI) extraction. The addition of 0.287 M (10%v/v) D2EHPA to 1.098 M TPB initially decreases E% from 49.60% to 37.62% but rises gradually to 53.21% at added 0.574 M (20%v/v) D2EHPA and later remained nearly constant. The non-synergistic extraction observed with D2EHPA might be due to relative unavailability MoO_2^{2+} ions in what otherwise would have been an enhanced extraction.

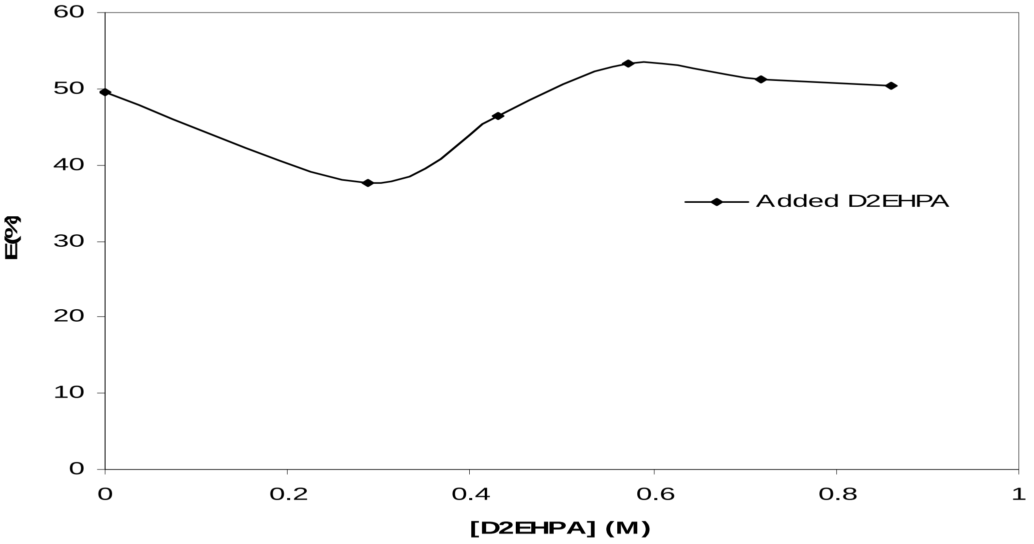

FIG. 5: Effect of the Addition of D2EHPA to TBP on Percentage Mo(VI) Extraction from HCl Solution [Mo(VI)] = 0.025 M; [KCl) = 0.1 M; [TBP] = 1.098 M ; pH = 1.0

Effect of Temperature

The effect of temperature on the distribution coefficient of Mo (VI) is presented in Fig.6.

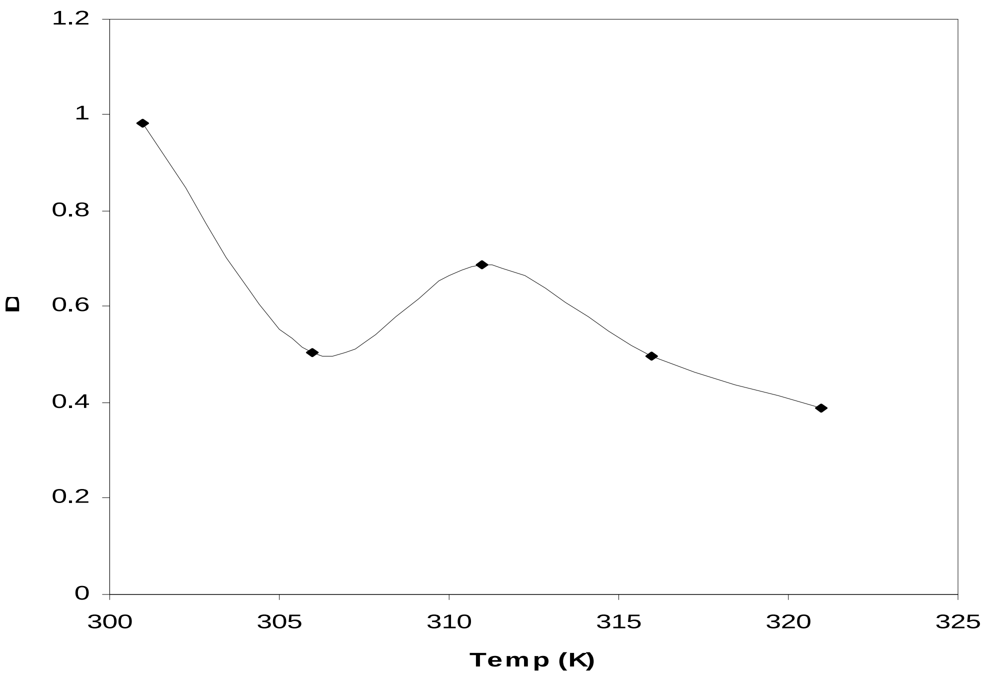

FIG. 6: Effect of Variation of Temperature on Distribution Coefficient of Mo (VI)

Table 2: Effect of temperature on distribution co-efficient and percentage Mo (VI) extraction from HCl solutions. pH = 1.0; [Mo(VI)] = 0.025 M; [KCl) = 0.1 M; [TBP] = 1.098 M

Temp (K)	D	E(%)
301	0.984	49.60
306	0.506	33.60
311	0.689	40.89
316	0.497	32.20
321	0.389	28.01

The percentage Mo(VI) extraction (as presented in Table 2) and distribution ratio both decrease with increase in temperature, suggesting an exothermic extraction process and a possible Mo(VI) overall mass transfer rate that is diffusion controlled. The E% varies from 49.60% at 301 K to 28.01% at 321K while distribution coefficient (D) at both temperatures are 0.984 and 0.389 respectively.

Electronic and Infrared Spectra

The electronic spectra for the TBP extract of Mo(VI) are shown in Table 3. The absorption bands observed at 44444 cm^{-1}, 40000 cm^{-1} and 30769 cm^{-1} have been assigned to ligand – metal – charge transfer (LMCT) of condensed molybdic acid while the band at 28571 cm^{-1} probably involves the molybdenyl species undergoing LMCT (Murata and Ikeda, 1970).

Table 3: The electronic spectra data (cm^{-1}) and assignment for the complexes.

Compound	Band(cm^{-1})	ε (M^{-1}cm^{-1})	Probable Assignment
n($MoO_3.2H_2O$).mTBP	44444	242	Charge transfer
	38462	242	Charge transfer
	32258	194	Charge transfer
	28571	32	Charge transfer
[$Mo.O_2Cl_2.2H_2O$].mTBP	44444	242	Charge transfer
	40000	240	Charge transfer
	30769	28	Charge transfer

The infrared spectra of the free TPB ligand and TPB- Mo (VI) extract are shown in Table 4.

Table 4: The infrared spectra data (cm^{-1}) and Assignments for TBP and complexes.

COMPOUND	BAND	ASSIGNMENTS
TBP	1278vs	ν(P=O)
	1028vs	ν(P-O-C)
n($MoO_3.2H_2O$).mTBP	3447s	ν(O-H)
	1271s	ν(P=O)
	1034vs	ν(P-O-C)
	990w	ν(P=O) -·-·- Mo
MoO_2Cl_2 (H_2O)$_2$.mTBP	3462s	ν(O-H)
	1272s	ν(P=O)
	1028vs	ν(P-O-C)
	990w	ν(P=O) -·-·- Mo

vs = very strong; s = strong; w = weak.

The band at 1278 cm^{-1} assigned to ν (P=O) vibration in the ligand shifts to 1271cm^{-1} in the complex while the ν (P-O-C) band at 1028 cm^{-1} shifts to 1034 cm^{-1} in the complex indicating the involvement of the phosphoryl group in coordination.

The weak band observed at 990 cm^{-1} in the complex and which is absent in the ligand has been assigned to ν (Mo=O) vibration . And finally, the presence of a very broad band at 3447 cm^{-1} assigned to ν (O-H) vibration confirms coordination or solvation by water molecules. (Ojo, 2003).

CONCLUSIONS

The extraction of Mo (VI) at moderately high concentration employed in this work poses no hinderance to its extraction and could be employed at any scale. The extraction of Mo(VI) from HCl with TBP could be carried out at the pH of 1.0 and 4.0 or concentrated HCl to attain a high extraction efficiency, but heating should be discouraged, since the extraction efficiency decreases with increase in temperature. Inspite of the higher E% (85.60-90.80%) obtained for Mo(VI) in concentrated HCl than dilute solutions (pH 1.0 and 4.0), we would recommend its large scale extraction at pH 1.0 because of the risk of TBP degradation already reported at high HCl concentration and more so when the E % (49.60) at pH 1.0 is high enough for a counter-current large scale process. The possible absence of anionic products serves also as an added advantage over pH of 4.0.

REFERENCES

Chen, Y., Feng. Q., Shao, Y., Zhang. G., Ou, L. and Lu, Y., 2006. Investigations on the extraction of molybdenum and vanadium from ammonia leaching residue of spent catalyst. International Journal of Mineral processing. 79(1): 42-48.

Cosar, T. and Ziyadangullari, R., 1998. Separation of molybdenum, vanadium and nickel by liquid - liquid extraction. Turk J Chem. 22: 379-386.

Cruywagen, J. J and Mckay, H. A. G., 1970. The extraction of molybdenum (VI) by tri-n-butyl phosphate. J. Inorg. Nucl. Chem. 32: 255-265.

Hirai, T., Onoe, N. O. and Kosamawa, N., 1993. Photo reductive stripping of vanadium in solvent extraction process for separation of vanadium and molybdenum J. Chem. Eng. Japan, 26 (4): 416-421.

Hirai, T., Hashimoto, T., Tsubio, I., Hino, A. and Kosamawa, I., 1995. Extraction and separation of molybdenum and vanadium using bis (2-ethylhexyl) monothiosphosphoric acid and bis (2-ethylhexyl) phosphoric acid. J. Chem. Eng. Japan, 28: 85-90.

Kolarik, Z., 1973. Acidic organophosphorous extractants. Extraction of molybdemum (VI) by di (2-ethylhexyl) phosphoric acid from weakly acid solutions. J. Inorg. Nucl. Chem. 35: 2025-2933.

Movsowitz, R. L., Kleinberger, R. and Buchaer, E. M., 1997. Application of Bateman Pulse columns for uranium SX. Uranium ore to yellow cake semiar, ALTAMelbourne.

Murata, K. and Ikeda, S., 1970. Extraction of molybdenum (VI) by propylene carbonate. J. Inorg. Nucl. Chem. 32: 267-275.

Ojo, J. O., 2003. Studies of the ploynuclear complexes of labile ligands of Vitamin B_1 and Zn (II), Cd (II) and Hg (II) with Fe (III). Pak.J . Sci. Ind. Res., 46(6): 432-435.

Saberyan, K., Maragheh, M. G. and Ganjali, M. R., 2004. Novel method for stripping of molybdenum (VI) after its extraction with Cyanex 301. Bull. Korean Chem. Soc. 25 (4): 60-465.

Spevack, P. A. and McIntyre, N. S., 1993. A raman and XPS investigation of supported molybdenum oxide thin film reactions with hydrogen sulphide. J. Phys. Chem. 97(42): 11031-11036.

Trijillo, R. A., 1987. Solvent extraction of molybdenum. Ph. D. Thesis, Arizona University, Tucson, USA, 181pp.

Wernick, I. K. and Themelis, N. J., 1998. Recycling metals for the environment, Annu. Rev. Energy Environ, 23: 465-497.

Zhang, P., Inoue, K., Yoshizuka, K. and Tsuyama, H., 1997. A new solvent extraction process for recovery of rare metals from spent hydrodesulphurization catalysts. Kagaku Kogaku ronbunshu 23(1): 1-10