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Mechanism of the extraction of Molybdenum(VI) from diluted HCl and HNO$_3$ solutions with di(2-ethylhexyl)phosphoric acid

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ABSTRACT

The mechanism of extraction of Mo (VI) from diluted HCl and HNO$_3$ solutions with di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in n-hexane has been investigated. The mechanism of extraction from both acids at pH 1.0 – 6.0 was found to be majorly by cation exchange of MoO_2^{2+} for H^+ of the extractant (H_2R_2), while at lower pH value, it was observed to be by neutral, unstable isopoly acid, $H_4Mo_8O_{26}$ or $nMoO_3 \cdot 2H_2O$ and MoO_2^{2+}. The extraction efficiency was maximal at pH 1.0 for both acids, E% = 84.8 and 80.0 for HCl and HNO$_3$ media respectively. From the method of slope analysis, the number of D2EHPA molecules associated with MoO_2^{2+} was found to be two at pH = 1.0.
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Keywords: Extractant, cation exchange, isopoly acid, slope analysis.

INTRODUCTION

The extraction of Mo(VI) from hydrochloric acid solution by tri-n-butyl phosphate (TBP) was the focus of the work reported recently (Ojo et al., 2008). The attendant attention on molybdenum is deserving in that it is an indispensable element in modern technology. Its application cuts across many spheres of human endeavours.

Molybdenum is a first-choice element in the manufacture of heat and corrosion-resistant alloys, a component of earth moving machines, a base metal in hydrodesulphurization catalysts (HDS) employed in crude oil refining. Its compounds are used as pigments and smoke suppressants. This element excitingly serves as an essential micronutrient to plants and thus artificially added to soils. As valuable as the metal is, its primary sources have become depleted, which necessitates a thorough understanding of its extraction mechanism in order to boost its recovery from process solutions. Mo(VI) is endowed with the presence of multi-species, some highly, and others lowly extractable, which very often depend on the acidity of the medium, making its solution chemistry unique and complex (Saberyan et al., 2003; Saberyan et al., 2004; Jin-Young et al., 2010).

The extraction of Mo (VI) in the alkaline pH range is well understood and proceeds majorly through molybdate species, MoO_4^{2-}, which is only extracted by anionic extractants like methyltrioctylammonium chloride or bromide ($R_4N^+X^-$) (Chen et al., 2006). At acidic pH range, many Mo(VI)

species of varying extractability are observed. These include H_2MoO_4, MoO_2^{2+}, $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$ making the acidity range exciting to study (Kordosky, 2010). The ions of some aqueous acids may also play influencing roles in the extraction of some metal species, thus affecting the efficiency of the overall extraction. For instance, the nitrate ion depending on its concentration was found to be the determinants of the extractable V(V) species from HNO_3 with di(2-ethylhexyl) phosphoric acid as extractant, in contrast to HCl medium (Ojo, 2010).

From diluted and concentrated HCl solutions, neutral polymeric and cationic Mo(VI)species, respectively have been extracted in which Cl^- acted as the counter-ion (Ojo et al., 2008).

The extraction of Mo(VI) in an admixture of W(VI) from HNO_3 and H_3PO_4 media with trioctylmethylammonium chloride has been reported, where the extractable species were found to be $HMoO_4^-$ and MoO_2^{2+} at lower and higher acid concentration, respectively (Johansson et al., 2003). In another study, where Mo(VI) was extracted from H_2SO_4 medium by Alamine 336 [tri- (C_8- C_{10}) amine] the extractable species was identified as $HMoO_4^-$ (Basualto et al., 2003). Some workers have also reported the formation of extractable mixed-valence polymolybdate species in their study of Mo(VI) extraction from aqueous solutions using aliquat 336 dissolved in n- heptane modified by n- decanol (Bal et al., 2004).

From the foregoing, it has become very obvious that if the pH is quite low, and with a careful choice of an acidic extractant such as D2EHPA, partial ionization could take place, that could be exploited for the quantitative extraction of cations and neutral Mo(VI) species.

The need to investigate the mechanism of Mo(VI) extraction from HCl and HNO_3 media at the acidic pH range with D2EHPA in order to optimize its recovery and also to determine the more suitable of the aqueous acid media prompted the present studies.

MATERIALS AND METHODS

The chemicals, MoO_3, NaOH , HCl, HNO_3, di(2-ethylhexyl)phosphoric acid (D2EHPA and tri-n-butyl-phosphate (TBP), and n-hexane were obtained from the British Drug House Limited (BDH). All the chemicals save for D2EHPA and TBP were of analytical grade and were used without further purification.

Preparation of reagents

Stock solutions of Mo(VI) were prepared by the dissolution of 0.025 mol MoO_3 in few cm^3 of fairly concentrated NaOH solution and made acidic with added HCl or HNO_3 solution to the 1-litre mark to obtain the desired pH (0.5-6.0). Stock solutions of D2EHPA were prepared by dissolving appropriate amounts of D2EHPA in n-hexane to obtain solutions of the concentration range of 0.287-0.861 mol dm^{-3}.

For D2EHPA mixtures with TBP, appropriate and varied amounts of TBP were dissolved in a fixed volume of D2EHPA with n-hexane added as diluent to give a TBP concentration of the range (0.366 – 1.098 mol dm^{-3}) and D2EHPA concentration of 0.861 mol dm^{-3}.

Extraction and analytical procedure

Ten cm^3 aliquots of stock Mo(VI) solution were shaken with appropriate volume of D2EHPA solution or D2EHPA – TBP mixtures in n-hexane for 1 hour (found optimum) with a mechanical shaker at 120 rpm. The phases were allowed to settle, disengage and separated. The organic phase was stripped with 14.5 mol dm^{-3} ammonia solution. Both phases were analysed (to

ensure a mass balance) to determine the Mo(VI) extracted using the modified Mo(VI) – thiocyanate Vogel's method (Ojo et al., 2008), which involves measuring the absorbance by UV-visible spectrophotometry of the isopentyl alcohol extract at 465 nm. For the procedure, 0.1 cm^3 of the Mo(VI) extracts was pipetted into a 25 cm^3 standard flask and with the following added in sequence; 2.0 cm^3 of concentrated HCl, 1.0 cm^{3}of 10% ammonium iron (II) sulphate in 0.05 M H$_2$SO$_4$, and 3.0 cm^{3}of 10% (w/v) KSCN. The solution was shaken gently and 3.0 cm^3 of 10% (w/v) SnCl$_2$ in 1 M HCl was added and made up to the 25 cm^3 mark with distilled water. It was extracted twice with 10 cm^3 portions of isopentyl alcohol and the extracts combined. The absorbance of the red couples was measured at 465 nm against isopentyl alcohol blank. The Mo(VI) concentration was finally obtained from a standard concentration curve.

RESULTS AND DISCUSSION
Effects of pH on Mo (VI) extraction

Figure 1 shows the effect of pH on percentage Mo(VI) extraction from HCl and HNO$_3$ solutions.

From HCl medium, the percentage Mo(VI) extraction (E%) was high and nearly constant at the pH range of 0.5-1.5 (E% = 83.6 – 84.4) and decreased subsequently to E% = 19.9 at pH of 4.0. It was worth noting that an intermittent variation in E% was also observed within the pH range of > 4.0 – 6.0. This trend agrees with the work reported by Ojo et al. (2008) on the solvent extraction of Mo (VI) from HCl solution with TBP, and Kalagbor et al. (2011).

This behavior can be attributed to the predominance of various Mo(VI) species at different pH values which is the peculiar feature of molybdenum aqueous solution chemistry (Kordosky, 2010). Mo(VI) species

extracted at the pH range of 0.5-1.5 would be predominantly MoO$_2^{2+}$ (since other co-present anionic species are not extracted by the extractant) of which equilibria can be expressed by equation 1.
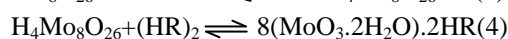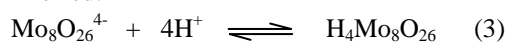
$$Mo_8O_{26}^{4-} + 20H^+ \rightleftharpoons 8MoO_2^{2+} + 10H_2O \quad (1)$$
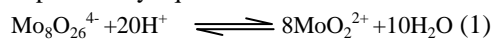
and the major extractive reaction, generally by equation 2.

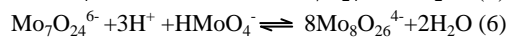$$MoO_2^{2+} + 2(HR)_2 \rightleftharpoons MoO_2R_2 . 2HR + 2H^+ \quad (2)$$

(where (HR)$_2$ represents the dimeric form of D2EHPA in hydrocarbon diluents)

While the minor reaction at pH of about 1.0 involving the extraction of H$_2$MoO$_4$ by unionized molecules of D2EHPA in accordance to equations 3 and 4 is strongly inferred.

$$Mo_8O_{26}^{4-} + 4H^+ \rightleftharpoons H_4Mo_8O_{26} \quad (3)$$
$$H_4Mo_8O_{26} + (HR)_2 \rightleftharpoons 8(MoO_3.2H_2O).2HR \quad (4)$$

This mechanism of extraction of neutral Mo(VI) species has been observed with TBP and mixed trialkylphosphine oxide (cyanex-923) extractants (Ojo et al., 2008; Talla et al., 2010).

At the pH range > 1.5 – 4.0, the observed decrease in E% could be explained on the decrease in the available MoO$_2^{2+}$ due to the predominance of unextractable anionic species arising from the equilibria described by equations 5 and 6.

$$7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O \quad (5)$$
$$Mo_7O_{24}^{6-} + 3H^+ + HMoO_4^- \rightleftharpoons 8Mo_8O_{26}^{4-} + 2H_2O \quad (6)$$

At the pH range of 4.0 – 6.0, MoO$_2^{2+}$ is also formed which is extractable by the highly ionized D2EHPA dimer as expressed by equation 2.

With HNO$_3$, the percentage Mo(VI) extraction (E%) follows a similar trend except the marked difference at pH of 0.5. At the pH range of 0.5-1.5, E% varies from 44.7 – 75.1%. The rather low E% at pH 0.5 might be due to the inability of HNO$_3$ to promote a high dissociation of D2EHPA arising from the poor ionization of HNO$_3$ at low pH value, in contrast to HCl, which is a stronger acid. The

extraction of Mo(VI) could therefore be majorly by neutral $n(MoO_3.2H_2O)$ polymer with unionized D2EHPA dimers, $(HR)_2$, expressed by equation 4. Above the pH range of 1.0 – 1.5, the Mo(VI) specie extracted was predominantly MoO_2^{2+}, as previously explained, which equilibrium can be expressed by equation 2.

Within the pH range of > 1.5 – 4.0, the percentage Mo(VI) extraction decreased gradually from E% = 75.2 to 22.4 similar to the trend observed with HCl, and the mechanism is expected to be the same as that expressed by equation 2. This could be explained on the basis of less availability of MoO_2^{2+} where undoubtedly more ionized

D2EHPA, that is $(HR)_2$ reacting species should be readily available.

At the pH range of 4.0-6.0, an increase / decrease in E% without a regular trend was observed. The E% reached an optimum of 69.3% at pH 5.5. The proposed mechanism for the extraction of MoO_2^{2+} is that expressed by equation 2.

Effect of D2EHPA concentration

The effects of D2EHPA concentration on the percentage extraction of Mo(VI) from HCl and HNO_3 media are presented in Figures 2 and 3.
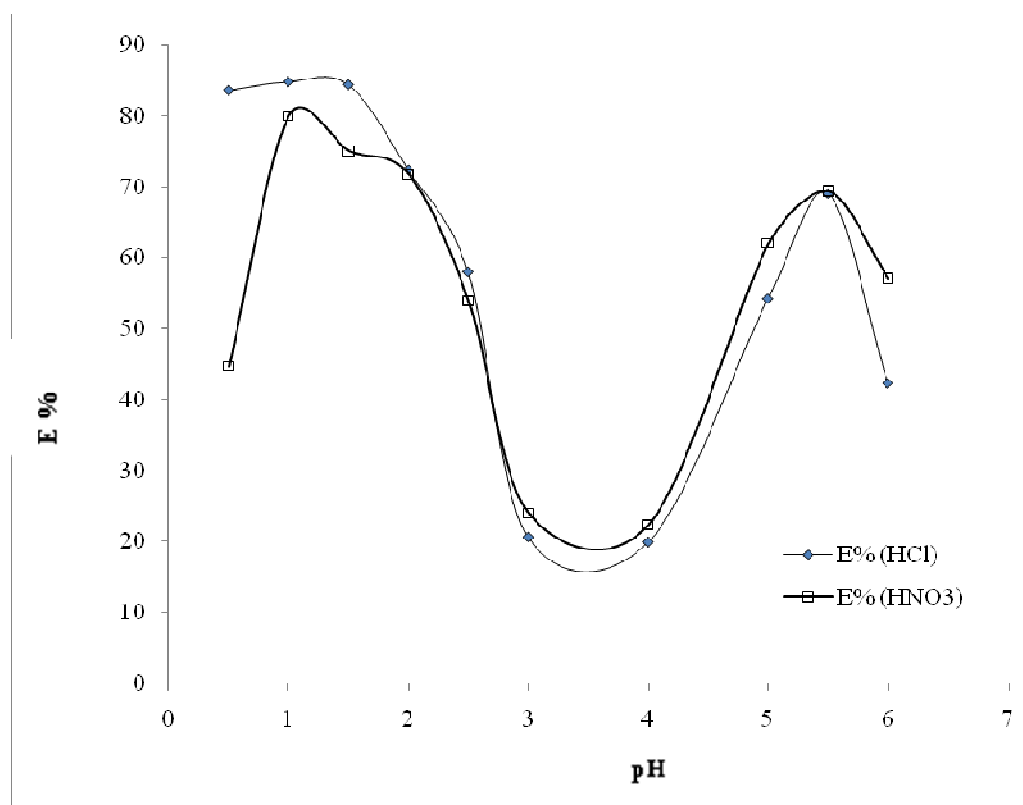

Figure 1: Effect of pH on percentage Mo(VI) extraction from HCl and HNO_3 solutions. $[Mo(VI)]= 0.025$ mol dm^{-3}; $[D2EHPA] = 0.861$ mol dm^{-3}; $[KCl]$, $[KNO_3] = 0.1$ mol dm^{-3}.
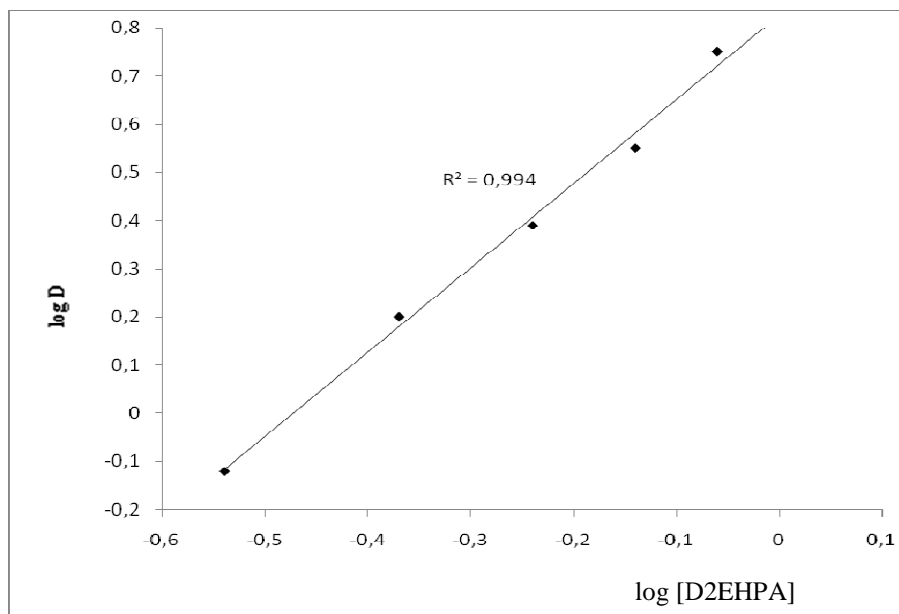
Figure 2: A log – log plot of distribution coefficient against D2EHPA concentration for Mo(VI) extracted from HCl solutions. pH = 1.0; [Mo(VI)]= 0.025 mol dm^{-3}.

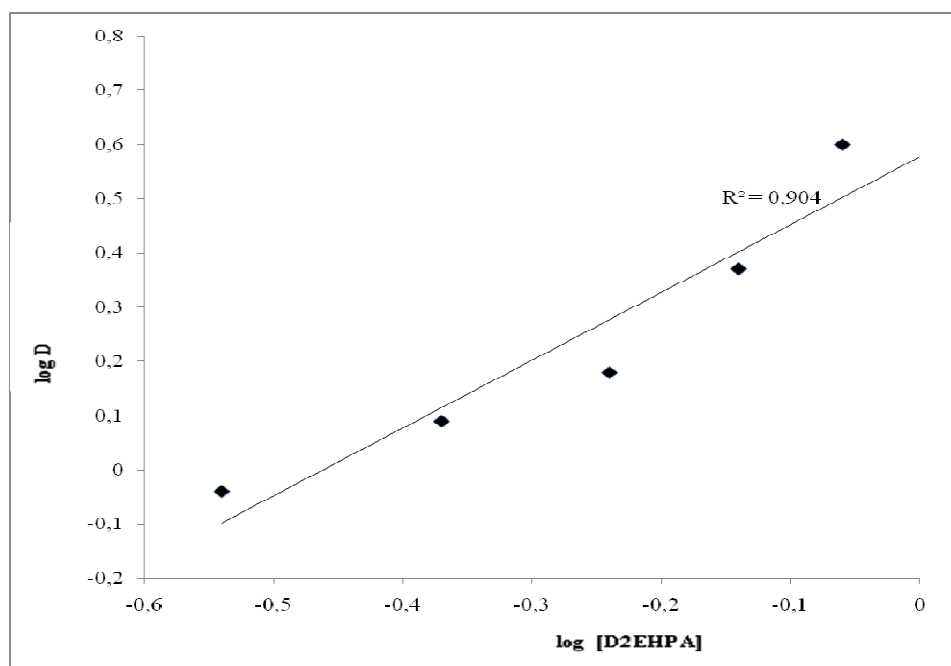

Figure 3: A log – log plot of distribution coefficient against D2EHPA concentration for Mo(VI) extracted from HNO$_3$ solutions. pH = 1.0; [Mo(VI)]= 0.025 mol dm^{-3}.

With HCl aqueous medium. Increase in D2EHPA concentration yielded an increase in percentage Mo(VI) extraction. The E% rose from 43.2% (log D = -0.12) at log [D2EHPA] = - 0.54 to 84.1% (log D = 0.75) at log [D2EHPA] = - 0.06.The plausible explanation is the availability of more ionized D2EHPA molecules for binding to the molybdenyl ion, MoO_2^{2+} leading to its extraction. This observation is similar to that reported by Saberyan et al. (2004) on the extraction of Mo(VI) from HNO_3 solution with bis (2,4,4-trimethylpentyl) dithiophosphinic acid which also is an organophosphorus extractant.

Since ionized D2EHPA dimers, HR_2^- are expected to be predominant at pH = 1.0, its extraction of MoO_2^{2+} can be represented by equation 7.

MoO_2^{2+} + n+1(HR)$_2$ $\rightleftharpoons$ MoO_2R_{2n}. n+1HR + n+1H$^+$ (7)
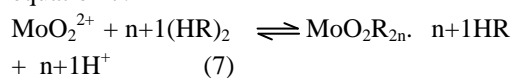
Therefore,

$$K_{ex} = [MoO_2R_{2n} . n + 1(HR)] . [H^+]_{org}^{n+1} / [MoO_2^{2+}]_{aq} . [(HR)_2]_{org}^{n+1}$$

$$K_{ex} = D[H^+]^{n+1}/ [(HR)_2]^{n+1}$$

where 'aq' and 'org' represent aqueous and organic phases respectively, while 'D' represents the ratio of the analytical concentrations of the Mo(VI) in organic and aqueous phases respectively. Keeping the pH constant and taking logarithms, we have

log D = log K_{ex} + (n+1) log [(HR)$_2$]

Hence, a log – log plot of 'D' against log [(HR)$_2$] would yield a straight line with a slope equal to 'n + 1', the number of reacting D2EHPA dimer molecules, and an intercept of log K_{ex} (K_{ex} = extraction equilibrium constant). The determined slope was 1.6 ($\approx$ 2), therefore, n = 1.

This implies that two molecules of ionized D2EHPA dimmers are bound to MoO_2^{2+}, and log K_{ex} = - 0.19 connoting a less

spontaneous extraction process, which justifies the initial rigorous and prolonged shaking at inception.

With HNO_3, increased D2EHPA concentration produced increased percentage Mo(VI) extraction. The E% increased from 47.6% (log D = 0.6) at [D2EHPA] = 0.861 mol dm^{-3}. The observed higher optimum E% in HCl medium when compared with HNO_3 at pH = 1.0 could be explained by the presence of more ionized D2EHPA molecules in the former, whose extraction could be described by equation 2.

As expected, a log – log plot should yield a straight line of slope n + 1. The determined slope was 1.7 ($\approx$ 2), hence n = 1, which suggests that two molecules of D2EHPA dimers are associated with MoO_2^{2+} which is in agreement with that observed in V (IV)- D2EHPA-H_2SO_4 (Biswas et al., 2004) and Zn (II)- D2EHPA-H_3PO_4 (Mellah and Benachour, 2006) systems. The log K_{ex} equals – 0.5 suggesting a low spontaneous extractive reaction which again warranted the rigorous and prolonged shaking during equilibration similar to what we reported in vanadium-HCl- d2EHPA sytem (Ojo et al., 2012).

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Effect of the addition of TBP to D2EHPA on Mo (VI) extraction

The effect of the addition of TBP to D2EHPA on Mo(VI) extraction is illustrated with Figure 4.

With HCl aqueous medium, at pH = 1.0, when TBP was added to D2EHPA, (0.861 mol dm^{-3}) at a concentration of 0.366 mol dm^{-3} (10% v/v of the total organic phase volume), the percentage Mo(VI) extraction decreased from E% = 84.1 (D2EHPA only) to 47.2, and when added further increased steadily to E% = 64.4 at [TBP] = 1.098 mol dm^{-3} (30% v/v). This trend has been reported by the author (Ojo, 2010) in the V(V) extraction from HNO_3 solution by D2EHPA/TBP mixture. The

decreased extraction could be explained on the basis of an association between D2EHPA dimers and TBP molecules, causing a reduction in the available ionized D2EHPA dimers responsible for the extraction of MoO_2^{2+}, while the subsequent increase might be due to increased solubility of extracted Mo(VI) – D2EHPA complex as a result of solvation by TBP, and also the extraction of only neutral Mo(VI) specie such as MoO_3 .

$2H_2O$ by TBP. This is in contrast with observations made in Zn(II)-D2EHPA/TBP-H_3PO_4 system where synergistic effect was noted (Guezzen and Didi, 2012).

With HNO_3, a similar trend in E% variation was observed. An initial decrease in E% (80.0 – 50.6%) followed by a steady increase up to 65.2% at added [TBP] = 1.1 mol dm^{-3}. The explanation offered with HCl medium is applicable in this circumstance.

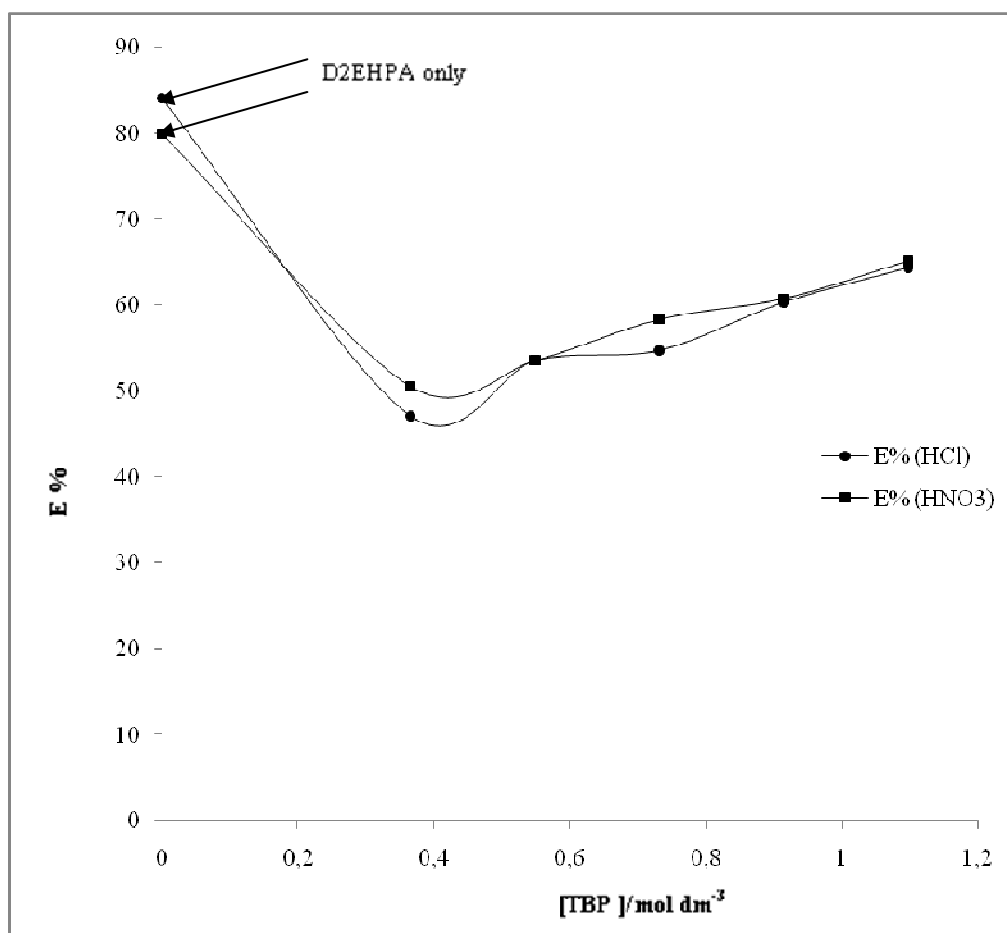**Figure 4:** Effect of the addition of TBP to 0.861 mol dm^{-3} D2EHPA at pH = 1.0 on percentage Mo(VI) extraction from HCl and HNO_3 solutions. [Mo(VI)]= 0.025 mol dm^{-3}; 6+[KCl], [KNO_3] = 0.1 mol dm^{-3}.

Conclusion

The mechanism of extraction of Mo(VI) from HCl and HNO$_3$ media by D2EHPA involved different species, MoO$_2^{2+}$ and n MoO$_3$.2H$_2$O (n = 8, H$_4$MoO$_8$O$_{26}$). At the pH range of 1.0 – 6.0, the major extractable specie was MoO$_2^{2+}$, while the mechanism at below pH = 1.0 involved n MoO$_3$. 2H$_2$O species (from H$_4$MoO$_8$O$_{26}$).

It is better to extract Mo(VI) at the pH range 1.0 – 6.0 where the prevailent specie MoO$_2^{2+}$ exists over a wide range, than at lower pH values where the neutral n(MoO$_3$. 2H$_2$O), existing at a narrow range is prevailent. The efficiency of the extraction from HCl solution is slightly higher than HNO$_3$ which will make HCl a better process acid (lixiviant).

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