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## COMPARATIVE STUDY OF THE EXTRACTION OF V(V) AND V(IV) FROM HYDROCHLORIC ACID SOLUTIONS WITH D1(2 ETHYLHEXYL) PHOSPHORIC ACID.

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(Received: 6th December, 2011; Accepted: 10th March, 2012)

### ABSTRACT

This study compared the extraction of V(V) and V(IV) from HCl solutions by di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in n-hexane with that of tri-n-butyl phosphate (TBP) extractant reported recently. The percentage vanadium extraction (E%) reached optimal levels of 78.0 and 83.3% for V(V) and V(IV) respectively, at optimum pHs of 1.3 and 2.0 in that order. The extraction of both species was found to increase with D2EHPA concentration up to experimental  $\log [D2EHPA] = -0.06 \text{ mol dm}^{-3}$  (i.e.  $0.86 \text{ mol dm}^{-3}$ ). The extraction of V(V) occurred through an exothermic process at the temperature range 301-321 K and V(IV) followed a similar order. From the method of slope analysis, UV visible and infrared spectra measurements, the stoichiometries of the extracted V(V) and V(IV) species were formulated as  $\text{VO}_2\text{HR}_2$  and  $\text{VO}(\text{HR})_2$  respectively. The study showed that V(IV) was adjudged to be better extracted than V(V) by D2EHPA under the prevailing experimental conditions.

**Key words:** Vanadium, Solvent Extraction, D2EHPA; Stoichiometries.

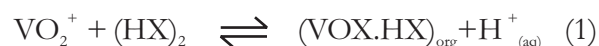
### INTRODUCTION

Solvent extraction of V(V) and V(IV) from HCl solutions with tri-n-butyl phosphate (TBP) was the focus of a recently reported study (Ojo and Adeeyinwo, 2011), The extraction of V(V) and V(IV) from the same medium utilising di(2-ethylhexyl) phosphoric acid (D2EHPA) has been undertaken in our current effort.

Di (2-ethylhexyl) phosphoric acid (D2EHPA) is an acidic extractant, which extracts cations by binding with them in its ionized form, and whose commercial use in the DAPEX (dialkylphosphate extraction) process for the extraction of  $\text{VO}^{2+}$  and  $\text{UO}_2^{2+}$  from sulphuric acid liquors of carnotite ore dated back to decades ago (Rigg and Garner, 1967).

The selective extraction of V(V) from associated metal ions from hydrochloric and hydrobromic acid solutions has been effected with tris (2-ethylhexyl) phosphate (TEHP) dissolved in toluene, and the extractable specie was formulated as  $\text{VOCl}_3 \cdot 2\text{TEHP}$  (Gaudh and Shinde, 1995). Some workers have also reported the mechanism of V(V) extraction from sulphuric acid solution with D2EHPA (Kurbatova and Kurbatov, 2006). A comparative study of the extraction of V(V) and V(IV) with 2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester (PC88A), itself an acidic extractant, have been carried out (Jayadas and Reddy, 2002). In the study, the equilibrium

extraction was represented by equation (1).



where  $(\text{HX})_2$  refers to the dimeric form of PC-88A while the equilibrium reaction for the V(IV) extraction has been formulated as in equation (2).



The extraction equilibrium constant  $K_{\text{ex}}$  for the V(V) and V(IV) extractions were 3.14 and 0.32 respectively which suggest a better recovery process for V(V).

Many anionic extractants (extracts complex anions) such as primary, secondary, tertiary and quaternary amines with the formulae  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$ ,  $\text{R}_3\text{N}$  and  $\text{R}^1\text{R}_3\text{N}^+\text{X}^-$  respectively have also been used to extract V(V) as vanadates ( $\text{VO}_4^{3-}$ ) with selectivity depending on the pH of the aqueous solutions (Miura *et al.*, 2001).

Very recently we have reported a comparative study of the extraction of V(V) and V(IV) from concentrate HCl solution with TBP was reported where it was found that V(V) was appreciably extracted in contrast to the poor extraction of V(IV) (Ojo and Adeeyinwo, 2011). It appears both the anionic and solvating extractants have not been found efficient for V(IV) extraction. From literature it is obvious that

most of the previous works have been carried out on metal ion concentration (an equilibrium condition) below those normally encountered in industrial liquors ( $>2\text{g L}^{-1}$ ) (Silver *et al.*, 2005). This and the fact that a comparative study of extractions involving the various and high concentration of vanadium species ( $\text{V}^{3+}$  has hitherto proved unextractable) by D2EHPA is significantly unreported, makes the present study a worthwhile venture. This is particularly important in that the efficiency of D2EHPA for the extraction of any of the vanadium species would have been addressed at both bench and large-scale or commercial levels of operation with an added advantage of providing a clue in the choice of suitable extractant. The present work concludes our report on the comparative study of the extraction of V(V) and V(IV) from HCl solutions.

## EXPERIMENTAL

### Reagents Used and their Sources.

The chemicals,  $\text{NH}_4\text{VO}_3$ , HCl, KCl,  $\text{KMnO}_4$ ,  $\text{H}_2\text{O}_2$ , ascorbic acid, tri-n-butyl phosphate (TBP), di (2-ethylhexyl) phosphoric acid (D2EHPA) and n-hexane (diluent) 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.

Ammonium metavanadate (5.85g, 0.05 mol) was dissolved in various concentrations of hydrochloric acid, followed by the addition of KCl (7.48g, 0.1mol) and finally made up to the 1 litre mark. The adjustment of pH was effected by adding NaOH or HCl and subsequently measured by the pH meter, LABEX LDA 861 model.

To the stock solution of V(V) prepared above was added ascorbic acid (19.11g, 0.1 mol) stirred, with the solution turning to blue. The amount of vanadium (IV) present was determined by titrating with 0.02 M  $\text{KMnO}_4$  at 333 K (Ipinmoroti, 1981). The reduction was complete in all the solutions.

Different concentrations of D2EHPA in the range 0.29 - 0.86 mol  $\text{dm}^{-3}$  were prepared by dissolving D2EHPA in appropriate volumes of n-hexane while D2EHPA/TBP solutions were prepared by mixing the appropriate volumes of TBP with a fixed volume of D2EHPA and diluted with n-hexane to give a TBP concentration in the range 0.37-0.73 mol  $\text{dm}^{-3}$  and D2EHPA of 0.86 mol  $\text{dm}^{-3}$ .

### Extraction and Analytical Procedure

25  $\text{cm}^3$  portions of V(V) and V(IV) solutions were transferred with 25  $\text{cm}^3$  portions of D2EHPA into 250  $\text{cm}^3$  separating funnel, and shaken with a mechanical shaker at 120 rpm for 5mins (found optimum from preliminary studies). The phases were allowed to settle, disengaged and separated. The lower aqueous layer (raffinate) was run out through the tap while the organic layer was poured out through the top to avoid contamination.

The effects of pH, initial V(V) and V(IV) concentrations, extractant and acid concentrations, and temperature were studied by varying the one under investigation while keeping the others constant as follows: pH varied in the range 0.4 - 2.0 with added few drops of concentrated NaOH or HCl to the V(V) and V(IV) aqueous portions with effort taken to minimize much changes in volume, and each of the aqueous portions was extracted with D2EHPA solution; variation of initial V(V) and V(IV) concentration was by the dilution of the 0.05 mol  $\text{dm}^{-3}$  stock solution of V(V) or V(IV) with 1.0 mol  $\text{dm}^{-3}$  HCl followed by extraction with D2EHPA; extractant (D2EHPA) concentration in the range of 0.29 - 0.86 mol  $\text{dm}^{-3}$ , was by shaking D2EHPA of the appropriate concentration with equivolume and equimolar V(V) and V(IV) solutions; mixed extractant (D2EHPA 0.86 mol  $\text{dm}^{-3}$ /TBP 0.37 - 1.1 mol  $\text{dm}^{-3}$ ), mixtures of D2EHPA and TBP, where the D2EHPA concentration was 0.86 mol  $\text{dm}^{-3}$  throughout and TBP varied between 0.37 and 1.1 mol  $\text{dm}^{-3}$  were equilibrated with a constant volume of V(V) or V(IV) aliquots; temperature was varied between 301 and 321K by heating separately the aqueous and organic portions on a hot plate to the desired temperature, measured with a thermometer, mixed and shaken with a mechanical shaker.

The amount of metal extracted was determined by spectrophotometry using ultraviolet visible spectrophotometer, Biochrom 4060 model by measuring the absorbance of the pink complex formed between vanadium and 3%  $\text{H}_2\text{O}_2$  in a 2.0 mol  $\text{dm}^{-3}$   $\text{H}_2\text{SO}_4$  medium at 450 nm, while the UV-visible spectra were recorded in the range 200-900 nm on the same instrument.

## RESULTS AND DISCUSSION

### Effect of pH

The effect of pH on the percentage V(V) and V(IV) extraction from HCl solutions with

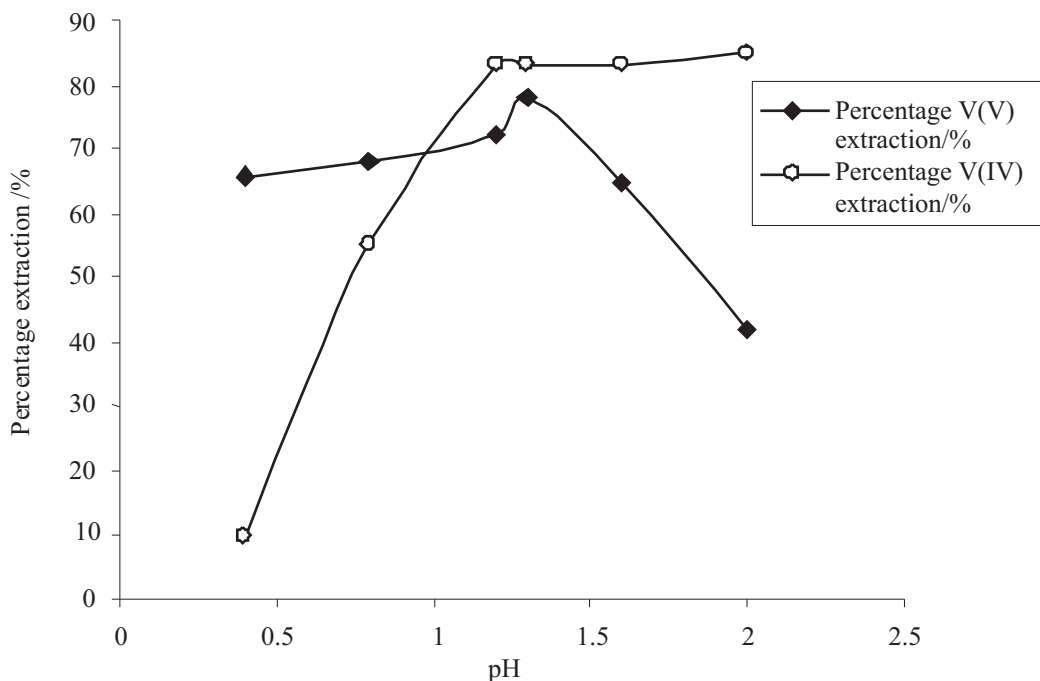


Figure 1: Effect of pH on Percentage V(V) and V( IV) Extraction from HCl Solutions with D2EHPA

$$[\text{VO}_2^+] = [\text{VO}^{2+}] = 0.05 \text{ mol dm}^{-3}; [\text{HCl}] = 0.1 \text{ mol dm}^{-3}$$

$$[\text{D2EHPA}] = 0.861 \text{ mol dm}^{-3}; \text{Temp.} = 301 \text{ K}$$

D2EHPA is presented in Figure 1.

The percentage V(V) extraction ( $E\%$ ) increased gradually to a peak of  $E\% = 78.0$  at pH 1.3, but above this pH, suffers a drastic reduction to  $E\% = 41.9$  at pH of 2. This trend has been observed by some researchers in V(V) extraction from sulphuric and nitric acid solutions with D2EHPA (Brunette *et al.*, 1979; Kurbatova and Kurbatov, 2006), which can be adduced to the possible formation of unextractable hydrolyzed species such as  $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-}$  and  $\text{H}_3\text{VO}_4$  (at about pH of 2) known to be the prominent feature of aqueous chemistry of V(V) (Greenwood and Earnshaw, 1997) and besides, it is a well understood fact that a metal extracts best below the pH where it hydrolyses. The extraction reaction of V(V) by the ionized D2EHPA dimer molecules can generally be expressed according to equation (4).



where “a” and “org” are aqueous and organic phases, respectively,  $(\text{HR})_2$  and  $\text{HR}_2$  represents the dimer and deprotonated dimer of D2EHPA in n-hexane diluent, respectively, and which is (i.e. dimer) the established state of D2EHPA at high concentration in aliphatic diluents (Brunette *et al.*, 1979).

With V(IV), an initial steep rise in percentage extraction was observed between pH 0.4 ( $E\% = 9.9$ ) and pH 1.2 ( $E\% = 83.2$ ) which remained nearly constant for the rest of the pH range (1.2-2.0) of study. This agrees closely with the optimum pH of about 1.8 observed by earlier workers in the extraction of V(IV) from  $\text{H}_2\text{SO}_4$  solutions with D2EHPA. The reaction can generally be represented by equation (5).



The higher  $E\%$  observed for V(IV) when compared to V(V) might be due to better complexation of V(IV) with D2EHPA as a result of the linear structure of V(IV) which would allow better coordination compared to  $\text{VO}_2^+$  which is angular, a factor that can impose a steric hinderance on its binding characteristics. This will be of great relevance in the separation of V(IV) from admixtures containing both ions or the prediction of extraction order among linear or angular shaped metal species.

### Effect of Initial V(V) and V(IV) Concentration

The effect of initial V(V) and V(IV) concentration on the percentage vanadium extraction is presented in Figure 2. At a moderate

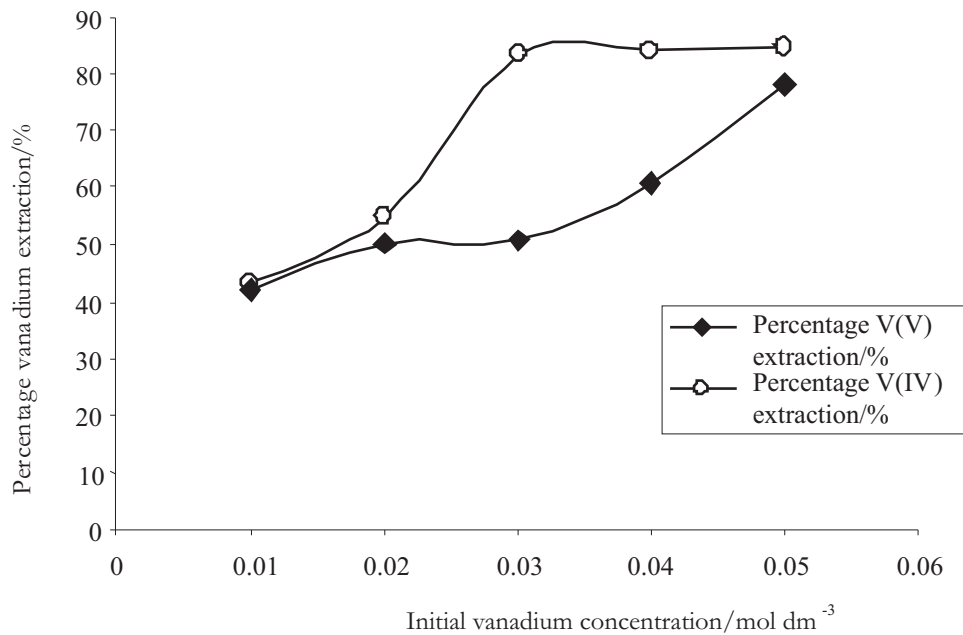


Figure 2: Effect of Initial Vanadium Concentration on Percentage V(V) and V(IV) Extraction from HCl Solutions

pH 1.3, V(V), pH 2.0, V(IV); [D2EHPA] = 0.861 mol dm<sup>-3</sup>;  
Temp. = 301 K; [HCl] = 0.1 mol dm<sup>-3</sup>

extractant concentration in the organic phase, the percentage extraction of both V(V) and V(IV) increased steadily with initial metal concentration until it reached a maximum at E% = 78.0 for V(V) and 84.8 for V(IV) at a vanadium ions concentration of 0.05 mol dm<sup>-3</sup> which agrees well with the studies of Alibrahim *et al.* (2008) but in

addition extended to higher metal loadings. The different portions on the curves infer the presence of different extractable vanadium species, however, not polynuclear.

#### Effect of D2EHPA Concentration

The effect of D2EHPA concentration on

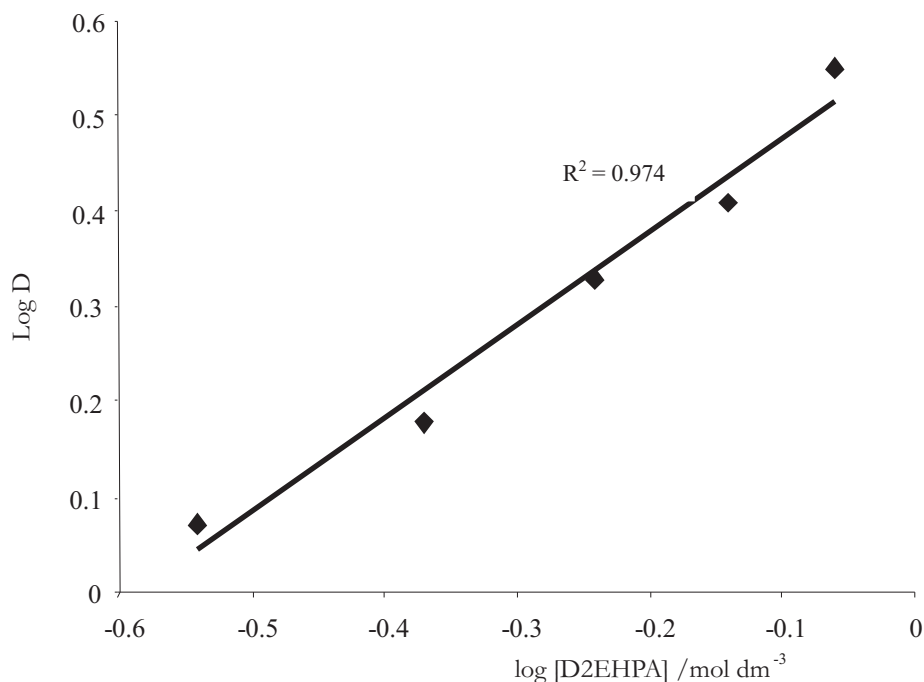


Figure 3: A Log-Log Plot of Distribution Coefficient of V(V) Extraction from HCl Solutions against D2EHPA Concentration

[VO<sub>2</sub><sup>+</sup>] = 0.05 mol dm<sup>-3</sup>; pH = 1.3; Temp. = 301 K



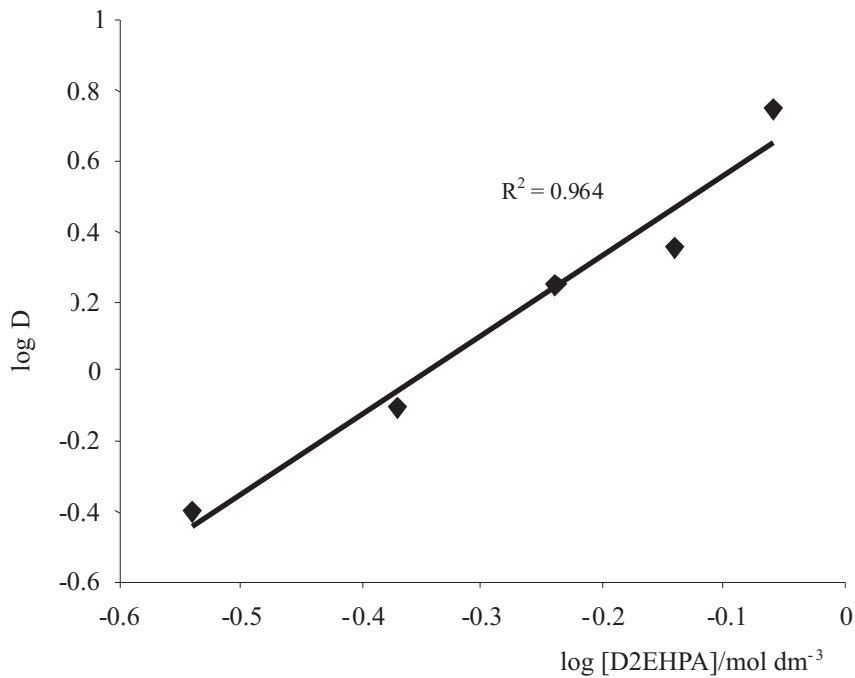


Figure 4: A Log-Log Plot of Distribution Coefficient of V(IV) Extraction from HCl Solutions against D2EHPA Concentration

$$[\text{VO}^{2+}] = 0.05 \text{ mol dm}^{-3}; \text{pH} = 2.0$$

V(V) and V(IV) extraction is illustrated in Figures 3 and 4 respectively. Both V(V) and V(IV) extractions increase with D2EHPA concentration. Vanadium (V) extraction reaches a maximum of  $\log D = 0.55$  at  $\log [\text{D2EHPA}] = -0.06 \text{ mol dm}^{-3}$  while V(IV) reaches  $\log D = 0.75$  at the same D2EHPA concentration.

If the extraction of  $\text{VO}_2^+$  by D2EHPA can generally be expressed by the equation 4.

Then,

$$K_{\text{ex}} = [\text{VO}_2 \text{HR}_2]_{\text{org}} [\text{H}^+] / [\text{VO}_2^+]_{\text{a}} [(\text{HR})_2] \quad (6)$$

$$K_{\text{ex}} = D[\text{H}^+] / [(\text{HR})_2] \quad (7)$$

Taking logarithm of both sides and keeping pH constant, we have

$$\log D = \log K_{\text{ex}} + n \log [(\text{HR})_2] \quad (8)$$

Therefore, a plot of  $\log D$  against  $\log [(\text{HR})_2]$  should yield a straight line of slope equal to 'n' and from the determination,  $n = 1.1(1)$  implying that one ionized D2EHPA dimer molecule ( $\text{HR}_2$ ) is coordinated to  $\text{VO}_2^+$ . From the intercept, the extraction equilibrium constant,  $\log K_{\text{ex}} = -0.53$  which is in agreement with the work of Brunnet *et al.* (2004) conducted in nitric acid solutions.

With V(IV), its extraction may be represented by equation 5.

Then,

$$K_{\text{ex}} = [\text{VO}(\text{HR}_2)_{n(\text{org})}] [\text{H}^+]^n / [\text{VO}^{2+}]_{\text{a}} [(\text{HR})_2]^n \quad (9)$$

The distribution coefficient, D, can be expressed by equation 10.

$$D = [\text{VO}(\text{HR}_2)_{n(\text{org})}] / [\text{VO}^{2+}]_{\text{a}} \quad (10)$$

Combining equations 9 and 10 we have,

$$\log D = \log K_{\text{ex}} + n \log [(\text{HR})_2] \quad (11)$$

Therefore, a log-log plot of D against  $[(\text{HR})_2]$  should yield a straight line of slope equal to 'n'. The slope was found equal to 2.1 (2). Therefore the number of ionized D2EHPA molecules coordinated to V(IV) is two, and from the intercept,  $\log K_{\text{ex}} = -0.5$  which is close to that observed by Biswas *et al.* (2004). in V(IV)-D2EHPA- $\text{H}_2\text{SO}_4$  system.

The  $\log K_{\text{ex}}$  values for the extraction of both V(V) and V(IV) are very low (negative) these portend to less spontaneous reactions, necessitating the need of initial vigorous agitations prior to the extractions.

The slightly higher value of  $\log K_{\text{ex}}$  of V(IV)

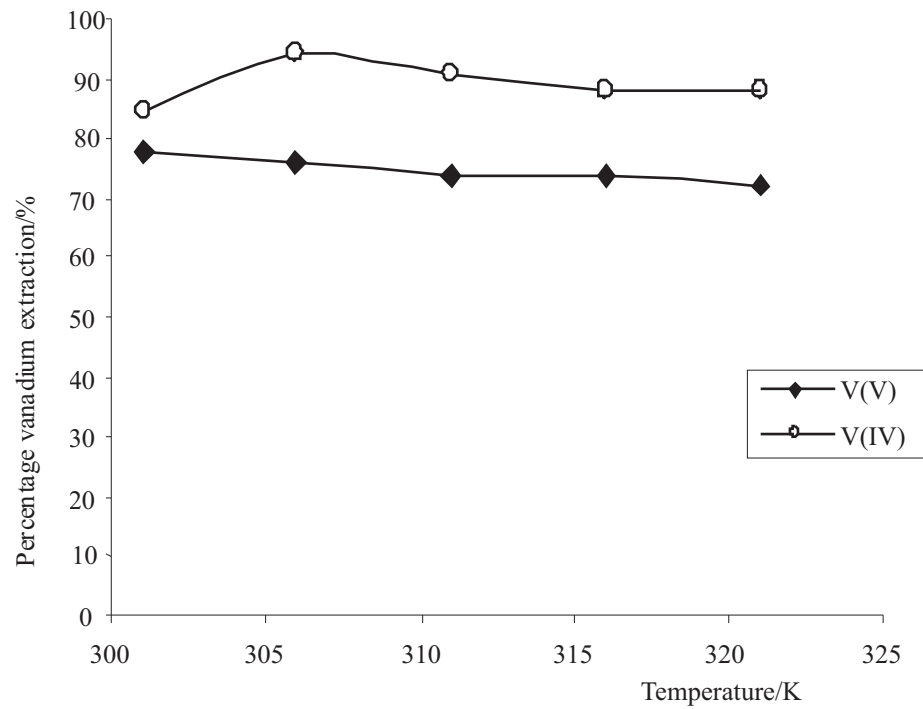


Figure 5: Effect of Temperature on Percentage V(V) and V(IV) Extraction from HCl Solutions with D2EHPA

$[\text{VO}_2^+] = [\text{VO}^{2+}] = 0.05 \text{ mol dm}^{-3}$ ;  $[\text{D2EHPA}] = 0.861 \text{ mol dm}^{-3}$ ;  
 pH 1.3, V(V); pH 2.0, V(IV)

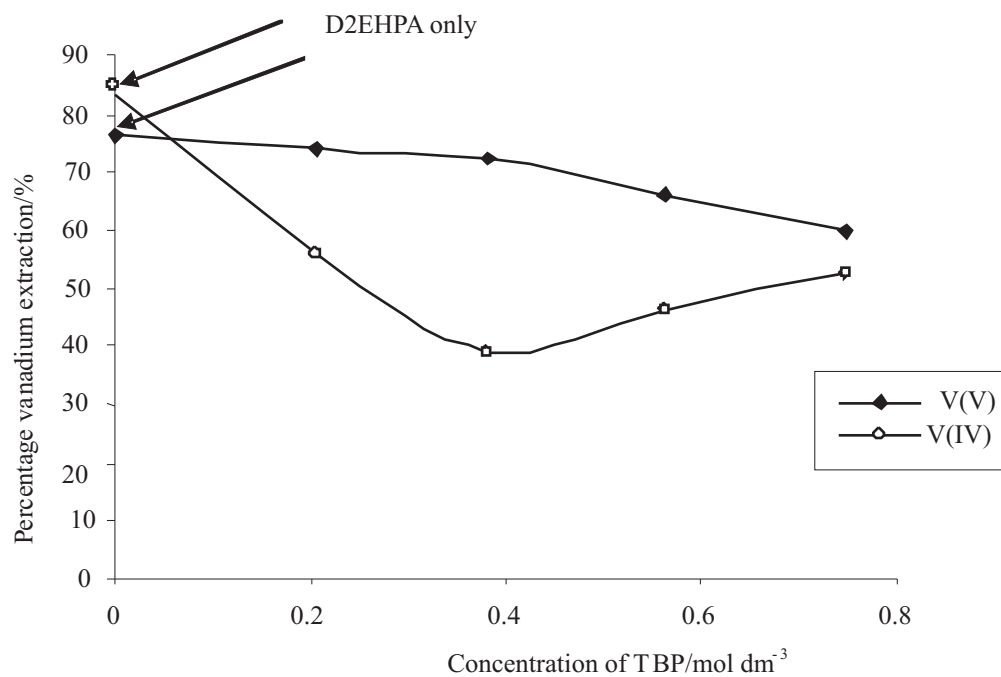


Figure 6: Effect of the Addition of TBP to D2EHPA on Percentage V(V) Extraction from HCl Solution

$[\text{D2EHPA}] = 0.861 \text{ mol dm}^{-3}$ ; pH = 1.3;  $[\text{VO}_2^+] = [\text{VO}^{2+}] = 0.05 \text{ mol dm}^{-3}$ ;  
 pH 1.3, V(V); pH 2.0, V(IV)

compared to V(V) lends credence to the observed higher percentage extraction of the former, and besides, the often encountered faster equilibration during the experiments is an added point. From the foregoing, the extraction of V(IV) by D2EHPA can be written as in equation (12).



### Effect of Temperature

The effect of temperature on percentage V(IV) extraction in the range 301-321K is shown in Figure 5.

The percentage V(V) extraction decreased with increasing temperature within the range 301-321K ( $E\% = 78.0-72.0$ ). This implies that the reaction is exothermic. With V(IV), a much higher percentage extraction was observed at temperature above ambient temperature (301K).

There was an initial increase in percentage extraction followed by a steady decrease ( $E\% = 85.0$  to  $94.2$  and further to  $91.2$ ) implying an exothermic process and probably a decrease in stability of the extracted complex at higher temperatures. In general, the extractions of both vanadium species are best at low temperatures and declined at elevated temperatures.

### Effect of the Addition of TBP to D2EHPA

The effect of the addition of TBP to D2EHPA on the percentage V(V) and V(IV) extraction is shown in Figure 6. The addition of increasing amount of TBP ( $0.37$ – $0.73$  mol dm<sup>-3</sup> i.e. 10-20% v/v) to D2EHPA ( $0.86$  mol dm<sup>-3</sup>) resulted into a decrease in the percentage extraction for both V(V) and V(IV). It is believed that the presence of TBP in the organic phase will result into association between its molecules and

Table 1: The electronic Spectra Data (cm<sup>-1</sup>) and Assignments for the Vanadium D2EHPA Complexes

Compound	$\nu/\text{cm}^{-1}$	$\epsilon/\text{M}^{-1} \text{cm}^{-1}$	Probable Assignment
V(V) complex	30,200	69	Charge transfer
V(IV) complex	29,412 14,710	71 30	Charge transfer

D2EHPA, and since TBP is less efficient than D2EHPA for V(V) and V(IV) extractions under the prevailing conditions, the interaction would have a deleterious effect on the extractions (Brunette *et al.*, 1979). The negative effect of TBP addition on extraction was more pronounced in V(IV) ( $E\%$  dropped to 40.6) probably because V(IV) naturally does not extract well with TBP as V(V), which therefore would make it feel the negative impact of added D2EHPA more. The sudden rise in percentage V(IV) extraction after added  $[\text{TBP}] \geq 0.37$  mol dm<sup>-3</sup> might be that the TBP molecules begin to solvate the extracted complex resulting in higher solubility. The addition of TBP to D2EHPA can be said to be antagonistic to the extractions of both V(V) and V(IV) in HCl solutions.

### Electronic and Infrared Spectra

The electronic spectra data for the D2EHPA complexes of V(V) and V(IV) are presented in Table 1 while the infrared spectra data for the D2EHPA ligand and complexes of V(V)

and V(IV) are presented in Table 2.

The electronic absorption spectrum for V(V) shows absorptions at  $30,200 \text{ cm}^{-1}$  with a strong intensity which has been assigned to ligand-to-metal charge transfer (LMCT) in the ultraviolet region, while the V(IV) D2EHPA complex shows absorption bands at  $29412 \text{ cm}^{-1}$  ( $=71 \text{ M}^{-1} \text{cm}^{-1}$ ) and  $14710 \text{ cm}^{-1}$  ( $=30 \text{ M}^{-1} \text{cm}^{-1}$ ) assigned to LMCT and d-d ( ${}^2\text{B}_1$ – ${}^2\text{B}_2$ ) respectively. These values are in the range observed for trigonal bipyramidal complexes ( $\text{C}_{4v}$ ) of vanadium by Sato *et al.*, (1978). Infrared spectra bands of D2EHPA were observed at  $3454$ ,  $1235$  and  $1033 \text{ cm}^{-1}$  assigned to (O-H), (P=O) and (P-O-C) vibrations. In the V(V) complex, the following changes were noticed; the (P=O) and (P-O-C) bands shift positively by  $6 \text{ cm}^{-1}$  and  $3 \text{ cm}^{-1}$  respectively. These shifts in the (P=O) and (P-O-C) bands coupled with the appearance of a new band at  $940 \text{ cm}^{-1}$  assigned to (V=O) vibration serve as evidences of coordination of the ligand through the phosphoryl end to the pervanadyl ion,  $\text{VO}_2^+$ . With



V(IV) complex, the following changes were observed; the (P=O), (P-O-C) bands shift negatively and with a decreased intensity by  $11\text{ cm}^{-1}$  and  $22\text{ cm}^{-1}$  respectively. The new band observed at  $920\text{ cm}^{-1}$  is ascribed to (V=O) vibration and which in conjunction with the recorded vibrational shifts confirm the coordination of the D2EHPA to the vanadyl ion,  $\text{VO}^{2+}$ . (Kurbatova and Kurbatov, 2006; Kurbatova *et al.* 2004)

The foregoing arguments support the formulated stoichiometries  $\text{VO}_2\text{HR}_2$  and  $\text{VO}(\text{HR}_2)_2$  for the extracted complexes of V(V) and V(IV) respectively, where  $\text{HR}_2$  represent the deprotonated dimer molecule of D2EHPA,  $[(\text{C}_{16}\text{H}_{34}\text{POO})_2\text{H}]$ , in which  $\text{R} = \text{C}_8\text{H}_{17}$ , 2-ethylhexyl.

## CONCLUSIONS

Based on the facts emanating from the present studies, it could be concluded that D2EHPA extracts V(IV) better than V(V), and furthermore, the observed high E% at high vanadium concentration employed in this work ( $5.85\text{ g L}^{-1}$ ) for both species should make the results applicable or relevant to commercial operations.

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