DEPENDENCE OF VANADIUM RECOVERY ON OXIDATION STATE IN ITS SOLVENT EXTRACTION FROM HYDROCHLORIC ACID SOLUTIONS WITH TRI N BUTYL PHOSPHATE

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ABSTRACT

The recovery of vanadium as V(V), VO_2^+ and V(IV), VO^{2+} from diluted and concentrated HCl solutions by tri-n-butyl phosphate (TBP) dissolved in n-hexane has been independently studied.

The oxidation state of the vanadium species was found to have a profound effect on the percentage vanadium extraction (E%).

At the pH range of 0.2-2.0, both V(V) and V(IV) were poorly extracted, with an optimum E% = 6.0 and 1.0 for V(V) and V(IV) respectively. However, at an optimum 6M HCl concentration, V(V) has a remarkable E% = 81.4 which was 2.0% for V(IV) and with both not much affected by temperature variation.

The extraction equilibrium constant, K_{ex}, was 1.52, and 0.02 for V(V) and V(IV) respectively.

Based on slope analysis, electronic and infrared spectra data, the organic extracts of V(V) and V(IV) complexes were formulated as $VO_2Cl(TBP)_2 \cdot 2HCl$ and $VOCl_2(H_2O)(TBP)$ respectively. The study reveals that V(V) is much better recovered than V(IV) from HCl solutions by TBP, and which might be informative in hydrometallurgical separation processes.

Keywords: Vanadium; Recovery; Oxidation State; TBP; Spectra

INTRODUCTION

The use of solvent extraction to recover economic minerals from lean ores has continued to generate waves of interest over the past few decades. Since vanadium is a component of various steels employed in machine parts and construction equipments (Greenwood and Earnshaw, 1997), the study of its extraction process deserves the attendant attraction in hydrometallurgy.

Both V(V) (cationic and anionic) and V(IV) (cationic) are extractable as neutral complexes into organic diluents but with varying quantitative extractions (Ritcey and Ashbrook, 1984). The DAPEX process (Agers *et al.*, 1962) extracts V(V) as VO_2^+, and V(IV) as VO^{2+} with di (2- ethylhexyl) phosphoric acid (D2EHPA) and with kinetics of the former in D2EHPA n-hexane thoroughly investigated (Ipinmoroti and Hughes, 1990). Some workers (Thomas *et al.*, 2003) studied the extraction of V(V) from HCl solutions with tri-n-butyl phosphate (TBP) in kerosene diluent and reported the extraction constants and isotherms. The extraction of complexes of anionic vanadium (VO_3) with tri-n-octylmethylammonium chloride (TOMAC) has been extensively investigated (Hirai and Kosamawa, 1990; Hirai *et a.l,* 1993).

Other researchers (Nasu *et al.,* 1999) have reported a comparative study of the relative extraction of iron as Fe (II) and Fe (III) from thiocyanate solutions but little effort has hitherto been made to address the relative extractions of V(V) and V(IV) under the same extraction conditions such as acid medium, extractant and diluent.

Since the relative quantitative extractions of V(V) and V(IV) from HCl solutions by TBP in n-hexane has not been much studied, it is hence thought worthwhile initiating independent studies on the species with a view of exploiting it later for a large-scale vanadium processing or separation processes where vanadium is a contaminant. However, the choice of the vanadium species would depend among other things on whether the vanadium is to be recovered from the acid leach or retained. In the present work, the extraction of V(V) and V(IV) from HCl solutions with TBP in n-hexane highlighting the dependence of vanadium extraction on the oxidation state is presented.

MATERIALS AND METHODS

The chemicals, NH_4VO_3, HCl, KCl, ascorbic acid, n-hexane, TBP, D2EHPA were obtained from the

British Drug House Limited (BDH). All the chemicals were of analytical grade except TBP and D2EHPA and were used without further purification.

Preparation of 0.05 M VO_2^+ Stock Solutions

Ammonium metavanadate (5.85 g, 0.05 mol) was dissolved in various concentrations of hydrochloric acid (1.0-6.0 M), followed by the addition of KCl (7.48 g, 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.

Preparation of 0.05 M VO^{2+} Stock Solutions

To the stock solution of V(V) prepared above was added ascorbic acid (19.11 g, 0.11 mol) with the solution turning to blue. The amount of vanadium (IV) present was determined (Ipinmoroti, 1981) by titrating with 0.02 M $KMnO_4$ at 60^0C. The reduction was complete in all the solutions.

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 mixed extractants were equilibrated separately with 15 cm^3 portions of V(V) and V(IV) solutions as the case may be at the appropriate pH and temperature in a separating funnel, swirled manually and later on a mechanical shaker operated at 120 rpm for 2 minutes (found optimum for equilibration). The

layers were allowed to separate out, 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 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% H_2O_2 in a 2.0 M H_2SO_4 medium at 450 nm. The infrared and electronic spectra were recorded on an infrared spectrophotometer, BUCK SCIENTIFIC M O D E L and ultraviolet-visible spectrophotometer respectively.

RESULTS

Figure 1 shows the effect of pH on percentage V(V) and V(IV) extraction. Both oxidation states are lowly extracted between pH of 0.2 and 2.0. Studies have been limited to this range to avoid hydrolysis for which the species are known (Sato, 1979). V(V) has higher percentage extraction (E% = 6.0) at a pH of 0.2 and subsequently decreased to E% = 4.03 at a pH of 0.4 which later remained constant thoughout, while for vanadium (IV) the percentage extraction was constant (E% = 1.0) throughout the pH range of study.

Fig. 2 shows the effect of increase in HCl concentration on the percentage V(V) and V(IV) extraction. The percentage V(V) extraction varies
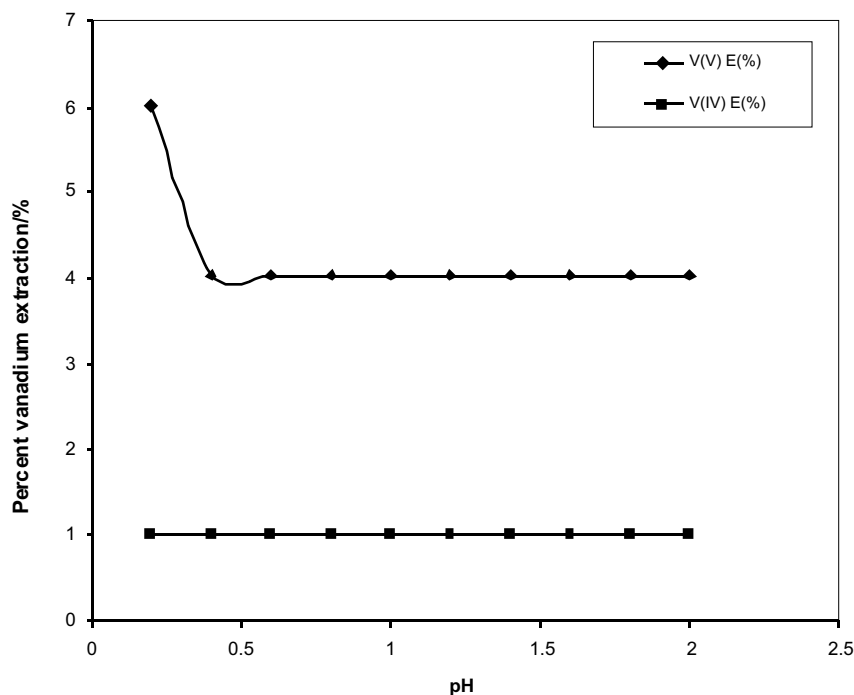

FIg.1: Effect of pH on Percentage V(V) and V(IV) Extraction from HCl solution
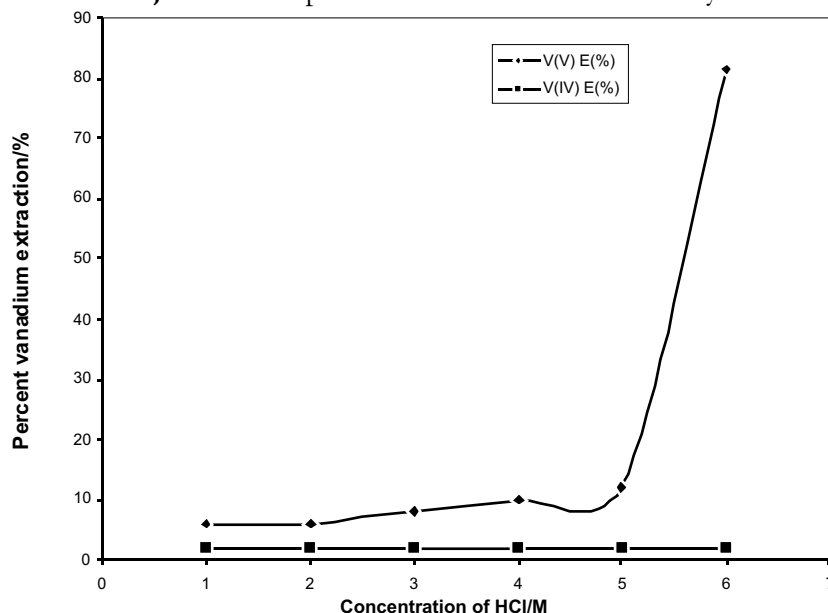[V(V)] = 0.05 M; [V (IV)] = 0.05 M; [TBP] = 1.098 M; [KCl] = 0.1 M

FIg.2: Effect HCI Concentration on Percentage V(V) and V(IV) Extraction
[V(V)] ; [V(IV)] 0.05 M; [TBP] = 1.098 M; [KCI] = 0.1 M

Table 1: Effect of Initial Vanadium (V) and (IV) Concentration on the Distribution
Co-efficient and Percentage Extraction of Vanadium (V) and (IV)
[TBP] = 1.098M (30% v/v); [KCl] = 0.1M, [HCl] = 6M

Conc (M)	V(V)		V(IV)	
	D	E (%)	D	E (%)
0.01	3.348	77.00	0.010	1.00
0.02	3.651	78.50	0.010	1.00
0.03	3.615	78.33	0.010	1.00
0.04	4.000	80.00	0.010	1.00
0.05	4.376	81.40	0.01	1.00

from 6.0% for 1.0 M HCl to 80.0% for 6.0 M HCl. In the case of V(IV), increase in HCl concentration had no effect on the percentage vanadium extraction as it remained constant at 2.0% throughout the concentration range and further works were therefore done at 6.0 M HCl.

Table 1 shows the effect of initial V(V) and V(IV) concentrations on percentage extraction. The percentage V(V) and V(IV) extractions were nearly constant when the initial V(V) and V(IV) concentrations were varied between 0.01 and 0.05 M. However, the concentration of 0.05 M where E% = 81.4 for V(V) and E% = 1.0 for V(IV) was used throughout the work.

The effect of TBP concentration on the percentage V(V) and V(IV) extraction is presented in Figure 3. The percentage vanadium (V) extraction reached a peak of E% = 81.4 at 1.1 M (30%v/v) TBP concentration and subsequently decreased, while the percentage V(IV) extraction (Figure 3) was nearly constant (E% = 1.0-1.96) when the TBP concentration was varied in the range 0.37-1.47 M.
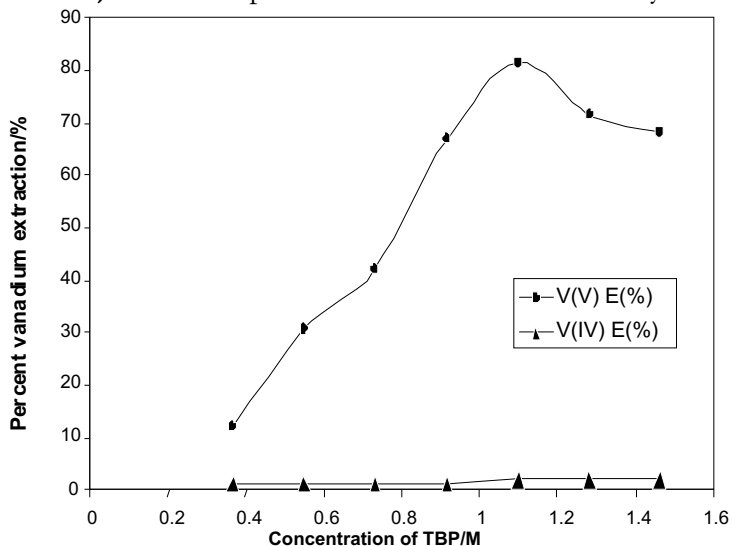
FIG. 3: Effect of TBP Concentration on Percentage V(V) and V(IV) Extraction from HCl solution [V(V)] = 0.05 M; [V(IV)] = 0.05 M ; [KCl] = 0.1 M
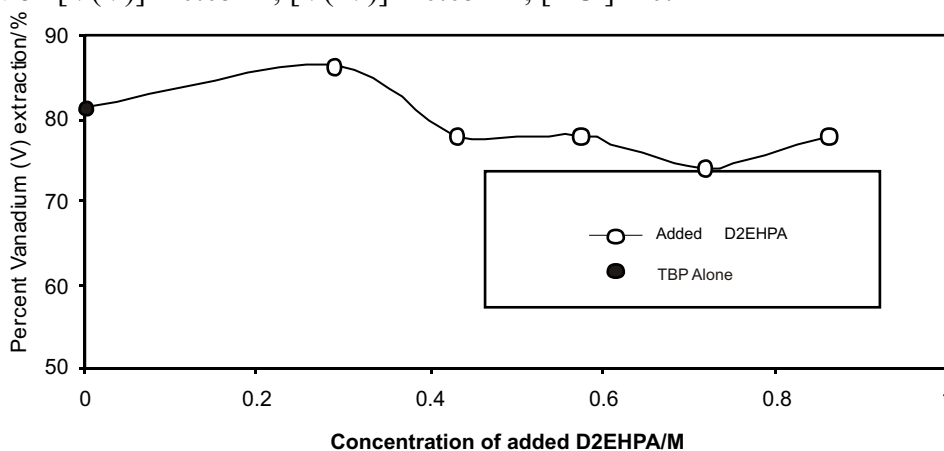

Fig 4: Effect of the Addition of D2EHPA to TBP on Percentage V(V) Extraction from HCl Solution [V(V)] =0.05 M; [HCI] = 6.0 M; [TBP] = 1.098 M

Table 2: Effect of Variation in Temperature on Percentage V(V) and V(IV) Extraction from 6.0 M HCl Solution with TBP. [V(V)], [V(IV)] = 0.05 M; [KCl] = 0.1 M; [TBP] = 1.098 M

Temp. (K)	V(V)		V(IV)	
	D	E (%)	D	E (%)
301	4.376	81.40	0.01	1.00
306	4.556	82.00	0.01	1.00
311	4.556	82.00	0.01	1.00
316	4.556	82.00	0.02	1.96
321	4.556	82.00	0.110	9.90

Table 3: The Electronic Spectra data (cm^{-1}) and Assignments for the Complexes

Compound	υ/cm^{-1}	ε/M^{-1}cm^{-1}	Probable Assignment
V(V) COMPLEX	30303	68	Charge transfer
	23529	22	
V(IV) COMPLEX	31250	1250	Charge transfer
	15152	1100	d – d allowed transition

Table 4: The Infrared Spectra Data (cm^{-1}) and Assignments for TBP and Complexes

Compound	Band (cm^{-1})	Assignments
TBP	1277vs	υ(P = O)
	1028vs	υ(P – O – C)
V(V) COMPLEX	2882w	υ(H - Cl)
	1270s	υ(P = O)
	1034vs	υ(P – O – C)
	980w	υ (V-Cl)
	960w	υ(V = O)
V(IV) COMPLEX	1269s	υ(P = O)
	1027vs	υ(P – O– C)
	980w	υ (V-Cl)
	857w	υ(V = O)

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

The effect of the addition of D2EHPA (0.29 0.86 M) to 1.1 M TBP is presented in Figure 4.

The effect of temperature on the percentage vanadium (V) and IV) extraction was investigated in the range 301-321 K and presented in Table 2.

It was observed that increase in temperature had no significant effect on V(V) extraction as the percentage extraction was nearly constant throughout; but in the case of V(IV) a slight increase in percentage extraction was observed (E % = 1.0 at 301 K and E% = 9.9 at 321 K).

The electronic spectra for TBP extracts of V(V) and V(IV) are shown in Table 3 while the i.r. spectra of the free TBP ligand and vanadium TBP extracts of V(V) are shown in Table 4.

DISCUSSION OF RESULTS
Effect of pH

The poor extraction of both vanadium (V) and (IV) at the pH range 0.2 - 2.0 could be explained on the basis of low concentration of H^+ which could have helped in removing coordinated water molecules from the complex as solvated ion needed for high extractability.

Effect of HCl Concentration

The observed high percentage V(V) extraction compared with V(IV), with increased HCl concentration (Figure 2) might be due to the fact that VO_2^+ is easily neutralized by the Cl^- counter-ion, more available at high acid concentrations or forms a more stable complex than VO^{2+} and this trend we have found agrees quite well with previous works done in CCl_4 (Tedesco and Rumi, 1978) and benzene (Sato, 1979) diluents with TBP as extractant. This position is further strengthened by the fact that no appreciable change in percentage extraction of V(V) and V(IV) was observed with pH variation.

Effect of TBP Concentration

With V (V), the initial increase in E% with increase in TBP concentration, was due to availability of more extractant molecules needed for solvation of the neutral complex thereby enhancing higher solubility and extractability in the organic phase (Ritcey and Ashbrook, 1984) while the decrease in E% at higher TBP concentration might be due to a hindrance in the

diffusion of the molecules of the solvated complex through the interfacial zone as a result of steric factor.

Since TBP extracts metals by solvation, the number of solvated TBP molecules, x, depends among many other things, on the coordination number of central atom, and the nature of the diluent (Ritcey and Ashbrook, 1984; Sato *et al.,* 1980). If the extraction of VO_2^+ into TBP can be expressed by equation 1,

$$VO_{2^{+}(aq)} + Cl_{(aq)}^- + xTBP_{(org)} = VO_2Cl. XTBP_{(org)} \quad (1)$$
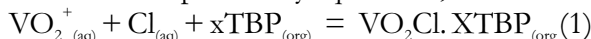
Then the equilibrium constant is given by

$$K_{ex} = \frac{[VO_2Cl. xTBP]_{org}}{[VO_2^+]_{aq}[Cl]_{aq}[TBP]^x_{org}} \quad (2)$$

$$K_{ex} = \frac{D}{[Cl]_{aq}[TBP]^x_{org}} \quad (3)$$

Where 'aq' and 'org' represent aqueous and organic phases respectively, and the distribution coefficient, D is given by the ratio of the analytical concentration of VO_2^+ in the organic and aqueous phases.

At constant [Cl], Equation (3) reduces to:

$$K_{ex} = \frac{D}{[TBP]^x_{org}} \quad (4)$$

$$i.e \quad D = K_{ex}[TBP]^x_{org} \quad (5)$$

hence,

$$\log D = x \log [TBP]_{org} + \log K_{ex} \quad (6)$$

It is therefore expected that a log - log plot of D against TBP concentration as shown in Figure 5, should yield a straight line with the slope equal to 'x', the number of TBP molecules (Forrest, 1969) solvated during VO_2^+ extraction. From the slope, x = 2.3, thus suggesting two as the possible solvation number for VO_2^+ extraction from acid-chloride medium into n-hexane and was found to agree with previous work done in kerosene
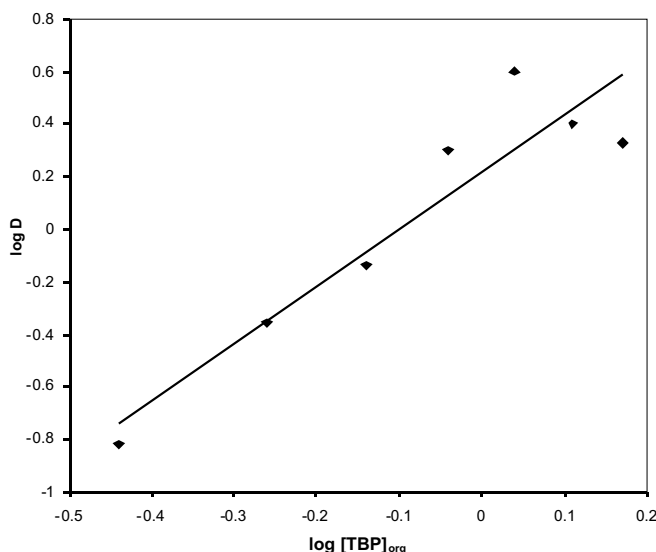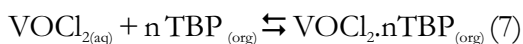
FIG 5: A Log-log plot of Distribution Coefficient Against TBP Concentration for V (V)

(Thomas *et al.,* 2003).

The value of $K_{ex} = 1.52$

For V(IV) extraction (Fig. 3) the percentage vanadium extraction varies from E% = 1.0 at 0.37 M (10% v/v) TBP, to 1.96 at 1.47 M (40% v/v) TBP and the relevant scheme for extraction would be according to Equation 7.

$$VOCl_{2(aq)} + n\,TBP_{(org)} \leftrightarrows VOCl_2.nTBP_{(org)} \quad (7)$$

where 'n' is the number of solvated TBP molecules.

Like the case of V(V) above, Equation 6 would express the distribution coefficient of V(IV).

Therefore, a log log plot of D against TBP concentration (Fig. 6) would yield a slope equal to 'n'

The value of 'n' was found to be 0.86 suggesting that one TBP molecule is solvated to a vanadyl ion.

The value of $K_{ex} = 0.02$

The values of K_{ex} for V(V) and V(IV) differs almost by a factor of 100 indicating that the extraction of V(V) is more favoured than V(IV).

Effect of the addition of D2EHPA to 1.098M TBP on V(V) Extraction.

The addition of D2EHPA to 1.1 M TBP (Figure 4) produced an initial slight increase from E% = 81.4 to E% = 86.0 perhaps due to a solvating behaviour of D2EHPA, but further
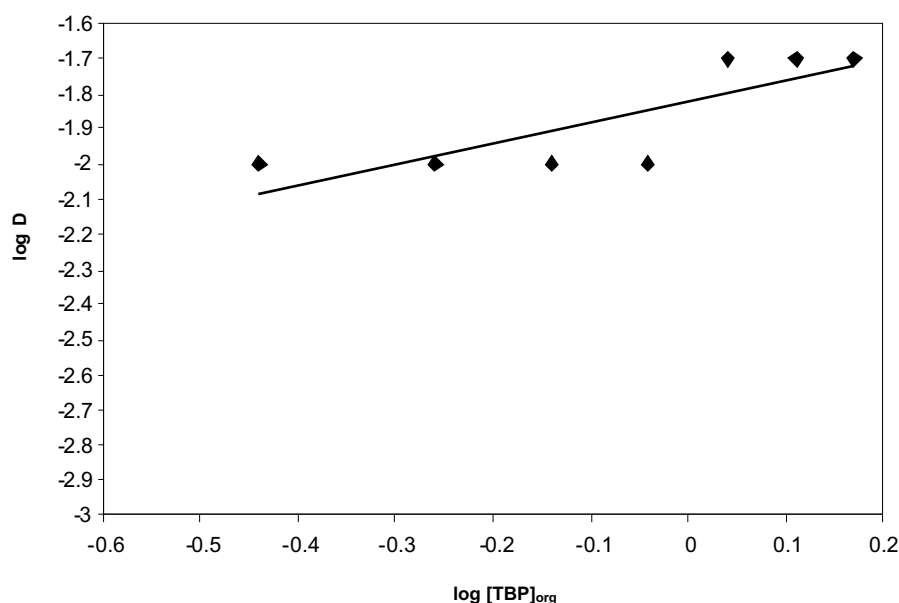
FIG. 6: A Log-log plot of Distribution Coefficient Against TBP Concentration for V (IV)

additions translated to a decrease from E% = 81.4 to E% = 74.0 which might be ascribed to increased interaction between the TBP and D2EHPA via hydrogen bonding (Brunette *et al.,* 1979). The addition of D2EHPA could therefore be viewed as having an unappreciable effect on V(V) extraction. Since there was insignificant extraction of V(IV) by TBP, no attempt was made to further investigate the effect of the addition of D2EHPA.

Effect of Temperature

The unappreciable increase in percentage extraction when the temperature was increased (Table 2) might point to an overall mass transfer of vanadium being dependent on a diffusion-controlled process, as increase in temperature is supposed to increase the vanadium extraction if chemically controlled, moreso that it is not exothermic.

Electronic and Infrared Spectra

V(V) shows absorptions (Table 3) at 30303 cm^{-1} (325 nm) and 23529 cm^{-1} (425 nm) ascribed to ligand-metal charge transfer (LMCT) since V(V) has a d$^{\circ}$ electronic configuration.

V(IV) shows weak absorptions (Table 3) at 31250 cm^{-1} (320 nm) and 15152 (660 nm) ascribed to charge transfer and d-d allowed transition respectively and both with surprisingly high molar extinction coefficient arising from a departure from octahedral geometry to a C$_{4v}$ symmetry (Sato, 1979 & Ojo, 2003).

The bands (Table 4) at 1277 and 1028 cm^{-1} assigned to (P = O) and (P-O-C) vibrations respectively, shift to 1270 and 1034 cm^{-1} in the complex, indicating the involvement of the phosphoryl group in coordination. The new but weak bands at 960 and 980 cm^{-1} assigned to (V = 0) and (V Cl) respectively, conclusively confirm the coordination of vanadium to TBP. And finally the band observed at 2882 cm^{-1} absent in the

ligand has been assigned to (H-Cl) vibration (Barrow, 1983), this band is absent in V(IV).

In the V(IV) complex, the (P = O), (P O - C) and (V = O) bands are observed at 1269, 1027 and 857 cm^{-1} respectively, and are similar to that of previous workers(Zhang *et al.,* 1996; Remya & Reddy, 2004). The (V = O) for V(IV) was much lower than V(V) probably due to the later exhibiting a more hard acid effect on the vanadyl bond. The possibility of the extracted [VOCl$_2$(H$_2$O)TBP] complex hydrolyzing to form species such as [VO(OH)Cl.TBP] and [VO(OH)Cl.TBP]$_2$ could not be ruled out as expressed by Equation 8.

$$VO^{2+} + H_2O \leftrightharpoons VO(OH)^+ + H^+ \qquad (8)$$
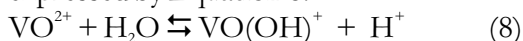
where the hydrolysis constant of 10^{-6} has been established (Sato, 1979) even though a magnetic moment data might be needed to confirm a dimerised structure.

From the foregoing, the extracted complexes of V(V) and V(IV) have been formulated as [VO$_2$Cl(TBP)$_2$].2HCl and [VOCl$_2$TBP(H$_2$O)] respectively, with the following proposed structures (Figs. 7 and 8):

CONCLUSIONS

It could be concluded from the present study that if vanadium is to be recovered from hydrochloric acid leach it would fair better if processed as V(V), VO$_2^+$ than V(IV), VO^{2+}, but if it is to be retained in the acid leach during
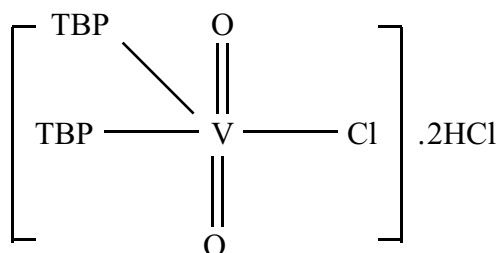
Figure 7: The Proposed Structure of V (V) TBP Complex, [VO$_2$Cl (TBP)$_2$].2HCl
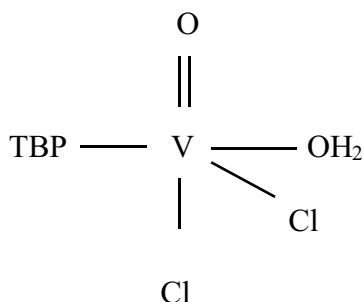
Figure 8: The Proposed Structure of V(IV) TBP Complex, [VOCl$_2$TBP(H$_2$O)]

separation from other metals, then V(IV), VO^{2+} is the viable alternative.

REFERENCES

Agers, D.W., Drobnick, J.L and Lewis, C.J. 1962. The *recovery of vanadium from acidic solutions by liquid ion exchange.* A paper presented at the Annual Meeting of the American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, 18-22 February, pp 1-21.

Barrow, G.M. 1983. *Physical Chemistry*, 4th edition, Japan, McGraw-Hill, 454pp.

Brunette, J.P., Rastegar, F. and Leroy, M.J.F. 1979. Solvent extraction of vanadium (V) by di(2-ethylhexyl)phosphoric acid from nitric acid solutions, *J. Inorg. Nucl. Chem.* 41: 735 -737

Forest, V.M.P., Scorgill, D. & Spickernell, D.R. 1969. Extraction of zinc & cadmium by TBP from aqueous chloride solution. *J. Inorg. Nucl. Chem.* 31: 187-197.

Greenwood, N.N. and Earnshaw, A. 1997. *Chemistry of the Elements*, 2nd edition, Pergamon Press Plc., England, 976 pp

Hirai, T. and Kosamawa, I. 1990. Separation and Purification of Vanadium & Molybdenum by solvent extraction followed by reductive stripping, *J. Chem. Eng. Japan* 23 (2): 208 213.

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

Ipinmoroti, K.O. and Hughes, M.A. 1990. The mechanism of vanadium extraction in a chemical kinetic controlled regime, *Hydrometallurgy* 24: 255-262.

Ipinmoroti, K.O. 1981. The Kinetics of solvent extraction of vanadium (IV) by di (2-ethyl hexyl) phosphoric acid. Ph.D. Thesis, University of Bradford, England.

Nasu, A., Takagi, H., Ohmiya, Y and Sekine, T. 1999. Solvent Extraction of Iron (II) and iron (III) as Anionic Thiocyanate Complexes with Tetrabutylammonium ions in chloroform, *Analytical Sciences*, vol

15, 177 180.

Ojo, J. O. 2003. Studies of the polynuclear 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.

Remya, P. N. and Reddy, M. L. 2004. Solvent extraction separation of titanium (IV), vanadium (V) and iron (III) from simulated waste chloride liquors of titanium minerals processing industry by the trialkylphosphine oxide Cyanex 923. *J. Chem. Technol. Biotech.* 79 (7): 734-741.

Ritcey, G.M. & Ashbrook, A.W. 1984. *Solvent extraction, Principles and applications to process metallurgy,* Part II, 2nd edition, Netherlands, Elsever Science Pub. Comp., 87pp.

Sato, T. 1979. The extraction of vanadium (IV) from hydrochloric acid solutions, by TOPO and TBP, *J. Inorg Nucl. Chem.* 41: 1605 1606.

Sato, T., Ikoma, S. & Nakamura, T. 1980. Solvent extraction of vanadium (IV) from hydrochloric acid solution by neutral organophosphorus compounds. *Hydrometallurgy* 6: 13-23.

Tedesco, P.H and Rumi, V.B. 1978. Vanadium (V) extraction by tri-n-butyl phosphate from hydrochloric acid solutions. *J. Inorg. Nucl. Chem.* 42: 269-272.

Thomas, J., Surender, G.D. and Reddy, M.L.P. 2003. Solvent Extraction Separation of Vanadium (V) from Multimetal Chloride Solutions using Tributylphosphate. *Separation Science and Technology* 38 (15): 3761 3774.

Zhang, P., Inove, K. and Yoshizuka, K. 1996. Solvent extraction of V(IV) from sulphuric acid solutions by bis (2,4,4-trimethylpentyl) phosphinic acid in exxsol D80. *J. Chem. Eng. Japan* 29 (1): 82 87.

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Tables of Contents: June Edition 2011; Vol. 13, No. 1