



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Solvent Extraction of Vanadium from Nigerian Bitumen Using Tri-Butylphosphate

I.I. Oguntimehin and K.O. Ipinmoroti

Department of Chemistry, School of Sciences, P.M.B. 704,
Federal University of Technology, Akure, Nigeria

Abstract: The equilibrium extraction of vanadium (V) from bitumen in Nigeria was carried out with Tributyl Phosphate (TBP) in nitric acid medium in pH range of 1.00-3.50. The extraction concentration was in the range 15-60% TBP in n-hexane and in temperature range of 27 to 50°C. The initial aqueous vanadium (V) concentration varied between 1×10^{-4} and 1×10^{-3} M. The extraction of the vanadium was most favorable at pH 2.8, 41.5°C ($\approx 315\text{K}$) and 7.8×10^{-4} M concentration of aqueous vanadium. However, increased concentration of the extractant beyond 40% did not favour the extraction of vanadium. The bitumen samples from Agbabu and Igbokoda analyzed contained $44.64 \pm 1.8 \times 10^{-1}$ and $31.58 \pm 2.3 \times 10^{-1}$ mg kg⁻¹ of vanadium, respectively.

Key words: Nigeria bitumen deposit, distribution coefficient, vanadium species, tri-butyl phosphate, spectrophotometric analysis, economic viability

INTRODUCTION

Bitumen is a naturally occurring, complex viscous mixture of hydrocarbons. It is the heaviest, thickest form of petroleum (Historica, 2007), in its natural state is not recoverable like conventional petroleum through wells but may be refined into petroleum products such as gasoline, kerosene, or gas oil without first being upgraded to crude oil. On the average, bitumen is composed of: carbon-83.2%, hydrogen-10.4%, oxygen-0.94% nitrogen-0.36%, sulphur-4.8%, others methane, hydrogen sulphide, traces of nickel, iron and vanadium (0.3%) Anonymous (2003).

The Nigerian bitumen belt is on the onshore areas of the southwestern Nigeria Eastern Dahomey (Benin) Basin. The probable reserve of bitumen and heavy oil in the entire Nigerian belt is approximately 120×4 km with an estimated 30-40 billion barrels in reserve (Adegoke and Ibe, 1982; Ekweozor and Nwachuku, 1989). Nigerian bitumen possesses relatively high amount of naphthenes, aromatics and asphaltenes that are similar to the conventional oil. This makes the Nigerian bitumen a very useful alternative source of petroleum hydrocarbon and a potential feedstock for petrol-chemical industries (Adegoke *et al.*, 1991).

Trace elements such as transition metals (V, Ni, Cu and As) get into bitumen in form of porphyrin complexes at its early stages of formation and the concentrations of

these elements as well as their relationships to one another are useful in generating information on the origin of its formation as well as oil-to-oil and oil-to-source rock correlation analyses (Adebiyi *et al.*, 2006).

Vanadium is present in petroleum and bitumen in the form of metalloporphyrin chelates, or mixed tetradentate complex of transition metals (Todorovic, 1987). The assessment of vanadium content of bitumen is very important from exploration, refining and eco-toxicological perspectives. V traces in refining process are capable of causing corrosion of columns or poison catalysts used during refining (Oluwole *et al.*, 1993).

Many methods had been reported for extraction and quantifying of vanadium in Bitumen (Adebiyi *et al.*, 2006), in this study, the solvent extraction using tri-butyl phosphate and spectrophotometric determination of vanadium was used. The spectrophotometric determination of the vanadium was carried out after its extraction with tri-butyl phosphate/hexane in an acidic medium. The easy availability of the instrument used in this work made the method suitable.

This work was designed in identification with the enormous deposit of Bitumen in South-west, Nigeria and aimed at estimating the amount of vanadium that can be obtained from her bitumen at Agbabu and Igbokoda in Ondo state, Nigeria (Fig. 1). Probably, we may be able to define the economy and industrial applicability of the extraction process.

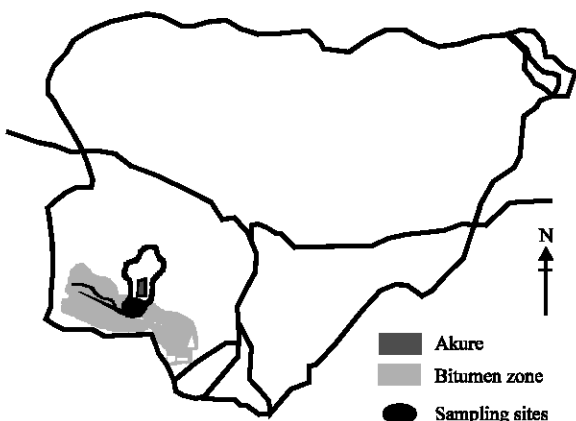


Fig. 1: Map of Nigeria showing the Bitumen belt (zone) and the sampling sites in Ondo state (capital: Akure)

MATERIALS AND METHODS

Tributyl phosphate (TBP) was obtained from the East Angela Chemicals, concentrated ammonia solution from Paul Hill Ltd., n-Hexane from BDH Chemicals and Ammonium metavanadate from May and Baker. Five Bitumen samples each from locations tagged S₁ and S₂ were collected from Agbabu and Igbokoda, respectively both in Ode-Irele Local Government Area of Ondo State (Fig. 1). This study was first carried out in Akure in the year 1997 but revised in 2004. Final samples were collected on March 5, 2004.

Kinetics studies of VO₂⁺ extraction using TBP: A particular metal may be extracted under various experimental conditions, some examined for the equilibrium studies of VO₂⁺ extraction are; variation of VO₂⁺ concentration in the aqueous phase, variation in TBP concentration in the organic phase, variation in the pH of the aqueous phase and variation in the temperature of extraction.

1 × 10⁻⁴ M NH₄VO₃ was prepared and 25 cm³ each pipetted into ten different 50 cm³ beakers. Their pH values were varied between 1.00 and 3.50 at 24°C using 1M NH₃ or 1 M HNO₃ solutions. These solutions were then allowed to equilibrate on shaking with 40% TBP in hexane in a separating funnel. The concentration of the vanadium in the aqueous medium was then determined spectrophotometrically at 450 nm. The difference between final concentration of vanadium and the initial is a measure of the amount transferred to the organic phase (Fig. 2).

The temperature of the extraction was varied between 300 and 323 K. Using 1 × 10⁻⁴, 2.5 × 10⁻⁴, 5 × 10⁻⁴, 7.5 × 10⁻⁴

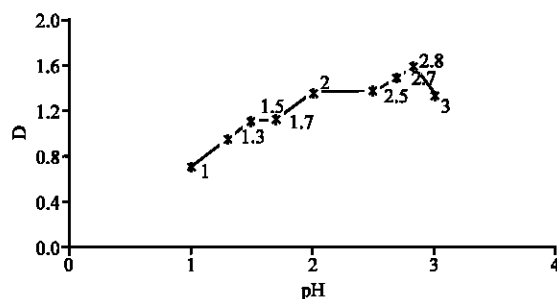


Fig. 2: Effects of aqueous vanadium (VO₂⁺) concentration on extraction with TBP

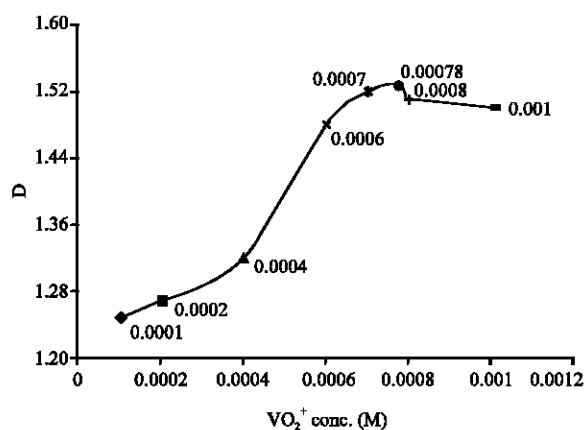


Fig. 3: Effects of aqueous VO₂⁺ concentration on Vanadium (V) extraction by TBP/Hexane

and 1 × 10⁻⁵ M, the temperature was adjusted to 297 K and the pH kept at 1.73. The various temperatures were obtained by gently warming 50 cm³ of the standard solutions in hot water bath thermostated to the desired temperature and keeping other variables constant. A graph of distribution coefficient (D) against temperature of extraction of VO₂⁺ was also obtained (Fig. 3).

The percentage of TBP in n-hexane were varied as 5, 10, 15, 20, 25 and 40%.

The bitumen was treated with concentrated sulphuric acid and the mixture reduced to acid free coke and dry ashed at 600°C in a muffle furnace. The inorganic sulphated ash with mixed acids was heated on a hot plate with subsequent addition of distilled water to put metals into solutions.

Extraction and determination of vanadium in bitumen: A 25 cm³ filtered solution containing the vanadium (V) was taken into a clean pretreated 50 cm³ beaker; 5 cm³ of 3% H₂O₂ were added. The absorbance of the red solution was measured using Camspec M201 u/v visible spectrophotometer at 450 nm.

Statistical analysis of result was performed with Microsoft Excel. Results are mean of five determinations (standard error of mean).

RESULTS

Effects of pH variation on VO_2^+ extraction with TBP: Percentage extraction of vanadium increased with pH to a maximum at pH of 2.8 at a percentage extraction of 60.47%. Beyond this pH the percentage vanadium extraction decreased rapidly (Fig. 2).

An increased initial aqueous vanadium concentration did not correspondingly favour higher degrees of vanadium extraction. Figure 3 shows that at a concentration of 1.0×10^{-4} M VO_2^+ a distribution coefficient (D) of 1.25 and 48.40% extraction into TBP. But at much higher concentration of 7.8×10^{-3} M VO_2^+ ; a higher distribution coefficient of 1.53 and 60.49% extractions into TBP were obtained. Beyond this point, higher increase in VO_2^+ concentration does not have an increase effect on the % E or D even at 1.0×10^{-4} M VO_2^3 concentration.

Effects of temperature on vanadium extraction with TBP: The temperature was varied between 300 and 320 K. There is a sharp increase in percentage extraction into TBP to a point of about 315 K (Fig. 4). The additional increase in temperature, beyond this point, only favours a decrease in the percentage extract of Vanadium.

Effects of TBP concentration on vanadium extraction with TBP: In this study, the quantitative amount of vanadium extracted did not increase with extractant concentration. The % extraction increased initially between 5-25%, then tends towards stability 25-40%, later it regressed sharply between 40-60%. There was a decrease in extraction at higher concentration of TBP (Fig. 5).

Extraction of vanadium from the bitumen samples: The samples from sites S_1 and S_2 were analyzed for vanadium, the samples contained on average of $44.64 \pm 1.8 \times 10^{-1}$ and $31.58 \pm 2.3 \times 10^{-1}$ mg kg^{-1} vanadium, respectively. Equilibration contact of the sample solutions with solvents revealed that only 23% of S_1 and 22.6% of S_2 could be extracted into TBP/hexane medium, from the aqueous medium in one contact, Moreover, further analysis with continuous extraction using the same aqueous solution thrice showed that the total percentage of extract into the TBP/hexane medium was 32%.

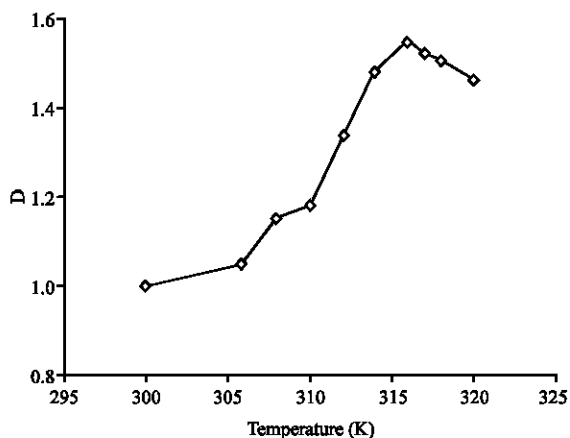


Fig. 4: Variation of D with temperature of extraction

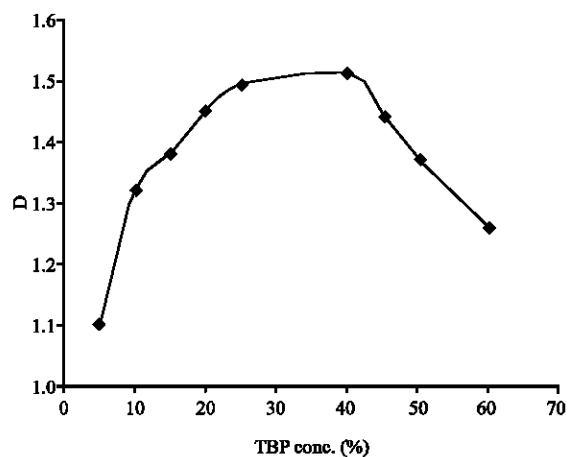


Fig. 5: A plot of variation of D with TBP concentration

DISCUSSION

The dependence of vanadium on pH (Fig. 2) can be attributed to the existence of several species of vanadium in the aqueous medium at different pH (Ritcey and Ashbrook, 1984). In very alkaline solutions (pH <13), simple vanadate anions are present; while in strong acid solutions the predominant species is the dioxovanadium (V) cation (VO_2^+). The increase in % extraction from pH 1.00 to 2.8 might be due to the presence of more (VO_2^+) cations in the solution but beyond pH 2.8 more of the tri and tetravanadate species may be present in solution and hence, the percent extraction of VO_2^+ decreases (Fig. 2). It is possible that polyvanadate anions such as $(\text{V}_{10}\text{O}_{28})^{-6}$, $(\text{HV}_{10}\text{O}_{28})^{-5}$ and $(\text{H}_2\text{V}_{10}\text{O}_{28})^{-4}$ ions might be present in the acidic solution at pH around 2 and slightly below 3.

More so, the result displayed by (Fig. 3) might also be dependent on the existence of various species of

vanadium such as $(V_4O_{12})^{-4}$ at higher concentrations rather than that of VO_2^+ , in which case the former predominates over the later.

The result explained by (Fig. 4) i.e., additional increase in temperature beyond 315 K did not favor further extraction is somehow common for most extraction characteristics. This characteristic is solvent specific. TBP is a viscous active liquid which readily forms emulsion that is promoted at higher temperatures, hence reduction in D or % extraction. In addition, mineral acids such as HNO_3 as well as water are readily extracted by this type of active solvent. (Ritcey and Ashbrook, 1984). A detailed kinetic study probably with a better time and temperature resolved techniques would be necessary to establish whether the system is controlled by diffusion or chemical kinetics (Chiarizia and Briand, 2007).

In Fig. 5, a decrease in extraction with increased extractant concentration might be due to the fact that TBP is capable of extracting nitric acid molecules at increased concentration leading to a sort of competition between the actual metal extraction and the acid species (Sarangi *et al.*, 2006).

Considering that the percentage of vanadium that was extracted by a single batch method, an average of about 23% from samples from the two sites. It can be established that TBP is able to extract vanadium from bitumen; therefore a more efficient process of extraction, based on counter current extraction using TBP/hexane was used to boost the percentage extraction from 23 to 32%. The final percentage (32%) is too poor for any commercial or industrial purpose. So, we cannot recommend this extraction procedure for an economic development. A better opportunity for research work is a challenge in this regards.

In recommendation, a more excellent extractant (solvent) such as Di-(2 ethyl hexyl) Phosphoric acid may also be an alternative solvent.

REFERENCES

Adebisi, F.M., O.I. Asubiojo and T.R. Ajayi, 2006. Multielement analysis of Nigerian bitumen by TXRF spectrometry and the physical constants characterization of its hydrocarbon component. *Fuel*, 85: 396-400.

Adegoke, O.S. and E.C. Ibe, 1982. The Tar sand and heavy crude resources of Nigeria. Proc. 2nd Int. Conf. on Heavy Crude and Tar Sands. Caracas, Venezuela, 32: 280-285.

Adegoke, O.S., M.E. Omatsola and J.L. Coker, 1991. The geology of the Nigerian Tar-sands. In: Heavy Crude and Tarsands Hydrocarbons for the 21st Century. Proc. 5th UNITAR Int. Conf. on Heavy Crude and Tar Sands, pp: 369-835.

Anonymous, 2003. Alberta Community Development. Oil sand Discovery Center, ACD, Fact Sheet.

Chiarizia, R. and A. Briand, 2007. Third phase formation in the extraction of inorganic acids by TBP in n-octane. *Solvent Extraction and Ion Exchange*, 25: 351-371.

Ekweozor, C.M. and J.I. Nwachukwu, 1989. Nigerian Association of Petrol Exploration Bull., 4: 82-94.

Historica, 2007. The Canadian Encyclopedia. Historica foundation of Canada website. <http://www.thecanadianencyclopedia.com>.

Oluwole, A.F., O.I. Asubiojo, J.I. Nwachukwu, J.O. Ojo, O.J. Ogunsola and J.A. Adejumo, 1993. *J. Radioanal Nucl. Chem. Articles*, 168: 145-152.

Ritcey, G.M. and A.W. Ashbrook, 1984. *Solvent Extraction Principle and Application to Process Metallurgy*. Elsevier Scientific Pub. Company Inc., New York, pp: 521-678.

Sarangi, K., E. Padhan, P.B. Sarma, K.H. Park and R.P. Das, 2006. Removal/recovery of hydrochloric acid using Alamine 336, Aliquat 336, TBP and Cyanex 923. *Hydrometallurgy*, 84: 125-129.

Todorovic, V.R., 1987. Determination of trace metals in petroleum and petroleum products by atomic emission spectroscopy methods. *J. Chem. Soc.*, pp: 52.