

## EXTRACTION OF VANADIUM (IV) INTO SINGLE DROP OF DI (2-ETHYL HEXYL) PHOSPHORIC ACID

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An experiment was carried out to study the rate of extraction of the vanadyl ion,  $VO^{2+}$  from sulphuric acid medium. The commercial metal extractant, Di (2-ethyl hexyl) phosphoric acid (D2EHPA) dissolved in n-hexane diluent was used in the study. The experimental technique was the single drop where the rate of metal extraction was related to the interfacial area for mass transfer. The results showed that the rate of vanadium (IV) extraction was proportional to the aqueous vanadium concentration and the organic concentration of D2EHPA. The rate was also inversely proportional to the aqueous hydrogen ion concentration especially at low acidities. The extraction process had a rate constant of  $1.71 \times 10^{-4} S^{-1}$  at  $28^\circ C$  with an activation energy of  $38.75 KJ mole^{-1}$ . The system appeared to be controlled by mass transfer with simultaneous chemical reaction.

**Key Words:** Vanadium (IV) extraction, single drop, D, (2-ethyl hexyl) phosphoric acid.

### Introduction

Vanadium is widely distributed in nature with many known commercially viable ore deposits [1]. These ores also contain other valuable metals as a result of which vanadium is often produced as a co- or by-product of other metals such as uranium, copper and iron [1].

When a typical vanadium ore is acid or alkaline leached, the aqueous composition is complex in terms of metal ions. Neither the DAPEX (Di-alkyl phosphoric acid extraction) nor the AMEX (Amine extraction)- two well known commercial hydrometallurgical extraction processes for vanadium [2], is sufficiently selective to effect rapid vanadium isolation from the complex aqueous medium. Several stringent operating conditions are usually necessary.

Most of the published information on the solvent extraction of vanadium (IV) with D2EHPA have been mainly on the extraction equilibria [3-5]. To build and operate a vanadium (IV) plant based on a solvent extraction route, the need to understand the kinetics of the system cannot be over-emphasized. Information on kinetics would influence the choice and design of the extractor and could be interpreted to achieve more selectivity. Some workers [6,7] have carried out limited work on the kinetics of vanadium (IV) extraction using some of the several available experimental techniques. In particular, Ipinmoroti and Hughes [7] have investigated the mechanism of Vanadium (IV) extraction in a chemical kinetic regime. In that work, the system was stirred rapidly to eliminate the influence of diffusion. However, there is a need to investigate  $VO^{2+}/D2EHPA$  system with an experimental method that can provide information on interfacial

area- one of the key factors that affects the rate of mass transfer. The single drop technique satisfies this condition despite its complex hydro-dynamics [8]. It can furnish data on interfacial area and its operation can simulate a column contractor.

The rate of vanadium (IV) extraction from a continuous aqueous phase into single drop of D2EHPA dissolved in n-hexane diluent is discussed in this paper.

### Experimental

**Reagents.** All chemicals were obtained from the British Drug Chemical Limited (BDH). Vanadium (IV) sulphate was supplied as  $(VO)_2SO_4 \cdot H_2O$  and had to be assayed before use. D2EHPA was purified using the method of Sato [9] but the diluent, n-hexane was used as supplied. Other reagents were of Analar grade and also used as supplied.

**Experimental conditions.** In all kinetic runs, the aqueous phase was maintained at 0.5M with respect to sodium sulphate in order to keep the ionic strength reasonably constant. Runs were carried out at  $28 \pm 0.5^\circ C$  except for the runs when the effect of temperature was investigated at some other temperatures.

**Analytical methods.** Macro concentration of vanadium in the aqueous phase was determined by titration with  $KMnO_4$  while micro concentration by spectrophotometric hydrogen peroxide method [10]. Vanadium in the organic phase was first stripped into the aqueous phase with  $2MH_2SO_4$  before analysis. The pH of the aqueous phase was measured with Orion pH-meter, model, 701A.

**Experimental Procedure.** The single drop technique has been extensively described elsewhere [8,11,12]. Drops of

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D2EHPA in n-hexane were produced at the tip of a stainless hypodermic needle (33 gauge size) and were made to rise through a vertical glass column filled with a continuum of aqueous vanadium (IV) sulphate. The drops were driven by pressure from an oxygen-free nitrogen gas cylinder. The travel period through the column was timed and after the drops had collapsed at the end of the column, a known volume of the loaded organic phase was sampled for analysis. A set of 4 Pyrex tube jacketed columns of uniform internal diameter (24 mm) and heights 37.5, 71.0, 132.0 and 167.5 cm was used for each experiment. By combining the results of the drop travel times through the columns, the average drop size, the quantity of metal transferred per unit volume and the rate of extraction across a unit interfacial area were calculated. The rate was always evaluated from the slope of the graphs of mass transfer per unit area against drop travel time as typified by Fig. 1.

Rising drops were used for the kinetic runs except for one experiment that was carried out to check the effect of phase inversion during which drops of the aqueous phases were made to fall through a continuous organic phase.

**Results and Discussion**

The effects of aqueous vanadium concentration, pH and organic phase concentration of D2EHPA on the rate of vanadium extraction are illustrated by Figs. 1-3. The results show that the rate increases with increase in aqueous concentration of vanadium, increase in the organic phase concentra-

tion of D2EHPA and with increase in aqueous pH. If the rate is expressed as:

$$r_v = K [VO^{2+}]_a^\alpha [D2EHPA]_o^\beta [H^+]_a^\gamma$$

where  $\alpha$ ,  $\beta$  and  $\gamma$  are constants and subscripts a and o imply aqueous and organic phases, then by a log-log plot of  $r_v$  against corresponding  $[VO^{2+}]_a$ ,  $[D2EHPA]_o$  and  $[H^+]_a$ ,  $\alpha$ ,  $\beta$  and  $\gamma$  can be evaluated from the limiting slopes since rate is measured as a function of each parameter when the other two are kept constant. Tables 1-3 summarise such measurements while

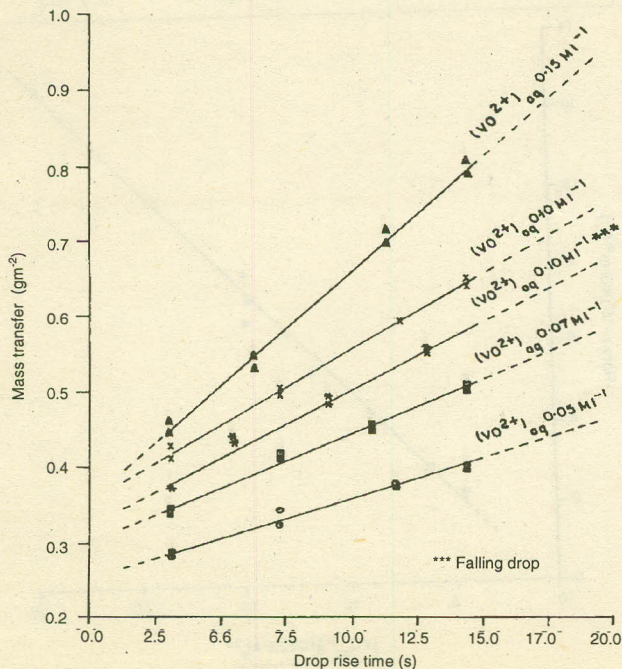


Fig. 1. Effect of aqueous vanadium concentration on the rate of vanadium transfer into the organic phase of D2EHPA.

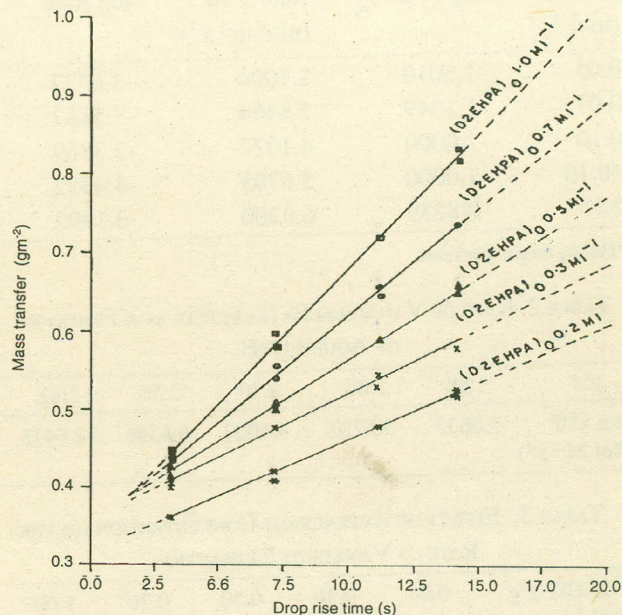


Fig. 2. Effect of the concentration of D2EHPA in the organic phase on the rate of transfer of vanadium into the organic phase of D2EHPA.

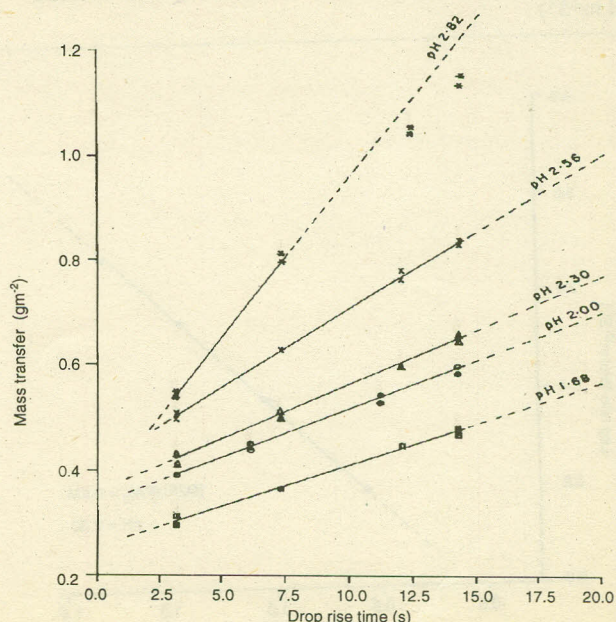


Fig. 3. Effect of aqueous pH on the rate of transfer of vanadium into the organic phase of D2EHPA.

Fig.4 is a typical plot from which  $\alpha$ ,  $\beta$  and  $\gamma$  are calculated to be 1.0, 0.8 and -0.9 respectively. Thus,

$$r_v = k[\text{VO}^{2+}]_a [\text{D2EHPA}]_o^{0.8} [\text{H}^+]_a^{-0.9}$$

The correlation is shown in Fig.5 with a slope of  $5.138 \times 10^{-5} \text{ M}^{-2} \text{ S}^{-1}$ . This value can be readily compared with some previous work by multiplying with the average specific area of

the drops. The average radius of the drops during the experimental work is 0.90 mm. Hence  $x = 1.71 \times 10^{-4} \text{ S}^{-1}$ . This value is much lower than the value of  $3.51 \times 10^{-3} \text{ S}^{-1}$  obtained by Ipinmoroti and Hughes [7] who used agitated vessels.

Within the working aqueous pH range during the rate measurement, vanadium is known to exist as  $\text{VO}^{2+}$  (or  $\text{V}(\text{OH})_2^{+2} (\text{OH})_2^{2+}$  alone [3] and hence the non-integer rate orders cannot be attributed to the effect of different metal species existing simultaneously in solution. Some workers [13-15] have also reported non-integer order dependency of the rate of metal extraction on pH and extractant concentration. Their observations have invariably been attributed to the influence of diffusion on chemical kinetics.

Although a slower rate of metal extraction is obtained for the falling drop mode of operating the column, the difference is not large and it can be attributed to some physical parameters of the system. For example, the falling drops move faster through the columns and are about 1.3 times bigger in size than the rising drops. These factors might combine to make the overall rate of mass transfer slower for the aqueous dispersed than the organic.

TABLE 1. RATE OF VANADIUM EXTRACTION AS A FUNCTION OF AQUEOUS VANADIUM CONCENTRATION.

| $[\text{VO}^{2+}]_{\text{aq}}$<br>(mol l <sup>-1</sup> ) | $\log (\text{VO}^{2+})_{\text{aq}}$ | Rate $\times 10^4$<br>(mol m <sup>-2</sup> s <sup>-1</sup> ) | log Rate |
|--|-------------------------------------|--|----------|
| 0.05   | -1.3010                             | 2.1004   | -3.6777  |
| 0.07   | -1.1549                             | 2.8464   | -3.5457  |
| 0.10   | -1.0000                             | 4.1027   | -3.3869  |
| *0.10  | -1.0000                             | 3.6708   | -3.4352  |
| 0.15   | -0.8239                             | 6.3200   | -3.1992  |

\*Falling drop experiment

TABLE 2. RATE OF VANADIUM EXTRACTION AS A FUNCTION OF AQUEOUS pH.

| pH   | 1.68   | 2.00   | 2.30   | 2.56   | 2.82    |
|--|--------|--------|--------|--------|---------|
| Rate $\times 10^4$<br>(Mol M <sup>-2</sup> s <sup>-1</sup> ) | 3.0623 | 3.5727 | 4.1027 | 6.6546 | 12.6418 |

TABLE 3. EFFECT OF EXTRACTANT CONCENTRATION ON THE RATE OF VANADIUM EXTRACTION.

| $[\text{D2EHPA}]_o^g$<br>(mol l <sup>-1</sup> )              | 0.20   | 0.30   | 0.50   | 0.70   | 1.00   |
|--|--------|--------|--------|--------|--------|
| (Rate $\times 10^4$<br>mol m <sup>-2</sup> S <sup>-1</sup> ) | 2.3933 | 2.9445 | 4.1027 | 5.2808 | 7.1650 |

TABLE 4. EFFECT OF TEMPERATURE ON THE RATE OF VANADIUM EXTRACTION

| Temperature<br>(°K) | $\frac{1}{T} \times 10^3$ | Rate $\times 10^4$<br>(mol m <sup>-2</sup> s <sup>-1</sup> ) | log Rate |
|---------------------|---------------------------|--|----------|
| 301                 | 3.3223                    | 4.1027   | -3.3869  |
| 306                 | 3.2680                    | 5.2020   | -3.2838  |
| 311                 | 3.2154                    | 6.7528   | -3.1705  |

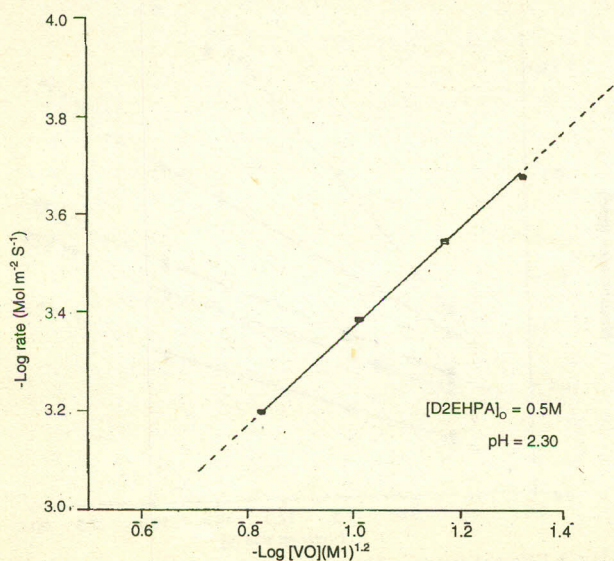


Fig. 4. The rate of extraction of vanadium as a function of the aqueous concentration of vanadium.

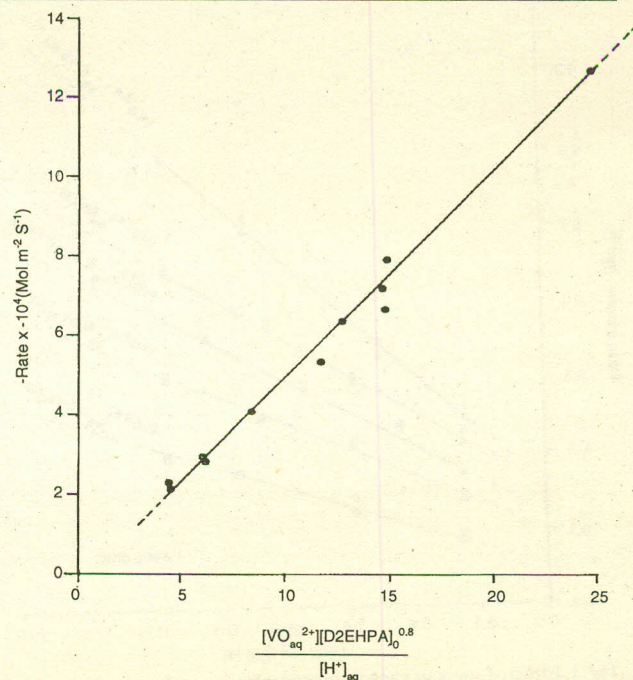


Fig. 5. Correlation of the rate of vanadium extraction with aqueous vanadium concentration, aqueous acidity and the concentration of D2EHPA in the organic phase.

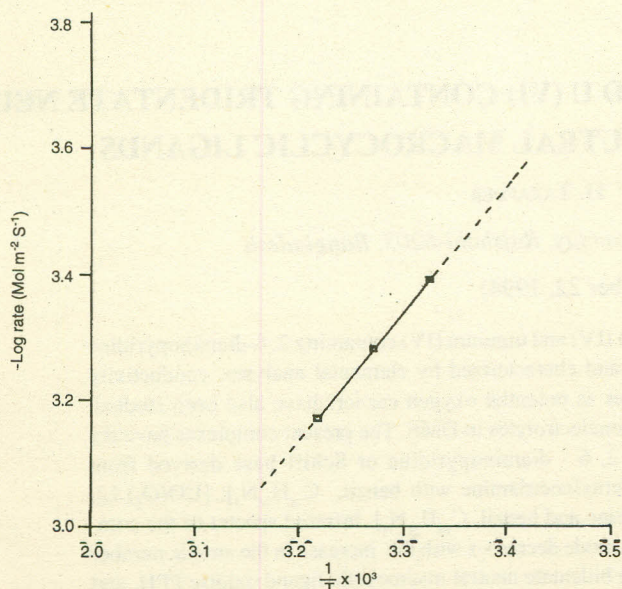


Fig. 6. Arrhenius plot for the extraction of vanadium by D2EHPA.

The data on the influence of temperature are presented in Table 4. From the Arrhenius plot (Fig.6), the activation energy is calculated to be 38.75 kJ/mole. This value is smaller than the value of 64.0 kJ/mole obtained when the system was controlled by chemical kinetics [7]. The magnitude of the activation energy also does not provide a clear-cut information as to whether the system is chemical or diffusion controlled. It appears to be a typical case of mass transfer with simultaneous chemical reaction.

### Conclusion

The results of mass transfer studies for the system vanadium/D2EHPA using the single drop technique suggest that the overall rate of mass transfer from the aqueous into the organic phase is influenced by both diffusion and chemical kinetics. The effects of the reactants concentration on the rate suggest that the processing of vanadium ore with D2EHPA would be more favourable when the aqueous vanadium concentration and the pH are high and when a large quantity of the extractant is available. There is a limit, however, to which the aqueous pH can be increased as  $\text{VO}^{2+}$  tend to oxidise rapidly to poorly extracted +5 vanadium species at high pH [16].

Since the rate of vanadium extraction increases with rise in temperature, extraction at high temperature would be

favourable for a commercial plant. This needs caution as some of the associated metals such as  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  have higher temperature coefficients [11] than vanadium and would therefore be extracted faster at high temperature to contaminate the primary product, vanadium.

Although the effect of dispersing the organic or the aqueous phase is minimal, the more expensive extractant, D2EHPA would always be available in a smaller quantity and hence for economic reasons should be preferably dispersed.

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