

## Solvent Extraction of Vanadium(IV) and Vanadium(V) with Di-o- tolylhydrogenphosphate in Benzene

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**Summary:**The extractions of V(IV) and V(V) from acidic sulphate-acetate media with di-o-tolylhydrogenphosphate (HDTP or  $H_2A_2$ ) in benzene have been investigated as functions of various experimental parameters. Reactions for extractions of V(IV) and V(V) have been proposed via chelation and solvation respectively. Temperature dependence data give the apparent enthalpy change ( $\Delta H$ ) for the reactions as  $-29.65$  kJ/mol (below  $50^\circ C$ ) and  $-26.78$  kJ/mol for V(V) and V(IV) respectively. The loading capacities of HDTP for V(IV) and V(V) are found to be 6g/100g HDTP and 3.6g/100g HDTP respectively. The value of the extraction equilibrium constant for the extraction of V(IV) has been calculated to be  $\log K_{ex} = 1.19$ . The diluent effect has also been investigated.

### Introduction

Although there are many reports on the extraction of metal ions with dialkylhydrogenphosphate, for example bis-(2-ethylhexyl) phosphoric acid (HDEHP), dibutylphosphoric acid (HDBP) etc. [1], relatively few reports are available on the extraction of metal ions by diarylhydrogenphosphates such as diphenylhydrogenphosphate [2-4] and ditolylhydrogenphosphate [5-7]. Recently, HDTP has been reported for the separation of Ti(IV) from Fe(III) and Fe(II) [8]. Moreover, the extractions of Cr(III) [9], Ni(II) [10] and Ti(IV) [11] with HDTP have been reported from our laboratories. Although there are many reports [12] on the extractions of V(IV) and V(V) from acidic solutions with various extractants, there appears to be little data available for these ions with respect to HDTP. This paper discusses the solvent extractive characteristics of V(IV) and V(V) relating to di-o-tolylhydrogen phosphate dissolved in benzene and compares the results obtained with those reported for HDEHP.

### Experimental

The following chemicals were used in the investigation: vanadyl sulphate (purified, F.S.C), ammonium metavanadate (reagent grade, B.D.H.), tri-o-tolylphosphate (pure, Koch Light Lab.), benzene (99%, B.D.H), sodium hydroxide (96%, B.D.H). All other chemicals were of reagent grade and were used without further purification. Di-o-

tolylhydrogenphosphate (HDTP) was prepared from tri-o-tolyl phosphate by the alkali hydrolysis method and purified as reported earlier [8-10]. HDTP was about 99%. It was diluted with benzene to make dimeric HDTP solutions of selected concentrations.

Aliquots of aqueous (0.20g/L V(V) at selected sulphuric acid concentration and 0.25 mol/L acetate concentrations or V(IV) containing 1 mol/L sulphate and 0.25 mol/L acetate concentrations at a selected pH) and organic phase were taken in a separating funnel and mixed well by an electric shaker at  $30 \pm 0.2^\circ C$ . A Corning 7A model pH meter was used to measure the pH of the V(IV)-solutions adjusted by anhydrous  $Na_2CO_3$ . After equilibration (5 min), the phases were settled and disengaged. The aqueous phase concentration of V(IV) (after oxidising to V(V) by boiling with conc  $HNO_3$ ) or V(V) was estimated by the  $H_2O_2$  method [13] using a Spectronic-20. The concentrations of V(IV) and V(V) in the organic phase were obtained by difference and occasionally verified by exhaustive back-washing of the organic phase with sulphuric acid solutions. The extraction ratio  $E_{OV}$  was then calculated by dividing the concentration of vanadium in the organic phase by the vanadium concentration in the aqueous phase each determined at equilibrium for a particular set of extraction parameters.

## Results and Discussion

Experiments were conducted to determine the time required to reach equilibrium in each system by measuring the change in the extraction ratios of V(IV) or V(V) as function of time. The results are shown in Fig.1. The plots  $E^O_V$  against time indicate that equilibrium is reached after about 1 min for V(IV) and after 45 sec for V(V). It has been reported that the equilibration time for the extraction of V(IV) by HDEHP in benzene is 1.50-2.00 min [14]. Thus, the extraction of V(IV) by HDTP is a little faster than by HDEHP. Similarly, the extraction of V(V) with HDTP is also faster than with HDEHP (5 min) [15]. In subsequent experiments, a phase mixing time of 5 minutes was allowed for both the systems to ensure the attainment of equilibrium under the various conditions.

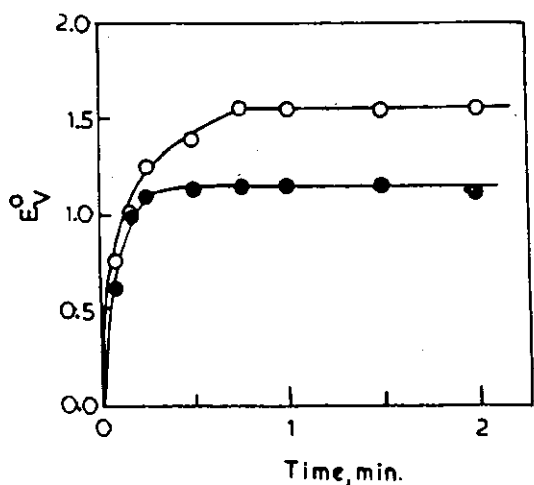


Fig.1: Determination of the time required to reach equilibrium. HDTP = 0.05M, (O),  $C^A_{V(IV)(ini)} = 180$  mg/L,  $pH_{ini} = 2.00$ ,  $pH_{eq} = 1.55$ ,  $[SO_4^{2-}]_T = 1M$  & (O),  $C^A_{V(V)(ini)} = 208$  mg/L,  $H_2SO_4 = 7M$ .

Figure 2 represents the variation of extraction ratio with initial V(IV) and V(V) concentrations in aqueous phase. The extraction ratio is found to increase linearly with initial V(IV) concentration in the aqueous phase. In the case of extraction with HDEHP, it has been reported [14] that the extraction ratio of V(IV) remains unchanged with variation of initial V(IV) concentration in the aqueous phase. On the other hand, the extraction ratio of V(V) is decreased with increasing V(V) concentration in the aqueous phase. Similar behaviour was also reported for extraction by HDEHP [15]. This

might be due to a change in the distribution of aqueous V(V) species upon increasing the metal ion concentration in the aqueous phase.

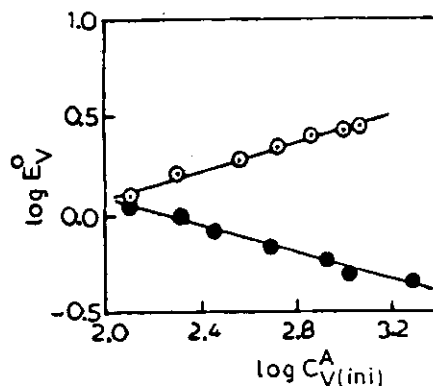


Fig.2: Dependence of extraction ratio,  $E^O_V$  on the initial vanadium concentration (mg/L) in the aqueous phase. HDTP = 0.05M, (O), 1.12 V(IV),  $[SO_4^{2-}]_T = 1M$ ,  $pH_{eq} = 1.42$ , slope(s) = 0.35 and (O), V(V),  $H_2SO_4 = 6M$ , s = -0.36.

The variations of the extractions of V(IV) and V(V) with acidity of the aqueous phase are shown in Fig. 3. It can be seen that the extraction of (IV) is increased with increasing aqueous equilibrium pH. The slopes of the lines indicate that the pH dependence of the extraction of V(IV) is unity. With HDEHP, the pH dependence of the extraction of V(IV) was reported to be two [14]. More than 92% V(IV) is extracted with 0.075 M HDTP at an equilibrium pH of 1.70. Here it should be pointed out that the equilibrium pH is decreased from its initial value when the extraction is made from solutions having pH higher than 1.20, whereas it is increased from its initial value when the extraction is made from solutions having pH lower than 1.20. It is thought that at higher pH, the ionization of HDTP in the aqueous phase and the liberation of  $H^+$  due to the extraction reaction decrease the pH of the aqueous phase. At lower pH, the increase in pH may be due to the extraction of  $H_2SO_4$  by HDTP. For V(V), the extraction is decreased with decreasing acidity (10 - 5 M  $H_2SO_4$ ). About 55% V(V) is extracted by 0.075M HDTP from 8M  $H_2SO_4$  medium. Vanadium(V) is not extracted appreciably in the pH range 0 to 3. The experimental points for each HDTP concentration do not yield straight lines and the nature of the curves depends largely on the extractant concentration level. With HDEHP, the acidity dependence curves for

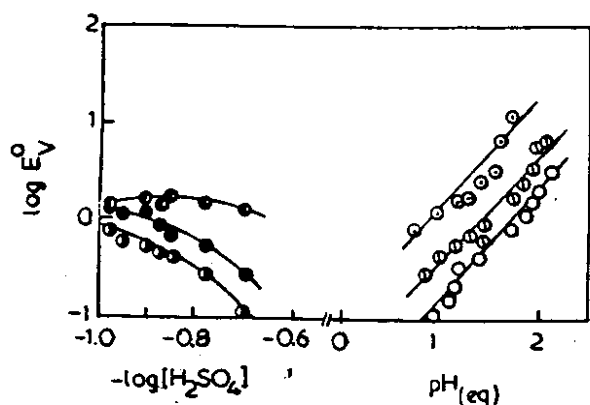


Fig. 3: Dependence of extraction of V(IV) and V(V) with HDTP on acidity of aqueous phase.  $C_{V(ini)}^A = 200$  mg/L,  $[SO_4^{2-}]_T = 1$  M for V(IV). (O), V(IV), HDTP = 0.025 M,  $s = 1.23$ , Intercept (I) = -2.07; (O), V(IV), HDTP = 0.05M,  $s = 1.09$ , I = -1.49; (O), V(IV), HDTP = 0.075M,  $s = 1.16$ , I = 1.12; (O), V(V), HDTP = 0.025M; (O), V(V), HDTP = 0.05M; (O), V(V), HDTP = 0.075M. Slopes and intercepts for V(IV) systems were calculated by the Least Square Analysis.

vanadium(V) pass through minima at about pH zero and maxima around pH 2.1 [15].

The extractant dependence of extraction ratios of V(IV) and V(V) are given in Fig.4, where  $\log E_{v_0}$  has been plotted against  $\log [HDTP]$ . A straight line relationship is obtained in the case of vanadium(IV) only. The slopes of the lines indicate that the extractant dependence for the extraction of V(IV) is about two. In the case of the extraction of V(V), the extractant dependence changes with HDTP concentration. It is about unity below 0.05 M HDTP but above this the HDTP dependence also changes with sulphuric acid concentration. For example, the HDTP dependence is about 4 in the presence of 5M  $H_2SO_4$ , whereas it is about 2 for 7M  $H_2SO_4$ .

The equilibrium constant for the extraction reaction of V(IV) has been calculated from the relationship [14].

$$\log E^0_V = \log K_{ex} + m \log [H_2A_2] + n \text{pH} \quad (1)$$

The calculated  $\log K_{ex}$  value is 1.19 with standard deviation of 0.114 and tabulated in Table 1. The value of  $\log K_{ex}$  for the extraction of V(IV) with HDEHP is only -1.812 [14]. Therefore, it may be concluded that HDTP, in comparison to HDEHP has higher affinity for V(IV) and may extract V(IV) from relatively higher acidic solutions.

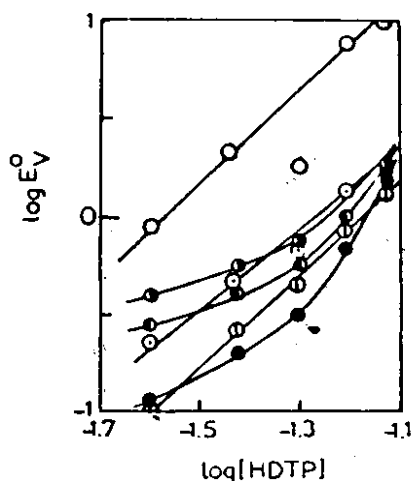
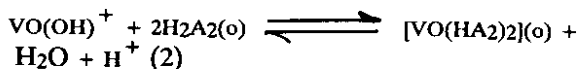


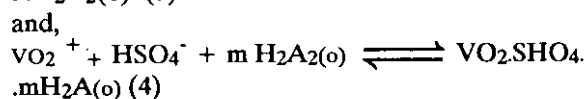
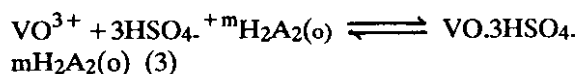
Fig. 4: Dependence of extraction of (IV) and V(V) on extractant concentration in the organic phase.  $C_{V(ini)}^A = 200$  mg/L,  $[SO_4^{2-}]_T = 1$  M for V(IV). (O), V(IV),  $\text{pH}_{eq} = 1.00$ ,  $s = 2.33$ , I = 2.34; (O), V(IV),  $\text{pH}_{eq} = 1.20$ , I = 2.62,  $s = 2.02$ ; (O), V(IV),  $\text{pH}_{eq} = 1.70$ ,  $s = 2.33$ , I = 3.06; (O), V(V),  $H_2SO_4 = 5$  M; (O), V(V),  $H_2SO_4 = 6$  M and (O), V(V),  $H_2SO_4 = 7$  M..

HDTP is dimeric in benzene like other dialkyl or diaryl esters [8,9,16]. The pH and HDTP dependences of extraction ratio of V(IV) indicate that the monohydroxylated V(IV) species is probably involved in the extraction reaction by the cation exchange and chelation mechanism:



The species  $VO(OH)^+$  is likely to be present in aqueous solution having a pH 1. In the case of extraction of V(IV) with HDEHP, the extraction of the species  $VO_2^{2+}$ ,  $VO(OH)^+$  and  $VO(OH)_2$  has been proposed [14] at lower ( $\text{pH} < 1$ ), medium ( $\text{pH} > 1$  but  $< 2$ ) and higher ( $\text{pH} > 2$ ) pH respectively, but extracted species is always  $VO(HA_2)_2$  in combination with  $VOA_2$ .

The results obtained in the case of V(V) are difficult to explain. No single extraction reaction appears to represent the extraction systems under all conditions. This might be due to change in the distribution of V(V) species on varying the acidity of the solution. It is well known that  $VO_2^{2+}$  and  $VO_3^{2+}$  are the principal V(V) species in highly acidic solutions [17]. The dependence of extraction ratio of V(V) on  $H_2SO_4$  and HDTP concentrations indicate the extraction *via* the following reactions which involve solvation rather than chelation or ion exchange:



Since the value of first ionization constant is large in comparison to the value of the second ionization constant of  $\text{H}_2\text{SO}_4$ , the concentration of  $\text{H}^+$  and  $\text{HSO}_4^-$  ions will be almost identical in absence of additional sulphate ion in the medium. This implies that  $\text{H}^+$  dependence of V(V) extraction may virtually represent the  $\text{HSO}_4^-$  dependence. Therefore, Fig. 3 indicates that reaction (3) is likely to occur in the lower sulphuric acid concentration region, whereas reaction (4) occurs in higher acid concentration region. The solvation number, 'cm' varies from 1 to 4 depending on the  $\text{H}_2\text{SO}_4$  and HDTP concentrations. Its values is about 1 for all the sulphuric acid concentrations examined within the 0.025 to 0.05M HDTP concentration range. On the otherhand, the value of 'cm' varies from 2 to 4 in the higher HDTP concentration region depending on the sulphuric acid concentration.

The effect of the total sulphate ion (sulphate, bisulphate plus undissociated  $\text{H}_2\text{SO}_4$ ) concentration of V(IV) and V(V) extractions can be seen from the  $\log E_{\text{Vo}}$  vs  $\log [\text{SO}_4]_{\text{T}}$  plots in Fig. 5. In the case of the extraction of V(IV), the extraction ratio

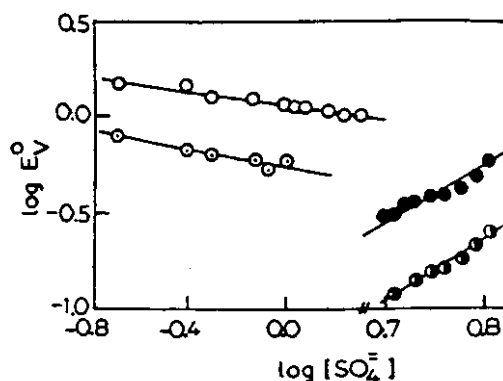


Fig. 5. Dependence of extraction of V(IV) and V(V) on total sulphate concentration in aqueous phase. (O), V(IV), HDTP = 0.025M,  $\text{pH}_{\text{eq}} = 1.50$ ,  $s = -0.15$ ; (O), V(IV), HDTP = 0.05M,  $\text{pH}_{\text{eq}} = 1.50$ ,  $s = -0.20$ ; (O), V(V), HDTP = 0.025 M,  $\text{H}_2\text{SO}_4 = 5\text{M}$ ,  $s = 3.40$  and (O), V(IV), HDTP = 0.05M,  $\text{H}_2\text{SO}_4 = 5\text{M}$ ,  $s = 3.00$ .

is slightly decreased linearly with increasing aqueous total sulphate concentration. The slopes of the lines are only about -0.20, which indicates that in conjunction with the extraction of  $\text{VO}(\text{OH})^+$  species, the aqueous solution might contain the  $\text{VO}(\text{OH}) \cdot \text{SHO}_4$  which may behave as follows

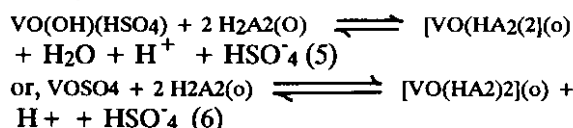


Table-1: Evaluation of extraction equilibrium constant of V(IV).

$C^{\text{V}}_{\text{(ini)}} = 0.20 \text{ g/L}$ ,  $[\text{SO}_4]_{\text{T}} = 1 \text{ M}$ ,  $[\text{Ac}^-] = 0.25 \text{ M}$ ,  $\text{temp.} = 30 \pm 0.2^\circ\text{C}$

| Fig. No | [HDTP],M | eq. Ph | Intercept, I | $\log K_{\text{ex}} = I - 2\log [\text{HDTP}]$ | $\log K_{\text{ex}} = I - 1.16 \text{ pH}$ | Mean $\log K_{\text{ex}}$ | St. dev. of $\log K_{\text{ex}}$ |
|---------|----------|--------|--------------|--|--|---------------------------|----------------------------------|
| 3       | 0.0250   | -      | -2.07        | 1.134  | -  | 1.185                     | 0.114                            |
|         | 0.0375*  | -      | -1.71        | 1.142  | -  |                           |                                  |
|         | 0.0500   | -      | -1.49        | 1.111  | -  |                           |                                  |
|         | 0.0625*  | -      | -1.33        | 1.078  | -  |                           |                                  |
|         | 0.0750   | -      | -1.12        | 1.130  | -  |                           |                                  |
| 4       | -        | 0.70*  | 2.24         | -  | 1.428                                      |                           |                                  |
|         | -        | 0.90*  | 2.38         | -  | 1.336                                      |                           |                                  |
|         | -        | 1.00   | 2.34         | -  | 1.180                                      |                           |                                  |
|         | -        | 1.20   | 2.62         | -  | 1.228                                      |                           |                                  |
|         | -        | 1.70   | 3.06         | -  | 1.088                                      |                           |                                  |

\*These conditions are not shown in figures 3 and 4.

Since the reactions (5) and (6) show the liberation of  $\text{HSO}_4^-$  ion during extraction, equilibria are shifted towards the left on increasing the sulphate or bisulphate ion concentration in the aqueous phase. These reactions might occur in conjunction with reaction (2). The decrease in the extraction of V(IV) with increasing sulphate ion concentration has also been reported for extraction by HDEHP [14]. On the other hand, the extraction of V(V) is found to increase with increasing the total sulphate ion concentrations. Since at high sulphuric acid concentration, bisulphate ion will be the predominant aqueous species, the slope of the line (3 for both parameters) supports the extraction of V(V) *via* equation (3) at 5M  $\text{H}_2\text{SO}_4$  medium.

The variations of the extraction ratios of V(IV) and V(V) with acetate (equimolar acetic acid and sodium acetate) concentration in the aqueous phase are presented in Fig. 6, which shows plots of  $\log E_{V^0}$  vs  $\log [\text{Ac}^-]$ . It is seen that the extractions of both metal ions are not influenced by acetate ion concentration in aqueous phase. There appear to be no reference to the formation of  $\text{VOAc}^+$  or  $\text{VO}(\text{Ac})_2$  and  $\text{V}(\text{V})\text{-Ac}^-$  species in aqueous solutions. The present extraction data also indicate that such acetate species are most probably not formed, at least in the presence of highly concentrated sulphate media. In the case of extraction with HDEHP, the extraction of V(IV) is very slightly increased with increasing acetate ion concentration in the aqueous phase [14]. The non-dependence on acetate ion concentration of the extraction of V(V) by HDEHP has been reported [15].

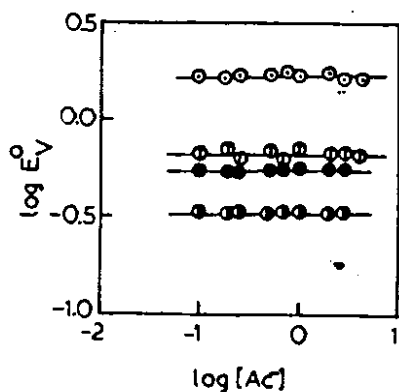


Fig. 6. Dependence of the extraction ratio of V(IV) and V(V) on acetate ion concentration in aqueous phase. HDTP = 0.05M. (O), V(IV),  $[\text{SO}_4^{2-}]_{\text{T}} = 1\text{M}$ ,  $\text{pH}_{\text{eq}} = 1.00$ ,  $s = 0$ ; (●), V(IV),  $[\text{SO}_4^{2-}]_{\text{T}} = 1\text{M}$ ,  $\text{pH}_{\text{eq}} = 1.50$ ,  $s = 0$ ; (○), V(V),  $\text{H}_2\text{SO}_4 = 5\text{M}$ ,  $s = 0$  and (○), V(V),  $\text{H}_2\text{SO}_4 = 6\text{M}$ ,  $s = 0$ .

The effect of temperature on the extraction of V(IV) and V(V) has been determined within the temperature range 30 to 60°C. The results are shown as  $\log E_{V^0}$  vs  $1/T$  (absolute temperature) plots in Fig. 7. The extraction of V(IV) is continuously decreased with increasing the extraction temperature, but the extraction of V(V) goes through a minimum at approximately 50°C. The apparent enthalpy change ( $\Delta H$ ) is about -26.78 kJ/mol for V(IV). It is about -29.65 kJ/mol for V(V) below 50°C and 32.50 kJ/mol for 7M  $\text{H}_2\text{SO}_4$  and 63 kJ/mol for 9M  $\text{H}_2\text{SO}_4$  systems above 50°C. The reported  $\Delta H$  value for the extraction of V(IV) with HDEHP [14] is about 19.81 kJ/mol. The change in the  $\Delta H$  value for the extraction of V(V) with temperature indicates the alteration of extraction reaction with temperature. It has been reported[9] that the extraction of Cr(III) with HDTP passes through a maximum at about 50°C.

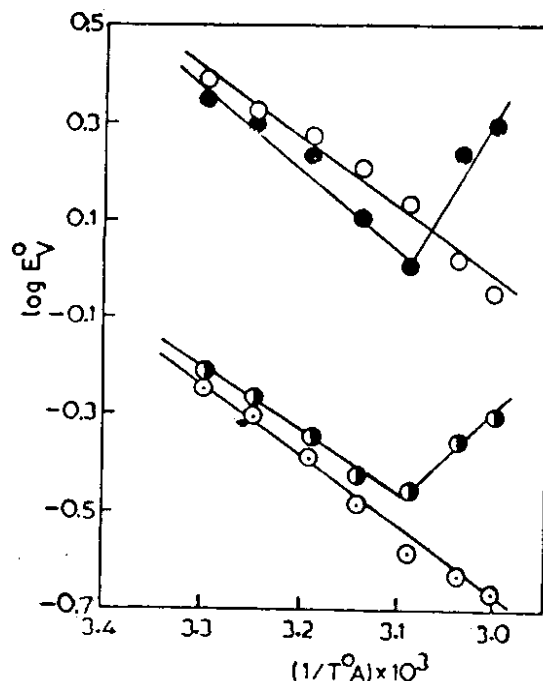


Fig. 7. Dependence of extraction on temperature. HDTP = 0.05M,  $[\text{SO}_4^{2-}]_{\text{T}} = 1\text{M}$  for V(IV). (O), V(IV),  $\text{pH}_{\text{eq}} = 1.80$ ,  $s = 1400$ ; (○), V(V),  $\text{H}_2\text{SO}_4 = 7\text{M}$ ,  $s = 1400$  (50°C) and (○), V(V),  $\text{H}_2\text{SO}_4 = 9\text{M}$ ,  $s = 1700$  (below 50°C), -3300 (above 50°C).

The loading of organic phase is important from an industrial point of view and for the elucidation of extraction mechanism at high loading particularly. Loading of HDTP with V(IV) has been effected at an initial pH of 1.50 for 0.05 and 0.10 M HDTP solutions and in the case of V(V) at 5M

Table-2: Effects of diluents for HDTP in the extractions of V(IV) and V(V).  $C^A_{V(IV)}(\text{ini}) = 230$  mg/L,  $C^A_{V(V)}(\text{ini}) = 215$  mg/L,  $[\text{SO}_4]_{\text{T}} = 1$  M for V(IV), pH = 1 for V(IV) solution,  $\text{H}_2\text{SO}_4 = 5$  M for V(V) solution, HDTP = 0.10 M, phase ratio = 1/1,  $[\text{Ac}^-] = 0.25$  M, temp. =  $3 \pm 0.2^\circ\text{C}$ .

| Diluent                 | Specification                             | Metal ion | Extraction ratio |
|-------------------------|---|-----------|------------------|
| Nitrobenzene            | M.C.& Bell, m.p. $5.6^\circ\text{C}$      | V(IV)     | 0.265            |
|                         |   | V(V)      | 0.608            |
| Carbon-tetrachloride    | E. Merck, 99%                             | V(IV)     | 0.265            |
|                         |   | V(V)      | 0.704            |
| Toluene                 | E.Merck, 99% b.p. $109-112^\circ\text{C}$ | V(IV)     | 0.181            |
|                         |   | V(V)      | 0.278            |
| Chloroform              | E.Merck, 99.2% b.p. $60-62^\circ\text{C}$ | V(IV)     | 0.593            |
|                         |   | V(V)      | 0.769            |
| Methyl iso-butyl ketone | B.D.H., 98%, b.p. $114-117^\circ\text{C}$ | V(IV)     | 0.181            |
|                         |   | V(V)      | 0.150            |
| Benzene                 | B.D.H., 99%, b.p. $79-81^\circ\text{C}$   | V(IV)     | 0.303            |
|                         |   | V(V)      | 0.797            |

$\text{H}_2\text{SO}_4$  for 0.05M HDTP solution. The results are shown in Fig. 8, as plots of cumulative vanadium concentrations in the organic phase,  $C^O_V$  versus increasing initial vanadium concentration (in successive steps) in the aqueous phase. About 1.68 g V(IV)/L and 3.005 g V(IV)/L in organic phase are obtained at the maximum loading for 0.05 and 0.10 M HDTP giving V(IV) to DTP ratio of 1:1.52 and 1:1.69 respectively. The V(IV) HDTP ratio of about 1:1.50 indicates that the extraction mechanism at high loading differs from that at low loadings. Similar behaviour was also found to occur in the case of extraction of Ti(IV) with HDEHP [18]. The maximum loading of 0.05M HDTP solution with V(V) is only 1.055 g V(V)/L, giving V(V) to HDTP ratio of 1:2.42. At high loading, the solvation number is therefore about 2.50. From the slope analysis (Fig. 4), it is also about 2.50 at 0.05M HDTP concentration level. The maximum capacities are about 6g V(IV)/100g HDTP and 3.60g V(V)/100g HDTP.

The effect of diluent type on the extraction of V(IV) and V(V) was investigated by determining extraction ratios in the various diluents while main-

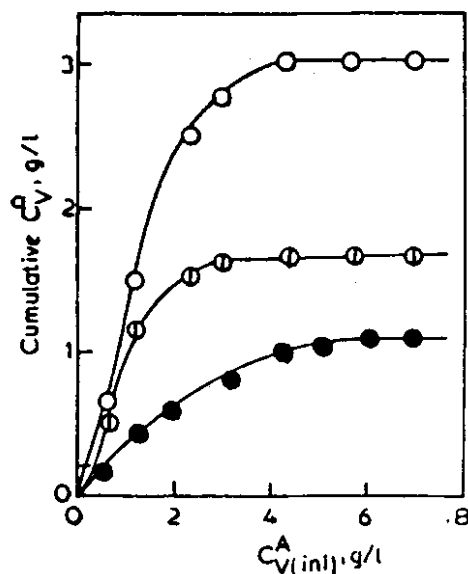


Fig.8. Loading of HDTP with V(IV) and V(V). temp. =  $30 \pm 0.2^\circ\text{C}$ ,  $[\text{AC}^-] = 0.25\text{M}$ ,  $[\text{SO}_4]_{\text{T}} = 1\text{M}$  for V(IV). (O), V(IV),  $\text{pH}_{\text{eq}} = 1.50$ , HDTP = 0.05M; (O), V(IV),  $\text{pH}_{\text{eq}} = 1.50$ , HDTP = 0.10M; (O), V(V),  $\text{H}_2\text{SO}_4 = 5\text{M}$ , HDTP = 0.05M.

taining the other parameters constants. Measurements with petroleumbenzene, cyclohexane, 1,2-dichloroethane, amyl alcohol, pyridine, n-hexane and kerosene were not possible either because of stable emulsion formation or insolubility of HDTP in the diluents. The results obtained with nitrobenzene, carbontetrachloride, toluene, chloroform, methyl iso-butyl ketone and benzene are given in Table 2. It appears that chloroform and benzene are good diluents for HDTP in extracting V(IV) and V(V).

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