Equilibrium of the Extraction of V(IV) in the
V(IV)-SO₄²⁻(H⁺, Na⁺)—Cyanex 302-Kerosene System

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ABSTRACT
The title system has been investigated from the equilibrium point of view. Significant extraction occurs above pH 2. Equilibration time is 20 min. The extraction ratio (D) remains constant with increasing [V(IV)] of at least 0.50 g/L. It is inversely proportional to [H⁺]², [H⁺] and [H⁺]⁰.³ in the lower pH (<2.25), medium pH (~2.90) and higher pH (~4.0) regions, respectively. Moreover, it is proportional to [Cyanex 302]²; and [SO₄²⁻]⁰ and [SO₂⁻]⁻¹ in the lower [SO₄²⁻] (<0.05 mol/L) and higher [SO₄²⁻] (>1 mol/L) regions, respectively. The apparent extraction equilibrium constant (Kₑ) in 0.02 mol/L SO₄²⁻ medium and at 303 K is found to vary from 10⁻³.⁴⁴⁷ to 10³.⁵⁰⁸ with increasing equilibrium pH from 2.25 to 4.00. Various sulphated, hydrolyzed, hydrated and mixed sulphated hydrolyzed species of V(IV) have been considered at different extraction conditions to propose the extraction equilibrium reactions to form always [VO(HA₂)₂] as the extractable species. The system is highly temperature dependent with ΔH value of ~90 kJ/mol and ~25 kJ/mol in lower and higher temperature regions, respectively. The calculated loading capacity is low (4.05 g V(IV)/100 g Cyanex 302). Kerosene is a better diluent over CHCl₃, Cyclo-C₆H₁₂ and CCl₄; but much better solvents are C₆H₆, C₆H₅CH₃, n-C₇H₁₆, C₆H₄(CH₃)₂, petroleum benzin, 1,2-C₂H₄Cl₂, C₆H₅Cl. Mineral acids (1 mol/L) are able to strip off V(IV) from the organic phase in a single-stage. Using Cyanex 302, almost complete separations of V(IV) from Cu(II) at pH 1.0 and from Ni(II) at pH(eq) 4.5 are possible in a single-stage of extraction; whereas, its separation from Zn(II) at pH(eq) 2.5, Co(II) at pH(eq) 3.5, Fe(III) at pH(eq) 2.0 and Ti(IV) at pH(eq) 2.5 will require counter-current multi-stage extractions.

Keywords: Extraction Equilibrium; Vanadium(IV); Cyanex 302; Kerosene; Sulphate

1. Introduction
Vanadium is used for alloying steel and the manufacture of oxidative catalyst. The rich deposits of its ores, viz: patronite (V₂S₃), vanadinite (3Pb₃(VO₄)₂·PbCl₂), carnotite (K₂U₂V₂O₁₁·3H₂O) etc. are rare on the earth’s crust now. Consequently, it is necessary to develop extraction processes for low grade ores and waste materials (tar sand, waste desulphurization catalyst etc.). Solvent extraction technique is convenient for such purpose. The technique can build up concentration by using low (O/A) ratio in extraction and high O/A ratio in stripping. Works on the solvent extraction of V(IV) by various extractants prior to 1976 were summarized by Sekine and Hasegawa [1]. Di-2-ethylhexyl phosphoric acid (D₂EHPA) is a promising extractant for V(IV) and V(V) [2-8]. Vanadium-(IV) and (V) have also been extracted by EHEHPA (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) [9]. A recent development in the field of solvent extraction is the use of organophosphinic acid derivatives and their sulphur analogues (Cyanex reagents) introduced by American Cyanamid Company and Cytec Canada Inc. Cyanex 302 and Cyanex 301 are the mono- and disulphide analogues of Cyanex 272 (di-2,4,4-trimethylpentyl phosphonic acid). The sulphur substitution decreases pKₐ values (viz. 6.4, 5.6 and 2.6 for Cyanex 272, Cyanex 302 [10,11] and Cyanex 301 [12], respectively) which permits to work at lower pH [13]. Cyanex reagents differ from other commercial organophosphorous reagents (e.g. D₂EHPA, DDPA, TBP, EHPEHPA etc.) in that the former reagents contain P-C bonding, whereas the latter reagents contain P-O-C bonding. The presence of P-C bonding in Cyanex reagents renders them to be less susceptible to hydrolysis and less soluble in water [14]. In recent past, the extraction behaviors of V(IV) from sulphuric acid solution by Cyanex 272 [15,16] and of V(IV) and V(V) from hydrochloric acid solution by Cyanex 272 and Cyanex 301 [14] had been reported. There is no report on the extraction behavior of V(IV) from any acid solution using Cyanex 302. The present paper reports the extraction characteristics of V(IV) from sul-
phosphate medium by Cyanex 302 dissolved in kerosene. The effects of the aqueous and organic phase variables (including diluent variation) have been investigated to determine the dependence of variables and to calculate the extraction equilibrium constant; and also to propose mechanism of extraction. The loading capacity is also elucidated. Finally, the possibility of separation of V(IV) from some cations of the first transition series in binary mixtures has been predicted.

2. Materials and Methods

2.1. Materials
Cyanex 302 was collected from Cytec Canada Inc. as a gift. It contains 78% - 80% R₂PSOH, 10% - 12% R₂PO, 2% - 3% R₂PO₂H, 2% R₂PS₂H and 8% unknown compounds [17] and has been used without further purification as R₂PO, R₂PO₂H and R₂PS₂H—all have the extracting power. Kerosene is bought from the local market and distilled to collect the colorless aliphatic fraction distilling over 200°C - 260°C. Ammonium vanadate (99%, Riedel-deHaen) and vanadium(IV) sulphate oxide (99.9%, Alfa Aesar-Johnson-Mathey), hydrogen peroxide (30%, Riedel-deHaen) and vanadium(IV) sulphate oxide (99.9%, Alfa Aesar-Johnson-Mathey), hydrogen peroxide (30%, Merck-Germany) are used in this study without further purification. Diluents other than kerosene are the products of Riedel-deHaen and E Merck-India; all are more than 99% pure.

2.2. Analytical
Concentrations of V(IV) in aqueous solutions have been measured by the HNO₃ oxidative-H₂O₂ method [18] at 450 nm using a UV-visible spectrophotometer (UV-1650 PC, Shimadzu, Japan). For standard and test solutions preparations NH₄VO₃ and VOSO₄·5H₂O, respectively, are used. A Mettler Toledo pH meter (model 320) is used for pH measurement and adjustment (by addition of either anhydrous Na₂CO₃ or dilute H₂SO₄ solution).

2.3. Procedure
Extraction and stripping procedures are given elsewhere [19]. In both cases, two phases are agitated at O/A=1 (O = 20 mL) and 303 K (otherwise stated) for a predetermined time (20 min in extraction and 1 h in stripping). The phase separation is quick; and the aqueous phase after equilibration is analyzed for its equilibrium pH and V(IV)-content. Then the value of extraction ratio or stripping percentage is calculated as usual [19].

2.4. Notations and Abbreviations

\[ K_{ex}, \text{ Extraction equilibrium constant; } \]

\[ D, \text{ Extraction or distribution ratio; } \]

\[ C, \text{ D at a constant equilibrium pH and extractant concentration; } \]

\[ \beta, \text{ Stability constant; } \]

\[ K_{sy}, \text{ A proportionality constant in sulphate dependence study; } \]

\[ \text{H}_2\text{A}_2, \text{ Cyanex 302 (dimeric); } \]

\[ A^{-}, \text{ Anion of monomeric Cyanex 302; } \]

\[ L^{-}, \text{ Uni-negative anion existing in the aqueous phase viz. OH}^{-} \text{ and HSO}_4^{-}; \]

\[ \Delta H, \text{ Apparent enthalpy change; } \]

\[ R, \text{ CH}_3-C(CH_3)_2-CH_2-CH(CH_3)-CH_2^-; \]

\[ l.c.r, \text{ Lower concentration region; } \]

\[ h.c.r, \text{ Higher concentration region; } \]

\[ l.pH.r, \text{ Lower pH region; } \]

\[ h.pH.r, \text{ Higher pH region; } \]

\[ i, \text{ Initial; } \]

\[ (eq), \text{ Equilibrium. } \]

2.5. Treatment of Extraction Equilibrium Data
The main constituent R₂PSOH of Cyanex 302 is dimeric in non-polar diluents [17,20]. In the aqueous solution, V(IV) virtually exists as VO₂⁺ (owing to high charge to radius ratio) which can form complex with co-existing OH⁻ and HSO₄⁻ (L⁻). Therefore, the extraction equilib-rium at a constant temperature can be represented by:

\[ \text{VOL}^{(2-z)+} + xH_2A_2(o) \rightarrow \text{VOL}_{n-z}A_{2-(n+z)}^{(2+)} \]

\[ \left( (2x-2+n-z)/2 \right) H_2A_2(o) + ZL^- + (2-n+z)H^+ \]

The \[ K_{ex} \] of Equation (1) can be expressed as:

\[ \log D = \log K_{ex} + (2-n+z)\text{pH} \]

\[ + x \log \left[ H_2A_2 \right]_{(o)} - z \log \left[ L^- \right] \]

Where, \[ D = [\text{VO}^{2+}]_{(o,eq)}/[\text{VO}^{2+}]_{(eq)} \]. Equation (2) represents the basic equation for chelate forming solvent extraction system by a dimeric acidic extractant. All concentrations and pH terms in Equation (2) refer to the equilibrium values. Consequently, Equation (2) represents that the value of log D should be independent of [VO₂⁺] at a set of constant equilibrium pH, [extractant] and [anion]. Corrected D-values (i.e. \( C D \)) at a set of constant equilibrium pH and [extractant] can be calculated by mass-balance (Equation (3)):

\[ \log CD = \log D + m \left( \text{pH}_{(ini)} - \text{pH}_{(eq)} \right) \]

\[ + x \left\{ \log \left[ H_2A_2 \right]_{(o,ini)} - \left[ \log \left[ H_2A_2 \right]_{(o,ini)} \right) \right\} \]

\[ + x \left( \text{VO}^{2+} \right)_{(o,eq)} \]

Where, \[ m = (2-n+z) \] and \( \text{pH}_{(eq)} \] = 1.5 and \( x = \text{extractant dependence} \]
= 2.00 and all concentration terms are in mol/L. Moreover, as $K_r$ is related to temperature by the Van’t Hoff equation, log $\text{CD}$ will also depend on temperature.

3. Results and Discussion

3.1. Extraction Equilibrium

Through running some preliminary experiments, it has been found that V(IV) is extractable by Cyanex 302 at pH around 3.0. When 0.20 g/L V(IV) existing in the aqueous phase at pH$_{\text{ini}}$ 4.00 containing 0.02 mol/L $\text{SO}_4^{2-}$ was extracted with 0.15 mol/L $\text{H}_2\text{A}_2$ in kerosene at 303 K and O/A = 1, then it was found that the $[\text{V(IV)}]_{(o)}$ was increased up to phase contact of 18 min. Therefore the equilibration time is about 18 min; but 20 min has been used subsequently in order to ensure equilibrations.

The variation of extraction ratio with $[\text{V(IV)}]$ was found out at two different set of experimental parameters. It is found in both cases that the $[\text{V(IV)}]_{(o)}$ is increased, but the value of D is decreased continuously with increasing $[\text{V(IV)}]_{(ini)}$. This is contrary to the general principle of solvent extraction chemistry as suggested by Equation (2) which is valid at constant $[\text{H}_2\text{A}_2]_{(o,eq)}$ and pH$_{eq}$. The observed decreasing behavior might be due to the non-constancy of $[\text{H}_2\text{A}_2]_{(o,eq)}$ and pH$_{eq}$ for various extents of V(IV) extraction. On calculating log $\text{CD}$ (by Equation (3)) on considering $n = 0.60$ (tangential slope at pH$_{eq}$ of 3.41 for 0.10 mol/L Cyanex 302 system) or 0.85 (tangential slope at pH$_{eq}$ of 3.10 for 0.20 mol/L Cyanex 302 system) and $m = 2.00$ (for both systems), the log $\text{CD}$ vs. log $([\text{V(IV)}]_{(ini)}$, mol/L) plots are drawn in Figure 1. The plots are horizontal up to at least $[\text{V(IV)}]_{(ini)}$ of 0.50 g/L. The decreasing behavior of log $\text{CD}$ value with increasing $[\text{V(IV)}]_{(ini)}$ over 0.50 g/L indicates the non-ideality of V(IV) bearing aqueous phase which might be due to the polymerization of V(IV) in the aqueous phase and/or in both phases.

At a constant equilibrium [extractant], the plot of log $\text{CD}$ vs. pH$_{eq}$ should be a straight line (cf. Equation (2)) with slope equaling to “$2 - n + z$” (the number of H$^+$ liberated). The log $\text{CD}$ values are calculated accordingly. Figure 2 represents log $\text{CD}$ vs. pH$_{eq}$ plots at constant $[\text{H}_2\text{A}_2]_{(o,eq)}$ of 0.10 and 0.20 mol/L. In both cases, straight lines are not obtained. Curves with limiting slopes of ~2 are obtained at $l.pH.r$ (below pH 2.25), whilst the tangential slope at pH = 4.0 is ~0.30 in both cases. At pH ~2.9, the tangential slope is unity. The unity sloped tangential lines have intercepts of ~3.04 and ~2.34 for 0.10 and 0.20 mol/L Cyanex 302 systems, respectively. The respective intercepts of lines having slope 2 are ~5.485 and ~4.845. It is concluded from this result that the pH dependence is dependent of equilibrium pH range used; two H$^+$ ions are liberated per V(IV) being extracted whence pH$_{eq}$ is kept below 2.25; and with increasing pH$_{eq}$ value, the number of H$^+$ ions liberated per V(IV) being extracted is decreased from 2 to 1 at pH$_{eq}$ of 2.9 and 0.3 at pH$_{eq}$ of 4.0.

According to Equation (2), the plot of log $\text{CD}$ vs. log $[\text{H}_2\text{A}_2]_{(o,eq)}$ at a particular constant pH$_{eq}$ should be a straight line with slope giving the mole ratio (x) of Cyanex 302/V(IV) in extractable species. The log $\text{CD}$ vs. log $[\text{Cyanex 302}]_{(o,eq)}$, mol/L plots at two sets of parametric conditions are shown in Figure 3. Straight lines are obtained with slopes equaling to ~2 in both cases. The intercepts of the lines are 2.07 and 2.30 for pH$_{ini}$ systems of 3.8 and 4.2, respectively. It is therefore
concluded that for the V(IV)-chelate extraction, 2 moles of Cyanex 302 is needed to extract 1 g ion of V(IV) i.e.
the value of “x” in Equations (2) and (3) is 2.

Co-existing anion in the aqueous phase often affects the extraction characteristics of a metal ion by an extractant, particularly when the extraction occurs via the ion-pair formation and solvation mechanisms. In chelate forming extraction systems, the co-existing anion may take part in chelate formation and also the chelate formation may be hindered by the prior formation of metal-co-existing anion complex. Since the extraction has been carried out from sulphate medium, the effect of [\text{SO}_4^{2-}] on extraction has been studied. The related plot is displayed in Figure 4. Experimental points fall on a curve rather than on a straight line. In l.c.r of \text{SO}_4^{2-}, CD is seldom changed, whilst in the h.c.r of \text{SO}_4^{2-}, it is considerably decreased with increasing[\text{SO}_4^{2-}]. Curves in figure are theoretical and represented by:

\[
\log C D = 0.14(\bullet), 0.95(\triangledown) - \log \left(1 + 2.24 \left[\text{SO}_4^{2-}\right]\right) \tag{4}
\]

Where, 2.24 is the value of \(K_{\text{SO}_4}\) as derived by the curve fitting method. Intercepts of the asymptotes at h.c.r of sulphate ion are −0.24 and 0.59 for 0.10 and 0.20 mol/L Cyanex 302 systems, respectively, whilst the respective intercepts at l.c.r of \text{SO}_4^{2-} are 0.14 and 0.95.

The Van’t Hoff plots for the investigated system at two sets of experimental parameters are shown in Figure 5. In both cases, it is found that the extraction ratio is increased with increasing temperature but the straight line relationship does not hold. Slopes of the lines at h.t.r are −1100 and −1400 and at l.t.r are −4600 and −4400 for 0.10 and 0.20 mol/L Cyanex 302 systems, respectively. From the slopes of the plots, the apparent ΔH values have been calculated as 21.80 and 27.7 kJ/mol at h.t.r and 91.1 and 87.1 kJ/mol at l.t.r for 0.10 and 0.20 mol/L Cyanex 302 systems, respectively. The extraction of V(IV) by Cyanex 302 is therefore, extensively increased with increasing temperature (endothermic) with ΔH value of ~25 kJ/mol at h.t.r and of ~90 kJ/mol at l.t.r. It is evident from these studies that the value of “x” is 2 irrespective of the experimental parameter but the value of “z” is 0 at low [\text{SO}_4^{2-}] and 1 at high [\text{SO}_4^{2-}]. The value of “2 − n + z” is 2 in low pH(eq), 1 in intermediate pH(eq), and 0.3 in high pH(eq). At l.c.r of \text{SO}_4^{2-} and at low pH(eq), 2 − n + z = 2 implies that n = 0; but at intermediate pH(eq), 2 − n + z = 1 implies that n = 1, and finally at high pH(eq), 2 − n + z = 0.30 implies that n = 1.70. On the other hand, at h.c.r of \text{SO}_4^{2-} and at low pH(eq), 2 − n + z = 2 implies n = 1; but at intermediate pH(eq), 2 − n + z = 1 implies n = 2 (possibly representing one bisulphate and one hydroxide.

\[
\text{Figure 3. Effect of [Cyanex 302]. [V(IV)] = 200 mg/L, Temp. = (303 ± 0.5) K, Eq. time = 20 min, O/A = 1 (O = 20 mL), }\]
\[

\text{[SO}_4^{2-}\text{]} = 0.02\text{mol/L. (●) pH(initial) = 3.8, pH(equil.) const. = 3.12; S = 2.00, l = 2.07; (○) pH(initial) = 4.2, pH(equil.) const. = 3.35; S = 2.00, l = 2.30.}
\]

\[
\text{Figure 4. Effect of [SO}_4^{2-}\text{]. pH(initial) = 4.2, [V(IV)] = 200 mg/L, Temp. = (303 ± 0.5) K, Eq. time = 20 min, O/A = 1 (O = 20 mL). (●), [Cyanex 302] = 0.10 mol/L, pH(equil.) const. = 3.85; (○), [Cyanex 302] = 0.20 mol/L, pH(equil.) const. = 3.79}
\]

\[
\text{Figure 5. Effect of temperature. [V(IV)] = 200 mg/L, Eq. time = 20 min, [SO}_4^{2-}\text{] = 0.02 mol/L, O/A = 1 (O = 20 mL). (●), pH(initial) = 4.40, pH(equil.) const. = 3.45, [Cyanex 302] = 0.10 mol/L; S = −1100, ΔH = 21.80 kJ/mol (h.t.r); S = −4600, ΔH = 91.1 kJ/mol (l.t.r); (○), pH(initial) = 3.80, pH(equil.) const. = 3.10, [Cyanex 302] = 0.20 mol/L; S = −1400, ΔH = 27.70 kJ/mol (h.t.r); S = −4400, ΔH = 87.1 kJ/mol (l.t.r).}
\]
being complexed with \( \text{VO}^{2+} \) and at high pH(eq), \( 2 - n + z = 0.30 \) implies \( n = 2.70 \) (possibly representing almost one/two bisulphate and two/one hydroxide being complexed with \( \text{VO}^{2+} \)).

3.2. Evaluation of Extraction Equilibrium Constant

The foregoing experimental results give the equation for \( \text{Cu} \) at 303 K as:

\[
\log \frac{\text{Cu}}{\text{D}} = \log K_{ex} + x \log \text{Cu}_{(o)} + 2 \log \text{Cyanex 302}_{(o)} - \log (1 + 2.24 \text{[SO}_4^{2-}]) \tag{5}
\]

Based on the Equation (5), the value of \( \log K_{ex} \) has been evaluated from intercepts of the straight lines or asymptotic lines in Figures 2-4. The evaluated values of \( \log K_{ex} \) from different parametric studies are shown in Table 1. It is observed that the value of \( \log K_{ex} \) is extensively increased with increasing the value of pH(eq) or decreasing the value of “x”. The log \( K_{ex} \) value of \( -3.447 \) for \( x = 2 \) is increased to \( -0.972 \) for \( x = 1 \) and to 1.508 for \( x = 0.3 \). The variation of the value of log \( K_{ex} \) with pH(eq) is given in Figure 6. The figure also shows the variation of “x” with pH(eq). It is seen that as the value of “x” decreases, the value of log \( K_{ex} \) increases tremendously.

3.3. Extraction Mechanism

The foregoing results lead to the following expression relating the equilibrium constant with extraction ratio in the extraction of 0.20 g/L V(IV) (which will also be valid up to 700 mg/L V(IV)) at 303 K:

\[
K_{ex} = \frac{\text{Cu}}{\text{D}} \left(1 + 2.24 \text{[SO}_4^{2-}]\right) \tag{6}
\]

At l.c.r of [SO\(_4^{2-}\)], \( 1 >> 2.24 \text{[SO}_4^{2-}] \), so that Equation (6) becomes:

\[
K_{ex} = \frac{\text{Cu}}{\text{D}} \left(\text{H}^+\right)^2 \tag{7}
\]

Equation (7) suggests the following general chemical reaction as the extraction equilibrium reaction:

\[
\text{VO(OH)}_{2-} + 2\text{H}_2\text{A}_{2(o)} \rightleftharpoons \text{VO(HA)}_{2-} \tag{8}
\]

When \( x = 2 \) i.e. at pH(eq) \( \leq 2.25 \), Equation (8) becomes:

\[
\text{VO}^{2+} + 2\text{H}_2\text{A}_{2(o)} \rightleftharpoons \text{VO(HA)}_{2-} + 2\text{H}^+ \tag{9}
\]

and when \( x = 1 \) i.e. at pH(eq) \( \approx 2.90 \), Equation (8) becomes:

\[
\text{VO(OH)}^+ + 2\text{H}_2\text{A}_{2(o)} \rightleftharpoons \text{VO(HA)}_{2-} + \text{H}^+ + \text{H}_2\text{O} \tag{10}
\]

and when \( x = 0 \) i.e. at pH(eq) somewhere greater than 4, Equation (8) becomes:

\[
\text{VO(OH)}_{2-} + 2\text{H}_2\text{A}_{2(o)} \rightleftharpoons \text{VO(HA)}_{2-} + 2\text{H}_2\text{O} \tag{11}
\]

It is therefore seen that the hydrolysis of \( \text{VO}^{2+} \) starts around pH 2.25 and consequently the pH dependence starts to decrease. It is reported that the values of \( \beta_{\text{VO(OH)}_2} \) and \( \beta_{\text{VO(OH)}_3} \) are \( 10^{0.56} \) and \( 10^{0.83} \), respectively [21]. As evaluated before, the equilibrium constant for the reaction given by Equation (9) is \( 10^{3.447} \) and that by Equation (10) is \( 10^{3.428} \). For Equation (11), the equilibrium constant will be somewhat greater than \( 10^{3.466} \). At h.c.r of \( \text{SO}_4^{2-} \), \( 1 \ll 2.24 \text{[SO}_4^{2-}] \); so that Equation (6) becomes:

| Fig. No. | pH(eq) | [H\(_2\text{A}_2\)]_{(o)} | [S\(_2\text{O}_4\)]_{(o)} | Intercept | Apparent log K\(_{ex}\) | Avg. log K\(_{ex}\) |
|----------|--------|--------------------------|--------------------------|------------|------------------------|------------------------|
| 1) pH\(_{eq}\) \leq 2.25; pH dependence = 2.0 | variable | 0.10 | 0.02 | -5.485 | -3.466 | -3.447 |
| 2 | variable | 0.20 | 0.02 | -4.845 | -3.428 |
| 2) pH\(_{eq}\) = 2.50; pH dependence = 1.5 | variable | 0.10 | 0.02 | -4.295 | -2.276 | -2.250 |
| 2 | variable | 0.20 | 0.02 | -3.640 | -2.223 |
| 3) pH\(_{eq}\) = 2.90; pH dependence = 1.0 | variable | 0.10 | 0.02 | -3.040 | -1.021 | -0.972 |
| 2 | variable | 0.20 | 0.02 | -2.340 | -0.923 |
| 4) pH\(_{eq}\) = 3.10; pH dependence = 0.8 | variable | 0.10 | 0.02 | -3.255 | -0.336 |
| 2 | variable | 0.20 | 0.02 | -1.740 | -0.323 |
| 3 | variable | 0.31 | 0.02 | 2.070 | -0.400 | 0.140 (l.c.r) | -0.356 | -0.360 |
| 4 | variable | 0.31 | 0.10 | -0.240 | -0.386 | (h.c.r) |
| 5) pH\(_{eq}\) = 3.35; pH dependence = 0.6 | variable | 0.10 | 0.02 | -1.61 | 0.409 |
| 2 | variable | 0.20 | 0.02 | -1.07 | 0.347 |
| 3 | variable | 0.35 | 0.02 | 2.30 | 0.309 | 0.346 |
| 4 | variable | 0.35 | 0.20 | 0.59 (h.c.r) | 0.328 |
| 6) pH\(_{eq}\) = 4.00; pH dependence = 0.30 | variable | 0.10 | 0.02 | -0.465 | 1.554 | 1.508 |
| 2 | variable | 0.20 | 0.02 | 0.045 | 1.462 | 1.388 |
increases in the following order with the variation of diluent: \( \text{CHCl}_3 \) (\( D = 0.85 \)) < \( \text{CCl}_4 \) (\( D = 3.01 \)) < cyclo-\( \text{C}_6\text{H}_{12} \) (\( D = 3.01 \)) < kerosene (\( D = 3.45 \)) < \( \text{C}_6\text{H}_5\text{Cl} \) (\( D = 4.01 \)) = \( \text{n-C}_6\text{H}_{16} \) (\( D = 4.01 \)) = 1.2-\( \text{C}_6\text{H}_4\text{Cl}_2 \) (\( D = 4.01 \)) < petroleum benzin (\( D = 4.72 \)) = \( \text{C}_6\text{H}_4\text{-CH}_3 \) (\( D = 4.72 \)) < \( \text{C}_6\text{H}_6 \) (\( D = 5.68 \)) = \( \text{C}_6\text{H}_5\text{-CH}_3 \) (\( D = 5.68 \)). The study helps draw the conclusion that \( \text{C}_6\text{H}_6 \) and \( \text{C}_6\text{H}_5\text{-CH}_3 \) are very good diluents followed by petroleum benzin and cyclo-\( \text{C}_6\text{H}_{12} \). 77.54% \( \text{V(IV)} \) extraction in kerosene phase can be increased to about 85.02% \( \text{V(IV)} \) extraction in \( \text{C}_6\text{H}_6 \) or \( \text{C}_6\text{H}_5\text{-CH}_3 \) phase whilst reduced to ~46% \( \text{V(IV)} \) extraction in the \( \text{CHCl}_3 \) phase.

### 3.5. Loading of Cyanex 302 with \( \text{V(IV)} \)

The loading of \( \text{V(IV)} \) into the kerosene solution of Cyanex 302 is presented in Figure 7. It is observed that the loading of the organic phase with \( \text{V(IV)} \) is ended up at the 11th contact. An aliquot of 1 L Cyanex 302 solution of concentration 0.20 mol/L is saturated with 4.96 g \( \text{V(IV)} \) and so the loading capacity is calculated to be about 4.05 g \( \text{V(IV)} \) per 100 g of Cyanex 302. The loading capacity is considerably low for the system, and so it cannot be recommended for a large scale separation of \( \text{V(IV)} \) from an aqueous solution. The extraction of 4.96 g \( \text{V(IV)} \)/L by 1 L 0.20 molar Cyanex 302 at saturated loading implies the Cyanex 302/\( \text{V(IV)} \) mole ratio of 2.05 which is slightly higher than that (2.00) obtained from the extractant dependence studies. This slight variation may be due to extractant loss for partitioning (aqueous solubility) on repeated contact with fresh amounts of the diluent.

### Table 2. Effect of diluent on extraction.

| Diluent            | \([\text{V(IV)}]_{\text{org}}\) mg/L | \([\text{V(IV)}]_{\text{aq}}\) mg/L | \( D \) | % of extraction |
|--------------------|--------------------------------------|-------------------------------------|--------|----------------|
| Carbon tetrachloride| 49.9                                 | 150.1                               | 3.01   | 75.04          |
| Chlorobenzene      | 39.9                                 | 160.1                               | 4.01   | 80.03          |
| Petroleum benzin   | 34.9                                 | 165.1                               | 4.72   | 82.53          |
| n-Heptane          | 39.9                                 | 160.1                               | 4.01   | 80.03          |
| Benzene            | 30.0                                 | 170.0                               | 5.68   | 85.02          |
| Toluene            | 30.0                                 | 170.0                               | 5.68   | 85.02          |
| Cyclohexane        | 49.9                                 | 150.1                               | 3.01   | 75.04          |
| 1,2-dichloroethane | 39.9                                 | 160.1                               | 4.01   | 80.03          |
| Xylene             | 34.9                                 | 165.1                               | 4.72   | 82.53          |
| Chloroform         | 108.2                                | 91.8                                | 0.85   | 45.92          |
| Kerosene           | 44.9                                 | 155.1                               | 3.45   | 77.54          |

assuming that \( \beta_{\text{VOHSO}} \) is \( 10^{24} \) [21].

### 3.4. Effect of Diluent

As the diluent may tremendously affect the metal-ion distribution in a solvent extraction process, the extraction ratios have been measured when \( \text{V(IV)} \) in the same aqueous phase has been extracted by 0.15 mol/L \( \text{H}_2\text{A}_2 \) solutions dissolved in different diluents keeping all other parametric conditions identical. The results are represented in Table 2. It is observed that the extraction ratio
aqueous phase by the same organic phase. The loading results indicate that the mechanism of extraction at high loading is not changed from that suggested at low loading i.e. in equilibrium studies.

3.6. Stripping of Ti(IV)-Loaded Organic Phase by Mineral Acids

The maximum V(IV) loaded organic phase containing 4.96 g/L V(IV) with theoretically no free-extractant, after proper dilution and adjustment of free extractant concentration, has been subjected for stripping study with 0.1, 0.3 and 1.0 mol/L H₂SO₄, HNO₃ and HCl solutions at 303 K and at O/A of 1. The stripping results are given in Table 3. It is found that stripping percentage is more or less acceptable in all three acids used alone. In all cases, stripping percentage is increased with increasing concentration of acid. It is seen that 90% stripping by 0.10 mol/L H₂SO₄ is increased to 100% stripping by 1.00 mol/L H₂SO₄. Similarly, 80% stripping by 0.10 mol/L HCl is increased to 95% stripping with 1.00 mol/L HCl; whereas, 86.42% stripping by 0.10 mol/L HNO₃ is increased to 100% stripping by 1.00 mol/L HNO₃. Sulfuric acid or nitric acid (1 mol/L) is sufficient to strip off V(IV) quantitatively. Hydrochloric acid can also be used in stripping if more than one-stage stripping is practiced or more concentrated solution being used.

3.7. Separation Ability of V(IV) from Some Other Metal Ions

In order to examine the effectiveness of Cyanex 302 towards the mutual separations of V(IV) from some 3d-block metal ions viz. Ti(IV), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II), the extraction percentages of these metal ions have been estimated while 0.20 g/L metal ion being extracted from 0.10 mol/L (or, [H₂SO₄] = [H₂SO₄] or 0.10 mol/L, Temp = 303 K, O/A = 1 (O = 20 mL), Equilibration time = 1 h. The extraction results given in Table 4, which predict the following:

Table 3. Stripping of V(IV) loaded organic phase using different acid solutions. [V(IV)]₀ = 200 mg/L, [Cyanex 302]₀ = 0.20 mol/L, pH (eq) = 0.04 mol/L, Equilibration time = 20 min, Temp. = (303 ± 0.5) K, O/A = 1 (O = 20 mL).

| Stripping agent | Acid concentration, mol/L | [V(IV)]₀mg/L | % of V(IV) stripped |
|-----------------|---------------------------|--------------|---------------------|
| H₂SO₄           | 0.10                      | 180.0        | 90.00               |
|                 | 0.30                      | 187.0        | 93.58               |
|                 | 1.00                      | 200.0        | 100.00              |
|                 | 0.10                      | 160.0        | 80.00               |
| HCl             | 0.30                      | 170.0        | 85.00               |
|                 | 1.00                      | 190.0        | 95.00               |
|                 | 0.10                      | 172.0        | 86.42               |
| HNO₃            | 0.30                      | 180.0        | 90.00               |
|                 | 1.00                      | 200.0        | 100.00              |

NE: non-extractable, CE: complete extraction, *aqueous solution becomes cloudy before extraction but becomes clear after extraction.

Table 4. Extraction data of some 3d-block elements by Cyanex 302 dissolved in kerosene. [Cyanex 302] = 0.10 mol/L (in kerosene), [Metal ion] = 0.20 g/L, Temp = 303 K, O/A = 1 (O = 20 mL), Equilibration time = 1 h.

| pH (eq) | V(IV) | Ti(IV) | Fe(III) | Co(II) | Ni(II) | Cu(II) | Zn(II) |
|---------|-------|--------|---------|--------|--------|--------|--------|
| 0.0     | NE    | NE     | 4.0     | NE     | NE     | CE     | NE     |
| 0.5     | NE    | NE     | 17.0    | NE     | NE     | CE     | NE     |
| 1.0     | NE    | 2.6    | 50.0    | NE     | NE     | 0.1    | 2.0    |
| 1.5     | 0.1   | 18.6   | 88.0    | NE     | NE     | 0.2    | 18.0   |
| 2.0     | 3.0   | 52.3   | 93.0    | NE     | NE     | 0.3    | 67.0   |
| 2.5     | 20.0  | 78.5   | 97.0    | 1.0    | NE     | 0.4    | 92.0   |
| 3.0     | 50.0  | 92.0   | 99.0    | 8.0    | NE     | 0.5    | 98.0   |
| 3.5     | 72.5  | 98.0   | 26.0    | NE     | 0.6    | 99.5   |
| 4.0     | 94.0’ | 99.5   | 0.7     | 56.0   | NE     | 0.8    | CE     |
| 4.5     | 98.6  | 0.9    | 83.0    | NE     | 0.10   | 0.11   |
| 5.0     | 99.0  | 0.12   | 0.13    | 94.0   | 2.0    | 0.14   | 0.15   |
| 5.5     | CE    | 0.16   | 0.17    | 99.0   | 8.0    | 0.18   | 0.19   |
| 6.0     | 0.20  | 0.21   | 0.22    | CE     | 21.0   | 0.23   | 0.24   |
| 6.5     | 0.25  | 0.26   | 0.27    | 0.28   | 70.0   | 0.29   | 0.30   |
| 7.0     | 0.31  | 0.32   | 0.33    | 0.34   | 92.0   | 0.35   | 0.36   |

NE: non-extractable, CE: complete extraction, *aqueous solution becomes cloudy before extraction but becomes clear after extraction.
1) V(IV) can be completely separated from Cu(II) at pH 1.0 in a single-stage extraction.
2) V(IV) can be separated almost completely from Ni(II) at pH_{eq} 4.50 in a single-stage extraction.
3) It is possible to separate V(IV) from Zn(II) at pH_{eq} 3.50, Co(II) at pH_{eq} 3.50, Fe(III) at pH_{eq} 2.00 and Ti(IV) at pH_{eq} 2.50 on using counter current multi-stage extractions.

4. Conclusions

The following conclusions are drawn:

1) Vanadium(IV) can be extracted by Cyanex 302 at pH above 3.0. The equilibration time is 20 min. Up to at least 0.7 g/L V(IV), the extraction ratio (D) is independent of [V(IV)] in the aqueous phase.

2) D is found to be proportional to [H^+]^{-2.5} at pH_{eq} \leq 2.50, Co(II) at pH_{eq} 3.50, Fe(III) at pH_{eq} 2.00 and Ti(IV) at pH_{eq} 2.50 on using counter current multi-stage extractions.

3) The extraction is highly sensitive to temperature, particularly at l.t.r with ΔH value of ~90 kJ/mol; but at h.t.r it is ~25 kJ/mol.

4) At various concentration levels of experimental parameters, the extraction equilibrium reactions have been proposed; and it is seen that at all conditions [VO(HA2)_2] is the extractable species through reacting V(IV) species in the aqueous phase may vary with its concentration and pH levels.

5) The loading capacity has been determined to be 4.05 g V(IV) per 100 g Cyanex 302; and it indicates that the mechanism of extraction at high loading does not change from that suggested at low loading (extracted species being [VO(HA2)_2]).

6) Aromatic diluents appear as better diluent over other categories; kerosene is a better diluent over CHCl_3, 1,2-C_2H_4Cl_2 and CCl_4.

7) The V(IV)-loaded organic phase can be quantitatively stripped by 1 mol/L H_2SO_4 and HNO_3 in a single stage.

8) Almost complete separations of V(IV) from Cu(II) at pH 1.0 and from Ni(II) at pH_{eq} 4.5 are possible in a single-stage of extraction; whereas, its separation from Zn(II) at pH_{eq} 2.5, Co(II) at pH_{eq} 3.5, Fe(III) at pH_{eq} 2.0 and Ti(IV) at pH_{eq} 2.5 will require counter-current multi-stage extractions.

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