

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

Ranjit Kumar Biswas, Aneek Krishna Karmakar

Department of Applied Chemistry & Chemical Engineering, Rajshahi University, Rajshahi, Bangladesh

Email: rkbiswas53@yahoo.com

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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 [SO₄²⁻]⁻¹ in the lower [SO₄²⁻] (<0.05 mol/L) and higher [SO₄²⁻] (>1 mol/L) regions, respectively. The apparent extraction equilibrium constant (K_{ex}) in 0.02 mol/L SO₄²⁻ medium and at 303 K is found to vary from 10^{-3.447} to 10^{1.508} 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(HA)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 benzine, 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), carnottite (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-trimethylpentylphosphinic acid). The sulphur substitution decreases pK_a 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-

phate 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% R₃PO, 2% - 3% R₂PO₂H, 2% R₂PS₂H and 8% unknown compounds [17] and has been used without further purification as R₃PO, 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-Matthey), 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} , Extraction equilibrium constant;
D, Extraction or distribution ratio;
^cD, D at a constant equilibrium pH and extractant concentration;

β , Stability constant;

K_{SO_4} , A proportionality constant in sulphate dependence study;

H₂A₂, Cyanex 302 (dimeric);

A⁻, Anion of monomeric Cyanex 302;

L⁻, Uni-negative anion existing in the aqueous phase viz.

OH⁻ and HSO₄⁻;

ΔH , Apparent enthalpy change;

R, CH₃-C(CH₃)₂-CH₂-CH(CH₃)-CH₂;

l.c.r., Lower concentration region;

h.c.r., Higher concentration region;

l.pH.r., Lower pH region;

h.pH.r., Higher pH region;

l.t.r., Lower temperature region;

h.t.r., Higher temperature region;

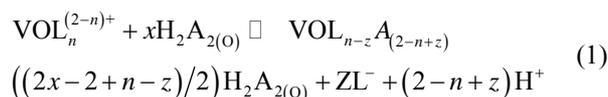
Suffix (o), Organic phase;

(ini), Initial;

(eq), 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 equilibrium at a constant temperature can be represented by:



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

$$\log D = \log K_{ex} + (2 - n + z) \text{pH} + x \log [\text{H}_2\text{A}_2]_{(o)} - z \log [\text{L}^-] \quad (2)$$

Where, $D = [\text{VO}^{2+}]_{(o, eq)} / [\text{VO}^{2+}]_{(aq)}$. 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.* ^cD) at a set of constant equilibrium pH and [extractant] can be calculated by mass-balance (Equation (3)):

$$\log {}^c D = \log D + m \left(\text{pH}_{(ini)} - \text{pH}_{(eq)} \right) + x \left[\log [\text{H}_2\text{A}_2]_{(o, ini)} - \left\{ \log [\text{H}_2\text{A}_2]_{(o, eq)} - x \left[\text{VO}^{2+} \right]_{(o, eq)} \right\} \right] \quad (3)$$

Where, $m = (2 - n + z) = \text{pH dependence} = 2$ (upto $\text{pH}_{(eq)} = 1.5$) and < 2 ($\text{pH}_{(eq)} > 1.5$) and $x = \text{extractant dependence}$

= 2.00 and all concentration terms are in mol/L. Moreover, as K_{ex} is related to temperature by the Van't Hoff equation, $\log {}^C D$ 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 $pH_{(ini)}$ 4.00 containing 0.02 mol/L SO_4^{2-} was extracted with 0.15 mol/L H_2A_2 in kerosene at 303 K and $O/A = 1$, then it was found that the $[V(IV)]_{(o)}$ 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 $[V(IV)]$ was found out at two different set of experimental parameters. It is found in both cases that the $[V(IV)]_{(o)}$ is increased, but the value of D is decreased continuously with increasing $[V(IV)]_{(ini)}$. This is contrary to the general principle of solvent extraction chemistry as suggested by Equation (2) which is valid at constant $[H_2A_2]_{(o,eq)}$ and $pH_{(eq)}$. The observed decreasing behavior might be due to the non-constancy of $[H_2A_2]_{(o,eq)}$ and $pH_{(eq)}$ for various extents of V(IV) extraction. On calculating $\log {}^C D$ (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 $\log {}^C D$ vs. $\log \{[V(IV)]_{(ini)}, \text{mol/L}\}$ plots are drawn in **Figure 1**. The plots are horizontal up to at least $[V(IV)]_{(ini)}$ of 0.50 g/L. The decreasing behavior of $\log {}^C D$ value with increasing $[V(IV)]_{(ini)}$ 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 $\log {}^C D$ vs. $pH_{(eq)}$ should be a straight line (*cf.* Equation (2)) with slope equaling to “ $2 - n + z$ ” (the number of H^+ liberated). The $\log {}^C D$ values are calculated accordingly. **Figure 2** represents $\log {}^C D$ vs. $pH_{(eq)}$ plots at constant $[H_2A_2]_{(o,eq)}$ 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.p.H.r* (below pH 2.25), whilst the tangential slope at $pH = 4.0$ is ~ 0.30 in both cases. At $pH \sim 2.9$, 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;

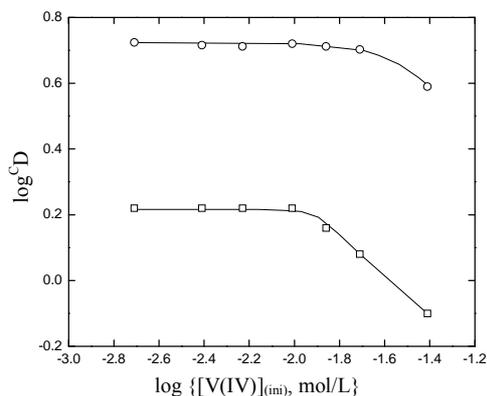


Figure 1. Effect of $[V(IV)]$ on ${}^C D \cdot [SO_4^{2-}] = 0.02 \text{ mol/L}$, Temp. = $(303 \pm 0.5) \text{ K}$, Equilibration time = 20 min, $O/A = 1$ ($O = 20 \text{ mL}$). (\square) $[Cyanex 302] = 0.10 \text{ mol/L}$, $pH_{(ini)} = 4.30$, $pH_{(eq)}$ const. = 3.41; (\circ) $[Cyanex 302] = 0.20 \text{ mol/L}$, $pH_{(ini)} = 3.80$, $pH_{(eq)}$ const. = 3.10.

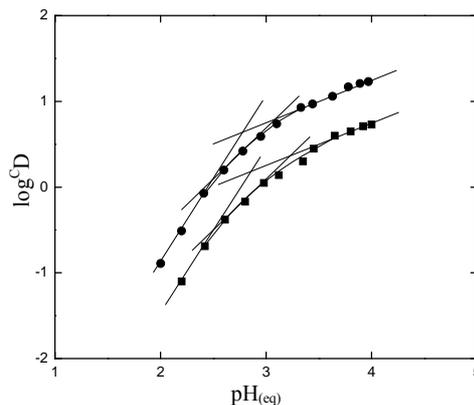


Figure 2. Effect of $pH_{(eq)}$. $[V(IV)]_{(ini)} = 200 \text{ mg/L}$, Temp. = $303 \pm 0.5 \text{ K}$, Eq. time = 20 min, $O/A = 1$ ($O = 20 \text{ mL}$), $[SO_4^{2-}] = 0.02 \text{ mol/L}$. (\square) $[Cyanex 302] = 0.10 \text{ mol/L}$; $S = 2$ ($pH_{(eq)} < 2.25$), 1 ($pH_{(eq)} = 2.9$) and 0.3 ($pH_{(eq)} = 4.0$); $I = -5.485$ (when $S = 2$) and -3.04 (when $S = 1$); (\circ) $[Cyanex 302] = 0.20 \text{ mol/L}$; $S = 2$ ($pH_{(eq)} < 2.25$), 1 ($pH_{(eq)} = 2.9$) and 0.3 ($pH_{(eq)} = 4.0$); $I = -4.845$ (when $S = 2$) and -2.34 (when $S = 1$).

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 $\log {}^C D$ vs. $\log [H_2A_2]_{(o,eq)}$ 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 $\log {}^C D$ vs. $\log \{[Cyanex 302]_{(o,eq)}, \text{mol/L}\}$ 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

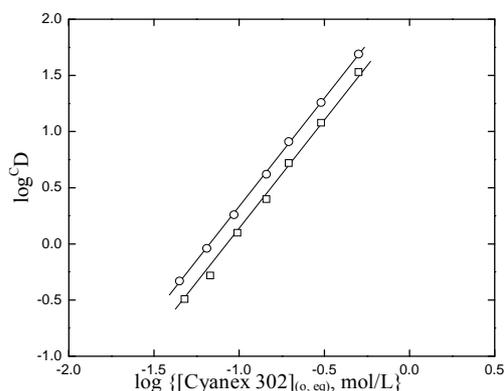


Figure 3. Effect of [Cyanex 302]. [V(IV)] = 200 mg/L, Temp. = (303 ± 0.5) K, Eq. time = 20 min, O/A = 1 (O = 20 mL), $[\text{SO}_4^{2-}] = 0.02$ mol/L. (□) $\text{pH}_{(\text{ini})} = 3.8$, $\text{pH}_{(\text{eq})}$ const. = 3.12; $S = 2.00$, $I = 2.07$; (○) $\text{pH}_{(\text{ini})} = 4.2$, $\text{pH}_{(\text{eq})}$ const. = 3.35; $S = 2.00$, $I = 2.30$.

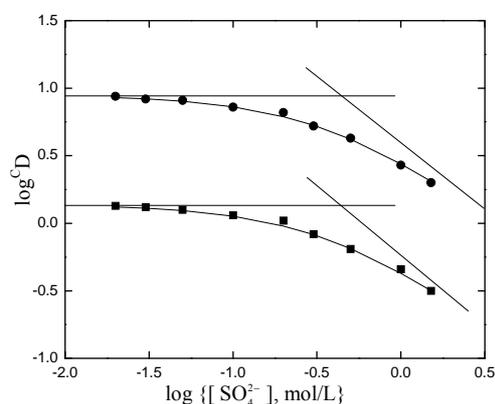


Figure 4. Effect of $[\text{SO}_4^{2-}]$. $\text{pH}_{(\text{ini})} = 4.2$, [V(IV)] = 200 mg/L, Temp. = (303 ± 0.5) K, Eq. time = 20 min, O/A = 1 (O = 20 mL). (■), [Cyanex 302] = 0.10 mol/L, $\text{pH}_{(\text{eq})}$ const. = 3.85; (●), [Cyanex 302] = 0.20 mol/L, $\text{pH}_{(\text{eq})}$ const. = 3.79

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 SO_4^{2-} , cD is seldom changed, whilst in the *h.c.r* of SO_4^{2-} , it is considerably decreased with increasing $[\text{SO}_4^{2-}]$. Curves in figure are theoretical and represented by:

$$\log ^c D = 0.14(\blacksquare), 0.95(\bullet) - \log(1 + 2.24[\text{SO}_4^{2-}]) \quad (4)$$

Where, 2.24 is the value of K_{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 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

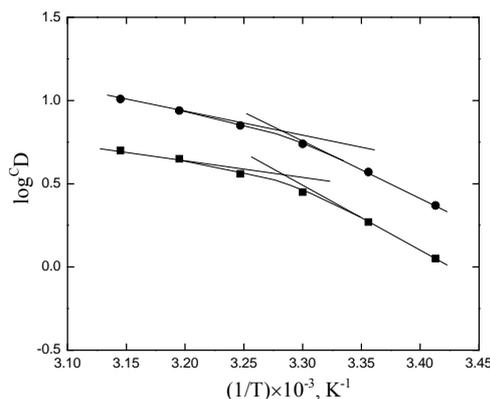


Figure 5. Effect of temperature. [V(IV)] = 200 mg/L, Eq. time = 20 min, $[\text{SO}_4^{2-}] = 0.02$ mol/L, O/A = 1 (O = 20 mL). (■), $\text{pH}_{(\text{ini})} = 4.40$, $\text{pH}_{(\text{eq})}$ const. = 3.45, [Cyanex 302] = 0.10 mol/L; $S = -1100$, $\Delta H = 21.80$ kJ/mol (*h.t.r*); $S = -4600$, $\Delta H = 91.1$ kJ/mol (*l.t.r*); (●), $\text{pH}_{(\text{ini})} = 3.80$, $\text{pH}_{(\text{eq})}$ const. = 3.10, [Cyanex 302] = 0.20 mol/L; $S = -1400$, $\Delta H = 27.70$ kJ/mol (*h.t.r*); $S = -4400$, $\Delta H = 87.1$ kJ/mol (*l.t.r*).

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 $\text{pH}_{(\text{eq})}$, 1 in intermediate $\text{pH}_{(\text{eq})}$, and 0.3 in high $\text{pH}_{(\text{eq})}$. At *l.c.r* of SO_4^{2-} and at low $\text{pH}_{(\text{eq})}$, $2 - n + z = 2$ implies that $n = 0$; but at intermediate $\text{pH}_{(\text{eq})}$, $2 - n + z = 1$ implies that $n = 1$, and finally at high $\text{pH}_{(\text{eq})}$, $2 - n + z = 0.30$ implies that $n = 1.70$. On the other hand, at *h.c.r* of SO_4^{2-} and at low $\text{pH}_{(\text{eq})}$, $2 - n + z = 2$ implies $n = 1$; but at intermediate $\text{pH}_{(\text{eq})}$, $2 - n + z = 1$ implies $n = 2$ (possibly representing one bisulphate and one hydroxide

being complexed with VO^{2+}) and at high $\text{pH}_{(\text{eq})}$, $2 - n + z = 0.30$ implies $n = 2.70$ (possibly representing almost one/two bisulphate and two/one hydroxide being complexed with VO^{2+}).

3.2. Evaluation of Extraction Equilibrium Constant

The foregoing experimental results give the equation for $^{\text{C}}\text{D}$ at 303 K as:

$$\log ^{\text{C}}\text{D} = \log K_{\text{ex}} + x\text{pH}_{(\text{eq})} + 2\log [\text{Cyanex 302}]_{(\text{o,eq})} - \log (1 + 2.24 [\text{SO}_4^{2-}]) \quad (5)$$

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

3.3. Extraction Mechanism

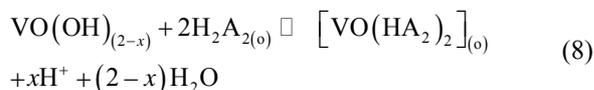
The foregoing results lead to the following expression relating the equilibrium constant with extraction ratio in the extraction of 0.20 g/L V(IV) (which will also be valid up to 700 mg/L V(IV)) at 303 K:

$$K_{\text{ex}} = ^{\text{C}}\text{D} [\text{H}^+]^x (1 + 2.24 [\text{SO}_4^{2-}]) / [\text{H}_2\text{A}_2]_{(\text{o})}^2 \quad (6)$$

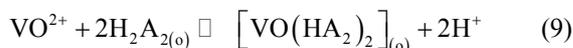
At *l.c.r* of $[\text{SO}_4^{2-}]$, $1 \gg 2.24 [\text{SO}_4^{2-}]$, so that Equation (6) becomes:

$$K_{\text{ex}} = ^{\text{C}}\text{D} [\text{H}^+]^x / [\text{H}_2\text{A}_2]_{(\text{o})}^2 \quad (7)$$

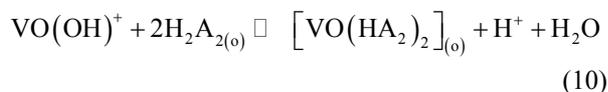
Equation (7) suggests the following general chemical reaction as the extraction equilibrium reaction:



When $x = 2$ *i.e.* at $\text{pH}_{(\text{eq})} \leq 2.25$, Equation (8) becomes:



and when $x = 1$ *i.e.* at $\text{pH}_{(\text{eq})} \approx 2.90$, Equation (8) becomes:



and when $x = 0$ *i.e.* at $\text{pH}_{(\text{eq})}$ somewhere greater than 4, Equation (8) becomes:



It is therefore seen that the hydrolysis of VO^{2+} starts around pH 2.25 and consequently the pH dependence starts to decrease. It is reported that the values of $\beta_{\text{VO}(\text{OH})^+}$ and $\beta_{\text{VO}(\text{OH})_2}$ are $10^{7.9}$ and $10^{18.31}$, 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 $10^{-0.972}$. For Equation (11), the equilibrium constant will be somewhat greater than $10^{1.508}$. At *h.c.r* of SO_4^{2-} , $1 \ll 2.24 [\text{SO}_4^{2-}]$; so that Equation (6) becomes:

Table 1. Evaluation of the approximate apparent K_{ex} values at various $\text{pH}_{(\text{eq})}$ and at 303 K ($[\text{V}(\text{IV})] = 0.20$ g/L).

Fig. No.	$\text{pH}_{(\text{eq})}$	$[\text{H}_2\text{A}_2]_{(\text{o})}$, mol/L	$[\text{SO}_4^{2-}]$, mol/L	Intercept (I)	Apparent $\log K_{\text{ex}}$	Avg. $\log K_{\text{ex}}$
1) $\text{pH}_{(\text{eq})} \leq 2.25$; pH dependence = 2.0						
2	variable	0.10	0.02	-5.485	-3.466	-3.447
		0.20	0.02	-4.845	-3.428	
2) $\text{pH}_{(\text{eq})} = 2.50$; pH dependence = 1.5						
2	variable	0.10	0.02	-4.295	-2.276	-2.250
		0.20	0.02	-3.640	-2.223	
3) $\text{pH}_{(\text{eq})} = 2.90$; pH dependence = 1.0						
2	variable	0.10	0.02	-3.040	-1.021	-0.972
		0.20	0.02	-2.340	-0.923	
4) $\text{pH}_{(\text{eq})} = 3.10$; pH dependence = 0.8						
2	variable	0.10	0.02	-2.355	-0.336	-0.360
		0.20	0.02	-1.740	-0.323	
3	3.12	variable	0.02	2.070	-0.400	-0.360
4	3.12	0.10	variable	0.140 (<i>l.c.r</i>)	-0.356	
				-0.240 (<i>h.c.r</i>)	-0.386	
5) $\text{pH}_{(\text{eq})} = 3.35$; pH dependence = 0.6						
2	variable	0.10	0.02	-1.61	0.409	0.346
		0.20	0.02	-1.07	0.347	
3	3.35	variable	0.02	2.30	0.309	0.346
4	3.35	0.20	variable	0.95 (<i>l.c.r</i>)	0.338	
				0.59 (<i>h.c.r</i>)	0.328	
6) $\text{pH}_{(\text{eq})} = 4.00$; pH dependence = 0.30						
2	variable	0.10	0.02	-0.465	1.554	1.508
		0.20	0.02	0.045	1.462	

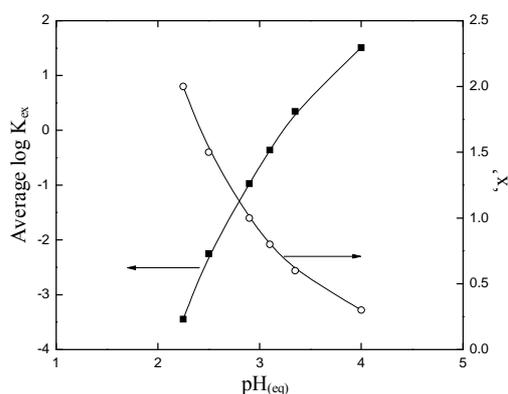
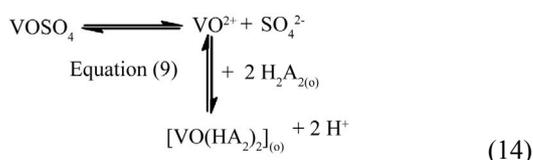
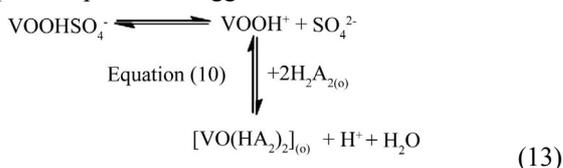


Figure 6. The approximate apparent extraction equilibrium constant (K_{ex}) at various equilibrium pH ($pH_{(eq)}$) at 303 K and for $[V(IV)]$ of 0.20 g/L.

$$K_{ex} = 2.24^C D [H^+]^x [SO_4^{2-}] / [H_2A_2]_{(o)}^2 \quad (12)$$

Equation (12) suggests the liberation of sulphate ion during extraction reaction. But at a certain pH, the values of K_{ex} obtained at *l.c.r* and *h.c.r* of sulphate are identical. It is suggested that at *h.c.r* of SO_4^{2-} , the general Equation (8) also represents the extraction equilibrium reaction. But in this case, as the sulphate concentration increases, the free non-sulphated/bisulphated V(IV)-species concentration decreases during the progress of extraction and this gradual depletion is probably compensated through dissociation of sulphated/bisulphated V(IV)-species. It appears therefore that the equilibrium shift occurs between sulphated/bisulphated and non-sulphated/bisulphated species as suggested below



at $pH \sim 2.90$ and ≤ 2.25 , respectively. It is reported that $\beta_{\text{VOHSO}_4^-}$ is $10^{2.44}$ [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 V(IV) in the same aqueous phase has been extracted by 0.15 mol/L H_2A_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

increases in the following order with the variation of diluent: CHCl_3 ($D = 0.85$) < CCl_4 ($D = 3.01$) = cyclo- C_6H_{12} ($D = 3.01$) < kerosene ($D = 3.45$) < $\text{C}_6\text{H}_5\text{Cl}$ ($D = 4.01$) = $n\text{-C}_7\text{H}_{16}$ ($D = 4.01$) = $1,2\text{-C}_2\text{H}_4\text{Cl}_2$ ($D = 4.01$) < petroleum benzin ($D = 4.72$) = $\text{C}_6\text{H}_4\text{-(CH}_3)_2$ ($D = 4.72$) < C_6H_6 ($D = 5.68$) = $\text{C}_6\text{H}_5\text{-CH}_3$ ($D = 5.68$). The study helps draw the conclusion that C_6H_6 and $\text{C}_6\text{H}_5\text{-CH}_3$ are very good diluents followed by petroleum benzin and $\text{C}_6\text{H}_4\text{-(CH}_3)_2$ for the extraction of V(IV) by Cyanex 302. Kerosene is a better diluent over CHCl_3 , CCl_4 and cyclo- C_6H_{12} . 77.54% V(IV) extraction in kerosene phase can be increased to about 85.02% V(IV) extraction in C_6H_6 or $\text{C}_6\text{H}_5\text{-CH}_3$ phase whilst reduced to ~46% V(IV) extraction in the CHCl_3 phase.

3.5. Loading of Cyanex 302 with V(IV)

The loading of 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 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 V(IV) and so the loading capacity is calculated to be about 4.05 g 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 V(IV) from an aqueous solution. The extraction of 4.96 g V(IV)/L by 1 L 0.20 molar Cyanex 302 at saturated loading implies the Cyanex 302/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

Table 2. Effect of diluent on extraction. $[V(IV)]_{(ini)} = 200$ mg/L, $pH_{(ini)} = 4.10$, $[\text{Cyanex 302}] = 0.15$ mol/L, $[\text{SO}_4^{2-}] = 0.02$ mol/L, Temp. = (303 ± 0.5) K, Equilibration time = 1 h, O/A = 1 (O = 20 mL).

Diluent	$[V(IV)]_{(eq)}$, mg/L	$[V(IV)]_{(o eq)}$, 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

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

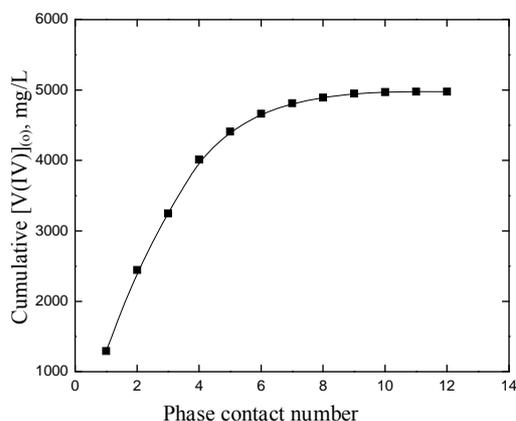


Figure 7. Loading of V(IV) in the organic phase. [V(IV)]_(ini) = 2000 mg/L, [Cyanex 302] = 0.20 mol/L, pH = 6.0, [SO₄²⁻] = 0.04 mol/L, Equilibration time = 20 min, Temp. = (303 ± 0.5) K, O/A = 1 (O = 100 mL).

Table 3. Stripping of V(IV) loaded organic phase using different acid solutions. [V(IV)]_(o) = 200 mg/L, [Cyanex 302]_(o) = 0.10 mol/L, Equilibration time = 1 h, Temp. = (303 ± 0.5) K, O/A = 1 (O = 20 mL).

Stripping agent	Acid concentration, mol/L	[V(IV)] _(aq) , mg/L	% of V(IV) stripped
H ₂ SO ₄	0.10	180.0	90.00
	0.30	187.0	93.58
	1.00	200.0	100.00
HCl	0.10	160.0	80.00
	0.30	170.0	85.00
	1.00	190.0	95.00
HNO ₃	0.10	172.0	86.42
	0.30	180.0	90.00
	1.00	200.0	100.00

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. Sulphuric 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 SO₄²⁻ (or, [SO₄²⁻] = H₂SO₄ when [H₂SO₄] > 0.10 mol/L) medium at different pH_(eq) values by 0.10 mol/L extractant (in kerosene) at 303 K and O/A = 1 (O = 20 mL) after phase mixing of 1 h. The extraction results given in Table 4, which predict the following:

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] = 0.2 g/L; [SO₄²⁻] = [H₂SO₄] or 0.10 mol/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	CE	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	CE	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 $pH_{(eq)}$ 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.

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 $[H^+]^{(-2)-(-0.3)}$, $[Cyanex\ 302]^2$ and $(1+2.24 [SO_4^{2-}])^{-1}$. Apparent K_{ex} value is found to be dependent of pH; it varies from $10^{-3.447}$ at $pH_{(eq)} \leq 2.25$ to $10^{1.508}$ at $pH_{(eq)} = 4.0$.

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 $[VO(HA_2)_2]$ is the extractable species though 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 $[VO(HA_2)_2]$).

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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