Liquid-liquid extraction equilibrium study of vanadium(V) from nitrate medium by technical grade D2EHPA dissolved in kerosene

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Research Article

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Abstract

The titled system was investigated as functions of aqueous pH, [V (V)] and [NO$_3^-$], and organic [D2EHPA]. The system is non-ideal as the log D value decreases with [V (V)]. Two types of mechanisms were identified through the pH dependence study; below pH 2.5, the log D value increases with increasing pH value with a limiting slope of 0.35, whereas, above pH 2.5, the limiting slope is -0.32. The extractant dependence is 0.24. The extraction ratio increases with increasing [NO$_3^-$], showing the salting out effect. Kerosene appears as a suitable diluent. The system is exothermic with $\Delta H = -12.34$ kJ/mol. The loading capacity was 6.11 g V (V)/100 g extractant. A 0.5 mol/L H$_2$SO$_4$ solution appeared to be a suitable stripping agent.

Article Highlights

- The study reports the liquid-liquid extraction equilibrium of vanadium (V) from a nitrate medium using D2EHPA.
- The equation for extraction equilibrium has been established.
- The mechanism and the selectivity for the present investigation have been provided.

1. Introduction

Vanadium and its compounds are in high demand for electronics and high-tech products. Vanadium is a metallic element that has a steel-grey color. It has oxidation states ranging from −1 to +5 [1]. According to the oxidation states, vanadium species show distinct types of color at different pH. The Eh-pH diagram for vanadium species illustrates the presence of vanadium in solution as divalent (violet up to pH 7.0), trivalent (green up to pH 3.5), tetravalent (blue up to pH ~ 4), and pentavalent (yellow up to pH ~ 4.5) ions [2, 3]. The equilibrium Eh-pH diagram for the vanadium-water system [2] demonstrates five solid substances of vanadium such as V, V$_2$O$_2$, V$_2$O$_3$, V$_2$O$_4$, and V$_2$O$_5$. A total of 10 aqueous species (V$^{+2}$, V$^{+3}$, V(OH)$^{+2}$, VO$^{+2}$, V$_4$O$_9$ $^{-2}$, VO$_2^+$, H$_2$V$_{10}$O$_{28}$ $^{-4}$, HV$_{10}$O$_{28}$ $^{-5}$, V$_4$O$_{12}$ $^{-}$, V$_2$O$_7$ $^{3-}$) appear on the diagram at the concentration level of around 1.0 g/L vanadium.

Vanadium is mainly used as an additive in the steel industry (i.e., ferrovanadium) [4]. This alloy produces rust-resistant, spring, high-speed steel apparatus [5].

The secondary sources for vanadium are petroleum desulfurization waste catalysts, tar sand, ash, etc. [6]. A vanadium slag is formed during the smelting of iron ore containing vanadium pentoxide. This slag is used to recover the vanadium metal. Various types of steps are used to retrieve the vanadium compounds (e.g., acid leaching [7], solvent extraction [8], etc.). A wide range of extractants can be used as solvents for the extraction of vanadium, such as tributyl phosphate (TBP) [9], Cyanex 272 [10], Cyanex 301 [11], EHEHPA [12], etc. Analytical grade D2EHPA has been used to extract vanadium (V) from chloride medium [13]. This paper describes vanadium (V) extraction behaviour by technical grade D2EHPA. Technical grade D2EHPA is five times cheaper than the analytical grade, but it contains 2/3 of the D2EHPA and 1/3 of the monoethylhexyl ester [M2EHPA]. It is used industrially as the latter also has the extracting power. This is why the technical grade D2EHPA has been used in this study.
During processing, $V_2O_5$ is formed in the solid state with gangue materials, and it can be readily leached by $HNO_3$ solution. Moreover, $VO^{2+}$ can be readily oxidized by $HNO_3$. Therefore, the extraction study is carried out in a nitrate medium.

$D2EHPA$ separates and purifies several metal ions (e.g., copper(II), cobalt(II), manganese(II), zinc(II), iron(III), cadmium(II), nickel(II), and rare earths) [14]. However, it is also used as an auxiliary extractant to achieve a synergistic effect with other extractants [15].

The study shows the ideal extraction conditions such as time, aqueous phase pH, metal ion concentration, extractant concentration, co-existing anion concentration, and temperature. The stripping of the extracted species by various reagents has been carried out. Furthermore, the best diluent for this system has been screened.

2. Materials and methods

2.1 Materials

Technical grade $D2EHPA$ was acquired from Fluka, Switzerland. Figure 1 displays the chemical structure of pure $D2EHPA$. Ammonium metal vanadate ($NH_4VO_3$) (99%, Riedel-deHain, Germany) was used as a source of vanadium (V). Kerosene was purchased from the local market. Collected kerosene was redistilled over 473–533 K. All the other chemicals were reagent grade and used without further purification.

2.2 Analytical

The aqueous phase vanadium (V) content was estimated spectrophotometrically at 450 nm using a T60 Visible Spectrophotometer (PG Instruments Limited, United Kingdom). The $H_2O_2-H_2SO_4$ method was used [16]. Accurately weighed 2.296 g of A. R. ammonium meta-vanadate, on dissolving with water and making up to 1.0 L, gave a standard vanadium (V) solution, in which 1.0 mL contained 1.0 mg vanadium (V). The aqueous phase pH was measured by the edge® dedicated pH/ORP meter (HI2002-01, Hanna Instruments, USA). Buffer solutions of pH 4 and 7 were used to standardize the pH meter. Moreover, the aqueous phase pH for the experimental purpose was adjusted by anhydrous $Na_2CO_3$.

2.3 Preparation of aqueous and organic phases

The requisite amount of $NH_4VO_3$ was dissolved in 535 mL of 15.44 mol/L $HNO_3$ solution and diluted to 2000 mL to obtain a stock solution containing 10.75 g/L vanadium (V) and 4.14 mol/L $HNO_3$. An aliquot of 25 mL of technical grade $D2EHPA$ was dissolved in redistilled kerosene in a 500 mL volumetric flask and made up to the mark to get a 500 mL stock solution of 5% $D2EHPA$ [17].

2.4 Procedure for equilibrium study

An aliquot of the aqueous phase (20 mL) containing vanadium (V) and nitrate ion at definite concentrations and having definite pH was agitated with an equal aliquot of the organic phase containing the extractant in kerosene (taken in a reagent bottle) for a predetermined time (30 min) at temperature 303 ± 1 K. The phase agitation was made effective by a Stuart Flask Shaker (220 V, 50 Hz, UK). The temperature was controlled by
putting the agitation flasks in a thermostatic water bath (LAUDA B 4 Stainless Steel Bath, Thomas Scientific, USA). After equilibration, phases were allowed to settle within the water bath and disengaged.

Separated aqueous solutions were subjected to determine equilibrium pH values followed by vanadium (V) concentrations. The vanadium (V) concentration in the organic phase at equilibrium was calculated by difference or mass balance. The extraction ratio, D, was then calculated using the following relation:

\[
D = \frac{(C_{V(V)} O (eq))}{(C_{V(V)} A (eq))} = \frac{(C_{V(V)} A (ini)) - C_{V(V)} A (eq))}{C_{V(V)} A (eq))} \quad (1)
\]

2.5 Procedure for loading of V(V) in the organic phase

In loading, an aliquot of 100 mL 5% (v/v) technical grade D2EHPA solution dissolved in kerosene was repeatedly equilibrated with 100 mL portions of the fresh aqueous solution containing 1.66 g/L vanadium (V) and 0.20 mol/L nitrate at pH of 2.00 and temperature 303 K. After each equilibration, the separated aqueous phase was analyzed for its vanadium (V) content. The organic phase vanadium (V) concentration was calculated by the difference. The process continued until the organic phase was saturated with vanadium (V).

2.6 Procedure for stripping study

The stripping procedure was performed by taking 10 mL of an organic phase containing 3.24 g/L vanadium (V) was equilibrated for 30 min at 303 K with an equal volume of either 0.10 mol/L NH₄OH, 0.50 mol/L NH₄OH, 0.10 mol/L NH₄OH + 0.10 mol/L NH₄Cl, 0.90 mol/L NaOH, 0.10 mol/L H₂SO₄, 0.50 mol/L H₂SO₄, 1.0 mol/L H₂SO₄, or 0.50 mol/L HNO₃ acid solutions. The stripping ratio was calculated by dividing vanadium (V) concentration in the aqueous phase by that in the organic phase at equilibrium [18].

3. Results and Discussion

3.1 Effect of phase contact time on the extraction ratio of vanadium (V)

The variation of log D with the variation of the contact time (min) is depicted in Fig. 2. It is found that the concentration ratio of vanadium (V) increases with the increase in phase contact time up to 30 min. With the further increase in the contact time, the value of log D remains unchanged. Therefore, it is concluded that the equilibration time for the current system is about 30 min.

3.2 Effect of metal ion concentration on the extraction ratio of vanadium (V)

The log D vs. log([V(V) (ini)], mol/L) plots are shown in Fig. 3. It is found that in both cases, the extraction ratio decreases with the increase in the initial concentration of vanadium (V) in the aqueous phase. The slope of log D vs log([V(V) (ini)], mol/L) plots are steeper at higher concentration regions than those at lower concentration regions. Therefore, the system appears as non-ideal. The non-ideality, i.e., the decrease in extraction ratio with the increase of vanadium (V) concentration, may be due to the following reasons:
i) Non-constancy of aqueous phase acidity, pH

The equilibrium pH may drop with the initial vanadium (V) ion concentration increase in the aqueous phase. The reason behind this phenomenon is the liberation of H\(^+\) during the extraction process (Eq. 2). It can also rise due to the consumption of H\(^+\) from the solution to form extractable species (Eq. 3).

\[
\begin{align*}
\text{VO}_2^+ + H_2A_2 & \xrightarrow{\text{chelation}} [\text{VO}_2H_2\text{A}_2]\text{(s)} + H^+ \\
V_{10}\text{O}_{26}(\text{OH})_2^{4+} + 4H^+ + H_2A_2& \xrightarrow{\text{Solvated ion pair formed}} H_4V_{10}\text{O}_{26}(\text{OH})_3H_2A_2\text{(s)}
\end{align*}
\] (2) (3)

In the present case, the decrease of pH\(_{\text{eq}}\) from pH\(_{\text{ini}}\) (Fig. 4) is noticed, and this indicates the extraction of the metal ion by a chelation mechanism [19].

<table>
<thead>
<tr>
<th>pH(_{\text{eq}})</th>
<th>% (approximate)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VO(_2^+)</td>
</tr>
<tr>
<td>1.0</td>
<td>99</td>
</tr>
<tr>
<td>1.5</td>
<td>98</td>
</tr>
<tr>
<td>2.0</td>
<td>65</td>
</tr>
<tr>
<td>2.5</td>
<td>24</td>
</tr>
<tr>
<td>3.0</td>
<td>4</td>
</tr>
<tr>
<td>3.5</td>
<td>-</td>
</tr>
<tr>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>4.5</td>
<td>-</td>
</tr>
<tr>
<td>5.0</td>
<td>-</td>
</tr>
<tr>
<td>5.5</td>
<td>-</td>
</tr>
<tr>
<td>6.0</td>
<td>-</td>
</tr>
</tbody>
</table>

ii) Non-constancy of equilibrium extractant concentration

With the increase in the initial vanadium (V) concentration, more extractants will be consumed to form the extractable complex. As a result, the equilibrium extractant concentration will be decreased with the increase in the initial vanadium (V) concentration in the aqueous phase, and the extraction ratio or percent extraction will be decreased, as indicated by the following equation.

\[
\log D = \log K_{\text{ex}} + z \text{pH} + z \log ([H_2A_2]_{\text{ini}} - S) \] (4)
where, $D =$ extraction ratio, $K_{ex} =$ extraction equilibrium constant, $pH =$ equilibrium $pH$ of the aqueous phase, $[H_2A_2]_{(ini)} =$ initial extractant concentration in the organic phase, $S =$ concentration of extractant which is used in forming the metal complex.

Besides these two causes, the decrease in extraction ratio with increasing the initial vanadium (V) concentration may be attributed to the non-ideality of the aqueous phase, i.e., hydrolysis and polymerization of vanadium (V) species in the aqueous phase.

It is known that $VO_2^+$ forms $V_{10}O_{26}(OH)_{24}^-$ on lowering acidity (increasing pH), and this conversion process is probably facilitated by the increase in $VO_2^+$ concentration in the aqueous phase. This conversion might be of the following type:

$$VO_2^+ + 8 H_2O \rightarrow V_{10}O_{26}(OH)_{24}^- + 14 H^+ \ (5)$$

### 3.3 Effect of aqueous pH on the extraction ratio of vanadium (V)

The plot of log $D$ vs. $pH_{(eq)}$ is depicted in Fig. 4. Figure 4 shows that the extraction of vanadium (V) increases with the aqueous equilibrium pH up to ~ 2.50. This phenomenon is the typical characteristic of ion-exchange or chelation type of extraction. However, vanadium (V) extraction is decreased with the increase of aqueous pH above $pH_{(eq)} = 2.50$, which indicates the formation of solvated ion pair. The limiting slopes of the two portions of the curve are calculated. For cation exchange reactions, the pH dependency (slope of log $D$ vs. $pH_{(eq)}$ plot) should be positive due to the liberation of $H^+$ by extraction reaction. This slope is 0.35. The negative pH-dependency (negative slope of log $D$ vs. $pH_{(eq)}$ plot) is indicative of the association of $H^+$ with existing vanadium (V) species to form the extractable species, and this slope is estimated as -0.32.

According to Zeng and Cheng [20], yellow colored $VO_2^+$ exists within pH 1–2, whereas, within pH 2-6.50, orange red $V_{10}O_{28}^{-6}$ exists. However, it is also reported that with the gradual increase of pH from zero, $VO_2^+$ is gradually transformed to VO(OH)$_3$ (to a small extent), $V_{10}O_{26}(OH)_{24}^-$, $V_{10}O_{27}(OH)_{5}^-$, $V_{10}O_{28}^{-6}$, $V_3O_9^{3-}$, $V_4O_{12}^{4-}$, $VO_2(OH)_{2}^{-}$ etc. $V_{10}O_{26}(OH)_{24}^-$ is virtually doubly protonated $V_{10}O_{28}^{-6}$; whereas $V_{10}O_{27}OH^{-5}$ is single protonated $V_{10}O_{28}^{-6}$. The distribution of these species as a function of pH is also available, as shown in Table 1.

Figure 4 also includes the % of existing vanadium (V) species at various pH values. It is seen that aqueous pH of value up to 1.50 in solution persists to exist $VO_2^+$ mainly (98%). Hence, the principal reaction responsible for V(V) extraction in this region follows the ion-exchange reaction.

$$VO_2^+ + nH_2A_{2(o)} \rightleftharpoons VO_2.HA_{2(o)}.{(n-1)H_2A_2(o)} + H^+ \ (6)$$

According to the above reaction, the pH dependence should be 1; but the experimental value is only 0.35. Therefore, it is considered that a parallel reaction product formation is also responsible for vanadium (V) extraction. It will be seen later that $[NO_3^-]$ enhances extraction. Moreover, it is thought that the ion-pair $VO_2NO_3$ is solvated by $H_2A_2$ and transferred to the organic phase. The probable equation for solvated ion-pair formation can be depicted as follows:
\[ \text{VO}_2^+ + \text{NO}_3^- + n\text{H}_2\text{A}_{2(o)} \rightleftharpoons \text{VONO}_3. n\text{H}_2\text{A}_{2(o)} \] (7)

The reaction in Eq. (7) is independent of \([\text{H}^+]\). Therefore, it is concluded that in the higher acidity region, 35% portion of V(\text{V}) is extracted following the reaction presented in Eq. (6) and the rest by the reaction shown in Eq. (7). Hence, the overall pH dependence becomes 0.35.

On increasing the pH of the aqueous solution, \(\text{VO}_2^+\) concentration in the system drops abruptly and becomes negligible at pH\(_{\text{eq}}\) 3. Consequently, the concentration of the hydrolysed product \(\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}\) increases proportionally and exists in the highest proportion at pH\(_{\text{eq}}\) 3. The prominent extractable aqueous vanadium (\text{V}) species is \(\text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-}\). The following type of reaction probably extracts this species:

\[ \text{V}_{10}\text{O}_{26}(\text{OH})_2^{4-} + 4\text{H}^+ + n\text{H}_2\text{A}_{2(o)} \rightleftharpoons 6\text{V}_{10}\text{O}_{28}.n\text{H}_2\text{A}_{2(o)} \] (8)

Moreover, the formation of \(\text{V}_{10}\text{O}_{27}(\text{OH})_5^{5-}\) starts at pH ~ 3 and becomes maximum at around pH 5. The extraction of this species is ruled out because the formation of \(6\text{V}_{10}\text{O}_{28}.n\text{H}_2\text{A}_2\) will require 5 \(\text{H}^+\) which is less likely supplied by the aqueous solution of high pH. In Eq. (8), 4 \(\text{H}^+\) are needed for 10 vanadium (\text{V}), so the pH dependence would be -0.40. The experimental value is -0.32, so the explanation given above conforms to the experimental results.

The pH functionality for the investigated system is found to be exceptionally low, which may act as a drawback of this system.

3.4 Effect of extractant concentration on the extraction ratio of vanadium (\text{V}):

Figure 5 represents the plot of log D vs. log ([D2EHPA], %) for two different metal ion concentrations. In both cases, straight lines are obtained. The slopes of these straight lines are 0.234 and 0.239 for 0.56 g/L and 0.72 g/L vanadium (\text{V}) systems, respectively. The results indicate that the more the extractant concentration, the more vanadium (\text{V}) extraction. This behavior is normal for any extraction process. The slope values indicate the requirement of one extractant molecule per four vanadium (\text{V}) extracted. As the equilibrium pH varies with the variation of extractant concentration, it is necessary to get log D versus log ([D2EHPA], %) plot at constant equilibrium pH values. The positive extractant dependence supports the general phenomenon of an extraction process.

3.5 Effect of nitrate ion concentration on the extraction ratio of vanadium (\text{V}):

The log D vs. log ([\text{NO}_3^-], \text{mol/L}) plot for two different D2EHPA concentrations is shown in Fig. 6. A curve is obtained instead of a straight line in each case. The extent of variation of extraction ratio with the [\text{NO}_3^-] depends on its concentration region. In both cases, the tangential positive slopes of these curves are increased gradually with the increase in the nitrate ion concentration. The slope approaches zero at lower nitrate ion concentration regions, whereas in the high concentration regions, it gradually increases to about 0.69 at [\text{NO}_3^-] of 1.50 mol/L. The nitrate ion thus exhibits the salting-out effect in the present system.
3.6 Effect of temperature on the extraction of V(V)

The effect of temperature in the present system has been determined at two different D2EHPA concentrations (5% and 7%). The experimentation related van’t Hoff (log D vs. (1/T), K⁻¹) plots are given in Fig. 7. In both cases, it is found that the extraction ratio is decreased with increasing temperature and the straight-line relationship holds in the van’t Hoff plots. Slopes of the line are 655.2 and 619.4 for 5% and 7% D2EHPA systems, respectively. From the plots’ slopes, the heat of extraction reaction (ΔH) values have been calculated as -12.54 kJ/mol and -12.14 kJ/mol for 5% and 7% D2EHPA systems, respectively. The extraction process is, therefore, exothermic with ΔH value of about -12.34 kJ/mol.

3.7 Loading of technical grade D2EHPA solution with vanadium (V):

The cumulative vanadium (V) concentration in the organic phase has been plotted against the phase contact number in Fig. 8. It is observed that the organic phase loading with vanadium (V) almost ends at the 4th contact. It is seen from Fig. 8 that the saturation of 5% or 53 g/L D2EHPA solution with vanadium (V) occurs at the 4th contact. The cumulative [vanadium (V)] increases gradually with the contact number and reaches the value of ~3.24 g/L in the organic phase. This result indicates that 53 g technical grade extractant can extract 3.24 g vanadium (V). It suggests a loading capacity of 6.11 g vanadium (V) per 100 g extractant. The loading capacity is low for its industrial implication.

<table>
<thead>
<tr>
<th>Diluent</th>
<th>V (V)_{(a,eq)} g/L</th>
<th>V (V)_{(o,eq)} g/L</th>
<th>Extraction ratio, D</th>
<th>% of extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kerosene</td>
<td>0.095</td>
<td>0.465</td>
<td>4.89</td>
<td>83.02</td>
</tr>
<tr>
<td>Xylene</td>
<td>0.147</td>
<td>0.413</td>
<td>2.81</td>
<td>73.75</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>0.205</td>
<td>0.355</td>
<td>1.73</td>
<td>63.37</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>0.217</td>
<td>0.343</td>
<td>1.58</td>
<td>61.24</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.218</td>
<td>0.342</td>
<td>1.57</td>
<td>61.08</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.242</td>
<td>0.318</td>
<td>1.31</td>
<td>56.71</td>
</tr>
<tr>
<td>Isobutyl methyl ketone</td>
<td>0.245</td>
<td>0.315</td>
<td>1.29</td>
<td>56.33</td>
</tr>
<tr>
<td>CCl₄</td>
<td>0.252</td>
<td>0.308</td>
<td>1.22</td>
<td>54.95</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.264</td>
<td>0.296</td>
<td>1.12</td>
<td>52.83</td>
</tr>
<tr>
<td>n-heptane</td>
<td>0.266</td>
<td>0.294</td>
<td>1.11</td>
<td>52.61</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.277</td>
<td>0.283</td>
<td>1.02</td>
<td>50.49</td>
</tr>
</tbody>
</table>
3.8 Effect of different diluents

Table 2 displays the result of the diluent effect for the present system. It is observed that the extraction ratio increases in the following order with the variation of diluent: chloroform (CHCl$_3$) < n-heptane (C$_7$H$_{16}$) < cyclohexane (cyclo-C$_6$H$_{12}$) < carbon tetrachloride (CCl$_4$) < isobutyl methyl ketone (C$_6$H$_{12}$O) < toluene (C$_7$H$_8$) < benzene (C$_6$H$_6$) < 1, 2-dichloroethane (C$_2$H$_4$Cl$_2$) < chlorobenzene (C$_6$H$_5$Cl) < xylene (C$_8$H$_{10}$) < kerosene. The study concludes that kerosene, xylene, and chlorobenzene are suitable diluents for extracting vanadium (V) using technical grade D2EHPA. Kerosene is preferable due to its availability, low volatility, low price, and high extraction power for this extraction system.

3.9 Stripping of V(V) loaded organic phase by base and acid

Table 3 presents the results obtained from the stripping process. The stripping percentage is much better with 0.50 mol/L H$_2$SO$_4$ than other stripping agents. Stage-wise stripping has been investigated with an H$_2$SO$_4$ solution of 0.50 mol/L concentration. About 91.35% can be stripped from the loaded organic phase with the repeated five contacts with the fresh 0.50 mol/L H$_2$SO$_4$ solution.
Table 3
Data on stage wise stripping. \([V(V)] = 3.24 \text{ g/L}, \ O/A = 1, \ (O = 10 \text{ mL})\)
Equilibration time = 30 min., Temperature = 303 K.

<table>
<thead>
<tr>
<th>Stripping agent</th>
<th>Stage No.</th>
<th>([V(V)]_{(a, \text{eq})} \text{ g/L}</th>
<th>% stripping</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 mol/L NH₄OH</td>
<td>1</td>
<td>0.743</td>
<td>22.96</td>
</tr>
<tr>
<td>0.50 mol/L NH₄OH</td>
<td>1</td>
<td>1.162</td>
<td>35.82</td>
</tr>
<tr>
<td>(0.10 mol/L NH₄OH + 0.10 mol/L NH₄Cl)</td>
<td>1</td>
<td>0.587</td>
<td>18.17</td>
</tr>
<tr>
<td>0.90 mol/L NaOH</td>
<td>1</td>
<td>0.899</td>
<td>27.75</td>
</tr>
<tr>
<td>0.10 mol/L H₂SO₄</td>
<td>1</td>
<td>1.307</td>
<td>40.29</td>
</tr>
<tr>
<td>*0.50 mol/L H₂SO₄</td>
<td>1</td>
<td>2.26</td>
<td>69.79</td>
</tr>
<tr>
<td>*0.50 mol/L H₂SO₄</td>
<td>2</td>
<td>0.435</td>
<td>13.42</td>
</tr>
<tr>
<td>*0.50 mol/L H₂SO₄</td>
<td>3</td>
<td>0.170</td>
<td>5.21</td>
</tr>
<tr>
<td>*0.50 mol/L H₂SO₄</td>
<td>4</td>
<td>0.059</td>
<td>1.85</td>
</tr>
<tr>
<td>*0.50 mol/L H₂SO₄</td>
<td>5</td>
<td>0.034</td>
<td>1.08</td>
</tr>
<tr>
<td>*1.0 mol/L H₂SO₄</td>
<td>1</td>
<td>1.98</td>
<td>61.08</td>
</tr>
<tr>
<td>*1.0 mol/L H₂SO₄</td>
<td>2</td>
<td>0.280</td>
<td>8.68</td>
</tr>
<tr>
<td>*0.50 mol/L HNO₃</td>
<td>1</td>
<td>1.74</td>
<td>53.70</td>
</tr>
<tr>
<td>2</td>
<td>0.232</td>
<td>7.15</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.049</td>
<td>1.48</td>
<td></td>
</tr>
</tbody>
</table>

*Organic phases are recycled with fresh aqueous stripping agents.

3.10 Selectivity:

The selectivity of the method will appear as low. D2EHPA extracts most metal ions in the pH range 1–5. In this pH range, vanadium (V) is extracted by more than 50% (log D = 0). Therefore, coextraction is possible.

4. Conclusion

The conclusions are:

The equilibration time for the current system is about 30 min. The study of metal ion dependency shows that the system is non-ideal.
Vanadium (V) extraction increases with the increase of aqueous equilibrium pH of ~ 2.50. This characteristic is typical for ion exchange or chelation type of extraction. On the other hand, the V(V) extraction is decreased with the increase of aqueous pH above pH_{eq} 2.50, which indicates the formation of a solvated ion pair. One molecule of extractant is needed to extract four vanadium (V). The nitrate ion causes salting out. The system is exothermic with the ΔH value of about − 12.34 kJ/mol.

A loading capacity is 6.11 g vanadium (V) per 100 g extractant. Kerosene is the best diluent for this system.

H_2SO_4 of 0.50 mol/L appears to be a better stripping agent than the other. A 5-stage stripping can strip off ~ 91.35% vanadium (V).

Declarations

Acknowledgements

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Conflict of Interest

The authors declare that they have no conflict of interest.

Data availability statement

The authors declare that the data supporting the findings of this study are available within the paper. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

Author Contribution

Dr. Aneek Krishna Karmakar wrote the whole manuscript and prepared all the graphs and tables. Amzad Hossen completed all the experimental work and revise the manuscript after prepared.

References


Appendix

AI. Notation and abbreviation

<table>
<thead>
<tr>
<th>Symbol or abbreviation</th>
<th>Meanings with the unit (where applicable)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2A_2$</td>
<td>Di (2-ethylhexyl) phosphoric acid (D2EHPA)</td>
</tr>
<tr>
<td>D</td>
<td>Distribution ratio or Extraction ratio</td>
</tr>
<tr>
<td>$K_{ex}$</td>
<td>Equilibrium constant from the equilibrium study</td>
</tr>
<tr>
<td>S</td>
<td>the concentration of extractant which is used in forming the metal complex</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>DH</td>
<td>Apparent enthalpy changes for extraction, kJ/mol</td>
</tr>
<tr>
<td>Suffix “eq”</td>
<td>Equilibrium</td>
</tr>
<tr>
<td>Suffix “o”</td>
<td>Organic phase</td>
</tr>
<tr>
<td>Suffix “a” or without suffix</td>
<td>Aqueous phase</td>
</tr>
<tr>
<td>Suffix “ini”</td>
<td>Initial</td>
</tr>
<tr>
<td>O</td>
<td>Organic phase</td>
</tr>
<tr>
<td>A</td>
<td>Aqueous phase</td>
</tr>
<tr>
<td>M2EHPA</td>
<td>Mono2-ethyl hexyl phosphoric acid</td>
</tr>
</tbody>
</table>

Figures

![Figure 1](image)

Figure 1
Chemical structure of D2EHPA.

Figure 2

Effect of phase contact time on the extraction of V (V) from nitrate medium by technical grade di(2-ethylhexyl) phosphoric acid dissolved in distilled kerosene. \([V \,(V)](\text{ini}) = 0.56 \, \text{g/L}, \text{pH}(\text{ini}) = 1.50, [\text{D2EHPA}] = 5\% \,(v/v), [\text{NO}_3^-] = 0.20 \, \text{mol/L}, O/A = 1, (O = 20 \, \text{mL}), \text{Temperature} = 303 \, \text{K} \).
Figure 3

Effect of metal ion concentration on the extraction of V (V) from nitrate medium by technical grade di(2-ethylhexyl) phosphoric acid dissolved in distilled kerosene. pH\textsubscript{(ini)} = 1, Temperature = 303 K, [NO\textsubscript{3}^-] = 0.20 mol/L, Equilibration time = 30 min, O/A = 1 (O = 20 mL).

Figure 4

Figure 4. Effect of equilibrium pH on the extraction of V (V) from nitrate medium by technical grade di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in distilled kerosene. [V (V)]\textsubscript{(ini)} = 0.56 g/L, [NO\textsubscript{3}^-] = 0.2 mol/L,
Temperature = 303 K, Equilibration time = 30 min, O/A = 1, (O = 20 mL). (□), [D2EHPA] = 5%, ( ); VO₂⁺, ( ); V₁₀O₂₆(OH)₂⁴⁻, (▲); V₁₀O₂₇(OH)⁵⁻ (Table 1)

Figure 5

Effect of extractant concentration on the extraction of V (V) from nitrate medium by technical grade di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in distilled kerosene. pHₐₚ = 1, Temperature = 303 K, [NO₃⁻] = 0.20 mol/L, Equilibration time = 30 min.

Figure 6
Effect of nitrate ion concentration on the extraction of V (V) from nitrate medium by technical grade di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in distilled kerosene. \([V \text{ (V)}]_{\text{(ini)}} = 0.56 \text{ g/L}, \text{pH}_{\text{(ini)}} = 1.50, \text{Temperature} = 303 \text{ K}, \text{Equilibration time} = 30 \text{ min. O/A} = 1 \text{ (O = 20 mL).}

\[\text{Figure 7}\]

Effect of temperature on the extraction of V (V) from nitrate medium by technical grade di(2-ethylhexyl) phosphoric acid (D2EHPA) dissolved in distilled kerosene. \([V \text{ (V)}]_{\text{(ini)}} = 0.56 \text{ g/L}, \text{pH}_{\text{(ini)}} = 1.50, [\text{NO}_3^-] = 0.20 \text{ mol/L}, \text{Equilibration time} = 30 \text{ min, O/A} = 1 \text{ (O = 20 mL).} \]
Figure 8

Loading of V (V) in the organic phase. V (V)\textsubscript{ini} = 1.66 g/L, [D2EHPA] = 5%, pH\textsubscript{ini} = 2, [NO\textsubscript{3}^{-}] = 0.20 mol/L, Temperature = 303 K, Equilibration time in each contact = 30 min, O/A= 1 (O = 100 ml).