Extraction of V(V) and Fe(III) from aqueous medium containing various concentrations of mineral acids and salts into 1-phenyl-3-methyl-4-butyrylpyrazolone in mixed organic phase

Bieluonwu Augustus Uzoukwu* & Usoro Monday Etesin
Coordination and Analytical Chemistry Unit, Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, Nigeria
Received 29 December 1993; revised 22 September 1994; accepted 24 October 1994

The extraction behaviour of V(V) and Fe(III) from aqueous medium containing various concentrations of acid and salt into chloroform-butanol and methylisobutyl ketone-butanol mixtures, each containing 0.05 M 1-phenyl-3-methyl-4-butyrylpyrazolone (HBuP) have been studied. Fe(III) was extracted quantitatively from 2.5-10 M HCl into 0.05 M HBuP-MIBK-BuOH. An optimum separation factor $D_{Fe}/D_{V} = 10^6$ has been obtained for mixtures of both metals. Hence, Fe(III) is separated from V(V) in 6 M HCl using 0.05 M HBuP-MIBK-BuOH as the extractant. With 0.05 M HBuP-CHCl$_3$-BuOH, V(V) is efficiently extracted from 0.9 M HNO$_3$ into the organic phase. The study shows that Fe(III) is extracted as Fe(BuPh) species between 0-4 M acid concentration, and as $H_2BuP^+FeCl_4^-$ species between 6-10 M (HCl) acid concentration. Vanadium is extracted as VO$_3$(BuP)$_2$, HBuP species from acid solutions.

1-Phenyl-3-methyl-4-acylpyrazolone-5 and its derivatives, especially the 4-benzoyl derivative have been used successfully as chelating reagents for the solvent extraction of metals from aqueous medium containing various acid concentrations. The 4-butyryl derivative (HBuP) has recently been shown to have more extraction capability for some metal ions than some of the 4-acyl derivatives studied along with it. In this present study mixed solvent systems have been employed to see if the distribution of some of these metal ions from acid and salt solutions into organic solvents containing the chelating agent will be improved.

Experimental
Deionized water was used for the aqueous phase and all aqueous preparations. 1-Phenyl-3-methyl-4-butyrylpyrazolone-5 (HBuP) was synthesised by methods described elsewhere. The pure product had a m.p. of 77°C after recrystallization from ethanol-water (4:1) mixture. Solution of 0.05 M HBuP in methyl isobutyl ketone (MIBK)-butanol (BuOH) (4:1, v/v) and chloroform-butanol (CHCl$_3$-BuOH) (4:1 v/v) were prepared afresh each time before use. A stock solution of 100 ppm Fe(III) was prepared in 10 M HCl by dissolving appropriate weight of NH$_4$Fe(SO$_4$)$_2$·12H$_2$O in HCl. Stock solution of 800 ppm of V(V) was prepared in 0.1 M HCl by dissolving appropriate amount of ammonium vanadate in HCl. The working solutions were 10 ppm Fe(III) and 80 ppm V(V) respectively and were prepared by diluting appropriate volumes of metal stock solutions.

Corked 20 ml polyethene extraction bottles were used for all phase equilibrations. Concentrations of the metal ions were determined with a Unicam SP 8-100 UV-visible spectrophotometer.

Measurement of distribution ratio
Equal volumes (5 ml) of the aqueous phase containing a metal ion, an acid or salt solution and an organic phase i.e. 0.05 M HBuP were shaken mechanically on a STUART flask shaker for 1 hour. Preliminary studies showed that 1 hour shaking is sufficient for equilibration to occur. The immiscible phases were allowed to settle and separated. The Fe(III) in the aqueous raffinate was determined using 1,10-phenanthroline method while the V(V) in the other raffinate was determined using the hydrogen peroxide method. The distribution ratio $D$ was calculated as the ratio of the concentration of metal ion in the organic phase to that in the aqueous phase. The % extraction ($E$) was calculated from $E = 100 \times D(D + 1)^{-1}$.

Results and discussion
Effects of mineral acids on the extraction of Fe(III) and V(V): Hydrochloric acid—The results for both the metal ions are shown in Fig. 1. It shows that the extraction of V(V) into both mixed solvent systems are identical at acid concentrations < 1 M. Beyond 2 M acid concentration CHCl$_3$-BuOH proved to be more efficient in the extraction of V(V) than MIBK-BuOH. In a similar study with Fe(III) an extraction curve similar to those in the published reports was obtained for CHCl$_3$-BuOH organic phase. Wine-red Fe(BuP)$_2$ chelates were extracted between 1-4 M HCl and colourless ion-pair complexes $H_2BuP^+FeCl_4^-$ were extracted above 6 M HCl.
With MIBK, however, quantitative extraction of Fe(III) was obtained up to 8 M HCl. Synergism was observed when HBuP-MIBK-BuOH solvent system was used, giving a 100% extraction of Fe(III) into the organic phase throughout the range of HCl concentration studied. The result obtained with HBuP-MIBK-BuOH solvent system showed that the organic phase has a higher extraction capacity for Fe(III) than those reported in results on the solvent extraction of Fe(III) from acidic media using 1,3-diketones.

**Sulphuric acid**—Extraction studies show that the distribution characteristics of V(V) from both HCl (Fig. 1) and H2SO4 solutions into both HBuP-MIBK-BuOH and HBuP-CHCl3-BuOH are basically identical. Subsequently, extraction curves similar to those already reported were obtained for the extraction of Fe(III) from H2SO4 solutions. This shows that the same extraction mechanism is operating from this acid into both mixed solvent systems.

**Nitric acid**—The extraction study on V(V) in HNO3 solution shows that the extraction mechanism for V(V) from acid media into HBuP-MIBK-BuOH as reported in Fig. 1 remains the same. However, a different distribution mechanism for V(V) into HBuP-CHCl3-BuOH was observed, resulting in a quantitative extraction of the metal from HNO3 solutions throughout the range of HNO3 concentrations studied. The study also shows that only one type of extraction mechanism is taking place in the distribution of Fe(III) from HNO3 solution into the mixed organic solvent systems studied. Hence, no depression was observed in the extraction curves but a monotonous decrease in the % extraction with increase in acid concentration.

**Effects of salts on the extraction of Fe(III) and V(V)**

The effects of various concentrations of Cl−, SO4−2 and NO3− solutions on the distribution of Fe(III) and V(V) into HBuP-MIBK-BuOH are shown in Fig. 2. Figure 2 shows that at low Cl− concentration ~ 0.5 M the % distribution of V(V) into HBuP-MIBK-BuOH is maximum. This may be due to the slight increase in the dielectric constant of the aqueous phase. However, at Cl− concentration > 0.5 M formation of stable chloro V(V) complexes in the aqueous phase may have been the cause of the fall in the % extraction of V(V). In SO4−2 and NO3− solutions a steady increase in % extraction with increase in anion concentration in the aqueous phase is observed. It is being suggested that formation of nitrate and sulphate adduct complexes of V(V) may have been responsible for this increase in V(V) distribution into the organic phase with increase in NO3− and SO4−2 concentrations.

Figure 2 shows that changes in Cl− concentrations do not significantly impede the distribution of Fe(III) into HBuP-MIBK-BuOH. It also shows that the distribution of Fe(III) into the organic phase increases to a maximum at 0.5 M sulphate and nitrate concentrations. Beyond these anion concentrations the distribution is observed to fall due to formation of anionic Fe(III) complexes in the aqueous phase.

**Determination of composition of extracted complex species**

Fe(III) complexes of 4-acylpyrazolones have been isolated and extraction studies showed that the wine-red Fe(III) complex has a molecular formula of Fe(BuP)3. Thus, the extraction process is

$$\text{Fe}^{3+} + 3\text{HBuP}_{(aq)} \rightleftharpoons \text{Fe(BuP)}_3{\text{(or)}} + 3\text{H}^+_{(aq)}$$

The stoichiometry of the extracted V(V) chelate was also established by the method described elsewhere and it showed that the metal-ligand mole

---

**Fig. 1**—Extraction curves for 10 ppm Fe(III) and 80 ppm V(V) from HCl solution into 0.05 M HBuP dissolved in 1, CHCl3-BuOH; 2, MIBK and 3, MIBK-BuOH.

**Fig. 2**—Extraction curves for 10 ppm (Fe III) and 80 ppm V(V) from solutions of 1, nitrate/2 M HNO3; 2, sulphate/1 M H2SO4 and 3, chloride/1 M HCl into 0.05 M HBuP-MIBK-BuOH.
Table I—Separation factor from various aqueous media containing 80 ppm V(V) and 10 ppm Fe(III) into various organic media each containing 0.05 M HBuP.

<table>
<thead>
<tr>
<th>Aqueous phase</th>
<th>Organic phase</th>
<th>DF_e/DF_v</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 M HCl</td>
<td>CHCl-BuOH</td>
<td>8.8 x 10^3</td>
</tr>
<tr>
<td>2.5-10 M HCl</td>
<td>MIBK-BuOH</td>
<td>1.0 x 10^6</td>
</tr>
<tr>
<td>4.5 M HNO_3</td>
<td>MIBK-BuOH</td>
<td>1.0 x 10^3</td>
</tr>
<tr>
<td>2 M Cl^- (3 M HCl)</td>
<td>MIBK-BuOH</td>
<td>1.3 x 10^2</td>
</tr>
<tr>
<td>8 M HNO_3</td>
<td>CHCl-BuOH</td>
<td>8.4 x 10^2</td>
</tr>
</tbody>
</table>

Table 2—Analysis of a synthetic mixture of Fe(III) and V(V) in 6 M HCl solution using 0.05 M HBuP-MIBK-BuOH organic phase.

<table>
<thead>
<tr>
<th>Amount in original aqueous phase (ppm)</th>
<th>Amount retained in original aqueous phase (%)</th>
<th>Amount back-extracted into 8.5 M HNO_3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(V)</td>
<td>Fe(III)</td>
<td>V(V)</td>
</tr>
<tr>
<td>80</td>
<td>10</td>
<td>99.2</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>99.5</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>98.4</td>
</tr>
</tbody>
</table>

ratio is 1:2. Complexes of V(V) with 4-acylpyrazolones were recently isolated and characterized and found to have a metal-ligand mole ratio of 1:2. Hence, the extraction mechanism can be written as

\[ \text{VO}^{2+}_{\text{aq}} + 2\text{HBuP}^{+}_{\text{or}} \rightarrow \text{VO}_2\text{(BuP)}^{+}_{\text{or}} + \text{H}_2\text{BuP}^{+}_{\text{aq}} \]

Extraction studies on V(V) in nitrate ion solutions showed that one mole of nitrate adduct complex species was extracted as indicated by the extraction mechanism.

\[ \text{VO}^{2+}_{\text{aq}} + \text{NO}_3^{-}_{\text{aq}} + \text{HBuP}^{+}_{\text{or}} \rightarrow \text{VO}_2\text{(BuP)}^{+}_{\text{or}} + \text{NO}_3^{-}_{\text{or}} \]

Separation of V(V) from Fe(III)

The differences between the distribution behaviour of Fe(III) and V(V) from 2-10 M HCl solution into HBuP-MIBK-BuOH (Fig. 1) have been used for the efficient separation of the two metals from one another. The separation factors D_Fe/D_V listed in Table 1 shows that extraction from 2-10 M HCl solution into HBuP-MIBK-BuOH offers an optimum separation condition since D_Fe/D_V = 10^6.

In principle, the method consists of extracting a mixture of both metal ions in a 6 M HCl solution with an equal volume of 0.05 M HBuP-MIBK-BuOH solution. Under this condition Fe(III) is quantitatively transferred to the organic phase while V(V) remained in the aqueous phase. After separation of the phases at the end of the extraction process Fe(III) is back extracted from the organic extract into the aqueous phase with 8.5 M HNO_3. Results shown in Table 2 indicate that the method efficiently separated both metal ions from one another.

Acknowledgement

The authors wish to thank the International Foundation for Science, Sweden for research grant awarded to B.A.U.

References