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Solvent Extraction Separation of Vanadium(V) from Multimetal Chloride Solutions Using Tributylphosphate

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ABSTRACT

The solvent extraction behavior of vanadium(V) from hydrochloric acid solutions was investigated using tributylphosphate (TBP) in kerosene as an extractant. The results clearly indicate that vanadium(V) is extracted into kerosene as $VO_2Cl \cdot 2HCl \cdot 2TBP$. The equilibrium constant of the extracted complex was determined. Extraction and stripping isotherms were generated using TBP in kerosene as an extractant with a typical feed solution containing 0.02 mol/dm^3 of vanadium(V) and 5.0 mol/dm^3 of hydrochloric acid. The effect of the nature of the diluent on the extraction of vanadium(V) with TBP was studied and correlated with dielectric constants. The separation and recovery possibilities of vanadium(V) from other associated metal ions, such as

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magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), and iron (III), present in the waste chloride liquors of titanium minerals processing industry, are discussed.

Key Words: Solvent extraction; Separation; Vanadium(V); Tributylphosphate; Multivalent metal chlorides.

INTRODUCTION

Vanadium is commercially important as a constituent of several alloys and catalysts. Nowadays, vanadium production is limited to the recovery from industrial wastes or low-grade ores, such as vanadium-bearing ferrophosphorus slag, iron slag, fly ash, spent catalysts, and titaniferrous magnetite ore. Selective separation and recovery of vanadium from titania waste streams for potential use is of paramount importance in view of the depleting resources of vanadium. Further, the more our economy recovers and recycles useful metals from industrial wastes, the less mining will be needed and less environmental damage will result from waste disposal. Hence, in the present work, an attempt was made to develop a solvent extraction-based separation method to recover vanadium from multivalent metal chloride solutions present in the waste chloride liquors of the titanium minerals processing industry.

A survey of published research showed that acidic organophosphorus extractants have been widely used for the extraction of vanadium(V) from acidic chloride solutions.[1–4] Recently, from our laboratory, a selective solvent extraction method was developed for the recovery of vanadium(V) from multivalent metal chloride solutions using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester.[5] However, as compared with acidic organophosphorus extractants, studies on the extraction of vanadium(V) from hydrochloric acid solutions using neutral organophosphorus extractants are limited.[6,7] The separation and recovery possibilities of vanadium(V) from other associated metal ions, such as magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), and iron(III), present in the waste streams of titanium minerals processing industry, were investigated using trialkylphosphine oxide (Cyanex 923) in kerosene as an extractant and reported poor selectivity.[7] The extraction equilibrium involved in the extraction of vanadium(V) from hydrochloric acid solutions, especially with tributylphosphate, is not well understood.[6] Hence, in the present study, tributylphosphate has been explored for the extraction of vanadium(V) from acidic chloride solutions to elucidate the nature of the complexes extracted into the organic phase and also to investigate the selectivity between vanadium(V) and other associated multivalent metal ions present in the titania waste chloride liquors.

EXPERIMENTAL

Reagents and Apparatus

Tributylphosphate supplied by Aldrich Chemical, USA, was used without further purification. Distilled kerosene (boiling range 160 to 200°C; composed of aliphatic hydrocarbons) was used as a diluent. All the other chemicals used were of analytical reagent grade.

Vanadium(V) stock solution was prepared by dissolving 5.85 g of ammonium monovanadate in hydrochloric acid and diluting to 1.0 dm^3 with distilled water. Freshly prepared solutions of vanadium(V) were used in all the experimental studies to prevent partial reduction to tetravalent vanadium in hydrochloric acid solutions with respect to time.[6] Titanium(IV) solutions were prepared from $TiCl_4$ (Spectrochem, India; purity = 99.0%) by diluting to the required concentration with hydrochloric acid. Stock solutions of magnesium(II), aluminium(III), chromium(III), manganese(II), and iron(III) were prepared by dissolving 12.32 g of $MgSO_4 \cdot 7H_2O$, 18.76 g of $Al(NO_3)_3 \cdot 9H_2O$, 25 g of $CrK(SO_4)_2 \cdot 12\ H_2O$, 8.45 g of $MnSO_4 \cdot H_2O$, and 8.11 g of $FeCl_3$ in 1.0 dm^3 of distilled water, respectively. Suitably diluted stock solutions of the previously mentioned metal ions were used in extraction and analytical studies. All organic phase solutions were prepared by dissolving weighed amounts of tributylphosphate in kerosene and then diluting to the required volume. A Hitachi 220 double-beam microprocessor-controlled spectrophotometer (Tokyo, Japan) was used for measuring absorbances. An Orion 720A ion analyser (USA) was used for the pH measurements. A Perkin Elmer AAnalyst 100 atomic absorption spectrophotometer (USA) was used for the analysis of metal ions in multicomponent mixtures.

Extraction and Analytical Procedures

Solvent extraction and stripping experiments were carried out by shaking the required volumes of aqueous and organic phase in a glass-stoppered vial using a mechanical shaker at 303 ± 1°K for 15 min. Preliminary experiments showed that the extraction equilibrium for vanadium(V) was attained within 5 min. After phase separation, the concentration of a particular metal ion remaining in the aqueous phase was determined using standard procedures. Thus, magnesium(II), aluminium(III), chromium(III), and iron(III) were analyzed spectrophotometrically using eriochrome black-T,[8] eriochrome cyanine-R,[8] 1,5 diphenyl carbazide[9] and 1,10 phenanthroline,[8] respectively. Vanadium(V) and titanium(IV) were analyzed spectrophotometrically using hydrogen peroxide method.[8] Manganese(II) was analyzed titrimetrically using EDTA.[8] The concentration of metal ion in the organic phase was then obtained by the mass balance. The distribution ratio, D, was taken as the ratio of the concentration of metal ion in the organic phase to that present in the aqueous phase. The batch-type counter-current extraction and stripping experiments were performed using separatory funnels of suitable volume. All the experiments were performed in duplicate and the general agreement in the distribution ratios obtained was within ± 5%.

RESULTS AND DISCUSSION

Effect of Hydrochloric Acid Concentration

The extraction behavior of vanadium(V) ($0.02\ \mathrm{mol/dm^3}$) with TBP in kerosene ($1.47\ \mathrm{mol/dm^3}$) as a function of hydrochloric acid concentration (1.0 to $5.0\ \mathrm{mol/dm^3}$) was studied and the results are shown in Figure 1. The extraction of vanadium(V) was found to increase with the increase in hydrochloric acid concentration. The effect of hydrogen (3.5 to $5.1\ \mathrm{mol/dm^3}$) and chloride (4.0 to $5.5\ \mathrm{mol/dm^3}$) ion concentrations on the extraction of vanadium(V), respectively, was investigated from HCl and NaCl

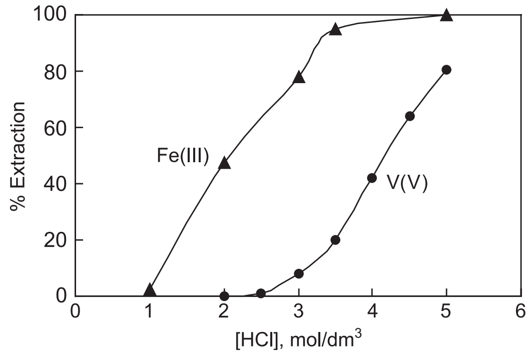

Figure 1. Effect of hydrochloric acid concentration on the extraction of vanadium(V) ($0.02\ \mathrm{mol/dm^3}$), magnesium(II) ($0.03\ \mathrm{mol/dm^3}$), aluminium(III) ($0.02\ \mathrm{mol/dm^3}$), titanium(IV) ($0.02\ \mathrm{mol/dm^3}$), chromium(III) ($0.01\ \mathrm{mol/dm^3}$), manganese(II) ($0.03\ \mathrm{mol/dm^3}$) and iron(III) ($0.01\ \mathrm{mol/dm^3}$) using $1.47\ \mathrm{mol/dm^3}$ TBP in kerosene.

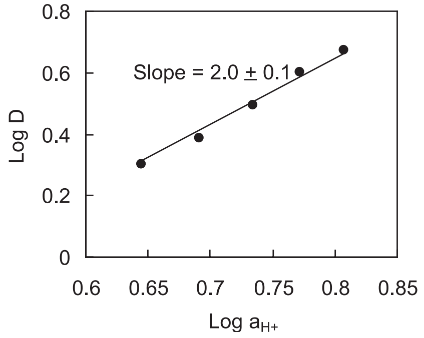

Figure 2. Effect of hydrogen ion concentration on the extraction of vanadium(V) at constant chloride ion concentration. $[Cl^-] = 5.1$ mol/dm^3, $[V(V)] = 0.02$ mol/dm^3, $[TBP] = 1.47$ mol/dm^3 in kerosene.

mixtures using 1.47 mol/dm^3 TBP in kerosene as an extractant. The results are depicted in Figures 2 and 3. From the slopes of the log-log plots, it is clear that vanadium(V) extracted as $VO_2Cl{\cdot}2HCl$ into the organic phase. The activity coefficients of hydrogen and chloride ions in the aqueous phase were calculated using Bromley's formulation.[10]

Effect of Extractant Concentration

The effect of TBP concentration (0.5 to 2.5 mol/dm^3) on the extraction of vanadium(V) was studied at constant metal ion (0.02 mo/dm^3) and

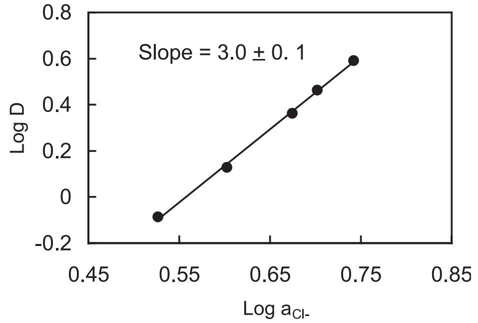

Figure 3. Effect of chloride ion concentration on the extraction of vanadium(V) at constant H^+ concentration. $[H^+] = 4.0$ mol/dm^3, $[V(V)] = 0.02$ mol/dm^3, $[TBP] = 1.47$ mol/dm^3 in kerosene.

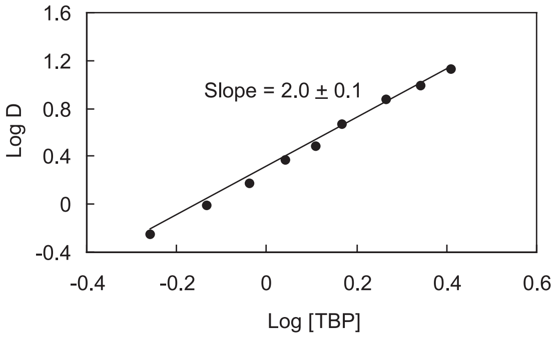

Figure 4. Effect of TBP concentration on the extraction of vanadium(V). [V(V)] = 0.02 mol/dm^3, [HCl] = 5.0 mol/dm^3.

hydrochloric acid (5.0 mol/dm^3) concentrations. The results are shown in Figure 4. The distribution ratio, D, of vanadium(V) increased linearly with increased TBP concentration. The slope of the log-log plot shows that two molecules of TBP were associated with the extractable complexes. However, Tedesco and Rumi[6] reported the involvement of two and three molecules of TBP in the extracted complexes of vanadium(V) from hydrochloric acid solutions at higher concentrations of the extractant.

Effect of Metal Ion Concentration

The effect of metal ion concentration (0.004 to 0.05 mol/dm^3) on the extraction of vanadium(V) was investigated from 5.0 mol/dm^3 hydrochloric acid solutions by employing 1.47 mol/dm^3 TBP in kerosene as an extractant. The log-log plot (Figure 5) of equilibrium organic-phase vanadium(V) concentration against aqueous-phase vanadium(V) concentration is linear with a slope of unity, indicating that only mononuclear species are extracted into the organic phase.

Extraction Equilibrium

Based on the preceding studies, the extraction equilibrium for vanadium(V) from hydrochloric acid solutions with TBP as an extractant can be represented by:

$$VO^+_{2aq} + 2H^+_{aq} + 3Cl^-_{aq} + 2TBP_{org} \overset{K_{ex}}{\Leftrightarrow} VO_2Cl \cdot 2HCl \cdot 2TBP_{org} \quad (1)$$

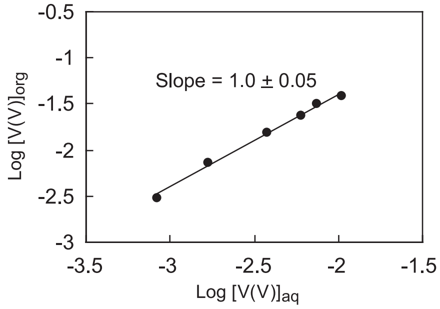

Figure 5. Effect of metal ion concentration on the extraction of vanadium(V). [HCl] = 5.0 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

where, K_{ex}, denotes the equilibrium constant.

$$K_{ex} = \frac{[VO_2Cl \cdot 2HCl \cdot 2TBP]}{[VO_2^+][H^+]^2[Cl^-]^3[TBP]^2} \tag{2}$$

Eq. (2) may also be represented in terms of concentrations and activity coefficients as:

$$K_{ex} = \frac{D\gamma_{VO_2Cl \cdot 2HCl \cdot 2TBP}}{[H^+]^2[Cl^-]^3[TBP]^2\gamma_{H^+}^2\gamma_{Cl^-}^3\gamma_{TBP}^2} \tag{3}$$

where γ represent the activity coefficient and the parentheses represent the concentration of the each species. However, in the present experiments, the concentration of metal ion (0.02 mol/dm^3) used is low as compared to the concentration of TBP (0.5 to 2.5 mol/dm^3) in the organic phase and hydrogen ion (3.5 to 5.1 mol/dm^3) and chloride ion (4.0 to 5.5 mol/dm^3) concentrations in the aqueous phase. Further, due to the unavailability of the activity coefficient data of TBP in the kerosene system, in the present study, the activities of the metal complex and TBP in the organic phase were considered as equal to their equilibrium concentration in the organic phase. The activity coefficients of the hydrogen ion and the chloride ion in the aqueous phase were calculated by Bromley's formulation.[10] The equilibrium constant was calculated from the distribution data and found to be 4.72 × 10^{-4}.

Effect of Diluent

The extraction efficiency of vanadium(V) from 5.0 mol/dm^3 hydrochloric acid solutions was studied using 1.47 mol/dm^3 TBP in various diluents. The results are shown in Table 1. The results clearly demonstrate that diluents, such as benzene, xylene, toluene, and kerosene, which have low dielectric constants, show higher extraction efficiency for vanadium(V). On the other hand, diluents having higher dielectric constants, such as chloroform, give poor extraction. This may be due to the strong interaction between TBP and chloroform through hydrogen bonding.[11] Among aromatic hydrocarbons, the extraction efficiency of vanadium(V) varies in the order benzene < toluene < xylene. In view of the commercial availability and high extraction efficiency, kerosene was used as the diluent in the present study.

Loading Capacity

Aliquots of 10 cm^3 of 1.47 mol/dm^3 TBP in kerosene were repeatedly extracted at $303 \pm 1°K$ for 10 minutes with equal volumes of the aqueous phase containing 0.02 mol/dm^3 vanadium(V) in 5.0 mol/dm^3 hydrochloric acid. The aqueous phases were analyzed for vanadium(V) after each stage of extraction and the cumulative vanadium(V) content transferred into the extractant phase was calculated. The plot of cumulative vanadium(V) in the organic phase per 100 g of TBP vs the number of stages of contact is presented in Figure 6. It is clear that the loading capacity of TBP in kerosene for the extraction of vanadium from hydrochloric acid solutions is 1.0 g of vanadium(V) per 100 g of TBP.

Table 1. Effect of nature of diluent on the extraction of vanadium(V) (0.02 mol/dm^3). [HCl] = 5.0 mol/ dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

Diluent	Dielectric constant	D
Kerosene	2.00	3.56
Cyclohexane	2.02	3.17
Xylene	2.24	1.75
Toluene	2.26	1.60
Benzene	2.28	1.51
Chloroform	4.90	0.01

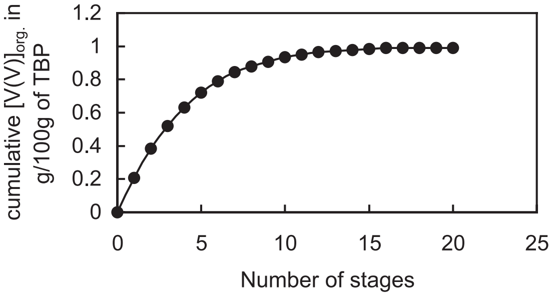

Figure 6. Loading capacity of TBP by vanadium(V). [HCl] = 5.0 mol/dm^3, [TBP] = 1.47 mol/dm^3.

Extraction and Stripping Isotherms

The extraction isotherm for a typical feed solution containing 1.1 g/dm^3 of vanadium(V) and 5.0 mol/dm^3 hydrochloric acid using 1.47 mol/dm^3 TBP in kerosene as an extractant was generated and the results are shown in Figure 7. The McCabe–Thiele plot for a feed solution containing 1.1 g/dm^3 of vanadium(V) showed that almost quantitative extraction of vanadium(V) is possible in three counter-current stages at an A:O (aqueous:organic) ratio of 1:1. The McCabe–Thiele plot (Figure 8) for a loaded organic phase containing 1.1 g/dm^3 vanadium(V) showed that quantitative stripping of vanadium(V) is possible in four counter-current stages using 4.0 mol/dm^3 hydrochloric acid as the stripping agent (O:A = 2:3).

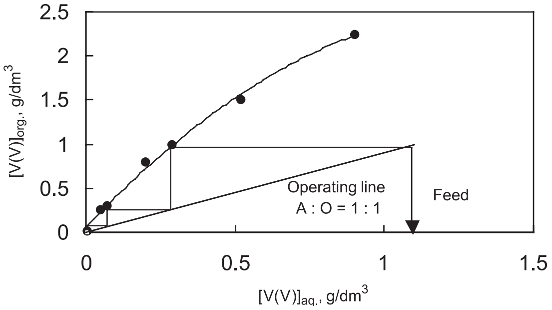

Figure 7. McCabe-Thiele plot for vanadium(V) extraction. [V(V)] = 1.1 g/dm^3, [HCl] = 5.0 mol/dm^3, [TBP] = 1.47 mol/dm^3 in kerosene.

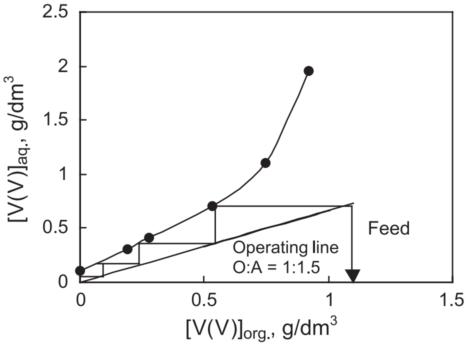

Figure 8. McCabe-Thiele plot for vanadium(V) stripping. $[V(V)]_{org} = 1.1$ g/dm^3, [HCl] = 4.0 mol/dm^3.

Comparison of Extraction and Stripping Behavior of Vanadium(V) with Other Associated Metal Ions

The extraction of vanadium(V) (0.02 mol/dm^3) and other associated metal ions, viz, magnesium(II) (0.03 mol/dm^3), aluminium(III) (0.02 mol/dm^3), titanium(IV) (0.02 mol/dm^3), chromium(III) (0.01 mol/dm^3), manganese(II) (0.03 mol/dm^3), and iron(III) (0.01 mol/dm^3) was investigated as a function of hydrochloric acid concentration using 1.47 mol/dm^3 TBP in kerosene as an extractant. The results are depicted in Figure 1. It is clear from the results that iron(III) is co-extracted along with vanadium(V) into the organic phase. On the other hand, magnesium(II), aluminium(III), titanium(IV), chromium(III), and manganese(II) were not extracted under the present experimental conditions. To develop a selective separation method for

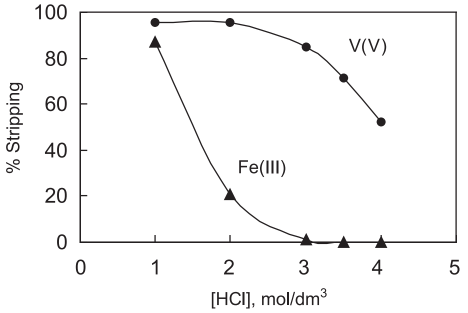

Figure 9. Stripping behaviour of vanadium(V) (0.02 mol/dm^3) and iron(III) (0.01 mol/dm^3) from loaded TBP phase (1.1 g/dm^3) using hydrochloric acid.

the recovery of vanadium(V) from the loaded organic phase, the stripping behavior of vanadium(V) and iron(III) from the loaded organic phase was investigated as a function of hydrochloric acid concentration and the results are shown in Figure 9. The results show that vanadium(V) can be selectively recovered from the loaded organic phase using 4.0 mol/dm^3 hydrochloric acid. On the other hand, the stripping of iron(III) was found to be negligible under this condition. Thus, vanadium(V) can be selectively separated from the loaded organic phase containing vanadium(V) and iron(III) using 4.0 mol/dm^3 hydrochloric acid as a stripping agent in four stages. Subsequently, iron(III) can be recovered from the organic phase using deionized water of pH 2.

Separation of Vanadium(V) from Simulated Waste Chloride Liquors

Based on the results, a simulated waste chloride liquor consisting of magnesium(II) (0.03 mol/dm^3), aluminium(III) (0.02 mol/dm^3), titanium(IV)

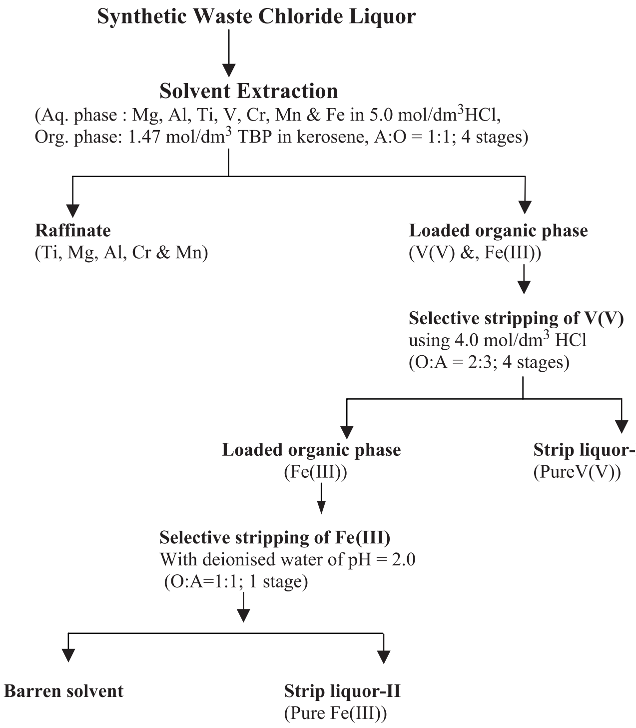

Figure 10. Separation scheme for the recovery of vanadium from simulated waste chloride liquor.

Table 2. Extraction and separation of vanadium(V) from simulated waste chloride liquor using 1.47 mol/dm^3 TBP in kerosene.

Metal ion	Feed (mol/dm^3)	Raffinate (mol/dm^3)	Strip liquor-I (mol/dm^3)	Strip liquor-II (mol/dm^3)
V(V)	0.022	ND	0.0146	ND
Fe(III)	0.011	ND	ND	0.011
Mg(II)	0.028	0.028	ND	ND
Al(III)	0.021	0.021	ND	ND
Ti(IV)	0.020	0.020	ND	ND
Cr(III)	0.010	0.010	ND	ND
Mn(II)	0.030	0.030	ND	ND

ND = not detectable.

(0.02 mol/dm^3), vanadium(V) (0.02 mol/dm^3), chromium(III) (0.01 mol/dm^3), manganese(II) (0.03 mol/dm^3), and iron(III) (0.01 mol/dm^3) in 5.0 mol/dm^3 hydrochloric acid was prepared and subjected to a batch-type solvent-extraction process using 1.47 mol/dm^3 TBP as an extractant to recover vanadium(V). The schematic diagram of the process and the typical results are shown in Figure 10 and Table 2. The results show that vanadium(V) and iron(III) are co-extracted into the organic phase, whereas other metal ions remain unextracted in the raffinate stream. Vanadium(V) is selectively stripped from the loaded TBP phase using 4.0 mol/dm^3 hydrochloric acid as a stripping agent in four stages (O:A = 2:3). Iron(III) was then recovered from the organic phase using deionized water of pH 2 in a single stage (O:A = 1:1). These results show that vanadium(V) can be selectively recovered from waste chloride liquors containing multivalent metal chlorides using TBP in kerosene as an extractant.

CONCLUSION

The extraction behavior of vanadium(V), magnesium(II), aluminium(III), titanium(IV), chromium(III), manganese(II), and iron(III) from acidic chloride solutions was investigated using TBP in kerosene as an extractant. The results clearly demonstrate that vanadium(V) and iron(III) are co-extracted into the organic phase, leaving behind other metal ions in the raffinate. Vanadium(V) was then selectively stripped from the loaded organic phase using 4.0 mol/dm^3 hydrochloric acid. Finally, iron(III) was recovered from the organic phase using deionized water of pH 2. This study clearly demonstrated that TBP can be used as an extractant for the extraction and separation of vanadium(V) from multivalent metal chloride solutions present in the waste chloride liquors of titanium minerals processing industry.

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