

Solvent Extraction of Vanadium (V) from Phosphate Solutions with Trioctylmethylammonium Chloride (TOMAC)

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Abstract: Different experimental conditions that could affect the extraction of vanadium (V) were investigated. These include acid concentration, metal ion concentration, extractant concentration, temperature, mixing of extractants, extraction stages and addition of foreign ions. TOMAC was found to be more efficient at lower acid concentration (1M). Optimum extraction conditions were reached at 38^oC and the use of TOMAC proved to be synergistic with the addition 2.5% TOPO. The infrared and UV-visible spectra data were used to propose VO₂H₂PO₄.nTOMAC as the stoichiometry for the organic extract.

Keywords: vanadium (V), extractant, phosphoric acid, solvent extraction, TOMAC.

I. Introduction

Solvent extraction is a simple technique for separating the components of homogeneous liquid mixture by distribution between the original liquid and a second liquid, which is either immiscible or only partially miscible with the first. Solvent extraction is the separation method of choice where distillation fails. Separation is achieved by adding a solvent to the original liquid carrying the component to be extracted (Sanchez, 1991). Liquid-liquid extraction also known as solvent extraction partitioning is a method used to separate compounds based on their relative solubility in two different immiscible liquids. It is an extraction of a substance from one liquid phase into another liquid phase. Liquid-liquid extraction is a basic technique in chemical laboratories, where it is performed using a separating funnel (Sanchez, 1991).

Solvent extraction is used in nuclear reprocessing, ore reprocessing (Ritcey and Ashbrook, 2000), the production of fine organic compounds, the processing of perfumes and other industries. This process is continuously by pumping an organic component with the aqueous component and allows ion transfer between them.

The solvent extraction of metals has become increasingly important in connection with hydrometallurgical extraction process. The main areas of application of solvent extraction with reversible chemical reaction are hydrometallurgy and liquid-liquid extraction as applied in metallurgical processing. Apart from separation, solvent extraction can be used for concentration and purification of solute (Scholz, 2000).

The three main separation processes between solid, gas and liquid have long been known, while solvent extraction is a relatively new separation technique. Nevertheless, because all solutes can be made more or less soluble in aqueous and organic phases, the number of applications of solvent extraction is almost limitless (Jan Rydberg et al; 2005).

Since large- scale industrial solvent extraction is a continuous process (in contrast to laboratory batch process) and can be made more selective than the conventional gas-liquid-solid separation technique, it offers numerous industrial possibilities to achieve desired separation efficiently and economically (Jan Rydberg et al; 2005).

II. Materials used

Trioctylmethylammonium chloride (TOMAC), phosphoric acid (H₃PO₄), ammonium metavanadate (NH₄VO₃), potassium dihydrogen phosphate (KH₂PO₄), nitric acid (HNO₃), isodecanol and n-heptane. Reagents were prepared by dissolving a given weight of the sample in aqueous acid in a volumetric flask.

III. Preparation of stock solutions

NH₄VO₃ (0.03M) was prepared by dissolving 0.0877g of the salt in H₃PO₄ (1-6M) in a 25 cm³ volumetric flask. 0.3402g KH₂PO₄ was added to the vanadium salt to make 0.1M solution. A yellow solution was obtained.

A stock solution of 8M H₃PO₄ was prepared by measuring 53 cm³ of conc. H₃PO₄ and made up to 100 cm³ with distilled water. Other concentrations (1M, 2M, 3M, 4M, 5M, and 6M) were prepared by appropriate dilutions. 15% (v/v) TOMAC was prepared by diluting 15 cm³ pure TOMAC to 100 cm³ with n-heptane. 2.5%, 5% and 10% concentrations were prepared by further dilution (Ojo, 2010).

IV. Experimental procedure for equilibrium studies of vanadium (V) extraction with TOMAC

Effect of variations in acid concentration, metal ion concentration, extractant concentration, temperature, mixing of extractants, extraction stages and addition of foreign ions on the extraction of VO_2^+ .

Vanadium (V) concentration of 0.03M was prepared in different H_3PO_4 concentrations of 1M, 2M, 3M, 4M, 5M and 6M. A volume of 10 cm^3 of each of the solutions was measured into a 100 cm^3 separating funnel and 10 cm^3 10% (v/v) extractant (TOMAC in n-heptane) was added to it. The mixture was manually shaken after the cork has been put in place for 5 minutes. The solution was allowed to stand for about a minute with the cork removed to release the pressure in the funnel and also for proper separation of the phases.

The bottom aqueous layer was drawn off into a clean 25 cm^3 measuring cylinder. The volume was recorded and stored in a clean reagent bottle labelled as sample 'A'. The small amount of liquid at the interphase was released from the tap and discarded. The upper organic layer was poured from the top of the funnel into a clean 25 cm^3 measuring cylinder and the volume recorded.

The organic layer was transferred to another separating funnel and equal amount of 2M HNO_3 was added as strippant to back extract the organic phase. The mixture was again shaken for another 5 minutes. After standing for about a minute for proper separation, the bottom aqueous layer was released into a measuring cylinder and the volume recorded. It was then transferred into a reagent bottle labelled as sample 'B'. The stored samples were kept for further analysis. The upper organic layer of extractant was collected in a bottle for possible reuse. Formation of three layers encountered was dispersed with addition of 3-5 drops of isodecanol (a modifier). Vanadium was determined by the phosphotungstate spectrophotometric method (Sanchez-Vinas et al, 1999) which was carried out as follows: 0.1 cm^3 of sample was pipetted into 10 cm^3 0.2M H_2SO_4 in a clean beaker. 2.5 cm^3 of 1:2 phosphoric acid and 2.5 cm^3 of 10% sodium tungstate were added to it. The solution was made up to 20 cm^3 with distilled water. It was heated to boiling, cooled and made up with distilled water in a 25 cm^3 standard flask. The absorbance was read at 400nm against a blank. The absorbance of standard vanadium solution was also read at the same wavelength (Thorton, 1992; Zygmunt, 1986). The amount of vanadium in sample was calculated from Beer-Lambert equation.

$A \propto CL$ Where, A is the absorbance, C is the concentration and L is the path length which is equal to 1cm (Vogel, 1989).

V. Results and discussion

Table 1 Effect of Acid Concentration on V(V) Extraction from Phosphoric Acid Slutions with TOMAC
 $[\text{V(V)}] = 0.03\text{M}$, $[\text{KH}_2\text{PO}_4] = 0.1\text{M}$, TOMAC = 10%(v/v)

$[\text{H}_3\text{PO}_4]$	$[\text{V(V)}]_a \text{ mol dm}^{-3}$	$[\text{V(V)}]_{org} \text{ mol dm}^{-3}$	D	E (%)
1M	0.012	0.018	1.500	60.0
2M	0.018	0.012	0.667	40.0
3M	0.020	0.010	0.500	33.3
4M	0.022	0.008	0.364	26.7
5M	0.019	0.011	0.579	36.7
6M	0.019	0.011	0.579	36.7

Table 2 Effect of Metal Ion Concentration on V(V) Extraction from Phosphoric Acid Solutions with TOMAC

$[\text{V(V)}]$	$[\text{V(V)}]_a \text{ mol dm}^{-3}$	$[\text{V(V)}]_{org} \text{ mol dm}^{-3}$	D	E (%)
0.01M	0.006	0.004	0.667	40.0
0.02M	0.012	0.008	0.667	40.0
0.03M	0.012	0.018	1.500	60.0
0.04M	0.016	0.024	1.500	60.0
0.05M	0.016	0.034	2.125	68.0

$[\text{H}_3\text{PO}_4] = 1\text{M}$, $[\text{KH}_2\text{PO}_4] = 0.1\text{M}$, TOMAC = 10% (v/v)

Table 3 Effect of Extractant Concentration on V(V) Extraction from Phosphoric Acid Solutions with TOMAC

$[\text{TOMAC}]$	$[\text{V(V)}]_a \text{ mol dm}^{-3}$	$[\text{V(V)}]_{org} \text{ mol dm}^{-3}$	D	E (%)
2.5%	0.014	0.016	1.143	53.3
5%	0.013	0.017	1.308	56.7
10%	0.012	0.018	1.500	60.0
15%	0.011	0.019	1.727	63.3

$[\text{V(V)}] = 0.03\text{M}$, $[\text{H}_3\text{PO}_4] = 1\text{M}$, $[\text{KH}_2\text{PO}_4] = 0.1\text{M}$

Table 4 Effect of Temperature on V(V) Extraction from Phosphoric Acid Solutions with TOMAC

Temp (°C)	[V(V)] _a mol dm ⁻³	[V(V)] _{org} mol dm ⁻³	D	E (%)
28.0	0.011	0.019	1.727	63.3
33.0	0.010	0.020	2.000	66.7
38.0	0.010	0.020	2.000	66.7
43.0	0.012	0.018	1.500	60.0
48.0	0.011	0.019	1.727	63.3

[V(V)] = 0.03M, [H₃PO₄] = 1M, [KH₂PO₄] = 0.1M, TOMAC = 15%(v/v)

Table 5 Effect of Mixing of Extractants on V(V) Extraction from Phosphoric acid Solutions

Extractant Mixture	[V(V)] _a mol dm ⁻³	[V(V)] _{org} mol dm ⁻³	D	E (%)
15%TOMAC+ 10%TRPO	0.018	0.012	0.667	40.0
15%TOMAC+ 2.5%TOPO	0.010	0.020	2.000	66.7
15%TOMAC+ 10%D2EHPA	0.011	0.019	1.727	63.3

[V(V)] = 0.03M, [KH₂PO₄] = 0.1M, Temp = 48°C

Table 6 Effect of Extraction Stages on V(V) Recovery from Phosphoric Acid Solutions with TOMAC

Stages	[V(V)] _a mol dm ⁻³	[V(V)] _{org} mol dm ⁻³	D	E (%)
1 st	0.0082	0.0218	2.659	72.7
2 nd	0.0042	0.0040	0.952	48.8
3 rd	0.0040	0.0002	0.050	4.8

[V(V)] = 0.03M, [H₃PO₄] = 1M, [KH₂PO₄] = 0.1M, TOMAC = 15% (v/v), Temp = 48°C

Table 7 Effect of Foreign Ions on V(V) Extraction from Phosphoric Acid Solutions with TOMAC

Foreign Ions mol dm ⁻³	[V(V)] _a mol dm ⁻³	[V(V)] _{org} mol dm ⁻³	D	E (%)
VO ₂ ⁺ alone	0.011	0.019	1.727	63.3
0.0015 Co ²⁺	0.008	0.022	2.750	73.3
0.0030 Co ²⁺	0.008	0.022	2.750	73.3
0.0015 Cu ²⁺	0.008	0.022	2.750	73.3
0.0015 Pb ²⁺	0.009	0.021	2.333	69.9
0.0015 Mo ⁶⁺ , Co ²⁺ , Cu ²⁺ , Pb ²⁺	0.007	0.023	3.286	76.7

[V(V)] = 0.03M, [H₃PO₄] = 1M, [KH₂PO₄] = 0.1M, TOMAC = 15% (v/v), Temp = 48°C

Table 8 Electronic Absorption Spectra for Extracted V(V) from H₃PO₄ Solutions with TOMAC

Compound	Wave number (cm ⁻¹)	Assignment
V(V)/H ₃ PO ₄ (aq)	34014(s)	charge transfer
V(V).TOMAC Complex	35211(s)	charge transfer

Table 9 Infrared Spectra Data for TOMAC and TOMAC Complex

Compound	Wave number (cm ⁻¹)	Assignment
TOMAC	2930(w)	v(C-H)
	1301(w)	v(C-N)
	723(s)	v(V=O)
	3404(br)	v(C-OH)
TOMAC Complex	2371(w)	v(C-H)
	1320(s)	v(C-N)
	717(s)	v(V=O)
	3327(br)	v(C-OH)

br = broad

VI. Discussion

The percentage VO₂⁺ extracted showed a gradual decrease with increase in acid concentration. The highest percentage extraction was recorded at 1M acid concentration (E% = 60.0). 1M H₃PO₄ concentration was subsequently used for the extraction of VO₂⁺ with TOMAC.

A step-like increase in the percentage extraction of VO₂⁺ was recorded. Higher concentrations of the metal ion favours a high extraction of VO₂⁺. 0.05M V(V) recorded the highest E% of 68.0. This contrasts with Khan et al., 2010 using cloud point extraction (CPE) method to determine trace quantity of vanadium in various pharmaceutical preparations.

There was a gradual increase in percentage extraction of V(V) as TOMAC concentration increases from 2.5% to 15%. The highest E% of 63.3 was recorded at 15% (v/v) TOMAC. 10% (v/v) TOMAC was favoured for further use due to the high viscosity of 15% concentration.

There was an initial increase in percentage extraction of V(V) up to 38°C after which a drop was recorded and later increase at 48°C. The increased efficiency of TOMAC at elevated temperatures indicates an endothermic process (Ojo, 2009).

The percentage extraction of V(V) with TOMAC was increased by the addition of 2.5% (w/v) TOPO from 63.3 (when TOMAC alone was used) to 66.7. This is reasonable as TOPO is a solvating extractant which increases the solubility of the metal in the organic phase. However, TBP has been shown to be antagonistic with D2EHPA in the extraction of VO_2^+ from HNO_3 solutions (Ojo, 2010).

The V(V) was well extracted from H_3PO_4 solution by TOMAC at 48°C. First stage recorded the highest E% of 72.7 which showed drastic reduction in the second and third stages of extraction.

All the foreign ions added to V(V) in extraction with TOMAC enhanced the extraction of V(V). The inclusion of 0.0015M each of all four ions (Mo^{6+} , Co^{2+} , Cu^{2+} and Pb^{2+}) recorded the highest E% for V(V) (E% = 76.7). TOMAC can therefore find application in the industrial recovery of vanadium from metal scraps in the presence of other metal ions.

The electronic absorption spectra of the aqueous phase and organic extract from H_3PO_4 solution by TOMAC recorded two important bands at 34014 cm^{-1} and 35211 cm^{-1} . The bands have been assigned to charge transfer and they are also of strong absorption. This relates well with the extraction of vanadium (V) from 12M sulphuric acid by Kurbatova and Kurbatov, 2006.

The IR spectra absorption bands for TOMAC and TOMAC complex obtained from the organic extract shows IR absorptions at 2371 cm^{-1} , 1320 cm^{-1} , 717 cm^{-1} and 3327 cm^{-1} which have been assigned to $\nu(\text{C-H})$, $\nu(\text{C-N})$, $\nu(\text{V=O})$ and $\nu(\text{C-OH})$ stretch respectively. The $\nu(\text{V=O})$ band is an evidence for vanadium extraction.

VII. Conclusion

The following conclusions are drawn from investigating the percentage extraction capabilities of trioctylmethylammonium chloride (TOMAC) as extractant for the extraction of V(V) from H_3PO_4 solutions.

1. TOMAC proved to be very efficient in the extraction of V(V) from phosphoric acid solutions.
2. TOMAC produced the highest percentage V(V) extraction when other metal ions were introduced into the solution.
3. The high viscosity of TOMAC limits its usage at higher concentrations.
4. The following is proposed for the stoichiometry of the organic extract of TOMAC $\text{VO}_2\text{H}_2\text{PO}_4 \cdot n\text{TOMAC}$.

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