**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Selective Extraction and Separation of Titanium(IV) from Multivalent Metal Chloride Solutions Using 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester

J. Saji[a]; M. L. P. Reddy[a]
[a] Inorganic and Analytical Chemistry Unit, Regional Research Laboratory (CSIR), Trivandrum, India

**To cite this Article** Saji, J. and Reddy, M. L. P.(2003) 'Selective Extraction and Separation of Titanium(IV) from Multivalent Metal Chloride Solutions Using 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester', Separation Science and Technology, 38: 2, 427 — 441

**To link to this Article: DOI:** 10.1081/SS-120016583

**URL:** http://dx.doi.org/10.1081/SS-120016583

MARCEL DEKKER, INC. • 270 MADISON AVENUE • NEW YORK, NY 10016

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, No. 2, pp. 427–441, 2003

# Selective Extraction and Separation of Titanium(IV) from Multivalent Metal Chloride Solutions Using 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester

**J. Saji and M. L. P. Reddy***

Inorganic and Analytical Chemistry Unit, Regional Research Laboratory
(CSIR), Trivandrum, India

## ABSTRACT

The extraction behavior of titanium(IV) from hydrochloric acid solutions was investigated using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA = HX) in kerosene as an extractant. The results demonstrate that the extraction of titanium(IV) follows the cation exchange mechanism:

$$TiO^{2+}_{aq} + 2(HX)_{2org} \Leftrightarrow TiO(HX_2)_{2org} + 2H^{+}_{aq}$$

where $(HX)_2$ refers to the dimeric form of EHEHPA. The equilibrium constant of the extracted complex was deduced by nonlinear regression

---

*Correspondence: M. L. P. Reddy, Inorganic and Analytical Chemistry Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India; Fax: +91-471-491712/490186; E-mail: mlpreddy@yahoo.co.uk.

DOI: 10.1081/SS-120016583 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

analysis by taking into account the aqueous phase complexation of metal ion with inorganic ligands and all plausible complexes extracted into the organic phase. The effect of the nature of diluent on the extraction of titanium(IV) with EHEHPA was investigated and found that the extraction efficiency varies in the order: chloroform $<$ benzene $\sim$ toluene $<$ xylene $<$ kerosene. IR spectral studies of the extracted complex were used to further clarify the nature of extracted complex. The separation possibilities of titanium(IV) from other associated multivalent metal ions, that is, magnesium(II), aluminum(III), vanadium(V), chromium(III), manganese(II), and iron(III), which are associated with titanium in the waste chloride liquors of titanium minerals processing industry was discussed.

*Key Words:* Selective extraction; Separation; Titanium(IV); 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester; Multivalent metal chlorides; Titania wastes.

## INTRODUCTION

Titanium finds the widest application as titanium dioxide pigment in the paint industry. Due to its excellent corrosion resistance in a chloride environment and also because of its special properties of high resistance, titanium has also been widely used in the aerospace industry. The manufacture of $TiO_2$ through “chloride process” generates large amounts of acidic waste chloride liquors containing multivalent metal ions such as magnesium(II), aluminum(III), titanium(IV), vanadium(V), chromium(III), manganese(II), and iron(III). Selective separation and recovery of valuable metal ions from these industrial wastes are gaining more importance because of the greater need for high-purity products and also due to environmental concerns. Nowadays, solvent extraction technique is being used for the recovery of metal values from waste streams as well as from mineral resources.[1,2]

A review of the literature indicates that di-2-ethylhexyl phosphoric acid (DEHPA) and trialkylphosphine oxides (TRPO) were the most widely studied extractants for the extraction of titanium(IV) from acidic aqueous solutions.[3] Sole investigated the extraction of titanium(IV) from sulfuric acid leach liquors of titaniferrous magnetite using DEHPA and reported poor selectivity for titanium due to the co-extraction of associated metal ions.[4] Islam et al. carried out extensive studies on the extraction of titanium(IV) from sulfuric acid solutions with a view to investigate the selectivity of titanium(IV) over Fe(II) and Fe(III).[5] The separation factors for Ti(IV)/Fe(III) and Ti(IV)/Fe(II) at 0.35 M $H_2SO_4$ with 0.2 M DEHPA are found to be 60 and 500, respectively. In the later studies, these investigators found better selectivity for titanium(IV) over iron(III) and iron(II) [separation factors for $Ti(IV)/Fe(III) = 175$ and $Ti(IV)/Fe(II) = 7800$] with di-o-tolyl phosphoric acid when extracted from sulfuric acid solutions.[6] Recently, from our laboratory, *bis*(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272 = HBTMPP) was proposed as a potential extractant for the selective extraction and separation of titanium(IV) from acidic chloride solutions containing multivalent metal ions such as magnesium(II), aluminum(III), vanadium(V), chromium(III), manganese(II), and iron(III).[7] As compared with dialkyl phosphoric and phosphinic acids, studies on the extraction of titanium(IV) from acidic chloride solutions using organophosphonic acids is lacking. Hence in the present work, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) was explored for the extraction of titanium(IV) from acidic chloride solutions with a view to elucidate the nature of the extracted complex in the organic phase and also to investigate the selectivity between titanium and other multivalent metal ions present in leach liquors of titanium mineral processing industry.

## EXPERIMENTAL

A Hitachi (Tokyo, Japan) 220 double-beam, microprocessor-controlled spectrophotometer was used for measuring absorbances. An Orion (Beverly, USA) 720A ion analyzer was used for the pH measurements. A GBC (Dandenong, Australia) 902 atomic absorption spectrometer was used for analysis of metal ions in multicomponent mixtures. All the computer programs were written in FORTRAN 77 and executed on a 32-bit minicomputer (HCL HORIZON III).

### Reagents

2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA), with a trade name Ionquest 801 (supplied by Albright and Wilson, USA), was used without purification. Distilled kerosene (boiling range 160–200°C; composed of aliphatic hydrocarbons) was used as a diluent in the present work. All the other chemicals used were of analytical reagent grade.

Titanium(IV) stock solution was prepared by dissolving 18.40 g of potassium titanyl oxalate and 5 g of ammonium sulphate in 100 mL of concentrated hydrochloric acid and diluted to 1 L with distilled water. Iron(III) stock solution was prepared by dissolving 8.11 g of ferric chloride in 20 mL of concentrated hydrochloric acid and diluted to 1 L with distilled water. Stock solutions of aluminum(III), chromium(III), manganese(II), and magnesium(II) were prepared by dissolving 18.75 g of $Al(NO_3)_3 \cdot 9H_2O$, 25 g of $CrK(SO_4)_2 \cdot 12H_2O$, 8.45 g of $MnSO_4 \cdot H_2O$, and 12.32 g of $MgSO_4 \cdot 7H_2O$ in 1 L each of distilled water, respectively. Vanadium(V) stock solution was prepared by dissolving 5.85 g of ammonium monovanadate in 20 mL of concentrated hydrochloric acid and diluted to 1 L with distilled water. Suitably diluted stock solutions of the above mentioned metal ions were used in the extraction and analytical studies.

## Extraction and Analytical Procedure

Liquid–liquid extractions were carried out by shaking equal volumes of aqueous and organic phases in a glass stoppered vial using a mechanical shaker at 303 ± 1K. Preliminary experiments showed that extraction equilibrium is attained within 90 min. To improve the phase disintegration, 20 vol.% isodecanol was used as a modifier, along with extractant, in the organic phase. After phase separation, the concentration of a particular metal ion left in the aqueous phase was determined using standard procedures. Thus, titanium(IV),[8] iron(III),[8] magnesium(II),[8] aluminum(III),[8] chromium(III),[9] and vanadium(V)[10] were analyzed spectrophotometrically using hydrogen peroxide, 1,10-phenanthroline, Eriochrome black-T, Eriochrome Cyanine R, 1,5-diphenyl carbazide, and oxine, respectively. Manganese(II) was analyzed volumetrically using EDTA.[11] The concentration of the metal ion in the organic phase was then obtained by 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 concentration of the above metal ions in a simulated waste chloride liquor was determined by atomic absorption spectrometer.

The Ti-EHEHPA complex was prepared by solvent extraction method by repeated contacts of fresh portions of metal solutions for 90 min. A Nicolet FTIR 560 Magna spectrometer, using KBr (neat), was used to obtain the IR spectra of the metal complex.

# RESULTS AND DISCUSSION

## Extraction Equilibrium

The extraction equilibrium of titanium(IV) with EHEHPA $[(HX)_2]$ from hydrochloric acid solutions may be represented as:

$$TiO^{2+}_{aq} + 2(HX)_{2org} \overset{K_{ex}}{\Leftrightarrow} TiO(HX_2)_{2org} + 2H^+_{aq} \qquad (1)$$

where $K_{ex}$ denotes the equilibrium constant and $(HX)_2$ refers to the dimeric form of EHEHPA. It has been reported elsewhere that the extractant will exist as a dimer in diluent such as kerosene.[12]

$$K_{ex} = \frac{[TiO(HX_2)_2][H^+]^2}{[TiO^{2+}][(HX)_2]^2} \qquad (2)$$

Titanium(IV) in the aqueous phase forms a variety of complexes in the presence of chloride ions. Then, the total Ti(IV) concentration can be expressed as:

$$\begin{aligned}[Ti^{4+}]_{Total} &= [TiO^{2+}] + [TiOCl^+] + [TiOCl_2] \\ &= TiO^{2+}(1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2) \qquad (3)\end{aligned}$$

where $\beta_1$ and $\beta_2$ are stability constants of the following reactions.

$$TiO^{2+} + Cl^- \overset{\beta_1}{\Leftrightarrow} TiOCl^+ \qquad (4)$$

$$TiO^{2+} + 2Cl^- \overset{\beta_2}{\Leftrightarrow} TiOCl_2 \qquad (5)$$

The values of stability constants, $\beta_1 = 3.55$ and $\beta_2 = 1.41$, were obtained from literature.[13] The distribution ratio, *D*, of titanium(IV) can be written from Eqs. (1) and (3) as:

$$D = \frac{K_{ex}[(HX)_2]^2}{[H^+]^2(1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2)} \qquad (6)$$

## Effect of Extractant Concentration

The effect of concentration of EHEHPA (0.05 to 0.3 M) on the extraction of titanium(IV) was investigated by keeping constant metal (0.01 M) and acid (1.0 M) concentrations and the results are depicted in the Fig. 1. It is clear from

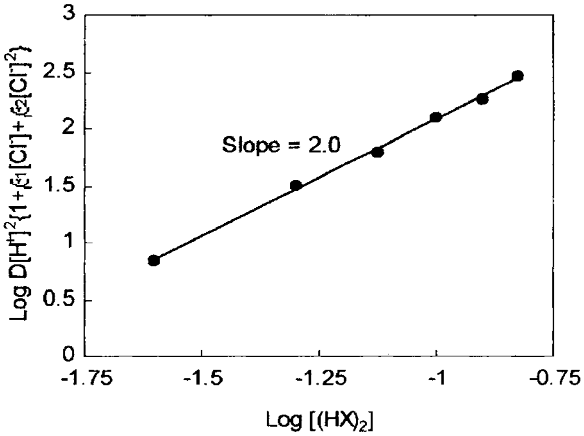

*Figure 1.* Effect of EHEHPA concentration on the extraction of titanium(IV). $[\mathrm{Ti(IV)}] = 0.01\,\mathrm{M}$; $[\mathrm{HCl}] = 1.0\,\mathrm{M}$.

the figure that the extraction of titanium(IV) increases with increase in extractant concentration. From the slope of the plot of log $D[H^+]^2\{1 + \beta_1[Cl^-] + [\beta_2[Cl^-]^2\}$ versus log $[(HX)_2]$, it is inferred that two dimeric molecules of EHEHPA are involved in the extracted complex of titanium(IV).

## Effect of HCl Concentration

The extraction of titanium(IV) with EHEHPA (0.2 M) in kerosene as a function of hydrochloric acid concentration has been studied and the results are shown in Fig. 2. The extraction behavior shows an inverse dependence with acidity. The plot of log $D\{1 + \beta_1[Cl^-] + [\beta_2[Cl^-]^2\}$ versus log $[H^+]$ gave a slope of $-2.0$, indicating the formation of $TiO(HX_2)_2$ as the extracted species. Reddy and co-workers[7] and Biswas and Begum[12] also reported the usual cation exchange mechanism for the extraction of titanium(IV) from hydrochloric acid solutions using HBTMPP or DEHPA as an extractant.

The formation of the extracted complex was further confirmed by analyzing equilibrium data presented in Figs. 1 and 2 using Eq. 6 with the aid of suitable chemically based model developed by taking into account complexation of chloride ions with titanium in the aqueous phase and all plausible complexes extracted into the organic phase. The best fit between the experimental and calculated *D* values was obtained only when the formation of the complex $TiO(HX_2)_2$ was assumed. The equilibrium constant

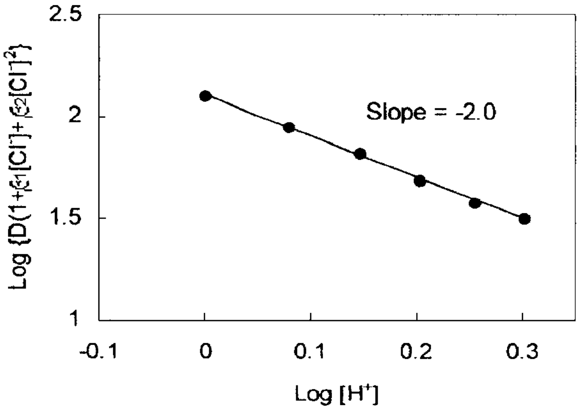

***Figure 2.*** Effect of hydrogen ion concentration on the extraction of titanium(IV). [EHEHPA] = 0.2 M; [Ti(IV)] = 0.01 M.

of the extracted complex was determined by nonlinear regression analysis as described in an earlier publication[14] and found to be log $K_{ex} = 4.09 \pm 0.03$. Table 1 gives the equilibrium constant values of various acidic organophosphorus extractants along with their pKa values for the extraction of titanium(IV) from acidic aqueous solutions. It can be concluded from these comparisons that the extraction efficiency of titanium with various acidic organophosphorus extractants increases in the order: HBTMPP < EHEHPA < DEHPA. Further, it is clear from these comparisons that log $K_{ex}$ values increase as the pKa value decreases.

## Effect of Metal Ion Concentration

The effect of titanium concentration on the extraction process was investigated at 0.1 M EHEHPA in kerosene from 1.0 M HCl solutions.

***Table 1.*** Two phase equilibrium constants of titanium(IV) with various acidic organophosphorus extractants.

| Extractant | pKa | Log $K_{ex}$ |
|---|---|---|
| DEHPA | 1.72[15] | 5.42[16] |
| EHEHPA | 3.42[17] | 4.09 ± 0.03 |
| HBTMPP | 6.37[7] | 2.27 ± 0.02[7] |

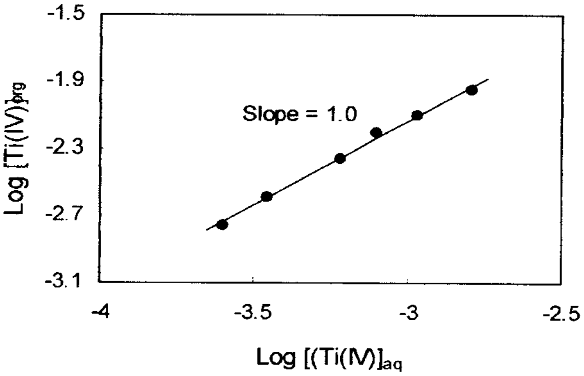

*Figure 3.* Effect of metal ion concentration on the extraction of titanium(IV). HCl = 1.0 M; EHEHPA = 0.1 M.

The extraction of titanium(IV) was found to be independent of metal ion concentrations in the range 0.002 M to 0.01 M. The log–log plot (Fig. 3) of equilibrium organic phase metal concentration against aqueous phase metal concentration is linear, with a slope of unity indicating that mononuclear species are extracted into the organic phase.

## IR Spectra of Ti-EHEHPA Complex

In the IR spectra of EHEHPA, the band at 1195 cm$^{-1}$ is due to P=O stretching and the band at 1038 cm$^{-1}$ is assigned to P—OH stretch (Fig. 4). The bands in the region 1700–2700 cm$^{-1}$ corresponds to the aggregative P—OH vibrations in the intermolecular hydrogen bonding of EHEHPA in dimeric form. In the spectra of Ti-EHEHPA complex, the band due to P—OH stretch is absent, indicating the complex formation through the replacement of hydrogen of P—OH by Ti. Further, the shift in the P=O stretching band from 1195 cm$^{-1}$ to 1065 cm$^{-1}$ reveals the participation of oxygen of P=O group in complex formation through coordination.

## Loading of EHEHPA by Titanium

Aliquots of 10 mL of 1 M EHEHPA in kerosene diluent were repeatedly extracted at 303 ± 1K for 90 min., with equal volume of aqueous phase containing 0.48 g/L of titanium and 2.0 M HCl. The aqueous phases were

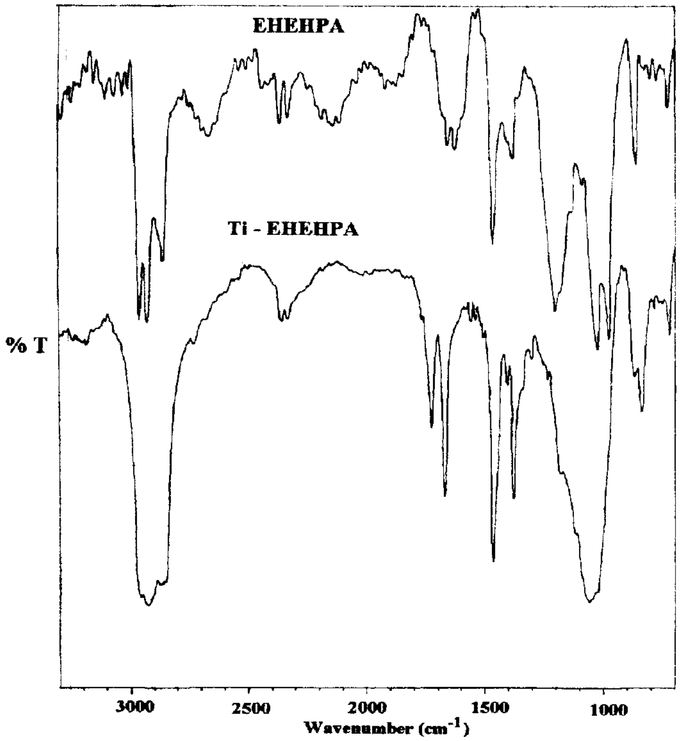

*Figure 4.* IR spectra of EHEHPA and Ti-EHEHPA.

analyzed for titanium after each stage of extraction and the cumulative titanium content transferred into organic phase was calculated. The plot of cumulative $[Ti(IV)]_{org}$ per 100 g EHEHPA versus contact number is presented in Fig. 5. It is clear from the figure that the loading capacity of EHEHPA in kerosene for the extraction of titanium from hydrochloric acid solutions is 5.92 g $Ti^{4+}$ per 100 g of the extractant. This is comparable to the loading capacity of HBTMPP [6.1 g $Ti^{4+}$ per 100 g[7]] and DEHPA [7.31 g $Ti^{4+}$ per 100 g[12]].

## Effect of Nature of Diluent on Extraction of Titanium

The extraction of titanium(IV) from 1.0 M hydrochloric acid solutions was studied using 0.1 M EHEHPA in various diluents and the results are

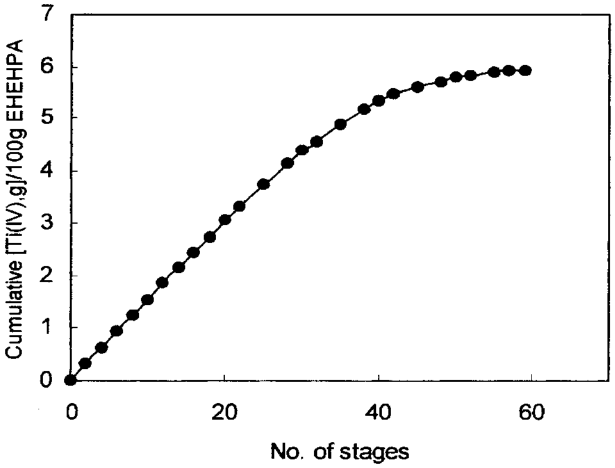

***Figure 5.*** Loading of EHEHPA by titanium(IV). HCl = 2.0 M.

shown in Table 2. The results clearly demonstrate that the extraction efficiency of titanium(IV) varies with the nature of diluent in the order: chloroform < benzene ∼ toluene < xylene < kerosene. Due to the high-extraction efficiency of titanium observed when kerosene was used as a diluent, subsequent studies were carried out using kerosene as a diluent.

## Stripping Studies

In any commercial extraction process, it becomes imperative to back-extract the metal from loaded organic phase. Titanium stripping from a loaded organic solvent system consisting of 0.2 M EHEHPA in kerosene and 0.01 M

***Table 2.*** Dependence of the nature of diluent on extraction of titanium(IV) using EHEHPA.

| Diluent | D |
|---|---|
| Chloroform | 1.15 |
| Benzene | 1.32 |
| Xylene | 1.59 |
| Toluene | 1.32 |
| Kerosene | 5.27 |

*Table 3.* Stripping of titanium(IV) from loaded extractant phase.

| Stripping agent | % Ti recovery |
|---|---|
| 1 M HCl | 0.5 |
| 2 M HCl | 3.0 |
| 3 M HCl | 10.0 |
| 4 M HCl | 11.7 |
| 2 M HCl + 1% $H_2O_2$ | 61.2 |
| 2 M HCl + 2% $H_2O_2$ | 95.5 |
| 2 M $H_2SO_4$ + 1% $H_2O_2$ | 68.2 |
| 2 M $H_2SO_4$ + 2% $H_2O_2$ | $>99.9$ |

titanium has been investigated using various stripping agents and the results are shown in Table 3. As the *D* values of titanium(IV) were found to be high (in the range of 0.5 M to 2.0 M HCl), stripping was impractical with hydrochloric acid alone. On the other hand, a mixture of hydrochloric acid and $H_2O_2$ as a stripping agent gave better stripping efficiency. Among the many strippants tried, a mixture of 2.0 M $H_2SO_4$ and 2% $H_2O_2$ was found to be effective stripping agent ($>99.9\%$) for titanium in a single stage with a phase ratio of unity.

## Comparison of Extraction Behavior of Titanium(IV) with Other Associated Metal Ions

The extraction behavior of magnesium(II), aluminum(III), titanium(IV), vanadium(V), chromium(III), manganese(II), and iron(III) has been investigated as a function of hydrochloric acid concentration and the results are depicted in Fig. 6. It is clear from these results that the percentage extraction of titanium(IV), iron(III), and vanadium(V) decreases with increasing hydrochloric acid concentration. On the other hand, the extraction of magnesium(II), aluminum(III), chromium(III), and manganese(II) were found to be negligible under the present experimental conditions. Further, it is also clear from the results that the extraction of vanadium(V) and iron(III) is also negligible at about 2.0 M HCl concentration. Thus, these results clearly indicate that it is possible to separate titanium from other associated multivalent metal ions such as magnesium(II), aluminum(III), vanadium(V), chromium(III), manganese(II), and iron(III), using 0.2 M EHEHPA in kerosene as an extractant by controlling the HCl concentration in the aqueous phase.

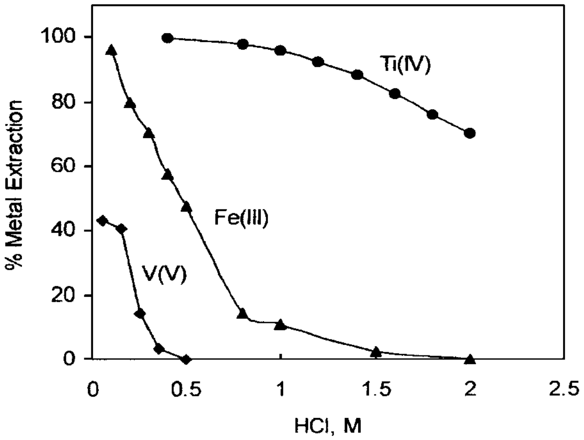

*Figure 6.* Effect of HCl concentration on the extraction of titanium(IV) (0.01 M), iron(III) (0.01 M) and vanadium(V) (0.001 M) using EHEHPA (0.2 M).

## Selective Extraction and Recovery of Titanium(IV) from Simulated Waste Chloride Liquor

Based on the results, a simulated waste liquor consisting of magnesium(II), aluminum(III), titanium(IV), vanadium(V), chromium(III), manganese(II), and iron(III) in 2.0 M HCl was prepared [The concentrations of various multivalent metal ions were chosen in such a way that they were

*Table 4.* Separation of titanium(IV) from multivalent metal chloride mixtures.

| | Amount of metal ion ( $\times 10^{-2}$ M) | | |
|---|---|---|---|
| Metal ion | Feed | Raffinate | Strip liquor |
| Ti(IV) | 0.80 | 0.01 | 0.79 |
| Mg(II) | 7.60 | 7.60 | ND |
| Al(III) | 1.30 | 1.30 | ND |
| V(V) | 0.90 | 0.90 | ND |
| Cr(III) | 0.20 | 0.20 | ND |
| Mn(II) | 3.10 | 3.10 | ND |
| Fe(III) | 0.80 | 0.80 | ND |

ND = not detectable.

equivalent to the waste chloride liquor at half dilution level.[18]] and subjected to extraction using 0.2 M EHEHPA in kerosene as an extractant (phase ratio A : O = 1 : 1) with a view to develop a selective extraction and separation method for the recovery of titanium from waste chloride liquors of titanium mineral processing industry. The results are shown in Table 4. It is clear from the table that titanium can be selectively separated from multivalent metal chloride solutions when extracted from 2.0 M hydrochloric acid solutions with 0.2 M EHEHPA in kerosene as an extractant in a single stage of extraction. Subsequently, titanium(IV) can be quantitatively recovered from the loaded organic phase in a single stage of stripping (O : A = 1 : 1) using a mixture consisting of 2 M $H_2SO_4$ and 2% $H_2O_2$ as stripping agent.

## CONCLUSIONS

This study clearly demonstrates the usefulness of EHEHPA as a selective reagent for the extraction of titanium(IV) over magnesium(II), aluminum(III), vanadium(V), chromium(III), manganese(II), and iron(III) from hydrochloric acid solutions. The extraction equilibrium of titanium(IV) can be explained by a simple chemically based model presented in this article. Furthermore, the results also indicate that EHEHPA can be used as a potential extractant for the selective extraction and separation of titanium(IV) from the waste chloride liquors of titanium minerals processing industry.

## ACKNOWLEDGMENTS

One of the authors, JS would like to thank CSIR, New Delhi, for the award of senior research fellowship.

## REFERENCES

1. Mikami, Y.; Iyatomi, N. Process for Recovering Sulfuric Acid from Metallic Sulfate-Containing Exhaust Sulfuric Acid. US Patent 5,489,423, February 6, 1996.
2. Duyvesteyn, W.P.C.; Sabacky, B.J.; Verhulst, D.E.V., et al. Processing Titaniferous Ore to Titanium Dioxide Pigment. WO 01/00531 A1, January 4, 2001.

3. Sole, K.C. Recovery of titanium from the leach liquors of titaniferous magnetites by solvent extraction. Part 1. review of the literature and aqueous thermodynamics. Hydrometallurgy **1999**, *51* (2), 239–253.
4. Sole, K.C. Recovery of titanium from the leach liquors of titaniferous magnetites by solvent extraction. Part 2. laboratory-scale studies. Hydrometallurgy **1999**, *51* (3), 263–274.
5. Islam, F.; Rahman, H.; Ali, M. Solvent extraction separation study of Ti(IV), Fe(III) and Fe(II) from aqueous solutions with di-2-ethylhexyl phosphoric acid in benzene. J. Inorg. Nucl. Chem. **1979**, *41*, 217–221.
6. Islam, M.F.; Biswas, R.K.; Mustafa, C.M. Solvent extraction of Ti(IV), Fe(III) and Fe(II) from acidic sulfate medium with di-o-tolyl phosphoric acid–benzene–hexan-1-ol system: a separation and mechanism study. Hydrometallurgy **1985**, *13* (3), 365–376.
7. Saji, J.; Saji John, K.; Reddy, M.L.P. Liquid–liquid extraction of tetravalent titanium from acidic chloride solutions by *bis*(2,4,4-trimethylpentyl) phosphinic acid. Solvent Extr. Ion Exch. **2000**, *18* (5), 877–894.
8. Vogel, A.I. *A Textbook of Quantitative Chemical Analysis*, 5th Ed.; ELBS, Longman: UK, 1989; 645–730.
9. Clesceri, L.S.; Greenberg, A.E.; Eaton, A.D., Eds. *Standard Methods for Examination of Water and Wastewater*, 20th Ed.; American Public Health Association: Washington, 1998; 3–65.
10. Morrison, G.H.; Freiser, H. *Solvent Extraction in Analytical Chemistry*; Wiley: New York, 1957; 244 pp.
11. Vogel, A.I. *A Textbook of Quantitative Chemical Analysis*, 5th Ed.; ELBS, Longman: UK, 1989; 329 pp.
12. Biswas, R.K.; Begum, D.A. Solvent extraction of tetravalent titanium from chloride solution by di-2-ethylhexyl phosphoric acid in kerosene. Hydrometallurgy **1998**, *49* (3), 263–274.
13. Kotrly, S. *Handbook of Chemical Equilibria in Analytical Chemistry*; Ellis Horwood: Chichester, UK, 1985; 414 pp.
14. Francis, T.; Meera, R.; Reddy, M.L.P. Extraction of mercury(II) with dicyclohexano-18-crown-6 and its application to industrial wastes. Sep. Sci. Tech. **2001**, *36* (10), 2341–2353.
15. Ritcey, G.M.; Ashbrook, A.W. *Solvent Extraction—Principles and Applications to Process Metallurgy, Part I*; Elsevier: Amsterdam, 1984; 101 pp.
16. Iio, K.; Takahashi, K.; Takeuchi, H. Solvent extraction of titanium(IV) from nitric acid solution by di-2-ethylhexyl phosphoric acid. Solvent Extr. Ion Exch. **1991**, *9* (1), 27–44.

17. Binghua, Y.; Nagaosa, Y.; Satake, M.; Nomura, A.; Horita, K. Solvent extraction of metal ions and separation of nickel(II) from other metal ions by organophosphorus acids. Solvent Extr. Ion Exch. **1996**, *14* (5), 849–870.
18. Saji, J.; Reddy, M.L.P. Liquid–liquid extraction separation of iron(III) from titania wastes using TBP–MIBK mixed solvent system. Hydrometallurgy **2001**, *61* (2), 81–87.

Received January 2002
Revised April 2002