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Solvent Extraction of tetravalent titanium from chloride and nitrate solutions by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) in Kerosene

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ABSTRACT

The extraction of titanium (IV) from chloride, and nitrate solutions has been studied using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) in kerosene as a solvent. The effect of acid concentration on extraction examined and it has been specified when concentration in aqueous solution (feed) is varied from 0.5-4 mol L^{-1}, the distribution ratios of titanium showed minimal values at 1-2 mol L^{-1} acid. The distribution ratio of titanium (IV) increases with the extractant concentration in the organic phase. The extraction of titanium (IV) has been done in presence of other metal ions viz. iron (III), silicon (IV), calcium (II), magnesium (II), manganese (II) and aluminum (III) which are associated with titanium in the titaniferous magnetite. At the next stage, the stripping of titanium was studied using H_2SO_4, $H_2SO_4+H_2O_2$ and Na_2CO_3. The kinetics of the stripping was very slow when sulphuric acid was used, but it was improved with complex forming stripping agents ($H_2SO_4+H_2O_2$) and Na_2CO_3. The titanium recovery was 97% using aqueous nitrate medium as an extractant and sodium carbonate as a stripper. Third phase formation was observed during extraction stage.

Keywords: Leaching, Solvent extraction, Hydrometa1llurgy, titanium.

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INTRODUCTION

Titanium and its alloys, due to their excellent characteristics are used for various purposes in industry. In particular, titanium has been widely used in the aerospace industry while titanium dioxide finds applications as pigment in the paint industry. Titanium ore can be effectively leached by HCl, H_2SO_4, HNO_3 and mixed acid solutions. A preliminary study shows that in terms of titanium yield, the best result was obtained by H_2SO_4+ HNO_3 [1].

Many solvents have been tested for the extraction of titanium (IV) from aqueous solutions. It is recognized that neutral organo-phosphorous compounds are effective extractants for tetravalent

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metals, particularly for titanium (IV). Among these, tri-n-butyl phosphate (TBP), tri-octyl phosphine oxide (TOPO) and Cyanex 923 (TRPO) have been used widely for the extraction of titanium (IV) from acidic solutions [2]. However, the use of TBP and TOPO leads to third phase formation when titanium (IV) is extracted [3]. Organophosphorus acid derivatives such as di-2-ethylhexyl phosphoric acid (D2EHPA) have been used by several investigators for the extraction of titanium (IV) from acidic aqueous solutions [4]. Biswas and Begum (1998) have studied the solvent extraction of tetravalent titanium from hydrochloric acid solutions using D2EHPA in kerosene as an extractant and have reported the usual cation exchange mechanism at lower loading of the metal ion [5]. On the other hand, these authors also reported the formation of TiOA2 species at higher loading of the metal ion. Further, these authors noticed slow kinetics for the extraction of titanium with D2EHPA. Fontana et al. (2005) have studied the extraction of titanium from nitric, sulfuric and hydrochloric acid solutions using EHEHPA in kerosene. Titanium extraction has been studied by Jayachandran and Dhadke [6]. John et al. (1999a) and Sing and Dhadke (2002) in H_2SO_4, HCl and $HClO_4$ solutions, respectively.

Among acidic organophosphonic extractants, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) has been used commercially due to its good ability to extract a large number of metal ions [7-8]. In this paper, the solvent extraction of titanium (IV) from chloride and nitrate solutions by EHEHPA has been studied to determine the best conditions of extraction and stripping for the effective recovery of titanium from other impurity elements.

MATERIALS AND METHODS

2.1. Materials
2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA) and low odor kerosene as diluent was used without further purification. All other chemicals used were of analytical grade. Titanium (IV) stock solution was prepared by leaching titaniferous magnetite in concentrated hydrochloric acid (37%) and nitric acid (68%) to check the effect of competing ions on titanium extraction. Unlike of other studies the composition of the titaniferous magnetite is natural and it was analyzed by XRF. The results of XRF analysis and the composition of leach solutions for two concentrations of Ti (leach solution A with 0.01 mol L^{-1} Ti and leach solution B with 0.02 mol L^{-1} Ti), by ICP–OES analysis are shown in Tables 1 and 2.

Table. 1. Composition of titaniferous magnetite (feed) with XRF analysis

Component	Concentration (%)	Component	Concentration (ppm)
SiO_2	9.30	Cl	340
Al_2O_3	1.52	S	30
Fe_2O_3	72.61	Ba	210
CaO	3.36	Sr	14
Na_2O	0.24	Zn	80
K_2O	0.32	V	1929
MgO	1.34	Ni	50
TiO_2	10.25	Cr	1372
MnO	0.353	Co	28
P_2O_5	0.372		

2.2. Procedure
Extraction and stripping was performed with equal volumes (50 mL) of aqueous and organic phases (A/O= 1) using a mechanical shaker at room temperature. Preliminary experiments showed that equilibrium in extraction stage was reached within 50 min and phase separation occurred within 8 min. EHEHPA concentrations of 0.2 and 0.5 mol L^{-1} were used throughout the

experiments. The titanium concentration was varied from 0.01 to 0.02 mol L^{-1}, while the effect of acid concentration was examined within the 0.5–4 mol L^{-1}. The concentrations of the titanium and other metals in the aqueous phase and strip solutions were determined using an inductively coupled plasma, (ICP–OES) and in organic phase were calculated by the method of mass balance [9-10].

Table. 2. Composition of leach solution with ICP (OES type) analysis

Component	Concentration (mol L^{-1})		Component	Concentration (mol L^{-1})	
	Leach solution(A)	leach solution (B)		Leach solution(A)	leach solution (B)
Si	0.0121	0.0242	Mg	0.00259	0.00518
Al	0.00232	0.00464	Ti	0.0100	0.0200
Fe	0.0710	0.142	Mn	0.000388	0.000776
Ca	0.00462	0.00924	Na	0.000604	0.00121

RESULTS AND DISCUSSION

3.1. Extraction equilibrium

The extraction equilibrium of titanium (IV) with an acidic organophosphorus extractant, EHEHPA ((HX)$_2$) may be represented as:

$$TiO^{2+} + 2 (HX)_2 \Leftrightarrow TiO(HX_2)_2 + 2H^+ \tag{1}$$

Where K$_{ex}$ denotes the equilibrium constant and (HX)$_2$ refers to the dimeric form of EHEHPA. The equilibrium constant, K$_{ex}$ for the above reaction is expressed as:

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

Titanium (IV) in the aqueous phase forms a variety of complexes in the presence of chloride or nitrate ions. Then the total [Ti (IV)] is expressed as:

$$[Ti(IV)]_{total} = [TiO^{2+}] + [TiOCl^+] + [TiOCl_2]$$
$$= [TiO^{2+}] \{1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2\} \tag{3}$$

Where β_1 and β_2 are the stability constants of the following reactions, respectively:
$$TiO^{2+} + Cl^- \Leftrightarrow TiOCl^+ \tag{4}$$
$$TiO^{2+} + 2Cl^- \Leftrightarrow TiOCl_2 \tag{5}$$
Then the distribution ratio of titanium (IV), *D* and is defined as titanium concentration at organic phase to titanium concentration at aqueous phase, can be written from Eqs. (1) and (3):

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

3.2. Effect of titanium concentration

About 1 mol L^{-1} aqueous solutions of HCl and HNO$_3$, with different amounts of titanium (0.01–0.02 mol L^{-1}) were equilibrated separately with 0.5 mol L^{-1} EHEHPA in kerosene solution. The results showed that distribution ratios in two used acidic media are influenced by the initial titanium concentration (the distribution ratio decreases with increasing initial titanium concentration). Sole (1999) noticed similar behavior for the extraction of titanium from sulfuric

solutions using TOPO [11] but Biswas and Begum (1998) noticed different behavior for the extraction of titanium from chloride solutions using D2EHPA and Fontana et al. (2005) for the extraction of titanium from sulfate, nitrate and chloride solutions using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (the distribution ratio is independent of initial titanium concentration in aqueous phase up to 1 gr L^{-1} and after that it decreases appreciably). From these data, it was seen that titanium extraction from a nitrate medium presents higher distribution coefficient values than Chloride medium. It may be due to the difference in the activity of Ti (IV) and ion-pairing nature of these anions (Fontana et al., 2005).

3.3. Effect of extractant concentration
The effect of EHEHPA concentration (0.2 to 0.5 mol L^{-1}) on Ti (IV) extraction has been studied at constant titanium (0.01 mol L^{-1}), HCl and HNO_3 (1 mol L^{-1}) concentrations and the results are shown in Fig. 1. It can be observed from the results that the extraction of titanium increases with increasing extractant concentration.
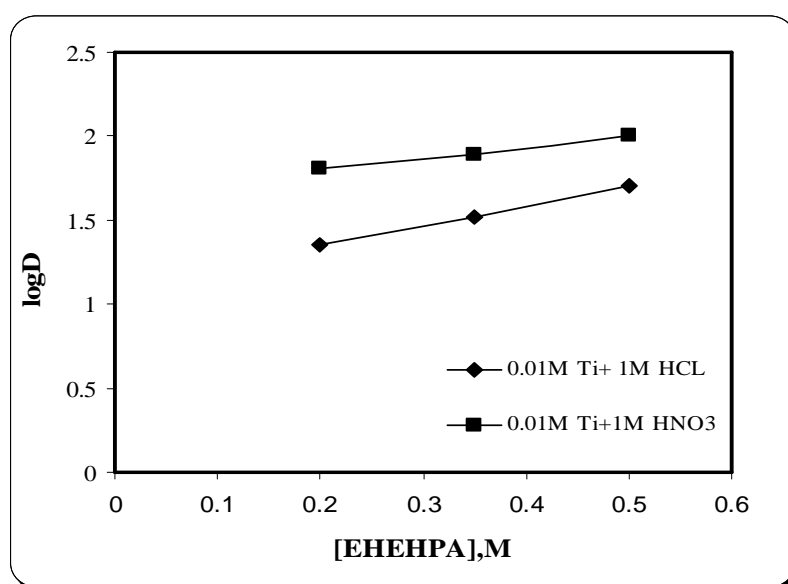

Fig. 1. Dependence of distribution ratio on extractant (EHEHPA) concentration

3.4. Effect of hydrochloric acid concentration
Many authors studied extraction of titanium from acidic chloride solutions, where Ti (IV) forms a variety of complexes. Seyfi et al. (1999a) used a neutral extractant (Cyanex 923) for the extraction of titanium and found an increase in extraction with the increase in chloride ion concentration. The plots of log D vs. [HCl] for 0.01 and 0.02 mol L^{-1} Ti (IV) and 0.2 and 0.5 mol L^{-1} EHEHPA systems are given in Fig.2.

Fig. 2 shows a very slight minimum in the distribution values at 1 M HCl concentration. It indicates that extraction of titanium using EHEHPA is much less dependent on the hydrochloric acid concentration; probably because at 4 M HCl the dominating species is still TiO^{2+} and the cation exchange mechanism occurs as reported for EHEHPA (Fontana et al., 2005; Saji and Reddy, 2003) and for D2EHPA (Biswas and Begum, 1998). It appears that Cl^- does not participate in the extracted species TiO $(HX_2)_2$ [12].
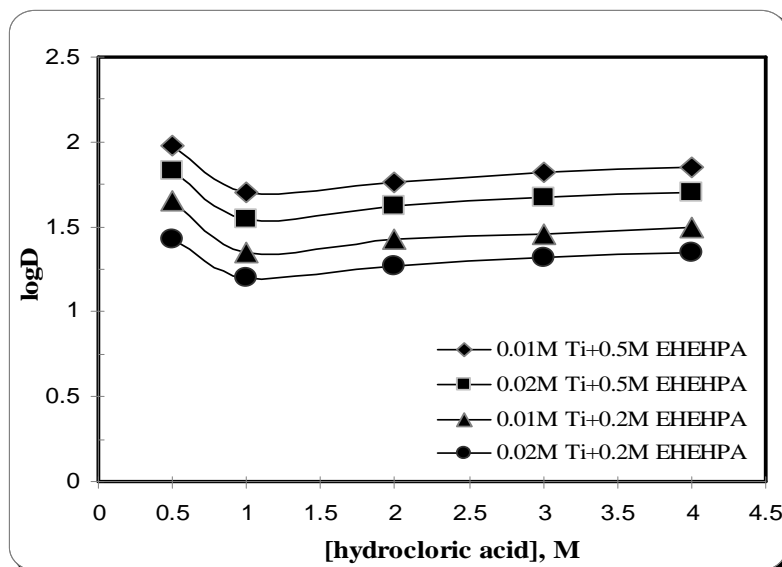
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Fig. 2. Dependence of distribution ratio on hydrochloric acid concentration

3.5. Effect of nitric acid concentration

Fontana et al. (2005) and Iio et al. (1999) have studied the extraction of titanium from nitric acid solutions using EHEHPA and D2EHPA, respectively. Extraction of titanium with different concentrations of nitric acid was performed in this study. The leach solution in this case is the same as Table 2. It was found that with increase of acid concentration, extraction increases up to 1 mol L^{-1} HNO3, but thereafter it passes through a minimum at 2 mol L^{-1} acid, instead of 1 mol L^{-1} as was the case when hydrochloric acid was used. The experimental curves are shown in Fig. 3.
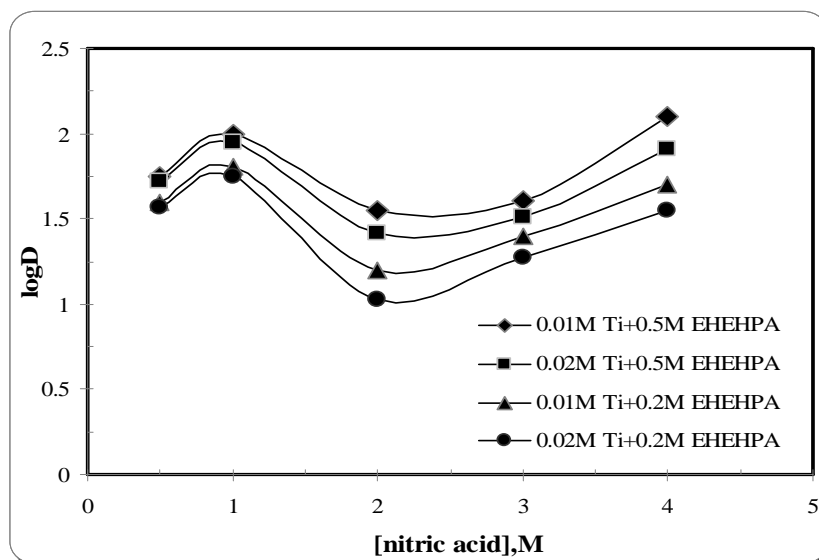

Fig. 3. Dependence of distribution ratio on nitric acid concentration

3.6. Effect of associated metal ions

Based on the percentage metal extraction obtained with leaching solution A, selective titanium separation can be done efficiently at 1 mol L^{-1} acid concentration (Table 3). In particular aluminum, calcium, manganese and magnesium do not interfere in any of the acids, while silicon is slightly extracted. Iron (III) seems to be the most competitive ion, reaching 65% extraction in nitric acid medium while the hydrochloric medium seems offer the lowest iron extraction. The extent of titanium extraction decreases in the following order HNO$_3$ > HCl.

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Table 3. Percentage of metals extraction from leaching solution A
(0.5 mol L^{-1} EHEHPA in Kerosene, O/A = 1, H$^+$ = 1 mol L^{-1})

Medium	Ti	Fe	Si	Al	Ca, Mg, Mn
Chloride	93	49.8	2.5	0	0
Nitrate	98	65.0	8.8	0	0

3.7. Stripping

The effect of stripping agents and their concentrations on titanium extraction from a loaded organic phase consisting of 0.5 mol L^{-1} EHEHPA and 0.01 mol L^{-1} Ti (IV) has been studied. A single stage experiment with 2 mol L^{-1} sulphuric acid shows that the titanium stripping kinetics is very slow (>160 min). The maximum percentage of stripping was found to be about 20% because of the strong Ti–TBP complex. Jayachandran and Dhadke (1998) reported that a mixture of H$_2$O$_2$ and sulphuric acid produces quantitative stripping of titanium as Ti(OH)$_4$(H$_2$O$_2$) SO$_4$. In this investigation, it was found that with increase in concentration of H$_2$O$_2$, the stripping of titanium increases to 82% as shown in Fig. 4.

A further interesting breakthrough was achieved when sodium carbonate was used as a stripping agent. The stripping of titanium was very fast and the yield was 99% (Fig. 4). The time required for the complete stripping was 60 min. More experiments showed that the time more than 60 min has no effective influence on equilibrium. The stripping of a loaded organic phase that also contained iron, using 2 mol L^{-1} Na$_2$CO$_3$, gave a promising result because 97% Ti was recovered with iron content below 9%. However separation of titanium from co-extracted iron (III) can be easily achieved, because iron can be stripped first by H$_2$SO$_4$ and subsequently titanium can be quantitatively stripped by 2 mol L^{-1} Na$_2$CO$_3$.
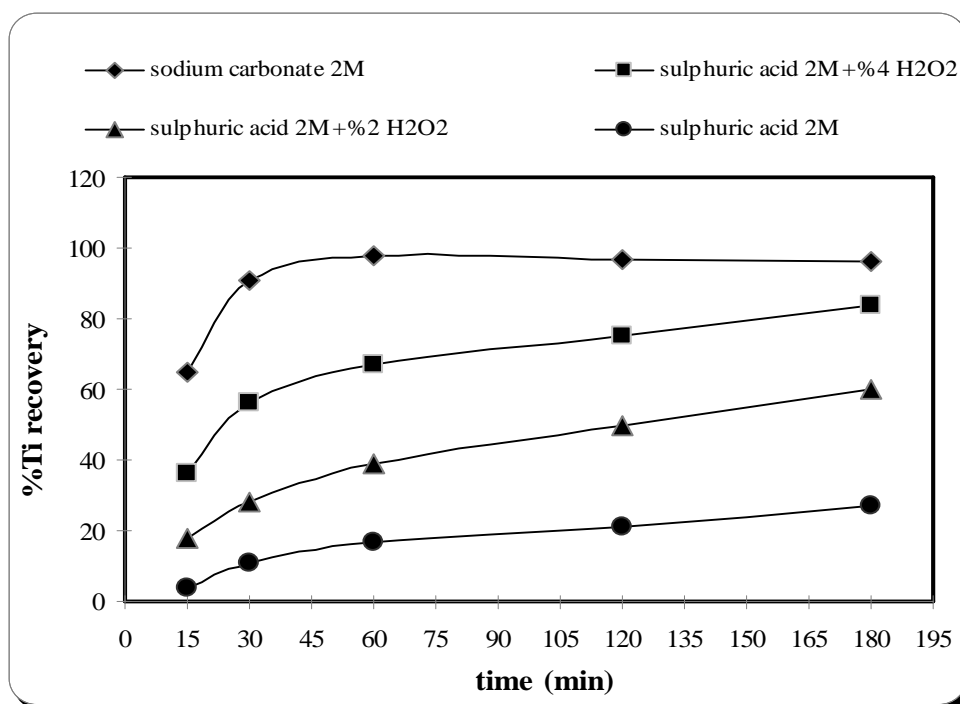

Fig. 4. Stripping rate of titanium from EHEHPA using different stripping agents

4. Third Phase Formation

Third phase formation is a phenomenon observed in solvent extraction during the loading of metal and/or mineral acid in the organic phase comprising of an extractant and non-polar diluent

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under some experimental conditions, under which the organic phase splits into two phases [13-14] .The light phase comprises mostly of the diluent and little extractant and metal solvate and is called diluent-rich phase. The heavy phase contains a high concentration of extractant and metal-solvate and little diluent and is known as third phase, with density intermediate between light organic and aqueous phases and hence usually accumulates in the interface.

Since solvent extraction plants are designed to operate only with two phases, formation of a third phase can complicate the operations. It creates density and viscosity effects, which affect the mixing of organic and aqueous phases [15-16] .In the case of titanium, the phenomenon has great significance with respect to the danger of criticality since the concentration of titanium in the third phase can be as high as 210 g/L .In order to avoid third phase formation, higher loading in the organic phase has to be restricted, and hence this phenomenon limits the metal loading, which can be practically achieved in the organic phase. Hence, preventing third phase formation is of paramount importance to improve the efficiency of solvent extraction processes.

CONCLUSION

Solvent extraction of titanium (IV) was investigated in order to study the effect of different acidic media, over the concentration range of 0.5–4 mol L^{-1} on the recovery by 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA). The extraction of titanium is dependent on the initial metal ion concentration. The highest distribution coefficient is observed for 1 mol L^{-1} nitric acid. The distribution ratios of titanium depend on the hydrochloric and nitric acid concentration in the aqueous phase and the extractant concentration in the organic phase. The stripping of titanium by sulphuric acid is much more effective adding H_2O_2, but is more complete and faster transfer when sodium carbonate is used.

 From the practical point of view, the results of this study suggest that the extraction of titanium can be performed using EHEHPA with each acidic solution. Regarding competition the among impurity metals, iron (III) seems to be the most competitive ion with 49.8–65% co-extracted, depending upon the acidic media.

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