

## **Extraction and separation of titanium(IV) with D2EHPA and PC-88A from aqueous perchloric acid solutions**

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(Received 20 August 2001, revised 1 March 2002)

The liquid-liquid extraction of Ti(IV) from perchlorate media using, di(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl prosthonic acid mono-2-ethylhexyl ester (PC-88A) in toluene as the extractant was studied. Quantitative extraction of Ti(IV) was observed in the lower acidity range of 0.01 to 0.1 mol dm<sup>-3</sup> with 0.003 mol dm<sup>-3</sup> D2EHPA and 0.01 mol dm<sup>-3</sup> PC-88A in toluene, respectively, and in the higher acidity range of 9.0 to 10.0 mol dm<sup>-3</sup> with 0.1 mol dm<sup>-3</sup> D2EHPA and PC-88A in toluene. Ti(IV) was completely stripped from the metal loaded organic phase of both the extractants with 3 % H<sub>2</sub>O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> and determined spectrophotometrically. The stoichiometry of the extracted species was determined on the basis of slope analysis. The extraction in the lower acidity range was found to proceed by a cation-exchange mechanism with the extracted species being TiOR<sub>2</sub>·2HR, while in the higher acidity range it was by solvation with the extracted species being Ti(OH)<sub>3</sub>ClO<sub>4</sub>·4HR. Separation of Ti(IV) was also carried out from some associated metals like Fe(III), Al(III), V(V), Ce(IV), Mg(II) and Mn(II). The developed methods were extended for the determination of Ti(IV) in real samples like ilmenite, magnetite and red mud in order to show the practical utility of the extractants.

*Keywords:* extraction, titanium, separation, D2EHPA, PC-88A and stripping.

### INTRODUCTION

Titanium metal has become known as a space-age metal because of its high strength-to-weight ratio and inertness to many corrosive environments. The present application areas of titanium include nuclear-waste canisters, pacemaker castings, medical implants, high performance automotive applications and ordnance armor. Although the principal application of high purity TiO<sub>2</sub> is as paint pigments, its utility as a photocatalyst has recently received widespread attention for the treatment of anthropogenic compounds in water.<sup>1</sup> Apart from being an important constituent of several alloys and catalysts, its future application area could include TiO<sub>2</sub> single-crystal electrodes, flue-gas denitrification catalysts and for the manufacture of barium titanate thermistors. Because of its widespread use, the primary sources of titanium are becoming exhausted and efficient methods have to be developed to recover it from

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low-grade ores and secondary sources. In view of the high purity requirements of the metal, solvent extraction offers and attractive alternative.

A literature survey revealed that over the years a variety of compounds, such as 8-hydroxyquinoline,<sup>2</sup> thenoyltrifluoroacetone,<sup>3</sup> cupferron,<sup>4</sup> molten biphenyl,<sup>5</sup> amidines,<sup>6</sup> catechol,<sup>7</sup> alizarin RS,<sup>8</sup> triisoamyl phosphate,<sup>9</sup> high molecular weight amines,<sup>10–12</sup> aliphatic carboxylic acids,<sup>13</sup> TBP,<sup>14</sup> TOPO<sup>15</sup> and most recently Cyanex-301 and Cyanex-302,<sup>16</sup> have been used for the extraction of Ti(IV). However, these methods have limitations such as interference of different ions and stringent control of pH,<sup>5–8</sup> emulsion formation and interference from co-existing metal ions,<sup>10–12</sup> the use of salting-out agents,<sup>2,4</sup> incomplete extraction<sup>3,9</sup> and use of high reagent concentrations.<sup>14,15</sup>

In recent years acidic organophosphorus compounds, such as di(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), have been widely used to extract and separate a number of metals.<sup>17–19</sup> D2EHPA and PC-88A have similar structures, differing only in the number of alkoxy (–RO) group directly attached to the phosphorus atom. This structural difference significantly affects the extractability and the separation efficiency of metal ions.

Though some studies on the extraction of Ti(IV) have been reported with D2EHPA<sup>20–24</sup> and PC-88A<sup>25,26</sup> from chloride, nitrate, sulphate and phosphate media, they have been confined to studying the extraction equilibria and the extraction kinetics. Extraction of Ti(IV) in chloride media by mixtures of mono-2-ethylhexyl phosphoric acid (MEHPA) and D2EHPA have also been reported.<sup>27</sup>

Perchloric acid, due to its oxidizing effect, acidic strength and high solubility of salts, is a stable reaction media which has long been used effectively. Hence it was preferred over other commonly used extraction media and has advantageously been used for the extraction of various metal ions.<sup>28,29</sup> No extraction and separation study of Ti(IV) from commonly associated metal ions with D2EHPA and PC-88A from perchloric acid medium has been reported to date.

The present work deals with a study of the extraction of Ti(IV) and its separation from some commonly associated metal ions, such as Fe(III), Al(III), V(V), Ce(IV), Mg(II), Mn(II), from perchlorate media with D2EHPA and PC-88A. The proposed method has been successfully employed for the recovery of pure Ti(IV) in ilmenite and red mud. The proposed method is simple, precise, rapid and free from the limitations described earlier.

## EXPERIMENTAL

### *Apparatus*

A GBC 991A UV-visible spectrophotometer and a Mitisubishi model CA-02 moisture meter were employed.

### *Reagents and chemicals*

The stock solution of Ti(IV) was prepared by dissolving appropriate amount of titanium dioxide, TiO<sub>2</sub> in perchloric acid and treating for about 2 h. The insoluble residue was filtered off and the filtrate standardized by the tannic acid and phenazone method.<sup>30</sup>

Other metal ion solutions were made from their salts in a similar way. The solutions were standardized<sup>30</sup> and working solutions of lower concentration were obtained by dilutions. The extractants di-(2-ethylhexyl)

phosphoric acid, D2EHPA, and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester, PC-88A, were obtained from Dai-hachi Chemical Industries Ltd., Japan and used for the extractions without further purification. All other chemicals used were of analytical reagent grade.

#### General extraction procedure

The extraction/stripping experiments were performed by shaking the appropriate organic and aqueous solution (10 ml each) at an O/A phase ratio of 1 for 20 min. All distribution equilibria studies were carried out at 25 °C. The initial concentration of Ti(IV) was maintained at 0.01 mol dm<sup>-3</sup> throughout the experiments (unless otherwise stated) and the metal content in the equilibrated aqueous phase was determined spectrophotometrically,<sup>31</sup> whereas the metal ions in the organic phase was calculated by mass balance. The distribution coefficient *D* was calculated as the ratio of the equilibrium concentration of Ti(IV) in the organic phase to that in the aqueous phase. The content of water in the organic phase was measured by a moisture meter.

All experiments were repeated on average three times and the accuracy determination of the metal concentration in the loaded phase was realized by mass balance and checked by complete stripping of the loaded organic phase followed by analysis of the stripped solution.

## RESULTS AND DISCUSSION

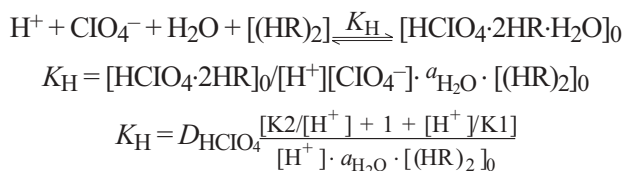
### Extraction mechanism of perchloric acid and water

The extraction of perchloric acid and water with D2EHPA and PC-88A was studied in order to describe comprehensively the extraction mechanism of Ti(IV) from perchloric acid solutions.

The extraction isotherms of perchloric acid and water are shown in Fig. 1. When the concentration of perchloric acid in the aqueous phase was less than 3 mol dm<sup>-3</sup>, the concentrations of perchloric acid and water in the equilibrium organic phases increase insignificantly with increasing acidity of the aqueous phase. However, when the concentration of HClO<sub>4</sub> in the aqueous phase was more than 3 mol dm<sup>-3</sup>, they increase sharply with increasing acidity of the aqueous phase. Therefore, perchloric acid and water is shown to be well extracted at higher acidities.

The slopes of all log *D*<sub>HClO<sub>4</sub></sub> and log [H<sub>2</sub>O]<sub>0</sub> plot against log [(HR)<sub>2</sub>]<sub>0</sub> are close to 1, where log *D*<sub>HClO<sub>4</sub></sub> denotes the distribution ratio of HClO<sub>4</sub>, log [H<sub>2</sub>O]<sub>0</sub>, the concentration of water in the equilibrium organic phase and log [(HR)<sub>2</sub>]<sub>0</sub>, the organic dimer concentration of D2EHPA and PC-88A. D2EHPA and PC-88A are known to exist as stable dimers in solvents of low polarity.<sup>32</sup>

Therefore, the extraction equilibrium of HClO<sub>4</sub> and water with D2EHPA and PC-88A in toluene can be expressed as follows:



where *K*<sub>H</sub> refers to the extraction equilibrium constant, *a*<sub>H<sub>2</sub>O</sub> is the activity of water, *K*<sub>1</sub> = [ClO<sub>4</sub><sup>-</sup>][H<sup>+</sup>]/[HClO<sub>4</sub>] and *K*<sub>2</sub> = [ClO<sub>4</sub><sup>-</sup>]/[HClO<sub>4</sub>].

There is a good relation between the low acidity range extraction by cation exchangers such as D2EHPA and PC-88A and that of cationic oxo- or hydroxo complexes of Ti(IV). How-

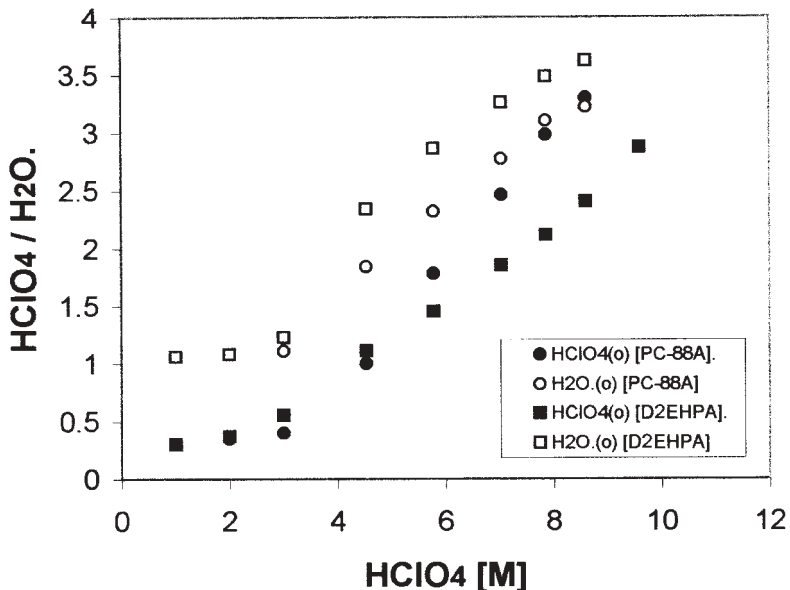


Fig. 1. Extraction isotherms of  $\text{HClO}_4$  and  $\text{H}_2\text{O}$  with D2EHPA and PC-88A.

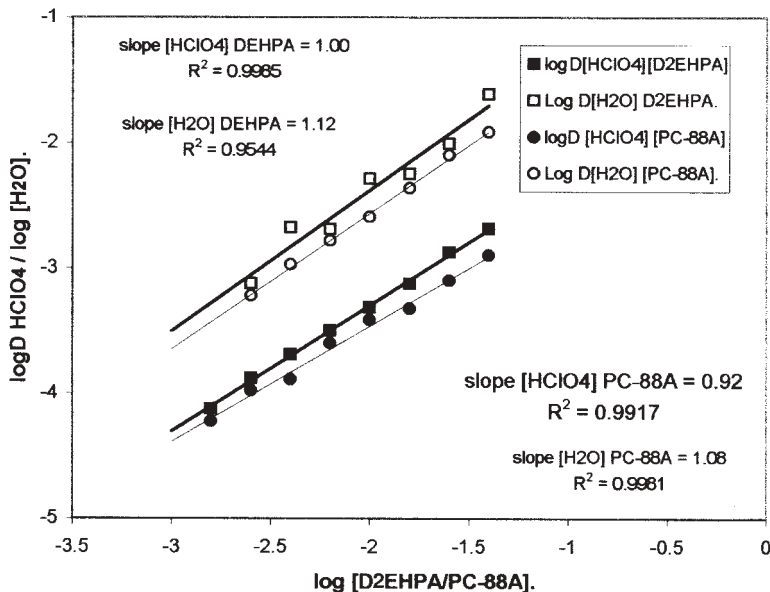


Fig. 2. Effect of the D2EHPA and PC-88A concentration on  $\log D_{\text{HClO}_4}$  and  $\log [\text{H}_2\text{O}]$ .

ever, in efficient extraction also occurs at high acidity, which is quite surprising considering that at high acidity the cation exchangers are present in their protonated form. The Ti(IV) cationic species are probably not strong enough acids to compete with  $\text{H}^+$  at high acidity. It seems more reasonable that these acids act as neutral complexants in the high acidity range, (Figs. 1 and 2).

### Effect of acidity

Perchloric acid has been found to play a dominant role in the extraction, hence the extraction of Ti(IV) was carried out in the perchloric acid media with D2EHPA and PC-88A.

The percentage extraction of Ti(IV) by D2EHPA decreases with increasing  $\text{HClO}_4$  concentration below  $3.5 \text{ mol dm}^{-3}$ , but above this acidity the extraction curve rises. In contrast, though the extraction curve for PC-88A resembles that of D2EHPA, a minimum appears at  $2.0 \text{ mol dm}^{-3}$ . It was observed that the extraction was quantitative in the range of  $0.01\text{--}0.1 \text{ mol dm}^{-3}$   $\text{HClO}_4$  with both D2EHPA and PC-88A. In this range the extraction proceeds by a cation exchange reaction. The extractions with D2EHPA and PC-88A are also quantitative in the  $\text{HClO}_4$  concentration range of  $9.0\text{--}10.0 \text{ mol dm}^{-3}$  but the extraction proceeds by a solvation reaction. (Fig. 3).

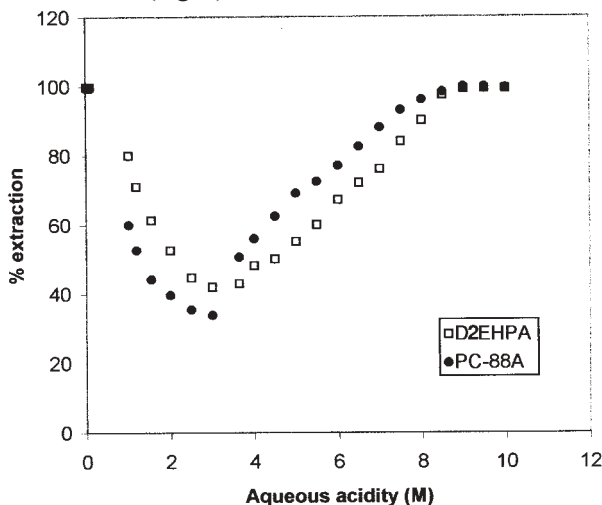


Fig. 3. Effect of the acidity of the aqueous phase on the percentage extraction of Ti(IV) with D2EHPA and PC-88A.

It was noted that the efficiency of Ti(IV) extraction with PC-88A is lower than that with D2EHPA at low acidity of the aqueous phase, while the reverse is true at high acidity. A similar behaviour was observed in case of antimony(V) and hafnium(IV) extraction with MEHPA<sup>33</sup> and D2EHPA,<sup>34</sup> respectively.

### Effect of the reagent concentration

Extraction of Ti(IV) was carried out by varying the reagent concentration from  $1 \times 10^{-4}$ – $1 \times 10^{-1} \text{ mol dm}^{-3}$ , while keeping the aqueous phase acidity constant at either  $0.1 \text{ mol dm}^{-3}$  or  $9.0 \text{ mol dm}^{-3}$   $\text{HClO}_4$ . (Fig. 4).

It was observed that the extraction increases with the reagent concentration and with the lower  $\text{HClO}_4$  concentration ( $0.1 \text{ mol dm}^{-3}$ ),  $3 \times 10^{-3} \text{ mol dm}^{-3}$  D2EHPA and  $1 \times 10^{-2} \text{ mol dm}^{-3}$  PC-88A dissolved in toluene gave quantitative extraction, while at the higher acidity  $\text{HClO}_4$  concentration ( $9.0 \text{ mol dm}^{-3}$ ), quantitative extraction was obtained with a minimum D2EHPA and PC-88A concentration of  $0.1 \text{ mol dm}^{-3}$ , respectively.

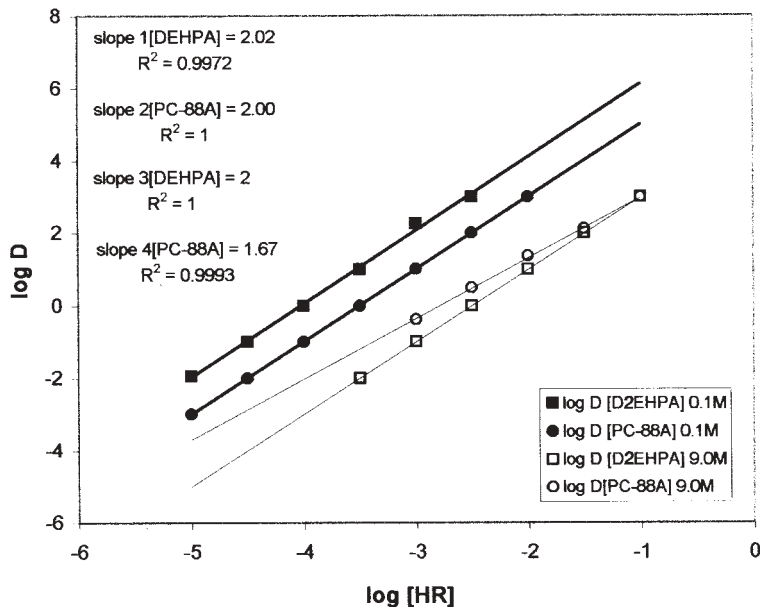


Fig. 4. Effect of the concentration of D2EHPA nad PC-88A on the extraction of Ti(IV) from aqueous  $HClO_4$ .

#### Effect of equilibration time

Ti(IV) was equilibrated with  $3.0 \times 10^{-2} \text{ mol dm}^{-3}$  D2EHPA and  $1 \times 10^{-2} \text{ mol dm}^{-3}$  PC-88A in toluene for a period of 1–20 min. With D2EHPA quantitative extraction of Ti(IV) was found within 1 min while with PC-88A the same result was attained only after 3 min, although 87.6 % Ti(IV) was extracted into the organic phase within 1 min. There was no adverse effect on the extraction yield up to 20 min with either of the extractants (Fig. 5).

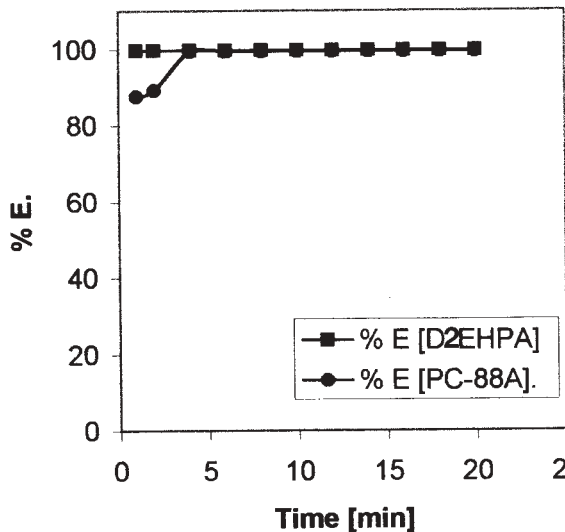


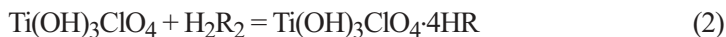
Fig. 5. Effect of the equilibration time on the percent extraction of Ti(IV) with D2EHPA and PC-88A from aqueous  $HClO_4$ .

### Nature of the extracted species

The nature of the extracted species was investigated by the slope analysis method (Fig. 4). The plots of  $\log D$  vs.  $\log [D2EHPA]/[PC-88A]$  for Ti(IV) at low acidity ( $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ ) and at high acidity ( $9.0 \text{ mol dm}^{-3} \text{ HClO}_4$ ) were linear with slopes of nearly 2.0. Therefore the metal to reagent stoichiometry of the Ti(IV): D2EHPA/PC-88A complex was 1:2. These results suggest that Ti(IV) was extracted from the perchlorate media with D2EHPA and PC-88A at low acidity as  $\text{TiOR}_2 \cdot 2\text{HR}$ , while the extraction takes place by solvation reaction at high acidities, where HR is the extractant D2EHPA and PC-88A in dimeric form<sup>32</sup> in the organic phase. The overall cation-exchange reaction can be expressed as follows:



and solvation reaction is



These extracted species are in close agreement with those proposed in earlier studies on the extraction of Ti(IV) which, based on spectroscopic data, reported that the extraction of Ti(IV) occurs by a cation-exchange reaction at low acidities and by a solvation reaction at high acidities.<sup>35,36</sup>

### Effect of diluents

Various aromatic and aliphatic organic diluents, such as toluene, chloroform, carbon tetrachloride, benzene, cyclohexane, *n*-hexane and xylene, have been employed for the extraction of Ti(IV). It was found that with both D2EHPA and PC-88A the extraction of Ti(IV) was quantitative only with toluene, xylene, *n*-hexane and benzene while chloroform, carbon tetrachloride and cyclohexane were comparatively less efficient.

Toluene was preferred as the diluent for both D2EHPA and PC-88A, as it provided better phase separation (Table I).

TABLE I. Effect of diluents on the extraction percentage of Ti(IV) with D2EHPA and PC-88A

Diluent	% E with	
	D2EHPA	PC-88A
Toluene	99.7	99.4
Xylene	99.7	99.4
Chloroform	78.8	77.3
Benzene	99.5	99.4
<i>n</i> -Hexane	99.5	99.4
Cyclohexane	89.7	87.8
Carbon tetrachloride	81.4	84.6

The results are the mean of triplicate values. Conditions: Aqueous phase:  $[\text{Ti}(\text{IV})] = 0.01 \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 0.1 \text{ mol dm}^{-3}$ . Organic phase:  $[\text{D2EHPA}/\text{PC-88A}] = 0.01 \text{ mol dm}^{-3}$ . Phase ratio: 1

### *Effect of various stripping agents*

Ti(IV) was stripped out from their loaded organic phases with different strength of stripping agents. Ti(IV) was stripped back from D2EHPA and PC-88A only with 4.5 mol dm<sup>-3</sup> HClO<sub>4</sub> and 3 % H<sub>2</sub>O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub>. The use of 3 % H<sub>2</sub>O<sub>2</sub> in 1 M H<sub>2</sub>SO<sub>4</sub> was preferred for the selective stripping of Ti(IV) as Fe(III) was also stripped when 4.5 mol dm<sup>-3</sup> HClO<sub>4</sub> was employed.

The back extraction of Ti(IV) was also carried out by varying the temperature while keeping the concentration of H<sub>2</sub>SO<sub>4</sub> constant and *vice-versa*. It was observed that the stripping was quantitative with 2 M H<sub>2</sub>SO<sub>4</sub> at a temperature of 333 K which may be attributed to the instability of the complex at that temperature and H<sub>2</sub>SO<sub>4</sub> concentration. The use of other strength acids did not give complete stripping. (Table II).

TABLE II. Efficiency of different stripping agents for the back extraction of Ti(IV)

Stripping agent/mol dm <sup>-3</sup>	% R of Ti(IV) from the organic phase of	
	D2EHPA	PC-88A
1.0 HCl	4.8	3.4
4.5 HCl	7.4	7.4
1.0 HNO <sub>3</sub>	16.8	15.7
4.5 HNO <sub>3</sub>	21.7	12.8
1.0 H <sub>2</sub> SO <sub>4</sub>	18.3	16.7
4.5 H <sub>2</sub> SO <sub>4</sub>	89.7	89.4
1.0 HClO <sub>4</sub>	38.3	36.7
4.5 HClO <sub>4</sub>	99.7	99.4
0.1 Tartaric acid	52.6	41.1
0.1 Oxalic acid	12.3	18.9
0.1 Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	68.7	64.8
3 % H <sub>2</sub> O <sub>2</sub> + 1 H <sub>2</sub> SO <sub>4</sub>	99.7	99.4

The results are the mean of triplicate values. Conditions: Aqueous phase: [Ti(IV)] = 0.01 mol dm<sup>-3</sup>, [HClO<sub>4</sub>] = 0.1 mol dm<sup>-3</sup>. Organic phase: [D2EHPA/PC-88A] = 0.01 mol dm<sup>-3</sup> in toluene. Phase ratio: 1

### *Metal loading capacity of the extractant*

The influence of the initial Ti(IV) concentration ( $1 \times 10^{-5}$  mol dm<sup>-3</sup> – 1.0 mol dm<sup>-3</sup>) on the extraction by D2EHPA and PC-88A in toluene was studied. It was observed that varying the initial Ti(IV) concentration in the concentration range  $1 \times 10^{-5}$  mol dm<sup>-3</sup> – 0.01 mol dm<sup>-3</sup> has no significant influence of Ti(IV) extraction with the extractant. This lack dependency of the metal distribution coefficient on the acidity of the aqueous phase indicates the probable absence of polynuclear species in the organic phase which is a clear indication of the mononuclear nature of the extracted species over the whole range of experimental conditions.

### *Effect of temperature*

The extraction of Ti(IV) was also studied at different temperatures [303 – 343 K] with  $3.0 \times 10^{-3}$  mol dm<sup>-3</sup> D2EHPA and  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> PC-88A in toluene as the extractant.



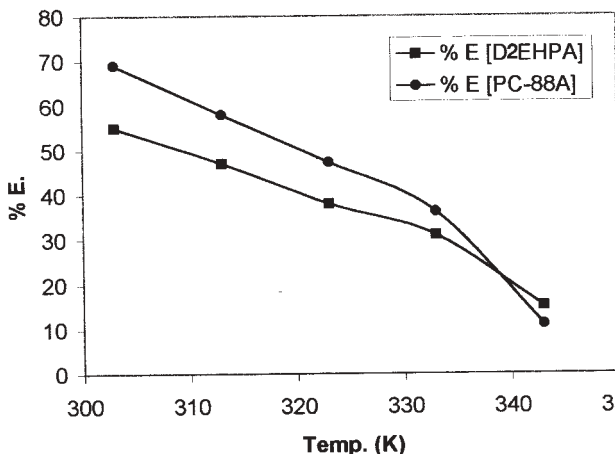


Fig. 6. Effect of the temperature on the percent extraction of Ti(IV) with D2EHPA and PC-88A.

It was observed that the percentage extraction of Ti(IV) decreases steadily with increasing temperature up to 333 K. However the percentage extraction of Ti(IV) decreases sharply when the temperature is greater than 333 K. This may be due to a sharp decrease in the stability of the extracted complex with D2EHPA and PC-88A at temperatures above 333 K.

Hence all the extractions were carried out at room temperature. (Fig. 6).

#### *Effect of diverse ion*

The effect of various diverse ions on the extraction of Ti(IV) was studied with D2EHPA and PC-88A in toluene. The tolerance limit of individual foreign ions was set so that the reduction of the percentage recovery was not more than  $\pm 2\%$ . Only EDTA and thiocyanate interfere seriously with the extraction of Ti(IV) by the proposed method. (Table III).

TABLE III. Effect of various diverse ions on the extraction of Ti(IV)

Diverse ions	Tolerance ratio Ti(IV) : Diverse ion	
	D2EHPA	PC-88A
$\text{SO}_3^{-3}; \text{SO}_4^{-2}; \text{ClO}_4^-$	1 : 35	1 : 33
$\text{Li}^{1+}; \text{Na}^{1+}; \text{K}^{1+}; \text{Ca}^{1+}; \text{Br}^-; \text{Cl}^-; \text{Citrate and tartarate}$	1 : 30	1 : 30
$\text{V}^{5+}; \text{Cr}^{3+}; \text{Mn}^{2+}; \text{Hg}^{2+}; \text{Cd}^{2+}; \text{Sr}^{2+}; \text{Zn}^{2+}$	1 : 15	1 : 15
$\text{Fe}^{3+}; \text{Co}^{2+}; \text{Cr}^{6+}; \text{Be}^{2+}; \text{Al}^{3+}; \text{Ni}^{2+}; \text{Pb}^{2+}; \text{Cs}^+; \text{Mg}^{2+}; \text{Cu}^{2+}$	1 : 8	1 : 6
EDTA and thiocyanate	1 : 0	1 : 0

The results are the mean of triplicate values. Conditions: Aqueous phase:  $[\text{Ti(IV)}] = 0.01 \text{ mol dm}^{-3}$ ,  $[\text{HClO}_4] = 0.1 \text{ mol dm}^{-3}$ . Organic phase:  $[\text{D2EHPA/PC-88A}] = 0.01 \text{ mol dm}^{-3}$  in toluene. Phase ratio: 1

#### *Hydrolytic stability and recycling capacity of the extractants*

The hydrolytic stability of D2EHPA and PC-88A towards  $0.05 \text{ mol dm}^{-3} \text{ HClO}_4$  were determined by keeping a toluene solution of the extractant in contact with the acid. No decrease was observed in the percent extraction of Ti(IV) with the two extractants even after a month of contact (Fig. 7).

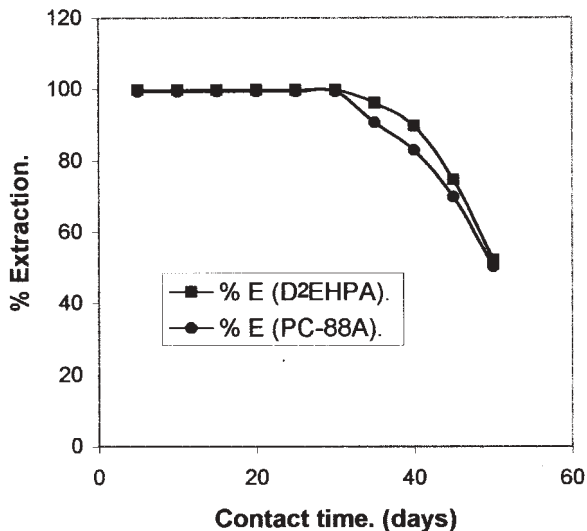


Fig. 7. Variation in the percentage extraction of Ti(IV) with D2EHPA and PC-88A.

Experiments were also conducted to determine the recycling capacity of the extractants by first loading them with Ti(IV) and then stripping with 3 %  $\text{H}_2\text{O}_2$  in 1 M  $\text{H}_2\text{SO}_4$ . The stripped organic phase was regenerated and used for extraction. The organic layers were regenerated by washing them with the corresponding stripping agents to remove other metal impurities. It was finally washed with water till the washings were neutral. The recovery of each step was calculated from the amount of Ti(IV) that was extracted into the organic phase in that particular cycle. The results reveal practically insignificant changes in the efficiency of the extraction up to 13 cycles for D2EHPA and 10 cycles for PC-88A (Figs. 7 and 8). Both the extractants, D2EHPA and PC-88A dissolved in toluene, showed a steady decrease (99.9 – 99.0 %) in metal recovery but the efficiency never fell below 99.0

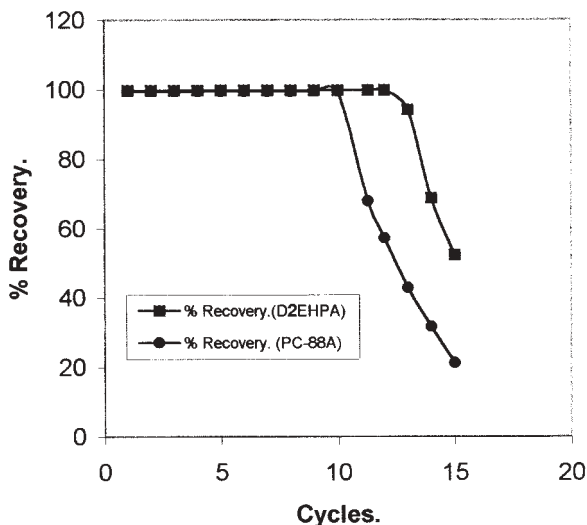


Fig. 8. Variation in the recovery of Ti(IV) in successive cycles.

% during the mentioned number of cycles. This result justifies the stability of the said extractants. However, on further extracting, the extraction efficiency of both the extractants, D2EHPA and PC-88A dissolved in toluene, decreases drastically. This can probably be attributed to a weakening of the extractants.

#### *Extraction behaviour of Ti(IV) and associated metal ions*

The extraction behaviour of Ti(IV) and of other commonly associated metal ions, namely Fe(III), Al(III), V(V), Ce(IV), Mg(II) and Mn(II) ( $0.01 \text{ mol dm}^{-3}$  each), from 0.01 to  $5.0 \text{ mol dm}^{-3}$   $\text{HClO}_4$  in  $0.01 \text{ mol dm}^{-3}$  toluene solutions of D2EHPA and PC-88A was studied.

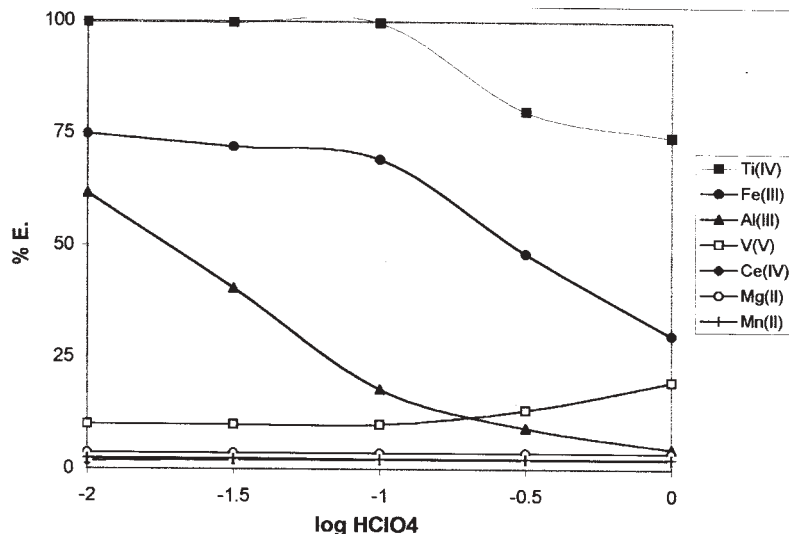


Fig. 9. Effect of the concentration of  $\text{HClO}_4$  on the extraction of associated metal ions by a toluene solution of D2EHPA.

With both the extractants, Ti(IV) was almost quantitatively extracted (above 99.7 %) up to  $0.1 \text{ mol dm}^{-3}$   $\text{HClO}_4$ , beyond which the extraction starts slowly to decline to a value of  $> 50 \%$ . Fe(III) and Al(III) shows a decreasing trend with increasing molarity of the acid. The extraction of V(V) was low ( $< 5 \%$ ) and almost constant between  $0.01 \text{ mol dm}^{-3}$  to  $0.1 \text{ mol dm}^{-3}$   $\text{HClO}_4$  and then showed a slight increase with increasing molarity of the acid. Mg(II), Mn(II) and Ce(IV) were negligibly extracted ( $< 3 \%$ ) over the entire investigated range of acid molarity (Figs. 9 and 10).

#### *Separation of Ti(IV) from associated metal ions*

Based on the partition data, the separation of Ti(IV) from some commonly associated metal ions, like Fe(III), Al(III), V(V), Ce(IV), Mg(II) and Mn(II), using D2EHPA and PC-88A can be achieved by taking advantage of the difference in the extraction and stripping conditions.

Both the extractants are equally effective for the separation of Ti(IV) from Mn(II), Mg(II) and Ce(IV). In these separations Ti(IV) is extracted into the organic phase leaving

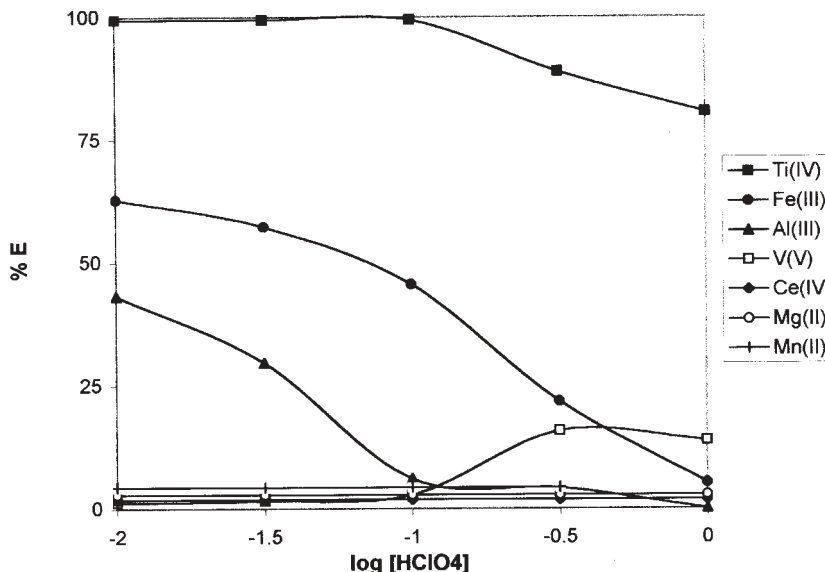


Fig. 10. Effect of concentration of HClO<sub>4</sub> on the extraction of metal ions by a toluene solution of PC-88A.

the other metal ions in the aqueous phase. Ti(IV) was then stripped with 3 % H<sub>2</sub>O<sub>2</sub> in 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>.

However, for the separation of Ti(IV) from Al(III) and V(V), PC-88A is preferred over D2EHPA because Al(III) and V(V) show relatively poor extraction when the former was employed.

For the separation of Ti(IV) from Fe(III), both the metal ions were first extracted into the organic phase. Ti(IV) was then selectively stripped employing 3 % H<sub>2</sub>O<sub>2</sub> in 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, this was followed by the stripping of Fe(III) using 0.5 mol dm<sup>-3</sup> HCl. D2EHPA is preferred over PC-88A for this separation because of the higher extraction of Fe(III) by it.

#### Determination of Ti(IV) in real samples

Ores like ilmenite, magnetite and red mud were analyzed by employing the proposed method. The ore was dissolved in a minimum amount of aqua-regia which was then evaporated to dryness. The residue obtained was dissolved in concentrated acid by digesting for 2 h, cooled, filtered and diluted to a known volume with distilled water. The analysis of Ti(IV) by the proposed method were carried out by the standard addition method. (Table IV).

TABLE IV. Analysis of Ti(IV) from real samples

Sample No.	Ore	Ti(IV)/μg Added	Ti(IV)/μg Found	% R of Ti(IV) from Ores
1.	Ilmenite	50 <sup>#</sup>	104 <sup>\$</sup>	98.1
		100 <sup>#</sup>	155 <sup>\$</sup>	99.3
		150 <sup>#</sup>	205 <sup>\$</sup>	99.6

TABLE IV. Continued

Sample No.	Ore	Ti(IV)/ $\mu\text{g}$ Added	Ti(IV)/ $\mu\text{g}$ Found	% R of Ti(IV) from Ores
2.	Magnetite	200 <sup>##</sup>	225 <sup>\$</sup>	98.6
		250 <sup>##</sup>	276 <sup>\$</sup>	99.2
		300 <sup>##</sup>	326 <sup>\$</sup>	99.2
3.	Red mud	100 <sup>##</sup>	160 <sup>\$</sup>	99.3
		150 <sup>##</sup>	209 <sup>\$</sup>	99.0
		200 <sup>##</sup>	257 <sup>\$</sup>	98.5

<sup>#</sup> 3 ml of a stock solution of ilmenite ore were added to a known amount of Ti(IV). <sup>##</sup> Known amount of Ti(IV) solution was added to 1 ml of the sample-2 and 3. <sup>\$</sup> Mean of triplicate analysis

### CONCLUSION

The above results of the extraction experiments with di-(2-ethylhexyl) phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) lead to the following conclusions:

(1). Both D2EHPA and PC-88A, due to their low  $\text{pK}_a$  values, extract Ti(IV) at higher acidity, this advantage is particularly important for Ti(IV), which requires a relatively high acidity to prevent its hydrolysis.

(2). The extraction of Ti(IV) proceed according to a cation-exchange reaction at lower acidity and to a solvating reaction at higher acidities.

(3). Both D2EHPA and PC-88A extract Ti(IV) quantitatively (> 99 %), while under similar extraction conditions, extractants such tri-*n*-butyl phosphate, thenoyltrifluoroacetone and triisooamyl phosphate provide incomplete extraction (< 95 %) of the metal ion.

(4). The extraction of Ti(IV) with both D2EHPA and PC-88A does not require strict control of the pH, and the separation from co-extracted Fe(III) can be easily achieved by selective stripping.

(5). Both D2EHPA and PC-88A extract Ti(IV) quantitatively unlike 8-hydroxyquinoline and cupferron which require the use of salting-out agents for similar result under similar extraction conditions.

(6). *N*-benzoyl-*N*-phenylhydroxyl amine extracts Ti(IV) quantitatively but the method suffers serious interference by Cu(II). The proposed method with both D2EHPA and PC-88A has the advantage of being free from such interferences.

(7). The use of comparatively lower D2EHPA and PC-88A concentration, as compared to TBP and TOPO under similar extraction conditions, encourages the commercial use of these extractants for the recovery of Ti(IV).

(8). Both D2EHPA and PC-88A were successfully used to separate Ti(IV) from some commonly associated metal ions, like Fe(III), Al(III), V(V), Ce(IV), Mg(II) and Mn(II), found in ilmenite, magnetite and red mud by control of the acidity of the aqueous phase.

(9). Extraction and separation of Ti(IV) with D2EHPA and PC-88A is commercially viable as both the extractants can be regenerated and utilized (>10 times) for the same purpose without compromising the efficiency of the metal recovery.

*Acknowledgement:* The authors are thankful to Dai-hachi Chemical Industries, Japan, for supplying working samples of D2ENPA and PC-88A.

## NOMENCLATURE

[ ] – Concentration [ mol dm<sup>-3</sup> / mmol dm<sup>-3</sup>]

*D* – Distribution ratio

% E – Percentage extraction

% R – Percentage recovery

aq. – Aqueous phase

org. – Organic phase

## ИЗВОД

### ЕКСТРАКЦИЈА И РАЗДВАЈАЊЕ ТИТАНА(IV) ПОМОЋУ D2ЕНРА И PC-88А ИЗ ВОДЕНИХ РАСТВОРА ПЕРХЛОРНЕ КИСЕЛИНЕ

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Проучавана је течно-течно екстракција Ti(IV) из перхлоратних медија коришћењем ди(2-етилхексил) фосфорне киселине (D2ЕНРА) и моно-2-етилхексил естра 2-етилхексил) фосфонске киселине (PC-88A) у толуену као екстракционог средства. Постигнута је квантитативна екстракција Ti(IV) у области мањих киселости (0,01 до 0,1 mol dm<sup>-3</sup>) са 0,003 mol dm<sup>-3</sup> D2ЕНРА и 0,01 mol dm<sup>-3</sup> PC-88A у толуену, а такође и у области великих киселости (9,0 до 10,0 mol dm<sup>-3</sup>) са 0,1 mol dm<sup>-3</sup> D2ЕНРА или PC-88A у толуену. Титан(IV) је у потпуности уклоњен из органске фазе оба екстрактанта помоћу 3 % H<sub>2</sub>O<sub>2</sub> у 1 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, а одређиван је спектрофотометријски. Стехиометрија екстрахованих врста одређивана је методом анализе нагиба. У области мање киселости екстракција тече по механизму катјонске измене, при чему је екстрахована врста TiOR<sub>2</sub>·2HR, док у области великих киселости процес тече солватацијом екстраховане врсте Ti(OH)<sub>3</sub>ClO<sub>4</sub>·4HR. Изведено је, такође, раздвајање Ti(IV) од неких пратећих метала као нпр. Fe(III), Al(III), V(V), Ce(IV), Mg(II) и Mn(II). Развијене методе су употребљене за одређивање Ti(IV) у реалним узорцима илменита, магнетита и црвеног муља у циљу демонстрације практичне употребљивости наведених екстракционих средстава.

(Примљено 20. августа 2001, ревидирано 1. марта 2002)

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