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Extraction of Titanium(IV) from its Hydrochloric Acid Solution with Indigenous Solvent, Tri-iso-Amyl Phosphate (TAP)

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The indigenously prepared solvent tri-iso-amyl phosphate (TAP) obtained from fusel oil, a by-product of Indian Alcohol Industry, has been successfully utilised to extract titanium(IV) from its aqueous hydrochloric acid solutions. The effect of various parameters viz. [ATP], [H_3O^+], [Cl^-], [Ti(IV)] on the extraction of the metal ion, has been investigated and discussed. The effect of using different diluents for TAP on the extraction reveals that the extraction is highest in the presence of non-polar diluents and this further substantiates the non-polar nature of the extracted species.

INTRODUCTION

During recent years a considerable amount of work has been reported which has widened the scope of application of the solvent extraction technique. Several phosphatic solvents such as tri-n-octyl phosphine oxide (TOPO), tri-n-butyl phosphate (n-TBP) and diethyl hexyl phosphoric acid (DEHPA) have been successfully and widely used[1–4]. It is reported that the extraction power of organo-phosphorus solvents for metal increases markedly with the increase in the number of direct carbon-phosphorus linkage.[5]

An indigenous solvent tri-iso-amyl phosphate (TAP), a higher homologue of n-TBP was prepared by us from fusel oil, a by-product of Indian Alcohol Industry and has proved to be a potential, economical and effective solvent for the extraction of several metals[6–13]. Thus, in continuation to our investigations the extraction of titanium(IV) from hydrochloric acid solutions was undertaken and the results are reported in this communication.

EXPERIMENTAL

(i) Preparation of tri-iso-amyl phosphate (TAP)

The fusel oil obtained from Indian Alcohol Industry was fractionally distilled and the fraction at 131°C was collected as *iso*amyl alcohol which was further

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purified by redistillation. In a three-necked flask (1 litre) 137 gm (3 moles) of the purified isoamyl alcohol, 133 ml (3.3 moles) of pure and dried pyridine and 138 ml of benzene (dried over sodium wire) were mixed. The reaction mixture was subjected to mechanical stirring at low temperature which was maintained at nearly –50°C. At this stage 46 ml (1 mole) of dry phosphorus oxychloride (b.pt. 107°C) was gradually and carefully added through a dropping funnel at such a rate (complete time of addition is nearly 8 hrs) so that the temperature of mixture did not exceed 5°C. When the addition was complete the reaction mixture was refluxed for 2 hrs, cooled and then 200–300 ml water was added to it to dissolve the white precipitate of pyridine hydrochloride. The mixture was transferred into a separatory funnel and the organic layer containing mainly crude tri-*iso*-amyl phosphate was separated, washed several times with water and kept overnight on anhydrous sodium sulfate.

Benzene and other unreacted materials were removed by distillation at low pressure (20 mm) till the temperature of the evaporating vapours reached 90°C. The ester tri-iso-amyl phosphate (TAP) was then collected at 160°C/4 mm as a colourless liquid. The analysis (found, C = 58.5, H = 10.6%; calculated for $C_{15}H_{33}O_4P$, C = 58.4, H = 10.7%, density = 0.976, yield = 75%) confirmed the purity of the ester. The ester TAP is freely miscible with all the common organic solvents. Tri-*iso*-amyl phosphate (TAP) thus prepared was diluted with carbon tetrachloride for the extraction experiments.

(ii) The stock solution of titanium(IV) in hydrochloric acid medium was prepared by dissolving air-dried and recrystallized potassium titanyl oxalate into concentrated hydrochloric acid and nitric acid. The mixture was gradually heated and then boiled for nearly 10 minutes. The solution was then cooled and ammonia solution was added to precipitate the titanium as its hydroxide. The precipitate was washed several times with deionized water to make it free from nitrate and chloride ions. The precipitate was then dissolved in hydrochloric acid of known strength.

The Ti(IV) content in the stock solution was determined by spectrophotometric method using hydrogen peroxide as a reagent[14].

All other reagents used were of A.R. grade.

Extraction procedure

15 Cm^3 of the properly diluted solvent was equilibrated for 15 minutes with an equal volume of an aqueous layer containing desired acidity but without Ti(IV). 10 Cm^3 of this pre-equilibrated solvent was then equilibrated with an equal volume of aqueous layer containing appropriate amount of Ti(IV). Preliminary experiments had shown that 15 minutes shaking at 25 ± 1°C was sufficient to attain the equilibrium.

There was no change in the volume of the two layers on standing. Concentration of the hydrogen ion in all these experiments was determined by potentiometric titration and the chloride ion was determined by Volhard's method[15]. It was also ascertained that carbon tetrachloride itself does not extract Ti(IV) from its aqueous hydrochloric acid solution.

RESULTS AND DISCUSSION

In the present work the system Ti(IV)-HCl-TAP (carbon tetrachloride) has been undertaken in which hydrogen ion concentration of aqueous phase has been maintained by the addition of hydrochloric acid.

Concentration of titanium(IV) in all the experiments was fixed at 1.0×10^{-3} mol dm^{-3}, except for the experiments where the effect of metal ion concentration on the extraction system has been investigated.

TAP was invariably diluted with carbon tetrachloride for equilibration with the aqueous phase since this gives clearly two layers with no observable change in their volumes.

In order to determine the equilibrium time, experiments were performed at 25 ± 1°C by shaking equal volume of aqueous and organic phases and it was observed that 15 minutes were sufficient to attain the equilibrium.

Preliminary experiments were carried out to obtain the optimum concentration of TAP in carbon tetrachloride to be used for the extraction of the metal keeping

TABLE 1

EFFECT OF TAP CONCENTRATION ON THE EXTRACTION OF TITANIUM(IV) FROM ITS HYDROCHLORIC ACID SOLUTIONS.

[HCl] = 5.0 dm^{-3}; [Ti(IV)] = 1.0×10^{-3} mol dm^{-3}
Vol. of aqueous layer = Vol. of organic layer = 10 cm^3

S. No.	[TAP] %	Amount in 5 cm^3 aliquot × 10^2 mg		D	% E
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$		
1.	2	—	—	—	—
2.	5	21.38	2.57	0.12	10.71
3.	7	17.87	6.08	0.34	25.37
4.	10	15.15	8.80	0.58	36.70
5.	12	13.92	10.03	0.72	41.86
6.	15	11.91	12.04	1.01	50.24
7.	17	9.97	13.98	1.40	58.33
8.	20	8.31	15.64	1.88	65.27
9.	22	6.96	16.99	2.44	70.97
10.	25	5.60	18.35	3.27	76.58
11.	27	4.77	19.18	4.02	80.08
12.	30	4.29	19.66	4.50	82.07
13.	31	4.08	19.87	4.87	82.98
14.	32	4.03	19.92	4.94	83.16
15.	33	3.87	20.08	5.18	83.81
16.	35	3.87	20.08	5.18	83.81
17.	40	3.87	20.08	5.18	83.81

hydrochloric acid concentration arbitrarily fixed at 5.0 mol dm^{-3} while the TAP concentration was varied. The results given in Table 1 reveal that the maximum extraction is obtained by 33% of TAP and further increase of TAP has no effect on the value of the distribution ratio. Thus, for the subsequent experiments 33% of TAP (in CCl_4) was used except for the effect of initial acidity and solvation number determination.

The results of preliminary experiments indicated that hydrochloric acid as such is not extracted by the dilute solution of TAP in carbon tetrachloride. In order to establish the optimum acidity for the extraction, experiments were performed by taking an arbitrary and fixed concentration of 20% TAP in carbon tetrachloride (v/v) while the hydrogen ion concentration was varied. The results thus obtained are given in Table 2 show that there is a gradual increase in the distribution coefficient with increasing initial aqueous hydrochloric acid concentration; the extraction reaches maximum at 11.5 mol dm^{-3} and after that there is no change in the distribution coefficient. To substantiate it further, elaborate experiments

TABLE 2
EFFECT OF VARIATION OF HYDROCHLORIC ACID CONCENTRATION ON THE EXTRACTION OF TITANIUM(IV)

[TAP] = 20% (vol/vol) in CCl_4; [Ti(IV)] = 1.0×10^{-3} mol dm^{-3}
Vol. of aqueous layer = Vol. of organic layer = 10 cm^3

S. No.	[HCl] mol dm^{-3}	Amount in 5 cm^3 aliquot × 10^{-2} mg		D	% E
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$		
1.	1.0	21.97	1.98	0.09	8.25
2.	2.0	20.12	3.83	0.19	15.96
3.	3.0	18.42	5.53	6.30	23.07
4.	3.5	16.74	7.21	0.43	30.06
5.	4.0	13.37	10.58	0.79	44.13
6.	4.5	10.50	13.45	1.28	56.14
7.	5.0	8.31	15.64	1.88	65.25
8.	6.0	7.21	16.74	2.32	69.87
9.	6.5	6.61	17.34	2.62	72.37
10.	7.0	5.78	18.17	3.14	75.84
11.	7.5	4.94	19.01	3.84	79.33
12.	8.0	4.53	19.42	4.28	81.06
13.	8.5	4.08	19.87	4.87	82.96
14.	9.0	3.58	20.38	5.69	85.05
15.	9.5	3.35	20.60	6.14	85.49
16.	10.0	3.28	20.67	6.30	86.30
17.	11.0	3.10	20.85	6.72	87.04
18.	11.5	2.96	20.99	7.09	87.63
19.	12.0	2.96	20.99	7.09	87.63

were carried out by taking other concentration of TAP *viz.* 30% and varying the hydrochloric acid concentration. The data given in Table 3 also supported that

TABLE 3

EFFECT OF VARIATION OF HYDROCHLORIC ACID CONCENTRATION ON THE EXTRACTION OF TITANIUM(IV)

[TAP] = 30% (vol/vol) in CCl_4; [Ti(IV)] = 1.0×10^{-3} mol dm^{-3}

Vol of aqueous layer = Vol. of organic layer = 10 cm^3

S. No.	[HCl] mol dm^{-3}	Amount in 5 cm^3 aliquot × 10^{-2} mg		D	% E
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$		
1.	1.0	20.82	3.13	0.15	13.04
2.	2.0	18.56	5.39	0.29	22.48
3.	3.0	16.29	7.36	0.47	31.97
4.	3.5	13.29	10.03	0.72	41.86
5.	4.0	7.53	16.64	2.18	68.55
6.	4.5	5.87	18.08	3.08	75.49
7.	5.0	4.29	19.66	4.57	82.04
8.	6.0	2.97	20.98	7.06	87.60
9.	6.5	2.52	21.43	8.50	89.47
10.	7.0	2.00	21.95	10.97	91.65
11.	7.5	1.52	22.43	14.75	93.65
12.	8.0	1.42	22.53	15.86	94.07
13.	8.5	1.28	22.67	17.71	94.65
14.	9.0	1.20	22.75	19.12	95.03
15.	9.5	1.12	22.83	20.38	95.32
16.	10.0	1.05	22.90	21.80	95.61
17.	11.0	0.92	23.03	25.03	96.16
18.	11.5	0.75	23.20	30.93	96.86
19.	12.0	0.75	23.20	30.93	96.86

the extraction of titanium(IV) is maximum at 11.5 mol dm^{-3} only and is same for higher hydrochloric acid concentration. Consequently it is inferred that the extraction of titanium(IV) depends upon the initial hydrochloric acid concentration and it has been observed that the percentage extraction is low at hydrochloric acid concentration < 4.0 mol dm^{-3} whereas ≥ 4.0 mol dm^{-3} [HCl] the extraction of titanium(IV) is appreciable. This is explained on the basis of aqueous chemistry of titanium(IV) which reveals that several hydrated species of titanium(IV) of the type $Ti(OH)_x(Cl)_y$ may be present at lower acidities,[16–18] whereas 4.0 mol dm^{-3} acidity hydrolysis may not be anticipated and sufficient extraction may be due to the predominance of non-hydroxy Ti^{4+} species[19–21].

The system was further investigated to determine the role of chloride ion on the extraction of titanium(IV). The experiment was conducted keeping hydrogen ion concentration arbitraily fixed at 3.0 mol dm^{-3} by the addition of perchloric acid and TAP concentration at 33% (v/v) and varying the initial chloride ion concentration of the aqueous solution by the addition of lithium chloride. It is observed (Table 4) that the distribution coefficient and hence the percentage extraction is siginificantly increased with increasing chloride ion concentration and a maximum of 92.14% extraction was recorded at 11.5 mol dm^{-3} chloride ion concentration. It can therefore be concluded that the extraction of titanium(IV) depends upon the concentration of chloride ion.

TABLE 4
EFFECT OF VARIATION OF CHLORIDE ION CONCENTRATION ON THE EXTRACTION OF TITANIUM (IV)

$[H_3O^+]$ = 3.0 mol dm^{-3}; [TAP] = 33% (vol/vol) in CCl_4;
[Ti(IV)] = 1.0×10^{-3} mol dm^{-3}
Vol. of aqueous layer = Vol. of organic layer = 10 cm^3

S. No.	$[Cl^-]$ mol dm^{-3}	Amount in 5 cm^3 aliquot × 10^{-2} mg		D	% E
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$		
1.	1.0	20.29	3.66	0.18	15.25
2.	2.0	18.42	5.53	0.30	23.49
3.	3.0	16.18	7.70	0.48	32.43
4.	4.0	15.25	8.70	0.57	36.30
5.	4.5	13.37	10.58	0.79	43.13
6.	5.0	12.15	11.80	0.97	49.23
7.	5.5	10.06	13.89	1.38	57.98
8.	6.0	8.64	15.31	1.77	63.89
9.	6.5	8.01	15.94	1.99	66.55
10.	7.0	6.26	17.69	2.82	73.82
11.	7.5	5.46	18.49	3.38	77.16
12.	8.0	4.80	19.15	3.98	79.91
13.	8.5	3.98	19.97	5.01	83.36
14.	9.0	3.61	20.34	5.62	84.89
15.	9.5	3.15	20.80	6.60	86.84
16.	10.0	2.68	21.27	7.94	88.81
17.	10.5	2.41	21.54	8.91	89.90
18.	11.0	2.17	21.78	10.00	90.90
19.	11.5	1.88	22.07	11.73	92.14
20.	12.0	1.88	22.07	11.73	92.14

Thus, the following equation can be written to describe the role of chloride ion on the equilibria involved for the extraction of titanium(IV) from hydrochloric acid solutions:

$$TiCl_n^m + xCl_{aq}^- \rightleftarrows TiCl_{(n+x)_{aq}}^{(m-x)} \qquad (1)$$

$$TiCl_{(n+x)}^{(m-x)} + yTAP \rightleftarrows [TiCl_{(n+x)}^{(m-x)}(TAP)_y]_{org} \qquad (2)$$

where m + n = 4.

If original TAP concentration in the organic phase is held constant

$$[TiCl_{(n+x)}^{(m-x)}(TAP)_y]_{org} = K[TiCl_{(n+x)}^{(m-x)}]_{aq} \qquad (3)$$

Hence

$$D = \frac{K[TiCl_{(n+x)}^{(m-x)}]_{aq}}{[TiCl_n^m]_{aq}} \qquad (4)$$

$$\log D = \log K + \frac{\log [TiCl_{(n+x)}^{(m-x)}]_{aq}}{[TiCl_n^m]_{aq}} \qquad (5)$$

$$\log D = \log K + \log k_1 + x \log [Cl^-]_{aq} \qquad (6)$$

Thus a plot of log D versus log $[Cl^-]_{aq}$ should give a straight line with a slope equal to x.

A graph is plotted between the effect of aqueous chloride ion on the extraction of titanium(IV) by TAP (Table 4). Since the graph is a straight line with a slope of nearly 3.0, indicating thereby that the value of x is 3 and the equilibrium can be depicted as follows:

$$TiCl_{n(aq)}^m + 3Cl^-_{aq} \rightleftarrows TiCl_{(n+3)_{aq}}^{(m-3)} \qquad (7)$$

$$TiCl_{(n+3)}^{(m-3)} + yTAP \rightleftarrows TiCl_{(n+3)}^{(m-3)}(TAP)_{y\,org} \qquad (8)$$

Consequently, it can now be assumed that the extracted moiety of titanium is $TiCl_4$ at higher hydrochloric acid concentration. The empirical formula of the extracted species was also supported by the analysis of the organic phase for the chloride ion and titanium(IV) concentration at 11.5 mol dm^{-3} acid concentration and the TAP concentration was varied from 2–40%. Results given in Table 5 indicate that the ratio of chloride ion and titanium (IV) ion $[Cl^-/Ti(IV)]_{org}$ is nearly 4 : 1. The results (Table 5) also show that maximum extraction of 97.45% was obtained by 33% of TAP in CCl_4 (v/v) at 11.5 mol dm^{-3} of hydrochloric acid.

In order to find out the nature and formula of the metal species present in the organic phase the solvation number of the species was evaluated by plotting log D against log C_{TAP} (Table 5) which gives a straight line with a slope of nearly 2.0. This indicats thereby that a disolvated species of titanium(IV) *viz.* $TiCl_4 \cdot 2TAP$ is formed in the organic layer.

The extraction rate constant (K) of the reaction can be evaluated mathematically as follows:

TABLE 5
EFFECT OF TAP CONCENTRATION ON THE EXTRACTION OF TITANIUM (IV) FROM HYDROCHLORIC ACID SOLUTIONS

[HCl] = 11.5 mol dm^{-3}; [Ti(IV)] = 1.0 × 10^{-3} mol dm^{-3}
Vol. of aqueous layer = Vol. of organic layer = 10 cm^3

Sl. No.	[TAP]%	Amount of 5 cm^3 aliquot × 10^{-2} mg			Ti : Cl	% E
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$	$[Cl^-]_{org}$		
1.	2	20.12	3.83	10.47	3.69	15.96
2.	5	11.68	12.27	35.37	3.89	51.22
3.	7	8.11	15.84	44.37	3.78	66.10
4.	10	4.72	19.23	54.86	3.85	80.27
5.	12	3.69	20.26	58.26	3.88	84.59
6.	15	2.41	21.54	62.41	3.91	89.92
7.	17	2.00	21.95	63.93	3.93	91.64
8.	20	1.58	22.37	64.82	3.91	93.39
9.	22	1.31	22.64	66.27	3.95	94.52
10.	25	1.07	22.88	67.14	3.96	95.53
11.	27	0.89	23.06	67.33	3.94	96.28
12.	30	0.75	23.20	68.08	3.96	96.86
13.	31	0.70	23.25	68.32	3.96	97.07
14.	32	0.67	23.28	68.58	3.98	97.20
15.	33	0.61	23.34	68.58	3.98	97.45
16.	35	0.61	23.34	68.84	3.98	97.45
17.	40	0.61	23.34	68.84	3.98	97.45

$$TiCl_4 \cdot 2TAP \rightleftarrows TiCl_4 \cdot 2TAP \tag{9}$$

$$K = \frac{[TiCl_4 \cdot 2TAP]_{org}}{[TiCl_4]_{aq}[TAP]^2_{org}} \tag{10}$$

Further,

$$[TAP]_{t \cdot org} = [TAP]_{org} + [TiCl_4 \cdot 2TAP] \tag{11}$$

$$[Ti(IV)]_{t \cdot org} = [TiCl_4 \cdot 2TAP] + [TiCl_4]_{org} \tag{12}$$

where $(TAP)_{t \cdot org}$ and $[Ti(IV)]_{t \cdot org}$ represent the total concentration of TAP and Ti(IV) in the organic phase. Since $[TiCl_4]_{org}$ is always negligible in comparison to $[TiCl_4 \cdot 2TAP]$ the value of K can be calculated by the following equation:

$$K = \frac{[Ti(IV)]_{t \cdot org}}{([TAP]_{t \cdot org} - 2[Ti(IV)]_{t \cdot org})^2 [Ti(IV)]_{aq}} \tag{13}$$

Thus with the help of the above equation (13) the extraction rate constant (K)

TABLE 6
CALCULATION OF EXTRACTION CONSTANT AT DIFFERENT TAP CONCENTRATIONS

[HCl] = 11.5 mol dm^{-3}; [Ti(IV)] = 1.0×10^{-3} mol dm^{-3}
Vol. of aqueous layer = Vol. of organic layer = 10 cm^3

Sl. No.	[TAP]%	Amount in 5 cm^3 aliquot × 10^{-2} mg		D	% E	log K
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$			
1.	2	20.12	3.83	0.19	15.96	1.71
2.	5	11.68	12.27	1.05	51.22	1.65
3.	7	8.11	15.84	1.95	66.10	1.63
4.	10	4.72	19.23	4.07	80.27	1.69
5.	12	3.69	20.26	5.49	84.59	1.61
6.	15	2.41	21.54	8.92	89.92	1.62
7.	17	2.00	21.95	10.97	91.64	1.60
8.	20	1.58	22.37	14.15	93.39	1.57
9.	22	1.31	22.64	17.28	94.52	1.58
10.	25	1.07	22.88	21.38	95.53	1.57
11.	27	0.89	23.06	25.91	96.28	1.57
12.	30	0.75	23.20	30.93	96.86	1.57
13.	31	0.70	23.25	33.21	97.07	1.57
14.	32	0.67	23.28	34.74	97.20	1.57
15.	33	0.61	23.34	38.26	97.45	1.58
16.	35	0.61	23.34	38.26	97.45	—
17.	40	0.61	23.34	38.26	97.45	—

Average log K = 1.60, Standard deviation = 0.0397

was calculated; the log K values at different solvent concentrations and their average value and standard deviation value are represented in Table 6.

The effect of concentration on the extraction of titanium(IV)

The extraction of titanium(IV) was performed for the above systems investigated at optimum conditions but varying the concentration of titanium(IV) in the range of 1.0×10^{-4} to 1.0×10^{-1} mol dm^{-3}.

The results given in Table 7 show a slight decrease only in the distribution ratio and percentage extraction values at 8.0×10^{-3} mol dm^{-3} but at higher concentration of titanium(IV) i.e. beyond 1×10^{-2} mol dm^{-3} a marked decrease in the percentage extraction is observed. This may be attributed to the polymerization of the titanium(IV) in the aqueous phase at higher initial metal concentrations. The existence of titanium polymers in acidic solution is not unlikely and has also been observed by other workers who have worked on the aqueous chemistry of titanium(IV)[16–18].

TABLE 7

EFFECT OF AQUEOUS TITANIUM(IV) ION CONCENTRATION ON THE EXTRACTION

[HCl] = 11.5 mol dm^{-3}; [TAP] = 33% (vol/vol) in CCl_4

Vol. of aqueous layer = Vol. of organic layer = 10 cm^3

Sl. No.	Initial $[Ti(IV)]_{aq}$	Amount in 5 cm^3 aliquot mg		D	% E
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$		
1.	1.0×10^{-4}	0.77×10^{-3}	23.18×10^{-3}	30.10	96.76
2.	5.0×10^{-4}	3.20×10^{-3}	116.55×10^{-3}	36.42	97.32
3.	8.0×10^{-4}	4.96×10^{-3}	186.84×10^{-3}	37.65	97.40
4.	1.0×10^{-3}	0.61×10^{-2}	23.34×10^{-2}	38.26	97.45
5.	5.0×10^{-3}	3.05×10^{-2}	116.70×10^{-2}	38.26	97.45
6.	8.0×10^{-3}	5.28×10^{-2}	186.52×10^{-2}	38.28	97.24
7.	1.0×10^{-2}	1.14×10^{-1}	22.81×10^{-1}	15.92	95.21
8.	5.0×10^{-2}	23.57×10^{-1}	96.18×10^{-1}	2.44	70.97
9.	8.0×10^{-2}	55.75×10^{-1}	136.06×10^{-1}	2.44	70.91
10.	1.0×10^{-1}	9.00	14.95	1.66	62.40

Effect of diluents on the extraction systems

The effect of some diluents other than carbon tetrachloride on the extraction systems under investigation while other parameters were identical was examined and the results are given in Table 8. This indicates thereby that the distribution

TABLE 8

EFFECT OF THE DILUENTS ON THE EXTRACTION OF TITANIUM(IV) FROM ITS HYDROCHLORIC ACID SOLUTION

[HCl] = 11.50 mol dm^{-3}; [TAP] = 33% (vol/vol);

[Ti(IV)] = 1.0×10^{-3} mol dm^{-3}

Vol. of aqueous layer = Vol. of organic layer = 10 cm^3

Sl. No.	Diluents used	Dielectric constant	Amount in 5 cm^3 aliquot $\times 10^{-2}$ mg		D	% E
			$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$		
1.	Carbon tetrachloride	2.24	0.61	23.34	38.26	97.45
2.	Benzene	2.28	0.65	23.30	35.28	97.24
3.	Kerosene oil	2.10	0.75	23.20	30.93	96.86
4.	Xylene	2.30	3.27	20.68	6.32	86.34
5.	Toluene	2.38	4.07	19.88	4.88	83.00
6.	n-Hexane	1.84	4.94	19.01	3.84	79.35
7.	Cyclohexane	2.50	5.41	18.54	3.42	77.40
8.	Chloroform	4.80	6.56	17.39	2.65	72.60

ratio values of the diluents including carbon tetrachloride decrease in the following order for the systems:
Carbon tetrachloride > Benzene > Kerosene oil > Xylene > Toluene
> n-Hexane > Cyclohexane > Chloroform.

The studies also reveal that in general the non-polar diluents are comparatively better than the polar diluents. This is attributed to the comparatively more structureless character of the nonpolar diluents and the extraction into these liquids is higher than into the more ordered polar diluents. This arbitrary differentiation correlates rather well with the dielectric constant of the polar and the non-polar diluents but does not very precisely explain the observed differences within a given class of diluents. However, it definitely proves the superiority of non-polar diluents over the polar ones.

Since non-polar diluent carbon tetrachloride has proved to be the best diluent for TAP, the formation and extraction of neutral species of titanium (IV) is further substantiated.

TABLE 9
EFFECT OF OTHER CATIONS ON THE EXTRACTION OF TITANIUM(IV) FROM ITS HYDROCHLORIC ACID SOLUTION

[TAP] = 33% (vol/vol) in CCl_4; [HCl] = 11.50 mol dm^{-3};
[Ti(IV)] = 1.0×10^{-3} mol dm^{-3}
Vol. of aqueous layer = Vol. of organic layer = 10 cm^3

S. No.	Cations added	%E	S. No.	Cations added	%E
1.	Li^+	97.45	13.	Ba(II)	97.20
2.	Na^+	97.45	14.	Pb(II)	97.18
3.	K^+	97.45	15.	Al(III)	95.00
4.	Rb^+	97.45	16.	Ga(III)	93.35
5.	Cs^+	97.45	17.	In(III)	95.65
6.	Mn(II)	97.45	18.	Tl(III)	94.84
7.	Mg(II)	97.40	19.	Eu(III)	89.58
8.	Sr(II)	97.32	20.	Zr(IV)	65.35
9.	Co(II)	97.24	21.	Th(IV)	70.28
10.	Ni(II)	97.12	22.	Hf(IV)	80.18
11.	Cu(II)	97.10	23.	Nb(V)	85.32
12.	Zn(II)	97.15	24.	U(VI)	75.35

Extraction of titanium (IV) in presence of other cations

The effect of some other cations on the extraction of titanium(IV) for the above systems was observed by mixing the equivalent amount of other cations with titanium(IV) solution and equilibration of mixed cations was performed with 33% TAP under the optimum conditions. The results are arranged in Table 9 which show that the precentage recovery of titanium(IV) is affected to some extent by the presence of Al(III), Ga(III), In(III) and Tl(III) and quite significantly by coextraction of Eu(III), Zr(IV), Th(IV), Hf(IV), Nb(V) and U(VI), hence making it rather difficult to separate titanium(IV) from these cations under the optimum conditions of the extraction.

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