Synergic Extraction of Titanium (IV) with the New Solvent Tri-iso-amyl Phosphate (TAP) and Thenoyltrifluoroacetone (TTA)

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ABSTRAK

Pengektrakan Ti(IV) dari larutan asid hidroklorik akueus telah diselidiki dengan menggunakan tiga sistem pelarut yang berbeza: Tenoiltrifluoroaseton (TTA), tri-iso-amil fostat (TAP) - satu pelarut baru dan campuran TTA dan TAP, yang mana semua pelarut tersebut dicairkan dengan karbon tetraklorida. Pengekstrakan optimum Ti(IV) adalah 90.34% dan 97.45% masing-masing dalam pelarut 4.0% TTA atau 33% TAP yang digunakan. Walau bagaimanapun kesan sinergi bererti telah dicapai bila setengah dari kepekatan kedua-dua pengekstrakan digunakan iaitu campuran terdiri dari larutan 2.0% TTA dan 16.0% TAP yang boleh mengekstrak sehingga 9.03% logam dari larutan HCl akueus.

Bagi ketiga-tiga sistem pengekstrakan, kepekatan Ti(IV) dan HCl masing-masing ditetapkan 1.0 x 10³ mol l¹ dan 11.5 mol l¹ adalah disimpulkan bahawa Ti(IV) membentuk disolvat dengan kedua-dua ligan iaitu TTA dan TAP tetapi campuran solvat 1:1 terbentuk bila sistem ligan bercampur TTA-TAP digunakan. Gabungan di antara TTA dalam bentuk tidak bercerai dengan ion logam pusat Ti(IV) telahpun diketahui. Pengolahan matematik bagi ketiga-tiga sistem pengekstrakan menunjukkan nilai purata log K_{ex} ialah 2.48 (TTA), 1.60 (TAP) dan 3.19 (sistem sinergi TTA-TAP). Nilai eksperimen bagi sistem solvat bercampur adalah 7.06 kali lebih besar dari nilai kiraan statistik juga ditunjukkan.

ABSTRACT

The extraction of Ti (IV) from aqueous hydrochloric acid solution was investigated by using three different solvent systems: thenoyltrifluoroacetone (TTA), a new solvent tri-iso-amyl phosphate (TAP) and a mixture of TTA and TAP, all diluted with carbon tetrachloride. An optimum of 90.34% and 97.45 % Ti(IV) was extracted when 4.0 % TTA or 33 % TAP was used, respectively. However, a significant synergic effect was observed even when half the concentration of the two extractants was used, i.e. a mixture of only 2.0% TTA and 16.0% TAP solution extracted as much as 99.03% of the metal from the aqueous HCl solutions.

For all these three extraction systems concentrations of Ti(IV) and HCl were maintained at 1.0 x 10³ mol l¹ and 11.5 mol l¹, respectively. It was concluded that Ti(IV) forms a disolvate with both the ligands, i.e. TTA and TAP, but a 1:1 mixed solvate is formed when a TTA-TAP mixed ligand system is used. It was also established that the TTA combines in its undissociated form with the central metallic ion Ti(IV). The mathematical treatment of the three extraction systems showed that the average values of log K_{ex} for the three systems were 2.48 (TTA), 1.60 (TAP) and 3.19 (TTA-TAP synergic system). It was also shown that the experimental value for the mixed solvate system is 7.06 times higher than the statistically evaluated value for the same system.

INTRODUCTION

In liquid-liquid synergic extraction, thenoyltrifluoroacetone (TTA) has been reported as being a better extractant than other chelating agents such as l-naphthoic acid, β-isopropyltropolone (IPT) and benzoylacetone (BA). TTA also exhibits an exceptionally strong tendency to form mixed adducts with neutral ligands (Sekine and Dyrssen 1967a). Consequently, it has been observed that the ligands having $R_3P=O$ donor groups give larger adduct formation constants with TTA compared to other donors such as α-naphthol, hexane, quinoline and coumarin. This tendency has been exploited for the synergic extraction of

a number of polyvalent metals from their aqueous acidic solutions (Taketatsu and Bauks 1966; Sekine and Dyrrsen 1964; Irving and Edgington 1965).

The extraction of Ti(IV) from acidic solution with TTA and synergic extraction with a mixture of TTA and different types of phosphatic solvents such a tri-n-octyl phosphine oxide (TOPO), tributylphosphine oxide (TBPO) and n-tributyl phosphate (TBP) have been reported in the literature (Marcus and Kertes 1969; Stary 1964; Komatsu 1980).

In view of the already well-established extractions of the metal ions by the solvent tri-iso-amyl phosphate (TAP) reported by us earlier (Pandey and Rupainwar 1979; Jaiswal and Rupainwar 1984; Singh *et al.* 1986; Hasan and Rupainwar 1987, 1990), it was of interest of investigate the efficacy of the new and more economic solvent TAP for the synergic extraction of titanium (IV) from aqueous hydrochloric acid solution. The results are described in this paper.

MATERIALS AND METHODS

Preparation of Solvents

Fusel oil obtained from Indian Alcohol Industry was fractionally distilled and the fraction at 131°C was collected as isoamyl alcohol which was redistilled. In a three-necked flask (1 l) 137g (3 moles) of the purified isoamyl alcohol was mixed with 133ml (3.3 moles) of pure and dried pyridine and 138 ml of benzene (dried over sodium wire). The reaction mixture was subjected to mechanical stirring at low temperature (-5°C). 46ml (1 mol) of dry phosphorus oxychloride (B.P. 107°) was gradually and carefully added through a dropping funnel at such a rate (time for complete addition took nearly 8 hours) that the temperature of the reaction mixture did not exceed 5°C. The reaction mixture was then refluxed for two hours, cooled and 200-300 ml water was added to dissolve the white precipitate of pyridine hydrochloride. The mixture was then transferred into a separating funnel and the organic layer containing mainly crude tri-iso-amyl phosphate (TAP) was separated, washed several time with water and kept overnight over anhydrous sodium sulphate. 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. Analysis of the product showed 58.5% C and 10.6% H. This agrees well with the theoretical values of 58.4% C, and 10.7%H for

$C_{15}H_{33}O_4P$. The density of 0.9476 g/cc and 75% yield confirmed the purity of the ester. The TAP ester 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.

Thenoyltrifluoroacetone (TTA) solution (0.5 M) was prepared by dissolving AnalaR grade reagent in ethyl alcohol. This stock solution was diluted with carbon tetrachloride as desired.

The stock solution of Ti(IV) was prepared by digesting potassium titanyl-oxalate in concentrated HCl and heating with concentrated nitric acid in order to remove oxalate.

All other reagents used were of AnalaR grade.

Determination of Ti(IV) by Spectrophotometric Method

Ti(IV) solution was determined in this investigation by two methods, viz. the hydrogen peroxide method and Tiron method (Sandel 1958). The hydrogen peroxide method was used in most cases since this method can be utilized even under highly acidic conditions and there is no interference by common metals. However, in certain cases where the amounts of Ti(IV) were rather low the estimation of Ti(IV) was also checked by an alternative method, i.e. the Tiron method.

Hydrogen Peroxide Method

A 5ml sample of aliquot containing Ti(IV) was taken and to this was added sulphuric acid of appropriate concentration to maintain an overall acidity of nearly 3.5 N. Colour was developed in this solution by the addition of 1.0ml of 3.0% hydrogen peroxide solution and the overall volume of the solution was made up to 25 ml. Absorbance of the mixed solution was determined using a spectrophotometer (Spectronic 20 Bausch and Lomb and Sicospec-200 G.L.) at 410 nm against a 10 ml aliquot sample mixed with 1.0 ml of water as reference solution.

Tiron Method

Disodium 1,2 hydroxy benzene 3,5 disulfonate (Tiron) gives a strong and stable yellow colour with Ti(IV) in the pH range 4.3-9.6. Beer's law is valid when a sufficiently high concentration of the reagent is used.

The sample solution was transferred to a 25 ml volumetric flask and 2.5ml of 4% aqueous reagent soluion and dilute ammonia was added until the mixture was neutral to congo-red paper. 2.5ml of buffer solution (equal volumes of 1.0

mol l⁻¹ acetic acid and sodium acetate) of pH 4.7 was added to the solution and diluted up to the mark. 12.5 mg of sodium dithionite was added to the above solution with minimum agitation. Absorbance of the mixed solution was determined with Sicospec-200 GL at 410 nm against a reference solution containing aliquot sample.

Extraction Procedure

The extraction of Ti(IV) has been studied by investigating the three systems as given below:

i) Ti(IV) - HCl - TTA (Carbon tetrachloride)

ii) Ti(IV) - HCl - TAP (Carbon tetrachloride)

iii) Ti(IV) - HCl - TTA + TAP (Carbon tetrachloride)

For all the above systems, 15 ml of properly diluted extractant was equilibrated for 15 minutes with an equal volume of aqueous layer containing the desired acidity but having no Ti(IV).

An amount (10ml) of this pr-equilibrated solvent was then equilibrated with an equal volume of an aqueous solution containing 1.0×10^{-3} mol l⁻¹ of Ti(IV).

There was no change in the volume of the two layers on standing. The H^+ ion concentration in all these experiments was determined by a potentiometric titration (Vogel 1978). It was ascertained that the diluent carbon tetrachloride itself does not extract Ti(IV) from HCl solution.

RESULTS AND DISCUSSION

The Ti(IV) synergic system studied in three stages as given in the experimental section has been discussed separately for the sake of clarity and to derive logical conclusions. However, the overall discussion of the system, the significant synergic effect and the mathematical treatment of the three systems leading to the evaluation of the extraction constant and also the effect of relevant parameters which have a bearing on the extraction systems have also been discussed.

Extraction of Titanium(IV) from Hydrochloric Acid Medium with Thenoyltrifluoroacetone (TTA) in Carbon Tetrachloride

The concentration of Ti(IV) for all the experiments was kept low and constant at 1.0×10^3 mol l⁻¹ in view of the formation of polymeric and inextractable species reported to be formed at

TABLE 1

Effect of variation of the hydrochloric acid concentration on the extraction of Ti(IV) using TTA
[TTA] = 2% (v/v) in CCl₄
[Ti(IV)] = 1.0×10^{-3} mol l⁻¹
Vol. of aqueous layer = vol. of organic layer = 10 ml.

S. No.	[HCl]$_{aq}$	Amount in 5 ml aliquot x 10^{-2} mg		D	%E
	mol l⁻¹	[Ti(IV)]$_{aq}$	Ti(IV)$_{org}$		
1	1.0	20.47	3.48	0.17	14.52
2	2.0	18.14	5.81	0.32	24.24
3	3.5	15.35	8.60	0.56	35.89
4	4.0	14.51	9.44	0.65	39.39
5	5.0	13.53	10.42	0.77	43.50
6	6.5	11.03	12.92	1.17	53.91
7	7.5	9.69	14.25	1.47	59.51
8	8.0	9.03	14.91	1.65	62.26
9	9.0	8.25	15.69	1.90	65.51
10	10.0	7.06	16.88	2.39	70.50
11	10.5	6.94	17.00	2.45	71.01
12	11.0	6.49	17.45	2.69	72.89
13	11.5	6.17	17.77	2.88	74.22
14	12.0	6.17	17.77	2.88	24.22

Distribution coefficient (D) $= \dfrac{[Ti(IV)]_{org}}{[Ti(IV)]_{aq}}$

Percentage extraction (% E) $= \dfrac{D \times 100}{D + 1}$

higher metal concentrations (Islam and Biswas 1978).

To establish the optimum acidity for the extraction of Ti(IV), experiments were performed at an arbitrary fixed TTA concentration of 2.0%. The initial HCl concentration was varied. The results given in Table 1 show a proportional and gradual increase in the percentage extraction with increasing acidity. A maximum of 74.22% extraction of the metal was recorded at 11.5 mol l⁻¹ HCl concentration, beyond which the distribution coefficient levels off. Consequently, all subsequent experiments were performed at an initial acidity of 11.5 mol l⁻¹.

The observed data can be further substantiated by the known aqueous chemistry of Ti(IV) in hydrochloric acid medium wherein the formation of hydroxy- and oxy-polymers has also been reported (Komatsu 1980; Pandey and Rupainwar 1979). Nevertheless, Ti(IV) has been reported to be present only at higher concentrations of the acid, i.e. > 4.0 mol l⁻¹ of the acid, while varying proportions of hydroxy species may be present at lower acidities.

The solvation number of the extracted species was evaluated by investigating the effect of TTA on the distribution ratio of Ti(IV). Thus, experiments were performed at 11.5 mol l⁻¹ HCl by varying concentration of the extractant (Table 2). The results reveal that the maximum extraction of 90.34% was obtained at 4.0% TTA. Also, a plot of log D against log C TTA (*Fig.1*) gives a straight line with a slope of nearly 2.0 indicating the association of two moles of TTA in the extracted moiety of Ti(IV).

Though carbon tetrachloride was used as a diluent in all these experiments, the role of other diluents such as benzene, toluene and chloroform was also investigated under the optimum conditions of the extraction, These tests showed that the maximum value of D was obtained when non-polar carbon tetrachloride was used.

Extraction of Titanium(IV) from a Hydrochloric Acid Medium with Tri-iso-amyl Phosphate (TAP).

Extraction of Ti(IV) from an HCl medium by TAP has already been reported from these laboratories (Hasan and Rupainwar 1987).

TABLE 2

Effect of TTA concentration on the extraction of Ti(IV) from hydrochloric acid solution.
Calculation of extraction constant (K) at different TTA concentration

[HCl] = 11.5 mol l⁻¹

[Ti(IV)] = 1.0 x 10⁻³ mol l⁻¹

Vol. of aqueous layer = vol. of organic layer = 10 ml.

| S. No.	[TTA] %	Amount in 5 ml aliquot x 10⁻² mg		D	% E	log K_{ex}
		[Ti (IV)]$_{aq}$	[Ti (IV)]$_{org}$			
1	0.5	18.56	5.39	0.29	22.48	2.70
2	1.0	12.53	11.42	0.91	47.64	2.59
3	1.25	10.36	13.59	1.31	56.70	2.55
4	1.50	18.49	15.46	1.82	64.53	2.54
5	1.75	7.39	16.56	2.24	69.13	2.50
6	2.0	6.17	17.77	2.88	74.22	2.48
7	2.25	5.36	18.58	3.46	77.57	2.45
8	2.50	4.55	19.40	4.26	80.98	2.44
9	2.75	4.14	19.80	4.78	82.69	2.42
10	3.00	3.61	20.33	5.63	84.89	2.42
11	3.25	3.15	20.79	6.60	86.84	2.42
12	3.50	2.91	21.04	7.23	87.86	2.39
13	3.75	2.57	21.38	8.31	89.25	2.39
14	4.00	2.31	21.64	9.36	90.34	2.39
15	5.00	2.31	21.64	9.36	90.34	-
16	8.00	2.31	21.64	9.36	90.34	-

Average log K_{ex} = 2.48 ± 0.0873
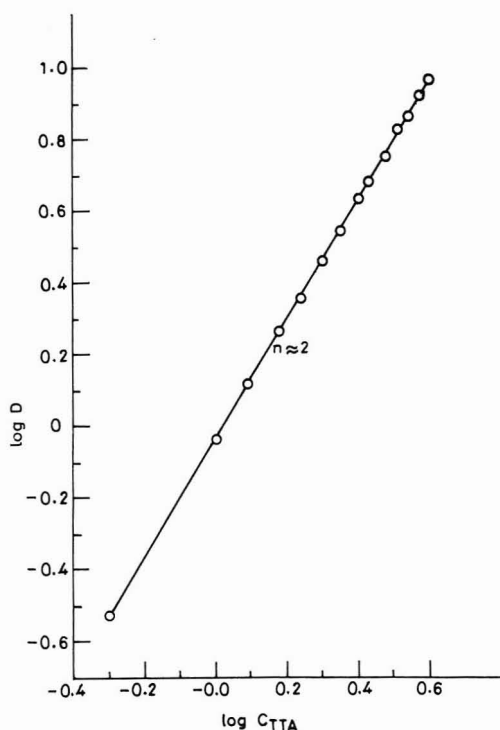
Fig. 1: *Effect of variation of the TTA concentration on the distribution coefficient (D) of Ti(IV) from aqueous hydrochloric acid solutions*
[HCl] = 11.5 mol l^1
[Ti(IV) = 1.0 x 10^3 mol l^1
n = Solvation number

However, the data relevant for this paper are given in Table 3, which shows that an optimum of 97.45% Ti(IV) is extracted from its 1.0 x 10^{-3} mol l^{-1} solution in hydrochloric acid by 33% TAP in carbon tetrachloride (v/v) at an acidity of 11.5 mol l^{-1}. The effect of diluents showed that the highest value of the distribution ratio was obtained when non-polar carbon tetrachloride was used as a diluent.

The formula of the predominant extracted moiety as evaluated from the slope of the graph (log C_{TAP} vs log D) was found to be $TiCl_4 \cdot 2TAP$ (*Fig. 2*).

The Synergic Extraction of Ti(IV) from Hydrochloric Acid with a Mixture of Tri-iso-amyl Phosphate (TAP) and Thenoyltrifluoroacetone (TTA)

After evaluating the extraction of Ti(IV) from a hydrochloric acid medium in the presence of individual ligands such as TAP and TTA, the extraction of Ti(IV) from hydrochloric acid medium was then performed by using a mixture of TAP and TTA in order to determine the effect of

the combined ligands. The acidity and concentration of Ti(IV) were kept constant at 11.5 mol l^1 and 1.0 x 10^{-3} mol l^1, respectively. Since two extractants were being employed, the concentration of one of the ligands was kept constant while that of the other was varied. Thus, when TAP was fixed at 10.0% (v/v in CCl_4) and TTA was varied from 0.5 to 5.0%, the results (Table 4) show that 96.57% Ti(IV) was extracted only at an initial TTA concentration of 2.0%. However, at concentration of TTA > 2.0% there was no appreciable change in the extraction. Again, when the TTA was kept constant at 2.0% and TAP was varied in the range of 1.0 to 20.0% it was clearly observed (Table 5) that the extraction was significantly increased even up to 99.05% with a much lower (i.e. only 16%) concentration of TAP.

The enhancement of the extraction of Ti(IV) by using a mixture of TTA and TAP at concentrations much lower than those used for individual ligands clearly reflects the synergic effect of the TTA. Further, a much lower TAP concentration is used, i.e. 16.0% in place of 33.0% for TAP alone, and the extraction increases from 97.45% to 99.05%. This is attributed to a stable and
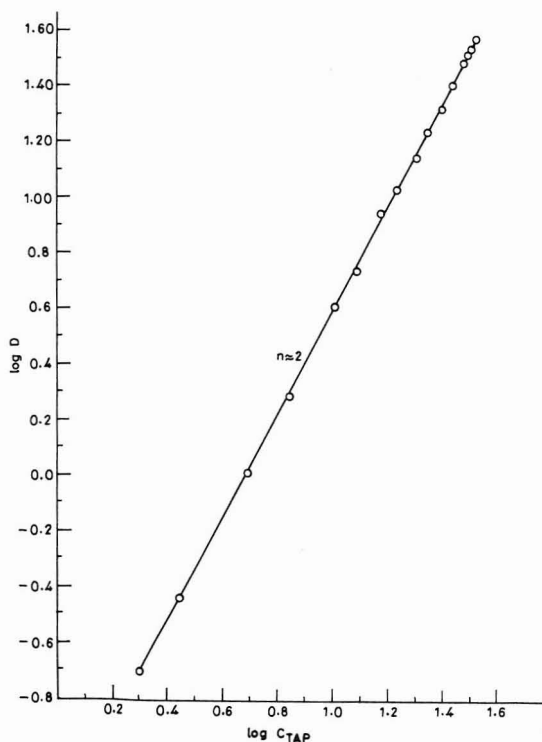

Fig. 2: *Effect of variation of the TAP concentration on the distribution ratio of Ti(IV) from its aqueous hydrochloric acid solutions*
[HCl] = 11.5 mol l^1, n = Solvation number

TABLE 3
Effect of TAP concentration on the extraction of titanium (IV)
from its hydrochloric acid solution
[HCl] = 11.50 mol l^{-1}
[Ti(IV)] = 1.0 x 10^{-3} mol l^{-1}
Vol. of aqueous layer = vol. of organic layer = 10 ml.

S. No.	[TAP] %	Amount in 5 ml aliquot x 10^{-2} mg		D	% E	log K$_{ex}$
		[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	1.64
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	22.68	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	27.20	1.58
15	33	0.61	23.34	38.26	97.45	-
16	35	0.61	23.34	38.26	97.45	-
17	40	0.61	23.34	38.26	97.45	-

Average log K$_{ex}$ = 1.60 ± 0.0397

readily extractable adduct of Ti(IV) with TAP and TTA. The system was further investigated to evaluate the number of moles of TTA and TAP used in the adduct formation. When log C$_{TTA}$ was plotted against log D keeping the [TAP] constant at 10.0% (Table 4) a straight line with a slope of nearly unity is obtained (*Fig.3*). Similarly when log D was plotted against log [TAP] from the data of Table 5, the results (depicted graphically in *Fig.4*) show a straight line also with a slope of nearly unity. Thus it can now be concluded that one mole each of the TAP and TTA is utilized in the adduct formation with Ti(IV), i.e. the ratio of Ti(IV):TTA:TAP in the organic phase is 1:1:1.

It had also been reported in an earlier paper (Stary 1964) that TTA reacts in the dissociated form but our results (given in Table 1) clearly show that the percentage extraction increases with the hydrogen ion concentration. This would not have been the case if the proton were being liberated from TTA. So it is concluded that in the present system the TTA is utilized in the completely undissociated form. This observation
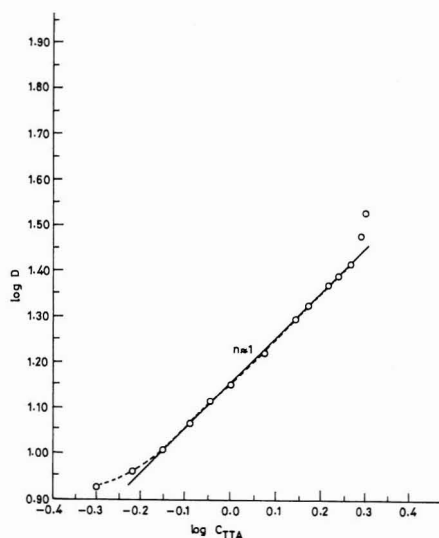

Fig. 3: *Effect of variation of the TTA concentration on the distribution coefficient of Ti(IV) at a fixed TAP concentration*
[HCl] = 11.5 mol^{-1}
[Ti(IV) = 1.0 x 10^3 mol l^1
[TAP] = 10% in CCl$_4$

TABLE 4
Effect of TTA concentration on the distribution coefficient (D) of Ti(IV)
when the TAP concentration was constant
[HCl] = 11.5 mol l^{-1}
[TAP] = 10% (v/v) in CCl$_4$
[Ti(IV)] = 1.0 x 10^{-3} mol l^{-1}

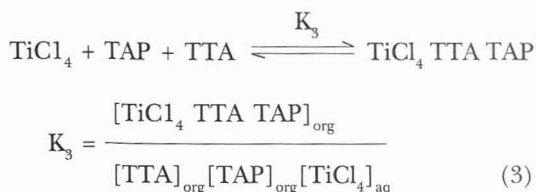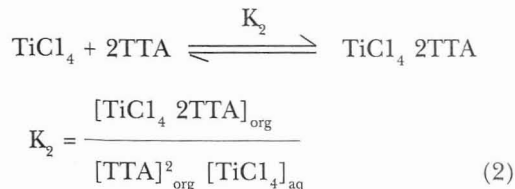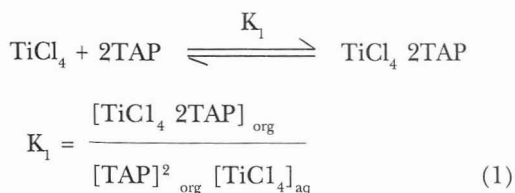| S. No.	[TTA]%	Amount in 5 ml aliquot x 10^{-2} mg		D	%E
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$		
1	0.50	2.57	21.38	8.31	89.25
2	0.60	2.37	21.58	9.10	90.09
3	0.70	2.13	21.82	10.24	91.10
4	0.80	1.92	22.03	11.47	91.98
5	0.90	1.65	22.30	13.48	93.09
6	1.00	1.58	22.37	14.15	93.39
7	1.20	1.37	22.58	16.48	94.28
8	1.40	1.17	22.78	19.47	95.11
9	1.50	1.07	22.88	21.38	95.53
10	1.65	0.97	22.98	23.44	95.90
11	1.75	0.93	23.02	24.47	96.07
12	1.85	0.90	23.05	25.61	96.24
13	1.95	0.84	23.11	27.51	96.49
14	2.00	0.82	23.13	28.20	96.57
15	3.00	0.82	23.13	28.20	96.57
16	5.00	0.82	23.13	28.20	96.57
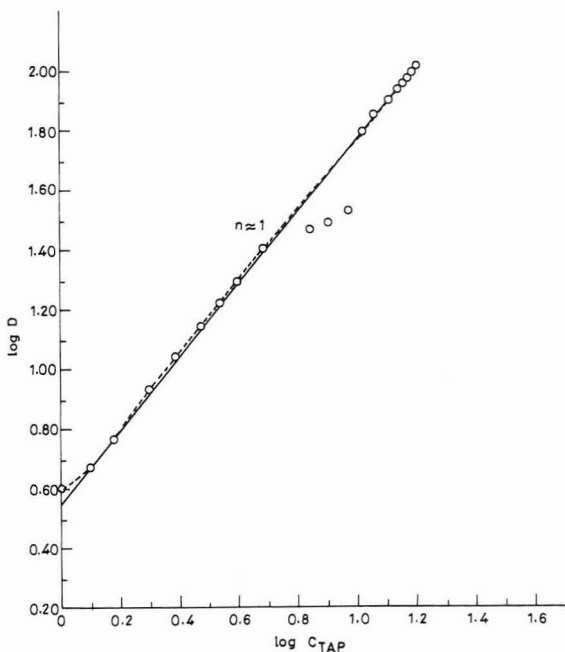
Fig. 4: Effect of variation of the TAP concentration on the distribution coefficient (D) of Ti(IV) when the TTA concentration is constant
[TTA] = 2.0% (vol./vol.) in CCl$_4$
[HCl] = 11.5 mol l^{-1}
[Ti (IV) = 1.0 × 10^3 mol l^{-1}
n = Solvation number

is also substantiated by earlier literature reports for certain analogous Ti(IV) extraction systems (Komatsu 1980; Stardy and Hladsky 1963). Thus the extraction systems can be mathematically represented as follows:

$$TiCl_4 + 2TAP \xrightleftharpoons{K_1} TiCl_4 \, 2TAP$$

$$K_1 = \frac{[TiCl_4 \, 2TAP]_{org}}{[TAP]^2_{org} \, [TiCl_4]_{aq}} \qquad (1)$$

$$TiCl_4 + 2TTA \xrightleftharpoons{K_2} TiCl_4 \, 2TTA$$

$$K_2 = \frac{[TiCl_4 \, 2TTA]_{org}}{[TTA]^2_{org} \, [TiCl_4]_{aq}} \qquad (2)$$

$$TiCl_4 + TAP + TTA \xrightleftharpoons{K_3} TiCl_4 \, TTA \, TAP$$

$$K_3 = \frac{[TiCl_4 \, TTA \, TAP]_{org}}{[TTA]_{org}[TAP]_{org}[TiCl_4]_{aq}} \qquad (3)$$

The value of K_1 and K_2 can be calculated from the results of Table 2 and Table 3 when TAP and TTA were used individually. The following equation may be written when only TAP is used for the extraction of Ti(IV).

$$[TAP]_{t.org} = [TAP]_{org} + 2[TiCl_4 \, 2TAP]_{org} \tag{4}$$

$$[Ti(IV)]_{t.org} = [TiCl_4 \, 2TAP]_{org} + [TiCl_4]_{org} \tag{5}$$

where $[TAP]_{t.org}$ and $[Ti(IV)]_{t.org}$ represent the total concentration of TAP and Ti(IV) in the organic phase. Since $[TiCl_4]_{org}$ is always negligible in comparison to $[TiCl_4 \, 2TAP]_{org}$ the value of K_1 can be calculated by the following equation:

$$K_1 = \frac{[Ti(IV)]_{t.org}}{([TAP]_{t.org}\text{-}2[Ti(IV)]_{t.org})^2 \, [Ti(IV)]_{aq}} \tag{6}$$

Similarly, K_2 can be calculated when it was expected that the TTA was not dissolved in the aqueous phase and the concentration of $[TTA]_{t.org}$ remained unchanged.

$$K_2 = \frac{[Ti(IV)]_{t.org}}{([TTA]_{t.org}\text{-}2[Ti(IV)]_{t.org})^2 \, [Ti(IV)]_{aq}} \tag{7}$$

The value of K_3 can be calculated if the details of the different complexes formed in the organic phase are written as follows:

$$[Ti(IV)]_{t.org} = [TiCl_4 2TAP]_{org} + [TiCL_4 2TTA]_{org} + [TiCl_4 TTA \, TAP]_{org} \tag{8}$$

$$[TAP]_{t.org} = [TAP]_{org} + 2[TiCl_4 2TAP]_{org} + [TICL_4 TTA \, TAP]_{org} \tag{9}$$

$$[TTA]_{t.org} = [TTA]_{org} + 2[TiCl_4 2TTA]_{org} + [TiCl_4 TTA \, TAP]_{org} \tag{10}$$

Replacing the concentration of the complexes in terms of the stability constant,

$$[Ti(IV)]_{t.org} = A \qquad [Ti(IV)]_{ag} = k$$

$$[TAP]_{t.org} = B \qquad K_1 = a \quad K_3 = z$$

$$[TTA]_{t.org} = C \qquad K_2 = b$$

$$[TAP]_{org} = x$$

$$[TTA]_{org} = y$$

The above equations (8), (9) and (10) become

$$A = kax^2 + kby^2 + kxyz \tag{11}$$

$$B = x + kax^2 + kxyz \tag{12}$$

$$C = y + 2kby^2 + kxyz \tag{13}$$

Combining these equations in the manner of 12 + 13 - 2 x 11

$$B + C - 2A = x + y \tag{14}$$

Thus using the values in equations (11) and (12) we get the following equation:

$$A - B = kby^2 - kax^2 - x \tag{15}$$

Further, replacing x with y from the equation (14) we get an equation of the second degree in y terms

$$y^2 (kb - ka) + y\varepsilon + \gamma = 0$$

where $\varepsilon = 1 + 2ka (B + C - 2A)$

$$\gamma = A - C - ka (B + C - 2A)^2$$

The value of $x = [TAP]_{org}$ drawn from the equation (14)

$$x = B + C - 2A - y$$

Concentrations of the $[TiCl_4 \, 2TAP]$ and $[TiCl_4 \, 2TTA]$ were calculated from their extraction constants

$$[TiCl_4 \, 2TAP]_{org} = K_1[TAP]^2 \, [Ti(IV)]_{aq} = kax^2$$

$$[TiCl_4 \, 2TTA]_{org} = K_2[TTA]^2 \, [Ti(IV)]_{aq} = kby^2$$

Thus the concentration of the adduct formed in the statements (8), (9) and (10) can be calculated by the following equation:

$$[TiCl_4 \, TTA \, TAP]_{org} = [TAP]_{t.org}\text{-}[TAP]_{org}\text{-}2[TiCl_4 \, 2TAP]_{org}$$

Finally K_3 can be calculated from its definition

TABLE 5
Effect of TAP concentration on the extraction of Ti(IV) when
the TTA concentration was constant
[TTA] = 2.0% (v/v) in CCl_4
[HCl] = 11.5 mol l^{-1}
[Ti(IV)] = 1.0 x 10^{-3} mol l^{-1}

S. No.	[TAP] %	Amount in 5 ml^{-1} aliquot x 10^{-2} mg		D	% E	log K_{ex} (mix)
		$[Ti(IV)]_{aq}$	$[Ti(IV)]_{org}$			
1	1.0	4.80	19.15	3.98	79.91	3.11
2	1.5	3.54	20.41	5.75	85.18	3.09
3	2.0	2.57	21.38	8.31	89.25	3.11
4	2.5	2.00	21.95	10.96	91.63	3.12
5	3.0	1.62	22.33	13.78	93.23	3.13
6	3.5	1.42	22.53	15.86	94.06	3.16
7	4.0	1.17	22.78	19.47	95.11	3.19
8	5.0	0.92	23.03	25.03	96.15	3.19
9	7.0	0.62	23.33	37.62	97.41	3.20
10	8.0	0.52	23.43	45.05	97.82	3.21
11	9.5	0.43	23.52	54.69	98.20	3.22
12	10.5	0.38	23.57	62.05	98.41	3.22
13	12.0	0.33	23.62	71.67	98.62	3.21
14	13.0	0.30	23.65	78.83	98.74	3.20
15	14.0	0.28	23.67	84.53	98.83	3.23
16	14.5	0.26	23.69	91.11	98.91	3.23
17	15.0	0.25	23.70	94.48	98.95	3.24
18	15.5	0.24	23.71	98.79	98.99	3.23
19	16.0	0.23	23.73	103.13	99.03	3.23
20	18.0	0.23	23.73	103.13	99.03	-
21	20.0	0.23	23.73	103.13	99.03	-

Average log $K_{ex (mix)}$ = 3.19 ± 0.0478

$$z = K_3 = \frac{B - x - 2kax^2}{kxy}$$

$$K_3 = \frac{[TAP]_{t.org}-[TAP]_{org}-2[Ti(IV)]_{ag}K_1[TAP]^2_{org}}{[Ti(IV)]_{aq}[TAP]_{org}[TTA]_{org}} \quad (16)$$

with the help of equations (6), (7) and (16) the extraction constants were calculated and represented in Tables 2, 3 and 5.

The average values for log K_{ex}(TTA) and log K_{ex}(TAP) were 2.48 and 1.60. The statistical value and observed value for $K_{ex.}$(mix) are represented as follows:

log $K_{ex.(mix)}$ (Stat.) log $K_{ex.(mix)}$ (Obs.)

TTA - TAP   2.34   3.19

The observed value of K_{ex} for TTA-TAP mixed ligand species was 7.06 times more than the statistical value.

Our results are also supported by the earlier work of Sekine and Dyrssen(1964) for the extraction of similar mixed chelate complexes of divalent metals with TTA and other ligands wherein it has been concluded that the extraction proceeds to a greater extent than the statistically evaluated values for the same ligand used separately.

Further, these workers have also evaluated the statistical extraction constant for divalent ions with the two ligands H_A and H_B using the relation

$$K_{(ex)(mix)} = 2\sqrt{K_{exA} \times K_{exB}}$$

where K_{exA} is the extraction constant for H_A and K_{exB} is that for H_B; the same statistical treatment has been used to evaluate the log $K_{ex(mix)}$ (Stat.).

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