

Statistical Experimental Design for the Extraction of Ti(IV) in the Ti(IV)- SO_4^{2-} (H^+ , Na^+) – Cyanex 301 – Kerosene – 5% (v/v) Heptane-1-ol System

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Received 24 February 2018, accepted in final revised form 24 June 2018

Abstract

The titled system has been investigated from the modelling point of view. The equilibration time for the system is 45 min, and 5% (v/v) heptane-1-ol in the organic phase is used as a de-emulsifier. The factors affecting the extent of extractions are [Ti(IV)], $\text{pH}_{(\text{eq})}$, [Cyanex 301], $[\text{SO}_4^{2-}]$ and temperature (T). The selected levels are high (+) and low (-) for these factors in the present investigation. Model equation for the extraction of Ti(IV) by Cyanex 301 is determined from 2^5 full factorial design. However, the success of the factorial design depends on the linear relationship between yield and factor. Plots of $\log C_D$ vs $\log [\text{Ti(IV)}]$, $\text{pH}_{(\text{eq})}$, $\log [\text{Cyanex 301}]$ and $\log [\text{SO}_4^{2-}]$ are curves. Logistic functions involving these factors are considered in designing. While $[\text{Ti(IV)}] < 1.00 \text{ g/L}$ and $[\text{HA}]_{(\text{o})} > 0.10 \text{ mol/L}$, considered logistic functions viz. $-\log(1+316.2 ([\text{Ti(IV)}], \text{mol/L}))$, $-\log(10^{-\text{pH}} + 229 \times 10^{-2\text{pH}})$, $\log ([\text{HA}]_{(\text{o})}, \text{mol/L})$, $-\log(1+0.79 ([\text{SO}_4^{2-}], \text{mol/L}))$ and absolute temperature are abbreviated as M, P, E, S and T, respectively. Model is $\log C_D = 5.847 + 0.964 M + 0.909 P + 2 E + 0.995 S - (1437.5/T)$. The experimental model illustrates that there is no interaction effect between the factors under investigation.

Keywords: Ti(IV); SO_4^{2-} ; Cyanex 301; Extraction; Factorial design; Kerosene.

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doi: <http://dx.doi.org/10.3329/jsr.v10i3.35748> J. Sci. Res. **10** (3), 275-289 (2018)

1. Introduction

In processing ilmenite (available in beach sand of south-eastern Bangladesh) for manufacturing pigment grade TiO_2 , it is required to extract Ti(IV) from the leach solution. In a review [1,2] it is concluded that the extraction of Ti(IV) from concentrated sulfuric acid medium by several organophosphorous extractants is the best achieved by using tri-octylphosphine oxide. However, the slow extraction kinetics, stripping difficulty and partial (~50% in a single stage) extraction are the disadvantages.

On the other hand, the extraction of Ti(IV) from $\text{Cl}^-/\text{SO}_4^{2-}$ medium by organophosphorous extractants have been investigated by several workers [3-21]. These

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are mostly reviewed by Reddy and Saji [22] and Zhu *et al.* [23]. In last review, Zhu *et al.* [23] have also included a number of new methods to purify titanium in chloride solution by solvent extraction established by Lakshmanan *et al.* [24-28]; Willem *et al.* [29]; Duyvesteyn *et al.* [30]; Verhulst *et al.* [31] and Wang *et al.* [32].

The equilibrium of the liquid-liquid extraction of Ti(IV) from acidic sulfate medium by Cyanex 301 has been reported by Biswas and Karmakar [33]; where the extraction isotherms are provided and reported the value of $\log K_{ex}$ as 1.117. In this paper, the same system is investigated from a modelling point of view. To model the system by factorial design, five logistic functions of the factors ([Ti(IV)], pH, [HA]_(o), [SO₄²⁻] and T (absolute temperature)) have been considered. The investigated factor levels are at high (+) and low (-). This statistical design is used to verify the extraction data obtained from the thermodynamic view point [33]. This has been done to cross-check the extraction data obtained from thermodynamic view point [33] and also to optimize the factors.

2. Materials and Method

2.1. Materials

Cyanex 301, containing 77.2% R₂PS₂H and the rest being R₂PSOH and R₃PSO etc. (where, R = CH₃-C(CH₃)₂-CH₂-CH(CH₃)-CH₂-) – a green viscous liquid of density 0.95 g/mL. It had a smell of rotten egg. Cyanex 301 was received from Cytec Canada Inc. as a gift and used in extraction studies without further purification as the impurities were reported to have similar extraction powers. Unlike other acidic organophosphorous acids, this reagent was monomeric as determined by the vapour pressure osmometry. Its molar solution was prepared considering its monomeric form. Kerosene was procured from the local market. It was then distilled to collect aliphatic colorless fraction distilling over 200-260 °C. All the other chemicals (TiO₂ (98%, BDH), H₂O₂ (30%, E. Merck), Heptane-1-ol (99%, BDH), H₂SO₄ (98%, E. Merck), H₃PO₄ (85%, Riedel-dettaen) etc.) were used without further purification.

2.2. Analytical

The concentration of Ti(IV) in the aqueous solution was measured by the 15% H₂SO₄ – H₂O₂ method 420 nm [34], using a UV-visible spectrophotometer (UV-1650 PC, Shimadzu, Japan). TiO₂ was used to prepare the standard solution of Ti(IV) on the complete fusion of 1 g TiO₂ with 10 g KHSO₄ in a platinum crucible followed by dissolution in 15% H₂SO₄ solution. The working solution of Ti(IV) was prepared by digestion TiO₂ with conc. H₂SO₄ followed by dilution with 15% H₂SO₄ and filtration. A pH meter (Mettler Toledo, MP 220) was used for pH measurement. The pH of test solution was adjusted by addition of either anhydrous Na₂CO₃ or diluted H₂SO₄ solution as required.

2.3. Extraction procedure

The extraction process is given elsewhere [33, 35]. Two phases at specified experimental parameters are stoppered in a quick fit reagent bottle. It is then agitated at O/A = 1 (O = 20 mL) for a predetermined time of 45 min. The phase separation after extraction is found to be quick; and on phase disengagement, the aqueous phase is analyzed for its equilibrium pH and Ti(IV)-content. Then the value of extraction or distribution ratio, D is calculated as follows:

$$D = ([\text{Ti(IV)}]_{(\text{ini})} - [\text{Ti(IV)}]_{(\text{eq})}) / [\text{Ti(IV)}]_{(\text{eq})} \quad (1)$$

2.4. Data treatment

The extraction isotherms, i.e. log D vs. pH and log D vs. log [HA]_(o) plots, at a constant temperature, are supposed to be valid at a constant free [HA]_(o) and a constant pH, respectively. In solvent extraction system, if the aqueous phase is not properly buffered (as usually the case; addition of foreign ions in the system not being practiced normally), the pH_(eq) - value is very much changed from the pH_(eq)- value (usually decreased for liberation of H⁺ due to extraction reaction), particularly when the latter value exceeds 1. The extent of this variation depends on the value of pH_(ini) and the extent of extraction. Similarly, due to different amounts of extraction, the free [HA]_(o) decreases, from its initial value at various extents.

It appears that the valid extraction isotherm in the pH-dependence plot would be only obtained when the experimental D- values are corrected to ^CD value at a constant [HA]_(o, eq) or, [HA]_(o, ini) - value. Hence, it requires the consideration of the change of D- value with [HA] change ([HA]_(o, ini) - [HA]_(o, eq)). On knowing the approximate [HA]-dependence from log D vs. log [HA]_(o, ini) as 'y', ^CD value at a constant [HA]_(o, ini) can be calculated from the following reaction:

$$\log {}^C D = \log D + y (\log [\text{HA}]_{(\text{o, ini})} - \log \{[\text{HA}]_{(\text{o, ini})} - y [\text{Ti(IV)}]_{(\text{o, eq})}\}) \quad (2)$$

where the concentration terms are in mol/L, y = 2 for this case [33] and the last term within the second bracket represents [HA]_(o, eq).

Similarly, the valid extraction isotherm in extractant dependence plot would be obtained when the experimental D- values are corrected to ^CD values at a constant pH_(eq) or pH_(ini) value on taking into consideration - the effect of pH variation (initial and equilibrium) on the value of experimental D value. Such a correction can be made by the equation given below (for value at constant pH_(ini)):

$$\log {}^C D = \log D - x (\text{pH}_{(\text{eq})} - \text{pH}_{(\text{ini})}) \quad (3)$$

where, x = 2 (pH dependence) as reported by Biswas and Karmakar [33], D is the experimental D- value for a pH_(ini)- value which is changed to a pH_(eq)- value and ^CD is the corrected D- value at a constant pH_(ini). When the correction for both parameters are required (as in the cases of [SO₄²⁻] and temperature dependencies), the following

combined equation can be used to get the corrected datum at a constant $\text{pH}_{(\text{ini})}$ and $[\text{HA}]_{(\text{o, ini})}$:

$$\log {}^{\text{C}}\text{D} = \log \text{D} - 2 (\text{pH}_{(\text{eq})} - \text{pH}_{(\text{ini})}) + 2 (\log [\text{HA}]_{(\text{o, ini})} - \log \{ [\text{HA}]_{(\text{o, ini})} - y[\text{Ti(IV)}]_{(\text{o, eq})} \}) \quad (4)$$

3. Results and Discussion

The theory of linearity in the factor effect is essential for the use of two-level factorial design [36]. In a previous paper of Biswas and Karmakar [33], the authors have reported that plots of $\log {}^{\text{C}}\text{D}$ vs. $\log [\text{Ti(IV)}]$ are curves which can be fitted to equation (5):

$$\log {}^{\text{C}}\text{D} = \text{constant} - \log (1 + 316.2 [\text{Ti(IV)}]) \quad (5)$$

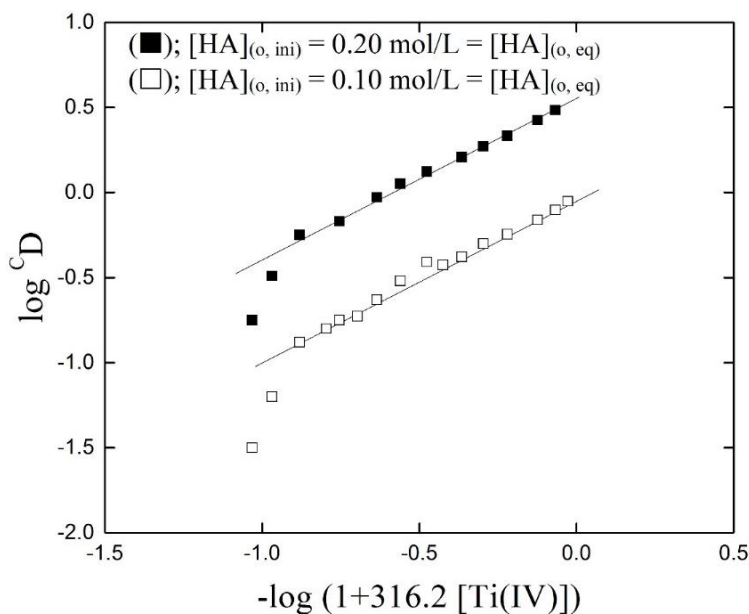


Fig. 1. Effect of $[\text{Ti(IV)}]$ on extraction. $[\text{SO}_4^{2-}] = 0.50 \text{ mol/L}$, temp. = 302 K, time = 45 min, O/A = 1, $\text{pH}_{(\text{eq})}$ chosen as constant = 1.80, pH dependence = 1.78.

where, the value of constant depends on pH and $[\text{HA}]_{(\text{o})}$ used in extraction at a constant temperature of 303 K and $[\text{SO}_4^{2-}]$ of 0.10 mol/L and $[\text{Ti(IV)}]$ in mol/L. However, the above equation holds good for $[\text{Ti(IV)}]$ of less than 1.1 g/L. Consequently, it is expected that $\log {}^{\text{C}}\text{D}$ vs. $-\log (1 + 316.2 [\text{Ti(IV)}])$ plots would be linear and such plots are shown in Fig. 1. It is therefore considered that the logistic function of $[\text{Ti(IV)}]$ is $-\log (1 + 316.2 [\text{Ti(IV)}])$.

The figures of $\log {}^{\text{C}}\text{D}$ vs $\text{pH}_{(\text{eq})}$ are also curves which can be fitted to the following equation:

$$\log {}^{\text{C}}\text{D} = \text{constant} - \log ([\text{H}^+] + 229 [\text{H}^+]^2) = \text{constant} - \log (10^{-\text{pH}} + 229 \times 10^{-2\text{pH}}) \quad (6)$$

where, the value of constant depends on $[HA]_{(o)}$ only at a constant temperature of 303 K, $[SO_4^{2-}]$ of 0.10 mol/L and $[Ti(IV)]$ of 0.50 g/L. It appears, therefore, that $\log C_D$ vs. $-\log (10^{-pH} + 229 \times 10^{-2pH})$ plots would be linear as shown in Fig. 2. Therefore, $-\log (10^{-pH} + 229 \times 10^{-2pH})$ can be regarded as the logistic function of the factor (pH).

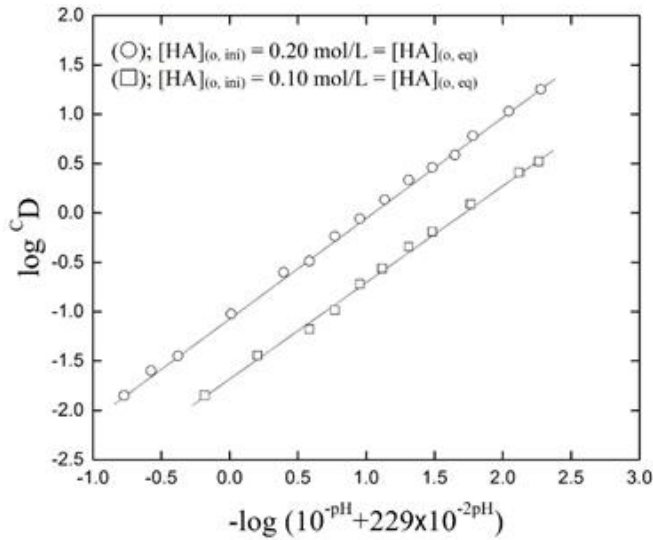


Fig. 2. Effect of pH on extraction. $[Ti(IV)] = 0.50 \text{ g/L}$, $[SO_4^{2-}] = 0.50 \text{ mol/L}$, temp = 303 K, time = 45 min, O/A = 1.

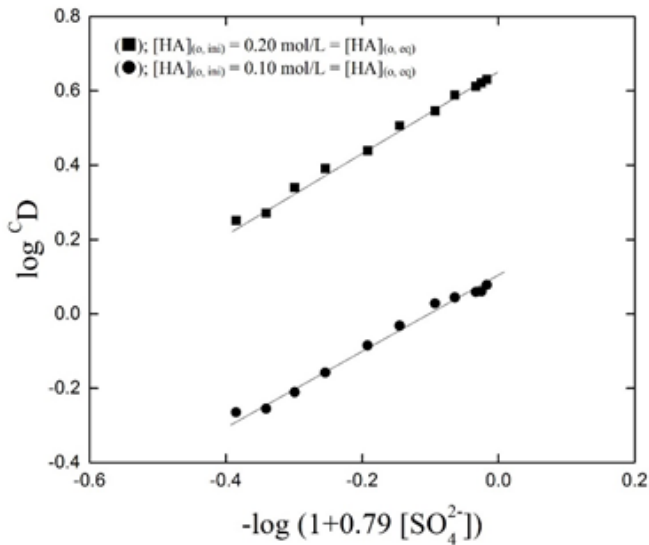


Fig. 3. Effect of $[SO_4^{2-}]$ on extraction. $[Ti(IV)] = 0.50 \text{ g/L}$, const. $pH_{(eq)} = 2.00$, Temp. = 303 K, Time = 45 min, O/A = 1.

Although $\log^C D$ vs. $\log [HA]_{(o)}$ plots are straight lines provided $[HA]_{(o)} > 0.10$ mol/L, the $\log^C D$ vs. $\log [SO_4^{2-}]$ plots are curves represented by following equation:

$$\log^C D = \text{constant} - \log (1 + 0.794 [SO_4^{2-}]) \quad (7)$$

where, the value of constant depends on pH and $[HA]_{(o)}$ used in extraction at a constant temperature and $[Ti(IV)]$. Fig. 3 shows linearity of $\log^C D$ vs. $-\log (1 + 0.794 [SO_4^{2-}])$ plots and hence $-\log (1 + 0.794 [SO_4^{2-}])$ is considered as the logistic function of the $[SO_4^{2-}]$ as factor. Moreover, it is reported that $\log^C D$ varies linearly with $1/T$ (K^{-1}) (Fig. 4). Therefore, $1/T$ is considered as the logistic function of temperature.

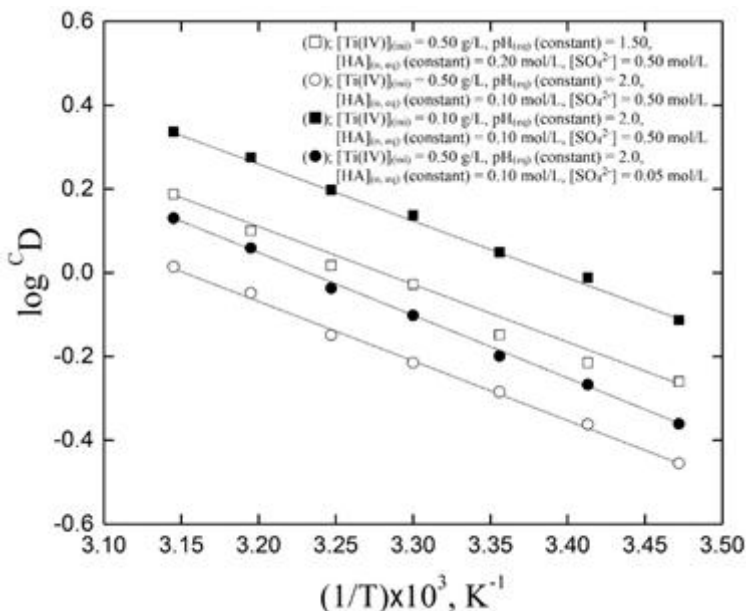


Fig. 4. Effect of temperature on extraction. Time = 45 min, O/A = 1.

The system under investigation has been demonstrated by a 2^k factorial design, where $k = 5$ (number of factors considered). Logistic function is considered for the present investigation [36]. All the factors under investigation are at 2 levels: high (+) and low (-) [37, 38, 14]. A 2^5 statistical experimental modelling would contain 1 ($5!/0!(5-0)! = 1$) mean effect, 5 ($5!/1!(5-1)! = 5$) single factor effects, 10 ($5!/2!(5-2)! = 10$) two-factor correlations, 10 ($5!/3!(5-3)! = 10$) three factor correlations, 5 ($5!/4!(5-4)! = 5$) four-factor correlations and, 1 ($5!/5!(5-5)! = 1$) five factor correlation.

The investigated system has been modelled by 2^5 factorial design which contains 32 trials. Subsequently, the 2^5 experimental model includes 32 trials and every trial run in twice. Hence, there will be 64 tests. At the middle point level of each factor, an extra test is repeated for four times. This additional trial is executed to analyze the inadequacy of fit due to curvature. The alteration of the average middle point value and the overall average value of the design points specify the severity of curvature.

Eqs. (8-12) [39,40] are used to determine \bar{Y} , the average yield and the variance for respective trial; the pooled variance (S_{pooled}^2), standard deviation_{pooled}, [MIN] and [MINC].

$$\text{Variance} = S^2 = \frac{(Y_1 - \bar{Y})^2 + (Y_2 - \bar{Y})^2 + \dots + (Y_n - \bar{Y})^2}{n-1} \tag{8}$$

The estimation of variances for respective trial is then used in the calculation of a weighted average, i.e. the pooled variance of the individual variances for each trial.

$$\text{Pooled variance} = S_{pooled}^2 = \frac{(n_1-1)(S_1^2) + (n_2-1)(S_2^2) + \dots + (n_k-1)(S_k^2)}{(n_1-1) + (n_2-1) + \dots + (n_k-1)} \tag{9}$$

$$\text{Standard deviation}_{pooled} = \sqrt{S_{pooled}^2} \tag{10}$$

$$[\text{MIN}] = t.s \sqrt{\frac{2}{m.k}} \tag{11}$$

$$[\text{MINC}] = t.s \sqrt{\frac{1}{m.k} + \frac{1}{c}} \tag{12}$$

The student's "t" table is used to find the "t" value (2.03) at 95% confidence level and 35 df (resulting from thirty-two (32) trials with two replicates and one trial with four replicates as $df = 32(2-1) + 1(4-1) = 35$).

Table 1. Process variables and response.

Factor	Level			Logistic Function	Level		
	(+)	(0)	(-)		(+)	(0)	(-)
(a) [Ti(IV)], mol/L	0.021	0.0069	0.001	a) $-\log(1 + 316.2[\text{Ti(IV)}])$	-0.881	-0.502	-0.123
(b) pH	2.60	1.69	1.0	b) $-\log(10^{\text{pH}} + 229 \times 10^{-2\text{pH}})$	2.263	0.9427	-0.378
(c) [HA], mol/L	0.63	0.07	0.01	c) $\log([\text{HA}], \text{mol/L})$	-0.20	-0.60	-1.00
(d) $[\text{SO}_4^{2-}]$, mol/L	1.50	0.64	0.05	d) $-\log(1 + 0.794[\text{SO}_4^{2-}])$	-0.3406	-0.1787	-0.0169
(e) T, K	288	302	318	e) $1/T, \text{K}^{-1}$	0.00347	0.00331	0.00315

Response: Y (yield) = value of \log^{CD}

The studied experimental parameters of variables in the present system under investigation are displayed in Table 1. The coded form of the factors (2⁵ experimental design) is given in the 3rd to 7th columns of Table 2. The measured values of these experiments are recorded in the 34th and 35th columns of Table 2. The 36th column of Table 2 represents the average values. The variance of two evaluations for individual trial is recorded in the end column of Table 2.

Table 2 also stands for the mathematical investigation of the present experiment. The model matrix is accompanied with a computation matrix in this research. This process is used to observe any interaction result between the factors under investigation. A definite arithmetical multiplication of the coded factor levels utilized for the development of the computation matrix. In the test run 1, a and b are positive, respectively, therefore ab is positive. Similarly, in the test run 2, a is minus and b is plus, therefore ab is minus. The

Table 2. Computation matrix for five factors two level experiment.

Trial	Design Matrix					Computation Matrix												Yield (log ⁵ D)		Response (μ)		Variance						
	a	b	c	d	e	ab	ac	ad	ae	abd	abe	acd	ace	ade	bcd	bce	bde	cde	abcd	abce	abde		acde	bcde	abcd	Y ₁	Y ₂	Average
1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	1.326	1.330	1.328	0.00001
2	-	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.060	2.056	2.058	0.00001
3	+	-	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.060	-1.084	-1.072	0.00029
4	+	-	+	-	+	-	-	-	-	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-0.350	-0.334	-0.342	0.00013
5	+	+	-	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.280	-0.264	-0.272	0.00013
6	+	+	-	-	+	-	-	-	-	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	0.460	0.456	0.458	0.00001
7	+	-	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-2.710	-2.634	-2.672	0.00289
8	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.990	-1.890	-1.940	0.00500
9	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.700	1.600	1.650	0.00500
10	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.420	2.340	2.380	0.00320
11	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.800	-0.700	-0.750	0.00500
12	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.010	-0.030	-0.020	0.00020
13	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.080	0.020	0.050	0.00180
14	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.800	0.760	0.780	0.00080
15	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-2.390	-2.310	-2.350	0.00320
16	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.570	-1.670	-1.620	0.00500
17	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.800	1.760	1.780	0.00080
18	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.540	2.490	2.515	0.00125
19	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.600	-0.620	-0.610	0.00020
20	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.140	0.096	0.118	0.00097
21	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.200	0.176	0.188	0.00029
22	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.960	0.876	0.918	0.00353
23	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-2.220	-2.200	-2.210	0.00020
24	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.500	-1.460	-1.480	0.00080
25	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.100	2.120	2.110	0.00020
26	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.800	2.880	2.840	0.00320
27	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.300	-0.280	-0.290	0.00020
28	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.400	0.480	0.440	0.00320
29	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.490	0.530	0.510	0.00080
30	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.260	1.220	1.240	0.00080
31	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.880	-1.900	-1.890	0.00020
32	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.180	-1.140	-1.160	0.00080
33	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.076	0.070	0.072	0.00001	
																									0.073	0.069		

$S^2_{pooled} = 0.0014$, Standard deviation_{pooled} = 0.0378, [MIN] = 0.019, [MINC] = 0.047 and curvature = 0.012

response values on an individual row with a positive sign for each column of Table 2 (e.g. for factor a, $1.328-1.072-0.272-2.672+1.650-0.750+0.050-2.350+1.788-0.612+0.188-2.212+2.110-0.290+0.510-1.890 = -4.496$). Similarly, the sum negative sign column (3rd factor and interaction results are found in Table 2, as follows and given in Table 3. The sum of positive column (2nd column of Table 3) accomplished by adding the column of Table 3) is achieved. The sum of these two columns value should be identical to the sum of all the average responses. It can be used as a check on arithmetic. The difference between the response values of the factor is at a high level (16 trails), and low level (16 trails), are displayed in the 4th column of Table 3. The difference value is divided by the number of plus signs in the column to achieve the effect of the factors under investigation. The system under investigation shows only the single factor effects with no other interaction effects.

Table 3. Evaluation of factor and interaction effects (based on Table 2).

Factor	Sum + ^{'s}	Sum - ^{'s}	Difference	Effect
Mean	2.688	0.000	2.688	0.084
a	-4.496	7.184	-11.680	-0.730
b	20.544	-17.856	38.400	2.400
c	14.144	-11.456	25.600	1.600
d	-1.232	3.920	-5.152	-0.322
e	-2.336	5.024	-7.360	-0.460

A first-order polynomial is used to express all the results as a numerical model. Table 3 displayed one-half values of the coefficient for the factor effects. Since the factor effects are created upon coded levels +1 and -1 that contrasted by two units. However, only factor effects are found in this investigation with no interaction effect. Therefore, the polynomial is:

$$Y = 0.084 + (-0.365) a + 1.200 b + 0.800 c + (-0.161) d + (-0.230) e \quad (13)$$

The factors are depicted as coded units in Eq. (13). These are transformed into real units by substituting:

i) for the concentration of metal ion $\{-\log(1+316.2[\text{Ti(IV)}]), \text{mol/L}\} = M$ let

$$a = \frac{M - \frac{-0.881+(-0.123)}{2}}{\frac{-0.881-(-0.123)}{2}} = -2.64 M - 1.3257 \quad (14)$$

ii) for pH $\{-\log(10^{-\text{pH}} + 229 \times 10^{-2\text{pH}})\} = P$ let

$$b = \frac{P - \frac{2.263+(-0.378)}{2}}{\frac{2.263-(-0.378)}{2}} = 0.7573 P - 0.7137 \quad (15)$$

iii) for extractant concentration $\{\log([\text{HA}], \text{mol/L})\} = E$ let

$$c = \frac{E - \frac{-0.20+(-0.10)}{2}}{\frac{-0.20-(-0.10)}{2}} = 2.5000 E + 1.5000 \quad (16)$$

iv) for SO_4^{2-} concentration $\{-\log(1 + 0.794[\text{SO}_4^{2-}])\} = S$ let

$$d = \frac{S - \frac{-0.3406 + (-0.0169)}{2}}{\frac{-0.3406 - (-0.0169)}{2}} = -6.1785 S - 1.1044 \quad (17)$$

v) for temperature (T being absolute temperature)

$$e = \frac{\frac{1}{T} - \frac{0.00347 + 0.00315}{2}}{\frac{0.00347 - 0.00315}{2}} = \frac{6250}{T} - 20.6875 \quad (18)$$

in Eq. (13) to obtain the following final equation:

$$Y = \log {}^C D = 5.847 + 0.964 M + 0.909 P + 2.000 E + 0.995 S - 1437.5/T \quad (19)$$

The measured yield is 1.3281 from the resulting hypothesis (Eq. (19)), for test 1 ($M = -0.881$, $P = 2.263$, $E = -0.20$, $S = -0.3406$ and $T = 288.2$); whereas, the experimental average yield is 1.328 which shows a deviation of only -0.0001. Table 4 displays all investigational average yield and the calculated yield resulting from model Eq. (19). The deviation of model yield and experimental yield in every investigational condition is negligible except the middle point value which is due to the curvature effect (less than [MINC] value). However, it should be memorized that the model is valid only when [Ti(IV)] in aqueous phase is kept below 1.10 g/L. The constant (5.847) is equivalent to $\log K_{ex}$ value shows in Eq. (19), at $M = 0$, $P = 0$, $E = 0$, $S = 0$ and $T = \infty$. At 303 K, Eq. (19) gives $\log K_{ex}$ value of 1.072 at $M = 0$, $P = 0$, $E = 0$ and $S = 0$ which matches well with that (1.117) obtained from the factor-dependence studies [33].

The model can competently guess investigational $\log {}^C D$ value which is displayed in Table 5, within a deviation of ± 0.20 , on any set of observational parameters. The optimization of the factors to acquire more than 95% Ex of Ti(IV) are shown in Table 6. The % Ex of >95% Ex-values on five optimized settings have been tested by the shake-out investigation at the optimized situations. These resulting values are found to be similar.

Table 4. Experimental average yield and calculated yield.

Trial	$Y_{(exp.)}$	$Y_{(cal.)}$	Deviation
1.	1.328	1.3281	-0.0001
2.	2.058	2.0581	-0.0001
3.	-1.072	-1.0718	-0.0002
4.	-0.342	-0.3417	-0.0003
5.	-0.272	-0.2719	-0.0001
6.	0.458	0.4581	-0.0001
7.	-2.672	-2.6718	-0.0002
8.	-1.942	-1.9417	-0.0003
9.	1.650	1.6501	-0.0001
10.	2.380	2.3801	-0.0001
11.	-0.750	-0.7498	-0.0002
12.	-0.020	-0.0198	-0.0002
13.	0.050	0.0501	-0.0001
14.	0.780	0.7801	-0.0001
15.	-2.350	-2.3498	-0.0002
16.	-1.620	-1.6198	-0.0002
17.	1.788	1.7884	-0.0004
18.	2.518	2.5184	-0.0004
19.	-0.612	-0.6115	-0.0005
20.	0.118	0.1185	-0.0005
21.	0.188	0.1884	-0.0004
22.	0.918	0.9184	-0.0004
23.	-2.212	-2.2115	-0.0005
24.	-1.482	-1.4815	-0.0005
25.	2.110	2.1104	-0.0004
26.	2.840	2.8404	-0.0004
27.	-0.290	-0.2895	-0.0005
28.	0.440	0.4405	-0.0005
29.	0.510	0.5104	-0.0004
30.	1.240	1.2404	-0.0004
31.	-1.890	-1.8895	-0.0005
32.	-1.160	-1.1595	-0.0005
33. (Middle point)	0.072	0.0839	-0.0119

Table 5. Comparison of model value with shake-out experimental value.

[Ti(IV)], g/L	pH _(eq)	[HA] _(o) , mol/L	[SO ₄ ²⁻], mol/L	Temp., K	log ^C D (exptl.)	log ^C D (model)	Deviation
0.10	1.8	0.10	0.50	303	-0.245	-0.223	0.015
0.70	1.8	0.10	0.50	303	-0.750	-0.738	0.012
0.50	1.5	0.10	0.50	303	-1.178	-1.223	0.045
0.50	2.4	0.10	0.50	303	0.412	0.273	0.139
0.50	1.8	0.20	0.50	303	0.046	0.003	0.043
0.50	1.8	0.50	0.50	303	0.789	0.775	0.014
0.50	2.0	0.20	0.10	303	0.612	0.426	0.186
0.50	2.0	0.20	1.00	303	0.391	0.206	0.185
0.50	2.0	0.10	0.50	293	-0.362	-0.468	0.106
0.50	2.0	0.10	0.50	318	0.014	-0.082	0.096

Table 6. Optimization of factor for extraction of 1.1 g/L Ti(IV) present in 0.10 mol/L SO₄²⁻ medium at 298 K.

pH _(eq)	P	[HA] _(o) , mol/L	E	log ^C D (calculated)	%E (calculated)	%E* (experimental)	Stand. Dev. of %Ex (exptl.)
1.0	-0.378	0.10	-1.000	-1.965	1.08		
		0.30	-0.523	-1.011	9.75		
		0.70	-0.155	-0.215	34.68		
1.5	0.584	0.10	-1.000	-1.091	7.50		
		0.30	-0.523	-0.137	42.18		
		0.70	-0.155	0.599	79.89		
2.5	1.483	0.10	-1.000	-0.274	34.73		
		0.30	-0.523	0.680	84.04		
		0.70	-0.155	1.416	96.30	96.00	0.32
2.5	2.263	0.10	-1.000	0.435	73.14		
		0.30	-0.523	1.389	96.08	96.20	0.25
		0.70	-0.155	2.125	99.26	99.40	0.10
3.5	2.910	0.10	-1.00	1.023	91.34		
		0.30	-0.523	1.977	98.96	99.00	0.08
		0.70	-0.155	2.713	99.81	99.90	0.12

M = -0.635, S = -0.033, T = 298, P = -log (10^{-pH} + 229×10^{-2pH}), E = -log [HA]_(o)

*Average of five experimental results.

4. Conclusion

In the titled system, Ti(IV) extraction has been demonstrated by five logistic functions of factors – two level factorial design. On symbolizing the logistic functions of [Ti(IV)], pH, [HA]_(o), [SO₄²⁻] and temperature as M = -log (1+316.2[Ti(IV)]), P = -log (10^{-pH} + 229×10^{-2pH}), E =log [HA]_(o), S = -log (1 + 0.794[SO₄²⁻]) and T (absolute temperature), the model obtained is: Y = log^CD = 5.847 + 0.964 M + 0.909 P + 2.000 E + 0.995 S – 1437.5/T, provided [Ti(IV)] is kept below 1.1 g/L. From this model, it is seen that there are only

effects of logistic functions of factors; i.e. there is no interaction between the logistic functions of factors. At $M = 0$, $P = 0$, $E = 0$ and $S = 0$, the $\log {}^C D$ value at 303 K (1.072) represents the equilibrium constant of the system at 303 K. Several conditions have been optimized for more than 95% extraction and at these conditions, the shake-out experiments yield % extractions which are very close to those predicted from the model.

5. Acknowledgment

Authors are grateful to Cytec Canada Inc. for providing Cyanex 301 as a gift.

Nomenclature

	Extraction or distribution ratio
${}^C D$	D at constant equilibrium pH and extractant concentration
K_{ex}	Extraction equilibrium constant
HA	Cyanex 301
%Ex	Percent extraction
Y	Response value
\bar{Y}	Average response value
n	Number of observation
t	Suitable value from Students 't-table'
S^2	Variance
m	Number of plus signs in a column
k	Number of replicates in each trial
c	Number of center point
df	Degree of freedom
[MIN]	Minimum significant factor effect
[MINC]	Minimum significant curvature effect
Suffix	
(o)	Organic phase
(ini)	Initial
(eq)	Equilibrium

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