



BCSIR

Available online at [www.banglajol.info](http://www.banglajol.info)

Bangladesh J. Sci. Ind. Res. 51(1), 47-54, 2016

**BANGLADESH JOURNAL  
OF SCIENTIFIC AND  
INDUSTRIAL RESEARCH**

E-mail: [bjisir07@gmail.com](mailto:bjisir07@gmail.com)

## Factorial (2<sup>5</sup>) design for the extraction of V(IV) in the V(IV)-[SO<sub>4</sub><sup>2-</sup>](H<sup>+</sup>, Na<sup>+</sup>) – Cyanex 302-kerosene system

R. K. Biswas\* and A. K. Karmakar

Department of Applied Chemistry and Chemical Engineering, Rajshahi University, Rajshahi-6205, Bangladesh

### Abstract

The title system has been investigated from the modeling points of view. Equilibration time is 20 min and the significant extraction occurs above pH 2. Considering the constancy of the organic to aqueous phase ratio (1:1), the factors affecting the extent of extraction (value of log D or log <sup>C</sup>D) are [V(IV)], pH<sub>(eq)</sub>, [Cyanex 302], [SO<sub>4</sub><sup>2-</sup>] and temperature (T). The levels of these factors chosen in experimentation are high (+) and low (-). Regression or model equation for the extraction of vanadium (IV) by Cyanex 302 is determined from 2<sup>5</sup> full factorial design. On abbreviating log[V(IV)], -log(1+4641.14x10<sup>-pH</sup> + (1.5x10<sup>6</sup>)x10<sup>-2pH</sup>), log[Cyanex 302], -log(1+2.24 [SO<sub>4</sub><sup>2-</sup>]) and absolute temperatures as M, P, E, S and T, respectively, the model obtained is: log <sup>C</sup>D = 10.452-0.16M+1.0047P+2.0011E+1.0003S-2425.3729/T. From the regression model it is seen that there is no interaction effect between the factors under investigation. The model can describe the system well.

**Keywords:** Extraction; Vanadium(IV); Cyanex 302; Kerosene; Sulphate; Factorial design

### Introduction

Vanadium is used for alloying steel and the manufacture of oxidative catalyst. The ores of vanadium are patronite (V<sub>2</sub>S<sub>3</sub>), vanadinite (3Pb<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>.PbCl<sub>2</sub>), carnotite (K<sub>2</sub>U<sub>2</sub>V<sub>2</sub>O<sub>11</sub>. 3H<sub>2</sub>O) etc. which are rare on the earth's crust. Consequently, it is necessary to develop extraction processes for low grade ores and waste materials (tar sand, waste desulphurization catalyst etc.). Solvent extraction technique is convenient for such purpose. The technique can build up concentration by using low (O/A) ratio in extraction and high O/A ratio in stripping. In a reference book (Sekine and Hasegawa, 1977) the works on the solvent extraction of V(IV) by various extractants prior to 1976 have been included. Di-2-ethylhexyl phosphoric acid (D2EHPA) is an effective extractant for V(IV) and V(V) (Sato *et al.*, 1978; Brunette *et al.*, 1979; Islam and Biswas, 1980a and 1980b; Hughes and Biswas, 1991; Juang and Lo, 1993; Biswas and Mondal, 2003). EHEHPA (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) (Saji and Reddy, 2002) can also extract V(IV) and V(V) efficiently. The organophosphinic acid derivatives and their sulphur analogues (Cyanex reagents) introduced by American Cyanamide Company and Cytec Canada Inc. are recent developed promising extractants. Cyanex 302 and Cyanex 301 are the mono- and di-sulphide analogues of Cyanex 272 (di-2,4,4-trimethylpentyl phosphinic acid). The sulphur substitution decreases the pK<sub>a</sub> values of the extractants permitting to work at lower pH

(Rickelton, 1992). Cyanex reagents differ from other commercial organophosphorous reagents (*e.g.* D2EHPA, DDPA, TBP, EHPEHPA etc.) in that the former reagents contain P-C bonding, whereas the latter reagents contain P-O-C bonding. The presence of P-C bonding in Cyanex reagents renders them to be less susceptible to hydrolysis and less soluble in water (Saily and Tandon, 1998).

Recently, the extraction behaviors of V(IV) from sulphuric acid solution by Cyanex 272 (Zhang *et al.*, 1995, 1996) and of V(IV) and V(V) from hydrochloric acid solution by Cyanex 272 and Cyanex 301 (Saily and Tandon, 1998) have been reported. As there was no report on the extraction behavior of V(IV) from any acid solution using Cyanex 302, this system have been investigated in Authors' Laboratories and as well reported by others (Sole and Hiskey, 1992).

In the present work, the factorial design considering five factors ([V(IV)], pH<sub>(eq)</sub>, [Cyanex 302], [SO<sub>4</sub><sup>2-</sup>] and temperature (T)) at two levels (low '-' and high '+') has been done to model the extraction of V(IV) in the V(IV)-[SO<sub>4</sub><sup>2-</sup>](H<sup>+</sup>, Na<sup>+</sup>) – Cyanex 302-kerosene system and the effectiveness of the derived model has been justified.

\*Corresponding author. e-mail: [rkbiswas694@gmail.com](mailto:rkbiswas694@gmail.com)

## Materials and methods

### Materials

Cyanex 302 containing 78-80%  $R_2PSOH$ , 10-12%  $R_3PO$ , 2-3%  $R_2PO_2H$ , 2%  $R_2PS_2H$  and 8% unknown compounds (Ali *et al.*, 2011) was collected from Cytec Canada Inc. as a gift. In extractions, it has been used without further purification as  $R_3PO$ ,  $R_2PO_2H$  and  $R_2PS_2H$  have extracting power. Kerosene is bought from the local market and distilled to collect the colorless aliphatic fraction distilling over 200-260°C.  $NH_4VO_3$  (99%, Riedel-deHaen),  $VOSO_4$  (99.9%, Alfa Aesar- Johnson-Mathey) and  $H_2O_2$  (30%, Merck-Germany) have been used without further purification.

### Analytical

Concentrations of V(IV) in aqueous solutions have been measured by the  $HNO_3$ , oxidative- $H_2O_2$  method (Ali *et al.*, 2011) at 450 nm using a UV-visible Spectrophotometer (UV-1650 PC, Shimadzu, Japan). For preparation of standard

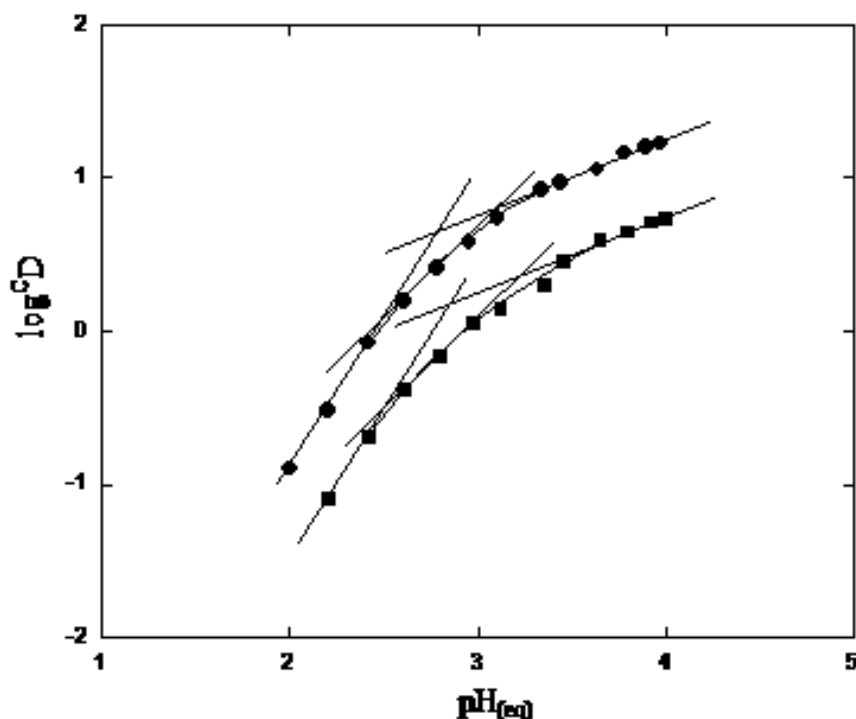
and test solutions,  $NH_4VO_3$  and  $VOSO_4 \cdot 5H_2O$  have been used respectively. A Mettler Toledo pH meter (model 320) was used for pH measurement. The pH was adjusted by addition of either anhydrous  $Na_2CO_3$  or dilute  $H_2SO_4$  solution when required.

### Procedure

Extraction procedures are given elsewhere (Paatero *et al.*, 1990). In this case, two phases at specified experimental parameters are agitated at  $O/A=1$  ( $O = 20$  mL) for a predetermined time of 20 min. The phase separation is found to be quick; and the aqueous phase after equilibration is analyzed for its equilibrium pH and V(IV)-content. Then the value of extraction ratio (D) is calculated as usual (Paatero *et al.*, 1990).

### Results and discussion

A potential concern in the use of two-level factorial design is the assumption of linearity in the factor effect. In the previous report (Biswas and Karmakar, 2012), though approxi-

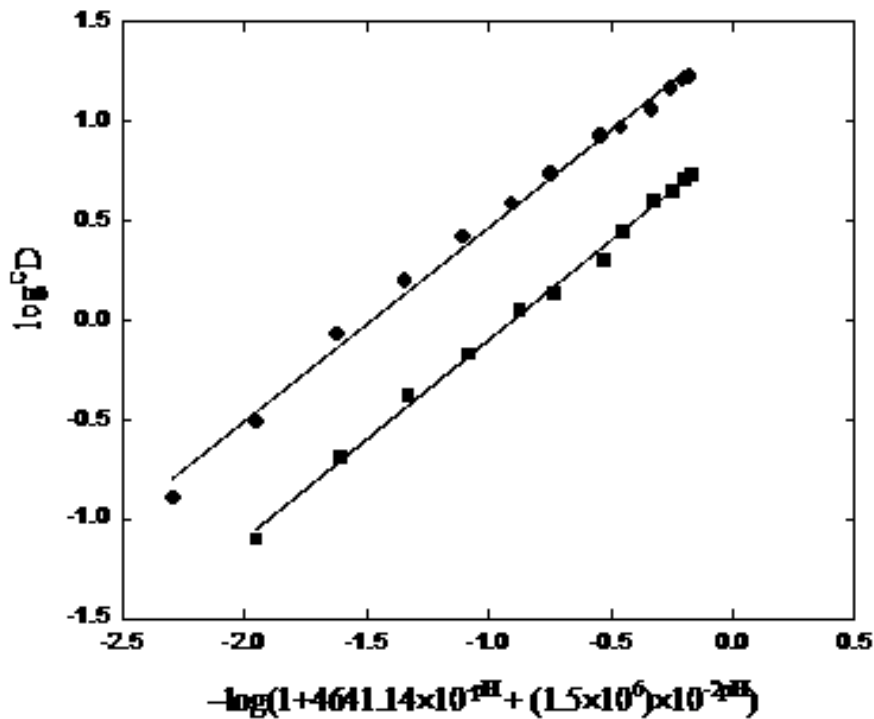


**Fig. 1.** Effect of equilibrium pH on the extraction of V(IV) Cyanex 302 in kerosene [14].  $[V(IV)]_{(ini)} = 200$  mg/L, Temp. =  $303 \pm 0.5$  K, Equilibration time = 20 min,  $O/A = 1$  ( $O = 20$  mL),  $[SO_4^{2-}] = 0.02$  mol/L.(n),  $[Cyanex\ 302] = 0.10$  mol/L; S = 2 ( $pH_{(eq)} < 2.25$ ), 1 ( $pH_{(eq)} = 2.9$ ) and 0.3 ( $pH_{(eq)} = 4.0$ ); I = -5.485 (when S = 2) and -3.04 (when S = 1); (□),  $[Cyanex\ 302] = 0.20$  mol/L; S = 2 ( $pH_{(eq)} < 2.25$ ), 1 ( $pH_{(eq)} = 2.9$ ) and 0.3 ( $pH_{(eq)} = 4.0$ ); I = -4.845 (when S = 2) and -2.34 (when S = 1)

mate linearity in the  $\log^c D$  versus  $\log[V(IV)]$ ,  $\log[\text{Cyanex 302}]$ ,  $-\log(1+2.24 [\text{SO}_4^{2-}])$  and  $1/T$  plots have been established, the pH effect was not linear. The  $\log^c D$  vs.  $\text{pH}_{(eq)}$  plots are reproduced in Fig.1. The non-linear curve fitting shows that  $\log^c D$  is proportional to  $-\log(1+4641.14 \cdot 10^{-\text{pH}} + (1.5 \cdot 10^6) \cdot 10^{-2\text{pH}})$ . It is therefore expected that the  $\log^c D$  vs.  $-\log(1+4641.14 \cdot 10^{-\text{pH}} + (1.5 \cdot 10^6) \cdot 10^{-2\text{pH}})$  should be straight line of unity slope. Such a plot is shown in Fig. 2.

duplicate. In order to check the lack of fit due to curvature, additional trial (four in number) is made at the midpoint level of each factor. The difference between the average center point value and the overall average of the design points indicates the severity of curvature.

The average yield,  $\bar{Y}$  and the variance for each trial; the pooled variance ( $S^2_{pooled}$ ), standard deviation<sub>pooled</sub>, [MIN] and [MINC] are calculated by using Eqs. (1) to (5) (Davies, 1979; Saha *et al.*, 2010).



**Fig. 2.** Effect of equilibrium pH on the extraction of V(IV) Cyanex 302 in kerosene.  $[V(IV)]_{(ini)} = 200 \text{ mg/L}$ , Temp. =  $303 \pm 0.5 \text{ K}$ , Equilibration time = 20 min, O/A = 1 (O = 20 mL),  $[\text{SO}_4^{2-}] = 0.02 \text{ mol/L}$ ,  $(n)$ ,  $[\text{Cyanex 302}] = 0.10 \text{ mol/L}$ ; S = 1.00; I = 0.90; (◻),  $[\text{Cyanex 302}] = 0.20 \text{ mol/L}$ ; S = 0.97; I = 1.44.

The investigated system has been modeled by  $2^k$  factorial design in considering logistic function (Hosmer and Lemeshow, 2000), where,  $k = 5$  (number of factors); each at 2 levels: high (+) and low (-) (Montgomery, 2001; Biswas and Karmakar, 2013). The statistical model for a  $2^5$  design includes  $5!/0!(5-0)! = 1$  mean effect,  $5!/1!(5-1)! = 5$  single factor effects,  $5!/2!(5-2)! = 10$  two-factor interactions,  $5!/3!(5-3)! = 10$  three factor interactions,  $5!/4!(5-4)! = 5$  four-factor interactions and  $5!/5!(5-5)! = 1$  five factor interaction.

In this case, there are  $2^5$  trials. Since the basic design involves 32 trials, there will be 64 trials when each is run in

Variance =

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

The variances calculated for each trial are then used in the calculation of a weighted average i.e. pooled variance of the individual variances for each trial.

Pooled variance =

$$S^2_{pooled} = \frac{(n_1 - 1)(S_1^2) + (n_2 - 1)(S_2^2) + \dots + (n_p - 1)(S_p^2)}{(n_1 - 1) + (n_2 - 1) + \dots + (n_p - 1)}$$

$$\text{Standard deviation}_{\text{pooled}} = t \sqrt{\frac{1}{nr} + \frac{1}{r}} \tag{3}$$

$$[\text{MIN}] = ts \sqrt{\frac{1}{nr} + \frac{1}{r}} \tag{4}$$

$$[\text{MINC}] = ts \sqrt{\frac{1}{nr} + \frac{1}{r}} \tag{5}$$

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

The experimental ranges of variables considered in this study are listed in Table I. The two level 5-factor design with factors in coded form is shown in the 3<sup>rd</sup> to 7<sup>th</sup> columns of the Table II. The results of these experiments are listed in the 34<sup>th</sup> and 35<sup>th</sup> columns with average in the 36<sup>th</sup> column in the Table II. The last column of Table II represents the variance of two measurements for each trial.

**Table I. Process variables and response**

Factor	Level			Logistic function	Level		
	(+)	(0)	(-)		(+)	(0)	(-)
(a) [V(IV)], mol/L	0.0195	0.0062	0.002	(a) log([V(IV)], mol/L)	-1.71	-2.21	-2.71
(b) pH	4.0	2.68	2.0	(b) $-\log(1+4641.14 \cdot 10^{-\text{pH}} + (1.5 \cdot 10^6) \cdot 10^{-2\text{pH}})$	-0.17	-1.23	-2.29
(c) [H <sub>2</sub> A <sub>2</sub> ], mol/L	0.50	0.07	0.01	(c) log ([H <sub>2</sub> A <sub>2</sub> ], mol/L)	-0.301	-1.1505	-2.00
(d) [SO <sub>4</sub> <sup>2-</sup> ], mol/L	0.01	0.50	1.50	(d) $-\log(1+2.24 [\text{SO}_4^{2-}])$	-0.0096	-0.3245	-0.6395
(e) T, K	293	305	318	(e) 1/T, K <sup>-1</sup>	0.003413	0.003279	0.003145

Response: Y ( yield ) = value of log <sup>C</sup>D

The computation analysis for this experiment is also shown in Table II. The design matrix is supplemented with a computation matrix, which is used to detect any interaction effect. This computation matrix is generated by simple algebraic multiplication of the coded factor levels. In trial 1, a is plus, b is plus, therefore ab is plus; in trial 2, a is minus, b is plus, therefore ab is minus. Based on Table II, the factor and interaction effects are determined as follows and presented in Table III. The sum +'s column (2<sup>nd</sup> column of Table III) is generated by totaling the response values on each row with a plus for each column of Table II: e.g. for factor a, 1.67-0.46-1.73-3.86+1.04-1.09-2.36-4.49+2.32+0.19-1.08-3.21+1.69-0.44-1.71-3.84= -17.36. In a similar manner the sum -'s column (3<sup>rd</sup> column of Table III) is generated. The sum of these

two columns should be equal to the sum of all the average responses and can be used as a check on calculations. The difference column represents the difference between the responses in the 16 trials when the factor is at a high level and the responses in the 16 trials when the factor is at a low level. The effect is then calculated by dividing the difference by the number of plus signs in the column. With the single factor effects there are no other interaction effects for the investigated present system.

These results are expressed as a mathematical model using a first order polynomial. The values for the co-efficient are one half the factor effects listed in Table III since these are based upon coded levels +1 and -1 that differed by two units. Since there is only factor effects with no interaction effect, the polynomial is

$$Y = -1.005 + (-0.080) a + 1.065 b + 1.700 c + 0.315 d + (-0.325) e \tag{6}$$

In Eq. (6), the factors are expressed in coded units. These are converted into real units by substituting:

i) for metal ion concentration (log[V(IV)], mol/L) = M let

$$c = \frac{t - \frac{r \cdot 30 + \sum 2.0^j}{2}}{-1 \cdot 30 + \sum -2.0^j} = 1.1771 E + \tag{7}$$

ii) for pH ( $-\log(1+4641.14 \cdot 10^{-\text{pH}} + (1.5 \cdot 10^6) \cdot 10^{-2\text{pH}})$ ) = P let

$$c = \frac{t - \frac{r \cdot 30 + \sum 2.0^j}{2}}{-1 \cdot 30 + \sum -2.0^j} = 1.1771 E + 1.3543 \tag{8}$$

iii) foreextractant concentration (log ([Cyanex 302], mol/L) = E let

$$c = \frac{t - \frac{r \cdot 30 + \sum 2.0^j}{2}}{-1 \cdot 30 + \sum -2.0^j} = 1.1771 E + 1.3543 \tag{9}$$

Table II. Computation matrix for five factor two level experiment

Trial	Design Matrix										Computation Matrix										Yield ( $\log^c D$ )		Response ( $\bar{Y}$ )		Variance						
	a	b	c	d	e	ab	ac	ad	ae	bc	bd	be	cd	ce	de	abc	abd	abe	bcd	acd	ade	abce	abde	acde		bcde	abcde	$Y_1$	$Y_2$	Average $\log^c D$	Response ( $\bar{Y}$ )
1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	1.64	1.70	1.67	0.0018	
2	-	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.90	1.76	1.83	0.0098	
3	+	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.44	-0.48	-0.46	0.0008	
4	-	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.28	-0.32	-0.30	0.0008	
5	+	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.76	-1.70	-1.73	0.0018	
6	-	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.65	-1.49	-1.57	0.0128	
7	+	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-3.84	-3.88	-3.86	0.0008	
8	-	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-3.62	-3.78	-3.70	0.0128	
9	+	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.02	1.06	1.04	0.0008	
10	-	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.25	1.15	1.20	0.0050	
11	+	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.10	-1.08	-1.09	0.0002	
12	-	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.90	-0.96	-0.93	0.0018	
13	+	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-2.29	-2.43	-2.36	0.0098	
14	-	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-2.15	-2.25	-2.20	0.0050	
15	+	-	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-4.41	-4.57	-4.49	0.0128	
16	-	-	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-4.29	-4.36	-4.33	0.0025	
17	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.28	2.38	2.32	0.0050	
18	-	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.44	2.52	2.48	0.0032	
19	+	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.15	0.23	0.19	0.0032	
20	-	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.33	0.37	0.35	0.0008	
21	+	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.02	-1.14	-1.08	0.0072	
22	-	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.94	-0.90	-0.92	0.0008	
23	+	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-3.16	-3.26	-3.21	0.0050	
24	-	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-3.02	-3.08	-3.05	0.0018	
25	+	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.66	1.72	1.69	0.0018	
26	-	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.81	1.89	1.85	0.0032	
27	+	-	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.42	-0.46	-0.44	0.0008	
28	-	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.26	-0.30	-0.28	0.0008	
29	+	-	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.69	-1.73	-1.71	0.0008	
30	-	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-1.50	-1.60	-1.55	0.0050	
31	+	-	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-3.78	-3.90	-3.84	0.0072	
32	-	-	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-3.61	-3.75	-3.68	0.0098	
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	0	0	-0.85	-0.84	-0.86	0.0003	
																												-0.87	-0.88		

$S^2_{\text{pooled}} = 0.0039$ , Standard deviation $_{\text{pooled}} = 0.0625$ , [MIN] = 0.03, [MINC] = 0.08 and curvature = -0.15

**Table III. Evaluation of factor and interaction effects (based on Table II)**

Factor	Sum +'s	Sum -'s	Difference	Effect
Mean	-32.16	0.00	-32.16	-1.01
a	-17.36	-14.80	-2.56	-0.16
b	0.96	-33.12	34.08	2.13
c	11.12	-43.28	54.40	3.40
d	-11.68	-21.76	10.08	0.63
e	-21.92	-11.52	-10.40	-0.65

**Table IV. Experimental average yield and calculated yield**

Trial	$Y_{(exp.)}$	$Y_{(cal.)}$	Deviation
1.	1.67	1.665	0.0049
2.	1.83	1.825	0.0048
3.	-0.46	-0.465	0.0048
4.	-0.30	-0.305	0.0048
5.	-1.73	-1.735	0.0047
6.	-1.57	-1.575	0.0047
7.	-3.86	-3.865	0.0047
8.	-3.70	-3.705	0.0047
9.	1.04	1.035	0.0049
10.	1.20	1.195	0.0049
11.	-1.09	-1.095	0.0049
12.	-0.93	-0.935	0.0049
13.	-2.36	-2.365	0.0048
14.	-2.20	-2.205	0.0048
15.	-4.49	-4.495	0.0048
16.	-4.33	-4.335	0.0048
17.	2.32	2.316	0.0041
18.	2.48	2.476	0.0041
19.	0.19	0.186	0.0041
20.	0.35	0.346	0.0041
21.	-1.08	-1.084	0.0040
22.	-0.92	-0.924	0.0040
23.	-3.21	-3.214	0.0039
24.	-3.05	-3.054	0.0039
25.	1.69	1.686	0.0042
26.	1.85	1.846	0.0042
27.	-0.44	-0.444	0.0041
28.	-0.28	-0.284	0.0041
29.	-1.71	-1.714	0.0040
30.	-1.55	-1.554	0.0040
31.	-3.84	-3.844	0.0040
32.	-3.68	-3.684	0.0040
33. Middle point-0.86		-1.009	0.1490

iv) for sulphate ion concentration ( $-\log(1+2.24 [\text{SO}_4^{2-}]) = S$  let)

$$c = \frac{1 - 0.3013(2.24^S)}{1 - 0.3013 - 2.24^S} = 1.1771E + 1.3543 \quad (10)$$

v) for temperature ( T being absolute temperature)

$$d = \frac{1 - 0.0096(293 - T)}{0.0096(293 - T) - 1} = \frac{1462.6886}{T} - 21.47 \quad (11)$$

in Eq. (6) to obtain the following final equation:

$$Y = 10.452 - 0.16 M + 1.0047 P + 2.0011 E + 1.0003 S - 2425.3729/T \quad (12)$$

For trial 1 ( $M = -1.71$ ,  $P = -0.17$ ,  $E = -0.301$ ,  $S = -0.0096$  and  $T = 293$ ), the yield calculated from the derived model represented by Eq. (12) is:  $Y_{(cal.)} = 1.665$  and the experimental average yield is  $Y_{(exp.)} = 1.67$  producing deviation = 0.0049.

All the values of the experimental average yield and the calculated yield using the derived equation (12) are shown in Table IV. It is seen in all cases that the deviation of modeled yield from the experimental yield is in between 0.15. At any set of experimental parameters the model can efficiently predict experimental  $\log^C D$  value which is shown in Table V. The optimization of the factors to obtain maximum possible %E of V(IV) are shown in Table VI. At three optimized conditions of ~99%E, values of %E have been verified by the shake-out experiments at the optimized conditions. These values are found to be comparable.

**Table V . Data for comparison of model value with shake-out experimental value**

[V(IV)], mg/L	pH <sub>(eq)</sub>	[Cyanex 302], mol/L	[SO <sub>4</sub> <sup>2-</sup> ], mol/L	Temp., K	log <sup>C</sup> D (experimental)	log <sup>C</sup> D (calculated)	Deviation
300	3.38	0.10	0.02	303	0.22	0.278	-0.058
700	3.27	0.10	0.02	303	0.16	0.128	0.032
200	2.60	0.20	0.02	303	0.20	0.067	0.133
200	2.80	0.10	0.02	303	-0.17	-0.275	0.105
200	3.35	0.10	0.02	303	0.30	0.282	0.018
200	3.20	0.05	0.02	303	-0.49	-0.445	-0.045
200	3.11	0.15	0.02	303	0.40	0.429	-0.029
200	3.12	0.10	0.05	303	0.10	0.052	0.048
200	3.22	0.10	0.50	303	-0.19	-0.134	-0.056
200	3.08	0.20	0.02	298	0.57	0.508	0.062
200	3.19	0.20	0.02	313	0.94	1.005	-0.065

**Table VI . Optimization of factors**

[V(IV)] <sub>x</sub> 10 <sup>3</sup> , mg/L	<sup>a</sup> M	pH <sub>(eq)</sub>	<sup>a</sup> P	[H <sub>2</sub> A <sub>2</sub> ], mol/L	<sup>a</sup> E	[SO <sub>4</sub> <sup>2-</sup> ], mol/L	<sup>a</sup> S	Temp.	log <sup>C</sup> D (cal)	%E	%E (exptl)
5.88	-2.230	4.5	-0.06	0.2	-0.699	0.02	-0.019	303	1.326	95.496	
13.73	-1.862	4.5	-0.06	0.5	-0.301	0.02	-0.019	303	2.064	99.144	98.9b
19.61	-1.708	4.5	-0.06	0.8	-0.097	0.02	-0.019	303	2.447	99.644	
5.88	-2.230	3.5	-0.42	0.5	-0.301	0.02	-0.019	303	1.761	98.296	98.01b
13.73	-1.862	3.5	-0.42	0.7	-0.155	0.02	-0.019	303	1.995	98.997	
19.61	-1.708	3.5	-0.42	1.0	0.000	0.02	-0.019	303	2.280	99.478	
5.88	-2.230	3.0	-0.85	0.9	-0.046	0.02	-0.019	303	1.840	98.574	
13.73	-1.862	3.0	-0.85	1.2	0.079	0.02	-0.019	303	2.031	99.077	
19.61	-1.708	3.0	-0.85	1.5	0.176	0.02	-0.019	303	2.200	99.373	99.21b

<sup>a</sup> M = log([V(IV)], mol/L); P = log(1+4641.14 10<sup>-pH</sup> + (1.5 10<sup>6</sup>) 10<sup>-2pH</sup>); E = log ([H<sub>2</sub>A<sub>2</sub>], mol/L); S = log (1+2.24 [SO<sub>4</sub><sup>2-</sup>]); T = Absolute temperature. <sup>b</sup> Average of 3 readings

### Conclusion

The extraction process has been successfully modeled by the five factor two level experimental design. On symbolizing log[V(IV)], -log(1+4641.14 10<sup>-pH</sup> + (1.5 10<sup>6</sup>) 10<sup>-2pH</sup>), log [Cyanex 302], -log (1+2.24[SO<sub>4</sub><sup>2-</sup>]) and absolute temperature as M, P, E, S and T, respectively; the model obtained is: log <sup>C</sup>D= 10.452-0.16 M+1.0047 P+2.0011 E+1.0003 S-2425.3729/T. From this model it has been seen that the extraction of V(IV) by Cyanex 302 is dependent on the factors.

### Notations and abbreviations

D Extraction or distribution ratio  
<sup>C</sup>D D at a constant equilibrium pH and extractant concentration  
 $\bar{Y}$  Response value  
 $\bar{Y}$  Average or mean of response value  
n Number of observations

t Appropriate value from "t-table"  
s Pooled standard deviation  
m Number of plus signs in 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

### References

Ali MR, Biswas RK, Salam SMA, Akhter A, Karmakar AK and Ullah MH (2011), Cyanex 302: An extractant for Fe<sup>3+</sup> from chloride medium. *Bangladesh J. Sci. Ind. Res.* **46**: 407-414.

- Bassett J, Denney RC, Jeffery GH and Mendham J (1979), Vogel's text book of quantitative inorganic analysis including elementary instrumental analysis, 4<sup>th</sup> Ed., ELBS and Longman, London, pp 752-753.
- Biswas RK and Mondal MGK (2003), Kinetics of VO<sup>2+</sup> extraction by D2EHPA. *Hydrometallurgy*. **69**: 117-133.
- Biswas RK and Karmakar AK (2012), Equilibrium of the extraction of V(IV) in the V(IV)-SO<sub>4</sub><sup>2-</sup> (H<sup>+</sup>, Na<sup>+</sup>) - Cyanex 302-kerosene system. *International Journal of Nonferrous Metallurgy*. **1**: 23-31.
- Biswas RK and Karmakar A K (2013), Solvent extraction of Ti(IV) in the Ti(IV)-SO<sub>4</sub><sup>2-</sup> (H<sup>+</sup>, Na<sup>+</sup>) - Cyanex 302-kerosene-5% (v/v) hexan-1-ol system. *Hydrometallurgy* **134-135**: 1-10.
- Brunette JP, Rastegar F and Leroy MJF (1979), Solvent extraction of vanadium (V) by di-(2-ethylhexyl)-phosphoric acid from nitric acid solutions. *J. Inorg. Nucl. Chem.*, **41**: 735-737.
- Davies O. L. (1979). Design and Analysis of Industrial Experiments. 2<sup>nd</sup> Ed., Longman, London, pp 636.
- Hosmer DW and Lemeshow S (2000), Applied Logistic Regression, 2<sup>nd</sup> Ed., John Wiley & Sons, New York, Chichester, Weinheim, Brisbane, Singapore and Toronto.
- Hughes MA and Biswas RK (1991), The kinetics of vanadium(IV) extraction in the acidic sulphate-D2EHPA-n-heptane system using the rotating diffusion cell technique. *Hydrometallurgy* **26**: 281-297.
- Islam F and Biswas RK (1980a), The solvent extraction of vanadium(IV) with HDEHP in benzene and kerosene: The solvent extraction of Vanadium(IV) from sulphuric acid solution with bis-(2-ethylhexyl) phosphoric acid in benzene and kerosene. *J. Inorg. Nucl. Chem.* **42**: 415-420.
- Islam F and Biswas RK (1980b), Kinetics of solvent extraction of metal ions with HDEHP-II: Kinetics and mechanism of solvent extraction of V(IV) from acidic aqueous solutions with bis-(2-ethylhexyl)phosphoric acid in benzene. *J. Inorg. Nucl. Chem.* **42**: 421-429.
- Juang RS and Lo RH (1993), Stoichiometry of Vanadium(IV) Extraction from Sulfate Solutions with Di(2-Ethylhexyl) Phosphoric Acid Dissolved in Kerosene. *J. Chem. Eng. Jpn.* **26**: 219-222.
- Montgomery DC (2001), Design and Analysis of Experiments, 5<sup>th</sup> Ed., John Wiley & Sons, USA.
- Paatero E, Lantto T and Ernola P (1990), The effect of tri-octylphosphine oxide on phase and extraction equilibria in systems containing bis (2,4,4-trimethylpentyl) phosphinic acid. *Solvent Extr. Ion Exch.* **8**: 371-388.
- Rickelton WA (1992), Novel uses for thiophosphinic acids in solvent extraction. *J. Met.* **44**: 52-54.
- Saha M, Islam STA, Saha D, Ismail M, Galib M and Sharif N (2010), Application of Statistical Experimental Design to Benzoylation of *p*-Chlorophenol. *Bangladesh J. Sci. Ind. Res.* **45**: 105-110.
- Saily A and Tandon SN (1998), Liquid-liquid extraction behavior of V(IV) using phosphinic acids as extractants. *Fresenius' J. Anal. Chem.* **360**: 266-270.
- Saji J and Reddy MLP (2002), Solvent extraction separation of vanadium(V) from multivalent metal chloride solution using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester. *J. Chem. Technol. Biotechnol.* **77**: 1149-1156.
- Sato T, Nakamura T and Kawamura M (1978), The extraction of vanadium(IV) from hydrochloric acid solutions by di-(2-ethylhexyl)-phosphoric acid. *J. Inorg. Nucl. Chem.*, **40**: 853-856.
- Sekine T and Hasegawa Y (1977), Solvent Extraction Chemistry: Fundamentals and Applications, Marcel Dekker Inc., New York and Basel, pp 564-567.
- Sole KC and Hiskey JB (1992), Solvent extraction characteristics of thio substituted organophosphinic acid extractants. *Hydrometallurgy*. **30**: 345-365.
- Zhang P, Inoue K and Tsuyama H (1995), Recovery of Molybdenum and Vanadium from Spent Hydrodesulfurization Catalysts by Means of Liquid-Liquid Extraction. *Kagaku Kogaku Ronbunshu* **21**: 451-456.
- Zhang P, Inoue K, Yoshizuka K and Tsuyama H (1996), Solvent Extraction of Vanadium(IV) from Sulfuric Acid Solution by Bis (2,4,4-Trimethylpentyl) Phosphinic Acid in Exxsol D80. *J. Chem. Eng. Jpn.* **29**: 82-87.

Received: 09 July 2013; Revised: 27 August 2015; Accepted: 19 October 2015.