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Experimental design modelling for the extraction of vanadium(IV) in V(IV)-SO$_4^{2-}$ (H$^+$, Na$^+$)-Cyanex 301-kerosene system

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Abstract

The vanadium(IV) extraction from acidic sulphate medium by Cyanex 301 (bis-(2,4,4-trimethylpentyl) dithiophosphinic acid) dissolved in kerosene is explored from the modelling point of view. The time of equilibration is only 10 min and above pH$_{(eq)}$ = 2, high extraction (>90%) occurs. On keeping organic to aqueous phase ratio of 1, factors affecting the extent of extraction (log D and log ^{C}D) are pH$_{(eq)}$, [V(IV)],[SO$_4^{2-}$], [Cyanex 301] and temperature (T). The high (+) and low (-) levels are considered for the factors. The 2^5 factorial design is used to find the regression equation for the V(IV) extraction by Cyanex 301. On symbolizing pH$_{(eq)}$, log [V(IV)], log [SO$_4^{2-}$], log [Cyanex 301], and 1/T (K^{-1}); where concentration terms are in mol/L, as P, M, S, E, and (1/T), respectively, the regression equation obtained is: log ^{C}D = 1.95 - 0.23 M + 1.83 P + 2.07 E + 0.84 S - (888.9/T) - 0.26 PS. The current system shows only the interaction effect among pH$_{(eq)}$ and [SO$_4^{2-}$]. The equation can well describe the system, and it can be used to optimize factors for satisfactory extraction.

Introduction

The essential technological metal, vanadium is used in high-speed alloying steels, and it, in pentoxide form, is used as an oxidative catalyst (Hofmann *et al.,* 1991). But its natural resources as ores on the earth crust are rare. As a result, vanadium is often recovered from fly ashes, tar sands, waste hydrodesulphurization-catalyst for petroleum fractions etc. In recovering vanadium from these materials, the principles of hydrometallurgy are applied (Henry *et al.,* 1992). The materials are acid or alkali leached to bring vanadium into aqueous solution either as V(IV) or V(V). The conversion of V(IV) to V(V) can be done by boiling with strong HNO$_3$; whereas, vanadium(V) can be effortlessly reduced to V(IV) by treatment with Na$_2$SO$_3$ or SO$_2$-water. Solvent extraction technique can be used for leach solution purification (Beaupré and Holland, 1980; Cox, 2004). Vanadium(IV) can be extracted by cation exchange/chelate formation mechanism when acidic extractants are used. On the other contrary, V(V) can be extracted by the mechanism of the solvated ion-pair formation when amines or neutral extractants are used. The

building up of concentration may be achieved by using low organic to aqueous phase ratio (O/A) in the extraction and in stripping O/A is high.

The V(IV) and V(V)- extractions by different extractants prior to 1976 have been included in a book of Sekine and Hasegawa (1977). Bis-2-ethylhexyl phosphoric acid (D2EHPA) is an effective extractant for both V(IV) and V(V) (Biswas and Mondal, 2003; Brunette *et al.,* 1979; Giavarini, 1982; Hughes and Biswas, 1991; Ipinmoroti and Hughes, 1990; Islam and Biswas, 1980a; Islam and Biswas, 1980b; Juang and Lo, 1993; Sato *et al.,* 1978). EHEHPA or PC88, i.e. of mono-2-ethylhexyl ester, 2-ethylhexylphosphonic acid, can extract V(IV) and V(V) proficiently (Jayadas and Reddy, 2002). Cyanex reagents are promising extractants for commercial application. Dialkyl (CH$_3$-C(CH$_3$)$_2$-CH$_2$-CH(CH$_3$)-CH$_2$-) derivative of H$_3$PO$_2$ is Cyanex 272. Its mono and di-substituted sulfur analogues are Cyanex 302 and Cyanex 301, respectively. The sulfur substitution decreases

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pKa values allowing to work at lower pH (Rickelton, 1992) Cyanex compounds vary from other marketable organophosphorous extractants, e.g. DDPA, D2EHPA, EHEHPA, TBP etc. In that later reagents comprise P-O-C bonding, whereas, P-C bonding is seen in the former reagents. Cyanex reagents are less susceptible to hydrolysis and less solubility in water due tothe presence of P-C bonding in their chemical structure (Saily and Tandon, 1998).

Within last two decades the extraction behaviours of V(IV) from sulfuric acid Medium by Cyanex 272 (Zhang, 1995; Zhang *et al.,* 1996), of both V(IV) and V(V) from HCl medium by Cyanex reagents(Saily and Tandon, 1998), of V(IV) from H_2SO_4 medium by Cyanex 302 (Biswas and Karmakar, 2012) and by Cyanex 301 (Biswas and Karmakar, 2013b) have been reported.

In this work, the reported data (Biswas and Karmakar, 2013b) have to be used to model the system. The model or equation to be derived will tell us the set of experimental parameters at which the highest percentage of extraction would be obtained. Otherwise, at a certain experimental setup, the model will predict the percentage of extraction. Only a model equation will justify all the results given in Ref. (Biswas and Karmakar, 2013b). In order to model vanadium(IV) extraction in V(IV)-SO_4^{2-}(H^+, Na^+)-Cyanex 301-Kerosene system, the factorial design using five factors viz., $pH_{(eq)}$, [V(IV)], [SO_4^{2-}], [Cyanex 301] and T, K at low '-' and high '+' levels has been carried out. Effectiveness of the derived model will be justified for optimization of factors for significant extraction.

Materials and methods

Materials

Cyanex 301was collected from Cytec Canada Inc. as a gift and used as it was received. It contains 72% R_2PS_2H and rests being R_2POSH and R_3PSO etc. (R = 2,4,4-trimethyl pentyl group). The impurities were reported to have similar extracting power. Vapour pressure osmometry suggest that this reagent was monomeric (Sole and Hiskey, 1992). The molar solution based on its monomeric form was prepared by diluting with white kerosene. Kerosene on buying from the local market was refined to collect aliphatic colourless fraction refining over 200-260 °C. $VOSO_4.xH_2O$ (99.9%, Alfa Aesar-Johnson-Mathey), NH_4VO_3 (99%, Riedel DeHaan) and H_2O_2 (30%, E. Merck) were used without further purification.

Analytical

The concentration of V(IV) in aqueous solution was measured by the HNO_3 oxidative -H_2O_2 method at 450 nm

(Bassett *et al.,* 1978) using a UV-visible spectrophotometer (UV-1650 PC, Shimadzu, Japan). $VOSO_4.5H_2O$ and NH_4VO_3 were used to prepare test and standard solutions, respectively. pH measurement was done by a Mettler Toledo pH meter (model MP 220). Addition of anhydrous Na_2CO_3 or dilute H_2SO_4 solution was required to adjust pH.

Extraction procedure

The extraction procedure is given elsewhere (Biswas and Karmakar, 2013b). Equal aliquots (20 ml) of two phases are taken in a quick-fit reagent bottle of suitable size, stoppered and shaken at organic to aqueous phase ratio (O/A) = 1 for 20 min. Preliminary studies indicate that the equilibration time is 20 min. The phases separated quickly; and on phase separation, the equilibrium pH and V(IV)-content of the aqueous phase are analyzed. Equation (1) is used to determine the D (extraction ratio) value.

$$D = ([V(IV)]_{(ini)} - [V(IV)]_{(eq)})/[V(IV)]_{(eq)} \qquad (1)$$

Data treatment

At a constant temperature,the logarithm of D vs. pH and log D vs. log [Cyanex 301] graphs are supposed to be valid at a constant free [Cyanex 301] and at a constant pH, respectively(Biswas and Karmakar, 2013b). In a non-buffered system, the equilibrium pH very much deviates from the initial pH value. Likewise, for variable extents of extraction, the free extractant concentration at equilibrium decreases invaribly from its initial value. It is therefore revealed that the valid pH-dependence plot is obtained only when the experimental D-values are corrected to ^CD-values on taking into consideration the effect of equilibrium [Cyanex 301] on the value of experimental D-value. The corrected equation is given below:

$$\log {}^CD = \log D + 2(\log[\text{Cyanex 301}]_{(o,ini)} - \log ([\text{Cyanex 301}]_{(o,ini)} - 2 [V(IV)]_{(o,eq)})) \qquad (2)$$

where concentrations are in mol/L and 2 is the extractant dependence(Biswas and Karmakar, 2013a; Biswas and Karmakar, 2013b), D is the experimental D-value for initial extractant concentration of [Cyanex 301]$_{(ini)}$ and ^CD is the corrected D-value at [Cyanex 301]$_{(ini)}$ as constant.

Similarly, the valid extractant-dependence figure would be attained if the investigational D-values are converted to ^CD-values on considering the result of pH variation (initial and equilibrium) on the value of investigational D-value. Equation (3) provided such type of rectification shown below:

$$\log {}^CD = \log D - 2 (pH_{(eq)} - pH_{(ini)}) \qquad (3)$$

where, 2 is the pH dependence (Biswas and Karmakar, 2013a; Biswas and Karmakar, 2013b) and D is extraction ratio at initial pH of $pH_{(ini)}$ and ^CD is the converted D-value at a constant $pH_{(ini)}$. When both parameters, correction is required as in sulphate ion concentration and temperature dependence, the following equation is used to get corrected datum at a constant $pH_{(ini)}$ and at a constant $[Cyanex\ 301]_{(ini)}$:

$$\log\ {}^CD = \log D - 2(pH_{(eq)} - pH_{(ini)}) + 2(\log\ [Cyanex\ 301]_{(o,ini)} - \log\ \{[Cyanex\ 301]_{(o,ini)} - 2[V(IV)]_{(o,eq)}\}) \qquad (4)$$

Results and discussion

An effective apprehension regarding the practice of the two-level factorial design is the hypothesis of factor effect linearly. In a previous paper (Biswas and Karmakar, 2013b), log ^CD and log D values at a const. $pH_{(eq)}$ and $[Cyanex\ 301]_{(eq)}$ value, respectively, are found to vary within only ±0.12 on varying $[V(IV)]$ from 0.10 to 1.00 g/L. This small variation does not appear linearly but may be regarded as if it occurs linearly with some deviation (experimental error). On the other hand, log ^CD vs. $pH_{(eq)}$, log D vs. log ([Cyanex 301], mol/L), and log ^CD vs. 1/T (K^{-1}) plots are perfectly linear (Figs 1, 2 and 3, respectively). However, the log ^CD vs. log

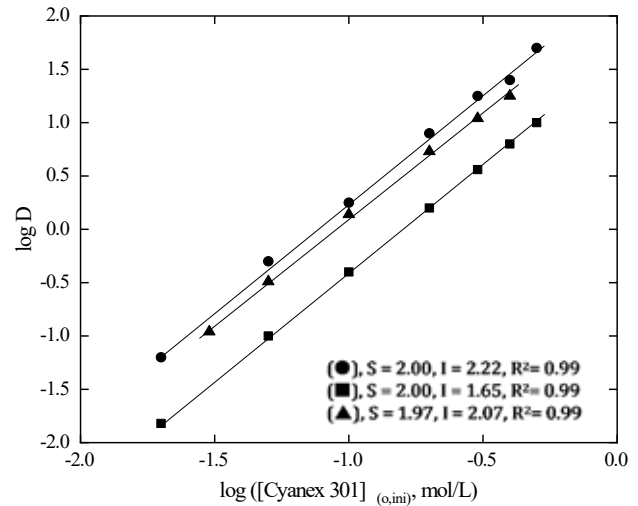**Fig. 2.** Effect of $[Cyanex\ 301]_{(o,\ eq)}$ on extraction. $[V(IV)]_{(ini)}$ = 200 mg/L, Temp. = 303 K, $[SO_4^{2-}]$ = 0.10 mol/L, Equilibration time = 15 min, O/A = 1 (O = 20 mL). (●), $pH_{(ini)}$ = 2.00; (■), $pH_{(ini)}$ = 1.50; (▲), $pH_{(ini)}$ = 1.40, $[SO_4^{2-}]$ = 1.50 mol/L
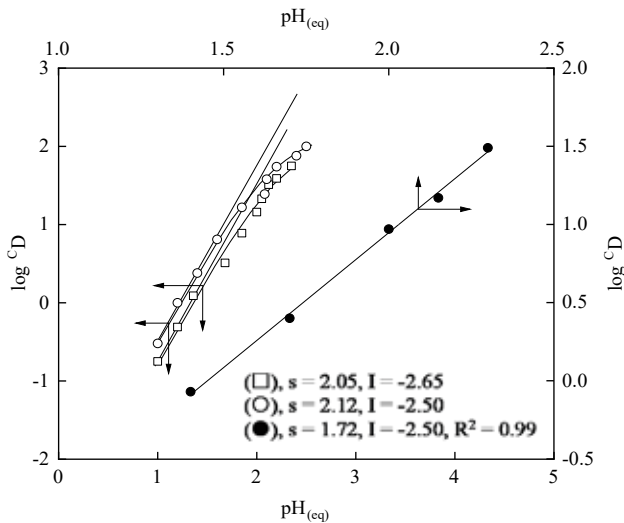
Fig. 1. Effect of $pH_{(eq)}$ on extraction. $[V(IV)]_{(ini)}$ = 200 mg/L, Temp. = 303 K, Equilibration time = 15 min, O/A = 1 (O = 20 mL). (○), $[SO_4^{2-}]$ = 0.10 mol/L, $[HA]_{(o,\ ini)}$ = 0.30 mol/L = $[HA]_{(o,\ eq)}$; (□), $[HA]_{(o,\ ini)}$ = 0.20 mol/L = $[HA]_{(o,\ eq)}$; (●), $[SO_4^{2-}]$ = 1.50 mol/L, $[HA]_{(o,\ ini)}$ = 0.15 mol/L,= $[HA]_{(o,\ eq)}$ and = 0.15 mol/L
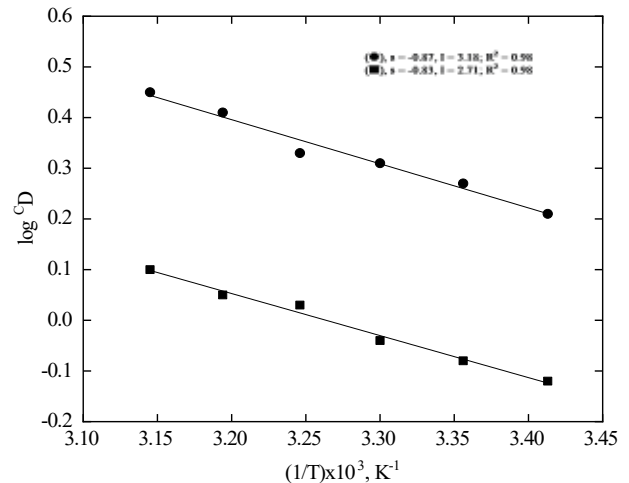
Fig. 3. Effect of temperature on extraction. $[V(IV)]_{(ini)}$ = 200 mg/L, $[SO_4^{2-}]$ = 0.10 mol/L, Equilibration time = 15 min, O/A = 1 (O = 20 mL). (●), $pH_{(ini)}$ = 1.35, $[HA]_{(o,\ ini)}$ = 0.30 mol/L = $[HA]_{(o,\ ini)}$,; (■), $pH_{(ini)}$ = 1.25, $[HA]_{(ini)}$ = 0.20 mol/L = $[HA]_{(o,\ ini)}$
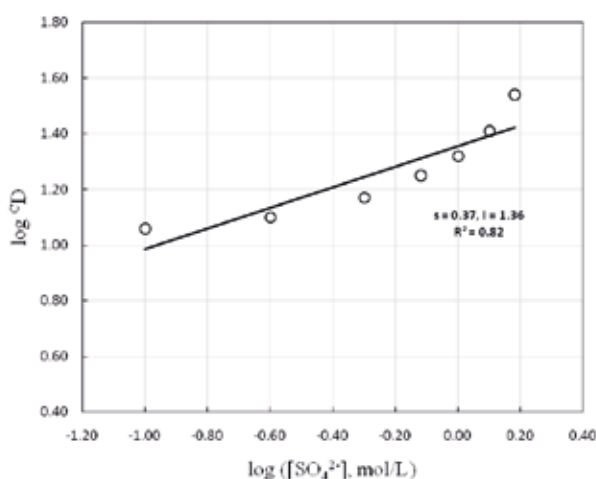
Fig. 4. Effect of sulphate ion concentration on the extraction of V(IV) by Cyanex 301. Equilibration time = 15 min, Temp. = (303 ± 0.5) K, [V(IV)]$_{(ini)}$ = 200 mg/L, pH$_{(ini)}$ = 2.00, [Cyanex 301] = 0.225 mol/L, ^{C}D = D at pH$_{(eq)}$ = 1.85 and [Cyanex 301]$_{(eq)}$ = 0.225 mol/L, O/A = 1 (O = 20 mL)

([SO$_4^{2-}$], mol/L)] plot is a curve; but can be regarded as linear on considering some experimental errors in higher and lower [SO$_4^{2-}$] regions. The log ^{C}D vs. log ([SO$_4^{2-}$], mol/L) plot is given in Fig. 4 for illustration as the case.

A 2^5 factorial design (5 number of factors) has been described for the present study. For the current investigation, the logistic function is considered(Davies, 1979; Yates, 1978). The 2 levels: high (+) and low (-) are taken for all the factors at current study(Biswas and Karmakar, 2013a; Davies, 1979; Hosmer and Lemeshow, 2000; Yates, 1978). The statistical modelling of 2^5 would contain 1 mean effect, 5 single factor effects, 10 two-factor correlations, 10 three-factor correlations, 5 four-factor correlations and, 1 five-factor correlation(Hosmer and Lemeshow, 2000; Kendüzler *et al.,* 2008; Li *et al.,* 2007; Montgomery, 2017).

The 2^5 factorial design has been used to model the investigated system. Subsequently, the statistical modelling system contains 32 trials and every single trial run double. Hereafter, the tests count would be 64. An extra test has been run at the midpoint level for the individual factor. It is run for four times. Middle point level trial is executed to observe the curvature. The alteration of the overall average value of the

design points and the average central point value and signified the severity of the curvature.

Eqs. (5-9) (Biswas and Karmakar, 2018; Islam *et al.,* 2010; Montgomery, 2017) is used to determine variance for the corresponding trial; the pooled variance (S$^2_{pooled}$), standard deviation$_{pooled}$, [MIN] and [MINC].

$$Variance = S^2 = \frac{(Y_1-\bar{Y})^2+(Y_2-\bar{Y})^2+.....+(Y_n-\bar{Y})^2}{n-1} \quad (5)$$

$$Pooled\ variance = S^2_{pooled} =$$
$$\frac{(n_1-1)(S_1^2)+(n_2-1)(S_2^2)+....+(n_k-1)(S_k^2)}{(n_1-1)+(n_2-1)+.....+(n_k-1)} = 0.005 \quad (6)$$

$$Standard\ deviation_{pooled} = \sqrt{S^2_{pooled}}$$
$$= 0.071 \quad (7)$$

$$[MIN] = t.s\sqrt{\frac{2}{m.k}} = 0.036 \quad (8)$$

$$[MINC] = t.s\sqrt{\frac{1}{m.k}+\frac{1}{c}} = 0.088 \quad (9)$$

From students 't' table at 95% confidence level, the "t" value is 2.03, and 35 *df* (Davies, 1979; Hosmer and Lemeshow, 2000; Montgomery, 2017) is taken.

Table I represents the variables used in the present study. The factors presented in the coded form are provided in the 3rd to 7th columns of Table II. The 34th and 35th columns in Table II display the measured yields (values) of these experimentations. The average values are convened in the 36th column of Table II. The last column of Table II shows up the variance of a particular trial.

The mathematical investigations are also assembled in Table II. In this study, a computation matrix is conveyed with the model matrix. To perceive any interaction effect between the factors this procedure is applied in the present study. The computation matrix is established by a definite arithmetic multiplication of the coded factor levels. The first test run illustrates that a and b are positive, respectively, hence ab is positive (+). Correspondingly, ab is minus when a is minus and b is plus for the case of second test run.

Table I. Process variables and response

Factor	Level			Logistic Function	Level		
	(+)	(0)	(-)		(+)	(0)	(-)
(a) [V(IV)], mol/L	2.00×10^{-2}	6.31×10^{-3}	1.96×10^{-3}	a) log ([V(IV)], mol/L)	-1.70	-2.20	-2.70
(b) pH $_{(eq)}$	2.50	1.50	0.50	b) pH $_{(eq)}$	2.50	1.50	0.50
(c) [Cyanex 301], mol/L	0.56	0.10	1.77×10^{-2}	c) log ([Cyanex 301], mol/L)	-0.25	-1.00	-1.75
(d) [SO$_4^{2-}$], mol/L	1.51	0.38	0.10	d) log ([SO$_4^{2-}$], mol/L)	0.18	-0.42	-1.00
(e) T, K	293	305	318	e) 1/T, K^{-1}	3.41×10^{-3}	3.27×10^{-3}	3.14×10^{-3}

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

Table II. Computation matrix for five factor two level experiment. S²$_{pooled}$= 0.005, Standard deviation$_{pooled}$ = 0.071, [MIN] = 0.036, [MINC] = 0.088 and curvature = 0.09

Trial	Mean	Yield Y1	Yield Y2	Average log ^CD	Variance
1	+	3.35	3.45	3.40	0.0050
2	+	3.68	3.58	3.63	0.0050
3	+	-0.18	-0.14	-0.16	0.0008
4	+	0.10	0.04	0.07	0.0018
5	+	0.28	0.32	0.30	0.0008
6	+	0.48	0.58	0.53	0.0050
7	+	-3.20	-3.32	-3.26	0.0072
8	+	-3.02	-3.04	-3.03	0.0002
9	+	3.10	3.26	3.18	0.0128
10	+	3.30	3.52	3.41	0.0242
11	+	-0.95	-1.05	-1.00	0.0050
12	+	-0.72	-0.82	-0.77	0.0050
13	+	0.07	0.09	0.08	0.0002
14	+	0.30	0.32	0.31	0.0002
15	+	-4.00	-4.20	-4.10	0.0200
16	+	-3.80	-3.94	-3.87	0.0098
17	+	3.68	3.60	3.64	0.0032
18	+	3.91	3.83	3.87	0.0032
19	+	0.09	0.07	0.08	0.0002
20	+	0.30	0.32	0.31	0.0002
21	+	0.50	0.58	0.54	0.0032
22	+	0.84	0.70	0.77	0.0098
23	+	-3.04	-3.00	-3.02	0.0008
24	+	-2.80	-2.78	-2.79	0.0002
25	+	3.33	3.51	3.42	0.0162
26	+	3.60	3.70	3.65	0.0050
27	+	-0.72	-0.80	-0.76	0.0032
28	+	-0.50	-0.56	-0.53	0.0018
29	+	0.31	0.33	0.32	0.0002
30	+	0.53	0.57	0.55	0.0008
31	+	-3.80	-3.92	-3.86	0.0072
32	+	-3.55	-3.71	-3.63	0.0128
33	0	-0.08 / 0.00	-0.02 / -0.10	-0.05	0.0018

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

Factor	Sum +'s	Sum -'s	Difference	Effect
Mean	1.28	0.00	1.28	0.04
a	-1.20	2.48	-3.68	-0.23
b	31.60	-30.32	61.92	3.87
c	25.44	-24.16	49.60	3.10
d	4.88	-3.60	8.48	0.53
e	-1.28	2.56	-3.84	-0.24
bd	-1.84	3.12	-4.93	-0.31

In other cases of two, three, four and five factor interactions, effects are absent

Table IV. Experimental average yield and calculated yield

Trial	$Y_{(exp.)}$	$Y_{(cal.)}$	Deviation
1.	3.40	3.402	-0.0020
2.	3.63	3.632	-0.0020
3.	-0.16	-0.168	0.0081
4.	0.07	0.062	0.0081
5.	0.30	0.303	-0.0030
6.	0.53	0.533	-0.0030
7.	-3.26	-3.267	0.0071
8.	-3.03	-3.037	0.0071
9.	3.18	3.182	-0.0020
10.	3.41	3.412	-0.0020
11.	-1.00	-1.008	0.0080
12.	-0.77	-0.778	0.0080
13.	0.08	0.083	-0.0030
14.	0.31	0.313	-0.0030
15.	-4.10	-4.107	0.0070
16.	-3.87	-3.877	0.0070
17.	3.64	3.640	-0.0005
18.	3.87	3.870	-0.0005
19.	0.08	0.070	0.0096
20.	0.31	0.300	0.0096
21.	0.54	0.541	-0.0015
22.	0.77	0.771	-0.0015
23.	-3.02	-3.029	0.0086
24.	-2.79	-2.799	0.0086
25.	3.42	3.420	-0.0005
26.	3.65	3.650	-0.0005
27.	-0.76	-0.770	0.0095
28.	-0.53	-0.540	0.0095
29.	0.32	0.321	-0.0015
30.	0.55	0.551	-0.0015
31.	-3.86	-3.869	0.0085
32.	-3.63	-3.639	0.0085
33. (Middle point)	-0.05	0.032	-0.0823

Table V. Comparison of model value with shake-out experimental value. [V(IV)] = 0.2 g/L as M = -2.407, 0.7 g/L as M = -1.862; $pH_{(eq)}$ as P = 1.4, 2.0, 2.15, 1.5, 1.85, 1.83, 1.22; $[HA]_{(o)}$, mol/L = 0.30 as E = -0.523, 0.2 as E = -0.699, 0.1 as E = -1.0, 0.5 as E = -0.301, 0.225 as E = -0.648; $[SO_4^{2-}]$, mol/L = 0.1 as S = -1.0; 1.5 as S = 0.176

[V(IV)], g/L	$pH_{(eq)}$	$[HA]_{(o)}$, mol/L	$[SO_4^{2-}]$, mol/L	Temp., K	log ^CD (exptl.)	log ^CD (model)	Deviation
0.2	1.40	0.300	0.10	303	0.31	0.540	-0.230
0.7	1.40	0.300	0.10	303	0.19	0.447	-0.257
0.2	2.00	0.200	0.10	303	1.51	1.460	0.050
0.2	2.15	0.200	0.10	303	1.75	1.776	-0.026
0.2	1.50	0.100	0.10	303	-0.40	-0.205	-0.195
0.2	1.50	0.500	0.10	303	1.00	1.240	-0.240
0.2	1.85	0.225	0.10	303	1.06	1.255	-0.195
0.2	1.83	0.225	1.50	303	1.54	1.641	-0.101
0.2	1.22	0.200	0.10	293	-0.12	-0.268	0.148
0.2	1.22	0.200	0.10	318	0.10	-0.029	0.129

Table VI. Optimization of factors

[V(IV)], g/L	[V(IV)], mol/L	log ([V(IV)], mol/L)	$pH_{(eq)}$=P	$[HA]_{(o)}$, mol/L	log ([HA], mol/L) = E	$[SO_4^{2-}]$, mol/L	log ($[SO_4^{2-}]$, mol/L) = S	T, K	log ^CD	%Ex	%Ex (exptl.)*
0.30	0.00588	-2.23	2.0	0.05	-1.301	0.10	-1.00	298	0.127	57.0	-
0.60	0.01176	-1.93	2.0	0.10	-1.000	0.10	-1.00	298	0.681	83.0	-
0.90	0.01764	-1.75	2.0	0.20	-0.699	0.10	-1.00	298	1.263	95.0	94.8±0.3
0.30	0.00588	-2.23	2.5	0.05	-1.301	0.10	-1.00	298	1.172	94.0	-
0.60	0.01176	-1.93	2.5	0.10	-1.000	0.10	-1.00	298	1.726	98.0	97.7±0.4
0.90	0.01764	-1.75	2.5	0.20	-0.699	0.10	-1.00	298	2.310	99.0	99.0±0.5
0.30	0.00588	-2.23	3.0	0.05	-1.301	0.10	-1.00	298	2.217	99.4	99.5±0.5
0.60	0.01176	-1.93	3.0	0.10	-1.000	0.10	-1.00	298	2.771	99.8	99.5±0.4
0.90	0.01764	-1.75	3.0	0.20	-0.699	0.10	-1.00	298	3.353	99.9	99.7±0.3

∗ Average of three readings

The estimated values of factor and interaction effects as calculated in Table II are accumulated in Table III. The 2nd column of Table III is produced by summing up the response values on an individual row with a positive sign for the individual column of Table II (*e.g.* for factor a, 3.40-0.16+0.30-3.26+3.18-1.00+0.08-4.10+3.64+0.08+0.54-3.02+3.42-0.76+0.32-3.86 = -1.20). On considering negative signs, in Table III the 3rd column is attained. The sum of all the average responses should be similar to the sum of these two columns value. This data is used to check on arithmetic. The 4th column of Table III represents the difference between Sum +'s and Sum –'s. The difference value is divided by the number of plus signs in the column to obtain the factor effect. The investigation displays only the single factor effects with one interaction effect (b and d).

To suggest a numerical model, the first-order polynomial is used. Table III shows half (1/2) of the coefficient for the factor effects. Consequently, the polynomial is:

$$Y = 0.04 + (-0.115)\, a + 1.94\, b + 1.55\, c + 0.265\, d + (-0.12)\, e + (-0.155)\, bd \qquad (10)$$

The factors in Eq. (10) are exhibited as a coded form. The coded units are altered into actual forms by replacing:

i) for [V(IV)] (let $M = \log([V(IV)], mol/L)$)

$$a = \frac{M - \frac{-1.70 + (-2.70)}{2}}{\frac{-1.70 - (-2.70)}{2}} = 2M + 4.4 \qquad (11)$$

ii) for pH (let $P = pH(eq)$)

$$b = \frac{P - \frac{2.50 + 0.50}{2}}{\frac{2.50 - 0.50}{2}} = P - 1.50 \qquad (12)$$

iii) for [Cyanex 301] (let $E = \log([Cyanex\ 301], mol/L)$)

$$c = \frac{E - \frac{-0.25 + (-1.75)}{2}}{\frac{-0.25 - (-1.75)}{2}} = 1.333\, E + 1.33 \qquad (13)$$

iv) for $[SO_4^{2-}]$ (let $S = \log([SO_4^{2-}], mol/L)$)

$$d = \frac{S - \frac{0.18 + (-1.0)}{2}}{\frac{0.18 - (-1.0)}{2}} = 1.695\, S + 0.695 \qquad (14)$$

v) for temperature (T in kelvin)

$$e = \frac{\frac{1}{T} - \frac{0.00341 + 0.00314}{2}}{\frac{0.00341 - 0.00314}{2}} = \frac{7407.4}{T} - 24.26 \qquad (15)$$

in Eq. (10) to acquire the model (16).

$$Y = \log {}^{C}D = 1.95 - 0.23\, M + 1.83\, P + 2.07\, E + 0.84\, S - (888.9/T) - 0.26\, PS \qquad (16)$$

In trial 1 (P = 2.50, M = -1.70, E = -0.25, S = 0.18 and T = 293), from the model (Eq. (16)) the evaluated yield is $Y_{(cal)}$ = 3.402; where as experimental yield is $Y_{(exp)}$ = 3.40. Deviation is 0.002 only.

All investigational average yield and the calculated yield are given in Table IV. The difference of model and experimental yields in all cases are negligible excepting the middle point value (-0.0823) which is for the curvature effect (less than [MINC] value).

The model is affortful to predict experimental $\log {}^{C}D$ value (Table V) within ±0.25 deviation. The factors optimization to acquire at least 99% Ex of vanadium(IV) are given in Table VI. At six optimized conditions of at least >95% Ex, extraction percentages have been justified by the equilibrium studies.

Conclusion

Vanadium(IV) extraction by Cyanex 301 has been modelled by the 2^5 experimental design. On abbreviating $pH_{(eq)}$, log ([V(IV)], mol/L), log ($[SO_4^{2-}]$, mol/L), log ([Cyanex 301], mol/L), and absolute temperature as P, M, S, E, and T, respectively; the model obtained is: $\log {}^{C}D = 1.95 - 0.23\, M + 1.83\, P + 2.07\, E + 0.84\, S - (888.9/T) - 0.26\, PS$. The model indicate that the extraction of V(IV) by Cyanex 301 is depended on factors and interaction between $pH_{(eq)}$ and log ($[SO_4^{2-}]$, mol/L).

Acknowledgement

Nomenclature

D	Extraction or distribution ratio
^{C}D	D at constant equilibrium pH and extractant concentration
HA	Cyanex 301
%Ex	Percent extraction
Y	Response value
	Average response value
n	Number of observations
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 the center point

df   Degree of freedom

[MIN]   Minimum significant factor effect

[MINC] Minimum significant curvature effect

Suffix

(o)   Organic phase

(ini)   Initial

(eq)   Equilibrium

(cal)   Calculated value

(exp.)   Experimental value

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