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A Statistical Model of the Extraction-Process Parameters of Uranium–*N*-Phenylbenzohydroxylamine–Trioctylphosphine Oxide Complex in Chloroform Solution

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The solvent extraction of uranium has been carried out with chloroform solutions of *N*-phenylbenzohydroxamic acid (BPHA) and Trioctylphosphine oxide (TOPO). The experiments were statistically planned to quantitatively assess the effect of the concentration of BPHA, the concentration of TOPO and the aqueous-phase pH of the solution on the percentage extraction of uranium. In addition, the interactional influence of the above-mentioned variables was also studied. A regression equation has been developed which successfully predicts the percentage extraction of uranium with the values of the variables lying between the selected range of experiments.

Solvent-extraction processes have attracted considerable attention from the view point of the analytical separation and extraction of metals in a pure state. Hydroxylamines were successfully employed as a spectrophotometric reagent for determining the concentration of metal ions in the organic phase.[1—3] When trioctylphophine oxide (TOPO)[4,5] is used with *N*-phenylbenzohydroxamic acid (BPHA), mixed-ligand complexes of uranium(VI) can be obtained. It has been reported[6] that *N*-arylhydroxylamines form a self adduct as well as neutral adducts with auxiliary ligand TOPO. The above-mentioned complex is formed by the replacement of one BPHA molecule from the self adduct. However, until now the effect of BPHA, TOPO, and pH of the aqueous solution has not been assessed quantitatively. Therefore, a need is felt to quantitatively assess the influence of the above-mentioned variables. This can be accomplished by developing an empirical model which will be useful for analyzing the reaction and predicting the extraction efficiency within a selected range of experiments. The design of experiments is one of the most important methods for building empirical models; recently, this technique is being applied to metallurgical and chemical extraction studies.[7—10] In the present investigation systematic efforts were made via a statistically planned series of extraction experiments to assess the influence of the important parameters likely to affect the extraction process, such as the concentration of BPHA, TOPO, and the aqueous-phase pH. All of the extraction experiments were carried out in a chloroform medium, since it is the best-known solvent.

Experimental

The extractant BPHA was prepared and purified by a known procedure.[11] TOPO was obtained by recrystallisation of the commercially available cyanex 921, (The American Cyanamid Co., N.J. USA). The purities of the reagents were confirmed by element analysis, the melting points and the IR spectra. A stock solution of uranium was prepared from AR-grade $UO_2(NO_3)_2 \cdot 6H_2O$ (BDH, AR-grade), and was standardized gravimetrically by 8-quinolinol.[12] The chloroform which was used as the organic diluent was always distilled and presaturated with water prior to use.

Preparation of a Uranium–BPHA–TOPO Complex. An aliquot of a 5 ml metal solution with a metal-ion concentration of 2.52×10^{-3} M was buffered to the desired experimental pH level by adding a solution of sodium acetate and acetic acid. This solution was added to 2.5 ml of a BPHA solution of desired concentration in chloroform. The resulting solution was taken in a 25 ml separatory funnel. To reach equilibrium the two phases were shaken thoroughly for 5 min, and then allowed to separate as an organic layer and an aqueous layer. The chloroform layer was drained out and an orange-yellow-colored organic layer was dried in a 25 ml beaker containing anhydrous Na_2SO_4. The organic phase free from water was transferred into a 5 ml volumetric flask, and the volume was made up to the mark by adding a small amount of solvent. This solution was used for measuring the absorbance against the corresponding reagent blank at 350 nm. The percentage extraction was computed from the absorbance data of the organic phases.

A Shimadzu UV-240 Spectrophotometer was used to obtain absorption data of the uranium complexes. A systronics 335 digital pH meter with a glass calomel electrode pair was used to measure the pH of the solutions. A box-type reciprocating shaker of Sambros (India) with a shaking speed of 200 oscillations per minute was used to equilibrate the aqueous and organic phases.

Statistical Design of Experiments. Experiments conducted according to statistically planned techniques of statistical design require a certain number of levels to be assigned to each experimental variable. These variables were then deliberately varied from experiment to experiment for all possible combinations. A regression equation was formed, from which the effect of each variable and their relative influence on the process can be readily assessed. This is done by comparing the magnitude of the coefficients of each variable. In addition, the interactional effect of two or more variables can be interpreted, which is not possible in the classical experiments. This method has the advantage of yielding optimum conditions in a relatively smaller number of experiments.

In the present investigation, a simple factorial design of experiments was selected where all the variables were varied in two levels. The variables considered were (i) the aqueous-phase pH, (ii) the concentration of BPHA, and (iii) the concentration of TOPO.

Results and Discussion

To study the effect of BPHA and TOPO as an extractant in the extraction process, the variable parameters and their selected range are presented in Table 1, where the actual (natural scale) and coded (dimensionless scale) values have been tabulated.

The design matrix and results showing the percentage extraction (%E) for the ternary complex of uranium-BPHA-TOPO system are given in Table 2.

The regression equation for the matrix is represented as

$$\%E = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3, \tag{1}$$

where a_0 is the value of percentage extraction when all of the variable parameters are at the base level. Coefficients a_1, a_2, and a_3 exhibit the effect of corresponding parameters and a_{12}, a_{13} and a_{23} exhibit the effect of interaction parameters.

The regression coefficients were estimated by

$$a_0 = \sum(\%E_i)/N.$$

Table 1. Actual and Coded Values of the Variables for the Complex of Uranium(VI) with N-Phenylbenzohydroxamato Acid and Trioctylphosphine Oxide as a Neutral Ligand

Levels	pH		BPHA		TOPO	
	Actual x_1	Coded X_1	Actual x_2 (M)	Coded X_2	Actual x_3 (M)	Coded X_3
Upper	4.50	+1	2.25×10^{-2}	+1	2.00×10^{-3}	+1
Lower	2.50	−1	2.2×10^{-2}	−1	0.4×10^{-3}	−1
Base	3.50	0	1.225×10^{-2}	0	1.2×10^{-3}	0

Table 2. Design Matrix and Percentage Extraction (%E) of U(VI)–BPHA–TOPO Complex

No. of obs.	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	Percentage extraction (%E)
1	−1	−1	−1	+1	+1	+1	37.11
2	−1	+1	−1	−1	+1	−1	69.08
3	−1	−1	+1	+1	−1	−1	41.21
4	−1	+1	+1	−1	−1	+1	84.02
5	+1	−1	−1	−1	−1	+1	58.12
6	+1	+1	−1	+1	−1	−1	79.02
7	+1	−1	+1	−1	+1	−1	52.28
8	+1	+1	+1	+1	+1	+1	99.78
9	0	0	0	0	0	0	70.90
10	0	0	0	0	0	0	68.58
11	0	0	0	0	0	0	65.68

$$a_i = \sum(X_{ij}\cdot\%E_i)/N,$$

$$a_{nj} = \sum[(X_{ni}\cdot X_{ji})\%E_i]/N \text{ and so on.}$$

The $\%E_i$ = Value of the percentage extraction in the i^{th} trial shown in the i^{th} row. N = Total number of trials. X_{ij} = Coded value in the i^{th} row and j^{th} column.

A student's t-test[12] was carried out at the 95%confidence level to test the significance of each coefficient. It was found that only the coefficients a_0, a_1, a_2, a_3, and a_{23} are significant. Therefore, the final regression equation obtained is

$$\%E = 65.07 + 7.22X_1 + 17.90X_2 + 4.245X_3 + 4.68X_2X_3. \tag{2}$$

It is worth mentioning that while testing the significance of each coefficient, the %E values of the three replicate observations at the base level were considered (refer to observation numbers 9, 10 and 11 in Table 2). This was done in order to assign due weight to the deviation in the %E values that may be caused by instrumental, manual or experimental errors or other factors.

The relationship between the coded values and the actual values are given by

$$X_1 = (x_1 - 3.50)/1.00,$$
$$X_2 = (x_2 - 1.255\times10^{-2})/1.025\times10^{-2},$$
$$X_3 = (x_3 - 1.2\times10^{-3})/0.8\times10^{-3}.$$

Using the above relationship, the regression Eq. 2 can be converted to an uncoded form. A Fisher test at the 95% confidence level indicates the model to be adequate.

Upon examining the regression Eq. 2, it was found that the concentration of BPHA and TOPO exerts a positive influence on the percentage extraction. In addition, the interactional effect of BPHA and TOPO was found to exert a positive influence. The extraction of uranium with BPHA and TOPO is favored in the higher acidic pH range. However, the concentration of BPHA appears to exert the strongest influence compared to the pH and concentration of TOPO.

The above-mentioned phenomena may be explained by the fact that two ligand molecules of BPHA remain bonded with the uranyl ion in the form of anions, and the third molecule of BPHA is adducted as a neutral ligand. A complex of the type $UO_2(BPHA)_2\cdot BPHA$ is formed. However, when TOPO is introduced into the system, one TOPO molecule forms an adduct complex $UO_2(BPHA)_2\cdot TOPO$ by replacing a BPHA ligand molecule from the self adduct. This increases the tendency of the uranyl complex to form an adduct complex through a stronger doner molecule. A synergistic extraction occurs which yields a higher absorbance, and subsequently leads to a higher extraction efficiency. Therefore, keeping all of the other variables fixed and only increasing the concentration of BPHA, the concentration of the uranyl ion in the organic phase increases (refer Table 2, observation number 1 and 2), which is attributed to an increase in the formation of $UO_2(BPHA)_2\cdot BPHA$ and $UO_2(BPHA)_2\cdot TOPO$ complexes. However, upon increasing both the BPHA and

Table 3. Results of Experimental Percentage Extraction and Calculated Percentage Extraction of U-BPHA-TOPO Complex System

No. of obsd	pH	Concentration of BPHA in M [a)]	Concentration of TOPO in M	%Extraction Expt.	Calcd
1	3.40	1.25×10^{-2}	1.8×10^{-3}	66.08	67.93
2	2.89	1.25×10^{-2}	1.8×10^{-3}	63.53	64.19
3	3.20	0.55×10^{-2}	1.8×10^{-3}	49.92	51.85
4	3.20	1.00×10^{-2}	1.8×10^{-3}	62.12	61.24
5	3.20	1.25×10^{-2}	1.58×10^{-3}	63.30	62.11
6	3.20	1.25×10^{-2}	1.38×10^{-3}	60.39	59.49

a) $1\ \mathrm{M} = 1\ \mathrm{mol\,dm^{-3}}$.

TOPO concentrations simultaneously, the formation of the $UO_2(BPHA)_2\cdot TOPO$ complex is favored, causing an increase in the synergistic extraction, which in turn causes the extraction efficiency to improve to a great extent. Although from Table 2 it is evident that extraction is favored at higher acidic pH values, it cannot be attributed as being the sole cause leading to an improvement in extraction efficiency. This is because of the fact that since the % extraction exhibits a variation of over 15% (refer Table 2 observation numbers 1, 2 and 4, 8), a change in the pH value alone cannot cause such a large deviation. Therefore, it can be concluded that such deviations can only be explained primarily on the basis of U–BPHA–TOPO complex formation.

Substituting the values of X_1, X_2, X_3, in Eq. 2, the regression equation for the actual values is obtained and is given by

$$\%E = 19.9325 + 7.33x_1 + 1061.47x_2 - 1681.25x_3 + 570725x_2x_3. \tag{3}$$

By using Eq. 3, the percentage extraction values can be predicted for all possible combinations of the variable parameters lying in the selected range of the experiments. Table 3 presents a comparison of the predicted percentage extraction values obtained from regression Eq. 3 and the experimental percentage extraction with identical values of the variable parameters. A student's t-test was performed to verify the significance of the difference between the experimental values and the predicted values. For the 95% confidence level (P) and for 5 degrees of freedom (F), the tested value in the student's t-test[12] is $t_p(F) = 2.57$. However, the estimated 't' value from the experimental values is 0.293. Since $t \ll t_p(F)$, the difference between the predicted and experimental percentage extractions values are insignificant. Therefore, by using Eq. 3 one can successfully predict the % extraction of uranium for any value of the variable parameter, whose value falls within the selected range of experiments.

Conclusion

A coded regression equation for the percentage extraction of the uranium-BPHA-TOPO system has been developed by taking recourse to the statistical design of experiments. The coded regression equation reveals that increasing the concentration of BPHA, TOPO, and the aqueous-phase acidic pH in the higher range exerts positive influences on the percentage extraction of uranium. However, the concentration of BPHA has been found to exert the strongest positive influence. The coded regression equation also indicates that the interactional effect of BPHA and TOPO is positive. This is attributed to the synergistic extraction characteristics exhibited by introducing TOPO in the uranium–BPHA system. The regression equation with actual values can be used to successfully predict the percent extraction values of uranium with any value of the variable parameters which lie within the selected range of the experiments.

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