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Statistical study of factors affecting the phase separation kinetics in solvent extraction for uranium recovery from phosphoric acid

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ABSTRACT

The phase separation kinetics for the process of recovering uranium from phosphoric acid medium (WPA) with 1.5 M D2EHPA + 0.2 M TBP is influenced by process variables such as D2EHPA/TBP concentration in the organic phase, acid concentration of the aqueous phase, temperature, phase ratio (A/O). To correlate the effect of these variables on phase separation kinetics (phase separation time, specific settling rate (SSR) for aqueous and organic), a statistical approach of data generation and analysis using factorial design of experimentation (DOE) has been adopted. The significance of individual variables and their mutual interactions on phase separation behaviour in WPA-D2EHPA + TBP process was statistically derived using the DOE data. Mathematical models representing a relation between the responses (phase separation time, SSR organic or SSR aqueous) and variables were established. The percentage effects of each variable on response were calculated from these models. Further a real variable mathematical equation is proposed, to predict the phase separation time in WPA-D2EHPA+TBP system for the given value of variable within the experimental range.

Keywords: Phase separation; Factorial design; D2EHPA-TBP; WPA; MGA; Kinetics; Phosphoric acid; Uranium

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1. Introduction

A process was developed to recover uranium from wet process phosphoric acid (WPA) by solvent extraction using 1.5M di-2- ethyl hexyl phosphoric acid (D2EHPA) + 0.2 M tri butyl phosphate (TBP) [1,2]. Merchant grade acid (MGA) is obtained by concentrating WPA from 6 M to 12 M phosphoric acid. In solvent extraction process after the operation of mixers, mixed phases are allowed to get separated in settlers which usually have a higher capacity (volume) as compared to mixers. So phase separation (settling) is a necessary step for the completion of extraction process. During the operations of mixers, coalescence and re-dispersion phenomenon are important as they influence the mass-transfer rates within the mixer [3]. Kinetics of mass transfer and phase separation helps in designing the equipment for better utilization of solvent inventory and economics of the process [4]. Although the settling characteristics of involved solvents play a vital role in design of settlers, very few references are available where kinetic aspects of phase separation have been dealt in detail [5].

The mass transfer kinetics of uranium was studied for D2EHPA+TBP-WPA process but phase separation kinetics was not investigated [6]. In the present investigation, attempts have been made to study the kinetics of phase separation behavior for the D2EHPA+TBP-WPA process. The effect of experimental variables such as D2EHPA/TBP

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concentration (organic phase), acid concentration (aqueous phase), temperature, aqueous to organic phase ratio (A/O), stirring speed on phase disengagement kinetics was investigated. In order to correlate the dependence of these variables and their mutual interactions on phase separation, a factorial design of experimentation has been adopted [7–10]. Similarly, the effects of process variables on specific settling rate (SSR) for the above process were also estimated. SSR is defined as the volume of the dispersed phase per unit area per unit time and it is an important factor in designing the settlers.

2. Experimental

2.1. Reagents

WPA (28% P_2O_5, density = 1.33 g/ml, viscosity = 4.86 cp) and MGA (50% P_2O_5, density = 1.65 g/ml, viscosity = 19 cp) were obtained from fertilizer companies. D2EHPA assaying (98% di-ester, Specific gravity (SG) = 0.9777, viscosity at 20°C (η) = 53 cps) was obtained from Orion chemicals and TBP (>98% pure, SG = 0. 973, η = 3.4 cps) from Heavy Water Board (India), were used as supplied. Petrofin (high flash point aliphatic fraction of refined kerosene) was used as diluent to obtain the desired concentrations of mixed extractants.

2.2. Procedure

WPA/MGA was taken as aqueous phase and 1.5 M D2EHPA + 0.2 M TBP/0.5 M D2EHPA + 0.06 M TBP as organic phase for phase separation studies. The dispersion of solvent (organic phase) and aqueous solution was carried out in a 500 ml beaker. The phases with predetermined A/O ratio were mixed using motorized stirrer at an rpm of 1200–1600. Stirring time of 5 min was given for uniform mixing. The mixed phase was transferred and allowed to separate in 250 ml stoppered graduated measuring cylinder which was marked with linear scale. The change in height of dispersed phase with time was noted.

2.3. Calculation of specific settling rate

From a plot of band width (*h*, height of mixed phase) versus time, SSR was calculated for each system using the Eq. (1):

$$\mathrm{SSR} = \frac{\nu(\mathrm{cm}^3)}{a(\mathrm{cm}^2) \times t(\mathrm{sec})} \tag{1}$$

where, ν is the volume of dispersed phase; *a* is the cross section area of cylinder; *t* is the time for phase dispersion.

2.4. Calculation of effects and interactions by factorial design of experiments

Five experimental variables namely, aqueous phase: X_1, phase ratio (A/O): X_2, temperature: X_3, stirring speed: X_4 and D2EHPA concentration: X_5 were studied for their influence on phase separation (response). For each variable, two values have been chosen X_1: WPA/MGA, X_2: 0.5/2, X_3: 30/55°C, X_4: 1200/1600 rpm and X_5: 0.5/1.5 M. In case of X_5, 0.5 M represents 0.5 M D2EHPA + 0.06 M TBP and 1.5 M means 1.5 M D2EHPA + 0.2 M TBP. It was observed from separate set of experiments that the effect of TBP concentration (0.06 to 0.2 M) in extractant on phase separation time was found to be negligible when added with D2EHPA at 1:7.5 mole ratio (which is due to similar density of D2EHPA and TBP).

The low value of each variable was assigned as '–1' where as high value was assigned as '+1'. These values are termed as dimensionless reduced variables. To quantify the effect of these variables and their interaction on response (t_p), total 2^5 i.e. 32 (all possible combinations of high and low) factorial designed experiments were carried out. Out of 32 experiments, run no. 10 (Table 1) was randomly selected and repeated 9 times to establish the reproducibility of the runs and to calculate standard deviation, which is used in subsequent calculations.

The results of 32 experiments led to the formulation of 32 different mathematical relations. Upon solving these relations using mathematical software (Mathematica 5.1), an empirical relation correlating response with variables and their interactions has been developed. The effects estimated from above relations are point estimates. This gives no idea of the reliability or precision of the estimates. The precision is generally stated in the form of a confidence interval, which is calculated using CL =(Main effect estimate) ± $ts/\sqrt{(N/4)}$; *s* = response error estimate, *N* = number of factorial run in the design, *t* = Student's '*t*' statistic with ν degree of freedom at stated confidence level. If confidence interval does not include zero, it can be said that the effect is significantly different from zero at the stated confidence level [11].

3. Results and discussion

3.1. Effect of variables on phase separation time

The experimental result (mean of phase separation time) of each run (replicated thrice) for 32 experiments and their corresponding standard deviation is shown in Table 1. '+' represent the high value whereas '–' low value of the variables studied. From this experimental data, the coefficients of regression were obtained using mathematical software (Mathematica 5.1), relationship as follows:

Table 1
Factorial design of experiment for phase separation time

Run no.	Factorial design of experiments						
	X_1 (MGA/WPA)	X_2 (A/O)	X_3 (Temp)	X_4 (rpm)	X_5 (molarity)	T_p (Sec)	Std. Dev.
1	+	+	+	+	+	481	34.6
2	−	+	+	+	+	125	4.2
3	+	−	+	+	+	370	18.4
4	−	−	+	+	+	139	15.6
5	+	+	−	+	+	765	28
6	−	+	−	+	+	206	4.9
7	+	−	−	+	+	736	4.2
8	−	−	−	+	+	215	5.7
9	+	+	+	−	+	447	8.5
10	−	+	+	−	+	129	13.2
11	+	−	+	−	+	369	18.4
12	−	−	+	−	+	142	12.7
13	+	+	−	−	+	741	7.8
14	−	+	−	−	+	206	2.1
15	+	−	−	−	+	744	4.2
16	−	−	−	−	+	218	8.5
17	+	+	+	+	−	350	14.1
18	−	+	+	+	−	114	11.3
19	+	−	+	+	−	70	2.8
20	−	−	+	+	−	80	1.5
21	+	+	−	+	−	608	29
22	−	+	−	+	−	189	7.8
23	+	−	−	+	−	114	2.8
24	−	−	−	+	−	181	2.8
25	+	+	+	−	−	370	33.2
26	−	+	+	−	−	105	2.1
27	+	−	+	−	−	74	3.4
28	−	−	+	−	−	85	2.8
29	+	+	−	−	−	610	1.4
30	−	+	−	−	−	193	4.9
31	+	−	−	−	−	111	3.5
32	−	−	−	−	−	159	18.4

$$\begin{aligned} t_p = {} & 295.19 + 139.81X_1 + 57.25X_2 - 79.56X_3 \\ & + 1.25X_4 + 81.87X_5 + 54.25X_1X_2 - 39.06X_1X_3 \\ & + 0.5X_1X_4 + 64.75X_1X_5 - 7.75X_2X_3 + 1.06X_2X_4 \\ & - 46.81X_2X_5 - 0.75X_3X_4 - 22.25X_3X_5 \\ & - 8.12X_1X_2X_3 + 1.68X_1X_2X_4 - 37.81X_1X_2X_5 \\ & + 0.37X_1X_3X_4 - 24X_1X_3X_5 + 0.82X_2X_3X_4 \\ & + 17.56X_2X_3X_5 + 3.125X_2X_4X_5 + 1.6875X_3X_4X_5 \\ & - 1.44X_1X_2X_3X_4 + 1.06X_1X_3X_4X_5 - 1X_2X_3X_4X_5 \\ & + 1.75X_1X_2X_3X_4X_5 \end{aligned} \tag{2}$$

The Eq. (2) represents a relationship between response (t_p) and X_j (j=1 to 5) dimensionless reduced variables. The coefficient of each term in Eq. (2) allows defining the extent of corresponding effect involved and the way it acts upon t_p. The absolute value of a coefficient with negative sign represented a favourable effect on t_p whereas positive sign associated with absolute value of coefficient indicated the adverse effect. The percentage effect of variables is defined as the ratio of coefficients of variables w.r.t. the constant term in Eq. (2).

Statistical analysis of calculated variable effects on phase separation time were carried out to show whether the effect is significant or not at 90, 95, 99% Confidence levels (CL). Stirring speed (X_4) had no effect on t_p even at 90% CL. As stirring speed (0.4%) had insignificant effect on phase separation time in the given range, its interactions with other variables were omitted from the Eq. (2). The simplified equation for phase separation time (t_p) in seconds is as follows:

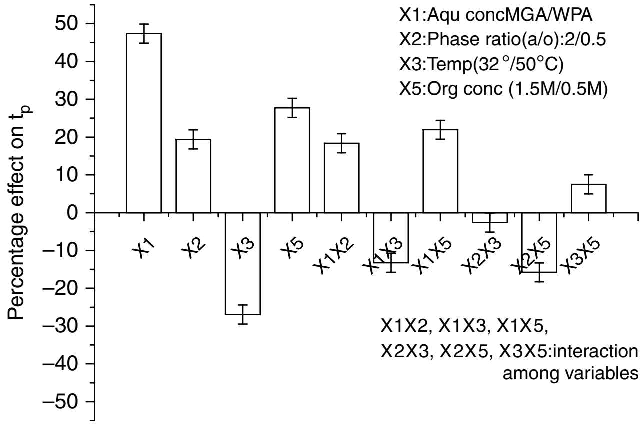

Fig. 1. Effect of variables on phase separation time.

$$\begin{aligned} t_p = {} & 295.19 + 139.81X_1 + 57.25X_2 - 79.56X_3 \\ & + 1.25X_4 + 81.87X_5 + 54.25X_1X_2 - 39.06X_1X_3 \\ & + 64.75X_1X_5 - 7.75X_2X_3 - 46.81X_2X_5 \\ & - 22.25X_3X_5 - 8.12X_1X_2X_3 - 37.81X_1X_2X_5 \\ & - 24X_1X_3X_5 \end{aligned} \tag{3}$$

From Eq. (3), the percentage effect of temperature, aqueous acid concentration, organic extractant concentration and phase ratio on t_p were –27%, 47%, 28% and 19% respectively (Fig. 1). Temperature was found to have favourable effect in terms of decrease in t_p with increase in temperature. Further the aqueous acid concentration, organic extractant concentration and phase ratio were observed to have adverse effect on t_p. The influence of variables on response was found to be significant at 99% CL.

3.2. Effect of interaction between variables on t_p

In order to determine whether two process parameters are interacting or not, a graphical tool called interaction graphs can also be used. If the lines in the interaction plot are parallel, there is no interaction between the process parameters. This implies that the change in the mean response from low to high level of a factor does not depend on the level of the other factor. On the other hand, if the lines are non-parallel, an interaction exists between the factors. The greater the degree of departure from being parallel, the stronger the interaction effect. The interaction graphs (Fig. 2) between acid concentration in aqueous phase and temperature (when X_2 and X_5 were fixed) show that the effect of temperature on phase separation time at two different levels of acid concentration (6 and 12 M) is not the same. This implies that there is a significant interaction between these two process parameters.

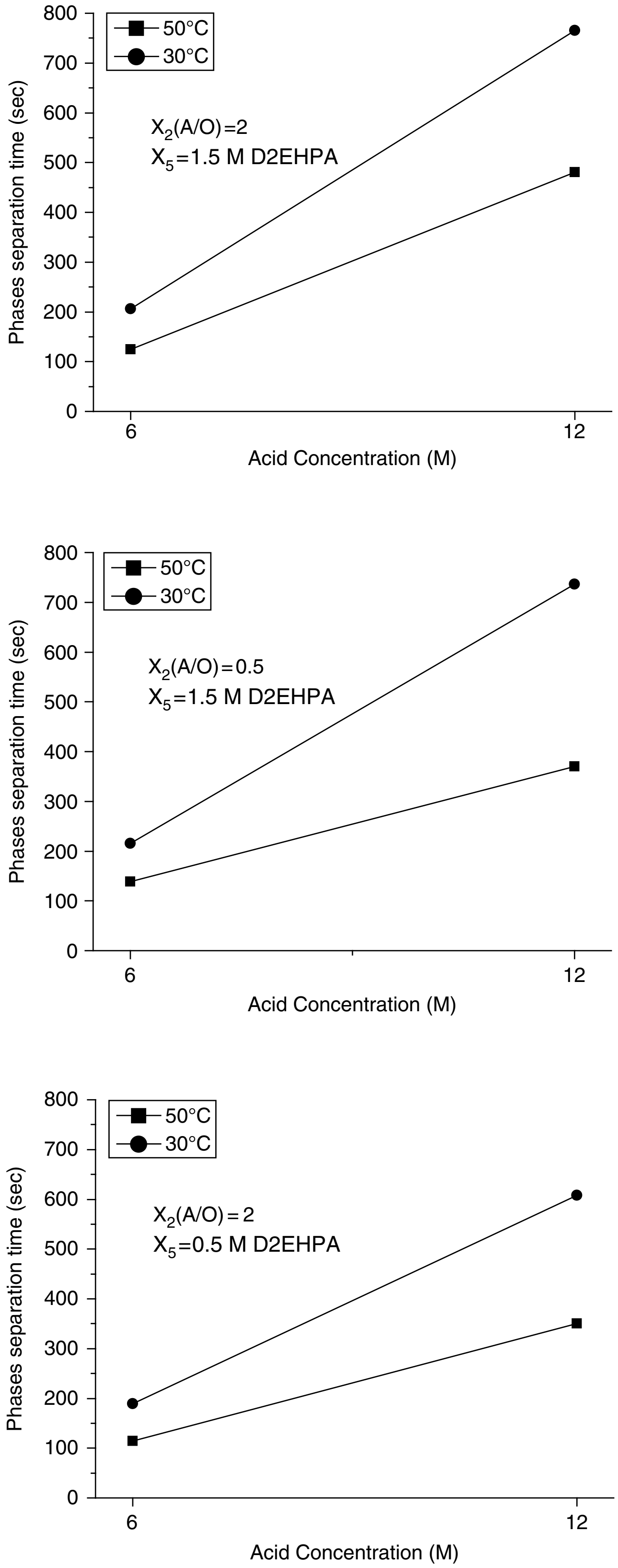

Fig. 2. Interaction plots between acid concentration and temperature.

The effect of binary interactions among X_1, X_2, X_3 and X_5 variables were estimated statistically, which show X_1X_2, X_1X_3, X_1X_5, X_2X_5, X_3X_5 interactions had significant effect on t_p at 99% CL. The interaction percentage effects were found to be 18%, −13%, 22%, −15.8%, 7.5% respectively (Fig. 2). Effect of interaction between X_2 and X_3 variables on t_p was not significant at 95% confidence limit. The observed binary interaction effects between X_1, X_2, X_5 (X_1X_2: 18%, X_2X_5: −16%) indicated the importance of interaction effect as the individual effect estimate was less or more than interaction effect. For example, X_2 and X_5 had positive individual effect on t_p but interaction effect X_2X_5 was negative. The effect of interaction among aqueous (X_1) and organic phase concentration (X_5) was 22% on t_p which clearly indicated the role of density and viscosity of individual phases and their interaction on the phase separation time. It can be concluded that individual effect and their interaction effects are many a times different. Hence, it is essential to study both individual as well as interaction effect.

3.3. Mathematical model for real system

To transform from dimensionless system (Eq. (3)) to a real system representing the real variables, X_j was substituted using the relation: X_j = 2(variable-mean)/range. Based on this, an empirical Eq. (4) for phase separation time was obtained. From this model, t_p can be estimated for different values of variables within defined experimental range.

$$\begin{aligned} t_p\,(\text{sec}) = {} & -164.78\ a - 1221.47\ o - 742.76\ p \\ & - 17.43\ T + 210.17\ a \times o + 126.47\ a \times p \\ & + 526.73\ o \times p - 90.08\ a \times o \times p + 2.26\ a \times T \\ & + 18.23\ o \times T - 2.94\ a \times o \times T + 9.98\ p \times T \\ & - 1.61\ a \times p \times T - 8.21\ o \times p \times T + 1.33\ a \\ & \times o \times p \times T + 1239.33 \end{aligned} \tag{4}$$

where, a is the aqueous phase concentration 6 M to 12 M H_3PO_4; p is the phase ratio A/O (0.5 to 2); o is the organic phase concentration 0.5 M to 2.0 M D2EHPA; T is the temperature (30 to 55°C).

Phase separation time data as obtained from 32 experimental runs were found to be in good agreement at 99% CL (paired t-test) with the results calculated by Eq. (4) within the experimental range as shown in parity plot (Fig. 3 (a)). New set of experiments were performed to validate the model. Fig. 3(b) represents the parity plot for calculated and experimental results obtained with 1.5 M D2EHPA + 0.2 M TBP, MGA, A/O = 0.5 at different temperature in the range of 20 to 55°C).

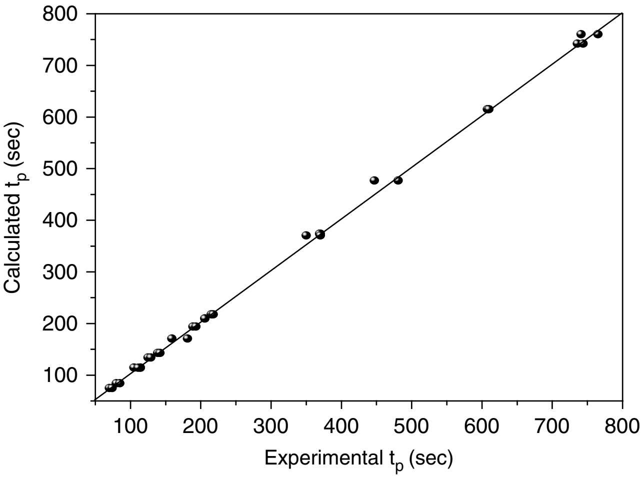

Fig. 3. (a) Parity plot of phase separation time for 32 experimental results.

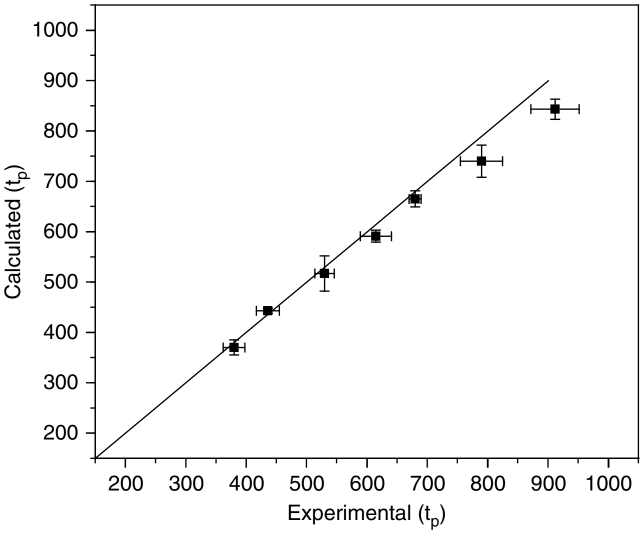

Fig. 3. (b) Parity plot of phase separation time at different temperature.

3.4. Effect of variables on SSR values

The SSR value of the phases involved determines the rate of phase disengagement. During the phase separation, SSR value of individual phase changes with the change in dispersion band (mixed phase) height (h). It was found that the SSR value was maximum when phase separation starts and goes on decreasing as the dispersed band height approaches to zero. The SSR value of dispersed phase plays an important role (being lower SSR value than the other phase) as it determines the rate of phase disengagement. Dispersed phase is the lower volume phase in the mixed mixture of two phases. The SSR values are more sensitive than phase separation time.

The maximum SSR (Δh=20 cm.) value was used as response of the experimental runs. The effect of X_1 X_2, X_3, X_5 on SSR values for both organic and aqueous phase were estimated employing 2^4 factorial design of experiments. Stirring speed (X_4) variable was not used because of its insignificant effect on t_p/SSR. By solving 16 relations obtained by factorial design of experiments, two mathematical models for aqueous and organic phase SSR values were obtained. Models representing the effect and interaction of variables on SSR value are given below:

$$\begin{aligned}\mathrm{SSR_{org}} = {}& 0.1061 - 0.0189X_1 - 0.0573X_2 + 0.0344X_3\\ & - 0.0392X_5 - 0.0101X_1X_2 - 0.0102X_1X_3\\ & - 0.0108X_1X_5 - 0.0219X_2X_3 + 0.0352X_2X_5\\ & - 0.0119X_3X_5 + 0.0008X_1X_2X_3\\ & + 0.0127X_1X_2X_5 + 0.0056X_1X_3X_5\\ & + 0.0103X_2X_3X_5 - 0.0043X_1X_2X_3X_5 \end{aligned} \tag{5}$$

$$\begin{aligned}\mathrm{SSR_{aq}} = {}& 0.0940 - 0.0312X_1 + 0.0100X_2 + 0.0235X_3\\ & - 0.0160X_5 - 0.0249X_1X_2 - 0.0071X_1X_3\\ & + 0.0026X_2X_3 - 0.0039X_3X_5 - 0.0097X_1X_5\\ & - 0.0054X_1X_2X_3 + 0.0151X_2X_5\\ & + 0.0103X_1X_2X_5 + 0.0018X_1X_3X_5\\ & + 0.0028X_2X_3X_5 + 0.0022X_1X_2X_3X_5 \end{aligned} \tag{6}$$

It is evident from Eq. (5) and also from Fig. 4 that temperature has a favourable influence (32%) on specific settling rate of organic phase whereas aqueous phase concentration (–17%), phase ratio A/O (–54%) and organic phase concentration (–36%) has negative effect on SSR organic. It was found that the effect of binary interaction between all the variables on SSR organic was significant. Higher coefficients of X_2X_4 (33.2%) and X_2X_3 (–20.6%) indicate the critical role of phase ratio on phase separation kinetics.

Fig. 5 represents the percentage effect of variables and their interaction on SSR aqueous phase In the case of SSR aqueous phase, temperature (+25%) and phase ratio (+10.6%) had positive effect. Aqueous phase concentration (–33%) and organic phase concentration (–17%) had negative effect on phase separation rate. Binary interaction effects between variables were also found to be significant for SSR of aqueous phase. All the effects were found to be significant at a confidence level of 95%.

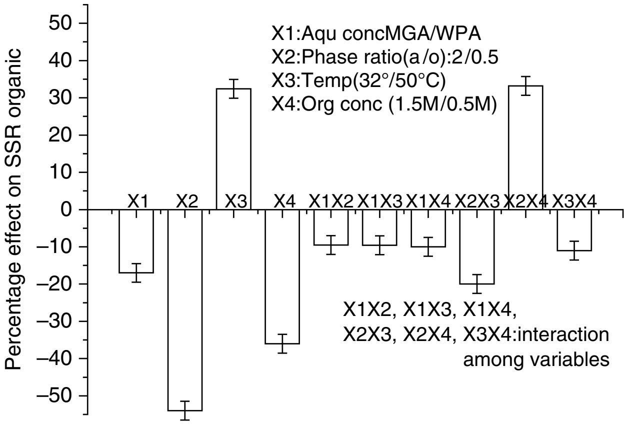

Fig. 4. Percentage effect of variables on SSR organic.

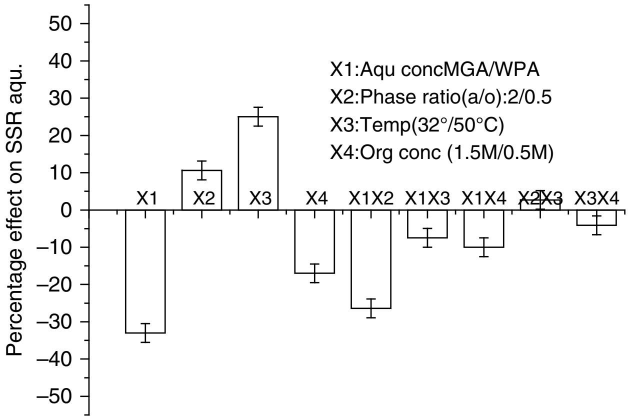

Fig. 5. Percentage response of variables on SSR aqueous.

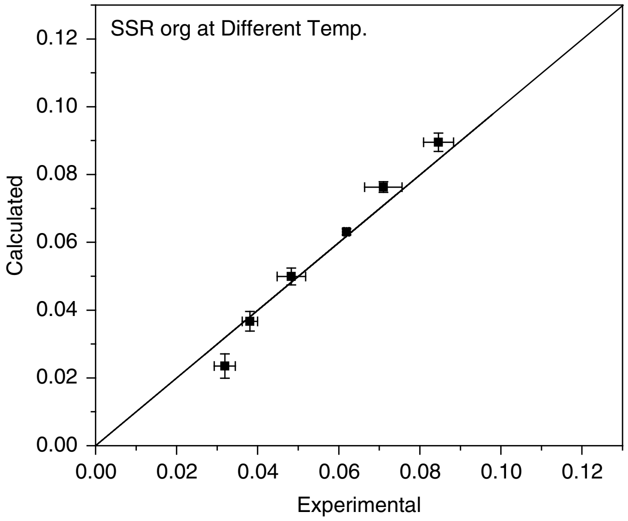

Fig. 6. Parity plot for SSR organic.

Eqs. (7) and (8) are derived from (5) and (6) equations respectively, which predict the SSR (organic/aqueous) for real variables within the experimental range. Fig. 6 shows the parity plot for experimental versus calculated SSR values for 1.5 M D2EHPA + 0.2 M TBP/MGA system, A/O=0.5 system at different temperature.

$$\begin{aligned}\mathrm{SSR_{org}} = {}& +\ 0.0631\ a + 0.4579\ o - 0.0506\ a\ o\\ & + 0.2943\ p - 0.0301\ a\ p - 0.2195\ o\ p\\ & + 0.0244\ a\ o\ p + 0.0193\ T - 0.0009\ a\,T\\ & - 0.0108\ o\,T + 0.0007\ a\ o\,T - 0.0075\ p\,T\\ & + 0.0003\ a\ p\,T + 0.0049\ o\ p\,T\\ & - 0.0003\ a\ o\ p\,T - 0.6103 \end{aligned} \tag{7}$$

$$\begin{aligned} \mathrm{SSR}_{\mathrm{aq}} = {} & + 0.0149\,a + 0.1009\,o - 0.0137\,a\,\mathrm{o} \\ & + 0.0337\,p - 0.0052\,a\,p - 0.0072\,o\,p \\ & + 0.0023\,a\,o\,p + 0.0016\,T + 0.0001\,a\,T \\ & - 0.0005\,o\,T - 0.0001\,a\,o\,T + 0.0029\,p\,T \\ & - 0.0004\,a\,p\,T - 0.0008\,o\,p\,T \\ & + 0.0002\,a\,o\,p\,T - 0.0994 \end{aligned} \tag{8}$$

where, a is the aqueous phase concentration 6 M to 12 M H_3PO_4; p is the phase ratio A/O 0.5 to 2; o is the organic phase concentration 0.5 M to 2.0 M D2EHPA; T is the temperature (30 to 55°C).

4. Conclusions

The significance of variables such as D2EHPA/TBP concentration in the organic phase, acid concentration of the aqueous phase, temperature, phase ratio (A/O) and their mutual interactions on phase separation behaviour in WPA/MGA - D2EHPA + TBP systems were statistically derived using the DOE data. Mathematical model representing a relation between the phase separation time/SSR and variables were established. The percentage effect of each variable on response was calculated from this model. Temperature was found to have favourable effect on t_p, whereas, aqueous acid concentration, organic extractant concentration and phase ratio were observed to have adverse effect on t_p. These effects were found to be significant at 99% confidence level, whereas interaction effects were significant at 95% confidence level. The mathematical models for SSR illustrates that the phase ratio and organic extractant concentration has maximum negative effect on SSR organic, whereas aqueous phase acidity had maximum negative effect on SSR aqueous. Temperature had significant positive effect on the SSR of both the phases. The real mathematical equations derived from above models can estimate the response value within the limited range of variables. Experimental data were found to be in good agreement with the results calculated by mathematical model.

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