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Reactive Extraction of Propionic Acid Using Tributyl Phosphate in Imidazolium-Based Ionic Liquids: Optimization Study Using Response Surface Methodology

Nilay BAYLAN [1,*]

[1] *Department of Chemical Engineering, İstanbul University-Cerrahpaşa, Avcılar 34320, İstanbul, Turkey*

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Abstract. In this work, the reactive extraction of propionic acid from aqueous solutions using imidazolium-based ionic liquids was examined. Ionic liquids, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf_2N]), and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]) were utilized as diluents. Tributyl phosphate (TBP) as an extractant in ionic liquids was used. D-optimal design based on the response surface methodology (RSM) has been exerted to specify the effect of different variables on the reactive extraction process. Initial propionic acid concentration (2-10% w/w), extractant (TBP) concentration (0-3.00 mol.L^{-1}) and temperature (25-45 °C) were chosen as numerical variables, and type of ionic liquid was chosen as a categorical variable. Extraction efficiency, selected as a dependent variable, was calculated from the experimental data. In addition to, the model equation for the extraction efficiency was created. The optimum extraction conditions were obtained as the initial propionic acid concentration of approximately 5% (w/w), TBP concentration in ionic liquids of 3 mol.L^{-1} and temperature of 45°C**.** Under these conditions, the values of extraction efficiency were determined as 85.64% for [BMIM][PF_6], and 81.91% for [BMIM][Tf_2N]. This study has indicated that the systems of TBP in ionic liquids is an efficient and green reactive extraction method for the removal of propionic acid from the aqueous media.

Keywords**:** Propionic acid, Imidazolium-Based Ionic Liquids, Tributyl phosphate, Reactive extraction, Response surface methodology.

İmidazolyum Bazlı İyonik Sıvılarda Tributil Fosfat Kullanarak Propyonik Asitin Reaktif Ekstraksiyonu: Yanıt Yüzey Metodolojisi İle Optimizasyon Çalışması

Özet. Bu çalışmada, propiyonik asidin sulu çözeltilerden imidazolyum bazlı iyonik sıvılar kullanılarak reaktif ekstraksiyonu incelenmiştir. İyonik sıvılar, 1-butil-3-metil imidazolyum bis(triflorometilsülfonil)imid ([BMIM][Tf_2N]), ve 1-butil-3-metil imidazolyum hekzaflorofosfat ([BMIM][PF_6]) seyreltici olarak kullanılmıştır. İyonik sıvılarda ekstraktan olarak tributil fosfat (TBP) kullanılmıştır. Farklı değişkenlerin reaktif ekstraksiyon işlemi üzerindeki etkisini belirlemek için yanıt yüzey metodolojisi (RSM) temelli D-optimal tasarım kullanılmıştır. Başlangıç propiyonik asit konsantrasyonu (ağırlıkça % 2-10), ekstraktan (TBP) konsantrasyonu (0-3.00 mol.L^{-1}) ve sıcaklık (25-45 °C) sayısal değişkenler olarak, ve iyonik sıvı türü ise kategorik değişken olarak seçilmiştir. Bağımlı değişken olarak seçilen ekstraksiyon etkinliği deneysel verilerden yararlanarak hesaplanmıştır. Ayrıca, ekstraksiyon etkinliği için model denklem oluşturulmuştur. Optimum ekstraksiyon koşulları, yaklaşık %5 (ağ/ağ) başlangıç propiyonik asit konsantrasyonu, 3 mol.L^{-1} iyonik sıvılar içerisinde TBP konsantrasyonu ve 45 °C sıcaklık olarak elde edildi. Bu koşullar altında, ekstraksiyon etkinliği değerleri [BMIM][PF_6] için %85.64 ve [BMIM][Tf_2N] için %81.91 olarak belirlenmiştir.

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* Corresponding author. *Email address: nilay.baylan@istanbul.edu.tr*

Bu çalışma, iyonik sıvılar içerisindeki TBP sistemlerinin, propiyonik asidin sulu ortamdan uzaklaştırılması için verimli ve yeşil reaktif ekstraksiyon yöntemi olduğunu göstermiştir.

***Anahtar Kelimeler*:** Propiyonik asit, İmidazolyum Bazlı İyonik Sıvılar, Tributil fosfat, Reaktif ekstraksiyon, Yanıt yüzey Metodolojisi.

1. INTRODUCTION

Propionic acid has large amount of using in different chemical applications and industries. Especially it is widely used in production of cellulose plastics, ester solvents, perfume bases, arthritis drugs, herbicides, and plasticizers. Also, it is utilized to prevent the growth of mold and rope in cakes and breads in food industry and it is used as mold preventives in hay and silage [1]. Propionic acid is generally obtained by the fermentation process and is acquired not only as a single product, but as by-product with aqueous solutions. The by-product formation is a major problem that reduces the production efficiency. It must be removed from the fermentation broths for the continuous fermentation process. [2, 3]. Hence, the removal of propionic acid from waste streams or aqueous media or fermentation broths has great importance.

A variety of separation methods such as solvent extraction [4, 5], electrodialysis [6], reverse osmosis [7], adsorption [8-10], ion exchange [11], membrane system [12] are utilized for the removal of propionic acid from aqueous media. In addition to these methods, reactive extraction is commonly used for the propionic acid removal from aqueous media or fermentation broths or industrial wastewaters [13-15].

Reactive extraction can be defined as a process in which solvent extraction occurs simultaneously with the chemical complexation [16]. The removal of carboxylic acid by reactive extraction from aqueous solutions ensures a higher distribution coefficient and removal yield [17]. Aliphatic amines such as trioctylamine (TOA), tributylamine (TBA), and organophosphorous compounds like tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), are broadly utilized as extractants for the removal carboxylic acids from aqueous. These extractants exhibit a high selectivity and solvent capacity [16]. The traditional organic solvents, such as alcohols, aliphatic hydrocarbons, ketones, ethers, are frequently used as diluents in the reactive extraction process [18].

Ionic liquids are organic molten salts which composed of specific anions and cations. Anions can be composed of organic or inorganic groups like bis (trifluoromethanesulfonyl) imide, hexafluorophosphate, tris (trifluoromethylsulfonyl) methyl, tetrafluoroborate, halides, acetate and nitrate. Cations are composed of organic groups like pyrrolidinium, ammonium pyridinium, sulfonium, phosphonium and imidazolium. Ionic liquids have negligible vapor pressure, and so they do not contribute to the atmosphere. Ionic liquids are non-flammable, good thermal stability, recyclable and good solubility for diverse compounds. Considering the substantial features of ionic liquids, they are also entitled “green solvents”. They have received great interest as an alternative to traditional solvents in many applications [19, 20].

Reactive extraction systems investigated in the literature for the uptake of propionic acid from aqueous solutions are summarized in Table 1. As shown in Table 1, the traditional organic solvents have been tested for the removal of propionic acid by reactive extraction. Nevertheless, these organic solvents cause environmental pollution due to they have toxic, volatile and flammable features. Therefore, the search for environmentally friendly solvent has emerged in the extraction. In this regard, ionic liquids have attention as alternative green solvents for the extraction processes instead of the traditional solvents [21].

Response surface methodology (RSM) is a technique consisting of mathematical and statistical methods used to determine the relation between independent variables and response, construct an experimental plan, build the model equation and specify the optimal conditions for response. RSM gives the minimum number of experiments that the maximum information about process behavior can be detected. Factorial Design, Box-Behnken, Central Composite and D-optimal designs are experimental design methods mostly used in RSM [36-38].

In this study, the use of imidazolium-based ionic liquids were investigated in the reactive extraction of propionic acid. TBP was utilized as an extractant in ionic liquids. D-optimal design based on RSM has been applied to specify the effect of initial propionic acid concentration, TBP concentration, temperature and ionic liquid type on the reactive extraction process. The mathematical model equation was created and the experimental data were evaluated using analysis of variance (ANOVA). And also, optimal conditions were determined for the reactive extraction process.

Table 1: Reactive extraction systems investigated in the literature for the removal of propionic acid.

Extractants	Diluent solvents	References
Amberlite LA-2	Cyclohexane, 1-octanol, 2-octanone, isooctane, toluene, methyl isobutyl ketone and hexane	[22]
TOA	1-octanol, methyl isobutyl ketone, chloroform and tetrachloromethane	[18]
TOA	Heptane, oleyl alcohol, ethyl acetate and petroleum ether	[23]
TOA	1-decanol and 2-octanol	[13]
TOA	Dichloromethane, n-butyl acetate and n-heptane	[24]
TBP	1-dodecanol, toluene, benzene, hexane, heptane, butyl acetate, paraffin liquid and petroleum ether	[25]
TBP	Kerosene and 1-decanol	[26]
TBP	Heptane, petroleum ether and toluene	[27]
TBP, TOA and Aliquat 336	1-octanol	[28]
TBP, TOA	Hexane	[29]
TOPO	Hexane	[30]
TRPO	Kerosene	[31]
Alamine 336	Toluene	[32]
Aliquat 336	Methyl isobutyl ketone	[33]
Aliquat 336	2-octanol	[34]
Aliquat 336	Cyclohexane, methyl isobutyl ketone, ethyl acetate hexane and toluene	[15]
Primary amine (N1923)	Hexane, n-octanol and butyl acetate	[35]

2. MATERIALS AND METHODS

Propionic acid solutions were prepared by dissolving of a certain amount of propionic acid (Merck, >99%) in distilled water. Organic solutions were prepared by dissolving of tributyl phosphate (TBP; Sigma-Aldrich, >99%) in ionic liquids. Imidazolium-based ionic liquids, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][Tf_2N]; Iolitec, >99%) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]; Iolitec, >99%), were utilized as diluents.

The volumes of propionic acid and organic solutions were 2 mL. Experiments were performed by shaking in a water bath (Nüve ST 30) at 150 rpm for 1 h. Then, the samples were centrifuged in 3000 rpm for 10 min to separate the phases. The propionic acid concentration in the aqueous phase was determined using an automatic Schott Titroline titrator with NaOH solution of 0.1 N. The concentration of propionic acid in the organic phase was calculated from the material balance.

The experimental results were appraised with using the distribution coefficient, extraction efficiency and loading factor [39]:

The distribution coefficient (D) is defined as the propionic acid extracted from the aqueous phase into the organic phase. It is declared as follows:

$$D = \frac{C_{A,org}}{C_A} \tag{1}$$

The extraction efficiency (E) is clarified as the ratio of extracted propionic acid to initial propionic acid concentration. It can be written in the following form:

$$E = \left(1 - \frac{C_A}{C_{A_0}}\right) * 100 \qquad (2)$$

The loading of extractant (Z), known as loading factor, is described as the total propionic acid concentration in the organic phase divided by the total extractant concentration in the organic phase. It is remarked as below:

$$Z = \frac{C_{A,org}}{C_{E,org}} \qquad (3)$$

where C_{A0} (mol.L^{-1}) is the initial propionic acid concentration in the aqueous phase, C_A (mol.L^{-1}) is the propionic acid concentration in the aqueous phase at the end of the extraction and $C_{A,org.}$ (mol.L^{-1}) is the propionic acid concentration in the organic phase at the end of the extraction. $C_{E,org.}$ (mol.L^{-1}) is the extractant concentration in the organic phase.

3. RESULTS AND DISCUSSION

3.1. Response Surface Methodology

D-optimal design based on RSM has been exerted to determine the effect of different variables on the reactive extraction process, specify the relation between the variables and response and create the mathematical model equation representing the extraction system. For the purposes, Design-Expert® Software Trial Version 11 (Stat-Ease, Inc.) was utilized. Design variables (numerical and categorical variables) and their levels were indicated in Table 2. The independent variables were selected as initial propionic acid concentration (X_1), initial TBP concentration in ionic liquid (X_2), and temperature (X_3). These variables were numerical variables. Other independent variable was ionic liquid type (X_4) and this variable was categorical variable. Dependent variable or response was selected as extraction efficiency. The variables and their levels given in Table 2 were entered into Design-Expert® Software. The experiment plan was determined according to four variables, namely three numerical variables and one categorical variable. As shown in Table 3, Design-Expert® Software proposed 24 experiment points and these experiments were carried out experimentally. Table 3 shows D-optimal design plan and experimental data obtained.

Table 2. D-optimal design variables and levels.

Variables	**Unit**	**Code**		**Levels**		
			Categorical	**1**	**2**	
			Numerical	**-1**	**0**	**1**
Initial propionic acid concentration	%	X_1	Numerical	2	6	10
TBP concentration	mol.L^{-1}	X_2	Numerical	0	1.5	3
Temperature	°C	X_3	Numerical	25	35	45
Ionic liquid type		X_4	Categorical	[BMIM][PF_6]	[BMIM][Tf_2N]	

Table 3. D-optimal design plan and experimental responses.

Experiment Number	Independent variables				Dependent variable
	Initial propionic acid concentration X_1	TBP concentration X_2	Temperature X_3	Ionic liquid type X_4	Extraction efficiency (%) Y_1
1	2	3	25	[BMIM][PF_6]	76.97
2	6	1.5	25	[BMIM][PF_6]	60.04
3	10	0	25	[BMIM][PF_6]	29.92
4	10	3	25	[BMIM][PF_6]	77.68
5	10	3	35	[BMIM][PF_6]	78.64
6	8	2.25	35	[BMIM][PF_6]	70.88
7	2	0	35	[BMIM][PF_6]	28.12
8	6	1.5	40	[BMIM][PF_6]	63.28
9	2	3	45	[BMIM][PF_6]	84.06
10	10	0	45	[BMIM][PF_6]	35.15
11	2	3	45	[BMIM][PF_6]	83.11
12	10	0	45	[BMIM][PF_6]	35.52
13	10	1.5	25	[BMIM][Tf_2N]	61.12
14	6	3	25	[BMIM][Tf_2N]	80.25
15	2	0	25	[BMIM][Tf_2N]	30.77
16	10	1.5	25	[BMIM][Tf_2N]	61.31
17	6	3	25	[BMIM][Tf_2N]	79.92
18	2	0	25	[BMIM][Tf_2N]	31.32
19	6	0.75	30	[BMIM][Tf_2N]	51.62
20	10	0	35	[BMIM][Tf_2N]	38.06
21	2	3	35	[BMIM][Tf_2N]	75.89
22	6	1.5	45	[BMIM][Tf_2N]	63.67
23	2	0	45	[BMIM][Tf_2N]	36.71
24	10	3	45	[BMIM][Tf_2N]	78.83

3.1.1. Analysis of Experimental Results

ANOVA table with numerous useful data is utilized to interpret of experimental results. The experimental results obtained were evaluated statistically using ANOVA. ANOVA table for extraction efficiency (Y) were indicated in Table 4. In ANOVA table, F-value and p-value of the model shows whether the model is significant or not [40]. As can be seen in Table 4, F-value of 1473.52 and p-value of < 0.0001 were obtained, these values showed that the model was significant for the extraction efficiency (Y). ANOVA table also shows effective parameters according to p-value. P-values of parameters less than 0.05 are important model terms and have an effect on the response [41]. In this case, X_1, X_2, X_3 and X_4 terms had the linear effects on the extraction efficiency; X_1X_2, X_1X_3, X_1X_4, X_2X_4 and X_3X_4 terms had the interaction effects on the extraction efficiency; X_1^2, X_2^2 and X_3^2 terms had exponential effects on the extraction efficiency. In other words, these terms had influential model terms and the model equation characterizing the extraction efficiency consists of these model terms. As a result, the model equation in coded factors was created with RSM as below:

$$Y = 61.78 + 1.17\,X_1 + 22.47\,X_2 + 2.11\,X_3 + 0.72\,X_4 - 0.97\,X_1X_2 - 0.77\,X_1X_3 + 0.58\,X_1X_4 - 1.93\,X_2X_4 - 0.81\,X_3X_4 - 3.54\,X_1^2 - 3.05\,X_2^2 + 1.06\,X_3^2$$

Table 4. ANOVA data for the extraction efficiency (Y).

Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value Prob>F**
Model	9493.66	13	730.28	1473.52	< 0.0001
X_1	17.19	1	17.19	34.69	0.0002
X_2	6623.59	1	6623.59	13364.69	< 0.0001
X_3	68.11	1	68.11	137.43	< 0.0001
X_4	10.14	1	10.14	20.46	0.0011
X_1X_2	10.97	1	10.97	22.13	0.0008
X_1X_3	6.22	1	6.22	12.54	0.0053
X_1X_4	4.12	1	4.12	8.32	0.0163
X_2X_3	2.05	1	2.05	4.13	0.0696
X_2X_4	47.96	1	47.96	96.78	< 0.0001
X_3X_4	9.91	1	9.91	19.99	0.0012
X_1^2	27.70	1	27.70	55.90	< 0.0001
X_2^2	18.26	1	18.26	36.85	0.0001
X_3^2	4.65	1	4.65	9.38	0.0120
Residual	4.96	10	0.4956		
Lack of Fit	4.21	5	0.8425	5.67	0.0400
Pure Error	0.7435	5	0.1487		
Cor. Total	9498.62	23	730.28	1473.52	< 0.0001

The model equation showed that all independent variables affect the extraction efficiency. Due to having the highest coefficient in the model equation, TBP concentration (X_2) was the most effective parameter on the extraction efficiency.

Table 5. Statistical parameters obtained in D-optimal design for extraction efficiency (Y).

Statistical parameters			
R^2	0.9995	**SD**	0.7040
Adjusted R^2	0.9988	**AP**	102.3903
Predicted R^2	0.9919	**CV %**	1.20

A number of statistical parameters are utilized to determine the adequacy and accuracy of model equation. Table 5 indicates the statistical parameters like the correlation coefficients (R^2, predicted R^2 and adjusted R^2), the coefficient of variation (CV), the standard deviation (SD) and adequate precision (AP). R^2 can be described as a measure of the grade of compliance. As can be seen in Table 6, R^2 value (0.9995) was found to be quite high. This has been proved that the experimental data was compatible with the model equation. R^2_{Adj} can be defined as a measure of the amount of variation around the average. If R^2 and adjusted R^2 (R^2_{Adj}) values are close to each other, it shows that the experimental data were represented sufficiently by the model. The difference between the predicted R^2 (R^2_{Pred}) and R^2_{Adj} is desirable to be less than 0.2. It indicates that these values are in reasonable agreement with each other. If the standard deviation is low, the model fit is better. Adequate precision (AP) measures the signal to noise proportion. It is desirable to be greater than 4. On the other hand, the coefficient of variation (CV) describes as the measure of proportion of the standard deviation of the average and is expected to be quite low [36, 37]. All statistical data indicate that the acquired model equation was accurate and adequate to design the reactive extraction of propionic acid.

Other control points for the verification of the experimental results are the analysis of diagnostic plots (predicted vs. actual plot or residuals vs. predicted plot) [42, 43]. The predicted vs actual plot and residuals vs. predicted plot were depicted in Figure 1. As depicted in Figure 1.a, the experimental data, namely actual values were aligned as a straight line. As indicated in Figure 1.b, all residual points were distributed within the range. Diagnostic plots denoted that the predicted values by the model equation were consistent with the experimental data.

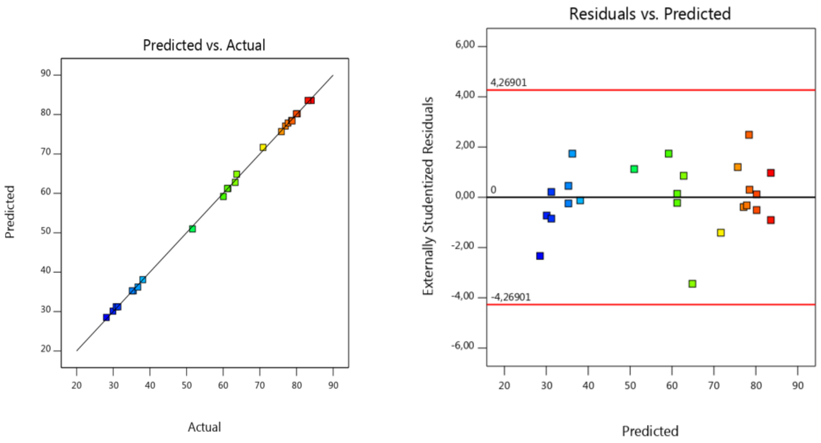
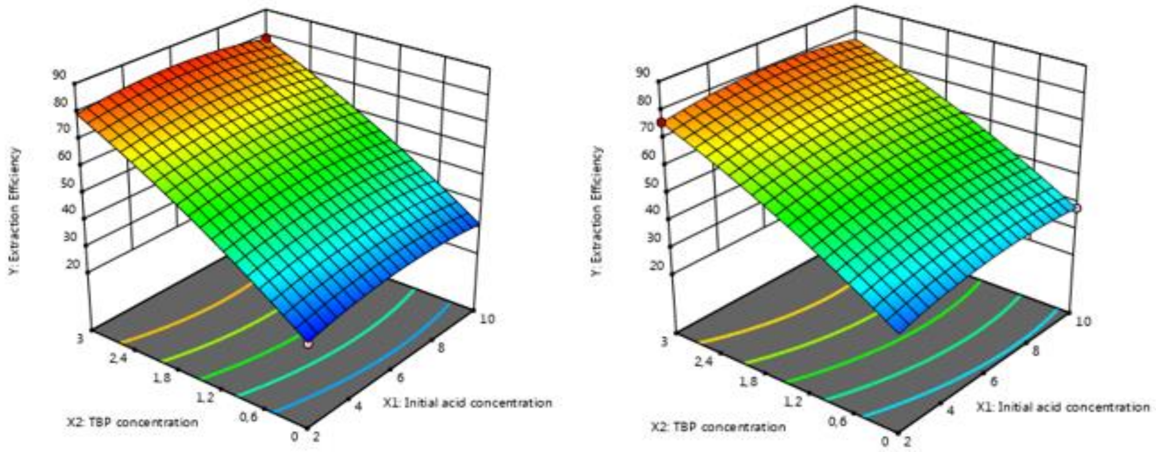


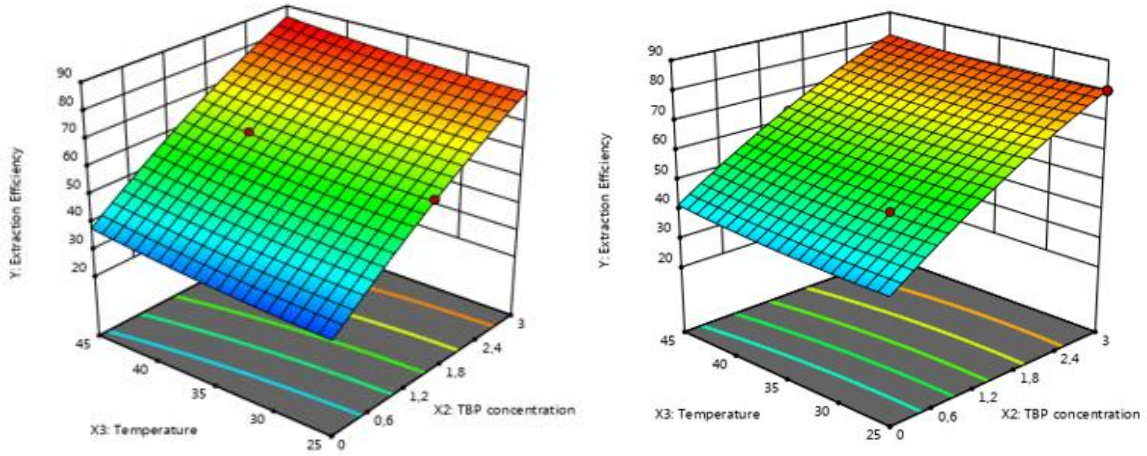
Figure 1. Diagnostic plots of D-optimal design model. (a) predicted vs actual plot (b) residuals vs. predicted plot.

3.1.2. Response Surface Plots

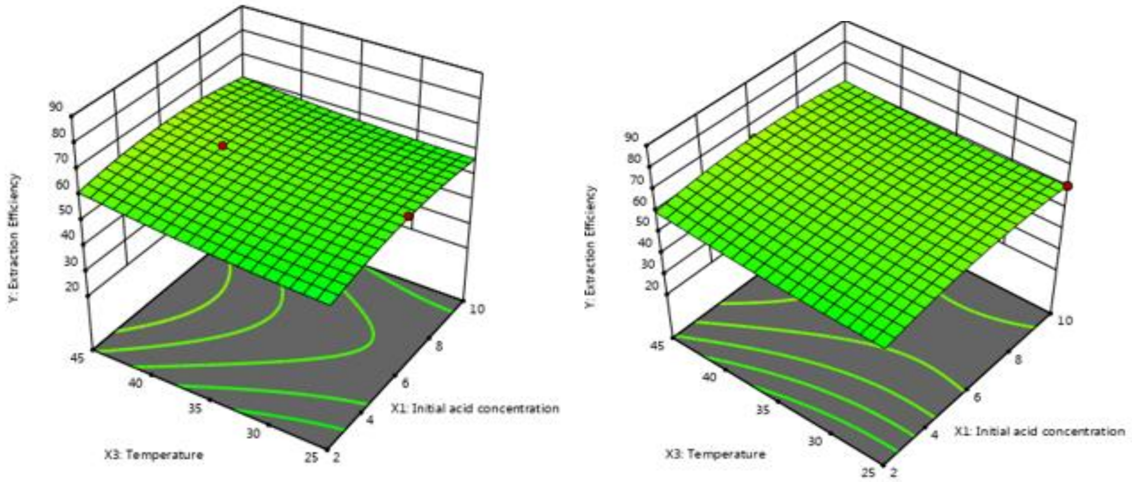
Response surface plots (3D plots) were depicted to specify the relation between the numerical variables and extraction efficiency. 3D plots were illustrated between two selected numerical variables. Other numerical variable was held at center levels. Figure 2 shows the effect of numerical variables on the extraction efficiency for both ionic liquids. As can be seen in Figures 2.a and 2.b, the extraction efficiency increased significantly with increasing TBP concentration in ionic liquids. When TBP is utilized as an extractant in the ionic liquid, the grade of extraction of propionic acid increases. So, more propionic acid molecules are extracted from the aqueous phase [44]. The trend observed acquired from this work were consistent with the reported studies in the literature [45]. From Figures 2.a and 2.c, the extraction efficiency slightly increased as the initial propionic acid concentration increased from 2% to 10%. In the literature, the reactive extraction of propionic acid with Aliquat 336 was investigated by Uslu and İnci [32]. Similarly, they observed that the extraction efficiency increased with increasing initial propionic acid concentration. In addition to, as the temperature was increased, the extraction efficiency increased slightly. From Figure 2.c, it increased from 60.04% to 63.67% with increasing the temperature varied range 25-45 °C. Athankar et. al. investigated gallic acid extraction with tri-n-caprylylamine and they reported that the extraction efficiency was only slightly increased (from 62% to 65%) with increasing temperature [46].



(a) **[BMIM][PF$_6$]** **(a) [BMIM][Tf$_2$N]**



(b) [BMIM][PF$_6$] **(b) [BMIM][Tf$_2$N]**



(c) [BMIM][PF$_6$] **(c) [BMIM][Tf$_2$N]**

Figure 2. 3D plots for the extraction efficiency in the reactive extraction of propionic acid with ionic liquids **(a)** the effect of initial propionic acid concentration (X_1) and TBP concentration (X_2) in case of temperature of 35 °C. **(b)** the effect of TBP concentration (X_2) and temperature (X_3) in case of initial propionic acid concentration of 6%. **(c)** the effect of initial propionic acid concentration (X_1) and temperature (X_3) in case of TBP concentration of 1.5 mol/L.

The final step of the design is the specification of the criteria for optimization. The optimization criterion was is to maximize the extraction efficiency. And also, all independent variables were kept within in the investigated range. These conditions were entered into Design-Expert® Software and the optimum conditions were obtained as shown in Table 6.

Table 6. Optimum reactive extraction conditions obtained by D-optimal design.

Ionic liquid type	Initial propionic acid concentration (% w/w)	TBP concentration (mol/L)	Temperature (°C)	Predicted Extraction efficiency (%)	Desirability
[BMIM][PF_6]	5.511	2.989	44.428	85.640	1.000
[BMIM][Tf_2N]	5.984	3.000	45.000	81.911	0.962

4. CONCLUSION

In the present design study, imidazolium-based ionic liquids, namely [BMIM][PF_6] and [BMIM][Tf_2N] were examined in the reactive extraction of propionic acid by using TBP. D-optimal design was conducted to determine the effect of various parameters on the extraction efficiency. The second-order model equation representing process parameters and extraction efficiency was obtained. The validity of model equation was evaluated by ANOVA and graphical analysis. The acquired model equation was in good agreement with the experimental data. The model equation indicated that all independent variables affect the extraction efficiency. Among independent variables, TBP concentration was obtained as the most effective parameter on the extraction efficiency. The optimum conditions were obtained as the initial propionic acid concentration of approximately 5% (w/w), TBP concentration in ionic liquids of 3 mol.L^{-1}, temperature of 45°C**.** Under optimum conditions, the values of extraction efficiency were determined as 85.64% for [BMIM][PF_6], and 81.91% for [BMIM][Tf_2N]. This study has also shown that ionic liquids [BMIM][PF_6] and [BMIM][Tf_2N] as green extraction solvents can be used in the reactive extraction of propionic acid.

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