Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 23, Sayı 3, 878-884, 2019

Süleyman Demirel University
Journal of Natural and Applied Sciences
Volume 23, Issue 3, 878-884, 2019

DOI: 10.19113/sdufenbed.524747

Experimental Design of Reactive Extraction of Levulinic Acid Using Green Solvents

Aslı GÖK*[1]

[1]Istanbul University- Cerrahpaşa, Faculty of Engineering, Department of Chemical Engineering, 34320, Istanbul, Turkey

(Alınış / Received: 08.02.2019, Kabul / Accepted: 11.11.2019, Online Yayınlanma / Published Online: 30.12.2019)

Keywords
Levulinic acid,
Reactive extraction,
Ionic liquids,
Carboxylic acid

Abstract: Levulinic acid is a carboxylic acid used in many different areas of the industry. It is used as pesticide and fertilizer in agriculture industry, and it is also used in the cosmetic industry due to its unique caramel odor and in the food industry due to its aromatic properties. Carboxylic acids are generally produced in the industry by fermentation processes, and the final product concentration is approximately 10% in aqueous solution. There are many different methods for the separation of acid from an aqueous solution. One of them is reactive extraction. In this study, it was aimed to remove levulinic acid from aqueous solution by reactive extraction using Tri-n-octylphosphine oxide and environmentally friendly solvents (Diethyl succinate+1-Butyl-3-methylimidazolium hexafluorophosphate). The experimental design was performed, and optimum experimental results were calculated, and data were analyzed with ANOVA. As a result of the experimental study, the maximum extraction efficiency was found as 55.1%. The model equation between the independent variables for the extraction efficiency was determined. According to these data, the obtained R^2 value was calculated as 0.9899.

Çevre Dostu Çözücüler Kullanarak Levulinik Asidin Reaktif Ekstraksiyonunun Deneysel Tasarımı

Anahtar Kelimeler
Levulinik asit,
Reaktif ekstraksiyon,
Iyonik sıvılar,
Karboksilik asit

Özet: Levulinik asit, endüstrinin birçok farklı alanında kullanılan bir karboksilik asittir. Tarım alanında pestisit ve gübre amaçlı olarak kullanılmaktadır ve ayrıca kendine özgü karamel kokusu nedeniyle kozmetik sektöründe ve aromatik özellikleri nedeniyle gıda sanayisinde kullanılır. Karboksilli asitler genellikle endüstride fermantasyon işlemleriyle üretilir ve nihai ürün konsantrasyonu sulu çözeltide yaklaşık % 10'dur. Asitin sulu çözeltiden ayrılması için birçok farklı yöntem vardır. Bunlardan biri reaktif ekstraksiyondur. Bu çalışmada, Tri-n-oktil fosfin oksit ve çevre dostu solventler (Dietil süksinat + 1-Bütil-3-metilimidazolyum hekzafulorofosfat) kullanılarak reaktif ekstraksiyon yoluyla sulu çözeltiden levulinik asidin uzaklaştırılması amaçlanmıştır. Deneysel tasarım uygulanmış ve optimum deney sonuçları hesaplanmış ve veriler ANOVA ile analiz edilmiştir. Deneysel çalışma sonucunda maksimum ekstraksiyon verimliliği % 55.1 olarak bulunmuştur. Ekstraksiyon verimliliği için bağımsız değişkenler arasındaki model denklemi belirlenmiştir. Bu verilere göre, elde edilen R^2 değeri 0.9899 olarak hesaplanmıştır.

1. Introduction

Levulinic acid (LA) is a monocarboxylic acid which contains a ketone group and a carboxylic acid group. These two functional groups make levulinic acid a potentially very versatile building block for the synthesis of various organic chemicals[1]. Levulinic acid is widely used in industrial sectors such as pharmaceuticals, polymers, food and plastics[2].

The conventional way of levulinic acid production is controlled degradation from C6-sugars by mineral acids such as sulfiric acid or hydrochloric acid (aprx. 1-5 %)[3,4]. However, as most of the carboxylic acid production process separation of levulinic acid from diluent solution or wastewater stream is very important because of production costs. The conventional way of purification carboxylic acids is precipitation. Apart from precipitation, there are purification methods such as liquid-liquid extraction,

---

*Corresponding author: aslig@istanbul.edu.tr

electrolysis, crystallization, distillation, liquid membrane, adsorption, reactive extraction[5-9]. Among these separation methods, reactive extraction stands out due to some advantages such as being effective at a high concentration of the substrate, easy reuse of solvents, acquire high purity product with good recovery[10].

Reactive extraction method is based on the reaction between reactant in the organic phase and analyte in aqueous phase. At the end of the reaction, complexes are dissolved in organic phase. Amines are generally selected as a reagent for reactive extraction. However, Tri-n-octylphosphine oxide (TOPO) was chosen as the reactant in this study. The main reason for using TOPO as a reactant is that it is less toxic than amines. [11] It must be diluted with a suitable solvent because it is a solid material. It is important to decide of diluents for reactive extraction because it has an important effect of extraction behavior of reactant [12]. In this study, Diethyl succinate (DES), a dibasic ester, was preferred as a solvent. Dibasic ester is environmentally friendly solvents, and it is preferred because of low toxicity, low cost, high boiling point, viscosity and density close to water in industrial applications [13-15]. However, because of its environmentally friendly, ionic liquids (ILs), such as dibasic esters, are one of the other important solvents. In recent years, the usage of ILs in chemical processes, such as carboxylic acid separation processes, increases due to the lack of vapor pressure. [6, 12] On the other hand, ILs have disadvantages such as have high viscosity and prices. Due to these disadvantages, ILs are used with other solvents such as DES.

This study aims to recover levulinic acid by utilizing IL which is 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIMPF6) and DES with experimental design method in the reactive extraction method.

2. Material and Method

2.1. Theoretical section

In the reactive extraction process, the reaction between an acid (LA) and TOPO can be expressed as the following [11]:

$$pLA(aq) + qTOPOorg \rightarrow (LA)pTOPOq(org) \qquad (1)$$

where p and q stand are the molecule number of LA and TOPO, respectively (aq, aqueous phase; org, organic phase). When the reaction is terminated, (LA)pTOPOq exists in the organic phase by complexing between LA and TOPO. For detailed analysis of the reactive extraction process, the loading factor (Z), the distribution coefficient (D) and the extraction efficiency (E) were determined as follows [16].

$$Z = \frac{C_{a,org}}{C_{e,org}} \qquad (2)$$

where Z is the loading factor which refers to the reactant activity. It is expressed by the ratio of the acid concentration (Ca,org) to the TOPO concentration (Ce,org) in the organic phase.

$$D = \frac{C_{a,org}}{C_a} \qquad (3)$$

where D is the Distribution coefficient which is the concentration ratio of LA in the organic phase to the concentration of LA in the aqueous phase.

$$E = \left(1 - \left(\frac{C_a}{C_{a0}}\right)\right) \times 100 \qquad (4)$$

Finally, Extraction yield or efficiency, defines the percentage of extracted acid from aqueous solution. According to formula, Ca0 is the initial acid concentration and Ca refers to the acid concentration at raffinate phase after extraction.

2.2. Materials

The materials used in the experiments listed in Table 1 with their physical properties.

Table 1. Physical properties of the pure components at 293.15 K

Substance	Source	Purity	ρ, (kg /m^3)
Water	Distilled		999.9
TOPO	Merck	> 98%	831
LA	Merck	> 98%	1130
DES	Merck	> 99%	1040
BMIMPF6	Io-li-tec	> 99%	1380

2.3. Method

For the conventional extraction procedure, LA solution was prepared with three different concentrations (0.6 mol/L, 0.8 mol/L, 1 mol/L) in distilled water and the conventional extraction method on these solutions was carried out separately with pure solvents which are 5 mL DES, 5 mL IL and the mixture of them (4.5mL DES + 0.5mL IL) [2].

The reactive extraction of LA performed according to procedure used by Bilgin et al. [11]. A trial version of Design-Expert 11 was used for experimental design. The reactive extraction experiment between LA and TOPO were optimized using the central composite design [17]. Independent variables; as initial acid concentration (Cao) (X_1), TOPO amount (mTOPO) (X_2) and phase ratio (organic:water) (X_3) were selected. Design table created by Design-Expert is given in Table 2 with coded variables.

According to this table, for each run, 5 mL of LA solution was mixed with different amounts of TOPO (0.1 g, 0.2 g, 0.3 g). BMIMPF6 was added to the same amount (0.5 mL) in all experiments and the mixture was completed with DES according to the designed phase ratio (1:5, 3:5, 5:5). The reactive extraction was carried out in a water bath (Nuve Shaker ST30 thermostated bath; Turkey) for 2 h at 298.15 K. At the end of the extraction time, the mixture was centrifuged (Nuve CN180; Turkey) at 4000 rpm for 10 min to separate the phases. The concentration of levulinic acid in the aqueous phase was determined by acid-base titration method (Schott Titroline Easy module 2; Germany).

Table 2. Experimental design table

Run	Ca_0 (mol/L)	TOPO amount (g)	Phase ratio (Organic: Water)
1	-1	-1	-1
2	1	1	-1
3	-1	1	-1
4	-1	-1	1
5	0	-1	0
6	-1	1	-1
7	-1	-1	-1
8	1	-1	-1
9	1	1	1
10	0	0	0
11	1	1	1
12	-1	1	1
13	0	0	-1
14	0	0	1
15	0	0	0
16	1	-1	1
17	0	0	0
18	0	0	0
19	1	-1	1
20	0	0	0
21	0	0	0
22	-1	0	0
23	1	0	0
24	-1	1	1
25	1	1	-1
26	0	1	0
27	1	-1	-1
28	-1	-1	1

3. Results and Discussion

3.1. Physical extraction

The conventional extraction method based on distribution of LA between two phases was carried out. The D and E values of IL, DES and IL+DES which were calculated with Eq 3-4, were shown in Fig 1, Fig 2. At the end of the extraction, it is observed that different initial acid concentration does not affect conventional extraction efficiency. Therefore, results were given as mean. According to Eq 3, higher D values mean LA amount in the organic phase is more than the water phase. As seen in Fig 1, the distribution coefficients were calculated as 0.26 for IL and 0.74 for DES when the solvents were used alone. However, when selecting the diluent, it is desirable to have higher D and E values.

According to Eq 4, increasing for E values indicates that the extraction was successful. When this value approaches 100%, this means that almost all of the acid is separated from the raffinate phase (15). As seen in Figure 2, the lower extraction efficiencies of IL and DES were obtained 19.4 and 40.25, respectively. However, when the mixture of these two solvents were used, better D (0.91) and E (45.38) values were obtained with respect to single solvent.

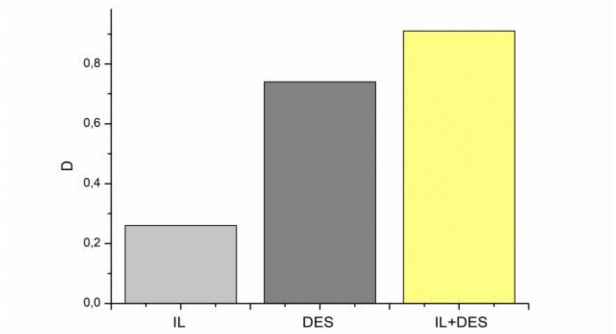

Figure 1. D values of the conventional extraction method with pure solvents

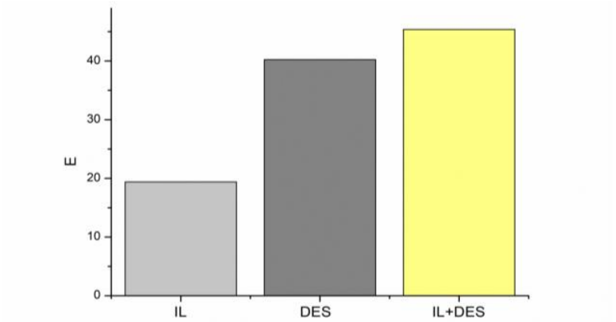

Figure 2. E values of the conventional extraction method with pure solvents

There are several studies in the literature in which conventional extraction methods were used [3, 18]. However, as these studies obtained less extraction efficiencies, trials were continued with reactive extraction [8, 19]. The further experiments was continued with these two solvent mixtures due to the high D and E values. (IL+DES).

3.2. Reactive extraction

The reactive extraction of LA with TOPO+IL+DES system was performed and response surface methodology (RSM) applied to experimental data. Process variables were chosen as Cao, mTOPO and (organic:water) phase ratio with three level -1, 0, 1. The experimental results (D, Z and E values) of the reactive extraction of LA with TOPO at 293.15 K for 1 atm, are given in Table 3. The highest E value (55.10 %) was obtained during the 12th run for 0.6 mol/L initial acid concentration, 0.3 g of TOPO amount and 5:5 Phase ratio of (organic:water).

Table 3. The reactive extraction results of levulinic acid

Run	$(Ce)^E$ (mol/L)	$(CA)^R$ (mol/L)	$(CA)^E$ (mol/L)	D	Z	%E
1	0.2664	0.5405	0.0595	0.1100	0.2232	9.91
2	0.7904	0.7713	0.2287	0.2965	0.2893	22.87
3	0.7775	0.4544	0.1456	0.3205	0.1873	24.27
4	0.0519	0.2918	0.3082	1.0562	5.9343	51.37
5	0.0876	0.4689	0.3311	0.7059	3.7795	41.38
6	0.7860	0.4580	0.1420	0.3099	0.1806	23.66
7	0.2703	0.4922	0.1078	0.2191	0.3990	17.97
8	0.2680	0.8220	0.1780	0.2165	0.6641	17.80
9	0.1565	0.4497	0.5503	1.2237	3.5168	55.03
10	0.1751	0.4576	0.3424	0.7483	1.9556	42.80
11	0.1578	0.4543	0.5457	1.2010	3.4587	54.57
12	0.1556	0.2694	0.3306	1.2273	2.1248	55.10
13	0.5287	0.6401	0.1599	0.2497	0.3024	19.98
14	0.1052	0.3799	0.4201	1.1057	3.9945	52.51
15	0.1752	0.4746	0.3254	0.6858	1.8577	40.68
16	0.0548	0.4897	0.5103	1.0421	9.3067	51.03
17	0.1761	0.4676	0.3324	0.7109	1.8883	41.55
18	0.1729	0.4717	0.3283	0.6962	1.8995	41.04
19	0.0560	0.4876	0.5124	1.0510	9.1471	51.24
20	0.1765	0.4660	0.3340	0.7166	1.8924	41.75
21	0.1783	0.4698	0.3302	0.7027	1.8519	41.27
22	0.1761	0.3469	0.2531	0.7295	1.4368	42.18
23	0.1767	0.5925	0.4075	0.6877	2.3067	40.75
24	0.1578	0.2779	0.3221	1.1590	2.0416	53.68
25	0.7823	0.7849	0.2151	0.2740	0.2749	21.51
26	0.2638	0.4557	0.3443	0.7556	1.3052	43.04
27	0.2623	0.8280	0.1720	0.2078	0.6560	17.20
28	0.0524	0.2937	0.3063	1.0432	5.8519	51.06

Uslu and Kırbaslar reported that LA reactive extraction efficiency was found that 85% with using Tri-octyl amine and diethyl carbonate [19]. Another study with Aliquat 336 and iso amyl alcohol system was also found that 72.1% extraction efficiency [20] . Eda et al. obtained more than 70% LA extraction efficiency with using tri methyl amine and tri-octyl amine which diluents are toluene, heptane and methyl iso butyl ketone[21].

Although the extraction efficiency was lower than all of these studies, the reactants used in these studies were more toxic than TOPO. Therefore, the extraction method obtained by this study is more environmentally friendly and so it is more useful and more suitable method among these reactive extraction methods.

Data obtained from reactive extraction studies were subjected to statistical analysis using one-way analysis of variance (ANOVA). $p < 0.05$ was considered to be indicative of significance according to data in Table 4. Thus, X_2,X_3,X_2X_3,X_3^2 are significant model terms and the model F value (195.44) also indicates that the model is significant. The model equation is given below.

$$Y = 41.63 + 2.49X_2 + 16.69X_3 - 0.98X_2X_3 - 5.55X_3^2 \quad (5)$$

where Y is extraction efficiency as response, X_2 amount of TOPO, X_3 phase ratio of (organic:water).

The "lack of fit F-value" of 1.17 implies the lack of fit is not significant relative to the pure error. There is a 37.33% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is desired and it indicates that the model is fit. The coefficient of regression (R^2) was calculated to be 0.9899 obtained by experimental data and the adjusted R^2 was calculated to be 0.9848 using Design Expert. The fact that both coefficients are close to each other indicates the suitability of this model. Moreover, according to the experimental data, the adequate precision (AP) value which measures the ratio of signal to noise and should be greater than 4, is 38.341. Therefore, this model is appropriate for applying three-dimensional response surface.

The three-dimensional response surface curve was plotted by statistically significant model to understand the relationship between the independent variables and E values (Fig 3, Fig 4, Fig 5). As seen in Fig. 3, the initial acid concentration does not significantly affect the extraction efficiency but TOPO amount effects positively on E%. In addition, the increasing organic phase in the solution increasing the extraction efficiency, too (Fig 4.). Moreover, as seen in Fig. 5, the effectiveness of phase ratio of organic:water on the extraction efficiency is much more than TOPO amount. Consequently, 53.72 %E value with 0.985 desirabilities was reached for 1 mol/L initial acid concentration, 0.3 g TOPO amount and 5:5 phase ratio of organic:water via the optimization the Design Space point using Design Expert.

Table 4. The reactive extraction results of levulinic acid

Source	Sum of Squares	df	Mean square	F	p-Value
Model	5342.03	9	593.56	195.44	<0.0001
X_1	0.43	1	0.43	0.14	0.7096
X_2	111.37	1	111.37	36.67	<0.0001
X_3	5013.9	1	5013.92	1650.9	<0.0001
X_1X_2	5.89	1	5.89	1.94	0.1806
X_1X_3	0.53	1	0.53	0.17	0.6819
X_2X_3	15.48	1	15.48	5.10	0.0367
X_1^2	0.31	1	0.31	0.1	0.7529
X_2^2	0.49	1	0.49	0.16	0.6935
X_3^2	86.7	1	86.7	28.55	<0.0001
Residual	54.67	18	3.04		
Lack of Fit	17	5	3.4	1.17	0.3733
Pure Error	37.66	13	2.9		
Cor Total	5396.7	27			

$R^2=0.9899$ $R_{adj}^2=0.9848$ AP=38.341 %CV=4.57 SD=1.74

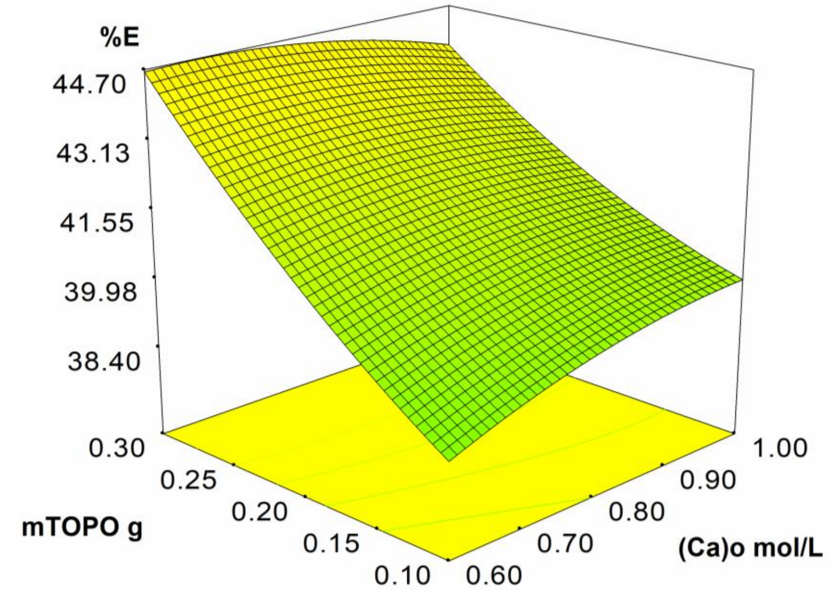

Figure 3. Extraction efficiency plot according to initial acid Ca_0 concentration and TOPO amount

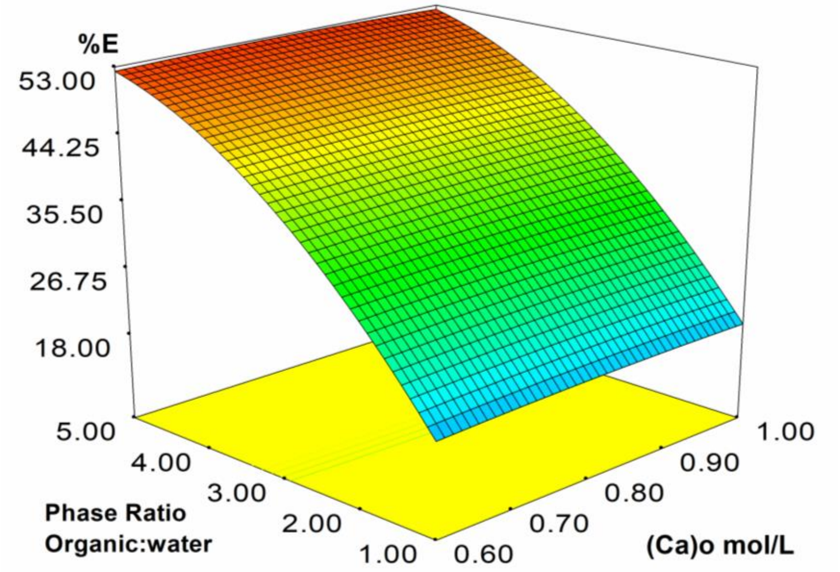

Figure 4. Extraction efficiency plot according to initial acid Ca_0 concentration and phase ratio of organic: water

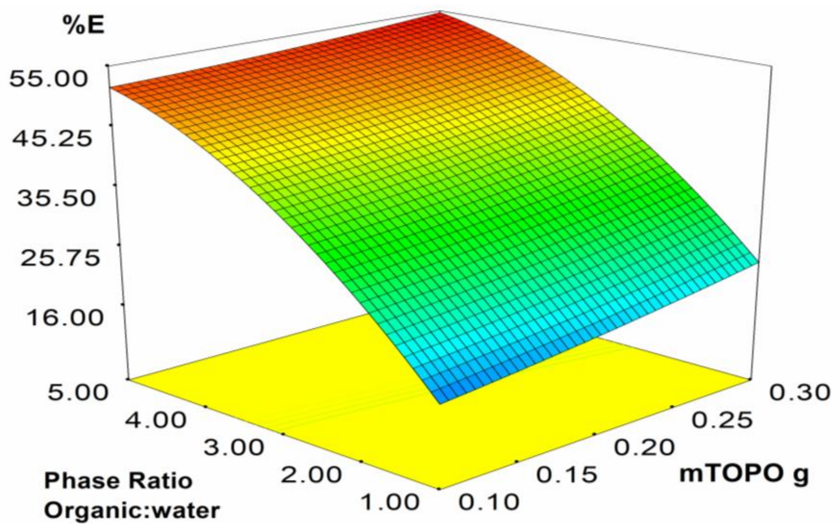

Figure 5. Extraction efficiency according to TOPO amount and phase ratio organic:water

4. Conclusion

This study introduces the removal of LA from aqueous solutions by reactive extraction using DES and IL solvents. RSM and the statistical analysis method were applied to the experimental data. The R^2 (0.9899) value obtained by the statistical analysis was found to be suitable with the adjusted R^2 (0.9848) value. Therefore, the model equation was found to be appropriate. Based on the data obtained in this study, it was concluded that the maximum extraction efficiency (55.10 %) was higher than the optimization the Design Space point using Design Expert (53.72 %). For further studies effect of increasing ILs amount can be investigated. Also different solvents can be investigate with ILs to see if there is a synergetic effect between different solvents.

Appendices

Symbols and abbreviations

BMIMPF6-1-Butyl-3-methylimidazolium hexafluorophosphate
TOPO- Tri-n-octylphosphine oxide
mTOPO- Amount of TOPO ,g
$(Ca)_R$ - Concentration of acid in the aqueous phase, mol/L
$(Ca)_E$ - Concentration of acid in the organic phase, mol/L
$(Ce)_E$ - Concentration of TOPO in the organic phase, mol/L
$(Ca)_0$ – Initial Acid concentration mol/L
D - Distribution coefficient
E - The efficiency of extraction
LA – Levulinic Acid
IL - Ionic liquid (BMIMPF6)
p - Number of acid molecules
q - Number of TOPO molecules
Z - Loading factor
aq - aqueous phase
org - organic phase

References

[1] Girisuta, B., Janssen, L. P. B. M., Heeres, H. J., 2006. Green chemicals a kinetic study on the conversion of glucose to levulinic acid. Chem. Eng. Res. Des., 84, 339–349.

[2] Datta, D., Marti, M. E., Pal, D., Kumar, S., 2017. Equilibrium study on the extraction of levulinic acid from aqueous solution with aliquat 336 dissolved in different diluents: solvent's polarity effect and column design. J. Chem. Eng. Data, 62(1), 3-10.

[3] Laitinen, A.T., Penttila, K. J. T., Kaunisto, J. M., 2016. Physical solvent extraction of levulinic acid from dilute aqueous solution with 2-methyltetrahydrofuran, Sep. Sci. Technol., 51(3), 465-473.

[4] Chang, C., Cen, P., Ma, X., 2007. Levulinic acid production from wheat straw, Bioresour. Technol. 98, 1448-1453.

[5] Baylan, N., Cehreli, S., Ozparlak, N., 2017. Transport and separation of carboxylic acids through bulk liquid membranes containing tributylamine, J. Dispersion Sci. Technol., 38(6), 895-900.

[6] Baylan, N., Cehreli, S., 2018. Ionic liquids as bulk liquid membranes on levulinic acid removal: A design study, J. Mol. Liq., 266, 299-308.

[7] Senol, A., 2000. Extraction equilibria of formic and levulinic acids using Alamine 308/diluent and conventional solvent systems, Sep. Purif. Technol., 21(1-2), 165-179.

[8] Uslu, H., Kirbaslar, S. I., 2008. Investigation of levulinic acid distribution from aqueous phase to organic phase with TOA extractant, Ind. Eng. Chem. Res., 47(14), 4598-4606.

[9] Lalikoglu, M., Gok, A., Gok, M. K., Asci, Y. S., 2015. Investigation of lactic acid separation by layered

double hydroxide: equilibrium, kinetics, and thermodynamics, J. Chem. Eng. Data, 60(11), 3159-3165.

[10] Datta, D., Marti, M. E., Uslu, H., Kumar, S., 2016. Extraction of levulinic acid using tri-n-butyl phosphate and tri-n-octylamine in 1-octanol: Column design. Journal of the Taiwan Institute of Chemical Engineers, 66, 407-413.

[11] Bilgin, M., Arisoy, C., Kirbaslar, S. I., 2009. Extraction equilibria of propionic and butyric acids with tri-n-octylphosphine oxide/diluent systems, J. Chem. Eng. Data, 54(11), 3008-3013.

[12] Aşçı, Y., S., 2017. Examination of the efficiency of ionic liquids in glycolic acid separation from aqueous solution by using reactive extraction method, JOTCSA, 4(3), 981-992.

[13] Gok, A., Kirbaslar, S. I., Uslu, H., Gilani, H. G., 2011. Liquid-liquid equilibria of (water plus butyric acid plus diethyl succinate or diethyl glutarate or diethyl adipate) ternary systems, Fluid Phase Equilib., 303(1), 71-75.

[14] Kirbaslar, S. I., Sahin, S., Bilgin, M., 2007. (Liquid + liquid) equilibria of (water + propionic acid + diethyl succinate or diethyl glutarate or diethyl adipate) ternary systems, J. Chem. Thermodyn., 39(11), 1463-1469.

[15] Kirbaslar, S. I., Sahin, S., Bilgin, M., 2007. Liquid-liquid equilibria of (water +acetic acid + diethyl succinate or diethyl glutarate or diethyl adipate) ternary systems. J. Chem. Eng. Data, 52(3), 1108-1112.

[16] Uslu, H., 2008. Reactive extraction of levulinic acid using TPA in toluene solution: LSER modeling, kinetic and equilibrium studies, Sep. Sci. Technol., 43(6), 1535-1548.

[17] Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., Escaleira, L. A.,2008. Response surface methodology (RSM) as a tool for optimization in analytical chemistry, Talanta, 76(5), 965-977.

[18] Uslu, H., Gok, A., Kirbaslar, S. I., 2009. Phase equilibria of (water + levulinic acid + dibasic esters) ternary systems", Fluid Phase Equilib., 282(1), 20-24.

[19] Uslu, H., Kirbaslar, S. I., 2008. Equilibrium studies of extraction of levulinic acid by (trioctylamine (TOA) + ester) solvents, J. Chem. Eng. Data, 53(7), 1557-1563.

[20] Uslu, H., Kirbaslar, S. I., 2009. Investigation of phase equilibria of levulinic acid distribution between aqueous phase to organic phase by Aliquat 336 in different modifiers", J. Chem. Thermodyn., 41(9), 1042-1048.

[21] Eda, S., Kota, B. J., Thella, P. K., Bankupalli, S., Bhargava, S. K., Parthasarathy, R., 2017. Regeneration of levulinic acid from loaded-organic phase: equilibrium, kinetic studies and process economics, Chem. Pap., 71, 1939–1951.