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Title: **RECOVERY OF LEVULINIC ACID FROM AN AQUEOUS PHASE BY REACTIVE EXTRACTION USING TRI-N OCTYLAMINE IN 1-DECANOL**
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RECOVERY OF LEVULINIC ACID FROM AN AQUEOUS PHASE BY REACTIVE EXTRACTION USING TRI-N-OCTYLAMINE IN 1-DECANOL

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Abstract

Reactive extraction of levulinic acid from aqueous solutions using tri-n-octylamine (TOA) in 1-decanol was investigated at room temperature. The experimental data were used to determine the distribution coefficient (K_D), extraction efficiency ($E\%$), loading ratio (Z), stoichiometric loading factor (Z_S) and modified separation factor (S_f). The distribution coefficient and extraction efficiency were found to be less by physical extraction. A maximum distribution coefficient (K_D) was obtained as 4.8575 using 40% TOA (0.9059 mol/L) while 82.92% of the levulinic acid was extracted. By increasing the initial concentration of levulinic acid resulted in a decrease in distribution coefficient and extraction efficiency. The distribution coefficient and extraction efficiency increased by increasing the tri-n-octylamine concentration from 10 to 40% (0.2264 mol/L to 0.9059 mol/L). The data obtained are useful in understanding the equilibrium characteristics.

Keywords: Reactive extraction, Levulinic acid, Tri-n-octylamine (TOA), 1-Decanol, Equilibrium

1. Introduction

Over the last few decades, carboxylic acids are produced using fermentation technology [1]. The separation and purification of carboxylic acids from fermentation broth are economically impracticable. The distribution coefficient and extraction efficiency were considered to be less by using conventional methods such as membrane separation, solvent extraction, liquid-liquid extraction, ultrafiltration, reverse osmosis, distillation, dialysis, electrodialysis, adsorption and ion exchange [2, 3, 4]. To overcome the drawbacks of conventional methods for the separation of carboxylic acids, scientists discovered an ingenious separation method known as reactive

extraction.

Reactive extraction is an efficient, economical and eco-friendly method of separation. The solute molecule in the aqueous phase is interacted with extractant molecule in the organic phase to form reaction complex which is dissolved in the organic phase [5]. To enhance the physical properties of extractant in the organic phase, diluents are added. There are many advantages of reactive extraction such as extraction efficiency is high, reactor productivity is increased, reduces cost of solvent recovery, better control of pH, decreases the downstream processing load and phase equilibrium is improved [6].

Levulinic acid ($C_5H_8O_3$, 4-Oxopentanoic

acid) is a carboxylic acid [7]. It has a ketone structure. It is soluble in water and polar organic solvents. It is produced from the degradation of cellulose. It was distinguished by the “US Department of Energy as one of the top 12 value-added biochemical” [8]. It has several applications in various industries like foods and beverages, pharmaceuticals, polymers, textiles, plastics, cosmetics etc [9, 10]. The demand for levulinic acid is increasing globally due to its potential uses.

In the present study, a probe on the extraction of levulinic acid from aqueous solution was aimed by using Tri-n-octylamine in 1-decanol. The equilibrium parameters such as distribution coefficient (K_D), extraction efficiency ($E\%$), loading ratio (Z), stoichiometric loading factor (Z_S) and modified separation factor (S_f) are evaluated using experimental data.

2. Theoretical Background:

2.1 Physical Extraction

Physical extraction involves the extraction of solute into inert non reacting hydrocarbons and substituted hydrocarbons and is relatively free of complexities. The chemical reactions take place during physical extraction as shown in Figure 1. (a) The ionization of levulinic acid in the aqueous phase. (b) The partial dissociation of the acids between two phases. (c) Dimerization of the levulinic acid in the organic phase.

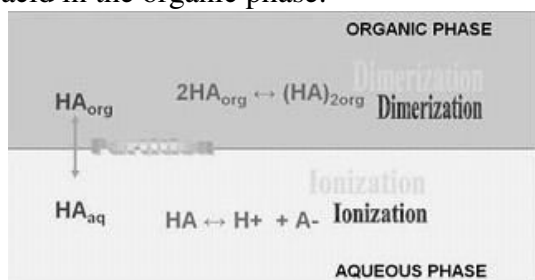


Figure 1: Illustration of Physical Extraction.

2.2 Reactive Extraction

The reactive extraction of levulinic acid ($[HA]$) with TOA ($[T]$) gives reaction complex ($T : (HA)_n$) which remains largely in the organic phase. Keeping in view that the exact chemistry involved in the uptake of extra acid is unknown, the distribution coefficient can be interpreted by the following set of equations:

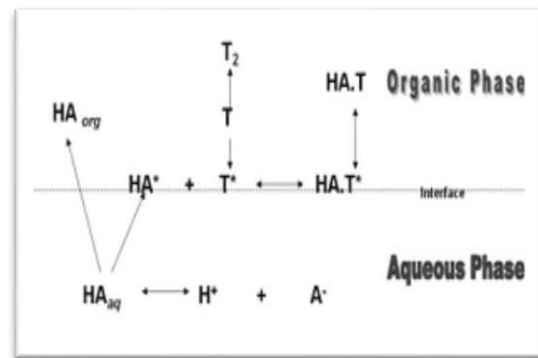
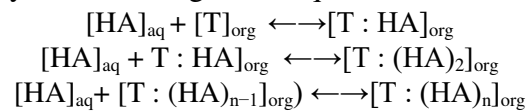


Figure 2: Illustration of Reactive Extraction.

The extraction process was analysed through the extraction efficiency and distribution coefficient. The extraction efficiency is defined as the ratio of Levulinic acid concentration in the organic phase $[HA]_{org}$ to the Levulinic acid concentration in aqueous solution by assuming no change in volume at equilibrium [11,12,13,14]. The distribution coefficient (K_D) is calculated with the relation as given

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \quad (1)$$

Extraction efficiency ($E\%$) is calculated as

$$E\% = \frac{K_D}{1+K_D} \times 100 \quad (2)$$

The extent to which the organic phase (TOA + 1-Decanol) can be loaded with organic acid is expressed as the loading

ratio. It is defined as the ratio of total concentration of acid in the organic phase $[HA]_{org}$ to the total concentration of solvent in the organic phase $[T]$ [15,16,17].

$$z = \frac{[HA]_{org}}{[T]} \quad (3)$$

The stoichiometric loading factor (Z_s), is the ratio of the overall complexed acid to total solvent in the organic phase [18]. This factor includes a correction term, ($v [HA]_{org}^{diluent}$) for the amount of acid extracted by the diluent in the solvent mixture. The stoichiometric loading Factor (Z_s), can be calculated using the equation (4).

$$z_s = \frac{[HA]_{org} - v [HA]_{org}^{diluent}}{[T]} \quad (4)$$

Where v is the volume fraction of diluent in the mixture and $[HA]_{org}^{diluent}$ is the concentration of acid extracted by the pure diluent alone not containing solvent.

Modified Separation Factor (S_f) is defined as the ratio of the complexed acid to overall extracted acid [19].

$$S_f = \frac{[HA]_{org}}{[HA]_{org} + [HA]_{org}^{diluent}} \quad (5)$$

3. Materials and methods:

3.1 Materials

Levulinic Acid ($C_5H_8O_3$, 4-Oxopentanoic acid), molar mass 116.12 g/mol, density 1.134 g/ml, 98 % purity was obtained from Sigma-Aldrich (India). Tri-n-octylamine ($C_{24}H_{51}N$), molar mass 353.67 g/mol, density 0.801 g/ml, 98 % purity, used as extractant from Sigma-Aldrich (India). 1-Decanol ($C_{10}H_{22}O$), straight-chain fatty alcohol with ten carbon atoms, molar mass 158.28 g/mol, density 0.8297 g/ml, 98 % purity was used as a diluent was obtained from Sigma-Aldrich (India). Distilled water was used to prepare the solutions of

various concentrations of levulinic acid. Sodium Hydroxide (NaOH) used for titration is of laboratory grade. Phenolphthalein solution with pH range 8.2 to 10 was used as an indicator was obtained from Ranbaxy, India. All chemicals were used without further purification.

3.2 Methods

3.2.1 Equilibrium Studies:

The optimal time (12 hours) to achieve a liquid-liquid equilibrium for physical and chemical extraction was calculated by analysing the samples at regular intervals of time. The initial concentrations of levulinic acid were 0.4686, 0.5467, 0.6248, 0.7029 and 0.781 mol / L, respectively.

3.2.2 Physical equilibrium:

For physical equilibrium, 20 ml of levulinic acid (aqueous phase) at different concentrations were added to different conical flasks and 20 ml of 1-decanol (organic phase) was added to each conical flask. The mechanical shakers were used to thoroughly mix the immiscible phases for 12 hours at room temperature. Both phases were allowed to stand for 2 hours in a separatory funnel. The aqueous phase was titrated with 0.1N NaOH using phenolphthalein as an indicator to measure the levulinic acid concentration in the aqueous phase. The mass balance was used to calculate the levulinic acid concentration in the organic phase.

3.2.3 Chemical equilibrium:

For the chemical equilibrium, 20 ml of levulinic acid (aqueous phase) and 20 ml of 10% tri-n-octylamine (TOA) (0.2264 mol/L) in 1-decanol (diluent) were added. (Organic phase). The immiscible mixture was sustained in mechanical shakers for 12 hours and then permitted to an impasse for 2 hours. Levulinic acid concentration was determined from the aqueous phase by titrating with 0.1N NaOH using

phenolphthalein as an indicator. The same procedure as shown in Figure 3, was repeated for 20%, 30% and 40% TOA.

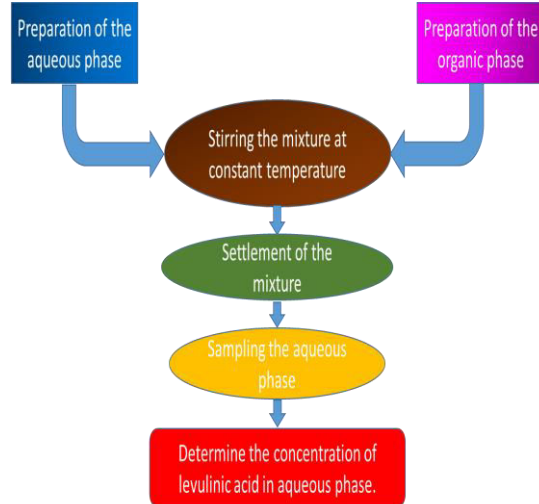


Figure 3: Experimental procedure

4. Results and discussion

The data obtained from the experiments are hoarded and evaluated to determine the amount of levulinic acid extracted from the aqueous solution using physical and chemical equilibrium methods with different concentrations of TOA (0.2264 mol/L to 0.9059 mol/L). Using the equilibrium data, the distribution coefficient (K_D), the extraction efficiency (E%), the loading ratio (Z), the stoichiometric load factor (Z_s) and the modified separation factor (S_f) are calculated.

4.1 Physical equilibrium

According to literature survey, low molecular weight diluents tend to be miscible with water while high molecular weight ones offer lower extraction efficiency due to their lower polarity [20]. Among the diluents explored, alcohols are flaunted to be the most effective ones. As they escalate the extraction of carboxylic acid [21]. The levulinic acid extracted in the physical equilibrium method with 1-decanol and various initial concentrations of the levulinic acid

showed that the concentration of the levulinic acid extracted in the aqueous phase and the organic phase is directly proportional to the initial concentration of the levulinic acid, as shown in Figure 4. It was observed that the highest distribution coefficient (K_D) is 0.157 was obtained by 1-decanol with only 13.57% recovery of levulinic acid. Thus, to amplify the extraction efficiency, Tri-n-octylamine is used as an extractant to recovery levulinic acid.

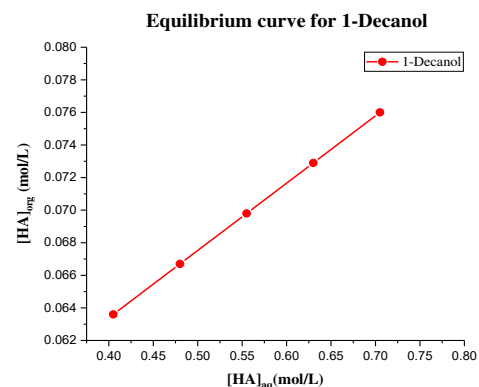


Figure 4: Physical extraction equilibrium curve for extraction of levulinic acid using 1-decanol.

Before progressing with chemical equilibrium, a pilot experiment was conducted to examine the change in the concentration of levulinic acid extracted in aqueous phase with the initial concentration of levulinic acid (0.4686 mol/L) in different TOA concentrations (10% to 60%). As shown in Figure 5, it was found that the distribution coefficient (K_D) and the extraction efficiency (E%) increased from 10% to 40% TOA (0.2264 mol/L to 0.9059 mol/L) and then steadily decreased, because of the back extraction. Therefore, the present study on chemical equilibrium considers the TOA concentration of 10 to 40% (0.2264 mol/L to 0.9059 mol/L).

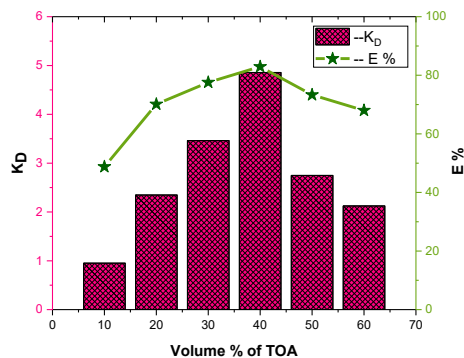


Figure 5: Effect of volume percentage of TOA in 1-decanol on distribution coefficient and extraction efficiency for extraction of 0.4686 mol/L levulinic acid.

4.2 Chemical Equilibrium

The experimental results obtained from chemical equilibrium with four different concentrations of TOA (0.2264 mol/L to 0.9059 mol/L) in 1-decanol and five different concentrations of levulinic acid (0.4686, 0.5467, 0.6248, 0.7029 and 0.781 mol/L) were considered. From Figure 6, there is an undeviating increase in the concentration of levulinic acid extracted in both phases. A maximum distribution coefficient (K_D) was obtained as 4.8575 using 40% TOA (0.9059 mol/L), as shown in Figure 7. From Figure 8, the maximum extraction efficiency (E %) was 82.92% of the initial levulinic acid was extracted using 40% TOA. The distribution coefficient (K_D) values obtained have indicated that the maximum distribution coefficient (K_D) of 0.9525 when the initial concentration of levulinic acid is 0.4686 mol/L and minimum distribution coefficient (K_D) of 0.627 when the initial concentration is 0.781 mol/L with 10% TOA (0.2264 mol/L). The same vogue was observed when levulinic acid is extracted with various concentrations of

the TOA i.e. 20%, 30% and 40%. The amount of levulinic acid extracted is found to be maximum when the initial concentration of the levulinic acid is 0.4686 mol/L because the concentration of levulinic acid in the aqueous solution of the fermentation broth was less than 10% w/w [22].

As the concentration of TOA increased from 10% to 40% (0.2264 mol/L to 0.9059 mol/L) there is a substantial increase in the distribution coefficient (K_D) and Extraction Efficiency (E%). From Figure 9, the loading ratio (Z) increases with increase in the concentration of levulinic acid in the aqueous phase. The loading ratio decreases with an increase in the concentration of TOA because more acid molecules involving complexes are formed at lower concentrations of TOA. From Figure 10, the stoichiometric loading ratio increases with an increase in the concentration of levulinic acid in the aqueous phase and decreases with increase in the concentration of TOA. From Figure 11, the modified separation factor slightly increases with an increase in the concentration of levulinic acid in the aqueous phase and concentration of TOA.

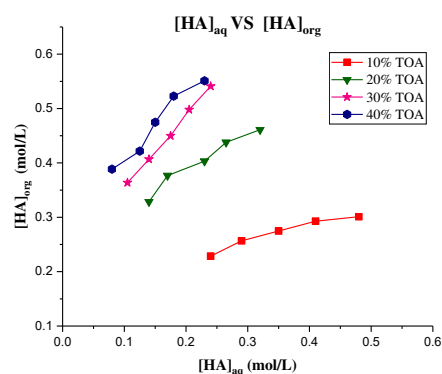


Figure 6: Equilibrium for reactive extraction of levulinic acid with various concentrations of TOA in 1-decanol.

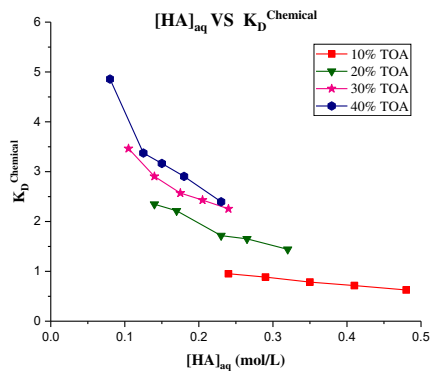


Figure 7: Effect of concentration of levulinic acid in the aqueous phase on Distribution Coefficient with variable TOA Concentration in 1-decanol

loading ratio (Z) with variable TOA concentration in 1-decanol

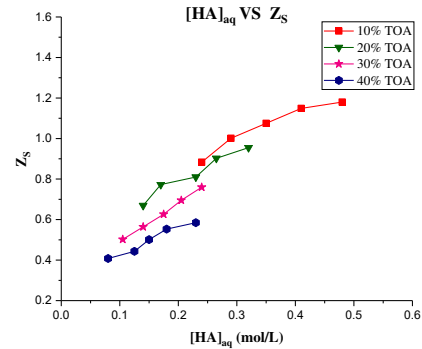


Figure 10: Effect of concentration of acid in aqueous phase on stoichiometric loading factor (Z_s) with variable TOA concentration in 1-decanol.

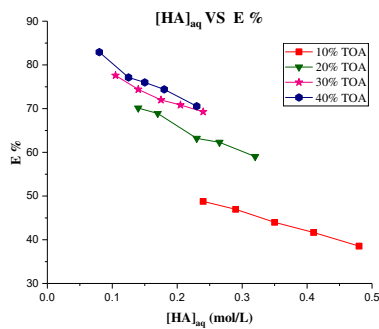


Figure 8: Effect of concentration of levulinic acid in the aqueous phase on extraction efficiency with variable TOA concentration in 1-decanol

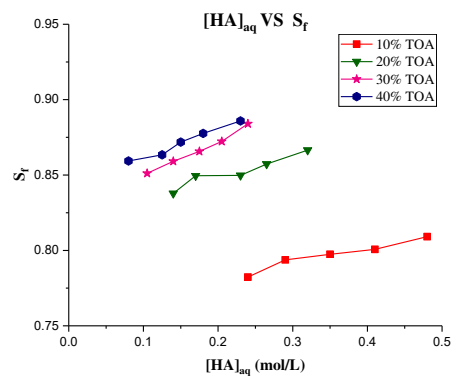


Figure 11: Effect of concentration of acid in the aqueous phase on Modified Separation Factor (S_f) with variable TOA concentration in 1-decanol.

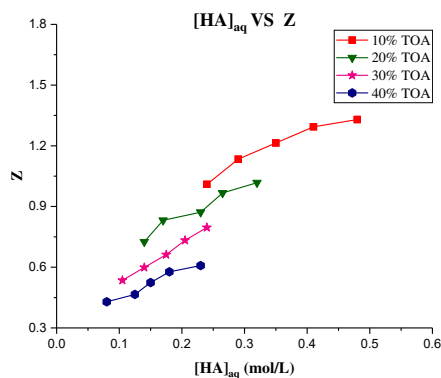


Figure 9: Effect of concentration of levulinic acid in the aqueous phase on loading ratio (Z)

5. Conclusion

In the present study, the reactive extraction of levulinic acid using TOA dissolved in 1-decanol was investigated. The time required for the maximum extraction is 12 hours. By comparing the physical and chemical equilibrium results, for the extraction of levulinic acid, chemical equilibrium provided maximum distribution coefficient and extraction efficiency. The extraction of levulinic acid using TOA increased with decrease in the

initial concentration of levulinic acid and increase in TOA concentration. The distribution coefficient, extraction efficiency and modified separation factor increases with an increase in the concentration of TOA. The loading ratio and stoichiometric loading factor decrease with increase in TOA concentration.

Nomenclature

K_D	distribution coefficient
$E\%$	extraction efficiency
Z	loading ratio
Z_S	Stoichiometric loading factor
S_f	Modified separation factor
[HA]	Concentration of levulinic acid (mol/L)
[T]	Concentration of Tri-n-octylamine (mol/L)
Subscripts	
aq	aqueous phase
org	organic phase

Declaration of Competition of interest:

The authors declare that there is no competing interest in publishing this article.

References:

[1] Sushil Kumar, B.V. Babu, Process Intensification for Separation of carboxylic acids from fermentation broths using reactive extraction, *i-manager's Journal on Future Engineering and Technology*, 2008, 3(3), 21-28. <https://doi.org/10.26634/jfet.3.3.643>

[2] Dipaloy Datta, Mustafa Esen Marti, Dharm Pal, Sushil Kumar, 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, *Journal of Chemical and Engineering data*, 2016

[3] Dipaloy Datta, Mustafa Esen Marti, Hasan Uslu, Sushil Kumar, 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*, 2016, 66, 407-413.

[4] A. Keshav, K.L.Wasewar, S.Chand, Extraction of propionic acid from model solutions: Effect of pH, salts, substrate, and temperature, *AIChE*, 2009, 55, 1705-1711

[5] T. Prathap Kumar, B. Vishwanadham, K.N.Prasanna Rani, M.Mallikarjun, V.V.Basava Rao, Reactive extraction of levulinic acid from aqueous solutions with Tri-n-octylamine(TOA) in 1-octanol: Equilibria, Kinetics, and Model Development, *Chem Eng Comm*, 2011, 198,572-589.

[6] Dipaloy Datta, Sushil Kumar, Hasan Uslu, Status of the Reactive Extraction as a Method of Separation, *Journal of chemistry*, 2015, 1-16.

[7] T. Prathap Kumar, B. Vishwanadham, K.N.Prasanna Rani, M.Mallikarjun, V.V.Basava Rao, Reactive extraction of levulinic acid from aqueous solutions with Tri-n-octylamine(TOA) in 1-octanol: Equilibria, Kinetics, and Model Development, *Chem Eng Comm*, 2011, 198,572-589.

[8] Dipaloy Datta, Mustafa Esen Marti, Hasan Uslu, Sushil Kumar, 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*, 2016, 66, 407-413.

- [9] Hasan Uslu, S. Ismail Kirbaslar, Kailas L. Wasewar, Reactive Extraction of levulinic acid by amberlite LA-2 extractant, *J. Chem. Eng. Data.*, 2009, 54, 712-718.
- [10] Hasan Uslu, S. Ismail Kirbaslar, Asli Gok, Phase equilibria of (water + levulinic acid + alcohol) ternary systems, *Fluid Phase Equilibria*, 2008, 273, 21-26.
- [11] A.Keshav, K.L.Wasewar, S.Chand, Extraction of propionic acid using different extractants (Tri-n-butylphosphate, Tri-n-octylamine, aliquat 336), *Ind. Eng. Chem. Res.*, 2008, 47, 6192-6196.
- [12] T. Prathap Kumar, B. Vishwanadham, K.N.Prasanna Rani, M.Mallikarjun, V.V.Basava Rao, Reactive extraction of levulinic acid from aqueous solutions with Tri-n-octylamine(TOA) in 1-octanol: Equilibria, Kinetics, and Model Development, *Chem Eng Comm*, 2011, 198,572-589.
- [13] Hasan Uslu, S. Ismail Kirbaslar, Kailas L. Wasewar, Reactive Extraction of levulinic acid by amberlite LA-2 extractant, *J. Chem. Eng. Data.*, 2009, 54, 712-718
- [14] A.Keshav, K.L. Wasewar, S.Chand, extraction of propionic acid with Tri-n-octylamine in different diluents, *Separation and Purification Technology*, 2008, 63,179-183
- [15] T. Prathap Kumar, B. Vishwanadham, K.N.Prasanna Rani, M.Mallikarjun, V.V.Basava Rao, Reactive extraction of levulinic acid from aqueous solutions with Tri-n-octylamine(TOA) in 1-octanol: Equilibria, Kinetics, and Model Development, *Chem Eng Comm*, 2011, 198,572-589.
- [16] Hasan Uslu, S. Ismail Kirbaslar, Kailas L. Wasewar, Reactive Extraction of levulinic acid by amberlite LA-2 extractant, *J. Chem. Eng. Data.*, 2009, 54, 712-718.
- [17] A.Keshav, K.L. Wasewar, S.Chand, extraction of propionic acid with Tri-n-octylamine in different diluents, *Separation and Purification Technology*, 2008, 63,179-183
- [18] A.Keshav, K.L. Wasewar, S.Chand, extraction of propionic acid with Tri-n-octylamine in different diluents, *Separation and Purification Technology*, 2008, 63,179-183
- [19] A.Keshav, K.L. Wasewar, S.Chand, extraction of propionic acid with Tri-n-octylamine in different diluents, *Separation and Purification Technology*, 2008, 63,179-183
- [20] Dipaloy Datta, Mustafa Esen Marti, Hasan Uslu, Sushil Kumar, 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*, 2016, 66, 407-413
- [21] Hasan Uslu, S. Ismail Kirbaslar, Investigation of levulinic acid distribution from aqueous phase to organic phase with TOA Extractant, *Ind. Eng. Chem. Res.*, 2008, 47, 4598-4606.
- [22] Dipaloy Datta, Mustafa Esen Marti, Hasan Uslu, Sushil Kumar, Extraction of levulinic acid using tri-n-butyl phosphate and Tri-n-octylamine in 1-octanol: Column design, *Journal of the Taiwan*



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