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Reactive Extraction of levulinic acid using tri-n-Octylamine in 1-hexanol

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ABSTRACT---Reactive extraction of levulinic acid using tri-n-octylamine (TOA) in 1-hexanol was investigated by physical and chemical extractions from aqueous solution at room temperature. Using the equilibrium data, the distribution coefficient (K_D), extraction efficiency (E %), loading ratio (Z), stoichiometric loading factor (Z_S) and modified separation factor (S_f) are evaluated. It was observed that chemical extraction provided a better yield than physical extraction. A maximum K_D was obtained as 10.715 using 40% TOA (0.9059 mol/L) while 91.46 % of the levulinic acid was extracted. By increasing the initial concentration of levulinic acid resulted in a decrease of K_D and E%. The K_D and E% increased by increasing the TOA concentration from 10 to 40 % (0.2264 mol/L to 0.9059 mol/L).

Keywords: Reactive extraction, Levulinic acid, 1-Hexanol, Tri-n-octylamine, Equilibrium

I. INTRODUCTION

The carboxylic acids like tartaric acid, formic acid, pyruvic acid, acetic acid, succinic acid propionic acid, lactic acid, citric acid, levulinic acid, malic acid etc., are produced using aerobic fermentation process from past few decades. Separation of carboxylic acids from fermentation broth is anintriguing task. Since the downstream processing of carboxylic acids not only account for up to 50-60% of the manufacturing cost but also generates a large amount of solid wastes[**Error! Reference source not found.**]. With the burgeoningemphasis of production of carboxylic acidfrom fermentation technology. It is significant to originate an efficient, eco-friendly and economical method to separate carboxylic acids from fermentation broth [**Error! Reference source not found.**]. Several separation techniques have been researched for the separation of carboxylic acids like membrane separation, solvent extraction, liquid-liquid extraction, ultrafiltration, reverse osmosis, distillation, dialysis, electrodialysis, adsorption and ion exchange [**Error! Reference source not found.**, **Error! Reference source not found.**, **Error! Reference source not found.**, **Error! Reference source not found.**]. These separation methods have certain drawbacks such as efficiency is less, expensive, the intricacy of operation and utilization of energy is huge. Reactive extraction with a desirable organic solvent has proved to be an efficient method to separate carboxylic acids from fermentation broth.

Reactive extraction is a separation technique used to enhance the extraction of solute from the AP to the OP. The extractant molecule reacts with the solute molecule to form a reaction complex, which will stabilize in OP due to the hydrogen bonding with 1-hexanol and hydrophobic nature of complex [**Error! Reference source not found.**]. Reactive extraction has variousrewardslikeenhanced reactor productivity, ameliorate control over pH in the bioreactor, reduces the downstream processing load, minimizes the solvent recovery cost, phase equilibrium enhanced and higher efficiency [**Error! Reference source not found.,Error! Reference source not found.**]. Therefore, it has fascinated several scientists to research the process and the effect of distinct parameters like the effect of pH, effect of temperature, kinetics of extraction and concentration of acid, extractant and diluents.

We know that Levulinic acid ($C_5H_8O_3$) is a carboxylic acid. It has a ketone structure. It is a sustainable chemical manufactured or produced from lignocellulosic materials like sugars, corn starch etc. It is classified as one of the 12 essential chemical building blocks due to its numerous potential uses as fuel additives, herbicides, pharmaceuticals, anti-inflammatory drugs, foods and beverages, plastics, synthetic fibres polymers and cosmetics [**Error! Reference source not found.,Error! Reference source not found.,Error! Reference source not found.,Error! Reference source not found.**]. With the ever increased demand for levulinic acid globally. Levulinic acid demand in growth rate is predicted to increase by 33.5% annually by 2021 [**Error! Reference source not found.**].

In thecurrentwork, an investigation on the recovery of levulinic acid from aqueous solution was aimed by employingTOA in 1-hexanol. The equilibrium parameters such as K_D, E %, Z, Z_S and S_f are evaluated using experimental data. There is no study available in the literature by using TOA as extractant and 1-hexanol as diluent. In this regard, this investigation will fill acrucial lack of literature.

II. THEORY

In reactive extraction, exclusively the undissociated form of the levulinic acid present in the AP reacts with TOA in the OP to form acid-amine complexes which remain mostly in the OP.

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Levulinic acid exists as a dimer in the OP due to intermolecular hydrogen bonding [**Error! Reference source not found.**]. By using mass action law, equilibrium data can be interpreted.

The extraction process was analysed through the K_D. It is a proportion of the concentration of levulinic acid in the OP ($[HA]_{org}$) to the concentration of levulinic acid in the AP ($[HA]_{aq}$) by assuming no change in volume at equilibrium [5,6,8,9, **Error! Reference source not found.**,12,13,].

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

The extraction efficiency (E%) is defined as the proportion of levulinic acid concentration in the OP ($[HA]_{org}$) to the sum of levulinic acid concentration in organic and AP[**Error! Reference source not found.**,**Error! Reference source not found.**,**Error! Reference source not found.**,**Error! Reference source not found.**].

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

The extent to which the OP (TOA+1-hexanol) can be loaded with levulinic acid is known as the loading ratio (Z)[**Error! Reference source not found.**, **Error! Reference source not found.**, **Error! Reference source not found.**,**Error! Reference source not found.**, **Error! Reference source not found.**, **Error! Reference source not found.**]. It is defined as the proportion of the total concentration of levulinic acid in the OP ($[HA]_{org}$) to the total concentration of TOA in the OP [T].

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

The stoichiometric loading factor (Z_S) is the proportion of the overall complexed acid to total solvent in the OP. This factor includes a correction term, ($v\,[HA]_{org}^{diluent}$) for the amount of acid extracted by the diluent in the solvent mixture [**Error! Reference source not found.**].

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

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 in the absence of solvent.

The modified separation factor (S_f) is defined as the proportion of complexed acid to overall extracted acid [**Error! Reference source not found.**,**Error! Reference source not found.**].

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

III. MATERIALS AND METHODS

Materials

Levulinic Acid ($C_5H_8O_3$), molar mass 116.11 kg/kmol, density 1.134 g/ml at 25^{0}C, 97 % purity was procured from Sigma-Aldrich (India). TOA (N,N-dioctyloctan-1-amine) ($C_{24}H_{51}N$), molar mass 353.67 kg/kmol, density 0.810 g/ml at 20^{0}C, 98 % purity, was procured from Sigma-Aldrich (India). 1-Hexanol (Hexyl alcohol, $C_6H_{14}O$), molar mass 102.17 kg/kmol, density 0.814 g/ml at 25^{0}C, 98 % purity was used as a diluent was obtained from Sigma-Aldrich (India). Distilled water has been utilized to make the solutions of respective concentrations of levulinic acid. Sodium Hydroxide (NaOH) used for volumetric analysis is of laboratory grade. Phenolphthalein solution with pH range 8.2 to 10 was used as an indicator was procured from Ranbaxy, India.

Methods

Equilibrium Studies:

Optimum time was calculated (12 hours) to attain liquid-liquid equilibrium for both physical extraction and chemical extraction by analyzing the samples at regular intervals of time. The initial concentrations of levulinic acid were 0.4686, 05467, 0.6248, 0.7029 and 0.781 mol/L respectively.

Physical equilibrium:

For physical equilibrium, 20 ml of levulinic acid (AP) of different concentrations were taken in different conical flasks and 20 ml of 1-hexanol (OP) was added in each conical flask. Mechanical shakers were used to thoroughly mix both the phases for 12hrs at room temperature. The organic and aqueous phases were permitted to steady down in a separating funnel for 2 hours. A sample fromAP was titrated with 0.1N NaOH using Phenolphthalein as an indicator to measure the concentration of levulinic acid in the AP. Mass balance was used to calculate the concentration of levulinic acid in the OP.

Chemical equilibrium:

For chemical equilibrium, 20 ml of levulinic acid and 20 ml of 10 % TOA (0.2264 mol/L) in 1-hexanol was added in a conical flask. The non-miscible solution was kept in shakers for 12 hours and then allowed to settle for 2hours. The levulinic acid concentration was determined from the aqueous phase by titrating a sample solution with 0.1N NaOH using Phenolphthalein as an indicator. The same procedure was repeated for 20%, 30% and 40% TOA.

IV. RESULTS AND DISCUSSION

Data obtained from the experiments are tabulated and compared to know the amount of the levulinic acid extracted from aqueous solution using the physical and chemical equilibrium methods with different concentration of the TOA. From the equilibrium data, the K_D, E %, Z, Z_S and S_f are calculated as shown in Table 1 and Table 2.

4.1 Physical equilibrium

According to D. Datta et al, the high molecular weight diluents are less miscible with water due to their lower polarity than compared to low molecular weight diluents [**Error! Reference source not found.**]. Therefore, intermediate molecular weight diluents are desired. The most effective diluents are alcohols since they enhance the extraction of carboxylic acids [3, **Error! Reference source not found.**, **Error! Reference source not found.**]. Therefore, 1-hexanol which is intermediate molecular weight alcohol is used as a diluent. The physical equilibrium data values for levulinic acid using 1-hexanol are shown in Table 1.

The levulinic acid extracted in the physical equilibrium method with 1-hexanol and various initial concentrations of the levulinic acid showed that the concentration of the levulinic acid extracted in both the phases is linearly proportional to the initial concentration of the levulinic acid. As shown in Figure 1, plotted against the concentration of levulinic acid in the AP and concentration of levulinic acid in the OP indicated a linear step-up in the concentration of the levulinic acid extracted. It was observed that the highest K_D is 0.464375 was obtained by 1-hexanol with only 31.71% recovery of levulinic acid. Thus, to enhance the E %, TOA is used as an extractant to recovery levulinic acid.

Table 1: Physical Equilibrium data of levulinic acid with 1-hexanol

$[HA]_{in}$ mol/L	$[HA]_{aq}$ mol/L	$[HA]_{org}$ mol/L	K_D	E%
0.4686	0.32	0.1486	0.464375	31.71148
0.5467	0.38	0.1667	0.438684	30.49204
0.6248	0.44	0.1848	0.42	29.57746
0.7029	0.5	0.2029	0.4058	28.86613
0.781	0.56	0.221	0.394643	28.29706

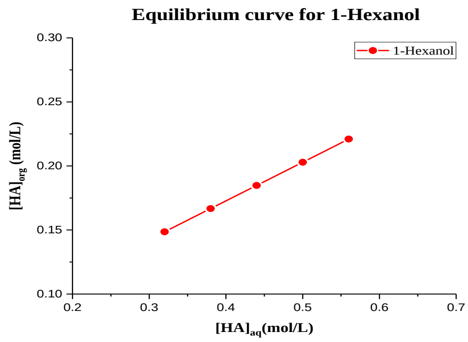

Figure 1: Physical extraction equilibrium curve for extraction of levulinic acid using 1-hexanol.

Before proceeding with the chemical equilibrium, a pilot run was conducted to examine the change in concentration of levulinic acid extracted in AP with the ICLA (0.4686 mol/L) in various concentrations of TOA (10% to 60%). Regarding Figure 2, the K_D and E % was found to increase from 10% TOA till 40% TOA (0.9059 mol/L) and then there was a steady decrease due to back extraction. Therefore, in the present study on chemical equilibrium, the concentration of TOA from 10 to 40% (0.2264 mol/L to 0.9059 mol/L) were considered.

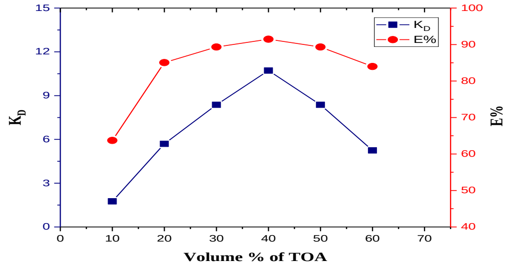

Figure 2: Effect of volume % of TOA in 1-hexanol on K_D and E % for extraction of 0.4686 mol/L levulinic acid.

4.2 Chemical Equilibrium

Reactive extraction of levulinic acid with four different concentrations of TOA in 1-hexanol revealed that the amount of the levulinic acid extracted in both AP and OP is directly proportional to the amount of the ICLA. A maximum K_D was obtained as 10.715 using 40% TOA (0.9059 mol/L). The maximum E % was 91.46 % of the initial levulinic acid was extracted using 40% TOA. The K_D values obtained have indicated that the maximum K_D of 1.7565 when the ICLA is 0.4686 mol/L and minimum K_D of 1.2314 when the ICLA is 0.7810 mol/L with 10% TOA (0.2264 mol/L). The same trend 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 ICLA is 0.4686 mol/L because the concentration of levulinic acid in the aqueous solution of the fermentation broth was below 10% w/w [**Error! Reference source not found.**].

As the concentration of TOA increased from 10% to 40% there is a significant increment in the K_D and E%. There was around 44% increase in the E % when the concentration of TOA is 40% than compared to the concentration of TOA at 10%. From Figure 6, the Zincrements with arise in the concentration of levulinic acid in the AP. The loading ratio decrements with arise in the concentration of TOA because more acid molecules involving complexes are formed at lower concentrations of TOA. From Figure 7, the stoichiometric loading ratio increments with arise in the concentration of levulinic acid in the AP and decrements with an increment in the concentration of TOA. From Figure 8, the modified separation factor marginally raises with an increment in the concentration of levulinic acid in the AP and concentration of TOA.

Table 2: Equilibrium for reactive extraction of levulinic acid with various concentrations of TOA in 1-hexanol.

$[HA]_0$ mol/L	[HA]in mol/L	$[HA]_{aq}$ mol/L	$[HA]_{org}$ mol/L	K_DChemical	E%	Z	Zs	S_f
0.2264 mol/L (10%	0.4686	0.1700	0.2986	1.7565	63.7217	1.3189	1.0235	0.6677
	0.5467	0.2050	0.3417	1.6668	62.5023	1.5093	1.1779	0.6721

TOA)	0.6248	0.2550	0.3698	1.4502	59.1869	1.6334	1.2661	0.6668
	0.7029	0.3050	0.3979	1.3046	56.6083	1.7575	1.3542	0.6623
	0.7810	0.3500	0.4310	1.2314	55.1857	1.9037	1.4644	0.6610
0.4529 mol/L (20% TOA)	0.4686	0.0700	0.3986	5.6943	85.0619	0.8801	0.7489	0.7284
	0.5467	0.0900	0.4567	5.0744	83.5376	1.0084	0.8612	0.7326
	0.6248	0.1200	0.5048	4.2067	80.7939	1.1146	0.9514	0.7320
	0.7029	0.1500	0.5529	3.6860	78.6598	1.2208	1.0416	0.7315
	0.7810	0.2100	0.5710	2.7190	73.1114	1.2608	1.0656	0.7210
0.6794 mol/L (30% TOA)	0.4686	0.0500	0.4186	8.3720	89.3299	0.6161	0.5396	0.7380
	0.5467	0.0700	0.4767	6.8100	87.1959	0.7016	0.6158	0.7409
	0.6248	0.0900	0.5348	5.9422	85.5954	0.7872	0.6920	0.7432
	0.7029	0.1100	0.5929	5.3900	84.3505	0.8727	0.7682	0.7450
	0.7810	0.1300	0.6510	5.0077	83.3547	0.9582	0.8443	0.7466
0.9059 mol/L (40% TOA)	0.4686	0.0400	0.4286	10.7150	91.4639	0.4731	0.4239	0.7426
	0.5467	0.0500	0.4967	9.9340	90.8542	0.5483	0.4931	0.7487
	0.6248	0.0650	0.5598	8.6123	89.5967	0.6179	0.5568	0.7518
	0.7029	0.0800	0.6229	7.7863	88.6186	0.6876	0.6204	0.7543
	0.7810	0.1000	0.6810	6.8100	87.1959	0.7517	0.6786	0.7550

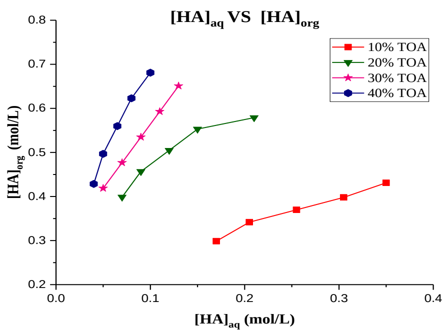

Figure 3: Equilibrium for reactive extraction of Levulinic acid with various concentrations of TOA in 1-Hexanol.

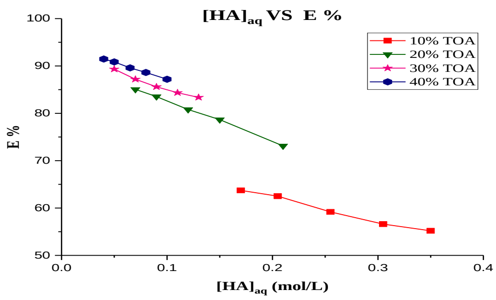

Figure 5: Effect of concentration of levulinic acid in the aqueous phase on extraction efficiency with variable TOA concentration in 1-Hexanol

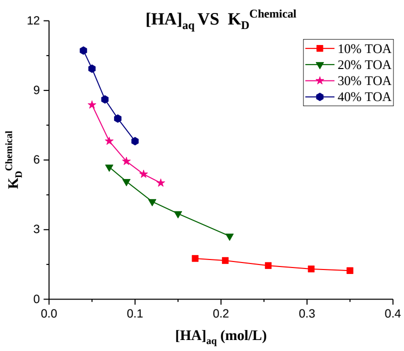

Figure 4: Effect of concentration of Levulinic acid in the aqueous phase on distribution Coefficient with variable TOA Concentration in 1 –Hexanol

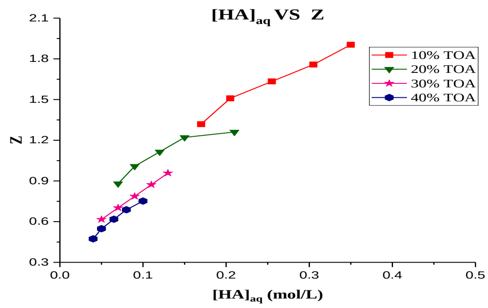

Figure 6: Effect of concentration of levulinic acid in the aqueous phase on loading ratio (Z)with variable TOA concentration in 1 – Hexanol

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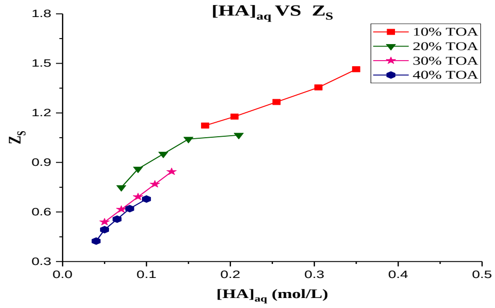

Figure7: Effect of concentration of acid in aqueous phase on stoichiometric loading factor (Z_S) with variable TOA concentration in 1-Hexanol.

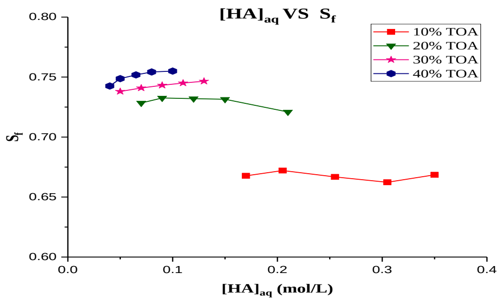

Figure 8: Effect of concentration of acid in the aqueous phase on Modified Separation Factor (S_f) with variable TOA concentration in 1-Hexanol.

ANOVA test was done, using the Microsoft Excel, to statistically compare the results. The results obtained showed that the F critical value is very less compared to F calculated value and p <0.005, which showed a significant difference in K_D at the various concentrations of TOA and ICLA.

Table 3: ANOVA analysis

ANOVA						
Source of Variation	***SS***	***df***	***MS***	***F***	***P-value***	***F crit***
Rows	0.061466	4	0.015367	17.40753	1.12E-05	3.006917
Columns	0.478786	4	0.119697	135.595	3.99E-12	3.006917
Error	0.014124	16	0.000883			
Total	0.554376	24				

V. CONCLUSION

The experiments conducted for the reactive extraction of levulinic acid with TOA in 1-hexanol were investigated. The key findings are as given below

(1) The optimum time required to attain physical and chemical equilibrium is 12 hrs.

(2) The chemical equilibrium showed a better yield than physical equilibrium.

(3) At 40 % concentration of TOA, the maximum K_D of 10.7150 and E % of 91.4639 % was obtained. The K_D and E % decrements with arise in the ICLA. The K_D and E % increments with a rise in the concentration of TOA (10% to 40%).

(4) The Zincrements with raise in the concentration of levulinic acid in the AP and decrements with raise in the concentration of TOA.

(5) The $Z_S$decrements with raise in the concentration of TOA.

(6) The modified separation factor increments with araise in TOA concentration.

VI. 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

VII. ABBREVIATION

TOA	Tri-n-octylamine
AP	Aqueous phase
OP	Organic phase
ICLA	Initial concentration of levulinic acid

Declaration of Competition of interest:

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

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