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Reactive Extraction of Levulinic Acid using Tri-n-octylamine in 1-Octanol: Equilibria and Effect of pH

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Abstract*—Reactive extraction is a sophisticated separation technique used for the recovery of carboxylic acids from fermentation broth. Levulinic acid is a versatile chemical. A right combination of extractant and diluent will provide a high yield. The reactive extraction of levulinic acid from aqueous solution with tri-n-octylamine (TOA) dissolved in 1-octanol was investigated at room temperature. The effect of pH was studied. From the physical and chemical equilibrium experimental results, the distribution coefficient (K_D), extraction efficiency (E%), loading ratio (Z), stoichiometric loading factor (Z_S) and modified separation factor (S_f) are calculated. It was found that physical extraction provided less yield compared to chemical extraction. A maximum K_D was obtained as 5.248 using 40% TOA (0.9059 mol/L) while 83.99 % of the levulinic acid was extracted. By increasing the initial concentration of levulinic acid increased the concentration of levulinic acid in both the organic phase and aqueous phase. As the concentration of TOA increases from 10 to 40 % (0.2264 mol/L to 0.9059 mol/L), the distribution coefficient and extraction efficiency also increase. By increasing the pH from 3 to 7, the distribution coefficient and extraction efficiency were drastically affected.

Key words: Reactive extraction, Levulinic acid, Tri-n-Octylamine, 1-Octanol, pH

I. INTRODUCTION

We know that Levulinic acid ($C_5H_8O_3$) is a carboxylic acid derived from lignocellulosic materials, sugars and starch [1]. It has legion potential uses and thus considered as an important basic chemical [2]. It is used as a food additive, fuel extender, antifreeze, plasticizer, fuel additive, textile dye, anti-inflammatory drugs, animal feed additive and food antimicrobial agent. It is used in plastics, pesticides, herbicides, polymers, synthetic fibers, polymer resin, cosmetics, foods, beverages and pharmaceuticals industries.

The downstream processing of levulinic acid from fermentation broth is inefficient by conventional separation methods like distillation, solvent extraction, membrane separation, adsorption, reverse osmosis, ultrafiltration, ion exchange etc.[3, 4, 5] Thus, reactive extraction with a proper extractant is been considered as a surrogate method of separation for obtaining carboxylic acids from a fermentation broth. According to reactive extraction, the extractant molecule in the organic phase reacts with the solute molecule in the aqueous phase to form reaction complexes. The reaction complexes were solubilized into the organic phase by hydrogen bonding through the diluent [6, 7]. The extraction of solute from the aqueous phase to organic phase is elevated due to the hydrophobic character of the reaction complex [6]. So we conclude that reactive extraction was an economical, efficient, and environmentally friendly separation method. It has many advantages such as re-extracted of acid, reuse of the solvent, high product purity, better control of pH, minimize the downstream processing load, phase equilibria enhanced and higher efficiency[8, 9]. The extraction efficiency could be enhanced by choosing organic phase solvents and optimizing equilibrium factors like the concentration of the acid, pH and temperature.

The "reactive extraction of propionic acid" was studied by Wasewar et al. (2008) and anticipated that TOA-oleyl alcohol system provided maximum extraction. Uslu et al. (2008) investigated the "reactive extraction of levulinic acid" using 5 different alcohols and 2 ketones and confirmed that Isoamyl alcohol is the most beneficial kind of diluent. A.Keshav et al. (2010) examined the effect of temperature and stated that when the temperature increases, the extraction efficiency decreases. Wasewar et al. (2011) investigated the "reactive extraction of caproic acid" and reported that the model of relative basicity was the most appropriate model. Hasan et al. (2015) stated that the disassociation constant of polar solvents was greater than non-polar solvents.

The objective of the work is to investigate the physical and chemical equilibrium, and the effects of pH for the recovery of levulinic acid using TOA in 1-octanol. So, the pH range used is from 3 to 7. The chemical extraction using various concentrations of TOA (0.2264 mol/L/ to 0.9059 mol/L) and physical extraction using pure diluent were conducted and the experimental results were compared based on the K_D, E%, Z, Z_S and S_f.

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II. MATERIALS AND METHODS

Materials

The physical properties of chemicals used in the paper were listed in Table 1. The various initial concentrations of levulinic acid were prepared by using distilled water. Laboratory grade sodium hydroxide (NaOH) was used for volumetric analysis of acid using Phenolphthalein as an indicator with a pH range 8.2 to 10. All the chemicals used in experiments with no additional purification.

Table 1: Physical properties of chemicals used in the experimental study.

Chemical	IUPAC name	Supplier	Formula	molar mass kg/kmol	density g/ml	purity
Levulinic Acid	4-oxopentanoic acid	Sigma-Aldrich, India	$C_5H_8O_3$	116.11	1.134	98 %
Tri-n-Octylamine	N,N-dioctyloctan-1-amine	Sigma-Aldrich, India	$C_{24}H_{51}N$	353.67	0.81	98 %
1-Octanol	Octan-1-ol	Himedia, India	$C_8H_{18}O$	130.23	0.83	99 %

Methods

Equilibrium Studies

The optimum time required to attain liquid-liquid equilibrium was found to be 12 hours from the experiments conducted for both physical and chemical extraction. The initial concentration of levulinic acid considers from 0.4686 mol/L to 0.781 mol/L because the concentration of levulinic acid in the fermentation broth was observed to be below 10% w/w [2].

Physical equilibrium

To study the physical equilibrium, 20 ml of the aqueous solution of initial levulinic acid concentrations 0.4686, 05467, 0.6248, 0.7029 and 0.781 mol/L were taken in a different conical flask. To this aqueous phase, 20 ml of pure 1-octanol is added. The mixture of both the phases is then placed in mechanical shakers for 12 hours at room temperature. The mixture was shifted into a separatory funnel. It was uninterrupted for at least 2 hours to attain a clear partition of the organic and aqueous phases. A sample solution from the aqueous solution was titrated with 0.1N NaOH using Phenolphthalein as indicator to obtain the concentration of levulinic acid in the aqueous phase. By using mass balance, the levulinic acid concentration in the organic phase is estimated.

Chemical equilibrium

In chemical equilibrium, the same procedure which was used in physical equilibrium was used to prepare an aqueous solution. The solution for organic phase was prepared by dissolving 0.2264 mol/L TOA (10 %) in 1-octanol. 20 ml of an aqueous solution of levulinic acid were directly contacted with 20 ml of organic solution in a 250 ml conical flask. This mixture was kept in shakers for 12 hours. It is then transferred to a separatory funnel and held uninterrupted for 2 hours for clear phase separation. The concentration of levulinic acid is measured by volumetric analysis using 0.1N NaOH solution and phenolphthalein as indicator. The same procedure was repeated for 20 %, 30% and 40 % TOA.

III. RESULTS AND DISCUSSION

Physical equilibrium:

Alcohols are considered as the best diluents because they improve the extraction efficiency of carboxylic acids [2, 5, 8, 10]. The physical equilibrium of levulinic acid (0.4686 mol/L to 0.781 mol/L) was examined using 1-octanol. From experimental data, we observed that the increase in the initial levulinic acid concentration increases levulinic acid concentrations in both phases, as shown in Fig 1. The K_D is calculated using equation (1). A maximum K_D of **0.2015** was obtained by 1-octanol for 0.4686 mol/L of the initial concentration of levulinic acid. It is found that the K_D while using pure 1-octanol is low.

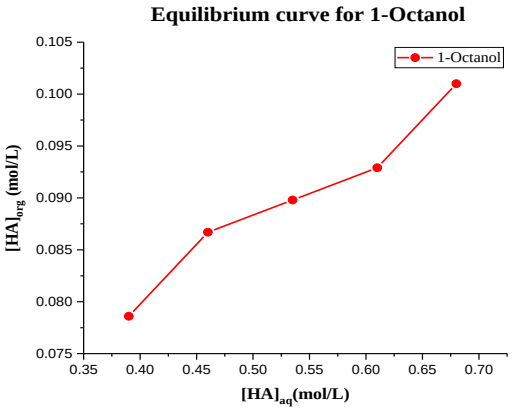

Fig 1: Physical extraction equilibrium curves for extraction of levulinic acid using 1-octanol.

A pilot run was carried to evaluate the effect of TOA concentration (10 % to 60%) in 1-octanol using 0.4686 mol/L of the initial concentration of levulinic acid. As shown in Fig 2, it was noticed that the K_D and E% increased from 10% TOA to 40% TOA and then gradually decreased due to back extraction. Thus, in the present paper, the concentration of TOA from 10 to 40% (0.2264 mol/L to 0.9059 mol/L) were considered.

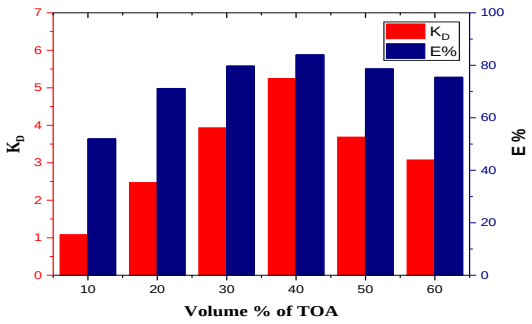

Fig 2: Effect of volume percentage of TOA in 1-octanol on distribution coefficient and extraction efficiency for extraction of 0.4686 mol/L levulinic acid.

Chemical Equilibrium

The chemical equilibrium data obtained using 5 different initial concentrations of levulinic acid (0.4686, 0.5467,0.6248,0.7029 and 0.781 mol/L), 4 different concentrations of TOA (0.2264 mol/L/ to 0.9059 mol/L) and 1-octanol, so the equilibrium parameters such as K_D, E %, Z, Z_S and S_f were calculated by using the equations (1),(2),(3),(4) and (5) respectively.

The distribution coefficient (K_D) is defined as the proportion of the levulinic acid concentration in the organic phase ($[HA]_{org}$) to the levulinic acid concentration in the aqueous phase ($[HA]_{aq}$) [2, 6, 7, 11, 14].

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

The extraction efficiency (E %) is defined as the proportion of levulinic acid concentration in the organic phase ($[HA]_{org}$) to the sum of levulinic acid concentration in both the phases [4, 6, 7, 11,14].

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

The maximum extent to which the organic phase (TOA + 1-Octanol) could be loaded with the acid is known as the loading ratio (Z) [6, 7, 10, 12, 13, 14].

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

Where [T] is the total concentration of TOA in the organic phase.

The proportion of the overall complexed acid to total solvent in the organic phase is called stoichiometric loading factor (Z_S). This factor contains the correction term, ($v\,[HA]_{org}^{diluent}$) for the amount of the levulinic acid extracted through the diluent in the solvent mixture [7, 12, 14].

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

From the equation (4), v is called a volume fraction of diluent in the mixture and $[HA]_{org}^{diluent}$ is the concentration of acid extracted through a 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 [14].

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

A graph plotted against the concentration of levulinic acid in the aqueous phase to the concentration of levulinic acid in the organic phase with various concentrations of TOA as shown in Fig 3. This graph shows the TOA increases, so does levulinic acid in the organic phase.

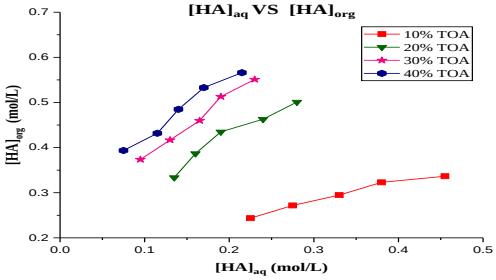

Fig 3: Equilibrium for reactive extraction of Levulinic acid with various concentrations of TOA in 1-Octanol.

A maximum K_D was obtained as 5.248 using 40% TOA and an initial concentration of levulinic acid is 0.4686 mol/L and a minimum K_D of 0.7165 using 10% TOA and an initial concentration of levulinic acid is 0.781. As shown in Fig 4, K_D increases as the concentration of TOA increases because the TOA enhances the extraction of levulinic acid from the aqueous phase to the organic phase. The K_D decreases with increasing the initial concentration of levulinic acid as it is found that the concentration of carboxylic acids in the fermentation broth is less than 10%.

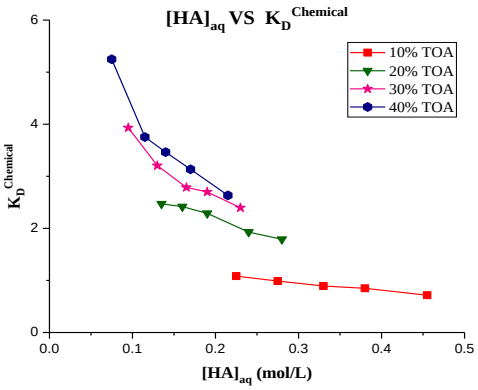

Fig 4: Effect of concentration of acid in the aqueous phase on distribution Coefficient with variable TOA Concentration in 1 –Octanol

The maximum E% was 83.99 % at 40 % TOA, as shown in Fig 5. Therefore, we have observed that the E% increases with increasing TOA concentration and decreases with increasing the initial concentration of levulinic acid.

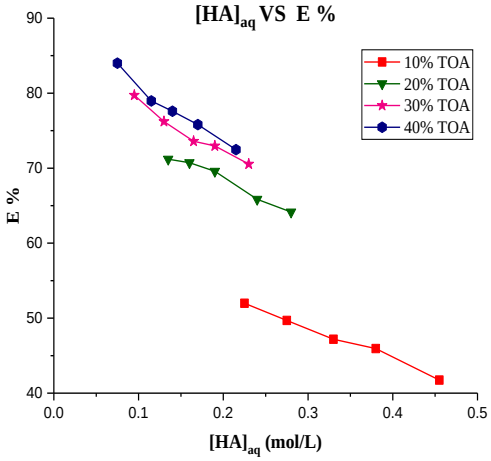

Fig 5: Effect of concentration of acid in aqueous phase on extraction efficiency with variable TOA concentration in 1-Octanol

From Fig 6, we observe that the loading ratio increases as the concentration of levulinic acid in the aqueous phase increases and decreases as the concentration of TOA increases. At low TOA concentrations, more levulinic acid molecules involving in reaction complexes (acid-amine complex) are formed.

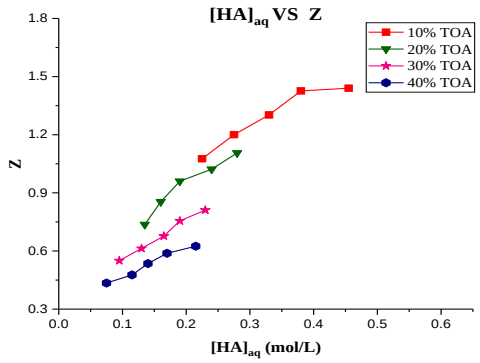

Fig 6: Effect of concentration of acid in aqueous phase on loading ratio (Z) with variable TOA concentration in 1 – Octanol

The stoichiometric loading factor increases with increasing concentration of levulinic acid in the aqueous phase and decreases with increasing TOA concentration as shown in Fig 7.

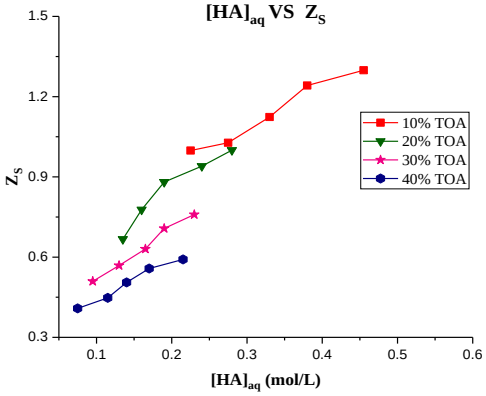

Fig 7: Effect of concentration of acid in the aqueous phase on stoichiometric loading factor (Zs) with variable TOA concentration in 1-Octanol.

The modified separation factor increases with increasing levulinic acid concentration in the aqueous phase and with increasing TOA concentration, as shown in Fig 8. Thus, it was observed that more reaction complexes are formed at 40 % TOA.

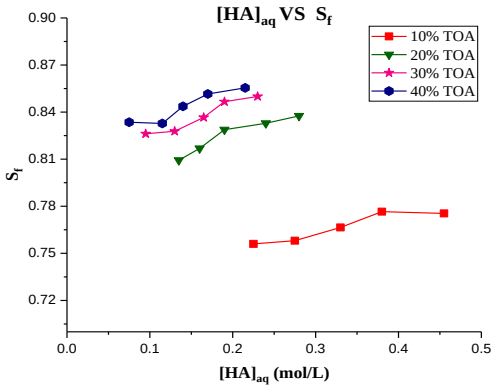

Fig 8: Effect of concentration of acid in the aqueous phase on Modified Separation Factor (Sf) with variable TOA concentration in 1-Octanol.

It is significant to examine the effect of pH during the recovery of levulinic acid as the pH of the fermentation broth changes during acid production [3]. Since the maximum extraction was found at 40% of TOA. In this study, we compared the effect of pH on K_D and E % with various concentrations of levulinic acid using 40% TOA in 1-octanol as shown in Fig 9. By increasing the pH from 3 to 7, we observed that K_D and E % drastically decreased. No levulinic acid extraction was carried out at a pH greater than 6, since most levulinic acid molecules are in a dissociated form at a high pH. During reactive extraction, only the undissociated form of levulinic present in the aqueous phase reacts with TOA in the organic phase to form reaction complexes. Therefore, it is better to maintain a pH of 3 to attain maximum extraction of levulinic acid.

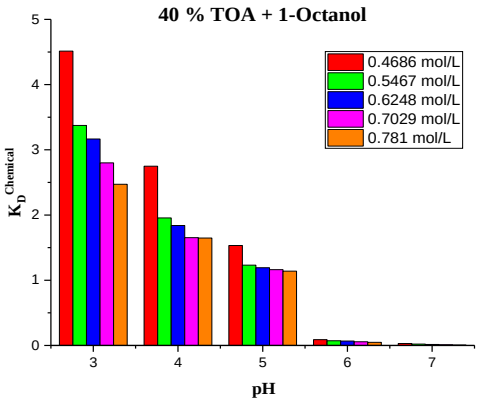

Fig 9: Comparison for effect of pH on distribution coefficient for various concentrations of levulinic acid using 40 % TOA in 1-octanol.

IV. CONCLUSION

From this study, we conclude that the reactive extraction of levulinic acid using TOA in 1-octanol was investigated and that the effect of pH was examined. The extraction of levulinic acid with 1-octanol alone results in a low K_D. At 40% TOA, the maximum K_D is 5.248 and E % is 83.99 %. As the concentration of TOA increases, the K_D, E% and S_f also increase. As the concentration of TOA increases, the Z and Zs decreases. By increasing the pH from 3 to 7, the K_D and E % drastically decreases. When pH is greater than 6, levulinic acid couldn't be extracted.

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

ABBREVIATION

TOA Tri-n-octylamine

DECLARATION OF COMPETITION OF INTEREST:

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

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