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Reactive Extraction of Carboxylic Acids (Lactic, Propionic and Succinic Acids) using Tri-n-Butyl Amine Dissolved in Various Diluents

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ABSTRACT

The current study intends to look into the extraction of lactic acid, propionic acid and succinic acids from aqueous solutions of these substances utilizing various solvent-extractant combinations to ascertain the most effective composition for the reactive extraction. The commercial value of succinic, propionic, and lactic acids in industrial processes led to their selection as the carboxylic acids. The process of recovering carboxylic acids from their aqueous solutions is accomplished by the Process Intensification method of reactive Tri-n-Butyl Amine was employed in the experiments because it has better stability, a lower water solubility, and is more eco-friendly than other extractants of the amine type. The extractants were dissolved in various diluents with various chemical structures, including 1-octanol, chloroform, and dimethylene chloride. Each experiment was conducted at 298.15 K. The distribution coefficient (KD), loading factor (Z), and extraction yield (%E) were used to compare the results in the range of 0.1 to 0.4 N acid concentration at various concentrations of Tri-n-Butyl Amine (10% to 40%). It was observed that at 0.1N and 40% amine concentration succinic acid attains a maximum distribution coefficient K_D is 8.01 and equilibrium complexion K_{E1} is 7.5 for Tri-n-Butyl Amine, followed by propionic acid and lactic acid and a (1:1) type of acid amine complex was observed. The kinetic studies that were carried out using stirred cells to figure out the kinetic parameters such as order of the reaction with respect to acid and amine, mass transfer coefficient, and rate constant are also reported. The reaction with the highest Hatta number, $M_H = 14$, occurs in an instantaneous regime in 1-octanol when succinic acid and Tri-n-Butyl Amine interact.

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Introduction

Fossil fuels are finite resources, and consuming them damages the ecosystem and promotes climate change. Over the past few decades, there has been a global push to replace fossil fuels with renewable energy sources. Biomass is a promising alternative to fossil fuels that is able to be used for producing valuable products [1,2]. A couple of chemicals with a great deal of promise and a wide range of industrial applications are carboxylic acids [3]. This chemical contains substantial economic significance and discovers application in food and beverage pharmaceutical, and personal care products. Its biotechnological production is gaining significant attention [4,5]. The fermentation procedures used in the biotechnological production of carboxylic acids result in multi-constituent aqueous solutions with an acid content of less than 10% (w/w). Consequently, it is economically significant for separating carboxylic acid from the fermentation environment or waste stream, because they have a wide range of applications across multiple industries, organic acids are widely recognized as essential target chemicals [6-8]. Additionally, microbial fermentation of naturally occurring biomass can also be used to create organic acids through chemical processes using fossil raw materials. Green technologies based on biotechnology are becoming more prevalent in production processes due to growing environmental concerns [8]. The primary products from the fermentation broth/aqueous stream must be recovered downstream, which poses the biggest barrier in the biological synthesis of organic acids [9]. Reactive (liquid) extraction is thought to present a major chance for this goal among the several downstream processing procedures. It is a highly selective and separated method that uses a lesser amount of energy and has flexible production scale possibilities [10]. Researchers are thinking about new recovery methods because of these factors as well as recovery's limitations. Authors suggested that a promising method for recovering carboxylic acids is reactive extraction [11]. One important method for removing organic acids like carboxylic acid, which are typically found in small amounts in aqueous solutions, is reactive extraction [12]. The design of the reactive separation technique for recovering carboxylic acids from fermentation broth and diluted aqueous waste streams [13,14].

It was successful to determine the extraction efficiency and distribution coefficient using the extractant and diluent, respectively [14,15]. Reactive extraction parameters such as the initial acid content and the composition of the extractant were used to systematically measure extraction efficiency [16,17]. An equilibrium model was used to calculate the reported equilibrium constants for each acid-amine complex. Compared to a mine-type extractants, it is more environmentally friendly and has a lower

water solvency in extraction tests [18]. To extract and recover carboxylic acids from aqueous solutions, aliphatic amines such as trioctylphosphine oxide (TOPO), tributyl phosphate (TBP), trioctyl butylamine (TBA), and trioctyl octylamine (TOA) have all been employed extensively. These substances have a high solvent capacity and selectivity [19-21]. Reactive extraction frequently uses conventional organic diluents including ethers, alcohols, ketones, and aliphatic hydrocarbons [22]. This article details the use of hydrophobic tertiary extractants, such as Tri-n-Butyl Amine, and active diluents, such as 1-octanol , dimethylene chloride, and chloroform, in the reactive extraction of carboxylic acids, such as lactic acid, propionic acid, and succinic acid, from an aqueous solution. By conducting equilibrium and kinetic analysis at amine and acid concentrations, a thorough design is evaluated.

Materials and Methods
Materials
Distilled water is combined with carboxylic acids such as succinic acid (Merck, 95%), propionic acid (Merck, 99%), and lactic acid (Merck, 95%) to produce an aqueous solution with a concentration range of 0.1N to 0.4N. Using extractants and diluents, the organic solution was made. Tri-n-Butyl Amine (Finar, 98%) was used as an extractant. Diluents included 1-octanol (Sisco, 98%), chloroform (Molychem, 98%), and dimethylene chloride (Molychem, 98%) The NaOH utilised was reagent grade, or 85% NaOH. PH=8–10 phenolphthalein indicator (Hi medium, 85%). All the chemicals were used immediately without any further purification.

Methods
Equilibrium Studies
The experiments employed atmospheric pressure (101.32 KPa) and room temperature (306 K). In order to conduct physical equilibrium and chemical equilibrium investigations, equivalent volumes of the aqueous and organic phases were maintained in separate conical flasks (100 ml) that were kept in temperature-controlled shaker bath. The two phases were allowed to stabilise until they reached equilibrium (1hour). Using NaOH and phenolphthalein as indicators, an acidbase titration was used to assess the acid concentration. The law of mass action was used to calculate the amount of acid in the organic phase. Diluents can be used to get physical equilibrium data in the organic phase.

Kinetic Studies
The kinetic investigations are carried out in a 500 ml cylindrical vessel with a double paddle impeller (diameter = 8 mm, thickness = 2 mm, and the spacing between impellers = 1 mm). 100 ml of the first aqueous phase are taken in a stirred cell. One millimetre exactly above and below the interface, the four-blade impeller is positioned is shown in Figure 1, 2. Without touching the interface, an equal volume (100 ml) of the organic phase was added to a cell. A very low speed of between 100 and 120 rpm was maintained. An aqueous sample (10ml) is taken periodically for every 10 min through syringe from the sample port and titrated it with 0.5N NaOH to determine the concentration of acid in the aqueous phase. The sample is collected until the steady state (1 hour) is attained. Acid in the organic phase was evaluated by mass balance. The above procedure is repeated with amine (Tri-n-Butyl Amine) for different diluents (1-octanol , Chloroform, and Dimethylene chloride) at various Lactic acid, Propionic acid and Succinic acid concentrations.

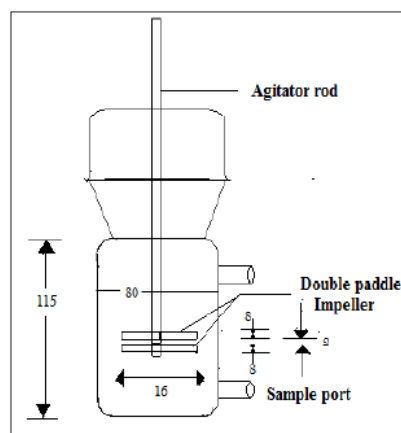**Figure 1:** Experimental Setup for Kinetic Studies (Stirred Cell)

Figure 2: Schematic Diagram of Stirred Cell (All dimensions are in mm)

Theory of Reactive Extraction
A process intensification method called reactive extraction is utilized to extract the carboxylic acids from an aqueous solution. It implies the existence of a mechanism at the interface between the extractant and the substance being removed [5]. Acid molecules pass through the aqueous and organic phases, where they combine with amine molecules to produce an acid-amine complex that is then dissolved in the diluent. A high distribution coefficient and improved selectivity of carboxylic acids are produced through reactive extraction [10].

$$[HA]aq \rightarrow [HA]org$$
$$A(solute) + E(Extractant) \leftrightarrow Complex$$
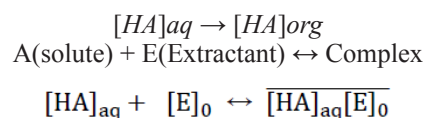
$$[HA]_{aq} + [E]_0 \leftrightarrow \overline{[HA]_{aq}[E]_0}$$

Equilibrium complexion constant (K_E) can be represented as

$$K_E = \frac{\overline{[HA]_{aq}[E]_0}}{[HA]_{aq} \ [E]_0}$$

The collection of equations offers the chemical equilibrium models for the simultaneous formation of acid-amine complexes, namely (1:1) (2:1).......(n:1) depending on the kind of acid, extractant, and diluent used in the experiment as well as their concentrations . As a mechanism for the reactive extraction of carboxylic acids, the following can be offered.

$[HA]_{aq} + [E]_0 \leftrightarrow [EHA]_{org}$

$[HA]_{aq} + [EHA]_{org} \leftrightarrow E[HA]_{2,org}$

$[HA]_{aq} + E[HA]_{n-1,org} \leftrightarrow E[HA]_{n,org}$

Where $K_{11}, K_{21} \ldots . K_{n1}$ represent the various equilibrium constants that the law of mass action can be used to compute.

Results and Discussion
Extraction Equilibria
Physical Equilibrium
Physical equilibrium was carried out at different acid concentrations with various diluents, and physical equilibrium isotherms were calculated in terms of (gm/cc). It denotes the amount of acid (in gm) diffused in one cc of solution. Figure 3 indicates that 1-octanol has a greater ability to extract acid from aqueous phase due to its active polar character and good function as a solvating medium for the creation of an ion-pair complex than chloroform and dimethylene chloride.
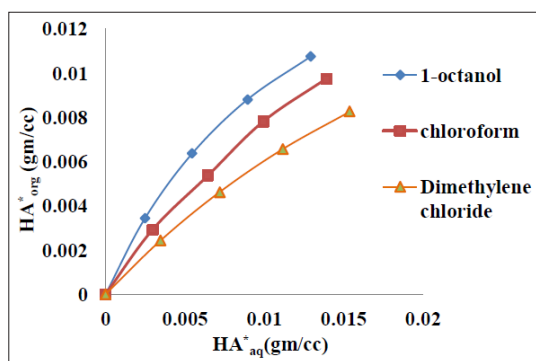

Figure 3: Physical Equilibrium Isotherms for Reacting Succinic Acid Extraction with Different Diluents
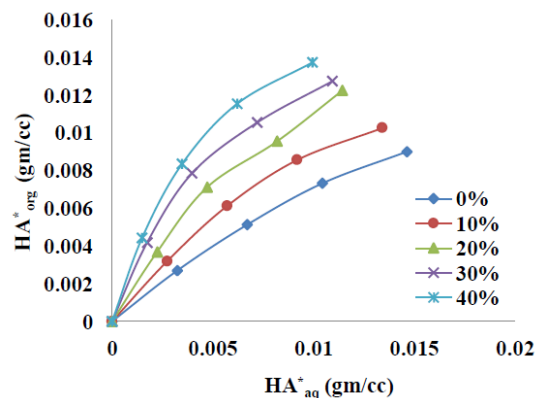
Chemical Equilibrium

Figure 4: Isotherms of Chemical Equilibrium at Various Concentrations of Succinic Acid and Tri-n-Butyl Amine in 1-Octanol

Because natural diluents have a larger affinity for water than carboxylic acids do, physical extraction with diluents is relatively ineffective. Instead, chemical reactions are carried out by adding amines to diluents in the organic phase. According to Figure 4, TBA significantly improves when amine concentrations rise because adding amines enhances the possibility that the acid-amine complex will form. Lactic acid and Propionic acid were also shown to exhibit comparable physical and chemical isotherms with all types of amine and diluents under study.

Loading Ratio (Z)
The loading ratio can be used to calculate how much carboxylic acid concentration can be loaded into the organic phase [10].

$$Z = \frac{[HA]_{org}}{[E]_0}$$

Z is relies on the bonding strength of the acid-extractant interaction, initial acid concentration in the aqueous phase and stoichiometry of the extraction process.
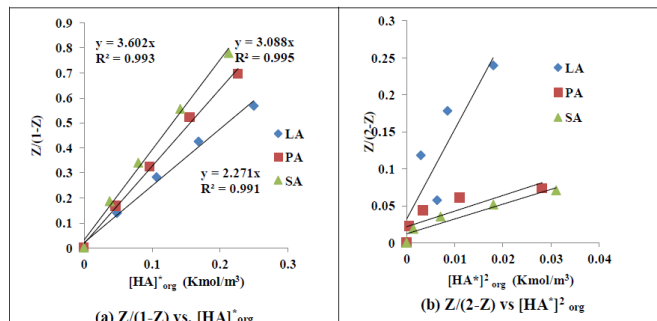

Figure 5: For the estimate of the Equilibrium Complexion Constant (1:1) and (2:1) Carboxylic Acids at 40% Tri-n-Butyl Amine in 1-octanol, a plot of (a) Z/(1-Z) vs. $[HA]^*_{org}$ and (b) Z/ (2-Z) vs $[HA^*]^2_{org}$ (Kmol/m³) is used

Figure 5 shows a linear trend for all carboxylic acids, i.e., a low loading ratio is attained (Z<0.5), indicating that a (1:1) type of acid-amine complex is created since there are not enough acid molecules to form a (2:1) reaction complex [7]. Succinic acid achieves the highest equilibrium complexion constant followed by Propionic and Lactic acid. The stable acid amine complex is favored by carboxylic acid, and high forward reaction rates lead to larger equilibrium coefficients in Tri-n-Butyl Amine.

Kinetic Studies
Distribution Coefficient
Some may be able to calculate the quantity of carboxylic acid that has diffused from the aqueous to the organic phase by determining the distribution coefficient (KD) and running the experiment at various amine concentrations. It measures how the solutes are distributed between the two phases [8].

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}}$$

Variation of distribution coefficient for different carboxylic acids at different concentrations of Tri-n-Butyl Amine (TBA)
Reactive extraction of carboxylic acids was measured in terms of distribution for different carboxylic acids, at 10%, 20 %, 30 % and 40 % of amine concentrations of Tri-n-Butyl Amine (TBA) with different diluents at 0.1 Kmol/m3 acid concentration.
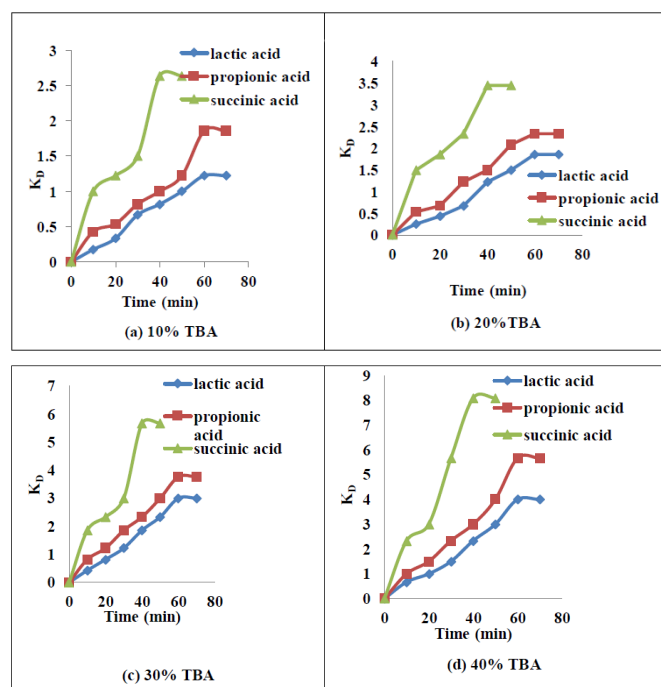
Figure 6: Effect of Carboxylic Acids on Distribution Coefficient with time for 0.1 Kmol/m³ Acid concentration at different amine concentrations of Tri-n-Butyl Amine (a) 10%, (0.4219 kmol/m³) (b) 20% (0.843 kmol/m³), (c) 30% (1.3 kmol/m³) and (d) 40% (1.7 kmol/m³)

Table 1: The Table Illustrates the Distribution Coefficient for Lactic, Propionic, and Succinic Acids in 1-octanol at 0.1N Acid Concentration with Varying TBA Concentrations

Concentration of Tri-n-Butyl Amine	K_D for Lactic Acid with 1- Octanol	K_D for Propionic Acid with 1- Octanol	K_D for Succinic Acid with 1- Octanol
	TBA	TBA	TBA
0%	1.04	1.16	1.38
10%	1.23	1.5	2.64
20%	1.9	2.3	3.44
30%	3	3.7	5.54
40%	4	5.67	8.09

As it can be observed from the Figure 6 and Table 1. It is found that the diffusion rate of carboxylic acids from the aqueous to the organic phase increases with increasing amine concentration, leading to a higher carboxylic acid distribution coefficient. Aliphatic amines interact with carboxylic acid molecules through proton transfer or the formation of ion pairs to form an acid-amine complex, which improves the distribution coefficient of the acid. All the investigated carboxylic acids, succinic acid has the highest distribution coefficient, followed by propionic and lactic acid.

Variation of Distribution Coefficient for Different Carboxylic Acids at Various Acid Concentrations
The amount of carboxylic acid is measured by calculating the distribution coefficient at different acid concentration varies from 0.1 to 0.4 Kmol m⁻³. It is evaluated at 40% of (TBA) amine concentration by varying the acid concentration.
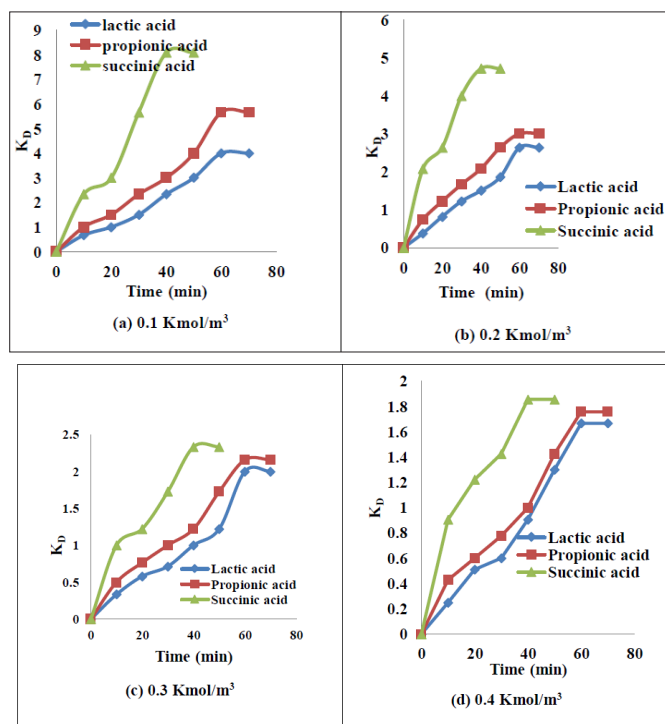

Figure 7: Distribution Coefficient for (a) 0.1N, (b) 0.2 N, (c) 0.3N and (d) 0.4N Concentrations of Lactic Acid, Propionic Acid and Succinic Acid at 40% TBA (1.7 Kmol/m³) in 1-octanol

Table 2: The Table shows the Distribution Coefficient for Various Carboxylic Acid Concentrations in 1-octanol at 40% TBA (1.7 Kmol/m³)

Carboxylic acid Concentration	K_D for Lactic Acid with 1- Octanol	K_D for Propionic Acid with 1- Octanol	K_D for Succinic Acid with 1- Octanol
	TBA	TBA	TBA
0.1N	4	5.67	8.09
0.2N	2.64	3	3.44
0.3N	2	2.16	2.33
0.4N	1.67	1.76	1.86

The amount of acid that has been transferred at various acid concentrations is determined using the distribution coefficient. As per Figure 7 and Table 2 demonstrates that the distribution coefficient decreased as the acid content increased. The amount and efficiency of different complexes varies with acid content, and the hydrogen bonding between acid molecules affects complex stoichiometry. It is important to note that TBA has the largest distribution coefficient for all carboxylic acids at lower acid concentrations.

Variations in KD with Time for Different Diluents
The lower the molecular weight of the diluents gives higher extraction efficiency of lactic acid, propionic acid, and succinic acid. Variations of the distribution coefficient for various diluents like 1-octanol, chloroform and dimethylene chloride were calculated in the concentration range of 0.1 to 0.4 kmol/m³ at different initial concentrations of Tri-n-Butyl Amine 10%, 20%, 30%, 40% (= 0.4219, 0.843, 1.3, 1.7 kmol/m³).

Table 3: Variation in Distribution Coefficient for 0.1 to 0.4 kmol/m³ Concentrations of Carboxylic Acid at 40% (1.7 kmol/m³) Tri-n-Butyl Amine in Different Diluents

Concentration of Carboxylic acid	KD for 1- Octanol with 40% TBA			KD for Chloroform with 40% TBA			KD for Dimethylene chloride with 40% TBA		
Carboxylic acid	LA	PA	SA	LA	PA	SA	LA	PA	SA
0.1N	4	5.67	8.09	2.25	2.32	3	1.4	1.95	2.6
0.2N	2.64	3	3.44	1.9	2.08	2.48	1.35	1.52	1.7
0.3N	2	2.16	2.33	1.5	1.73	2	1.2	1.31	1.42
0.4N	1.67	1.76	1.86	1.3	1.4	1.5	0.9	1.0	1.25

Table 4: Variation in Distribution Coefficient for Tri-n-Butyl Amine (TBA) 10%, 20%, 30%, 40% (= 0.4219, 0.843, 1.3, 1.7 kmol/m³) Concentrations of Amine at 0.1 kmol/m³ in Different Diluents

Concentration of TBA	KD for 1- Octanol with 0.1 kmol/m³ acid concentration			KD for Chloroform with 0.1 kmol/m³ acid concentration			KD for Dimethylene chloride with 0.1 kmol/m³ acid concentration		
	LA	PA	SA	LA	PA	SA	LA	PA	SA
10%	1.23	1.5	2.64	1	1.2	1.8	0.54	0.67	0.82
20%	1.9	2.33	3.44	1.2	1.4	3	0.8	1.2	1
30%	3	3.76	5.54	1.9	1.75	4	1.2	1.5	1.9
40%	4	5.67	8.09	2.3	2.5	7	1.5	1.9	2.3

From the Tables 3 and 4 it is found that 1-octanol shows maximum distribution coefficient compared to chloroform and dimethylene chloride due to its high polarity and extractability.

High polarity of the active diluents causes an increase in the Lewis-basicity of tertiary amine consequently, an increase in the distribution coefficient of the carboxylic acids takes place. Ranking of distribution coefficient for the reactive extraction of acid with diluents are as follows 1-octanol > chloroform > dimethylene chloride for better extraction. Succinic acid achieves the highest Distribution coefficient followed by Propionic and Lactic acid in three types of diluents.

Effect of Extraction Efficiency at Various Concentrations of Amines
Extraction efficiency can be calculated based upon the obtained values of the distribution coefficient of acid with TBA in different diluents.

$$\eta = \frac{K_D}{1+K_D}$$

Extraction efficiency depends upon the type of diluents, acids, and amines. In the following graphs, isotherms were plotted for extraction efficiency of (Lactic acid, Propionic acid, and Succinic acid) in the concentration range of 0.1N to 0.4N at various concentrations of amines (10%, 20%, 30% and 40% of Tri-n-Butyl Amine) with different diluents (1-octanol , chloroform, and dimethylene chloride).

Variation of Extraction Efficiency of Carboxylic Acids at Different Amine Concentrations Using TBA
Extraction efficiency of carboxylic acid was calculated for different concentrations of amines (10%, 20%, 30% and 40%) Tri-n-Butyl Amine at a particular acid concentration by using different diluents.
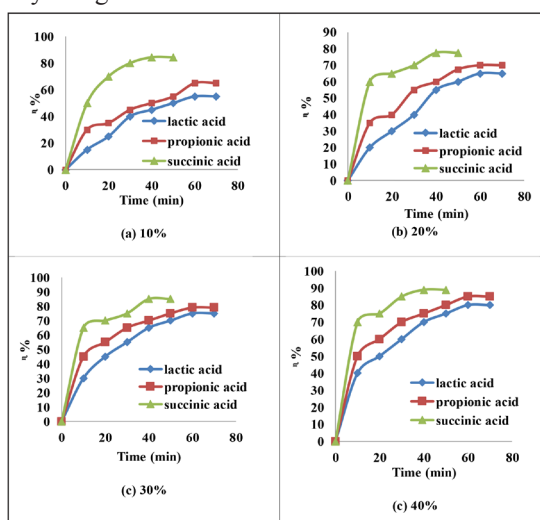

Figure 8: Variation of Extraction Efficiency of Carboxylic Acids for 0.1Kmol/m3 acid Concentration at (a) 10%, (b) 20%, (c) 30% and (d) 40% (0.4219 ,0.843, 1.3 and 1.7 Kmol/m3) of TBA in 1-octanol

Table 7: Extraction Efficiency for Various Concentrations of Tri-n-Butyl Amine in 1-octanol at 0.1N of Acid

Concentration of amine	η (%) for 1- Octanol Lactic acid	η (%) for 1- Octanol Propinic acid	η (%) for 1- Octanol Succinic acid
	TBA	TBA	TBA
0%	33	35	40
10%	55	65	72.5
20%	65	70	77
30%	75	79	85
40%	80	85	92

From Figure 8 and Table 7 it is observed that for all the carboxylic acids as the concentration of amine increases extraction efficiency also increases with TBA in 1-octanol . It is argued that succinic acid shows highest extraction efficiency (η =92% for TBA in 1-octanol) due to its less hydrophilic in nature and flavors better for the forward reaction compare with propionic acid (η =85% for TBA in 1-octanol) and lactic acid (η =80% for TBA in 1-octanol).

Variation of Extraction Efficiency at Various Concentrations of Carboxylic Acids with TBA in 1-octanol
Extraction efficiency of carboxylic acid was calculated for different concentrations of acids (0.1N, 0.2N, 0.3N, and 0.4N) at particular amine concentration Tri-n-Butyl Amine by using different diluents.
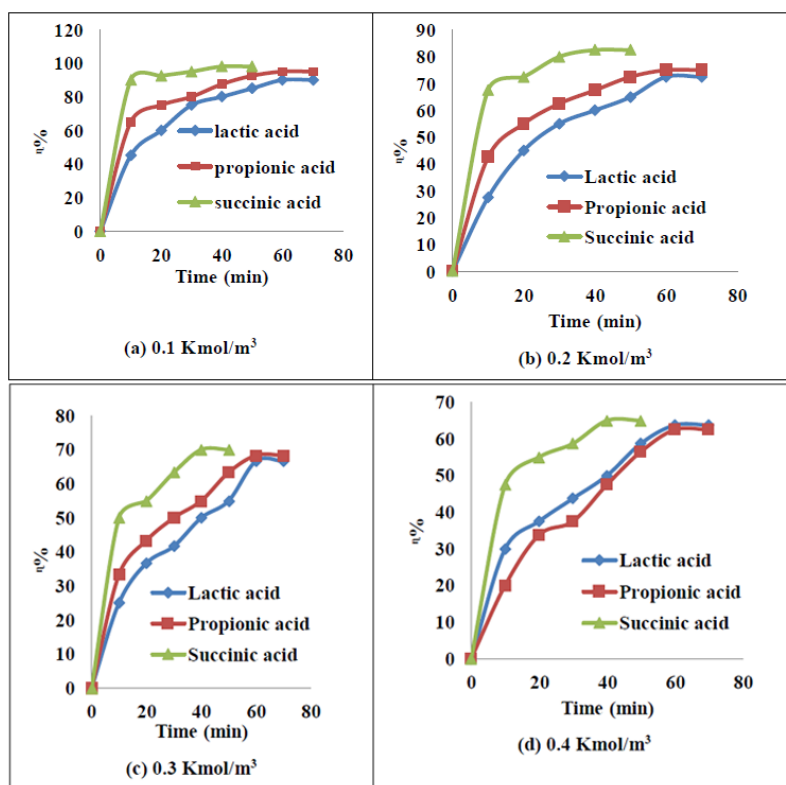

Figure 9: Variation of Extraction Efficiency of Carboxylic Acids for 40% (1.7Kmol/m³) TBA at (a) 0.1, (b) 0.2, (c) 0.3 and 0.4 Kmol/m³ of Acid Concentration

Table 8: Extraction Efficiency for Various Concentrations of Acids at 40% Tri-n-Butyl Amine in Different Diluents

Concentration of acids	η (%) for Lactic acid with 1-octanol	η (%) for Propionic acid with 1-octanol	η (%) for Succinic acid with 1-octanol
	TBA	TBA	TBA
0.1N	80	85	92
0.2N	70	75	77.5
0.3N	66.7	78.3	70
0.4N	62.5	63.75	65

From Figure 9 and Table 8. It is observed that as the acid concentration increases the reactive extraction of carboxylic acid decreases. Extraction efficiency of succinic acid slightly decreases from 92% to 65% for TBA with 1-octanol . A similar effect is observed for the other carboxylic acids like propionic acid (85% to 63.75% for TBA 1-octanol) and lactic acid (80% to 62.5% for TBA 1-octanol).

It is also noticed that from the Table 8 for TBA as the acid concentration increases extraction efficiency gets decreases. Extraction efficiency of dicarboxylic acids (succinic acid) and monocarboxylic acids (propionic acid and lactic acid) decreases with increase in acid concentration at all studied range of acid concentrations.

Physical Mass Transfer Coefficient

To determine the kind of regime for distinct carboxylic acids, physical extraction and kinetic studies are used to derive the mass transfer coefficient [8].

A batch-type reactive system's differential mass balance is represented as

$$V_{org} \frac{d[HA]_{org}}{dt} = K_L A_c ([HA]^*_{org} - [HA]_{org})$$

By integrating the preceding equation, we obtained to the following findings:

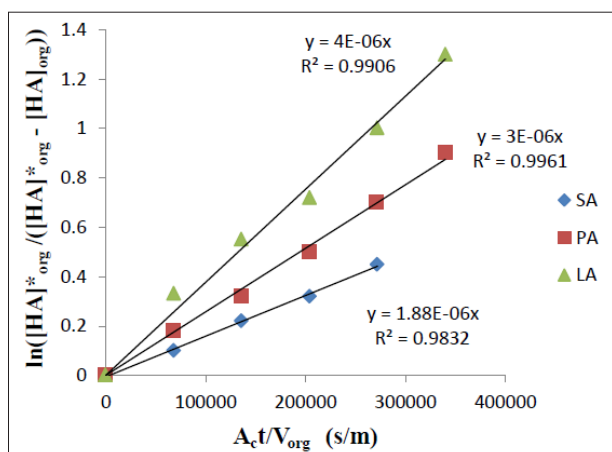$$\ln\left(\frac{[HA]^*_{org}}{[HA]^*_{org} - [HA]_{org}}\right) = K_L \frac{A_c t}{V_{org}}$$

Figure 9: The Overall Mass Transfer Coefficient for Various Carboxylic Acids in 1-octanol can be Calculated by Plotting the Values of $\left(\frac{[HA]^*_{org}}{[HA]^*_{org} - [HA]_{org}}\right)$ vs $\frac{A_c t}{V_{org}}$.

Concentration of carboxylic acid increases, lactic acid exceeded propionic acid and succinic acid in terms of mass transfer coefficient.

Specific Rate of Reaction, $R_{HA}\left(\frac{kmol}{m^2 s}\right)$:

Cross-sectional area (A_c=0.0058 m^2) divided by volume of organic solution (100 ml), or the slope between C_{org} Vs time and divided by interfacial area 23.8 m^{-1}, will give the value of R_{HA} the following list includes a specific rate of reaction.

$$R_{HA} = \left(\frac{V_{org}}{A_C} \frac{dC_{org}}{dt}\right)_{at\ t=o}$$

Order of the Reaction

Order can be found by the "Method of least squares" a linear approximation method was applied on the data of specific rate of extraction to find the order w.r.t acid or amine for different acid concentrations (0.1 to 0.4N) at particular amine concentration (40%).
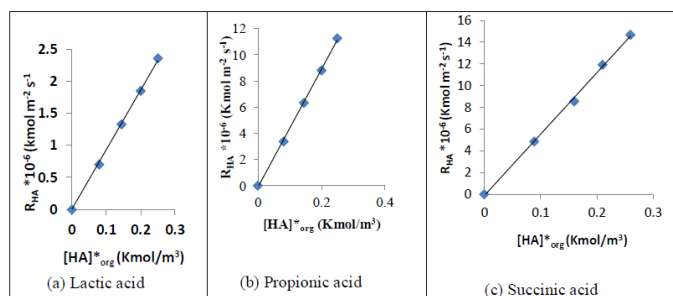

Figure 10: The Specific Rate of Extraction for the Reactive Extraction of Acid with 40% TBA=1.7 Kmol/m^3 in 1-octanol is Affected by the Initial Concentrations of (a) Lactic Acid, (b) Propionic Acid, and (c) Succinic Acid

From the Figure 10. It is observed that there is an effect of initial lactic acid, propionic acid and succinic acid concentration for TBA at various concentrations of amine (10% to 40%), with 1octanol, since the format trend line passes through origin with slope m=1, for carboxylic acids, so order w.r.t. acid may be considered as first order for TBA with 1-octanol .
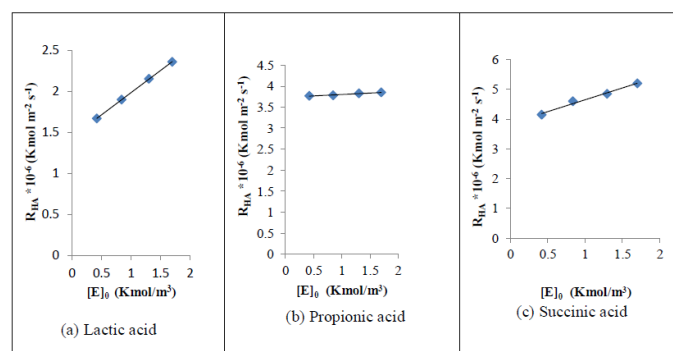

Figure 11: Reactive Extraction of (a) Lactic Acid, (b) Propionic Acid, and (c) Succinic Acid at 0.1N, with Tri-n-Butyl Amine (0.4219, 0.843, 1.3, and 1.7) Kmol/m^3 in 1-octanol , shows the Effect of Starting Amine Concentration on Specific Rate of Extraction

From Figure 11. It is observed that Amine effect is not observed (n=0) for TBA since the trend line does not passes through origin and it is considered as zero order for TBA. It is found for for all the studied type of Lactic acid, Propionic acid and Succinic acid, Hence it is concluded that the overall order is first order for TBA with different diluents.

Rate Constant

The equation to calculate the rate constant for an acid amine complex with a specified m, n order was provided by Doraiswamy and Sharma. Kmn (mol/m^2*s) [23].

$$R_{HA} = [HA]^*_{org}\left(\sqrt{D_A K_{mn} [HA]^{m-1} [E]_0^n}\right)$$

Where DA is the diffusion coefficient given as,

$$D_A = 7.4 * 10^{-12} \left(\frac{T\sqrt{\varphi M_B}}{\mu \vartheta_{acid}^{0.6}}\right)$$

Where φ, is the association factor, M_B (gm/mol) is molecular weight of diluent, μ (Ns/m^2) represents the dynamic viscosity, ϑ_{acid} (m^3/Kmol) is the molar volume of carboxylic acid.

Table 4: Diffusivity of Carboxylic Acids with 1-octanol

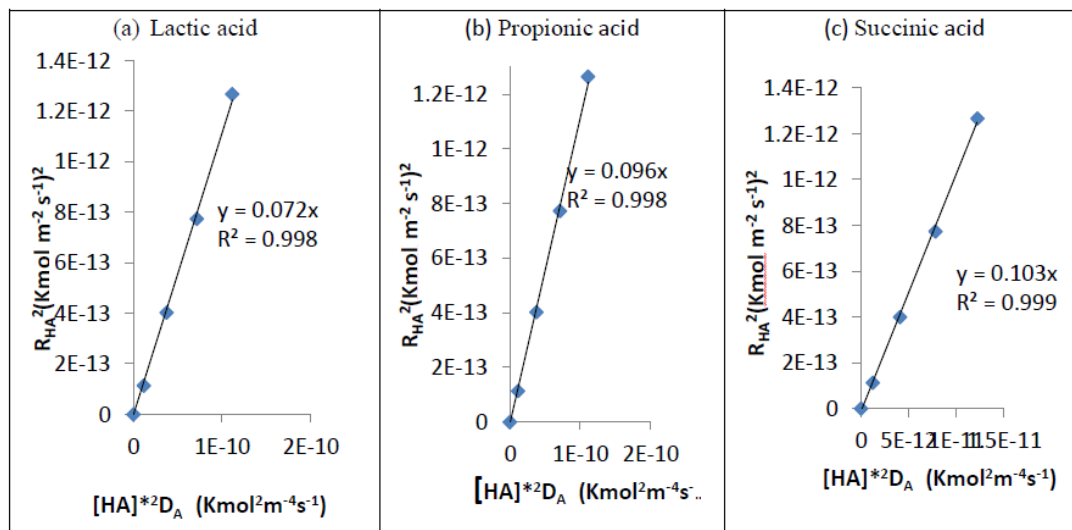| Carboxylic acid	Diffusivity (m²/s) with 1-octanol
Succinic acid	1.78×10^{-6}
Propionic acid	1.63×10^{-6}
Lactic acid	1.56×10^{-6}

Figure 9: Finding the First Order Rate Constant for the Reaction TBA=1.7 Kmol/m3 in 1 Cctanol at Various Carboxylic Acid Concentrations between 0.1N and 0.4N

Table 5: Determination of Rate Constant at Various Concentrations of TBA in 1-octanol for Different Carboxylic Acids

Concentration of amine	Lactic acid	Propionic acid	Succinic acid
	TBA (k_1)	TBA (k_1)	TBA (k_1)
10%	0.023	0.034	0.046
20%	0.04	0.052	0.064
30%	0.051	0.074	0.091
40%	0.072	0.093	0.103

It is found that Table 5, as the amine concentration increases the value of first order rate constant k_1(s^{-1}). It is observed that TBA has high rate constant due to its high affinity towards the carboxylic acids. Dicarboxylic acids shows maximum rate constant compared to mono carboxylic acids due to its hydrophobic in nature.

Hatta Number (MH)

The four sorts of regimes have been classified by Doraiswamy and Sharma (very slow, slow, fast and instantaneous) Depending on the value of the Hatta number, which is defined as the ratio of the amount of reactant [HA] reacting in the film to that reacting in the bulk, it is possible to determine the type of regime for a particular reaction order (m,n) [24-26].

$$M_H = \left(\frac{\sqrt{\frac{2}{m+1} K_{mn} D_A [HA_*]^{m-1} [E]_0^n}}{K_L} \right)$$

Enhancement Factor (Φ):

The effect of reaction of carboxylic acids can be determined by using enhancement factor and is defined as the ratio of take up of solute when reaction occurs to the rate of take up of solute for straight mass transfer [26].

$$\emptyset = \frac{\text{Rate of take-up of solute when reaction occurs}}{\text{Rate of taking up of solute for straight mass transfer}} = \frac{R_{HA}}{K_L [HA]_{org}^*}$$
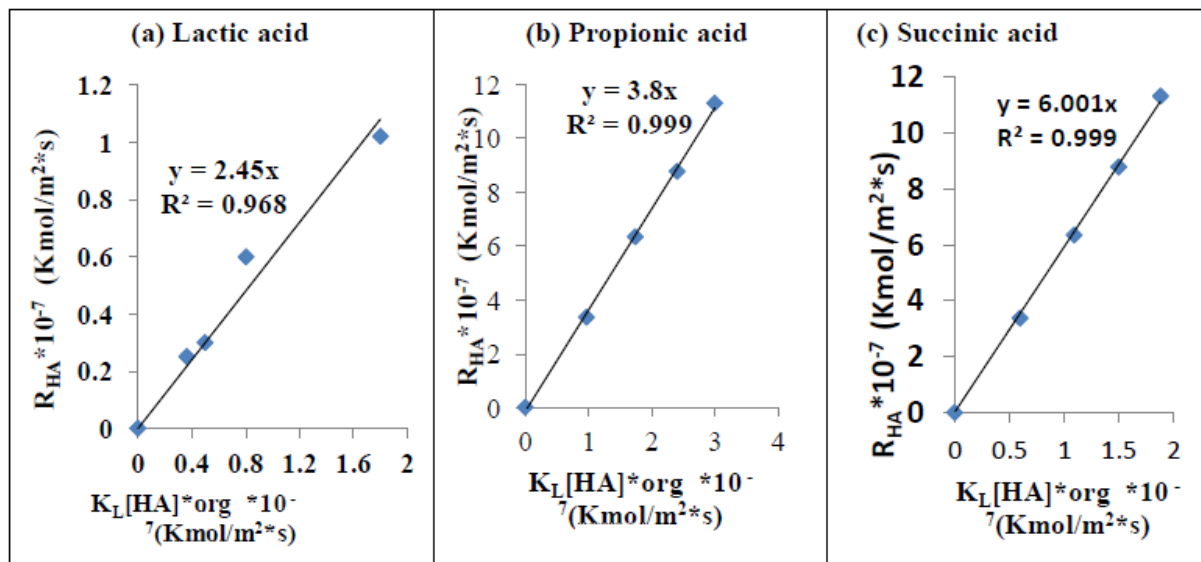
Figure 10: Estimation of Enhancement Factor for Different Carboxylic Acid Concentration with Tri-n-Butyl Amine at 40% (1.7kmol/m^3) in 1-octanol

Table 6: Range of Hatta Number and Enhancement Factor at Various Amine Concentrations with 1-octanol for Different Carboxylic Acids

concentration of amines	Lactic acid		Propionic acid		Succinic acid	
	TBA		TBA		TBA	
	M_H	Φ	M_H	Φ	M_H	Φ
10%	1.5	1.1	3.1	1.7	5.1	2.5
20%	2.1	1.8	4.8	2.2	8.5	3.6
30%	3.3	2.1	6.6	2.9	10	4
40%	4.1	2.5	8.4	3.8	14	6.1

Succinic acid achieves maximum Hatta number (M_H=14 for TBA) followed by Propionic acid (M_H=8.4 for TBA) and lactic acid (M_H=4.1 for TBA). For all the carboxylic acids the value of M_H is found to be >>1 with TBA. It is also observed that from Table 6 there is an increase in hatta number as the amine concentration increases.

$$M_H \gg \frac{[E]_0}{Z[HA*]}\left(\sqrt{\frac{D_B}{D_A}}\right) \qquad D_A K_2 [E]_0 \gg K_L^2 \quad \text{for m=1, n=1 Instantaneous reaction regime}$$

$$M_H \ll \frac{[E]_0}{Z[HA*]} \qquad D_A K_1 \gg K_L^2 \qquad \text{for m=1, n=0 Fast reaction regime [26].}$$

By checking all the above validity conditions, it is concluded that TBA in 1-octanol falls in fast reaction regime occurs simultaneously in the film itself. The ranking of enhancement factor is as follow succinic acid> propionic acid> lactic acid this is due to less hydrophilic nature of dicarboxylic acid compared to mono carboxylic acids so that it can be extracted very easily. Finally it is concluded that TBA in 1-octanol can be chosen as a best solvent and diluent combination for the reactive extraction of carboxylic acids.

Conclusion
A detailed design on reactive extraction of carboxylic acids is studied through equilibrium and kinetic studies. Extraction power of the organic phase was found to be increased significantly due to the presence of tertiary amine when compared to physical extraction. Order w.r.t. TBA is found to be first order. Rate constant is high for TBA since it has more capability to extract the carboxylic acids from the aqueous phase to organic phase and increases the prospect of forming the acid amine complex. Succinic acid with TBA gives maximum M_H=14, followed by propionic acid and lactic acid. It is found that TBA in 1-octanol falls in fast reaction regime for all the type of Lactic acid, Propionic acid and Succinic acid. Among all various carboxylic acids, amines and diluents the effect of reaction is more for Succinic acid with TBA in 1-octanol.

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