

A Study on Reactive Extraction of Succinic acid

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Abstract- Succinic acid has received increasing attention in various fields and hence reactive extraction has been employed to recover by using tri pentyl-amine and try butyl amine in different diluents (1-octanol, chloroform and dimethylen chloride). Distribution coefficient (k_D), loading ratio(Z), physical and chemical equilibrium isotherms were measured through an acid-amine complex at room temperature and pressure. In a batch type reactive system, order with respect to acid and amine, mass transfer coefficient, rate constant was determined by conducting kinetic studies at different succinic acid concentrations. Based upon the value of hatta number and other criterion conditions, enhancement factor and type of reaction regime for TPA and TBA with 1-octanol have been evaluated.

Keywords- Chloroform, Dimethylene chloride, Equilibrium, Kinetic, Succinic acid, Reactive Extraction, Tri-n-pentyl amine, Tri-n-butyl amine and 1-octanol.

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1. Introduction:

Succinic acid has four carbon atoms and is a dicarboxylic acid. It can be found in the tissues of both plants and animals. The body's intermediate metabolism must work properly. Because it's utilised as a monomer in biodegradable polymers, it's gained a lot of interest recently. [1,21].

Carboxylic acids are organic acids of the carboxylic group consisting of a carbonyl-bonded hydroxyl group. They are both polar and form hydrogen links. In the chemical industry, polymers, pharmaceuticals, solvents and food products are manufactured.

The most effective chemicals for fermentation are lactic acid, propionic acid, succinic acid, citric acid, tartaric acid, itaconic acid and other carboxylic acids. [2,17].

Extraction, precipitation, distillation, electro dialysis and adsorption were typical methods for the separation of succinic acid. A new reactive extraction process has been developed for separation, which is clean, safe, economical and eco-friendly. When reactive extraction takes place, a reaction occurs through diffusion and solubilization mechanisms between the solution and the extractant. [3,26].

Due to its high viscosity and corrosive nature, aliphatic amines were used with diluents. The three groups of amines are primary, secondary and tertiary. Primary amines are organic hydrophilic compounds that are at microorganism level become poisonous and at the interface form gel, which creates a third phase that is hard to disconnect. The tertiary amines are highly extractable, and have a hydrophobic nature, leading to high succinic acid recuperation. [4,27].

Diluent helps to keep the complex stable by preventing succinic acid from being back-extracted from the organic to the aqueous phases. Diluents can improve the extraction efficiency and distribution coefficient of succinic acid due to their polar nature and tendency for the formation of complexes. [5,19].

The two forms of diluents employed are active and inactive diluents. The active diluent used to form acid-amine complexes is polar in nature and has a highly soluble medium. Such compounds include carbon-bonded oxygen donor atoms (1-octanol, MIBK, 1-decanol) and chlorine atoms (dichloromethane, chloroform, chlorobenzene, 1-chlorobenzene) [6,18].

This study is mainly concerned with using equilibrium and kinetic experiments to determine the impact of chemical reactions on the specific rate of mass transfer. It can be attained by using Succinic acid (solute), Tri-pentyl amine, and Tri-butyl amine (extractants) diluted with 1-octanol, chloroform, and dimethylene chloride (Active diluents).

2. Materials and Methods:

2.1. Materials

Tri-pentylamine (TPA), $[\text{CH}_3(\text{CH}_2)_4\text{N}]$, ($\rho=0.782\text{g/ml}$) were extractants used in Sigma Aldrich and in Finar chemicals were Tri-butyl amine (TBA), $[(\text{CH}_3)_3\text{CNH}_2]$, ($\rho=0.778\text{g/ml}$). 1-octanol $[\text{CH}_3(\text{CH}_2)_7\text{OH}]$, ($\rho=0.83\text{g/ml}$) from Sisco Research Laboratory Private Limited, Molychem Manufacturers & Importers of Laboratory Reagents & Fine Chemicals supplied the diluents chloroform $[\text{CHCl}_3]$ ($\rho=1.489\text{ g/ml}$) and dimethylene chloride $[\text{CH}_2\text{Cl}_2]$ ($\rho=1.325\text{ g/ml}$). Merck Specialities Private Limited provided the succinic acid $[\text{C}_4\text{H}_6\text{O}_4]$ ($\rho=1.56\text{ g/ml}$), and the NaOH utilised was reagent grade. The phenolphthalein indicator ($\text{pH}=8.00$ to 10) was given by Hi media lab pvt ltd. An aqueous solution with a concentration range of 0.1 N to 0.4N is made using distilled water. All of the compounds were utilised without any further purification.

2.2. Methods

2.2.1. Equilibrium studies:

The experiment was carried out at room temperature (304K) and under normal pressure (101.32K Pa). A 0.5N NaOH solution is prepared, and oxalic acid was used to standardise it. Succinic acid was diluted with distilled water to make an aqueous solution (0.1N to 0.4N). Only organic phase diluents were used to achieve physical equilibrium. In a separate conical flask (100 ml), equal volumes of aqueous and organic phases were combined and placed in a temperature-controlled shaker bath (provided by REMI laboratory instruments) until equilibrium was reached (1 hour). Titrating with NaOH and phenolphthalein indicator can be used to determine the concentration of Succinic acid. By diluting the extractant with the organic phase, similar chemical equilibrium data can be obtained. The concentration of succinic acid in the organic phase can be estimated using the law of mass action.

2.2.2. Kinetic studies:

The kinetic tests were carried out in a 500mL cylindrical vessel (diameter 80mm , length 115mm) with a double paddle impeller (diameter 8mm , thickness 2mm , spacing between impellers 1mm). In a cylindrical cell, equal volumes of aqueous and organic phases (100ml each) are taken. To maintain the same concentration levels in both phases, the impeller is located exactly at the interface. At atmospheric temperature and pressure, very low rpm in the range of $100\text{-}120\text{ rpm}$ was maintained so that the interface would not be disturbed. To assess the concentration of Succinic acid in the aqueous phase, a sample (10ml Aqueous phase) is obtained every 10 minutes and titrated with 0.5N NaOH. Mass balance can be used to determine the amount of succinic acid in the organic phase. Because the reaction is reversible, there is a possibility of backward extraction of

Succinic acid molecules from the organic to aqueous phases. Kinetic studies allow for the verification of back mixing by measuring the initial specific rate of reaction, R_{HA} ($\text{mol/m}^2\cdot\text{s}$), which is only directed by the forward reaction. [14,22]

$$R_{HA} = \left(\frac{V_{org} dC_{org}}{A_C dt} \right)_{\text{at } t=0}$$



Figure.1. Experimental setup for kinetic studies (Stirred cell)

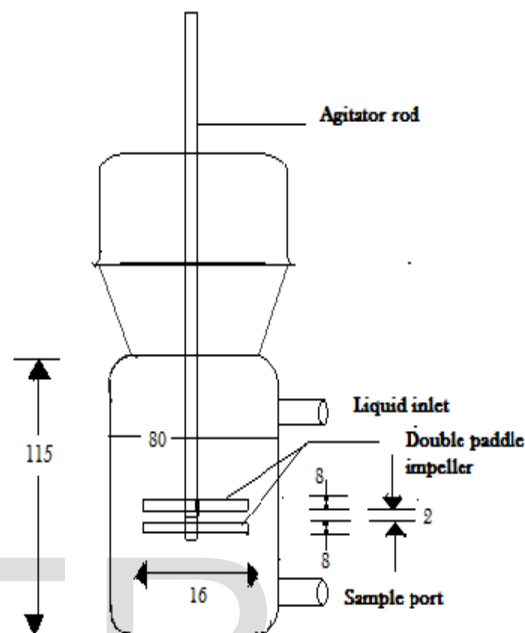
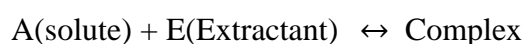
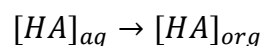


Figure. 2. Schematic diagram of stirred cell (All dimensions are in mm)

2.3. Theory of reactive extraction:

Reactive extraction with a specific extractant that results in a higher distribution coefficient has been suggested as a promising technique for recovering Succinic acid. The concentration of the aqueous phase, organic phase, a form of complex, extractant, and temperature all affect reactive extraction. Acid's hydroxyl group reacts with the carbon atom's hydrogen atom to produce a complex and water. Succinic acid transfers from the aqueous phase to the interface and interacts with the extractant to form a complex, which is subsequently solubilized in the diluent. [7,24].



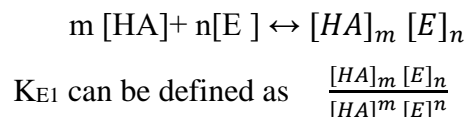
The distribution coefficient can be used to calculate the amount of Succinic acid that has diffused from the aqueous to the organic phases. (K_D) It is the measure of the solute distribution in the two phases. [8].

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

Succinic acid extraction efficiency can be determined as the ratio of acid concentration to the initial acid concentration of the extractant.[9,20].

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

The equilibrium complexation constant (K_{E1}) for the reaction of m acid molecules and n-Amine molecules to form m:n complex [10].



For convenience, the systems can be divided into four regimes based on the relative rates of diffusion and reaction:

- Regime 1, very slow reactions;
- Regime 2, slow reactions;
- Regime 3, fast reactions;
- Regime 4, Instantaneous reactions.

In general, depending on the value of M_H and the criterion conditions provided by doraiswamy and Sharma, liquid chemical reactions can be fast or instantaneous. At the current concentration of the different species, bulk liquid can be considered to be in equilibrium in most situations. When a liquid-phase reaction occurs instantly, equilibrium can be assumed at all points in the liquid, including the interface. Fast reactions, on the other hand, do not always achieve equilibrium. [11,25].

3. Results and discussions:

3.1. Extraction equilibria:

Equilibrium experiments with only diluents in the organic phase are used to achieve physical equilibrium isotherms. Isotherms were plotted with different diluents at different Succinic acid concentrations ranging from 0.1 to 0.4 kmol/m³ (Figure 3). Because of its polar composition, 1-octanol has the highest extraction efficiency as compared to chloroform and dimethylene chloride, and it serves as a strong solvating medium for the formation of ion-pair complexes.

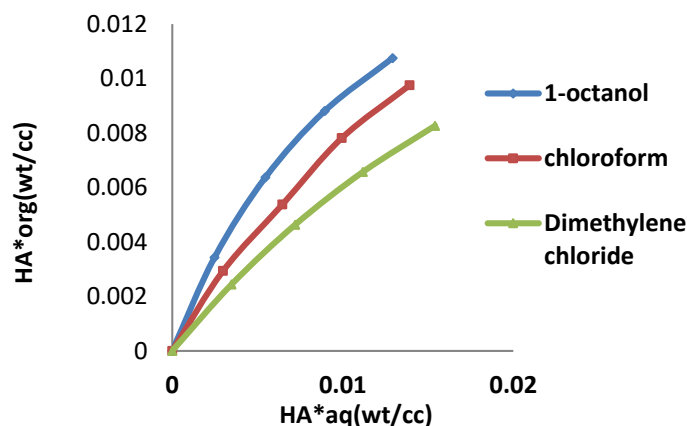
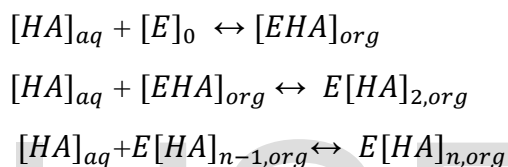


Figure. 3 The reactive extraction of succinic acid with various diluents isotherms of physical equilibrium.

The equations describe equilibrium models for the formation of Acid-amine complexes at the same time, i.e. (1:1). (2:1)... (1: n) [12,29]



The individual equilibrium constants K_{11} , K_{21} , K_{n1} can be calculated using the law of mass action.

Chemical equilibrium isotherms for various concentrations of Tri-pentyl amine and Tri-butyl amine (kmol/m^3) at various Succinic acid concentrations ranging from 0.1 to 0.4 kmol/m^3 were measured. It can be seen in the figure.4 That as the amine concentration increases, the extraction efficiency of Succinic acid increases as well, and then stays constant.

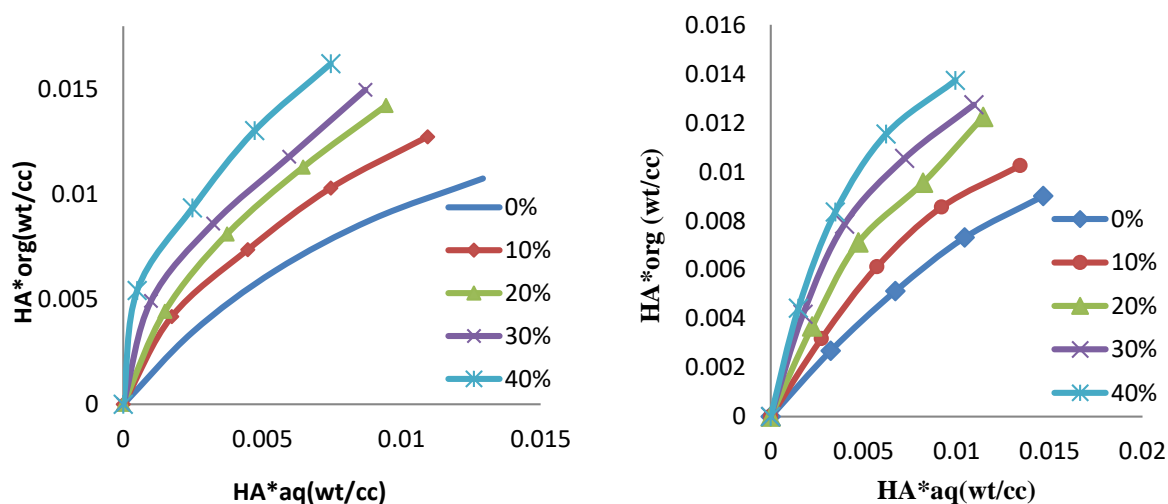


Figure.4. Chemical equilibrium isotherms for reactive extraction of 0.1N Succinic acid in 1-octanol at different concentrations of TPA = 0%, 10%, 20%, 30%, 40% (=0, 0.343, 0.687, 1.03,

1.4Kmol/m³) and TBA= 0%, 10%, 20%, 30%, 40% (=0, 0.4219, 0.843, 1.3, 1.7Kmol/m³), T=304K.

Loading ratio:

The loading ratio (Z) determines the quantity of Succinic acid concentration that can be added in the organic phase (Tri pentyl amine in 1-octanol). [13,28]

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

The extractability of Succinic acid (the strength of the acid-base interaction) and its aqueous concentration affect Z, although Amine concentration is unaffected.

A plot of Z/((1-Z)) vs [HA] for a very low loading ratio of Succinic acid in the organic phase (Z<0.5), i.e. for (1:1) acid-amine complex, yields a straight line with a slope as the equilibrium complexation is constant K_{EI}=14.06 for TPA and K_{EI}=7.5 for TBA.

Table 1

Equilibrium complexation constant for the reactive extraction of (1:1) Succinic acid at 40% TPA and TBA with various diluents.

Diluent	K _{EI} for TPA in 1octanol	K _{EI} for TBA in 1-octanol
1-octanol	14.06	7.5
Chloroform	6.31	3.83
Dimethylene chloride	4.6	2.23

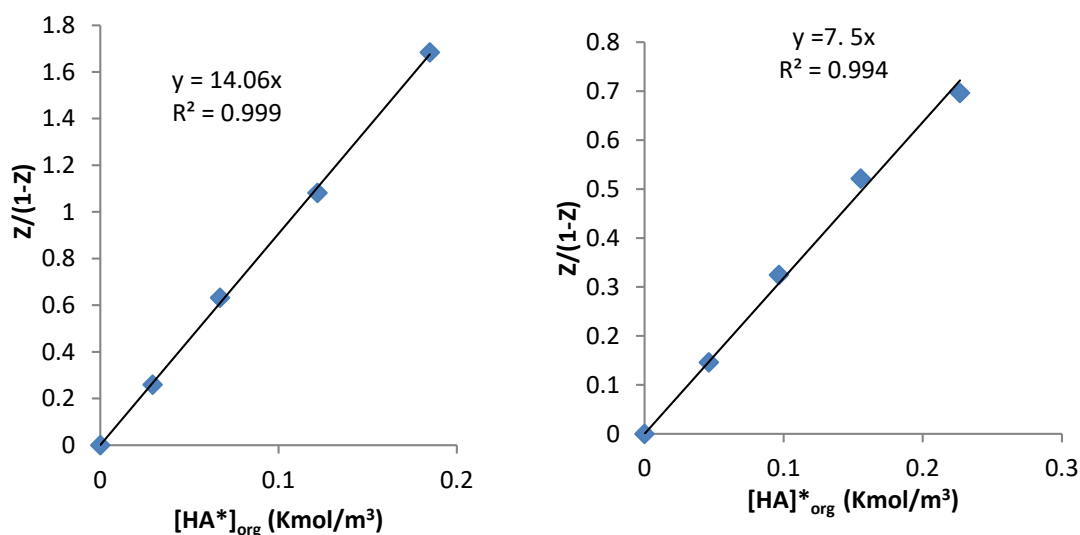


Figure.5. The equilibrium complexion constant (1:1) Succinic acid at 40% Tri pentyl amine and Tri butyl amine in 1-octanol was estimated using a plot of Z/((1-Z)) vs. [HA]*_{org}.

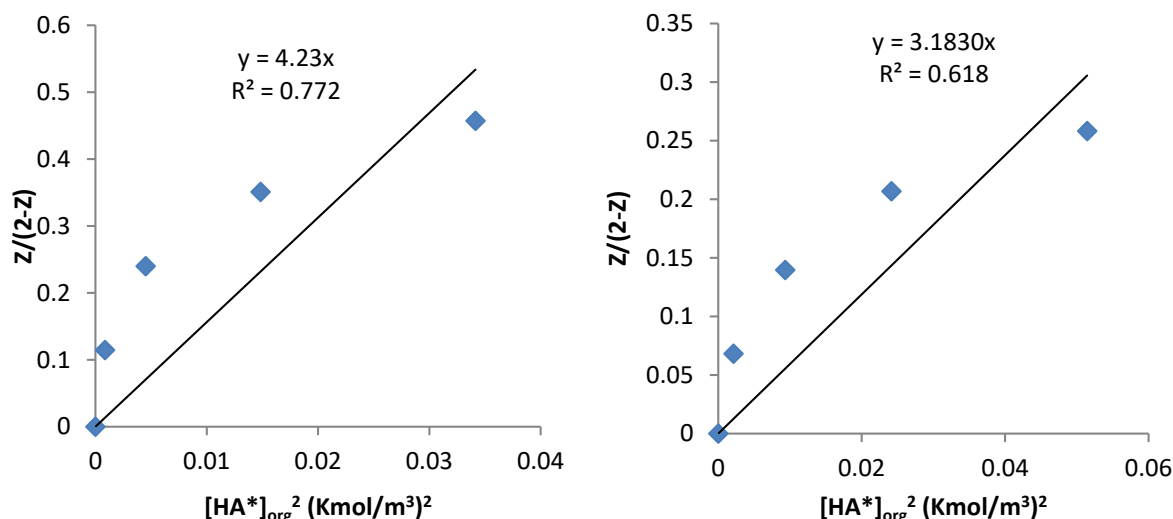


Figure.6. For (2:1) Succinic acid at 40 percent Tri pentyl amine and Tri butyl amine in 1-octanol, a plot of $Z/(2-Z)$ vs. $[HA]^*_{org}$ was used to estimate the equilibrium complexation constant.

Because of the high equilibrium Succinic acid concentration in the organic phase, it is possible to form only (1:1) acid-amine complexes, as shown in fig. 5. In The organic phase, there are not enough Succinic acid molecules to create a (2:1) Succinic acid-amine complex is observed in fig 6.

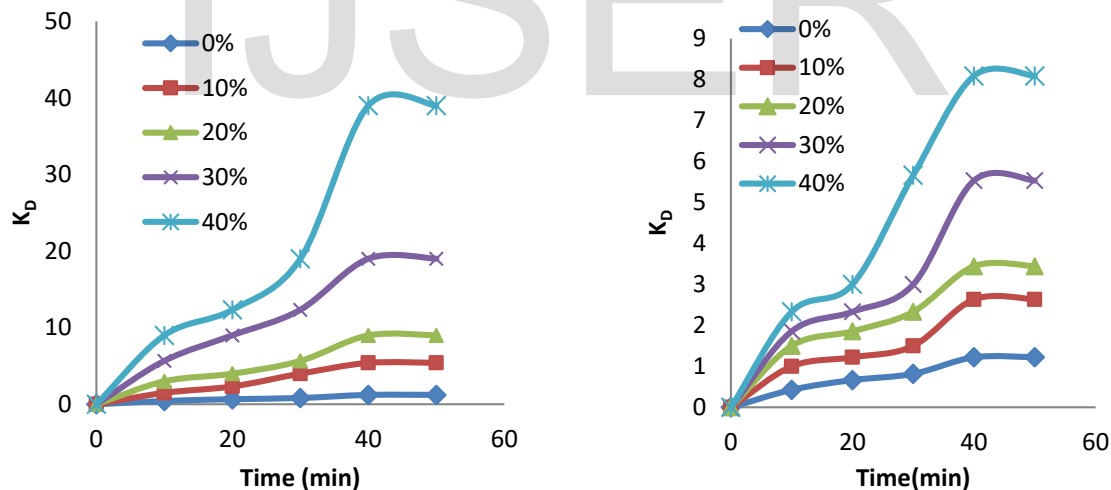


Figure.7. Effect of distribution coefficient on time for different concentrations of Tri-pentyl amine and Tri-butyl amine at 0%, 10%, 30%, 40%, and 0.1N, Succinic acid with 1-octanol.

As the above figure shows. The distribution coefficient increases with rising TPA and TBA concentrations, as well as w.r.t. time, after reaching a steady state, until it becomes constant. When compared to TBA with 1-octanol ($K_D = 8.09$), TPA with 1-octanol ($K_D = 32$) extracts the most Succinic acid. This is due to the higher amount of carbon atoms available in Succinic acid, which allows for more complex formation.

Effect of Initial Acid Concentration:

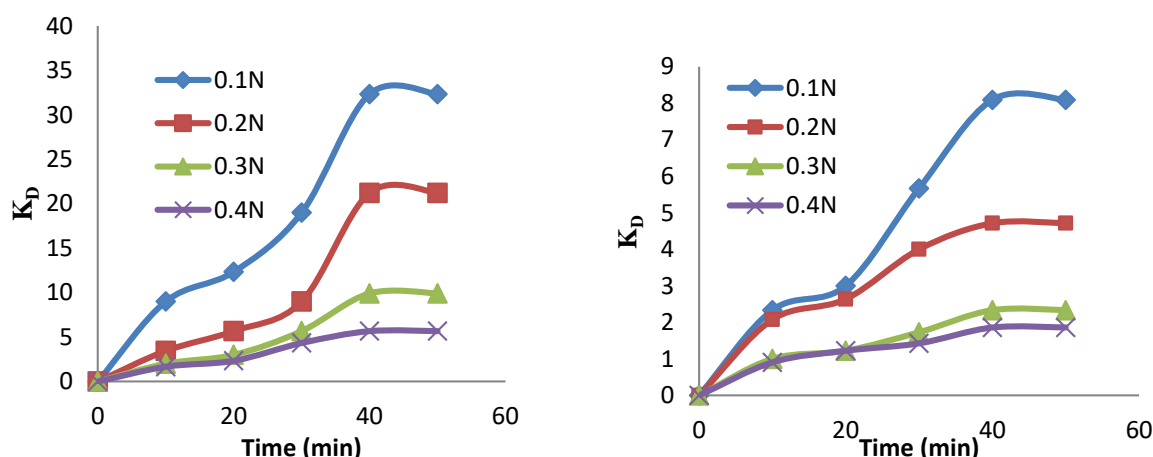


Figure.8. Variation of distribution coefficient with time for different concentrations of Succinic acid and concentration of 40% (1.4, 1.7Kmol/m³) TPA and TBA in 1-octanol

The variation of the distribution coefficient is studied with various concentrations of TBA and TPA diluted in various diluents at different acid concentrations (0.1 to 0.4 kmol/m³). figure 8, is evaluated. As the concentration of acids rises, the distribution coefficient (K_D) reduces. The ratio of the concentration of acid bound to the amine [HA]_{org} to the concentration of acid molecules remaining in the aqueous phase [HA]_{aq} is expected to be higher at low acid concentrations (0.1 kmol/m³) than at higher acid concentrations (0.4 kmol/m³) in the aqueous phase, so K_D drops significantly with an increase in acid concentration.

Table 2

At 40 % TPA and TBA, the distribution coefficient for the reactive extraction of 0.1N Succinic acid with various diluents.

Diluent	K _D for TPA in 1octanol	K _D for TBA in 1-octanol
1-octanol	32.00	8.09
Chloroform	9.00	7.00
Dimethylene chloride	4.00	2.3

When compared to chloroform and dimethylene chloride, 1-octanol has the highest distribution coefficient due to its high polarity and carboxylic acid extractability (fig.9).

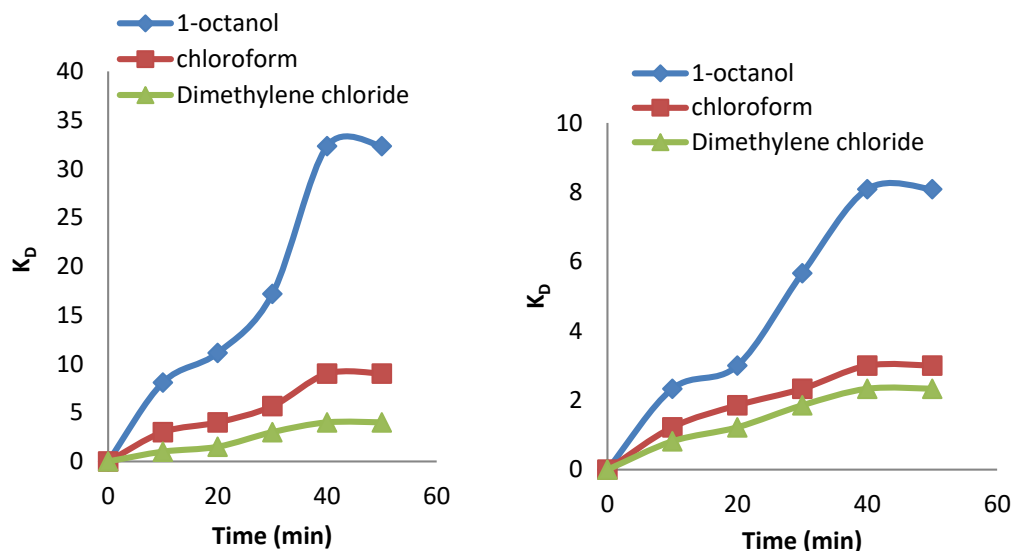


Figure.9. Effect of diluents on distribution coefficient for 0.1 Kmole/m³ succinic acid 40% (1.4, 1.7Kmole/m³) of TPA and TBA.

Effect of extractants efficiency:

Extractants were used to increase the extracting power of carboxylic acids and it gave positive results for all the studied amine concentrations. In the present study, tertiary extractants like Tri-n-pentylamine and Tri-n-butylamine were used for the extraction of succinic acid.

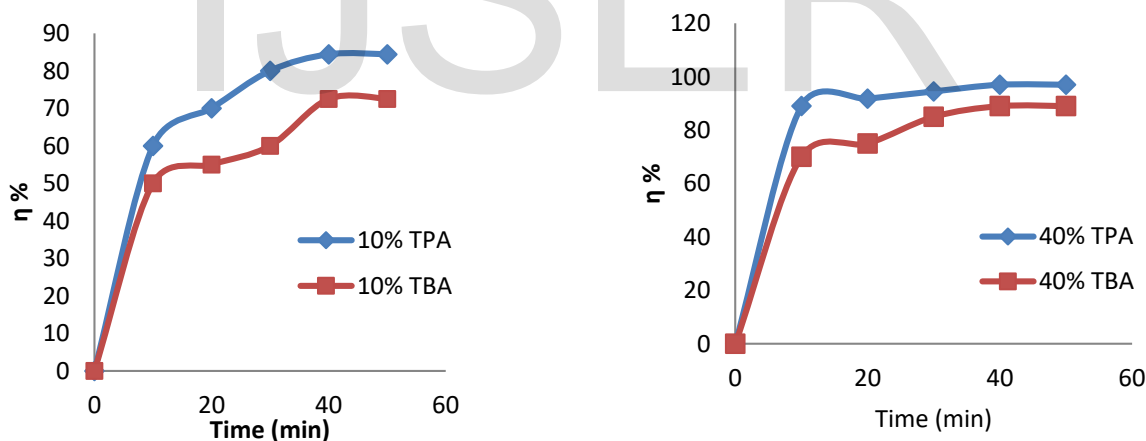


Figure.10. Effect of extractants on reactive extraction for 0.1N succinic acid concentration Tri-pentyl amine and Tri-butyl amine concentration at 10% and 40%.

From fig.10. As amine concentration increases extraction efficiency of succinic acid increases for both TPA and TBA with different diluents. At 40% of amine concentration extraction efficiency of succinic acid (0.1N) for TPA with 1-octanol reaches 97% for TPA and 89% for TBA with 1-octanol.

Kinetic studies:

Physical mass transfer coefficient:

The mass transfer coefficient, K_L (m²/s), is determined to confirm the reactive system's regime. Physical extraction of Succinic acid in a batch type reactive system using only pure diluent can be accomplished. [14,25].

For a batch type reactive system, the differential mass balance can be stated as

$$V_{org} \frac{dC_{org}}{dt} = K_L A_c (C^*_{org} - C_{org})$$

We have achieved this by integrating the above equation.

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

A plot between $\ln \left(\frac{C^*_{org}}{C^*_{org} - C_{org}} \right)$ versus $\frac{A_c t}{V_{org}}$ yields a straight line gives the slope as the value of

$$K_L = 1.88 \times 10^{-6} \text{ m}^2/\text{s}.$$

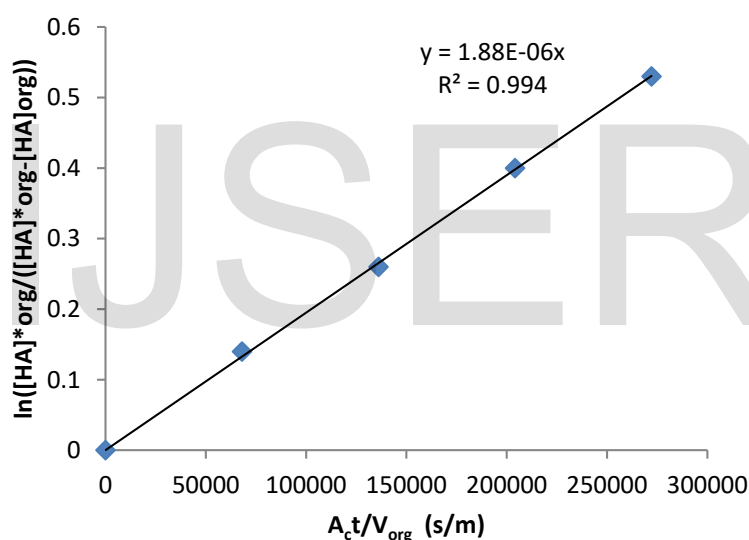


Figure.11. Determination of overall mass transfer coefficient at 0.1N Succinic acid in 1-octanol.

Order of the reaction w.r.t initial Succinic acid concentration:

To identify the order of specific extraction reaction rates for various Succinic acid (0.1 to 0.4 kmol/m³) concentrations at a concentration of 40 percent for TPA (1.4 kmol/m³) and TBA (1.7 kmol/m³) in particular. By performing a regression analysis on the data from fig.12, it was discovered that for both TPA and TBA, the order with relation to the initial Succinic acid concentration is m=1.

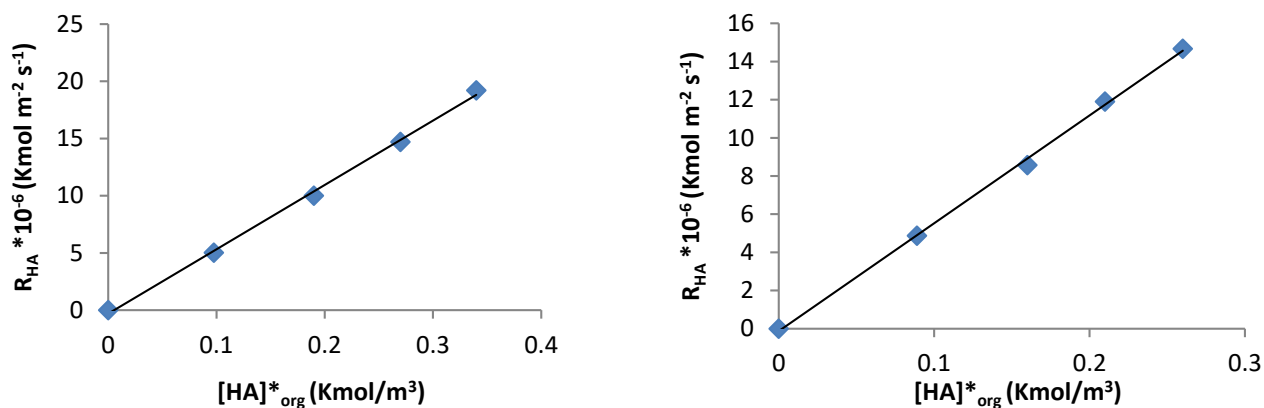


Figure.12. Effect of initial concentration of Succinic acid on specific rate of extraction for the reactive extraction of 0.1N Succinic acid with TPA=40 percent =1.4 Kmol/m^3 and TBA= 40 percent =1.7 Kmol/m^3 in 1-octanol.

Order of the reaction w.r.t initial amine concentration:

The specific rate of extraction for various concentrations of TPA at 10%, 20%, 30%, 40% (0.343, 0.687, 1.03, 1.4) Kmol/m^3 and TBA (0.4219, 0.843, 1.3, 1.7) Kmol/m^3 at suitable Succinic acid concentration i.e. 0.1 kmol/m^3 may be analysed using regression analysis. From fig.13, it can be deduced that TPA(n=1) has an amine effect. For TBA, it is noticed that n=0.

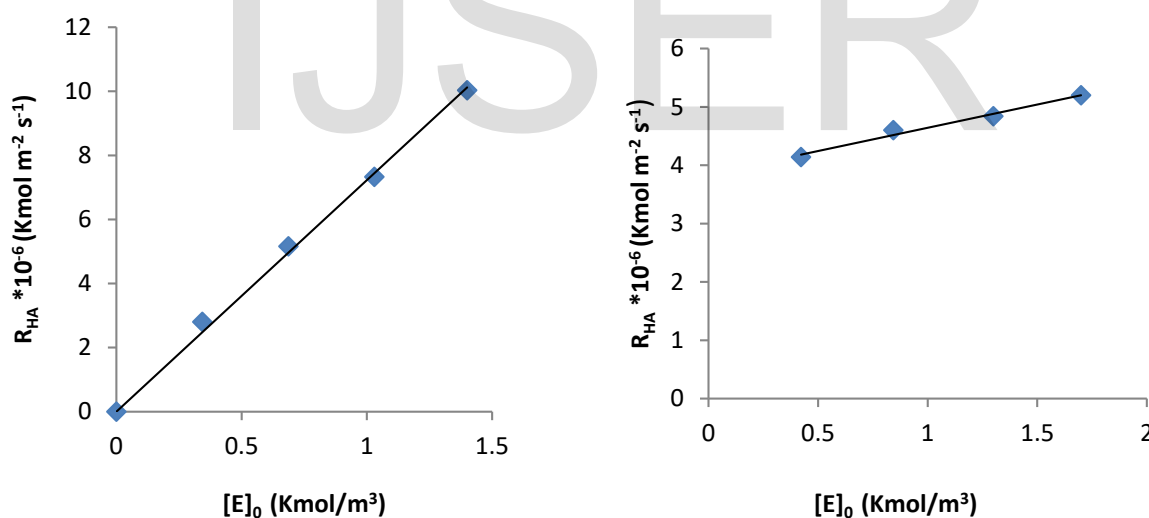


Figure.13. For the reactive extraction of Succinic acid with Tri-pentyl amine and Tri-butyl amine in 1-octanol, the effect of initial amine concentration on specific rate of extraction (at 0.1N of Succinic acid, T=304K).

Rate constant:

To ascertain the rate constant for a certain m,n acid, amine complex order the Doraiswamy and Sharma have provided the equation. K_{mn} ($\text{mol/m}^2\text{s}$). [15,22]

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

Where D_A is the diffusion coefficient of Succinic acid in 1-octanol. It can be evaluated from the equation given by Doraiswamy and Sharma.

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

Where Molecular weight (M_B), Association factor (φ), and viscosity (μ) for 1-octanol are $M_B=130.23$ g/mol, $\varphi=1$, $\mu=7.36*10^{-3}$ Ns/m², the molar volume of Succinic acid is 0.0756 m³/Kmol, D_A can be obtained as $1.78*10^{-9}$ m²/s.

For the obtained order (m,n) the rate expression can be reduced to

$$R_A = [HA]_{org}^* (\sqrt{D_A K_2 [E]_0^n}) \quad \text{For } m=1, n=1$$

$$R_A = [HA]_{org}^* (\sqrt{D_A K_1}) \quad \text{For } m=1, n=0$$

The value of the second-order rate constant can be found by doing a regression analysis between R_A^2 versus $D_A [E]_0 [HA]_{org}^*{}^2$ and K_2 was calculated to be $0.185 \text{ m}^3 \text{ kmol}^{-1} \text{ s}^{-1}$ (see fig.14). Plotting a graph of R_A^2 versus $[HA]_{org}^*{}^2 (K_1)$ provides a straight line with a slope of 0.103 s^{-1} , which is the value of the first-order rate constant. When compared to Tri-butyl amine with 1-octanol, the rate constant for Tri-pentyl amine is shown to be higher.

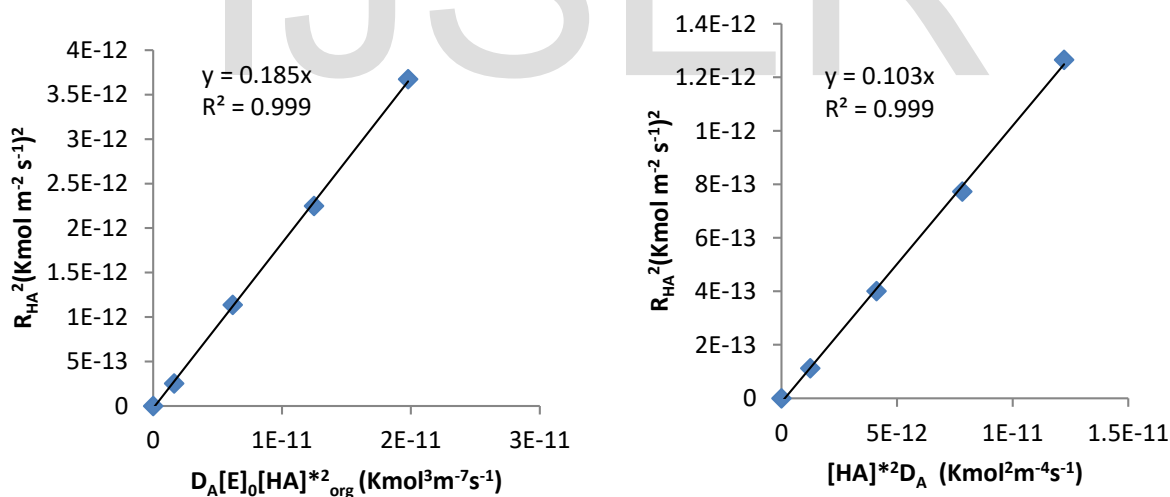


Figure.14. In 1-octanol at varied Succinic acid concentrations ranging from 0.1N to 0.4N, the second order rate constant for 40% TPA= 1.4 kmol/m^3 and the first order rate constant for 40% TBA= 1.7 kmol/m^3 were determined.

Hatta number (M_H):

The four sorts of regimes have been classified by Doraiswamy and Sharma [16] (Very slow, slow, fast and instantaneous). The value of the hatta number can be used to determine the type of regime for a particular reaction order (m,n).

$$M_H = \frac{\text{Maximum possible conversion in the film}}{\text{Maximum diffusional transport through the film}}$$

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

For varied concentrations of TPA (0.343 to 1.4) Kmol/m³ with 1-octanol, the hatta number ranges from 8.5 to 21, and for TBA (0.4219 to 1.7) Kmol/m³, it ranges from 5.09 to 14. The reaction is in the instantaneous or fast reaction domain because $M_H \gg 1$. The validity of the regime must be confirmed in order to certify the kind of regime for a specific reaction order.

$$M_H \gg \frac{[E]_0}{Z[HA^*]} \left(\sqrt{\frac{D_B}{D_A}} \right) ; \quad D_A K_2 [E]_0 \gg K_L^2 \quad \text{for } m=1, n=1 \quad \text{Instantaneous (regime 4)}$$

$$M_H \ll \frac{[E]_0}{Z[HA^*]} ; \quad D_A K_1 \gg K_L^2 \quad \text{for } m=1, n=0 \quad \text{Fast reaction (regime 3)}$$

TPA has a value of $\frac{[E]_0}{Z[HA^*]} \left(\sqrt{\frac{D_B}{D_A}} \right)$ ranging from 3.4 to 5.2, and $D_A K_2 [E]_0 \gg K_L^2$, and TBA has a value of $\frac{[E]_0}{Z[HA^*]}$ and $D_A K_1 \gg K_L^2$ ranging from 1.2 to 3.8. Because the criterion conditions for the intended regimes were met. As a result, for TPA, instantaneous reaction takes place at the interface in the organic phase of the reactive system, while for TBA, fast reaction takes place simultaneously in the film itself.

Enhancement factor:

To identify the effects of a reaction on pure mass transfer of Succinic acid from the aqueous to the organic phase, an enhancement factor has been developed, which is defined as follows:[15]

$$\phi = \frac{\text{Rate of take-up of a solute when reaction occurs}}{\text{Rate of taking up of a solute for straight mass transfer}} = \frac{R_{HA}}{K_L [HA]_{org}^*}$$

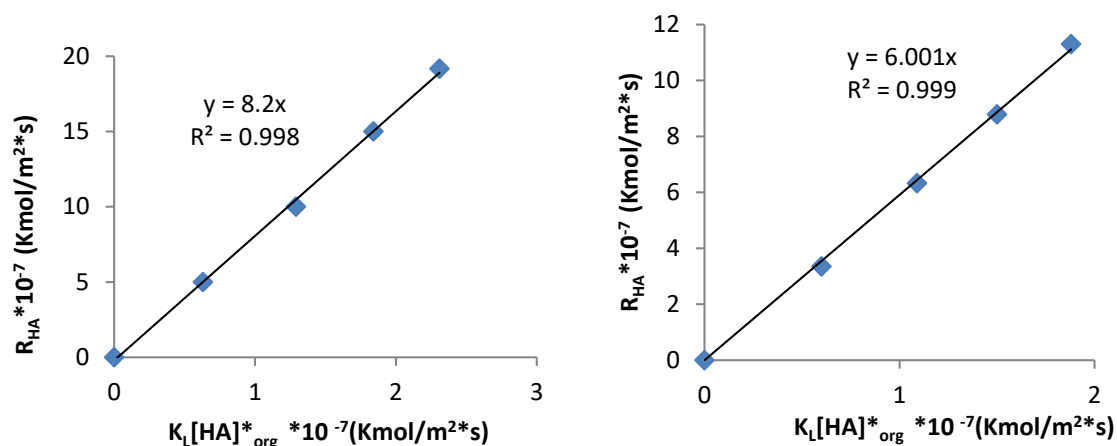


Figure.15. Estimation of enhancement factor in 1-octanol using 0.1N Succinic acid concentration with 40% Tri-pentyl amine (1.4 kmol/m^3) and 40% Tri-butyl amine (1.7 kmol/m^3).

TPA has an enhancement factor of 8.2 while TBA has an enhancement factor of 6.001, as shown in fig.15. As a result, the effect of Succinic acid extraction reaction with TPA in 1-octanol is greater.

4. Conclusions:

Equilibrium and kinetic experiments have been used to demonstrate the design of Succinic acid extraction. TPA, as compared to TBA, has a higher distribution coefficient and loading ratio due to its better extractability and longer chain length. TPA and TBA have the same order as Succinic acid, $m=1$, whereas TPA and TBA have the same order as Amine, $m=1$ for TPA and $n=0$ for TBA. TPA with 1-octanol has been proposed as the optimal extractant-diluent combination based on $K_D=32$ and $Z=4$. The value of K_L was calculated as $1.88 \cdot 10^{-6} \text{ m/s}$ using the differential mass balance equation. $K_2=0.185 \text{ m}^3\text{kmol}^{-1}\text{s}^{-1}$ for TPA and $K_1=0.103 \text{ s}^{-1}$ for TBA were found to be the rate constants. For varied concentrations of TPA (0.343 to 1.4) Kmol/m^3 with 1-octanol, the hatta number ranges from 8.5 to 21, and for TBA (0.4219 to 1.7) Kmol/m^3 , it ranges from 5.09 to 14. The reaction regime was discovered to be instantaneous for TPA and fast for TBA based on the value of the hatta number. Because the enhancement factors for TPA and TBA were found to be 8.2 and 6.001, respectively, it can be assumed that the effect of the reaction for Succinic acid is greater for TPA with 1-Octanol.

5. List of abbreviations

The following are the list of abbreviations used in the paper.

1. $[HA]_{org}$: Concentration of Succinic acid in the organic phase (Kmol/m^3)
2. $[HA]_{aq}$: Concentration of Succinic acid in the aqueous phase (Kmol/m^3)
3. $[HA]_{in}$: Initial Succinic acid concentration (Kmol/m^3)
4. $[HA]_{org}^*$: Concentration of Succinic acid in organic phase at equilibrium (Kmol/m^3)
5. $[E_0]$: Initial Amine concentration (Kmol/m^3)

6. K_D : Distribution coefficient
7. η : Extraction efficiency
8. Z : Loading ratio
9. D_A : Diffusivity of Succinic acid in 1-octanol (m^2/s)
10. R_{HA} : Specific rate of extraction of Succinic acid ($Kmol/m^2s$)
11. K_L : Mass transfer coefficient (m/s)
12. M_H : Hatta modulus
13. Φ : Enhancement factor
14. $[A_c]$: Cross sectional area of the stirred cell (m^2)
15. V_{org} : Volume phase(m^3)
16. t : Time of extraction(min)
17. K_2 : Second order rate constant ($m^3/Kmol*s$)
18. K_1 : First order rate constant (s^{-1})
19. K_{E1} : Equilibrium complexion constant for 1:1 Acid amine complex
20. K_{E2} : Equilibrium complexion constant for 2:1 Acid amine complex

Acknowledgements

Prof V.V. Basava Rao, Professor of Chemical Engineering and Principal, University College of Technology, Osmania University, Hyderabad provided valuable guidance and support to the authors.

References:

- [1] Hong, Y. K.; Hong, W. H.; Chang, Y. K. Effect of pH on the Extraction Characteristics of Succinic and Formic Acids with Tri-n-octylamine Dissolved in 1-Octanol. *Biotechnol. Bioprocess Eng.* 2001, 6, 347–351.
- [2] Murali, N.; Srinivas, K.; Ahring, B. K. Biochemical Production and Separation of Carboxylic Acids for Biorefinery Applications. *Fermentation.* 2017, 3, 22–47.
- [3] Hong, Y. K.; Hong, W. H.; Han, D. H. Application of Reactive Extraction to Recovery of Carboxylic Acids. *Biotechnol. Bioprocess Eng.* 2001, 6, 386–394.
- [4] Keshav, A.; Wasewar, K. L.; Chand, S. Extraction of Propionic Acid using Different Extractants (Tri-n-Butylphosphate, Tri-n-Octylamine, and Aliquat 336). *Ind. Eng. Chem. Res.* 2008, 47, 6192–6196.

- [5] Shitanshu Pandey and Sushil Kumar. "Reactive Extraction of Gallic Acid Using Aminic and Phosphoric Extractants Dissolved in Different Diluents: Effect of Solvent's Polarity and Column Design", *Industrial & Engineering Chemistry Research*, 2018, vol.57 (8), page: 2976-2987.
- [6] Keshav, A.; Wasewar, K. L.; Chand, S. Extraction of Propionic Acid using Different Extractants (Tri-n-Butylphosphate, Tri-n-Octylamine, and Aliquat 336). *Ind. Eng. Chem. Res.* 2008, 47, 6192–6196.
- [7] Madhumala, M. et al., "Extraction of acetic acid from aqueous media using indigenous Liquid-Liquid membrane contactor system, *Journal of Chemical Engineering Research Studies*, 2015, vol. 2, Page: 1-9.
- [8] Uslu, H.; Hasret, E.; Kirbaslar, S., İ . Extraction of Propionic Acid from Aqueous Solutions Using Tri-n-octyl phosphine Oxide and Dioctylamine in Different Solvents. *J. Chem. Eng. Data* 2019, 64, 4369–4375.
- [9] Eda, S.; Kumari, A.; Thella, P. K.; Satyavathi, B.; Rajarathinam, P. Recovery of Volatile Fatty Acids by Reactive Extraction using TriN-Octylamine and Tri-Butyl Phosphate in Different Solvents: Equilibrium Studies, pH and Temperature Effect, and Optimization using Multivariate Taguchi Approach. *Can. J. Chem. Eng.* 2017, 95, 1373–1387.
- [10]) Datta, D.; Kumar, S. Intensification of Recovery of Formic Acid from Aqueous Stream using Reactive Extraction with N, NDioctyloctan-1-Amine: Effect of Diluent and Temperature. *Chem. Eng. Commun.* 2013, 200, 678–700.
- [11] Octave levenspiel *Chemical Reaction Engineering*, third edition, Jhon Wiley & sons: Singapore, 2011, Chapter 23, page: 529.
- [12] Keshav, A.; Wasewar, K.; Chand, S.; Uslu, H. Reactive Extraction of Propionic Acid Using Aliquat-336 in 2-Octanol: Linear Solvation Energy Relationship (LSER) Modeling and Kinetics Study. *Chem. Biochem. Eng. Quart.* 2010, 24, 67–73.
- [13] Eda, S. et al., "recovery of Succinic acid by Reactive Extraction using Tri-n-octylamine in 1-deconol Equilibrium optimization using Response Surface method and kinetic studies.",

International journal of chemical separation Technology, 2016, Vol. 2, page:1-14.

[14] T. Prathap Kumar, B.Vishwanadham, K.N.Prasanna Rani, and V.V. Basavarao,"Reactive extraction of Levulinic acid from aqueous solutions with tri-n-octylamine(TOA) in 1-octanol: Equilibria, kinetics, and model development" chemical engineering communication 2011, 198:572-589.

[15] Mustafa, E., Marti, Turker Gurkan, "Equilibrium and kinetic studies on reactive extraction of pyruvic acid with Tri octylamine in 1-octanol". Industrial and Engineering Chemistry Research, 2011, vol. 50, page: 13518–13525.

[16] Doraiswamy, L. K., and Sharma, M. M. Heterogeneous Reaction: Analysis, Examples and Reactor Design, Fluid-Fluid-Solid-Reactions, John Wiley, New York, 1984, vol. 2.

[17] Kumar, S.; Datta, D.; Babu, B. Differential Evolution Approach for Reactive Extraction of Propionic Acid using Tri-n-Butyl Phosphate (TBP) in Kerosene and 1-Decanol. Mater. Manuf. Processes 2011, 26, 1222–1228.

[18] Senol, A.; Cehreli, S.; Ozparlak, N.; Andreatta, A. Optimization of Reactive Extraction of C1-C4 Aliphatic Monocarboxylic Acids from Aqueous Solutions: Modeling Solvation Effect with Extended-LSER, A-UNIFAC and SPR. Asia-Pac. J. Chem. Eng. 2017, 12, 919–937.

[19] Sunderlal, P., Diwaker, Z.S., Shahida, A., Rathore, A.K. "Reactive extraction of Itaconic acid Using Tri-n- Butyl phosphate in 1- Butanol, 1-Octanol and 1-Dodecanol", International Journal of Research in Science, Engineering and Technology, 2016, vol. 5, page: 14251433.

[20] Asc 1, Y. S.; Inci, I. Extraction Equilibria of Propionic Acid from Aqueous Solutions by Amberlite LA-2 in Diluent Solvents. Chem. Eng. J. 2009, 155, 784–788.

[21] Asc 1, Y.S., Inci, I. "Extraction equilibria of succinic acid from aqueous solutions by Amberlite LA-2 in various diluents." Journal of Chemical and Engineering Data, 2010, vol. 55 page: 847-851.

[22] Dharmapala, and Keshav, A. "kinetics of reactive extraction for the separation of pyruvic acid using Tri-n-butylamine dissolved in butyl acetate"International journal of chemical reactor engineering, 2015, vol 13, page: 63-69.

[23] Asci, Y.S., and Inci I. "Extraction of glycolic acid from aqueous solutions by amberlite la-2 in different diluent solvents," Journal of Chemical and Engineering Data, 2009, vol. 54, no. 10, page: 2791–2794.

[24] Barbari, T.A., King, C.J. "Equilibrium distribution coefficients for extraction of chlorinated hydrocarbons and aromatics from water into n-decane." Environmental Science and Technology, 1982, vol 16, page: 624-627.

[25] Bhaurao, P.N., Moulijn, J. A., and Pangarkar, V.G. "reactive extraction of citric acid by Alamine 336 in MIBK: equilibrium and kinetics", Chemical technology and biotechnology, 2004, vol 79, page: 1155-1161.

[26] Cascaval, D., Galaction, A.I. New separation techniques on bioseparations 1. Reactive extraction. Chemical Industry, 2004 vol. 58, page: 375-386.

[27] Dai, Y., King, J. "Selectivity between lactic acid and glucose during recovery of lactic acid with basic extractants and polymeric sorbents," Industrial and Engineering Chemistry Research, 1996, vol. 35, page: 1215-1224.

[28] Erdem Hasret, Sah İsmail KırbaSlar, and Hasan Uslu . Extraction of Citric Acid and Maleic Acid from Their Aqueous Solutions Using a Phosphorus-Bonded Extractant, Tri-n-octylphosphineoxide, and a Secondary Amine, Diocetylamine. Journal of Chemical & Engineering Data, 2018, vol.63 (1), page: 39-48.

[29] Keshav, A., and Norge, P., Wasewar, K.L. "Reactive extraction of citric acid using tri-n-octylamine in nontoxic natural diluents: part 1—equilibrium studies from aqueous solutions," Applied Biochemistry and Biotechnology, 2012, vol. 167, no. 2, page: 197–213.

[30] Shitanshu Pandey and Sushil Kumar. "Reactive Extraction of Gallic Acid Using Aminic and Phosphoric Extractants Dissolved in Different Diluents: Effect of Solvent's Polarity and Column Design", Industrial & Engineering Chemistry Research, 2018, vol.57 (8), page: 2976-2987.