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Reactive Extraction of Gluconic Acid Using Tri-n-octylamine in 1- Hexanol

K. Laila, Dr. B. Sarath Babu,G. Jyothsna Deepika

Department of Chemical Engineering
Sri Venkateswara University College of Engineering, Tirupati, India

Abstract-Gluconic acid is an important carboxylic acid widely used in chemical, pharmaceutical, food and other industries. The growing importance of biological production (fermentation) expressed with new routes and increasing production rates, leads to look for technologies of downstream processing for product separation.

Tertiary amines are effective extractants for separation of carboxylic acid from dilute solutions. The basic principle of recovery of acid by tertiary amines is through reaction with extraction. Generally, amines are used in diluents to improve their physical properties and to provide salvation of the complexes formed by them with the acids. The recovery of Gluconic acid with Trioctylamine and 1-hexanol is carried out for different Concentrations of acid, Trioctylamine (TOA) and 1-Hexanol

Key words: Reactive Extraction, Gluconic Acid, Tri-n-Octyl amine, 1-hexanol

1. INTRODUCTION

The carboxylic acids like tartaric acid, formic acid, pyruvic acid, acetic acid, succinic acid propionic acid, lactic acid, citric acid, gluconic 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. 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. 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. 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 Reactive extraction has variousrewardslikeenhanced reactor productivity, amelioratecontrol over pH in the bioreactor, reduces the downstream processing load, minimizes the solvent recovery cost, phase equilibrium enhanced and higher efficiency. 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.

Gluconic acid is a carboxylic acid (pentahydroxycaproic acid, $C_6H_{12}O_7$) is the oxidation product of glucose, naturally occurring in plants, fruits, wine (up to 0.25%), honey (up to 1%), rice, meat, vinegarand other natural sources.Gluconic acid is the largest commercially produced of fungal organic acids, from glucose. Demand for metal gluconates is steadily increasing due to their multiple applications in different industries.

In the current work, an investigation on the recovery of gluconic acid from aqueous solution was aimed by employing TOA in 1-hexanol. The equilibrium parameters such as K_D, E %, Z are evaluated using experimental data.

2. THEORY

The extraction process was analyzed through the K_D.The distribution coefficient (K_D) is defined as the ratio of total concentration of acid in all forms (partition, dimers & as complexes) in the organic phase to total concentration of all existing forms (ionized & un-ionized) in the aqueous phase by assuming no change in volume at equilibrium.

$$K_D = \frac{[\overline{GA}]_{total}}{[GA]_{total}}$$

Where, $[\overline{GA}]_{total}$= Concentration of acid in organic phase.
$[GA]_{Total}$= Concentration of acid in aqueous phase.

The extraction efficiency (E %) is defined as the proportion of gluconic acid concentration in the OP to the sum of gluconic acid concentration in organic andAP

$$E\% = \frac{K_D}{1+K_D} \times 100$$

The value of Z depends on the extractability of the acid (strength of the acid base interaction) and its aqueous concentration. The stoichiometry of the overall extraction equilibrium depends on the loading ratio in organic phase (Z). If the organic phase is not highly concentrated by acid, i.e., at very low loading ratios (Z < 0.5), 1:1 complex of acid and extractant is formed.

The extent to which organic phase (TOA+Decanol) can be loaded with carboxylic acid is expressed as the loading ratio, Z;

$$Z = \frac{[GA]_{Org}}{[T]_{Org}}$$

Where, $[GA]_{org}$= Concentration of acid in organic phase after extraction.
$[T]_{org}$= Concentration of TOA in organic phase before extraction.

3. MATRIALS AND METHODS

Materials

Gluconic Acid ($C_6H_{12}O_7$)(49-53 wt % of H_2O), molar mass 116.11 kg/kmol, density 1.134 g/ml at 250C, 97 % purity was procured from Sigma-Aldrich (India). TOA (N,N-dioctyloctan-1-amine) ($C_{24}H_{51}N$)a tertiary amine is a colour less liquid with the molecular weight of 353.66 g/mol, density 0.81 g/cm3at 200C, 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 250C, 98 % purity was used as a diluent was obtained from Sigma-Aldrich (India). Sodium Hydroxide (0.1 N of NaOH) used for volumetric analysis is of laboratory gradeused for titration. Phenolphthalein solution with pH range 8.2 to 10 was used as an indicator was procured from Ranbaxy, India. Distilled water was used to prepare the solutions of various initial concentrations of Gluconic acid solutions. The initial concentration of TOA in 1-hexanol was varied from 10% to 50% on volume basis. The aqueous phase consists of Gluconic acid and water and the organic phase consists of TOA and 1-hexanol.

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 gluconic acid were 0.0634, 0.12653, 0.1897, 0.25306, 0.31632 mol/L respectively.

Physical equilibrium:

For physical equilibrium, 20 ml of gluconic 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 gluconic acid in the AP. Mass balance was used to calculate the concentration of gluconic acid in the OP.

Chemical equilibrium:

For chemical equilibrium, 20 ml of gluconic 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 2 hours. The gluconic 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.

4. RESULTS AND DISCUSSION

Data obtained from the experiments are tabulated and compared to know the amount of the gluconic 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, are calculated as shown in Table 1 and Table 2.

Physical equilibrium

The most effective diluents are alcohols since they enhance the extraction of carboxylic acids. Therefore, 1-hexanol which is intermediate molecular weight alcohol is used as a diluent. The physical equilibrium data values for gluconic acid using 1-hexanol are shown in Table 1. It is observed that an increase in the initial concentration of acid increases the concentration of acid in both aqueous and organic phase. It is observed that distribution coefficient K_D decreases with increase in initial concentration of gluconic acid because the increase in concentration of acid in aqueous phase is higher than the concentration of acid in organic phase.

[GA]In Mol/L	[GA]Aq	[GA]Org	K_D	E%
0.03	0.01	0.019	1.9	65.517
0.06	0.02	0.03	1.5	60

0.12	0.04	0.046	1.15	53.48
0.18	0.06	0.055	0.916	47.807
0.2	0.07	0.06	0.857	46.149
0.3	0.13	0.07	0.538	34.98

Table 1:Physical equilibrium of water – Gluconic acid – 1-Hexanol

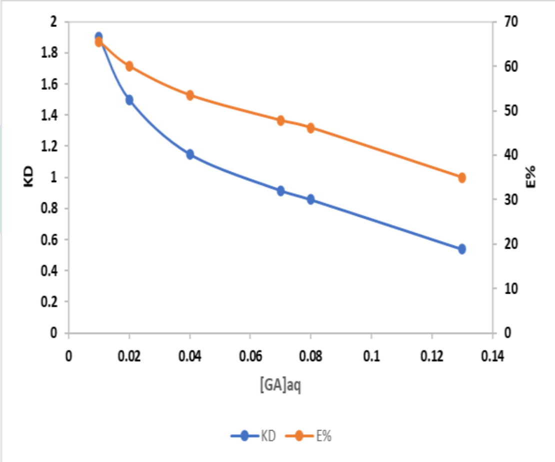

Fig 1: Equilibrium distribution of water – Gluconic acid – 1-Hexanol

Chemical equilibrium

The most effective diluents are alcohols since they enhance the extraction of carboxylic acids. Therefore, 1-hexanol which is intermediate molecular weight alcohol is used as a diluent. The chemical equilibrium data values for gluconic acid using 1-hexanol are shown in Table 2.

In this chemical equilibrium TOA is added 10-50%.It is observed that an increase in the initial concentration of gluconic acid increases the concentration of acid in both aqueous and organic phase. It is observed that distribution coefficient K_D decreases of Gluconic acid in aqueous phase $[HA]_{aq}$ because K_D is the ratio of concentration of acid in organic phase to the concentration of acid in aqueous phase. The chemical extraction distribution coefficient is found to be higher than physical extraction for all acid concentrations.
It is observed that extraction efficiency E% decreases, increases concentration of Gluconic acid in aqueous phase $[HA]_{aq}$ because E% is the ratio of concentration of acid in organic phase to the sum of acid concentration in aqueous and organic phase. It is observed that Loading Ratio Z increases with an increase in the concentration of acid in aqueous phase. The loading ratio decreases with an increase in the concentration of TOA because complexes involving more acid molecules are formed at lower concentrations of TOA.

10% TOA				
[GA]aq	[GA]org	KD	E%	Z
0.01	0.064	6.4	86.486	2.11
0.02	0.0808	4.04	80.158	2.39
0.05	0.11514	2.3028	69.715	3.36
0.07	0.1313	1.8757	65.2258	3.76
0.11	0.15554	1.414	58.57	4.56
0.211	0.1818	0.8616	46.2827	4.83
20% TOA				
[GA]aq	[GA]org	KD	E%	Z
0.01	0.064	6.4	86.486	1.95
0.02	0.0909	4.545	81.9657	2.26
0.05	0.1313	2.626	72.4214	3.25

0.07	0.14948	2.1354	68.106	3.58
0.11	0.1717	1.5609	60.951	4.32
0.211	0.19796	0.93819	48.405	4.64
30% TOA				
[GA]aq	[GA]org	KD	E%	Z
0.01	0.064	6.4	86.486	1.83
0.02	0.10504	5.252	84.005	2.13
0.05	0.14746	2.9492	74.678	3.11
0.07	0.16968	2.424	70.79	3.39
0.11	0.18988	1.72618	63.318	4.14
0.211	0.21412	1.01478	50.36	4.49
40% TOA				
[GA]aq	[GA]org	KD	E%	Z
0.01	0.064	6.4	86.486	1.74
0.02	0.1212	6.06	85.835	1.99
0.05	0.16564	3.3128	76.813	2.88
0.07	0.18584	2.6548	72.368	3.26
0.11	0.20604	1.87309	65.194	3.97
0.211	0.23028	1.09137	52.188	4.26
50% TOA				
[GA]aq	[GA]org	KD	E%	Z
0.01	0.064	6.4	86.486	1.65
0.02	0.13332	6.666	86.955	1.84
0.05	0.1818	3.636	78.429	2.68
0.07	0.19998	2.8568	74.07	3.11
0.11	0.22624	2.0567	67.284	3.63
0.211	0.25048	1.1871	54.277	4.12

Table 2: Equilibrium for reactive extraction of gluconic acid with various concentrations of TOA (10-50%) in 1- hexanol

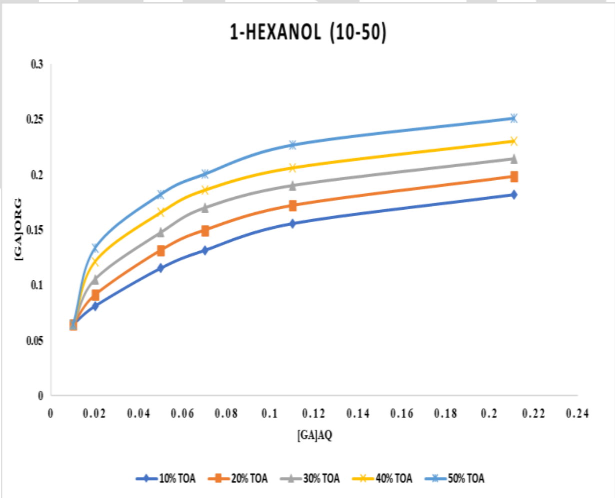

Fig 2: Equilibrium for reactive extraction of Gluconic acid with various concentrations of TOA in 1-Hexanol

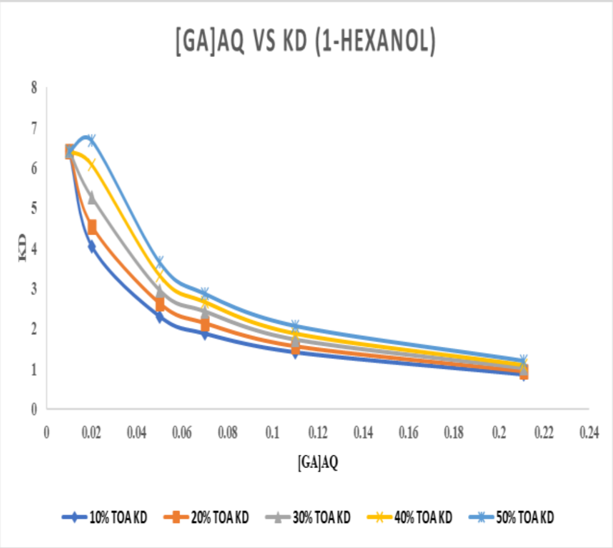

Fig 3: Effect of concentration of acid in aqueous phase on Distribution Coefficient with variable TOA Concentration in 1-Hexanol

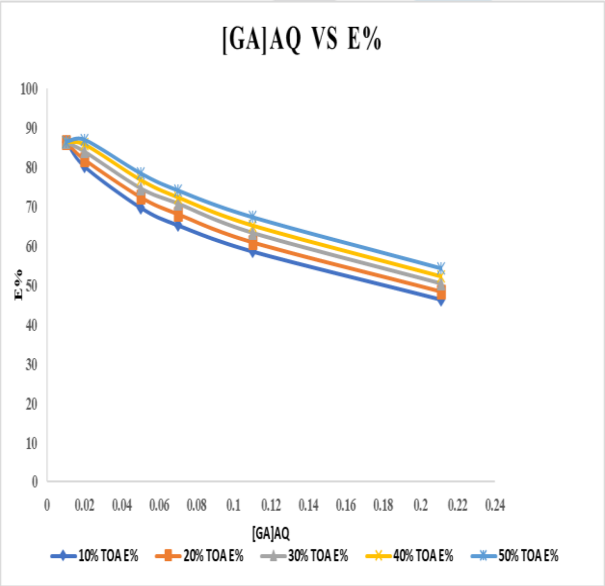

Fig 4: Effect of concentration of acid in aqueous phase on Extraction Efficiency with variable TOA Concentration in 1-Hexanol

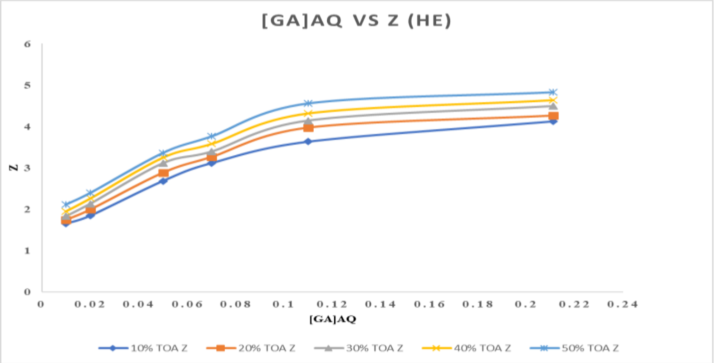

Fig 5: Effect of concentration of acid in aqueous phase on Loading Ratio (Z) with variable TOA concentration in 1-Hexanol

V. CONCLUSION

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

- The physical and chemical equilibria for the extraction of gluconic acid by tri-n-octyl-amine in 1-hexanol are determined. The chemical extraction is found to be superior over to physical extraction.
- The optimum TOA concentration is found to be 50% at which K_D values for 1-hexanol is 6.66.
- The loading ratio Z decreases with an increase in TOA initial concentration in 1-hexanol is 4.83. It increases with an increase in concentration of acid in aqueous phase.
- The degree of extraction of acid increased with decreased in initial concentration of acid and increase in TOA concentration is 86.95%.

VI. NOMENCLATURE

K_DDistribution coefficient

E%Extraction efficiency or degree of extraction

ZLoading ratio

[GA] Concentration of Gluconic acid (mol/L)

[T] Concentration of Tri-n-octylamine (mol/L)

HEHexanol

Subscripts

aq aqueous phase

org organic phase

VII. ABBREVIATION

TOA Tri-n-octylamine

AP Aqueous phase

OP Organic phase

ICGA Initial concentration of Gluconic acid

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AUTHOR PROFILE

Korivi Laila, is a PhD research scholar in the department of chemical engineering, Sri Venkateswara University College of engineering, Tirupati. She completed her undergraduate from AP IIIT RK Valley, Idupulapaya, kadapa, A.P. and postgraduate from Sri Venkateswara University College of engineering. She is currently working on Reactive extraction of Gluconic acid.

Dr.B.SarathBabu is working as Associate professor in the Department of Chemical Engineering, Sri Venkateswara University College of engineering, Tirupati. His research areas are separation processes, environmental Engineering and process control. He is Associate Professor ,worked as Head of Chemical Engineering, has 22 years of teaching experience, specialized in reactive separations, guided 3 Ph.D.'s and one ongoing, organized10 National Conferences, chaired for 4 Conferences, 6 International Conferences and 11 National Conferences attended, 30 Publications, 3 book chapters ,2 book published, 7 FDP's attended, 38 workshops attended, worked as Deputy Warden, NSS program Officer, Additional Chief superintendent of Examinations and NCC officer for S V U College of Engineering.

G. Jyothsna Deepika is a PG student, Department of Chemical engineering, Sri Venkateswara University College of engineering, Tirupati. She completed her under-graduationfromSri Venkateswara University College of engineering.