Reactive Extraction of Gluconic Acid Using Tri-n-Octylamine in 1- Octanol

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Abstract- Reactive extraction is a separation method which is used for the recovery of carboxylic acids from fermentation broth. Gluconic acid is a carboxylic acid which is used in chemical, pharmaceutical and food industries. Tertiary amines are effective extractants for separation of carboxylic acid from dilute solutions. An Adequate combination of extractant and diluent will provide a high yield. The reactive extraction of Gluconic acid with Trioctylamine and 1-octanol is carried out for different Concentrations of acid, Trioctylamine (TOA) and 1-octanol at room temperature. From the physical and chemical equilibrium experimental results, the distribution coefficient (K_D), extraction efficiency (E %), loading ratio (Z) are calculated. It was found that physical extraction provided less yield compared to chemical extraction. A maximum K_D was obtained as 3.57 using 40% TOA (0.02 mol/L) while 78.13 % of the gluconic acid was extracted. By increasing the initial concentration of gluconic acid increased the concentration of gluconic acid in both phases. As the concentration of TOA increases from 10 to 40 % (0.0229mol/L to 0.02 mol/L), the distribution coefficient and extraction efficiency also increases.

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

I. INTRODUCTION

Gluconic acid is a carboxylic acid. Gluconic 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, vinegar and 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.

The separation and purification of Gluconic acid from fermentation broth is inefficient by conventional methods like adsorption, distillation, solvent extraction, reverse osmosis, ion exchange, ultra filtration etc. Reactive extraction is a separation method which is used to enhance the extraction of solute from the Aqueous Phase to the Organic Phase. The extractant molecule reacts with the solute molecule to form a reaction complex, which will stabilize in Organic Phase due to the hydrogen bonding with 1-Octanol and hydrophobic nature of complex. Reactive extraction has various rewards like enhanced reactor productivity, control over pH in the bioreactor, reduces the downstream processing load, and minimizes the solvent recovery cost and higher efficiency. In the current work, an investigation on the recovery of Gluconic acid from aqueous solution was conducted by using TOA in 1-Octanol. The equilibrium parameters are studied such as K_D, E %, Z using experimental data.

II. THEORY

The extraction process was analyzed by using the Distribution Coefficient K_D. The distribution coefficient (K_D) is defined as the ratio of total concentration of acid in all forms in the organic phase to total concentration of all existing forms in the aqueous phase. Consider that 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

Organic Phase to the sum of Gluconic acid concentration in organic phase and Aqueous Phase.

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

The value of Z depends on the extractability of the acid i.e. 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+Octanol) 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.

III. MATERIALS AND METHODS

Materials

Gluconic Acid (pentahydroxycaproic acid ,$C_6H_{12}O_7$) (49-53 wt % of H_2O), molar mass 196.16 kg/kmol, density 1.134 g/ml at 25^0C, 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 molar mass 353.66 g/mol , density 0.81 g/cm3 at 20^0C, 98 % purity, was procured from Sigma-Aldrich (India). 1-octanol, molar mass 130.23 g/mol, density 0.827 g/ml at 250C, 98 % purity was used as a diluent was obtained from Sigma-Aldrich (India). 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. 0.1 N of NaOH and phenolphthalein indicator used for titration. The initial concentration of TOA in 1-octanol 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-Octanol.

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 0.03, 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-octanol (OP) was added in each conical flask. Mechanical shakers were used to mix both the phases for 12hrs at room temperature. The organic and aquennnous phases were allowed to steady down in a separating funnel for 2 hours. A sample from aqueous phase was titrated with 0.1N NaOH using Phenolphthalein as an indicator to measure the concentration of Gluconic acid in the Aqueous Phase. By using Mass balance calculated the concentration of Gluconic acid in the Organic Phase.

Chemical equilibrium:

For chemical equilibrium, 20 ml of gluconic acid and 20 ml of 10 % TOA (0.2264 mol/L) in 1-octanol was added in a conical flask. The immiscible solution was kept in shakers for 12 hours and then kept under separation for 2hours. 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 10%, 20%, 30% and 40% TOA.

IV. 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. Among those 1-octanol is the one alcohol which is used as a diluent here for extraction of Gluconic acid. The physical equilibrium data values for Gluconic acid using 1-octanol are shown in Table 1.

[GA]$_{in}$ mol/L	[GA]$_{aq}$ mol/L	[GA]$_{org}$ mol/L	K$_D$	E%
0.03	0.01	0.018	1.80	64.29
0.06	0.02	0.023	1.15	53.49
0.12	0.04	0.039	0.98	49.37
0.18	0.07	0.049	0.70	41.18
0.2	0.08	0.054	0.68	40.30
0.3	0.13	0.056	0.43	30.11

Table 1: Physical equilibrium of Gluconic acid & 1-octanol

GA(Aq) Vs [GA]org mol/L
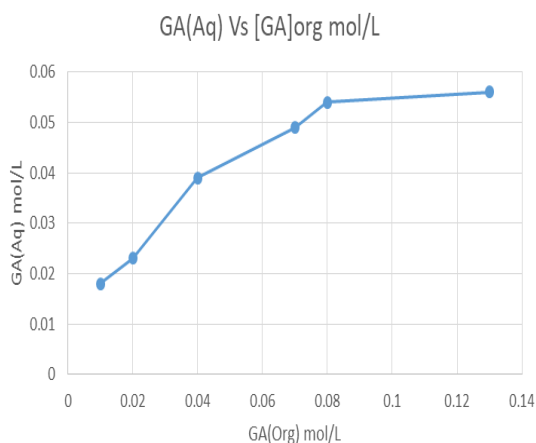
Figure 1 physical extraction equilibrium curves for extraction of Gluconic acid using 1-octanol
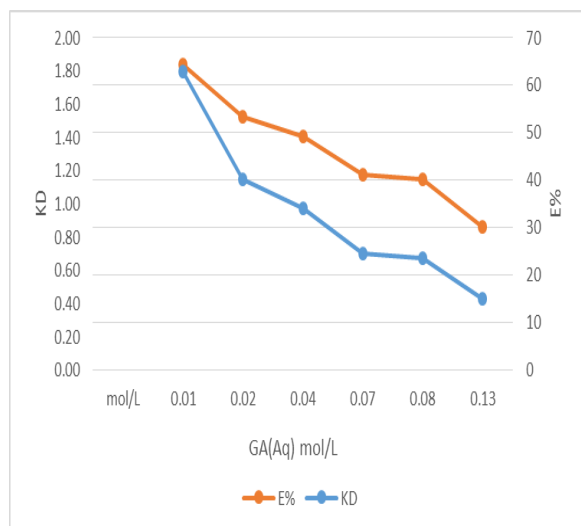

Fig 1: Equilibrium distribution of water -Gluconic acid &1-octanol

Chemical equilibrium

The Chemical Extraction of Gluconic Acid was studied with 1-Octanol in the presence of Tri-octylamine solution. Reaction extraction of Gluconic acid with five different concentrations of TOA in 1-octanol revealed that the amount of Gluconic acid extracted in both Aqueous Phase and Organic Phase is directly proportional to the ICLA The phase equilibrium data of octanol was measured by varying the Gluconic Acid concentration in feed phase in the range of 0.03-0.3 mol L^{-1}.The maximum K$_D$ was obtained is using 40% TOA (mol/L). As the concentration of TOA increased from 10%-40%, K$_D$ and E% Increased.

10% TOA				
[GA]aq	[GA]org	K$_D$	E%	Z
0.012	0.013	1.08	52.00	0.5677
0.03	0.03	1.00	50.00	1.3100
0.06	0.05	0.83	45.45	2.1834
0.09	0.07	0.78	43.75	3.0568
0.12	0.08	0.67	40.00	3.4934
0.16	0.09	0.56	36.00	3.9301
20% TOA				
[GA]aq	[GA]org	K$_D$	E%	Z
0.01	0.02	2.00	66.67	0.8811
0.025	0.04	1.60	61.54	1.7621
0.055	0.06	1.09	52.17	2.6432
0.085	0.08	0.94	48.48	3.5242
0.1	0.09	0.90	47.37	3.9648
0.15	0.1	0.67	40.00	4.4053
30% TOA				
[GA]aq	[GA]org	K$_D$	E%	Z
0.005	0.015	3.00	75.00	0.7009
0.02	0.04	2.00	66.67	1.8692
0.05	0.065	1.30	56.52	3.0374
0.08	0.085	1.06	51.52	3.9720
0.09	0.09	1.00	50.00	4.2056
0.15	0.11	0.73	42.31	5.1402
40% TOA				
[GA]aq	[GA]org	K$_D$	E%	Z
0.007	0.025	3.57	78.13	1.2500
0.01	0.035	3.50	77.78	1.7500
0.04	0.07	1.75	63.64	3.5000
0.08	0.09	1.13	52.94	4.5000
0.095	0.1	1.05	51.28	5.0000
0.15	0.12	0.80	44.44	6.0000

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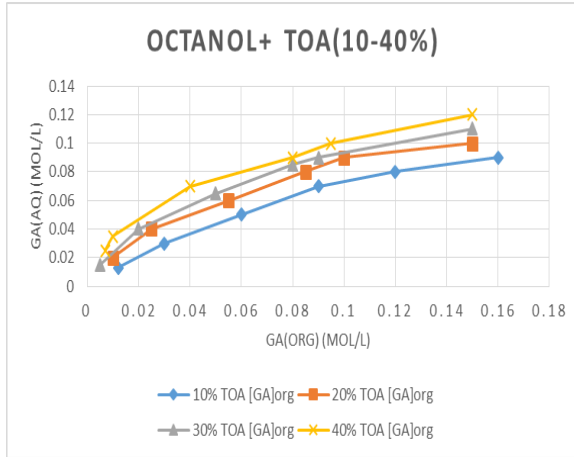

Fig 2: Equilibrium for reactive extraction of Gluconic acid with various concentrations of TOA in 1-octanol
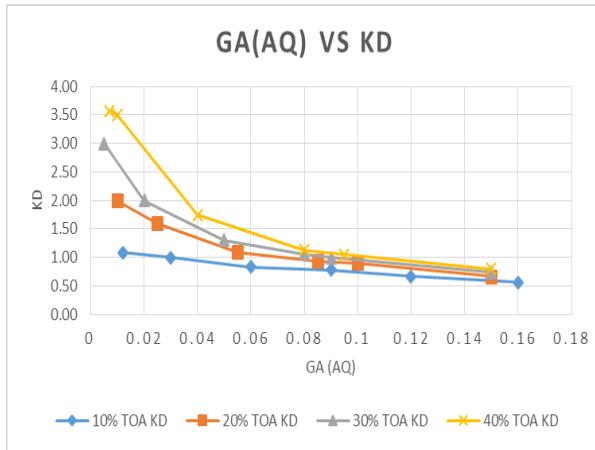

Fig 3: Effect of concentration of acid in aqueous phase on Distribution Coefficient with variable TOA Concentration in 1-octanol
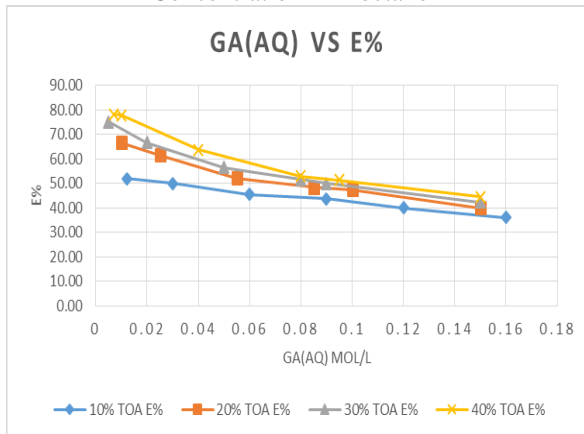

Fig 4: Effect of concentration of acid in aqueous phase on Extraction Efficiency with variable TOA Concentration in 1-octanol
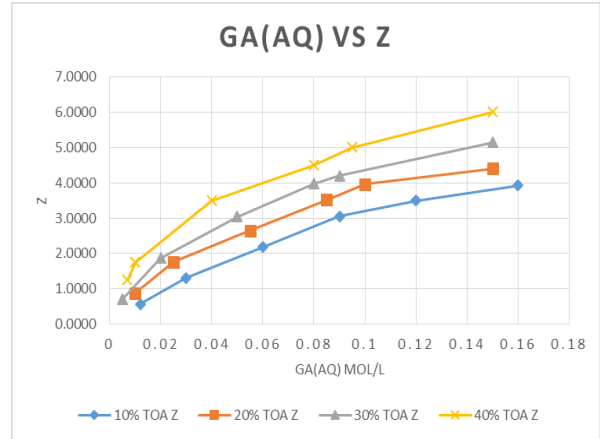

Fig 5: Effect of concentration of acid in aqueous phase on Loading Ratio (Z) with variable TOA concentration in 1-octanol

V. CONCLUSION

The Reactive extraction of Gluconic acid using TOA in 1-octanol experiment was conducted. The key findings are as given below Chemical extraction was found to have high distribution coefficient and extraction efficiency than Physical extraction. The distribution coefficient and extraction efficiency decrease with increase in acid concentration. The loading ratio of TOA with acid Z increases with increasing in Gluconic acid concentration. The optimum TOA concentration is found to be 40% at K_D values for 1-octanol is 3.57

VI. NOMENCLATURE

K_D distribution coefficient
E% extraction efficiency
Z loading ratio
[GA] Concentration of Gluconic acid (mol/L)
[T] Concentration of Tri-n-octylamine (mol/L)
Subscripts
aq aqueous phase
org organic phase

VII. ABBREVIATION

TOA   Tri-n-octylamine
AP Aqueous phase
OP Organic phase
ICGA Initial concentration of Gluconic acid

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