



REACTIVE EXTRACTION OF GLUCONIC ACID USING TRI BUTYL PHOSPHATE IN 1- OCTANOL

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Abstract- Reactive extraction of Gluconic acid from aqueous solutions by using tri butyl phosphate (TBP) in 1-octanol was studied at room temperature. Reactive extraction is a separation method which is used to treat carboxylic acids from fermentation broth. An Adequate combination of extractant and diluent will provide a high yield. The physical and chemical extraction equilibrium studies were conducted at room temperature. From the physical and chemical equilibrium experimental data, 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 distribution coefficient K_D was obtained as 0.35 using 40% TBP (0.02 mol/L) while 25.93% 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 TBP

increases from 10 to 40 % the distribution coefficient and extraction efficiency increases.

Key words: Reactive Extraction, Gluconic Acid, Tri-n-butyl phosphate, 1-octanol.

I. INTRODUCTION

Gluconic acid (pentahydroxycaproic acid, $C_6H_{12}O_7$) is a carboxylic acid. It 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 membrane separation, 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 with a suitable extractant. 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 is an economical, efficient and eco-friendly method. 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. The extraction efficiency can be enhanced by selecting organic phase solvents and optimizing equilibrium parameters like the concentration of the acid, PH and temperature. In the current work, an investigation on the recovery of Gluconic acid from aqueous solution was conducted by using Tri-n-butyl phosphate (TBP) 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.

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

Where, $[GA]_{org}$ = 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 (TBP+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 TBP 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 $25^{\circ}C$, 97 % purity was procured from Sigma-Aldrich (India). TBP (Tri butyl phosphate) ($C_{12}H_{27}O_4P$) a tertiary amine is a colour less liquid with the molar mass 266.32 g/mol, density 0.977 g/cm³ at $20^{\circ}C$, 98 % purity, was procured from Sigma-Aldrich (India). 1-octanol, molar mass 130.23 g/mol, density 0.827 g/ml at $25^{\circ}C$, 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 TBP 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 TBP and 1-Octanol.

Chemical	IUPAC name	Supplier	Formula	Molar mass kg/kmol	Density g/ml	Purity
Gluconic acid	pentahydroxypropionic acid	Sigma-Aldrich, India	C ₆ H ₁₂ O ₇	196.16	1.134	97%
Tri-n-butyl phosphate	Tri butylphosphate	Sigma-Aldrich, India	C ₁₂ H ₂₇ O ₄ P	353.67	0.81	98%
1-octanol	Octan-1-ol	Sigma-Aldrich, India	C ₈ H ₁₈ O	130.23	0.83	98%

Table 1: PHYSICAL PROPERTIES OF CHEMICALS USED IN THE EXPERIMENTAL STUDY

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.

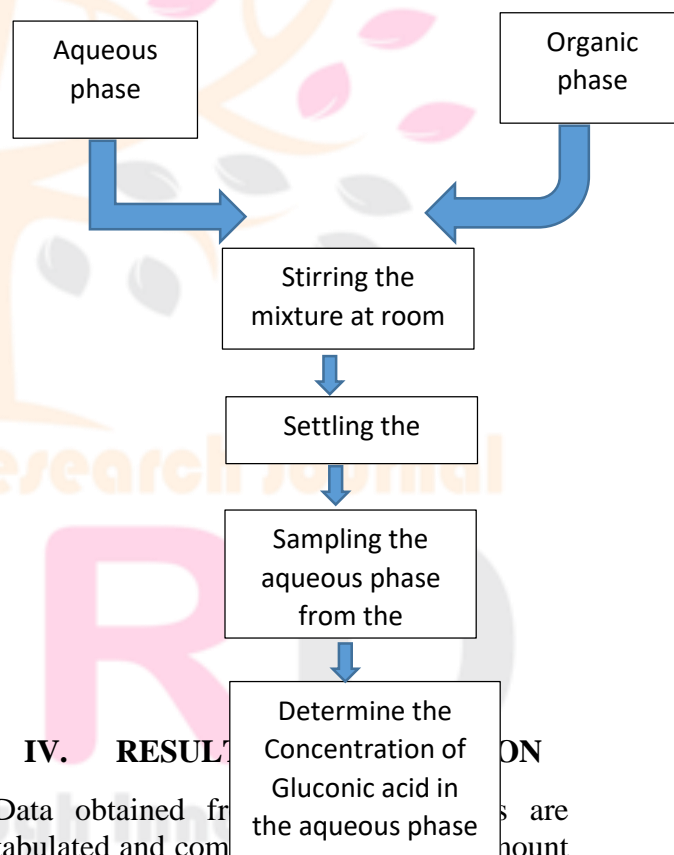
Physical equilibrium:

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 aqueous 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:

To study the chemical equilibrium, the same procedure which was used in the physical equilibrium was used to prepare an aqueous

solution. The organic solution was prepared by dissolving 0.03 mol/L & TBP (10%) in 1-octanol. A 20 ml of an aqueous solution of Gluconic acid was directly contacted with 20 ml of organic solution in 250 ml conical flasks. I.e. For chemical equilibrium, 20 ml of gluconic acid and 20 ml of 10 % TBP (0.2264 mol/L) in 1-octanol was added in a conical flask. The immiscible solution was kept in mechanical shakers about 12 hours and then mixture was kept under separation for 2 hours in separatory funnel. The gluconic acid concentration was determined by using volumetric analysis 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%, 40% and 50% TBP.



Data obtained from the experiment are tabulated and compared with the amount of the Gluconic acid extracted from aqueous solution using the physical and chemical equilibrium methods with different concentration of the TBP. From the equilibrium data, the K_D , $E\%$, Z , are calculated as shown in Table 1 and Table 2.

Physical equi

Figure 1: Experimental Procedure

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 of Gluconic acid (0.03 to 0.3 mol/L) was examined using 1-octanol. It was observed that an increase in the initial concentration of gluconic acid, increases the concentration of Gluconic acid in the organic and aqueous phase as shown in below fig. the distribution coefficient was calculated 0.18 and extraction efficiency is 14.89%. The distribution coefficient is found to be low by using only 1-octanol.

[GA] _{in} mol/L	[GA] _{aq} mol/L	[GA] _{org} mol/L	K _D	E%
0.03	0.02	0.0035	0.18	14.89
0.06	0.03	0.005	0.17	14.29
0.12	0.05	0.0085	0.17	14.53
0.18	0.08	0.012	0.15	13.04
0.2	0.09	0.013	0.14	12.62
0.3	0.14	0.017	0.12	10.83

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

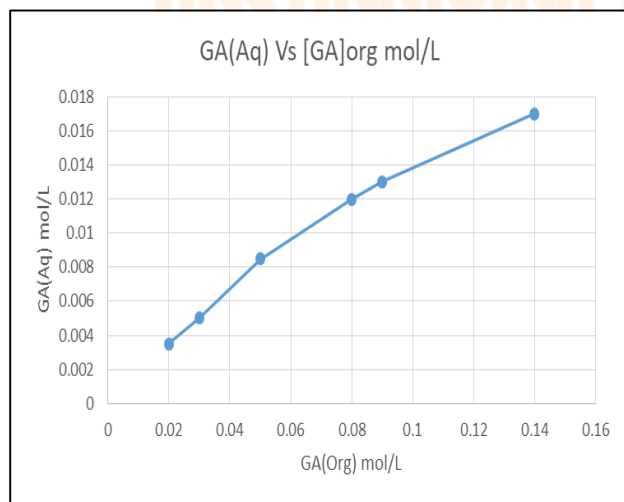


Figure 1: physical extraction equilibrium

curves for extraction of Gluconic acid using 1-octanol

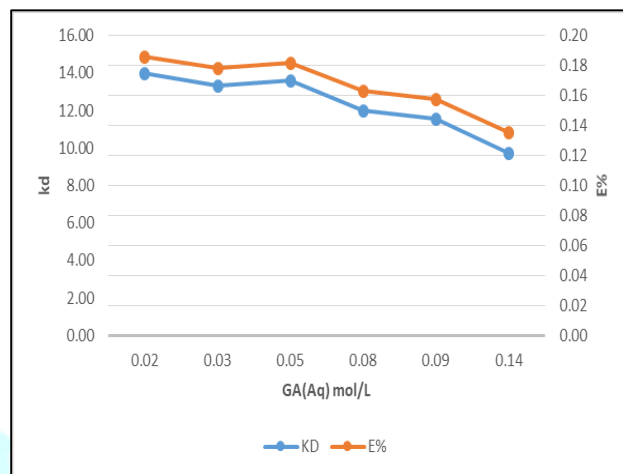


Figure 2: Equilibrium distribution of water -Gluconic acid &1-octanol

Chemical equilibrium

The Chemical Extraction of Gluconic Acid was studied with 1-Octanol in the presence of Tri butyl phosphate solution. Reaction extraction of Gluconic acid with five different concentrations of TBP 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 0.3 using 40% TBP and extraction efficiency is 23.08. As the concentration of TBP increased from 10%-40%, K_D and E% increased. Consider the below equilibrium graphs for reactive extraction of Gluconic acid with various concentrations of TBP in 1-octanol.

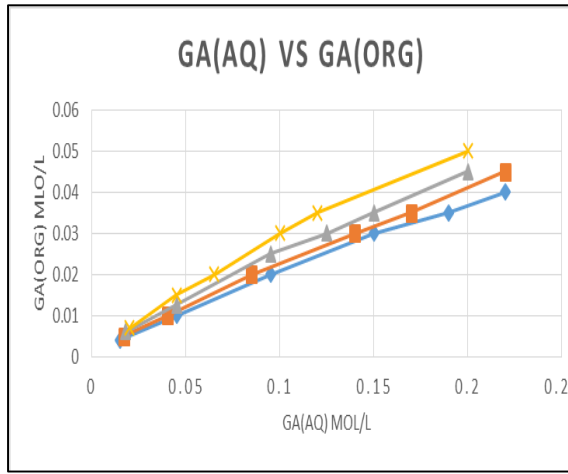


Figure 3: Equilibrium for reactive extraction of Gluconic acid with various concentrations of TBP in 1-octanol

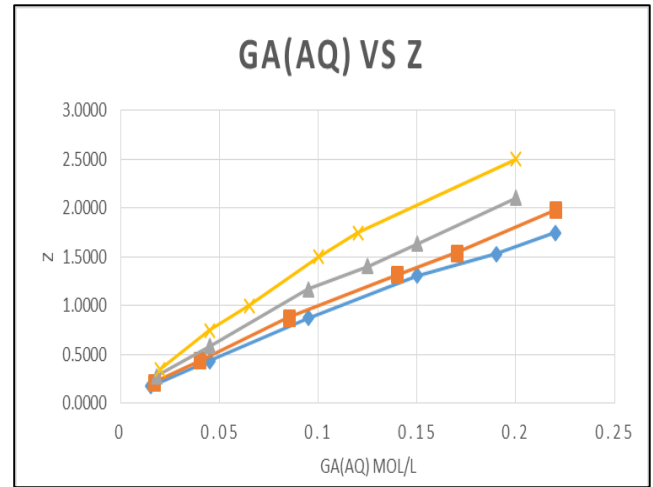


Figure 6: Effect of concentration of acid in aqueous phase on Loading Ratio (Z) with variable TBP concentration in 1-octanol

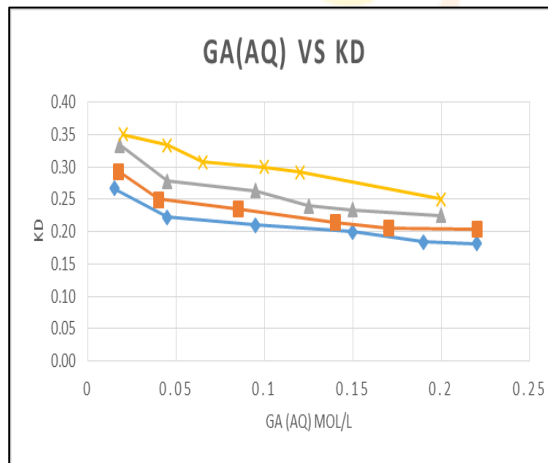


Figure 4: Effect of concentration of acid in aqueous phase on Distribution Coefficient with variable TBP Concentration in 1-octanol

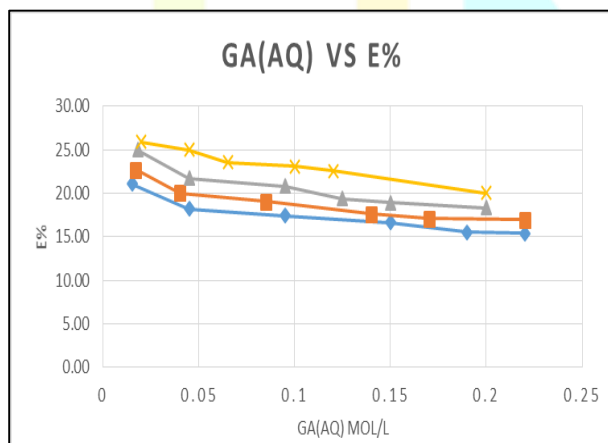


Figure 5: Effect of concentration of acid in aqueous phase on Extraction Efficiency with variable TBP Concentration in 1-octanol

V. CONCLUSION

The Reactive extraction of Gluconic acid using TBP in 1-octanol experiment was conducted. The key findings are as given below

The extraction of Gluconic acid by 1-octanol alone results in a low distribution coefficient. At 40% Tri butyl phosphate, the maximum distribution coefficient is 0.35 and extraction efficiency is 25.93%. The distribution coefficient and extraction efficiency increase with increase in the concentration of tri butyl phosphate. Chemical extraction was found to have high distribution coefficient and extraction efficiency than Physical extraction.

NOMENCLATURE

K_D distribution coefficient

E% extraction efficiency

Z loading ratio

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

[T] Concentration of Tributylphosphate (mol/L)

Subscripts

aq aqueous phase

org organic phase

VI. ABBREVIATION

TBP Tributylphosphate

AP Aqueous phase

OP Organic phase

ICGA Initial concentration of Gluconic acid

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