Recovery of Gluconic Acid from an Aqueous Phase by Using Reactive Extraction with TRI-N-OCTYL Amine in Different Diluents

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Abstract: **- Gluconic acid is an important carboxylic acid which is widely used in chemical, pharmaceutical, food and other industries. Reactive extraction is a separation technique which is used for the recovery of carboxylic acids from fermentation broth. Tertiary amines are effective extractants for separation of carboxylic acid from dilute solutions. A right combination of extractant and diluent will provide a high yield. The reactive extraction of Gluconic acid from aqueous solution with tri-n-octylamine (TOA) dissolved in different diluents was studied at room temperature. From the physical and chemical equilibrium experimental results, the distribution coefficient (K_D) and extraction efficiency (E %) are calculated. It was found that physical extraction provided less yield compared to chemical extraction. By increasing the initial concentration of Gluconic acid increased the concentration of Gluconic acid in the both organic phase and aqueous phase. As the concentration of TOA increases from 10 to 40 %, the distribution coefficient and extraction efficiency increases. The recovery of Gluconic acid with Tri-n-octylamine with different diluents (1-hexanol, 1-octanol & 1-decanol) is carried out for different Concentrations of acid. The order in which diluents recover the Gluconic acid from aqueous solution is found to 1-hexanol > 1-octanol > 1-decanol.**

Key words: **Reactive Extraction, Gluconic Acid, Tri-n-Octyl amine, 1-hexanol, 1-octanol & 1-decanol.**

I. INTRODUCTION

Carboxylic acids are the organic acids described by the presence of a carboxyl group (-COOH) which included a hydroxyl group (O-H) clung to a carbonyl group (C=O). Its molecular formula $CnH_{2n+1}COOH$.

$$RCOOH \rightarrow RCOO^- + H^+$$

Carboxylic acids can be synthetically blended by oxidation of primary alcohols or aldehydes. Alkyl group on a benzene ring will be completely oxidized to produce a carboxylic acid, regardless of chain length. Carboxylic acids such as Gluconic acid, acetic acid, formic acid, propionic acid, butyric acid, valeric acid, levulinic acid,,succinic acid, caproic acid, citric acid,, lactic acid, pyruvic acid, tartaric acid, malic acid. Etc.

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 diluents like 1- hexanol, 1-octanol and 1-decanol. 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. In the current work, an investigation on the recovery of Gluconic acid from aqueous solution was conducted by using Tri-n-Octyl amine (TOA) in different diluents. The equilibrium parameters are studied such as K_D & E %, 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.

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

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(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^{oC}, 98 % purity, was procured from Sigma-Aldrich (India). 1-octanol, molar mass 130.23 g/mol, density 0.827 g/ml at 25^{oC}, 98 % purity , 1-hexanol, molar mass 102.17g/mol, density 0.814g/ml at 25^{oC} and 1-decanol, molar mass 158.28g/mol, density 0.8297g/ml at 25^{oC} were used as a diluent was obtained from Sigma-Aldrich (India).

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, 0.1265, 0.1897, 0.25306, 0.31632 mol/L respectively**.**

Physical equilibrium:

For physical equilibrium, 25 ml of Gluconic acid (AP) of different concentrations were taken in different conical flasks and 25 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 & TOA (10%) in diluent. A 25 ml of an aqueous solution of Gluconic acid was directly contacted with 25 ml of organic solution in 250 ml conical flasks. I.e. For chemical equilibrium, 25 ml of Gluconic acid and 25 ml of 10 % TOA (0.229 mol/L) in diluent 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 2hours 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% 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.

Physical equilibrium

The physical equilibrium of Gluconic acid (0.03 to 0.3 mol/L) was examined using different diluents. 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. The distribution coefficient was calculated 2 and extraction efficiency is 66.6% respectively for hexanol.

Chemical equilibrium

The phase equilibrium data of different diluents were 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 6.34 using 40% TOA and extraction efficiency is 86.38%. As the concentration of TOA increased from 10%-40%, K_D and E% Increased. Consider the below equilibrium graphs for reactive extraction of Gluconic acid with various concentrations of TOA with different diluents.

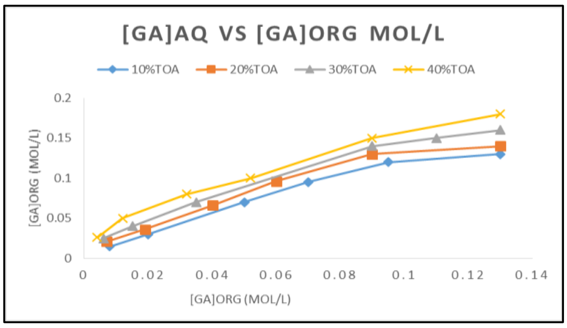

Figure 1 Equilibrium for Reactive extraction of Gluconic acid with diff conc. Of TOA in 1-Hexanol

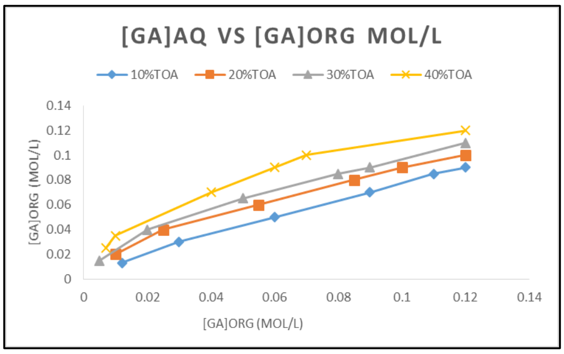

Figure 2 Equilibrium for Reactive extraction of Gluconic acid with diff conc. Of TOA in 1-octanol

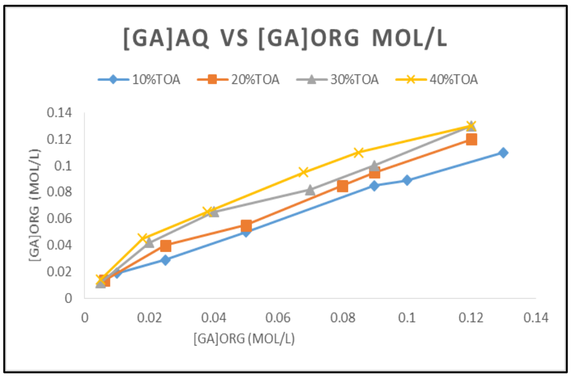

Figure 3 Equilibrium for Reactive extraction of Gluconic acid with diff conc. Of TOA in 1-decanol

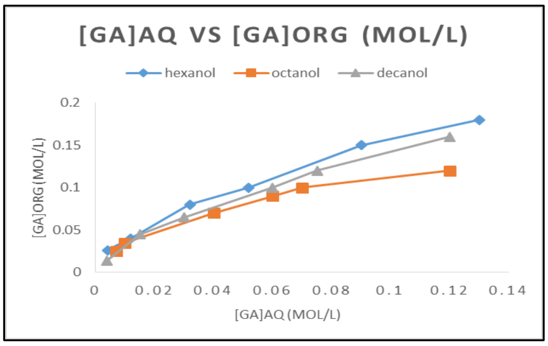

Figure 4 comparison of effect of conc. of acid in aq. phase vs org phase w.r.t 40%TOA in 1-Hexanol, 1-Octanol & 1-Decanol

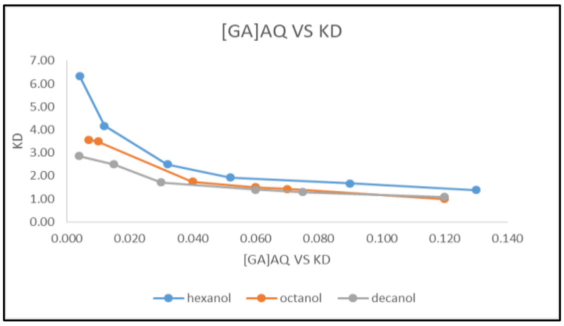

Figure 5 comparison of effect of conc of acid in aq. phase on K_d w.r.t 40%TOA in 1-Hexanol, 1-Octanol & 1-Decanol

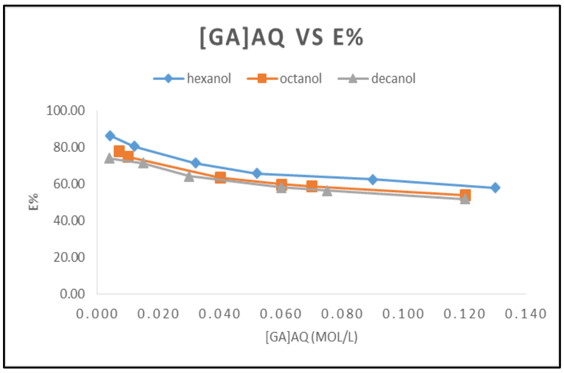

Figure 6 comparison of effect of conc of acid in aq phase on E% w.r.t 40%TOA in 1-Hexanol, 1-Octanol & 1-Decanol

V. CONCLUSION

Reactive extraction of Gluconic acid (mol/L) using tri-n-Octyl amine (mol/L) in 1-hexanol, 1-octanol and 1-decanol from aqueous solutions are carried out. The distribution coefficient and extraction efficiency increase with increase in the concentration of tri-n-Octyl amine. Chemical extraction was found to have high distribution coefficient and extraction efficiency than Physical extraction. As the concentration of TOA increases from 10 to 40 %, the distribution coefficient and extraction efficiency increases. The order in which the diluents recover the Gluconic acid from aqueous solution is found to 1-hexanol > 1-octanol > 1-decanol.

NOMENCLATURE

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

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

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