



# EQUILIBRIUM STUDIES ON REACTIVE EXTRACTION OF PROPANOIC ACID USING TRIBUTYL AMINE IN DIFFERENT DILUENTS

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## ABSTRACT

Propanoic acid is an important commercial product and separating it out of aqueous solution is a growing requirement in fermentation based industrial waste stream. The recovery techniques should provide high selectivity and yield. In the present work equilibrium study for the reactive extraction of propanoic acid is carried out. Various diluents and extractants are used for equilibrium studies and data are presented in terms of distribution coefficient and equilibrium complexation constant. In the present paper, equilibrium with propionic acid using tri-butyl amine as solvent, in three different diluents (1-octanol, ethyl acetate and petroleum ether) has been studied. On the basis of higher distribution coefficient and equilibrium complexation constant, the best combination of diluents, extractant is suggested. In physical equilibria, distribution coefficient ( $K_D = 2.15$ ) with 1-octanol is maximum at concentration of 0.5M of propionic acid. Distribution coefficient ( $K_D = 2.25$ ) is enhanced with tri-butylamine (60%) in 1-octanol for the reactive extraction of propionic acid. Presented data can be used for the design of reactive extraction process for the recovery of propionic acid.

**Keywords:** Propanoic acid, tributylamine, 1-octanol, ethyl acetate, distribution coefficient ( $K_D$ ), reactive extraction, complexation constant, petroleum ether.

## 1. INTRODUCTION

Propionic acid ( $\text{CH}_3\text{CH}_2\text{COOH}$ ) is a colorless liquid with a boiling point of  $141^\circ\text{C}$ , which has a pungent, rancid-type odor. It occurs naturally in

the form of esters in essential oils and in mammals as a metabolic intermediate. Major applications include animal feed and grain preservation, and mold inhibition in human foods, mainly in baked goods and cheeses. Propionic acid is also used as a synthetic intermediate in the manufacture of herbicides and pharmaceuticals, cellulose acetate propionate (CAP) plastics, in alkyl propionate esters for solvents, and in flavors and fragrances.

Preservation of animal feed, grain and food (calcium and sodium propionates) accounted for 78.5% of world propionic acid consumption in 2012, followed by various herbicides and diethyl ketone. Other smaller-volume applications include cellulose acetate propionate; pharmaceuticals; solvent esters; flavors and fragrances; plasticizers; dyes; and textile, leather and rubber auxiliaries. Demand for propionic acid is largely dependent on production of animal feed and grain, followed by packaged food and bakery products. World growth prospects for propionic acid and its salts in animal feed/grain preservation and food are significant. Other fast-growing markets include propionate esters for solvents, such as n-butyl and pentyl propionate; these esters are increasingly being used as replacements for solvents listed as hazardous air pollutant. Propionic acid is also useful as an intermediate in the production of other chemicals, especially polymers. Cellulose-acetate-propionate is a useful thermoplastic. Vinyl propionate is also used. In more specialized applications, it is also used to make pesticides and pharmaceuticals.

Presently the commercial production of propionic acid is entirely by petrochemical routes (Jin and Yang 1998). Since the petrochemical reserves are gradually depleting, research efforts are being directed towards the production of propionic acid by alternative renewable resources mainly by fermentation. Batch propionic acid fermentation takes about 3 days to reach approximately 2 % (w/v) propionic acid. Propionic acid fermentation by *P. acidipropionici* is a multiproduct fermentation, with low cost. The esters of propionic acid have fruit-like odors.

The prospective function of a novel energy efficient fermentation technology has been getting great attention in the past fifty years due to the quick raise in petroleum costs. Fermentation chemicals are still limited in the modern market in huge part because of trouble in recovery of carboxylic acids. Therefore, it is needed considerable development in the current recovery technology.

Many separation processes are available like, stripping, adsorption, electro-dialysis, liquid-liquid extraction, per traction, pervaporation, and membrane solvent extraction. All these processes have their own advantages and disadvantages

This paper presents a state-of-the-art review on the reactive extraction of propanoic acids from fermentation broths. This paper principally focuses on reactive extraction that is found to be a capable option to the proper recovery methods.

Liquid-liquid extraction (LLE) is a process in which a particular solute is removed from a liquid phase (feed phase) by another liquid phase (solvent or extract phase).

## 2. THEORY

The main difference between reactive extraction and solvent extraction is the reaction between the extractant and the solute in the organic phase. Aliphatic amines and phosphoric solvents are proposed as effective extractants by earlier researchers. While extractants play the major role in the reaction, diluents also have a significant effect on the level of extraction. Non-aromatic, water immiscible and polar solvents with intermediate molecular weights and high boiling points are commonly preferred for the extraction to have high distribution and selectivity. The solvents (diluents) control the

physical properties (viscosity, density, surface tension, etc.) of the solvent phase and also affect the stability of the complex structure formed between the solute and the extractant.

The reactive extraction is found to be a promising method for the recovery of the propionic acids from a dilute fermentation broth.

This separation method has advantages such as the following: (i)effective at high concentration of substrate in the extractive fermentation, (ii)the acid can be re-extracted and the solvent can be reused, (iii)better control of pH in the bioreactor, (iv)better recovery of acid with higher product purity, (v)reduction of downstream processing load and recovery cost, (vi)reactants are relatively immiscible, (vii)product(s) undergoes subsequent undesired reactions in reaction phase, (viii)reaction products to be separated are immiscible with the reaction phase, (ix)phase equilibrium can be positively influenced, (x)heat transfer is to be improved during the reaction, (xi)product-catalyst separation can be affected by a liquid-liquid separation.

The extractants as three major types: (i) carbon bonded oxygen bearing extractants, (ii) phosphorus bonded oxygen bearing extractants, (iii) high molecular weight aliphatic amines.

The first two categories are nonreactive in nature and extract the acid molecules by solvation. The distinction between the first two categories is based on the strength of the solvation bonds and the specificity of solvation. The coordinate bonds between carbon bonded oxygen donor extractant and the acid are too weak for a specific solvation but it is significantly more for phosphorus bonded oxygen bearing extractants. The extractants in the second category make the solvation process more specific and the number of solvating molecules per extracted acid molecule can be accessible experimentally. The aliphatic amines in the third category can react with the carboxylic acid molecule and form acid-amine complexes by proton transfer or by ion pair formation. This causes a significant increase in the distribution coefficient of the carboxylic acid. Among aliphatic amines, primary alkyl amines are observed to be excessively soluble in water at room temperature while secondary amines form a gel phase (third phase) at the interface which creates difficulty in phase separation. The

extractability of tertiary amines is found to be more than that of the primary and secondary amines. Aliphatic tertiary amines having more than six carbon atoms per chain are found to be effective extractants for the recovery of carboxylic acids.

Although a tertiary amine has good extractability, it must always be used with a diluent due to its viscous and corrosive nature.

Further, the stability of the formed acid-amine complexes in the reactive extraction is affected by the basicity of the amine which can be manipulated by using different types of diluents. Moreover, use of a diluent controls the physical properties such as density, viscosity, and surface tension of the organic phase.

Diluents can be broadly divided into two groups: (i) active diluents and (ii) inactive diluents. Generally, the active diluents are polar in nature due to the presence of functional groups.

They are good solvating media for an ion-pair such as an acid-amine complex. The category includes chlorinated hydrocarbon, ketone, alcohol, and halogenated aromatic solvents.

Inactive diluents being nonpolar provide very low distribution of the acid and poor solvation of the polar complexes. Alkanes, benzene, alkyl substituted aromatics, and so forth fall in this category.

These diluents limit the formation of the third phase at higher concentrations of acid in the organic phase and are useful in the stripping of acid. The equilibrium curve can be shifted towards the aqueous phase by increasing the concentration of the inert diluent in the mixture of diluents.

Reactive extraction represents a reaction between the acid (solute) and extractant molecule at the interface of aqueous and organic phase where transfers of acid molecules take place by the diffusion and solubilization mechanism.

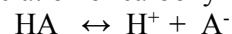
Reactive extraction strongly depends on various parameters such as aqueous phase composition, organic phase composition, types of complexes (1 : 1, 2 : 1, etc.) formed, properties of the solvent (extractant and diluent), type of solvent, temperature, and pH.

The purpose should be achieving a high distribution coefficient with higher selectivity. This can be realized by utilizing an appropriate

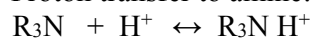
organic phase at optimum conditions. There are two stages in extractive separation. The first is the extraction of the solute to produce a solute-extractant complex and a relatively solute free aqueous raffinate.

The second step is necessary for stripping the solute from the organic complex to obtain amine free aqueous solute as a product and also for simultaneously regenerating the extractant recycled back to the extraction unit. In the second stage of reactive extraction, it is necessary to regenerate the organic phase. Two approaches for the regeneration of extractant-diluent system: (i) temperature swing regeneration and (ii) diluent swing regeneration. The following reactions occur in the reactive extraction of acids with tertiary amine extractants.

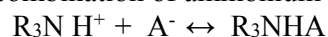
Dissociation of carboxylic acid:



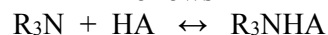
Proton transfer to amine:



Recombination of ammonium salt:



Thus, the overall reaction can be given as follows



### 3. EXPERIMENTAL PROCEDURES

Propionic acid is dissolved in distilled water to prepare the aqueous solutions with initial concentration of the range of 0.1N to 0.5N. It is known as aqueous phase.

The organic solutions are prepared by dissolving TBA in different diluents as 10%, 20%, 40%, and 60% of the organic phase solution.

Equal volumes of the aqueous and organic solution (50ml of each phase) are poured into a 200 ml capacity beaker and stirred using motor stirrer. Stirring is carried out for 60 minutes. After attaining equilibrium, both the phases are separated in 125 ml separating funnel.

After separation, the aqueous phase is analyzed to determine the concentration of acid by titration using fresh 0.5N NaOH solution and phenolphthalein as an indicator.

The acid concentration in the organic phase is calculated by mass balance.

The extraction process is analyzed by means of the degree of extraction and distribution coefficient.

Distribution Coefficient,  $K_D = C_{LA,org} / C_{LA,aq}$   
Efficiency,  $E\% = (C_{LA,aq} - C_{LA,org}) * 100 / C_{LA,aq,i}$

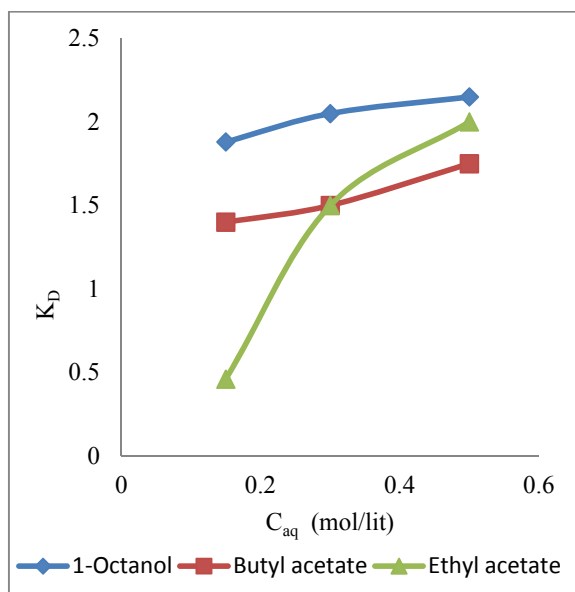
#### 4. RESULTS & DISCUSSIONS:

Experiments were carried out to describe the physical and chemical equilibria for propionic acid using pure diluents and tri-butyl amine with different diluents (Ethyl acetate, Butyl acetate, Petroleum ether and 1-Octanol.)

##### 4.1 Physical Equilibria:

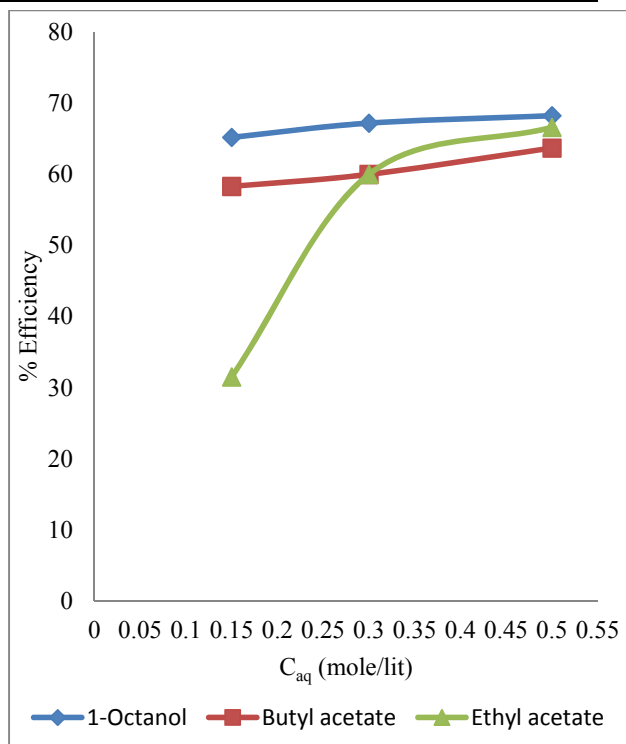
The physical equilibrium was studied for propionic acid using various solvents. Ethyl acetate, Butyl acetate, Petroleum ether and 1-Octanol to find the distribution coefficient of propionic acid.

Experiments were carried to know the effect of initial acid concentration on distribution coefficient and percentage of extraction for a particular solvent. The results are shown in Fig. 1 and 2.



**Fig 1:** The distribution coefficient for propionic acid with initial concentration of acid using different solvents

Our experimental studies show that there is maximum distribution coefficient ( $K_D = 2.15$ ) with 1-Octanol at concentration of 0.5 mol/lit the amount solvent is the limiting factor for low concentration.



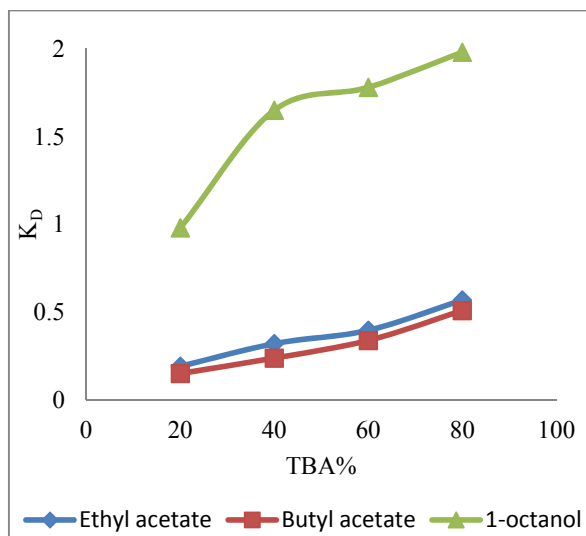
**Fig 2:** The effect of concentration of propionic acid on percentage of efficiency

The equilibrium curves with 1-Octanol and ethyl acetate are more but butyl acetate giving high percentage extraction and distribution coefficients with butyl acetate even with low concentration of propionic acid. Petroleum ether giving low distribution coefficients due low cost further studies extending with that solvent. The equilibrium distribution coefficients and percentage extraction efficiency summarized in figure 1 and 2.

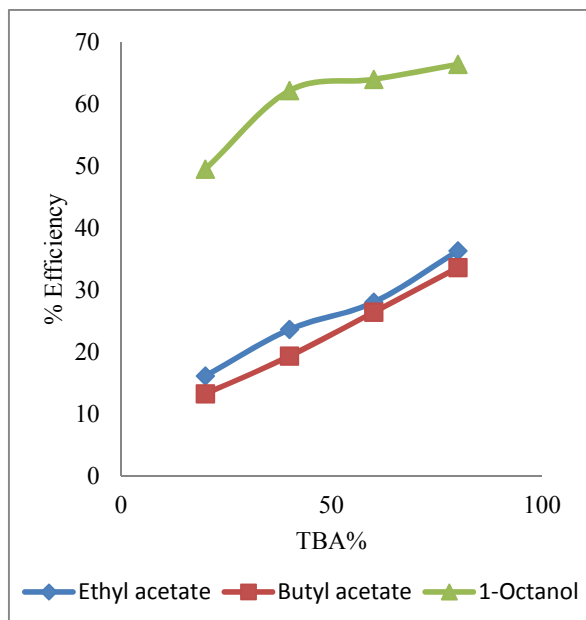
##### 4.2 Reactive Extraction:

Aliphatic amines are effective and relatively inexpensive extractants that have been used successfully to extract propionic acid. Tertiary amine extractants are effective, with  $K_D$  strongly dependent upon the nature of the diluents used and the concentration of amine in that diluent. Tertiary amines are found to be effective in extracting propionic acid completely. In this study the propionic acid extraction with tributyl amine, the variation of  $K_D$  and percentage extraction with initial propionic acid of 0.3 M is given in below figures. The difference among distribution coefficient and equilibrium values for same acid in different diluents indicates that salvation of complex by diluents is critical factor in extraction of acid. Active diluents have

functional groups that enable greater salvation of acid-amine complex, so due to the presence of active diluents 1-octanol gives higher equilibrium values in tri-butyl amine as solvent.



**Fig 3 :** Effect of tri-butyl amine volume % on distribution coefficient in reactive extraction of 0.30M propionic acid with ethyl acetate ,butyl acetate and 1-Octanol.



**Fig 4 :** Effect of tri-butyl amine volume percentage on percentage efficiency in reactive extraction

The increase of volume of tri-butyl amine brings about the gradual increase of efficiency of extraction and distribution coefficient. This is due to basicity and polarity of amine increase with their chain length.

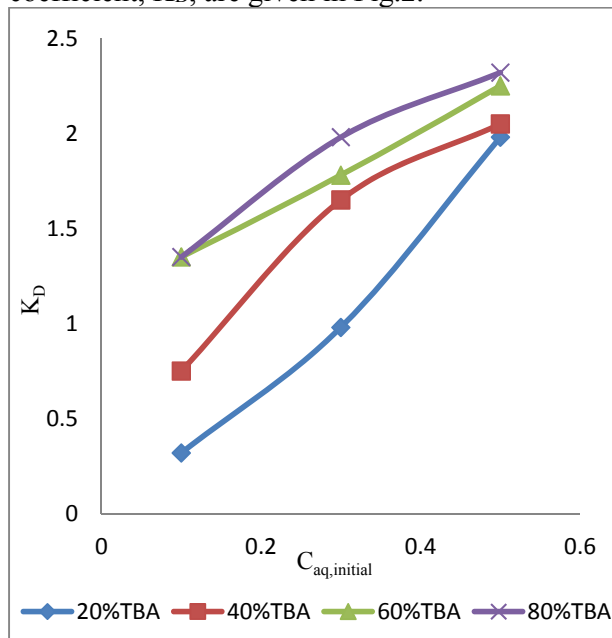
The reactive extraction is carried out using tri-butyl amine which is a low cost solvent

.The extractability of tri-butyl amine is studied with three diluents namely ethyl acetate ,butyl acetate and 1-octanol.In the present study 1-octanol showed optimum extractability rate when compared to others.

The chemical equilibrium isotherms, for (20%, 40%, 60%, and 80%) tri-butyl amine in 1-Octanol , for the distribution of propionic acid between water and organic phase (in 1:1 volume ratio) within the range of 0.1M to 0.5 M initial propionic acid concentrations were determined at 30 °C and are shown in Figure 1. It can be inferred from figure 1 that the distribution of lactic acid increased with the increase of concentration of tri-butyl amine in 1-Octanol.

#### 4.3 Distribution Coefficient, $K_D$

The effect of tri-butyl amine in 1-Octanol on the extraction is effectively. The amount of acid extracted from aqueous solutions at any initial acid concentration increased with increasing amine concentration. The values of distribution coefficient,  $K_D$ , are given in Fig.2.



**Fig 5:** Distribution Coefficient for reactive extraction of propionic acid with % soln of tri-butyl amine in 1-Octanol

#### 5. CONCLUSION:

The acid concentrations are not expected to be high. Hence low concentration range (0.1 moles/lit to 0.5 moles/lit) of propionic acid concentration is used. The extraction of propionic acid from aqueous solution by Tri-butyl amine dissolved in ethyl acetate, butyl

acetate and 1-Octanol were studied. The effect of concentration of propionic acid on distribution coefficient and percentage of efficiency is studied and 1-octanol had the high efficient values.

In the present study 1-octanol showed optimum extractability rate when compared to others diluents with low cost recovery. The extraction efficiency increases with increase in the composition of solvent up to 60% volume.

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