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Acrylic acid recovery using Tri-n- butyl phosphate in laboratory made nontoxic non- edible diluent and efficiency comparison with Tri-n-octyl amine.

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ABSTRACT

The present work was aimed to study the usefulness of laboratory modified nontoxic nonedible natural diluent for the extraction of acrylic acid with tri-n-butyl phosphate (TBP) and Tri-n-octyl amine extractants. Partition coefficient (P=0.2389) and Dimerization coefficient (D=13.39 m^3/kmol) were calculated using graphical method. Extraction equilibrium constant (K_{E11}=2.23154 m^3/kmol) and loading factors (Z<0.5) were determined for TBP extraction of acrylic acid. The values of Z provided a base to postulate that there is formation of 1:1 complexes between TBP and acrylic acid. As most of the work on acrylic acid is done using TOA, an attempt is made to compare the results with TBP. The effect of alcohols on extraction efficiency of TOA was studied to develop a bio compatible extractant for extraction of acrylic acid.

Keywords: Nontoxic Non-edible Solvent, Acrylic Acid, Tri-n-Butyl Phosphate (TBP), Tri-n-Octyl Amine (TOA), Extractant.

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INTRODUCTION

Acrylic acid is a simplest form of versatile unsaturated carboxylic acid which is produced from petroleum feed stock by partial oxidation of propylene. Acrylic acid is widely used to make polymers. Esters of acrylic acids is used for manufacturing of consumers goods such as adhesives, surface coatings, textiles, binders for leather (accounts for 65-70% of products)and remaining products uses glacial acrylic acid (plastics, polyacrylic acids, copolymers in emulsions etc). Global warming (due to rapid industrialization across the world) and unstable prices of petroleum feedstock is forcing the manufacturers of acrylic acid to reduce their dependency on petroleum by seeking and developing biotechnology based methods. These methods utilize abundant and cheap biomass as their raw material. The extraction of acrylic acid from low concentrated (often < 10%) aqueous solution (fermentation broth & waste water stream) is a major challenge in making biobased method a viable option for sustainable development of mankind. The production of these acids via fermentation of biomass generated by increasing population of humans will ensure reduced carbon emission and clean environment .The recovery of acrylic acid from waste water will ensure good living conditions for aquatic fauna and flora(in view of toxicity of acrylic acid) and will also result in reduction in considerable amount of oxygen demand of waste water. As there is commercial value attached with recovered acid (used for commercial production of polymers; paints etc.) so it can bring reduction in the cost of waste treatment [1].

Presently most of acrylic acid is manufactured from propene (derived as byproduct during ethylene production) by catalytic partial oxidation with yield around 50-60%. A high yield (90%) two step acrolien is preferred over former method. The volatile price of crude oil and growing awareness for sustainable development is encouraging the industries to look towards renewable alternatives for production of acrylic acid. The successful commercialization of any organic acid by fermentation is dependent upon the recovery of acid cheaply (presently accounts for 40-60% of production cost). A large amount of organic waste is generated by rising population and during farming. These cheap sources of sugar provide us an unique opportunity to develop a low cost acrylic acid with commercial success (same purity and reactivity).[2] .

Fermentation process in near future can be used for production of carboxylic acids commercially only when there is development of low cost downstream process to crystallization (presently mostly used).Recovery methods such as extraction, electro dialysis, precipitation, adsorption etc are challenging crystallization and are undergoing continuous investigation and improvement..One of the major problems of fermentation process is low yield (due to product inhibition). There is a need to develop insitu method for recovery of acids. This will guarantee the commercialization of acids from fermentation. Reactive extraction is receiving a lot of attention for recovery of acids but very little work is done of recovery of acrylic acids [3]-[5]. Researchers [7]-[14] have shown that petroleum based diluent can be replaced by some non toxic eco friendly solvent. Recently A Kar [6] has used natural oils as diluents to overcome toxity of extractants for recovery of acrylic acid. The whole objective of carrying out this work is to test laboratory made eco friendly nontoxic nonedible diluent for the recovery acrylic acid using TBP and TOA as extractants.

EXPERIMENTAL SECTION

Materials Procured

Chemicals in the experiments were used as supplied (without undergoing any treatment) and de-ionized water was used for preparing solutions. Acrylic acid, Tri-n-butyl phosphate (TBP) and TOA were supplied by SRL Pvt. Limited through local vendor. The nontoxic nonedible natural diluent was prepared in the lab. A solution of phenolphthalein was prepared in lab for determining the end point during titration of aqueous phase. A freshly prepared NaOH was used to determine acid concentrations (after standardizing NaOH with the laboratory prepared solution of 0.1 N Oxalic acids).

Experimental setup used and Procedure adopted

A concentrated stock solution of acrylic acid was prepared using de-ionized water and then solution of desired concentrations were prepared by diluting with de-ionized water. The extractant (TBP) was dissolved in laboratory prepared natural nonedible non toxic diluent to prepare organic solution of 10%-30% by volume whereas with or Tri-n-octyl amine (TOA) 10-40% by volume solution is prepared in similar manner .10 mL of

aqueous and 10 ml organic solution was poured in 250 ml conical flask and then shaked in Orbital shaking incubator at 25^{O}C, at 150 rpm for 16 hours. The Centrifuge (Make: REMI) was used to separate the mixed phases by operating centrifuge at 10,000 rpm for 10 minutes. The mass balance was carried out to determine amount of acids in the organic phase. Only few runs were repeated to determine the data reproducibility and were observed to be within ±2% of accuracy.

Theory:

Physical extraction:

The physical extraction acrylic acid was carried out to determine the ability of nontoxic nonedible diluents ability to extract the acrylic and to calculate the partition coefficient (P) and Dimerization Coefficient (D) graphically by determining the values of distribution coefficient. The theory involved in physical extraction is given below [15]:

1. Ionization of the acid occurs in the aqueous phase but for weak acids this is small:

$$[HA]_{aq} \leftrightarrow [H^+] + [A^-] \quad (1)$$

$$K_{HA} = [H^+]\,[A^-] / [HA] \quad (2)$$

2. Extraction of the un dissociated molecular acid by the diluent results in partition between the two phases, aqueous (aq) and organic (org) as:

$$[HA]_{aq} \leftrightarrow [HA]_{org} \quad (3)$$

$$P = [HA]_{org} / [HA]_{aq} \quad (4)$$

3. As acid is polar in nature so in the organic phase so dimerization of the acid occurs as:

$$2[HA]_{org} \leftrightarrow [HA]^2_{org} \quad (5)$$

$$D = [HA]_{2,org} / [HA]^2_{org} \quad (6)$$

Distribution coefficient for physical extraction ($K_D^{diluent}$) can be written in terms of above defined parameters for graphical determination as:

$$K_D^{diluent} = \frac{[HA]_{org\,Total}}{[HA]_{aq\,Total}} = \frac{[HA]_{org} + 2[HA]_2}{[HA]_{aq} + [A^-]} = \frac{P + 2P^2 D[HA]_{aq}}{1 + K_{HA}/[H^+]_{aq}} \quad (7)$$

For the dilute concentration of acid (used in the study), it can fairly be assumed that second term in the denominator of above equation can be neglected, thus

$$K_D^{diluent} = P + 2P^2 D[HA]_{aq} \quad (8)$$

The degree of extraction (*E* %) of carboxylic acid in diluent is expressed as:

$$E\,\% = K_D^{diluent} \times 100 / (1 + K_D^{diluent}) \quad (9)$$

Equations of Reactive extraction with TBP:

The extraction of carboxylic acid by TBP in natural non toxic diluent can be represented as (mass law):

$$[HA]_{aq} + p[E]_{org} \quad <\xrightarrow{K_S}> \quad [HA.(E)_p]_{org} \quad (10)$$

The Extraction equilibrium constant (K_S) and reacting molecules number (of extractant) are computed as given below

$$K_S = [(HA).(E)_p]_{org} / [HA]_{aq}\,[E]^p_{org} \quad (11)$$

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Where $[HA]_{aq}$, $[E_{org}]$ & $[HA.(E)_p]_{org}$ or $[HA]_{org}$ represents acid ,extractants and complex concentrations in the respective phases and K_s depends upon proprties of the acids and the solvation efficiency of the diluent used.

It is well known fat that organic acids exist in undissociated format pH below pKa, the extraction process can also be analyzed by means of the distribution coefficient (K_D)

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \quad (13)$$

and Overall degree of extraction as given below:

$$\% E = K_D \times 100 / (1 + K_D) \quad (14)$$

Equations of Reactive extraction with TOA:

In reactive extraction of Acrylic acid (HA) with tertiary amine TOA (E) there is a formation of reaction complex ($[HA]_{org}$) and which solvates in organic phase. The distribution coefficient is by following equation

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \quad (15)$$

And percentage extraction (%E) for TOA also as

$$\% E = [K_D / (1 + K_D)] \times 100 \quad (16)$$

Model for Prediction of Simultaneous Formation of Various Complexes between TBP and acrylic acid

Loading ratio (Z) values here tells the extent to which the organic phase (extractant + diluent) can be loaded with acrylic acid and is given as:

$$Z = \frac{[HA]_{org}}{[E]} \quad (17)$$

The formation of various types of complexes (1:1, 2:1 and 3:1) between acid and extractant depends on the values of Z. For low values of Z<0.5 a complex of (1:1) is formed as given by

$$Z/(1-Z) = K_{E(1:1)}[HA]_{aq} \quad (18)$$

A plot of Z/(1-Z) versus $[HA]_{aq.}$ (from above equation) should yield a straight line passing through origin. The slope of this line gives the value of extraction complexation constant ($K_{E(1:1)}$) .For higher values of Z> 0.5, complexes such as [1:2]and [1:3] are assumed to be formed.

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RESULTS AND DISCUSSIONS

Physical Extraction:

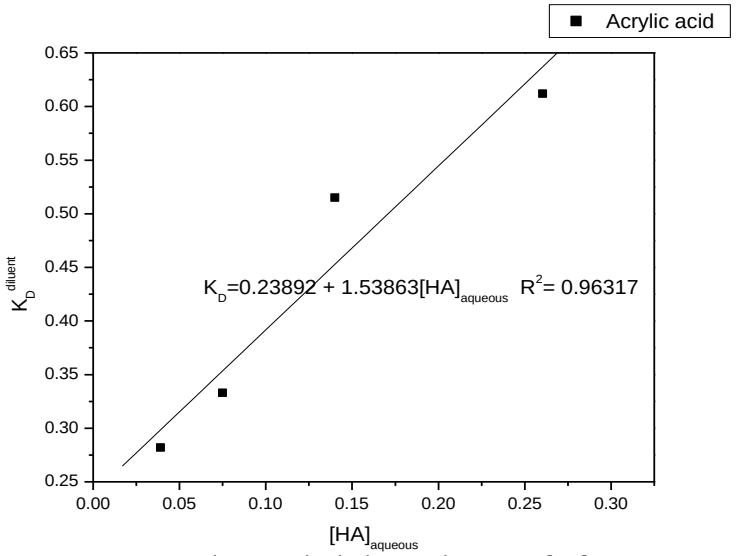

Figure 1: Physical Extraction : K_D vs $[HA]_{aqueous}$

The extractability of any acid by pure non toxic diluent depends on two factors; one is the ability of acid to lose hydrogen (extent of hydration) and other is the bond strength of acid with water molecule. The extraction efficiency (in terms of E *%*) was found to increase with an increase in the concentration of acrylic acid. The extraction of acrylic acid by pure nontoxic natural solvent (without extractant) was studied to find out the Partition coefficient (P) and Dimerization coefficient (D) and Distribution coefficient ($K_D^{diluent}$) graphically. The results are calculated from Figure 1 and tabulated in Table 1. The small value of D indicates that extracted acid molecule dimerizes to a small extent only.

Acid	*P*	*D(m^3/kmol)*	*Range of E%*
Acrylic Acid	0.2389	13.39	22—35%)

Table 1: Partition coefficient (P), Dimerization coefficient (D) & Percentage Extraction efficiency (%E) values for extraction of acrylic acid without extractants.

Effect of Extractant concentration:

The results of physical extraction (low extraction efficiency) can be enhanced by using phosphorus or amine extractant (in sufficient concentration) in order to make the process commercially viable. These extractants when used along with diluents get associated with acrylic acid (in aqueous phase) via reversible complexion reaction to form organic phase solvable complex product and this may be regarded as advanced form of liquid extraction or reactive extraction**.** These reactants are toxic in nature and thus preventing *insitu* extraction of acids from aqueous solutions (fermentation broth). The judicious use of these extractants and non toxic diluent can overcome the toxicity problem. Here an attempt is made to study the usefulness of laboratory prepared non toxic solvent for extraction purpose.

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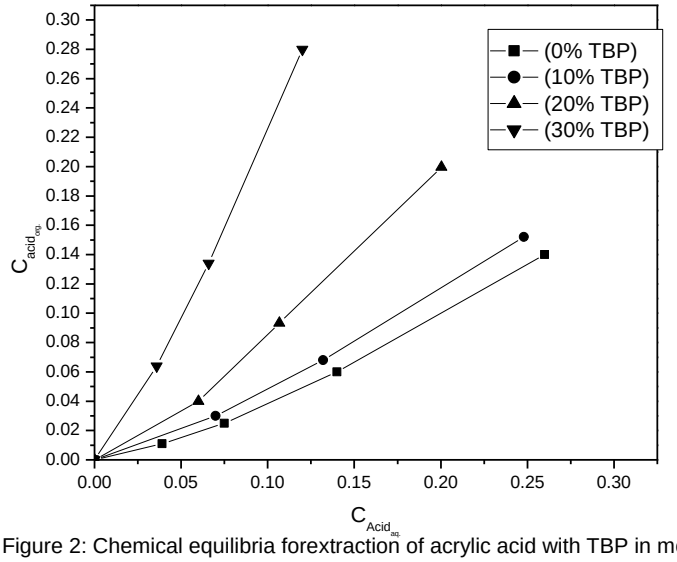

Figure 2: Chemical equilibria forextraction of acrylic acid with TBP in modified oil

Figure 2 shows the equilibrium isotherms for acrylic acid obtained by performing experiments with varying percentages of TBP in nontoxic diluent. The isotherms show the major influence of TBP on extraction of acrylic acid. The extraction was found to increase with the increase in TBP concentration and the increase is significant at composition of 30% TBP (consistent with the literature available). The results also show that the lab made nontoxic natural diluent is capable of solvating the reversible complex during the process. The extraction efficiency (E %) is found to increase up to 70% with the in the increase in TBP concentration (40%)

Loading ratios (Z):

The stoichiometric relation that exists between acid and extractant in the complex depends on the value of Z (estimated and plotted). The values of Z strongly depend on acid and extractant concentrations as shown in the Figure3. The low values of Z (Z < 0.5) at all initial acid concentrations indicate a strong possibility for formation of formation of 1:1 complex between acid and extractant [due to low concentration range of acrylic acid (0.05-0.4 moles/liter) is used for extraction with TBP]. The loading values of Z are lower than 0.5 were consistent with the available literature(A Keshav [2] & a Kar [6]).

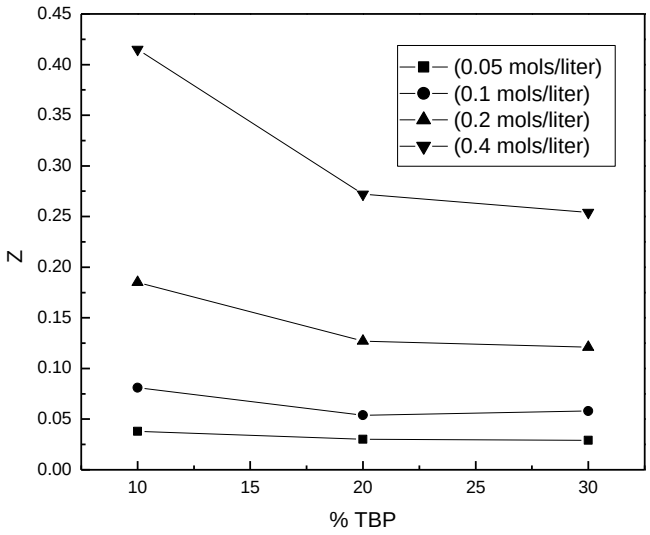

Figure 3:Loading ratios for the extracion of Acylic acid using modified oil

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The overall loading ratio (Z) values were also found to decrease with the increase in percentage of TBP concentration for all initial acid concentrations .As all the values of Z were found to be lower than 0.5, we can conclude that there is formation of only 1:1 complex of TBP with acrylic acid without overloading when laboratory prepared non toxic non edible oil was used as diluent.

Estimation of $K_{E(1:1)}$ based on Z:

The values of $K_{E(1:1)}$ for the extraction of acrylic acid was estimated by fitting a straight line through origin on a plot between Z/(1-Z) vs $[HA]_{aq.}$. The corresponding values of slope and R^2 are shown in the Figure 4. The Equilibrium extraction constant ($K_{E(1:,1}$) for 1:1 complex between acrylic acid and extractant (TBP) was found to be2.23154(m^3/kmol). The obtained values of $K_{E(1:1)}$ are very similar to the values obtained by A Kar[6] while using natural oils for extraction of acrylic acid using TBP.

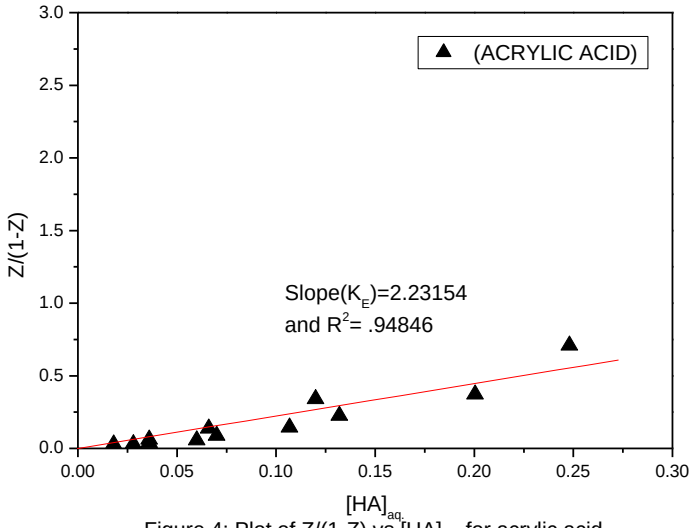

Figure 4: Plot of Z/(1-Z) vs $[HA]_{aq.}$ for acrylic acid

Extraction with TOA:

The literature showed TOA is more effective than TBP for extraction of acrylic acid so few runs were taken to check the utility of lab prepared non toxic diluent. The amount of TOA is varied from 10-40% in the organic phase. The extraction efficiency of around 90% was obtained with 40% TOA as compared to 70% with TBP.

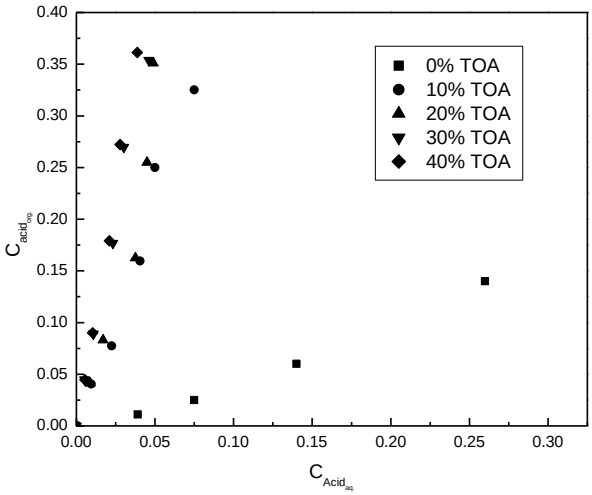

Figure 5: Chemical equilibria for extraction of acrylic acid with TOA in modified oil

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Extraction with TOA with Modifiers (Decanol & Octanol): The studies conducted by Hong Y K [5] showed that the polar alcohols are very effective for extraction of acrylic acid from aqueous solution when used along with TOA. The extractants consisting of TOA, Decanol and Dodecane are often referred as biocompatible by researchers such as S Kumar [16].Figure 6 shows that on adding 30% Octanol or 30% Decanol to 30% TOA increases the extraction efficiency because of increase in the solubility of acrylic acid-TOA complex in organic phase due to increase in polarity. The above results are consistent with the literature (Hong Y K [5]).

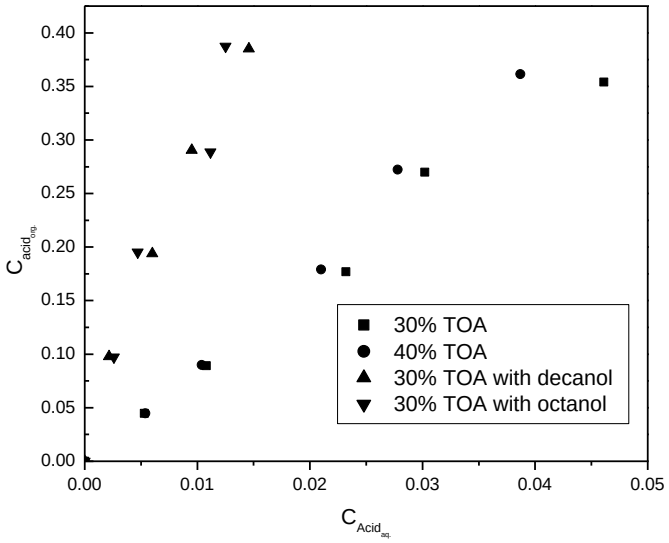

Figure 6: Chemical equilibria for extraction of acrylic acid with TOA(with and without higher alcohols) in modified oil

CONCLUSIONS

Most of the studies of reactive extraction were aimed to recover the solute fro aqueous phase without taking toxity into consideration .The successful commercialization of fermentation process depends upon insitu extraction of acids for which there is need and scope. In this study, laboratory modified non toxic natural diluent provided comparable results with petroleum based diluents for recovery of acrylic acid from aqueous solution. The addition of extractants such as TBP and TOA to non toxic diluent increases the recovery of acrylic acid. The average % extraction of acrylic acid at 30% TBP is 66.98% whereas for 40% TOA is 89.87%.On adding 30% of higher alcohols such decanol and octanol, the percentage efficiency increases to 96.93% for decanol and 97.04% for octanol. There is only marginal difference in the extraction efficiency between octanol and decanol promoted extraction but due to toxity issues the decanol based system is recommended over octanol. The values of loading ratios (Z) for acrylic acid are always less than 0.5 so the formation of 1:1 complex is presumed. The Equilibrium extraction constant ($K_{E(1:1)}$) for 1:1 acrylic acid and extractant (TBP) is found out to be 2.23154(m^3/kmol) .

Symbols Used

$[A^-]$ = Dissociated acid concentration in aqueous phase (kmol/m^3)
[E] = Extractant concentration in organic phase (kmol/m^3)
$[H^+]$ = Concentration of H^+ ion in aqueous phase (kmol/m^3)
[HA] = Concentration of acid, (kmol/m^3)
(K_S)=Extraction equilibrium constant
D = Dimerization constant (m^3/kmol)
E% =Extraction efficiency
K_D = Acid distribution coefficient
$K_{E(1:1)}$ = Extraction equilibrium constant for (1:1) acid-extractant complex, (m^3/kmol)
P = Partition coefficient
Z= loading ratio

Subscripts

aq = aqueous phase
org = organic phase

Superscript

diluent = for diluent only

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