Reactive Extraction of Caproic Acid using Tri-n- Butyl Phosphate (TBP) in Non Toxic Diluents

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Abstract : The present paper deals with the study of reactive extraction of caproic acid using tri-n-butyl phosphate in non-toxic diluents (oils obtain from sunflower, soybean, and rice bran) in different proportions and combinations of extractant and the non-toxic diluents. Results were presented in terms of distribution coefficients, loading ratio, degree of extraction, equilibrium complexation constants and the kinetics of reaction involved. The data obtained were found to be useful for process engineers to efficiently design reactive extraction process for the recovery of caproic acid by thorough understanding of the equilibrium characteristics. Also, the problem of toxicity in reactive extraction could be reduced by using the natural non-toxic diluents with the extractant.

Keywords : Reactive extraction, TBP, Nontoxic diluent, Caproicacid, Toxicity, batch process.

Introduction

Reactive extraction is a showing a lot of promise for the recovery of carboxylic acid with respect to other processes such as distillation(not suitable for low concentration), electro dialysis (high cost of membrane and fouling)and other conventional precipitation processes(by product disposal). The success stories of reactive extraction has been increasing in the recovery of carboxylic acids from dilute solutions or fermentation broths but toxicity problems of the diluents and extractants employed is hampering its wider acceptability. Therefore, it is felt study various combinations of non-toxic diluents and extractants or by using less toxic extractants in a non-toxic diluents(oils) that can recover the acid efficiently and ineco friendly manner[1-7].

Caproic acid, technically known as n-hexanoic acid $\{CH_3 (CH_2)_4COOH\}$ is a member of fatty acids series and is often found in oils and fats of animals[8]. It is widely used in organic synthesis, pharmaceuticals and perfumes, medicine, lubrication, grease, dye, latex, plastics, rubbersand flavorings. It has pungent smell and is

a colourless light yellowish transparent oily liquid. Caproic acid is used in organic synthesis, pharmaceuticals and perfumes, medicine, lubricating, grease, dye, rubber& latex, plastics and flavorings.The market is ready to welcome caproic acid but the demand would be greatlyexpanded greatly if it could be produced from renewable waste materials (inexpensive starting materials).

Presently Caproic acid is produced commercially by carbonylation of ethylene with carbon monoxide and water or by oxidation of propanal or by direct oxidation of hydrocarbons. Although the petrochemical route promises good yield, but due to high cost of petroleum feed stock it is wiser to find ecofriendly and regenerative route alternate like fermentation (most preferred way of producing caproic acid)[9-10].

The downstream process of separation of caproic acid from fermentation broth or aqueous streams is of great importance. The neutralization followed by extraction is the most preferred way to recover the carboxylic acids. Generally inorganic acids such as H_2SO_4 and HClare used to neutralize, followed by solvent extraction using suitable extractant and whenever sulfuric acid is used to neutralize the waste than low value sodiumsulphate results as waste (by-product).

The oxygen present in the carboxylic acids makes them as promising intermediates for further reaction resulting in different kinds of products. Generally low concentrations of carboxylic acids (<10%) are achieved in fermentations even for lactic acid and citric acid (now commercialized) from carbohydrates. Chemical reaction combined with extraction by employing immiscible phases can be considered as an alternative to the conventional calcium salt precipitation techniques for the recovery of carboxylic acids from aqueous stream. For the recovery of caproic acid by extraction using the common organic solvents such as ketones and alcohols shows low distribution ratio. The high affinity of acid for water shows that physical extraction with conventional solvents is not an efficient method for recovery of caproic acid.

Reactive liquid-liquid extraction involving organic immiscible phase has the advantage that caproic acid can be removed easily from aqueous stream, recoveredcaproic acid can be re-extracted easily and the extractant generated after re extraction can be recycled. The selected extractant should be cheaply available; easily regenerated, very high distribution coefficients, and low toxicity (betterif extractant is environmentally friendly). In other words, the extractant should be immiscible in water as far as possible, so that it does not add substantially to COD of the aqueous raffinate.

Lots of work on the reactive extraction of various carboxylic acids[11-24] using tertiaryamines(TOA) and quaternary amines(Aliquat) has been done but very little work using organophosphorus extractants for caproic acid extraction using natural diluents is hardly available in the literature. The distribution coefficient of caproic acid between water and TBP dissolved in diluents (vegetable oils) were studied at isothermal conditions, in the present work.

THEORY

The recovery of caproic acid with TBP may be due to the formation of a complex (due to interfacial reaction) may be represented as:

$[HA]_{aq} + pB_{org} \leftrightarrow (HA. B_p)_{org}$ …… (1)
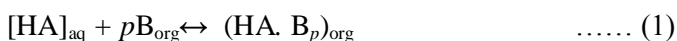
The caproic acid is rapidly extracted into the organic phase as the acid-TBP complex is formed. Extraction constant (K_E) and the number of reacting molecules of extractant have been computed by applying law of mass action*. According to the general equation of interaction between the extractant and the extracted species the relation may be expressed as:

$K'_E = [(HA).(B)_p]_{org} / [HA]_{aq} [B]^p_{org}$ ………(2)

It is expected that the values of K_E might depend on acid properties and the solvation efficiency of the diluent (oils in present case) used. The little dissociation of the acid in the aqueous phase may be given as:

$HA \leftrightarrow H^+ + A^- \quad K_{HA} = \dfrac{[H^+][A^-]}{[HA]}$ ..... (3)
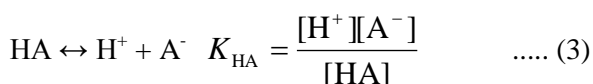
*is the ratio between concentrations of reactant molecules and concentration of the product species.

The values of Distribution ratio (K_D) (defined as the ratio of total (analytical) concentration of acid in all its forms (by partition, dimmers and as complexes) in organic phase to total (analytical) concentration of all its existing forms (dissociated and undissociated) in aqueous raffinate) might affect ionic strength, nature of ion concentration of H$^+$ etc. of solution constituents.

$$K_D = \frac{[HA]_{org}}{[HA]_{aq}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots..\ldots..(4)$$

Degree of extraction (*E*) is defined in terms of distribution coefficient and is generally a the ratio of caproic acid concentration in organic phase to the sum of acid concentration in organic and aqueous phase as:

$$E\% = \frac{K_D \times 100}{1 + K_D} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

It is foundthat solvation number of the acid depends on carboxylic group and is equal to the number of -COOH group on the acid molecule[25]. As caproic acid contains one -COOH group so the solvation number (*p*) can be assumed to be unity.

Considering *p* = 1, and using,

$$[B]_{org} = [B]^o_{org} - [HA.B]_{org} \qquad \ldots\ldots\ldots\ldots\ldots\ldots.. \quad (6)$$

equation (2) can be written as,

$$K'_E[HA]_{aq} = \frac{[HA.B]_{org}}{[B]^o_{org} - [HA.B]_{org}} = \frac{[HA]^{total}_{org}}{[B]^o_{org} - [HA]^{total}_{org}}$$

$$= \frac{z}{1-z} \quad \ldots\ldots\ldots\ldots\ldots \quad (7)$$

where *z* (loading ratio) represents the extent to which the organic phase (extractant + diluent) can be loaded with carboxylic acid, and is represented as,

$$z = \frac{[HA]_{org}}{[B]_{o,org}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

The value of *z* indicates the extractability of the acid (strength of the acid-base interaction) and its aqueous concentration. The stoichiometry of the overall extraction reaction depends on the loading ratio (z) in the organic phase *z*.

Experimental

Tributyl phosphate (TBP) {Purity : 99%; M/sCDH Laboratory Reagent, India; Mol Wt ; 266.32 g mol^{-1}; Density : 0.975 g cm^{-3}}, is a light colorless liquid. Caproic acid was purchased from M/s Himedia, India. Diluents, as manufactured from natural products are used without modifications (sunflower oil, soya oil), rice bran oil). Sodium hydroxide (NaOH) was procured from M/s S.D. Fine Chemicals Ltd, India. Phenolphthalein solution (pH range 8.2 - 10.0) was used as an indicator and procured from M/s S.D. Fine Chemicals Ltd, India. Low initial aqueous concentration of acid (0.05 to 0.2 kmol/m^3) was used in view to find the effectiveness of the reactive extraction for recovery of dilute caproic acid (as concentration greater than 0.2 kmol/m^3 in waste streams and in fermentation broths is not expected)

Reactive extraction experiments were carried out by shaking 20 cm^3 volumes of aqueous and organic phases for 12 hours in shaking water bath (Remi, India) at constant temperature (305 K), followed by settling (phase separation) of the mixture for at least 2 hours at a same temperature (305 K). an Orion 3 star pH bench top (Thermo Electro Corporation) was used to measure aqueous phase pH . Aqueous phase acid concentration was then determined by titration (phenolphthalein indicator) with NaOH (freshly prepared). The acid content in the organic phase was computed by mass balance. Only few experiments were repeated to verify the consistency and found within limit of ±2%.

Results and Discussion

Chemical Extraction of caproic acid using TBP

TBP (Viscosity : 3.56 · 10^{-3} Pa·s) contains a phosphoryl group and shows a stronger Lewis base character and intermolecular hydrogen bonding than the carbonyl group. It shows a very low solubility in aqueous phase (Mass Fraction ; 0.039) and low water co-extraction (Mass Fraction : 4.67). All these features could facilitate good phase separation in continuous extraction process and so, it attracted us to use TBP, in the present study. The TBP also undergoes specific interactions (like self association and molecular complex formation with low density diluents or other solutes) due to the presence of both electron donor and electron acceptor groups in phosphoryl group [=P (O) OH]

Chemical Equilibrium Curves

Figs. 1-3 shows the chemical equilibrium curves for extraction of caproic acid using 0, 20 and 40% TBP in natural diluents like sunflower oil (Fig. 1), rice bran oil (Fig. 2) and soya oil (Fig. 3). It is evident from the figures that there found some improvement in extraction, at 0% TBP, but that was not large enough to choose sunflower oil as diluent. The only advantage with natural diluents is its non toxic characteristics which might make it suitable while using *In-Situ* extraction of acid.

The values of K_D were obtained in the range of 0.00142 – 24.2, 0.59 – 20, and 1.59 – 16.4 with 0, 20 and 40 percent TBPin sunflower oil, rice bran oil, and soya oil, respectively. Higher extractions were obtained at higher concentrations of acid with TBP.The value of E% was found to increase from the average value of 88.2 to the average value of 91.3% in the case of sunflower oil with the increase of TBP from 0-40 %. However, in case of rice bran oil (14.1%) and soya oil (12.7%) the increase was higher as with sunflower oil. Nevertheless the highest value of E% was obtained in case of sunflower oil, viz. 91.3% . Loading ratios were less than 0.5, thus suggesting that only (1:1) acid-TBP complexes were formed. The value of K'_E was obtained as 11.29, 8.73 and 8.33 m^3/kmol in sunflower oil, rice bran oil and soya oil respectively. The low extraction by TBP is accounted to the non polar nature of both extractant and diluents.
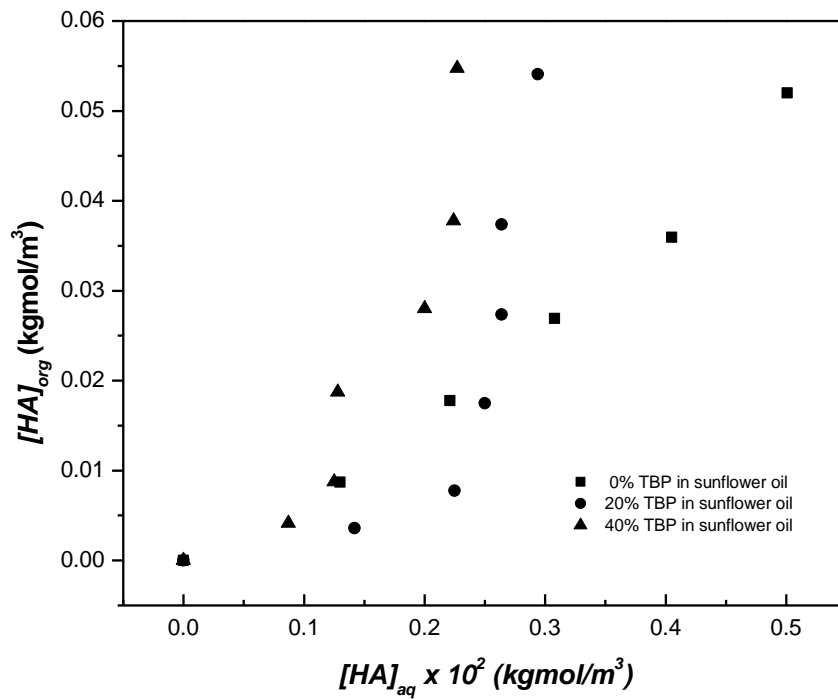
Fig. 1. : Chemical equilibria for extraction of caproic acid using various percentages of TBP in sunflower oil.
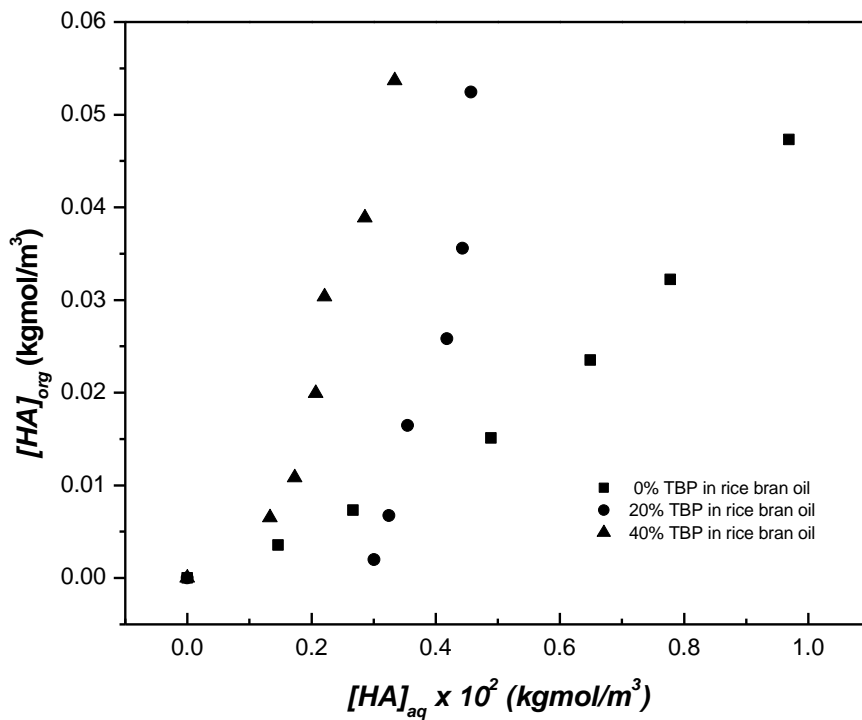

Fig. 2. : Chemical equilibria for extraction of caproic acid using various percentages of TBP in Rice Bran Oil.
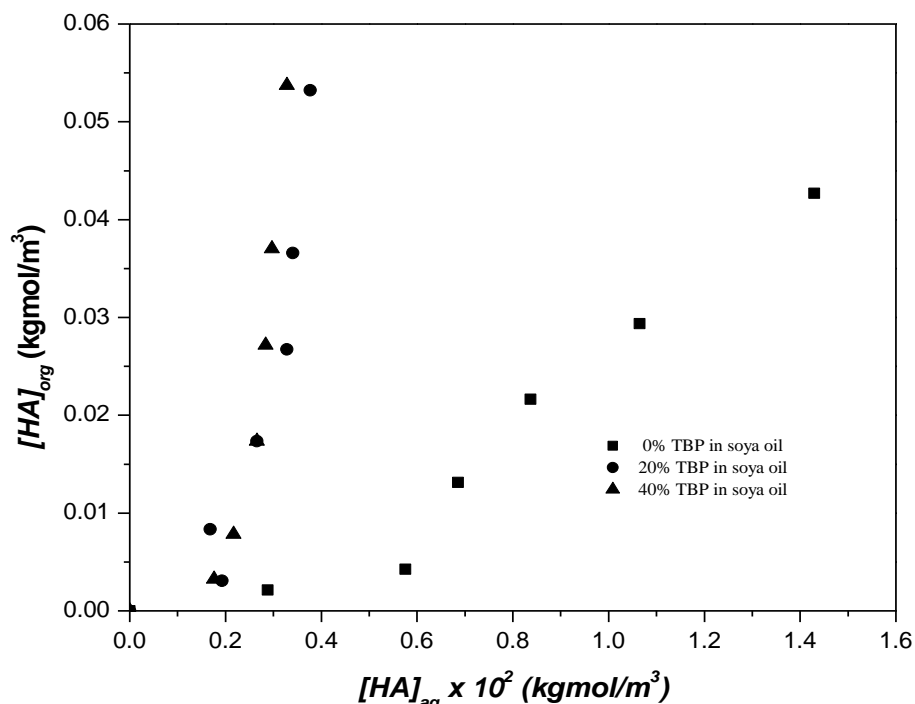
Fig. 3.: Chemical equilibria for extraction of caproic acid using various percentages of TBP in soya oil.

Conclusion

TBP was used in different percentages in various diluents. It was found that the K_D values improve much as the reactive extraction involves extraction with chemical reaction. The trend of K_D (average) for extraction using TBP in different diluents follows sunflower oil > rice bran oil > soya oil.

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