

# Intensification of Recovery of Nicotinic Acid Using Reactive Extraction: Equilibrium Study

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## ABSTRACT

Nicotinic acid is widely used in the food, pharmaceutical and biochemical industries. Fermentation technology for the production of nicotinic acid in particular has been known for more than a century and acid have been produced in aqueous solutions. Reactive liquid-liquid extraction for the recovery of the organic acids by a suitable extractant has been found to be a promising alternative to the conventional processes. For the design of extraction process, equilibrium data of extractant is required to select the proper extractant for reactive extraction. The conventional extractants, such as simple hydrocarbon, ketone, kerosene oil and alcohol are used to carryout the physical equilibrium experiments for reactive extraction of nicotinic acid. These extractants are not able to fulfill the basic requirements often because of their low distribution coefficients. The maximum distribution coefficient ( $K_D = 0.51$ ) is obtained with 1-octanol. Tri-n-butyl phosphate (TBP) with various diluents is used to perform equilibrium experiments of reactive extraction of nicotinic acid. The distribution coefficients are calculated with various extractant systems in equilibrium. Effect of nicotinic acid concentration on distribution coefficient has also been studied. Pure TBP is showing maximum recovery of nicotinic acid with distribution coefficient ( $K_D = 0.87$ ).at an initial acid concentration of  $0.105 \text{ kmol/m}^3$ .

## INTRODUCTION

Over the last 3 decades, there has been a resurgence of interest in large-scale production of fermentation chemicals due to the sharp increase in petroleum cost. So the potential role of a new energy efficient fermentation technology is receiving growing attention. The current economic impact of fermentation chemicals, however, is still limited, in large part because of difficulties of product recovery. Thus, for fermentation products to penetrate the organic chemicals industry, substantial improvements in the existing recovery technology are needed.

Organic acids, widely used in the food, pharmaceutical and chemical industries, are important chemicals. Fermentation technology for the production of organic acids in particular has been known for more than a century and acids have been produced in aqueous solutions. Reactive liquid-liquid extraction of the organic acids by a suitable extractant has been found to be a promising alternative to the conventional processes [1]. This method is advantageous for alcohol and organic fermentations [2]. Some of the advantages include increased reactor productivity, ease in reactor pH control without requiring base addition, and use of a high-concentration substrate as the process feed to reduce process wastes and production costs. This method may also allow the process to produce and recover the fermentation product in one continuous step and reduce the down stream processing load and the recovery costs. Nicotinic Acid (also called Niacin) is an important carboxylic acid. Severe lack of niacin causes the deficiency disease pellagra. Niacin has proved to be useful as a food additive and in pharmaceuticals. The main sources of nicotinic acid are fruits, plants and seeds [3].

Three major factors have been found to influence the equilibrium characteristics of extraction of carboxylic acids from aqueous solutions, i.e., the nature of the acid, concentrations of acid and Tributyl Phosphate (TBP), and the type of diluent [4-6]. Process considerations dealing with the competition between physical extraction and the chemical interaction of hydrophobic acids remain a challenging problem since such systems show extremely nonideal behavior.

The extraction of carboxylic acids from aqueous solution is structured according to three extraction categories [1]:

1. Acid extraction by solvation with carbon-bonded oxygen-bearing extractants (inert aliphatic and aromatic hydrocarbons and some of their substituted homologs).
2. Acid extraction by solvation with phosphorous- bonded oxygen- bearing extractants.
3. Acid extraction by proton transfer or by ion pair formation, the extractant being high molecular weight aliphatic amines.

The distribution of nicotinic acid (3-pyridine carboxylic acid) between water and TBP dissolved in various diluents, and a comparison with the extraction capacity of pure diluent alone were studied at isothermal conditions. Equilibrium experiments are also carried out to study the effect of TBP concentration within extractants.

## EXPERIMENTAL

To carry out the equilibrium experiments, experimental set-up consists of temperature controlled shaker bath, conical flasks, separating funnels and burette for potentiometric titration.

### Materials

In the experiments, TBP- tributyl phosphate (Sd Fine Chemicals Co.) and Nicotinic acid (Sd Fine Chemicals Co) were used. Various solvents and diluents like 1-octanol (Sd Fine Chemicals Co.), MIBK (Sd Fine Chemicals Co), diethylether (SpectroChem Co.), kerosene (Sd Fine Chemicals Co), toluene (Sd Fine Chemicals Co) and benzene (SpectroChem Co.) were also used.

### Reactive Extraction

Aqueous nicotinic acid solution of the required concentration was prepared by diluting the nicotinic acid (99.5%v/v) with distilled water. Aqueous acid solutions for nicotinic acid were prepared in the range of 0.00752 to 0.13 kmol/m<sup>3</sup>. Various diluents are used to study physical equilibrium of extraction of nicotinic acid. phosphorous- bonded oxygen- bearing extractant, tri-n-butyl phosphate (TBP) with diluents are used for studying of chemical equilibria. Various phosphorous based organic solutions were prepared in the range of 20-80%TBP (v/v) with various diluents. Experiments were carried out in 150 ml shake flasks with a working volume of 50 ml in the temperature controlled reciprocal shaker bath with capacity of 12 flasks. Equal volumes (25 ml) of the aqueous phase and the organic phase in 150 ml. of flasks were shaken for 12 hrs. at room temperature.

Our preliminary studies had shown that 12 hrs. of mixing time is sufficient to reach equilibrium. The initial pH of the propionic acid solution was taken as such by initial concentration of solutions. After attaining equilibrium, the phases were brought into contact for separation.

### Analytical Method

After settling, organic and aqueous phases were separated and the volume of each phase was determined. The propanoic acid concentration in equilibrium aqueous phases was determined by potentiometric titration using 0.05N NaOH solution normalized with 0.05N oxalic acid solution. The acid concentration in the organic phase was obtained by the mass balance. The extraction ability was represented by the distribution coefficient. The calculated distribution coefficient,  $K_D$ , is calculated with following relation as given by Eq. 1.

$$K_D = \frac{C_{org}}{C_{aq}} \quad (1)$$

Where,  $C_{org}$  is the concentration of propionic acid in organic phase and  $C_{aq}$  is the concentration of propionic acid in aqueous phase after reaching equilibrium.

## RESULTS AND DISCUSSION

Experiments were carried out to intensify the recovery of nicotinic acid from aqueous solution by studying the physical and chemical equilibria using pure diluents and phosphorous- bonded oxygen- bearing extractant, tri-n-butyl phosphate (TBP).

### Carbon bonded Oxygen-bearing Extractants

The distribution of the acid between water and the hydrocarbon is relatively free of complexities and can be regarded as physical distribution. The acid partially dissociates in the aqueous phase and its dimerization occurs in the hydrocarbon phase. While, the acids extracted by the carbon bonded oxygen-bearing solvents are strongly hydrated by varying number of water molecules. The exact solvation number of the acid molecules in the organic phase is undetermined [4].

The physical equilibrium was studied for nicotinic acid using various solvents. MIBK, 1-octanol, diethyl ether, kerosene, toluene and benzene were used to find the distribution coefficient of nicotinic acid. Experiments were carried to know the effect of initial acid concentration on distribution coefficient for a particular solvent. The results are shown in Fig. 1 and 2.

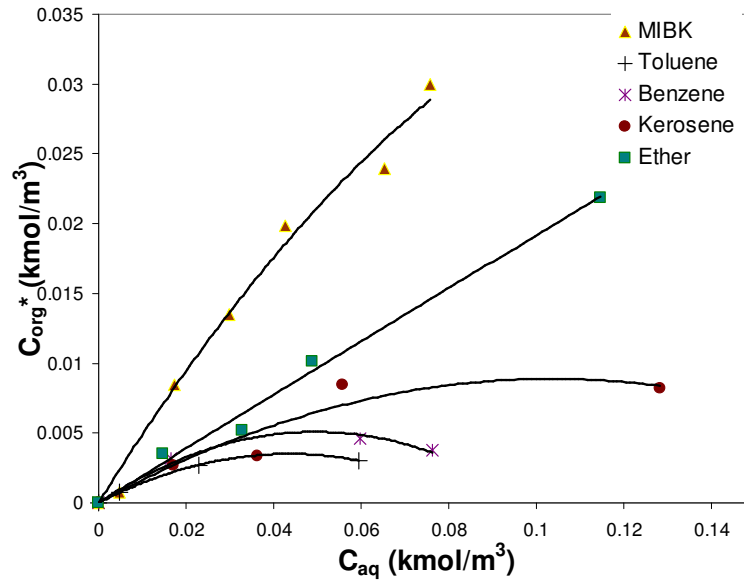


Fig. No. 1: Physical Equilibria for the Extraction of Nicotinic Acid with Pure Diluents

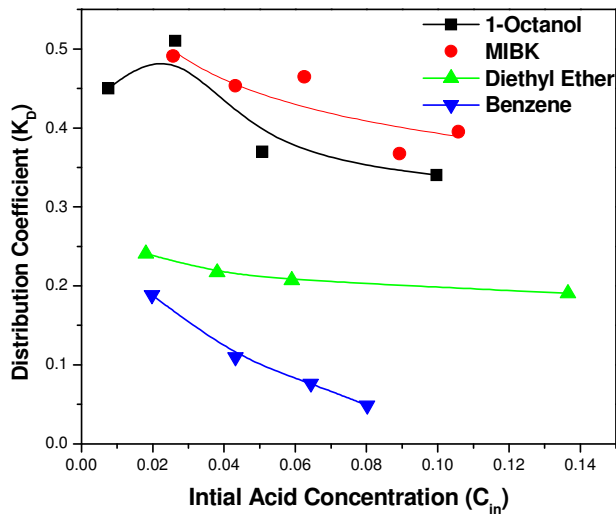


Fig. No. 2: Distribution Coefficient for Nicotinic acid with Initial Concentrations of Acid using Diluents

The equilibrium curves with 1-octanol and MIBK are much steeper from Fig. 1. So 1-octanol and MIBK solvents show better recovery of propionic acid in organic phase than benzene, xylene and heptane. Solvation strength is less for aromatic and hydrocarbon solvents. Conventional solvents such as 1-octanol, heptane, MIBK, xylene and benzene and aliphatic hydrocarbons are not efficient when applied to dilute, carboxylic acid solutions because of the low aqueous activity of carboxylic acids resulting in low distribution coefficients. Our experimental studies show that there is maximum distribution coefficient ( $K_D = 0.51$ ) of nicotinic acid with 1-octanol at initial acid concentration of  $0.0263 \text{ kmol/m}^3$ , as shown in Fig 2. At higher initial propionic acid concentration, the amount of solvent may be the limiting factor for the strength of solvation of the complex.

**Phosphorous bonded Oxygen- bearing Extractants:**

Weak organic acids are extracted by phosphorous- bonded oxygen- bearing extractants with a significantly higher distribution ratio than carbon-bonded oxygen-bearing extractants under comparable conditions. Tri-n-butyl phosphate (TBP) is used to study chemical equilibria. the results for extraction of nicotinic acid from aqueous solution are shown in Fig. 3 and 4.

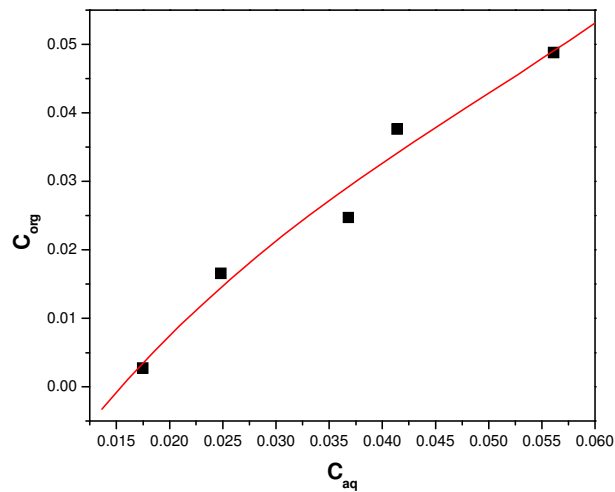


Fig. No. 3: Chemical Equilibria for the Extraction of Nicotinic Acid with TBP

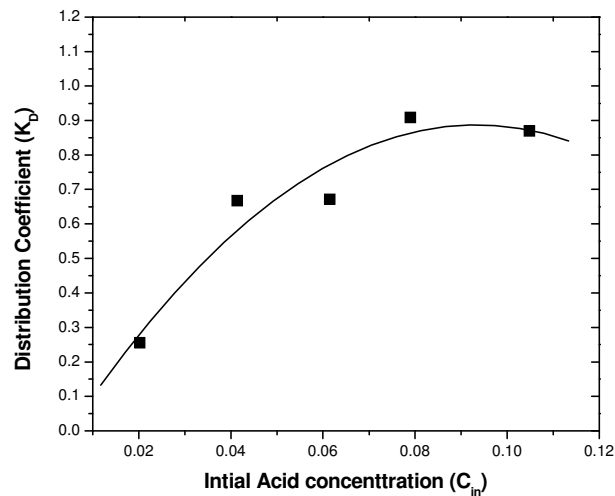
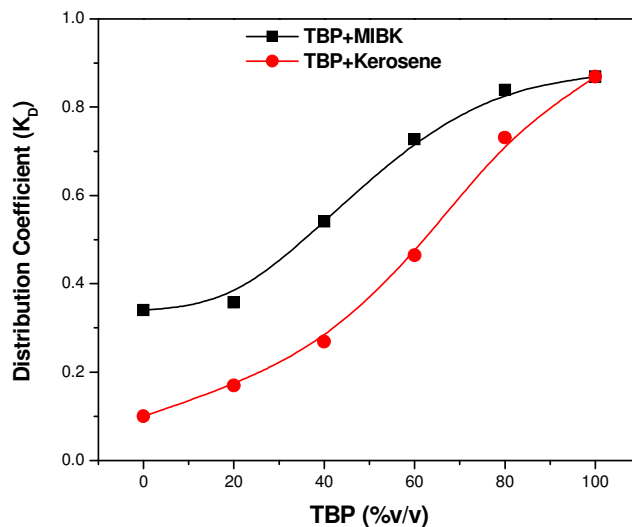


Fig. 4 Distribution Coefficient with Initial Acid Concentration using TBP as Extractant.

Figure 4 shows the effect of acid concentration on the extraction of nicotinic acid by TBP used as an extractant. With Tri-n-butyl phosphate (TBP) and unit  $V_{org}$  to  $V_{aq}$  ratio,  $K_D$  increased from 0.26 to 0.91 upon increasing initial nicotinic acid concentration from 0.02 to 0.08 kmol/m<sup>3</sup>. But At higher initial nicotinic acid concentrations, the amount of TBP may be the limiting factor for the reactive extraction. So at high acid concentration,  $K_D$  decreased upon increasing initial acid concentration



**Fig. 5 Distribution Coefficient with Variation of TBP Conc. at Initial Acid Concentration of 0.105 kmol/m<sup>3</sup>.**

Experiments are also carried out to study the effect of concentration of TBP on the recovery of nicotinic acid. With increasing conc. of TBP in the diluents,  $K_D$  is also increased from 0.34 to 0.87 with MIBK and from 0.1 to 0.87 with kerosene as shown in Fig. 5. TBP extractant is tested with two diluents- MIBK and Kerosene for the extraction of acid. As can be seen that the distribution coefficient of acid for diluents is enhanced using with TBP.

Our experimental study shows that nicotinic acid is recovered from aqueous solution to organic solvent. So an extractive separation and recovery process normally involves two steps: extraction and solvent regeneration. Extractant can be easily regenerated by stripping with a small volume of alkaline solution. There are various methods for back extraction such as temperature swing, diluent swing, and gas anti-solvent methods using NaOH, HCl, ammonia and trimethyl amine. Wasewar et al. (2004) have given the exhaustive discussion on these processes for the back extraction of carboxylic acids [7].

## CONCLUSION

Conventional solvents such as 1-octanol, MIBK, kerosene, diethylether and benzene are not efficient when applied to dilute, nicotinic acid solutions because of the low aqueous activity of carboxylic acids resulting in low distribution coefficients. Physical and chemical equilibria for nicotinic acid extraction TBP dissolved in MIBK and Kerosene have been determined. It has been found that Pure TBP and the combination of TBP and diluent gave a higher distribution coefficient as compared to pure solvent. The polar diluents may be more effective with phosphorous- bonded oxygen- bearing extractants. Distribution coefficients for extraction of nicotinic acid using TBP was higher than pure solvents.

## REFERENCES

1. Kertes, A.S. and King, C., Extraction chemistry of fermentation product carboxylic acids. *Biotechnology and Bioengineering*. 1986, 28: 269-282.
2. Wasewar, K. L.; Heesink, A. B. M., et al., 2003, Intensification of Enzymatic Conversion of Glucose to Lactic Acid by Reactive Extraction, *Chem. Eng. Sci.*, **58**(15), pp. 3385-3394.

3. Category: Niacin, Wikipedia, free encyclopedia (database on Internet). [Updated: September 8, 2006].  
Available from: [http://en.wikipedia.org/wiki/Nicotinic\\_acid](http://en.wikipedia.org/wiki/Nicotinic_acid)
4. Tamada, J. A., Kertes, A. S. and King, C. J. (1990). Extraction of carboxylic acids with amine extractants. 1. equilibria and law of mass action modeling. *Ind. Eng. Chem. Res.*, **29**, pp. 1319-1326.
5. Yang, S., White, S. A., Hsu, S. 1991. Extraction of carboxylic acids with Tertiary and Quaternary Amines: Effect of pH. *Ind. Eng. Chem. Res.*, **30**, pp. 1335-1342.
6. Bizek, V., Horacek, J. and Kousova, M. (1993). *Chem. Eng. Sci.*, **48**, pp. 1447-1457
7. Wasewar, K. L., Yawalkar, A., et al, 2004, Fermentation of glucose to lactic acid coupled with reactive extraction: A review, *Ind. Eng. Chem. Res.*, **43**, pp. 5969-5982.