REACTIVE EXTRACTION OF NICOTINIC ACID WITH TRI-ISO-OCTYLAMINE (TIOA) IN 1-DECANOL

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ABSTRACT

Nicotinic acid also known as pyridine-3-carboxylic acid mainly used in food, pharmaceutical, biochemical industries. The production of nicotinic acid by enzymatic conversion of 3-cynopyridine is an efficient process and reactive extraction is a most useful separation technique among other separation processes. The reactive extraction of nicotinic acid with tri-iso-octylamine (TIOA) in 1-decanol has been studied in the present work. It includes the effect of initial concentration of nicotinic acid (0.025-0.15 kmol/m^3) and TIOA (0.02-0.25 kmol/m^3) on the degree of extraction of nicotinic acid. The highest value of distribution coefficient (K_D) is found to be 13.66 with initial acid concentration of 0.125kmol/m^3.

Keywords: Nicotinic Acid, Reactive Extraction, TIOA, 1-Decanol, Distribution Coefficient.

I. INTRODUCTION

Nicotinic acid also known as niacin, pyridine 3- carboxylic acid, vitamin B3, vitamin PP and is one of the vitamin of B-complex. The derivatives of nicotinic acid are NAD (nicotinamide-adenine-dinucleotide) and NADP (nicotinamide- adenine- dinucleotide- phosphate). These are the coenzymes and play important role in the redox reaction in the cells. Deficiency of vitamin B3 or nicotinic acid causes a dangerous disease pellagra which has paralyzed mankind [1,2,3]. As human body does not have ability to produce vitamin B3, for avoiding deficiency it will be taken by food or nutritional supplements [2,3]. Nicotinic acid is widely used in food, pharmaceutical, biochemical industries and is an important raw material for fine chemicals. Nicotinic acid is produced mainly in Western Europe, Japan, India, Romania, China and some other countries. The world-wide production of nicotinic acid is about 22,000tonnes/year [4]. Industrial production of nicotinic acid is carried out by using 5-ethyl 2-methyl pyridine and 3-methylpyridine (3-picoline) as a starting material. The chemical synthesis route for nicotinic acid production includes, oxidation of 5-ethyl 2-methyl pyridine with nitric acid at 230- 270^{0}C and pressure of 6-8MPa. It is also produced by gas phase ammoxidation of 3-picoline to 3-cynopyridine which on hydrolysis either form nicotinamide or nicotinic acid. Vanadium oxide catalyst is used for production of nicotinic acid in both the gas phase oxidation and ammoxidation processes. One main drawback of the chemical hydrolysis process for nicotinic acid production is that the formation of nicotinate salt due to over hydrolysis of 3-cynopyridine [5]. Excluding the technical aspect other parameters such as desired quality, a physical and chemical property of the final product and the ecological problems make the chemical synthesis methods difficult. Due to these reasons, the chemical synthesis route for the acid production not effective [3,4]. Biologically nicotinic acid can be synthesized by using an improved nitrilase mediated

bioprocess from 3-cynopyridine with hyperinduced Nocardia globerula NHB-2. [6] It can also be synthesized using the intracellular nitrilase of Nocardia globurula NHB-2 promoted by propionitrile which catalyses the hydrolysis of 3-cynopyridine to nicotinic acid without considerable formation of nicotinamide [7]. Other biological processes includes batch and continuous stirred membrane bioreactor using Microbacterium imperial CBS 498-74 resting cells as a catalyst for biological conversion of nicotinamide into nicotinic acid [8]. The thermostable nitrilase produced by the thermophilic bacterium Bacillus pallidus Dac521 catalyzes the direct hydrolysis of 3-cynopyridine to nicotinic acid without detectable formation of nicotinamide [9]. Carboxylic acids synthesis by fermentation processes produces multicomponent, aqueous solution with maximum product acid concentration 10% w/w [10]. There is need to develop new and effective separation techniques for recovery of carboxylic acids from fermentation broth to make fermentation process effective and economic [11]. Separation processes for recovery of carboxylic acid from fermentation broth such as crystallization, distillation, ion exchange, reverse osmosis electrodialysis, liquid-liquid extraction, and precipitation are mostly employed [11,12]. These separation techniques–require high energy and material consumptions and depend on the concentration of the acid in the feed [4]. The conventional method for recovery of acid from fermentation broth includes the precipitation of calcium salt with calcium hydroxide [13]. Reactive extraction have observed to be an effective separation method for extraction of carboxylic acid from a dilute fermentation processes [3,14]. Reactive extraction process was selected due to its high efficiency of separation at high concentration of substrate in the extractive fermentation, at higher concentration maximum acid can be extracted and reduction of downstream processing load and the cost for back extraction [15]. In addition to this, after back extraction the solvent can be reused and the pH of bio-reactor can be controlled [4,11,13]. Three important factors that influences the equilibrium extraction characteristics are the nature of the acid extracted, the concentration of the extractant and the type of the diluent [11,15,16]. Carboxylic acids have low aqueous activity into conventional solvents. Thus, solvent extraction with conventional solvents would require very high flow rates and results in substantial dilution of the acid [10]. Organophosphoric solvating agents such as tributyl phosphate (TBP) [2,17,18], tributyl phosphine oxide (TBPO), Trioctyl phosphine oxide (TOPO) [17,18], Cyanex@923 (mixture of four trialkyl phosphine oxide), di-(2-ethylhexyl)-phosphoric acid (D2EHPA) [1] have been employed as an extractants for many carboxylic acid with different diluents. Long chain aliphatic amines are effective extractants for separation of carboxylic acids from dilute aqueous solution. High molecular weight aliphatic amines such as quaternary alkylammonium salt (Aliquat 336) [19], lauryl-trialkylmethylamine (Amberlite LA-2) [1], tri-n-(octyl-decyl)-amine (Alamine 336) [20], tri-n-octylamine (TOA) [2,21,22], tri-iso-octylamine (HOSTRAREX A 24) [12], tri-n-dodeocylamine have been successfully used as extractants in reactive extraction. The amine extractants are dissolved in diluents because it dilutes the extractants to the desired concentration and controls the viscosity and the density of the organic phase [15]. Diluents are either inert or active diluents. Inert diluent does not take part in solvation of solute to extractant molecule in the organic phase as it is nonpolar. It modifies the physical properties of the extractant in the organic phase. The active diluent increases the salvation efficiency of the solute to extractant molecules [23,24,25]. In the present research work, the reactive extraction of nicotinic acid has been studied with extractant from the group of aliphatic amines such as tri-iso-octylamine (TIOA) using active diluent 1-decanol.

II. EXPERIMENTAL

2.1 Materials

Nicotinic acid (Assay 99%, Spectrochem), tri-iso-octylamine (TIOA) (Sigma Aidrich), 1-decanol (Himedia Lab Pvt. Ltd, India). For preparing aqueous solution of different concentrations of nicotinic acid deionised water was used.

2.2. Method

The aqueous solution of various concentrations of nicotinic acid were prepared in the range 0.025-0.15 kmol/m^3, as concentration of nicotinic acid in fermentation broth is found to be 0.041-0.132 kmol/m^3. The concentration of extractant tri-iso-octylamine (TIOA) has been varied in the range 0.02-0.25 kmol/m^3. 1-decanol has been used as the diluent for preparing different concentrations of TIOA in organic phase. The equal volume (15 cm^3) of each phase was equilibrated in 100 ml Erlenmeyer flask using magnetic stirrer (REMI, 2MLH) for 2 hours. All the experiments have been performed at the temperature of 25^{0}C. Centrifuge has been used for effective separation of two phases for 15 min. Concentration of acid in aqueous phase has been analysed by potentiometric titration with 0.01 N NaOH (Merck Specialities Pvt. Ltd) solution using phenolphthalein as an indicator. UV- spectrophotometer (Chemito, Spectroscan UV- 2600, Double beam UV- spectrophotometer) and HPLC (Agilent 1260) have also been employed to determine aqueous phase acid concentration. HPLC system was composed of quaternary pump with diode array detector (DAD) and mobile phase as H_2SO_4 solution of molarity 0.00625M.

III. RESULTS AND DISCUSSION

The results obtained from the reactive extraction of nicotinic acid (0.025 to 0.15kmol/m^3) with TIOA (0.02-0.25 kmol/m^3) dissolved in 1-decanol a polar diluent have been discussed. The parameters like distribution coefficient (K_D), degree of extraction (E) and loading ratio (Z) are calculated to analyze the reactive extraction process. Mathematically they are express by following equations

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

$$E = \frac{C_{org}}{C_{in}} \times 100 \quad (2)$$

$$Z = \frac{C_{org}}{S_0} \quad (3)$$

The effect of concentration of acid and the concentration of TIOA on the distribution coefficient and the degree of extraction have been studied in the present study.

3.1 Effect of Initial Acid Concentration

It has been observed that the degree of extraction has not changed appreciably with the increase in initial concentration of nicotinic acid. Fig.1 indicates that the highest value of degree of extraction is found to be 93.18% at acid concentration of 0.125kmol/m^3. The equilibrium results for various acid concentrations are represented in Table 1.

Table 1. Equilibrium Results for Reactive Extraction of Nicotinic Acid with TIOA in 1-Decanol for Various Acid Concentrations

C_{in}	S_0	C_{aq}	C_{org}			
kmol/m^3	kmol/m^3	kmol/m^3	kmol/m^3	K_D	$E\%$	Z
0.025	0.15	0.00173	0.02326	13.3893	93.05	0.155
0.05		0.00344	0.04655	13.5137	93.11	0.3103
0.075		0.00517	0.06983	13.5067	93.10	0.4655
0.1		0.00691	0.09308	13.4661	93.08	0.6205
0.125		0.00852	0.11640	13.6661	93.18	0.776
0.15		0.01192	0.13807	11.5775	92.05	0.9204

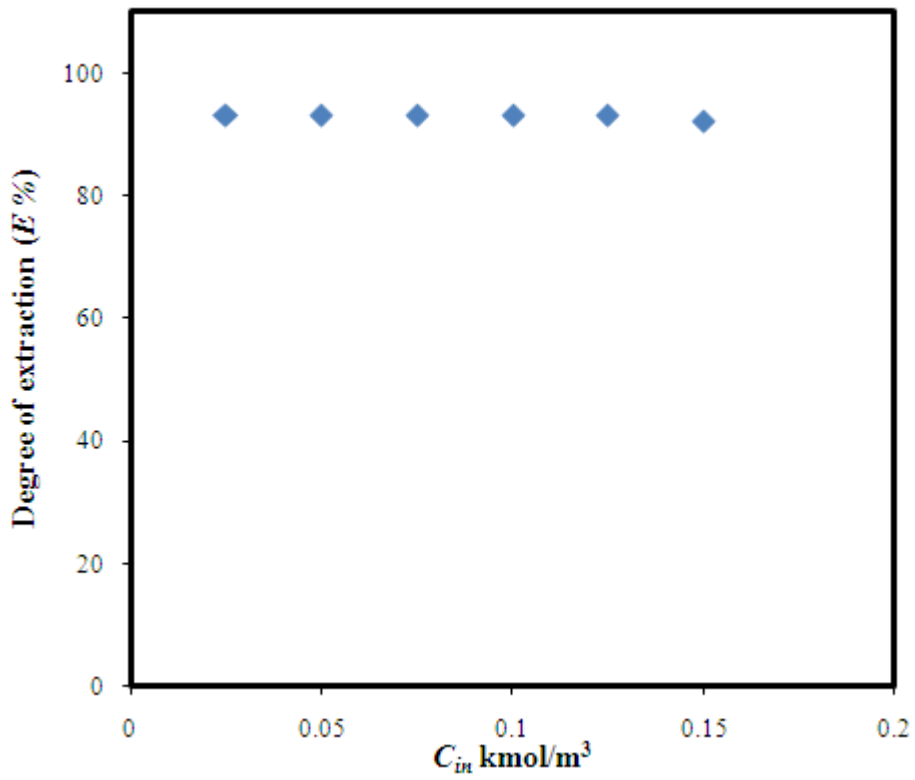

Figure 1. Effect of initial concentration of nicotinic acid on degree of extraction using TIOA in 1-decanol

3.2 Effect of Extractant Concentration

The effect of increase in the initial concentration of extractant has been studied using 1-decanol as a diluent. Fig.2 shows that with increase in concentration of TIOA, the extraction efficiency increases. This is due to the fact that 1-decanol contains –OH group (proton donating) which increases the extraction power of low polar amine (TIOA). With increasing concentration of TIOA in 1-decanol the Lewis basicity of the amine and the number of direct C-N linkages increases, which results increase in degree of extraction. The equilibrium results are shown in Table 2.

Table 2. Equilibrium results for reactive extraction of nicotinic acid with TIOA in 1-decanol for various TIOA concentrations

C_{in}	S_0	C_{aq}	C_{org}			
kmol/m^3	kmol/m^3	kmol/m^3	kmol/m^3	K_D	$E\%$	Z
0.1	0	0.0616	0.0384	0.6233	38.4	-
	0.02	0.0459	0.0541	1.1786	54.1	2.705
	0.05	0.0271	0.0729	2.6900	72.9	1.458
	0.10	0.0115	0.0885	7.6956	88.5	0.885
	0.15	0.00691	0.09309	13.4717	93.09	0.6206
	0.20	0.00524	0.09476	18.0839	94.76	0.4738
	0.25	0.0042	0.0958	22.8095	95.8	0.3832

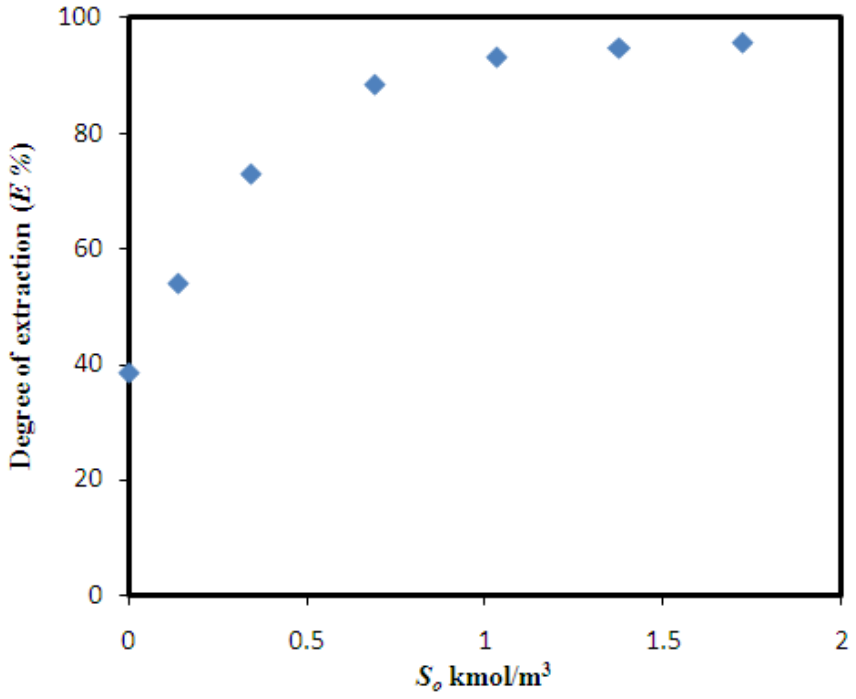

Figure 2. Effect of initial concentration of TIOA in 1-decanol on degree of extraction

3.3 Effect of Loading Ratio (Z)

The value of loading ratio (Z) obtained is less than 1 therefore there is formation of 1:1 (one number of acid molecule per amine molecule) complex in the organic phase for all acid concentrations [26]. This nature might be occurred due to the formation of H- bond between the solute and the extractant molecule.[27] In the present study 1-decanol used as an active (polar) diluent and it can solvate the acid-amine complex easily by making H-bond.

IV. CONCLUSION

The study on reactive extraction of nicotinic acid with TIOA in 1-decanol shows that the extraction of nicotinic acid from aqueous phase occur due to the reaction at the interface of two phases. The formation of 1:1 complex in the organic phase is observed. The degree of extraction increases with TIOA concentration in 1-decanol. The distribution coefficient increases with acid concentration in the aqueous phase and the highest value of K_D is found to be 13.66 with initial acid concentration of 0.125kmol/m^3.

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VI. NOMENCLATURE

C_{in}- initial concentration of nicotinic acid in aqueous phase, (kmol/m^3)
S_0- initial concentration of extractant (TIOA), (kmol/m^3)
C_{aq}- concentration of nicotinic acid in aqueous phase, (kmol/m^3)
C_{org}- concentration of nicotinic acid in organic phase, (kmol/m^3)
K_D- distribution coefficient
E- degree of extraction
Z- loading ratio

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