# RECOVERY OF ITACONIC ACID AND NICOTINIC ACID BY REACTIVE EXTRACTION

**A DISSERTATION**

*Submitted in partial fulfillment of the requirements for the award of the degree of*

MASTER OF TECHNOLOGY

*in*

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

*By*

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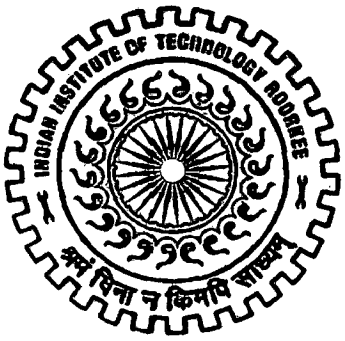


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# ABSTRACT


## RECOVERY OF ITACONIC ACIDAND NICOTINIC ACID BY REACTIVE EXTRACTION

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**June 2008,**

Carboxylic acids recovery from dilute aqueous solutions is a growing requirement due to the increasing demand for use of pure acids. Reactive extraction is proposed as an alternative to conventional methods of recovery, since the selectivity of separation is remarkably enhanced in reactive extraction.

The aim of this study is to perform the equilibrium studies for the recovery of itaconic acid and nicotinic acid from their synthetic aqueous solutions by reactive extraction and investigate the effects of various parameters such as initial acid concentration in the aqueous phase (0.05 – 0.4 M for itaconic acid and 0.05 – 0.14 M for nicotinic acid), temperature (20°C – 60°C), organic phase extractant concentration (10% - 30%), type of the extractant (Methyl tri-Capryl Ammonium Chloride, tri-Butyl Phosphate) and types of diluent.

The results of the experiments showed that the degrees of extraction increased with decreasing use of diluent with the extractant. The degree of extraction decreased with increasing initial acid concentration of the aqueous phase. the performance of the diluents were investigated by performing reactive extraction with pure diluents and solution of Aliquat 336 (Methyl tri-Capryl Ammonium Chloride) and tri-Butyl Phosphate in aromatics, esters and inerts at different concentrations of extractant. It was observed that esters had higher salvation power and resulted

higher degree of extraction. Higher equilibrium coefficient was obtained for aliquat 336 in ethyl acetate for both the carboxylic acids.

Among the different extractants highest degree of extraction was with 30% Aliquat 336 in ethyl acetate for both the acids for the extraction of 0.05 M acid solution.

The present work is a first step in the design of industrial reactive extraction process that is going to attempt forward and backward extraction of itaconic acid and nicotinic acid simultaneously to achieve continuous product recovery. The equilibrium data can be combined with further studies as the next step of designing a separation module.

*Keywords:* Reactive extraction, Itaconic acid, Nicotinic acid, Equilibrium studies, Aliquat 336, TBP, Temperature studies, Kinetics.

## CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in the dissertation entitled, "RECOVERY OF ITACONIC ACID AND NICOTINIC ACID BY REACTIVE EXTRACTION" submitted towards partial fulfillment of the requirements for the award of degree of **Master of Technology** in Chemical Engineering with specialization in "**INDUSTRIAL POLLUTION ABATEMENT**" submitted in the Department of **CHEMICAL ENGINEERING**, Indian Institute of Technology, Roorkee, India, is an authentic record of my own work carried out under the supervision of **Dr. KAILAS L. WASEWAR**.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree.

Date: 30|6|2008

Place: Roorkee

B. V. Suresh Kumar

(BOTTA VENKATA SURESH KUMAR)

## CERTIFICATE

This is to certify that above statement made by candidate is correct to best of my knowledge and belief.

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B. V. Suresh Kumar

(BOTTA VENKATA SURESH KUMAR)

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# LIST OF SYMBOLS AND ABBREVATION

| | |
|---|---|
| $[B]_{i,\ org}$ | Initial concentration of extractant in the diluent |
| $[B]_{org}$ | Concentration of unreacted extractant in the organic phase |
| $[BHA]_{org}$ | Equilibrium concentration of the complex in the organic phase |
| $C_{aq}$ | Equilibrium concentration of acid in the aqueous phase in all forms |
| $C_{org}$ | Equilibrium concentration of acid in the organic phase in all forms |
| D | Degree of extraction |
| $[HA]_{i,\ aq}$ | Initial concentration of carboxylic acid in the aqueous phase |
| $[HA]_{aq}$ | Equilibrium concentration of acid in the aqueous phase |
| $K_{11}$ | Equilibrium complexation constant of (1, 1) acid – extractant complex |
| $K_{12}$ | Equilibrium complexation constant of (1, 2) acid – extractant complex |
| $K_D$ | Distribution constant of acid |
| $(-)r_A$ | Rate of reaction with respect to equilibrium acid concentration in the aqueous phase |
| Z | Loading factor |

# CHAPTER 1

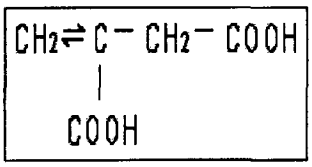
# INTRODUCTION

## 1.1 ITACONIC ACID

Itaconic Acid (also called Methylene Succinic Acid) is a white crystalline carboxylic acid obtained by the fermentation of carbohydrates. It is soluble in water, ethanol and acetone. It is an unsaturated diprotic acid. The total market for IA has been quoted as being between 10,000 and 15,000 metric tonnes per year worldwide with a price that is 10-times that of citric acid, a more widely used fermentation product. It is an organic acid, one of three acids obtained by distillation of citric acid. Itaconic acid is an unsaturated diprotic acid. It has a unsaturated double bond.

Itaconic acid is insoluble in water, ethanol and other solvents. Itaconic acid is crystalline white carboxylic acid, occurs in some fermentation sugars.

The structural formula of itaconic acid is




The physical and chemical properties are given in table T1

| | |
|---|---|
| Appearance | White or cream colored acicular crystal |
| Molecular formula | $CH_2$=C(COOH)$CH_2$COOH |
| Molecular weight | 130.1 |
| Specific gravity | 1.5-1.6 |
| Melting point | 153-156°C |
| Loss on drying | 0.5% max. |
| $pK_a$ | 3.85 |

Table T 1: Properties of Itaconic acid

Generally the itaconic acid is under ordinary conditions, hygroscopic in nature Avoid heat, flames, sparks and other sources of ignition. The itaconic acid on contact with the skin has certain acute effects like irritation, on inhalation causes irritation to mucus membrane and upper respiratory tract. It emits toxic fumes when burnt.

Itaconic acid is the third polymer of acrylic acid. Itaconic acid forms a number of esters. There are almost infinite esters obtained from thousands of potential starting materials. Esters are formed by removal of water from an acid and an alcohol, e.g., carboxylic acid esters, phosphoric acid esters, and sulfuric acid esters.

Carboxylic acid esters are used as in a variety of direct and indirect applications. Lower chain esters are used as flavoring base materials, plasticizers, solvent carriers and coupling agents. Higher chain compounds are used as components in metalworking fluids, surfactants, lubricants, detergents, oiling agents, emulsifiers, wetting agents textile treatments and emollients. They are also used as intermediates for the manufacture of a variety of target compounds. The almost infinite esters provide a wide range of viscosity, specific gravity, vapor pressure, boiling point, and other physical and chemical properties for the proper application selections. To obtain suitable monomers for emulsion polymerization itaconates are synthesized by means of esterification using itaconic acid or itaconic anhydride and the appropriate fatty alcohol as starting materials (Vymetalikova, B., 2007)

Itaconic acid and its polymers can be made into effective deodorant by adding a little natural substance, they can react with alkaline or acidic odor such as ammonium, amine, and hydrogen sulfide. They can also be utilized in paper and plastic thin film with deodorant function.

Itaconic acid can copolymerize with styrene and butadiene to prepare latex which is widely used in paper coatings, metal and concrete paint. It is used in paints to improve quality and used as fiber carpet sizing agent to make carpet more endurable.

Itaconic acid can react with acrylic and methacrylic acid or their esters to prepare resins which can be widely used in emulsion coating, leather coating, coatings for car, refrigerator and other electrical appliances to improve adhesion, color and weather resistance. They are also used in eletroporetical coating with excellent adhesion, in dental binder with the help of metal oxides. With chloroalkyl dimethyl- benzyl- ammonium chloride added, they can be used to prepare water soluble coating for food packaging to reduce bacteria contamination.

Esters of itaconic acid can be used in paint, ion-exchange resin, lubricant, binder, plasticizer, and sealant and molding plastics.

Itaconic acid derivatives are used in medicine, cosmetics, lubricant, thickener, herbicide and wool modifier.

Bond for teeth: bond for teeth made by itaconic acid, acrylic acid and high bond metallic oxide has good anti-pressure and physiology applicability.

Specialized lens: polymer which contains itaconic acid has special luster and transparency, it is fit for making synthetic cut stone and special lens.

Eradicator: polymer produced by itaconic acid and acrylic acid is a kind of macromolecule chelate agent, it has special effect to resist filth form of basification calcium and basification magnesium in water treatment, so it can be used in boiler or cooling equipment purification.

Conventional hair gels usually contain a combination of gel formers and hair-fixing polymers. The cosmetic hair-fixing polymers usually used for this purpose are characterized by good fixing properties, which more or less satisfactorily hold and fix the hair in a predetermined shape, in aqueous, alcoholic or aqueous-alcoholic media. Water treatment system to prevent contamination by metallic alkali

## 1.2 NICOTINIC ACID

Nicotinic acid is known as niacin (3-pyridine carboxylic acid). Vitamin $B_3$ is made up of niacin (nicotinic acid) and its amide, niacin amide, and can be found in many foods, including yeast, meat, fish, milk, eggs, green vegetables, and cereal grains. The demand for nicotinic acid is growing, especially for its use in the production of various polymers. Co-enzyme I (Nicotinamide-adenine dinucleotide NAD) and Co-enzyme II (Nicotinamide-adenine dinucleotide phosphate NADP) are required by all living cells. Niacin is required for the synthesis of the active forms of vitamin$B_3$, nicotinamide adenine dinucleotide ($NAD^+$) and nicotinamide adenine dinucleotide phosphate ($NADP^+$).Both $NAD^+$ and $NADP^+$ function as cofactors for numerous dehydrogenase. Niacin is not a true vitamin in the strictest definition since it can be derived from the amino acid tryptophan. However, the ability to utilize tryptophan for niacin synthesis is inefficient (60 mg of tryptophan are required to synthesize 1 mg of niacin). Also, synthesis of niacin from tryptophan requires vitamins $B_1$, $B_2$ and $B_6$ which would be limiting in them on a marginal diet. The recommended daily requirement for niacin is 13 - 19 niacin equivalents (NE) per day for a normal adult. One NE is equivalent to 1 mg of free niacin).

. Both nicotinamide and nicotinic acid are building blocks for these co-enzymes. They enable both the conversion of carbohydrates into energy as well as the metabolism of proteins and fats.

Nicotinic acid was first discovered (Weidel, 1873) in his studies of nicotine. Niacin is a pellagra preventing factor, a typical skin disease. Niacin is a precursor to NADP, NAD, $NAD^+$, and NADP, which play essential DNA repair and the production of steroid hormones in the adrenal gland (COX teal, 2000). Since the human body produces neither nicotinic acid nor the amide, it is dependent on intake via foodstuffs. After the recognition of the importance of niacin, the number of deaths due to the vitamin deficiency disease pellagra dropped from 7500 to 70 in the years from 1929 to 1956 E. (Codices, *Nut. Diet.*) The total market quoted being 15,000 to 22,000 metric tone of niacin and 8000 metric tones of niacin amide per year worldwide (Lonza, 1995).

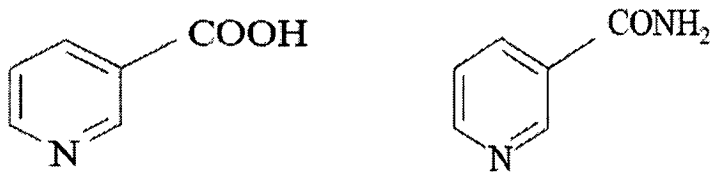
A review has been recently compiled on the preparations and applications of nicotinic acid and nicotinamide, including most recent developments in the treatment of schizophrenia, diabetes, auto-immune diseases and cholesterol-related diseases and in cosmetic skin care (Guiot, P., 1996).

The physical and chemical properties of nicotinic acid are given in table T2.

| | |
|---|---|
| Molecular formula | $C_6H_5NO_2$ |
| Molecular weight | 123.11 |
| Melting point | 236.6 °C |
| Boiling point | Decomposes |
| Colour | White |
| Appearance | Amorphous |
| $pK_a$ | 4.85 |

Table T2: Properties of Nicotinic acid

The structure of niacin and nicotinamide




Nicotinic Acid (Niacin) Nicotinamide (Niacinamide)

Co-enzyme I (nicotinamide-adenine dinucleotide NAD) and co-enzyme II (nicotinamide-adenine dinucleotide phosphate NADP) are required by all living cells. They enable both the conversion of carbohydrates into energy as well as the metabolism of proteins and fats. Both nicotinamide and nicotinic acid are building blocks for these co-enzymes. The common name for vitamin $B_3$ is niacin, and strictly speaking, refers only to nicotinic acid.

Since the human body produces neither nicotinic acid nor the amide, it is dependent on intake via foodstuffs. After the recognition of the importance of niacin, the number of deaths due to the vitamin deficiency disease pellagra dropped in the US from over 7500 to 70 in the years from 1929 to 1956 (Kirk –Othmer, 1998).

Nicotinic acid finds its application in food, pharmaceuticals and biochemical industries. It appears in small doses in some fruits, flowers and vegetables as raw food.

The concentration of niacin in roots and tubers (527µgm/ 100gm), legumes like peas, beans (1480µgm/ 100gm).

The nicotinic acid is consumed to prevent some of the diseases. Niacin (vitamin B3) and niacinamide are U.S. Food and Drug Administration (FDA)-approved for the treatment of niacin deficiency. Pellagra is a nutritional disease that develops due to insufficient dietary amounts of vitamin B3 or the chemical it is made from, tryptophan. Symptoms of pellagra include skin disease, diarrhea, dementia, and depression. In the prevention of heart attack, Niacin may benefit the choroidal blood vessels, which underlie the region of the retina called the macula. Age-related macular degeneration (AMD) may result from disrupted blood flow in the choroidal vessels. (Metelitsina TI et. al, 2004). Niacin is a well-accepted treatment for high cholesterol. Multiple studies show that niacin (not niacinamide) has significant benefits on levels of high-density cholesterol (HDL or "good cholesterol"), with better results than prescription drugs such as "statins" like atorvastatin (Lipitor). There are also benefits on levels of low-density cholesterol (LDL or "bad cholesterol"), although these effects are less dramatic. Adding niacin to a second drug such as a statin may increase the effects on low-density lipoproteins Whitney EJ(et.al) 2005. Studies suggest that niacin may be used to treat AMD, Preliminary human studies suggest that niacinamide may be useful in the treatment of osteoarthritis. Niacinamide has been used in skin care products, including moisturizers, anti-aging products, and rosacea treatments.

Nicotinic acid undergoes several reactions. When reacts with ethylene oxide reacts with nicotinamide under very mild conditions to yield, after acidification with HCl, the chloride of (2-hydroxyethyl)-nicotinamide chloride, and with nicotinic acid to produce the betaine of (2-hydroxyethyl)-nicotinic acid Windmueller .H. G (1958)

Many thermal and chemical reactions occur during the roasting process: Decarboxylation, fractionization, isomerization, polymerization, and complex sugar reactions. The principal thermally reactive components are mono saccharides and sucrose, chlorogenic acids, free amino acids, and trigonelline. Both aravinose and calactose of polysaccharides are split off and the basic sulfur containing and hydroxyamino acids decompose. Nicotinic acid melts in pure crystalline form at 457 degrees F. Naturally occurring Nicotinic Acid is bound to the polysaccharide cellulose structure. Nicotinic Acid is also derived in soluble form during roasting. Higher levels of Nicotinic Acid for any given degree of roast are associated with better cup quality. Since it is I 00% soluble, it will end up in the cup. Nicotinic Acid contributes to favorable acidity and clean finish. It's derivation rate is one of the key constituent control flags for determining the best reaction ratio temperature and chemistry propagation rates. Additionally, the interaction of melted Nicotinic acid with other constituents contributes significantly to the intensity associated with darker roasts.

Due to its expanding area of applications, the demand for nicotinic acid is increasing and the recovery of nicotinic acid from fermentation broths and aqueous streams is growing year by year.

Suresh Kumar, Kailas Wasewar, Reactive extraction of itaconic acid using Aliquat-336 and tri-n-butyl phosphate, Forwarded to CABEQ

Kailas L. Wasewar, Suresh Kumar, Effect of temperature on recovery of itaconic and nicatonic acid from aqueous solutions, *International Symposium & 61st Annual Session of IIChE in association with International Partners* (CHEMCON-2008), *27-30th December, Punjab University, Chandigarh, INDIA*

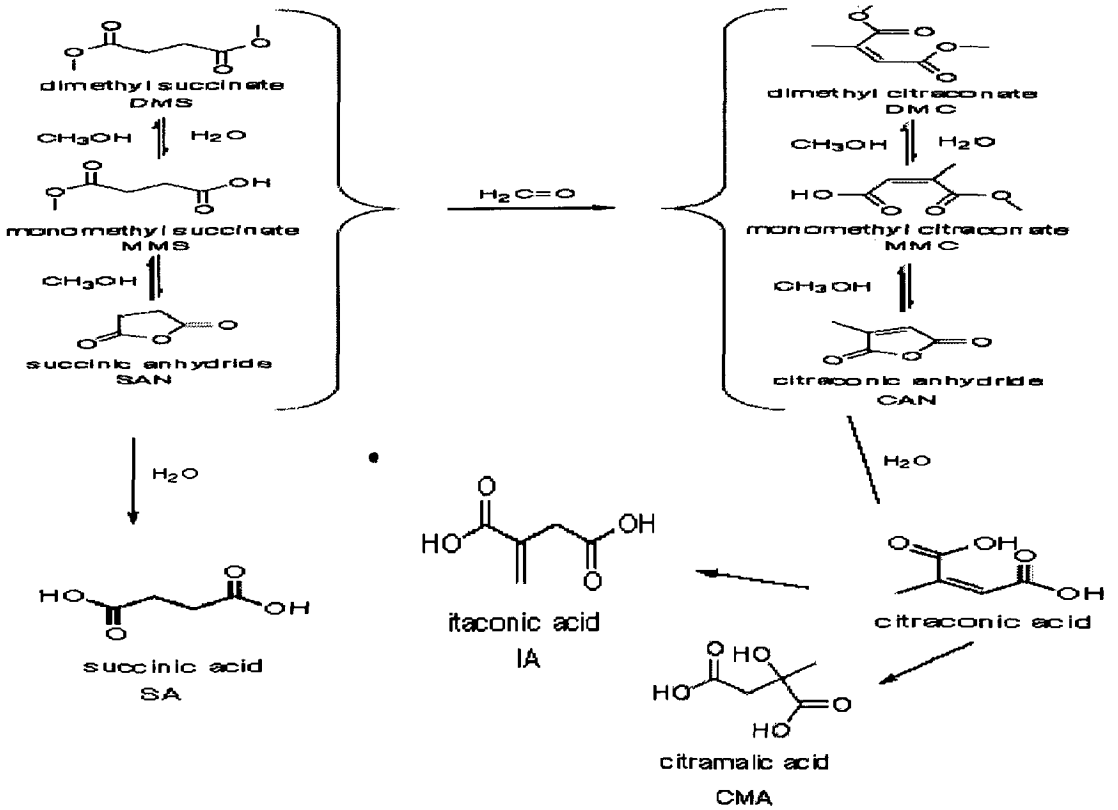
Suresh Kumar and Kailas L. Wasewar, Recovery of Itaconic Acid From Aqueous Streams, *National Conference On Clean Technology And Cleaner Production, DCRUST, Murthal, 8-9 May, 2008 India*

Suresh Kumar, Kailas Wasewar, Reactive extraction: A clean technology for recovery of itaconic acid, *Proceedings of Indo-Italian Conference on Green and Clean Environment (GCE 2008), MITCOE, Pune, 20-21 March 2008 pg.691-699* (2008)

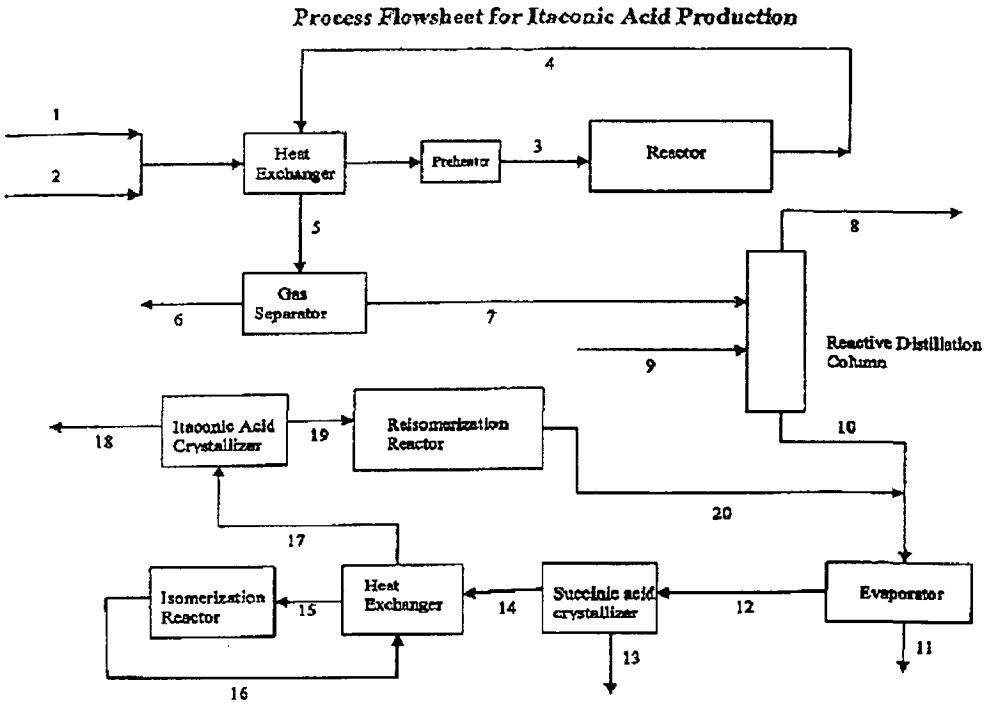
## 1.3 PRODUCTION METHODS FOR ITACONIC ACID

### *1.3.1 Catalytic condensation of Succinic acid and Formalin*

Itaconic acid (IA) is a valuable monomer because of its unique chemical properties, which derive primarily from the conjugation of one of its two carboxylic acid groups with its methylene group. Itaconic acid is thus a functionalized analog of acrylic acid, the simplest conjugated-alkenoic acid. Like acrylic acid, IA is able to take part in addition polymerization, giving polymers with many free carboxyl groups that confer advantageous properties on the resulting polymer. The itaconic acid is commercially produced by fungal fermentation of glucose using Aspergillus Terreus at a relatively high cost. The fungal fermentation is expensive because it requires dilute feed solutions (approximately 10 wt. % glucose) and 8- to 10-day batch times, yet gives a yield of only 50–60% (Fujii, C., Shimizui, T., 1974). The catalytic route to itaconic acid has several distinct advantages over fermented route. The rate of the catalytic reaction is several orders of magnitude faster than biological reaction. Secondly, The difficulties involved with the fungal fermentation (product inhibition, sensitivity of micro-organism to process changes are avoided. The separation and recovery costs via catalytic process are lower. Itaconic acid can also be formed via the catalytic condensation of succinic acid derivatives with formaldehyde (Fumagalli, C., Spa, L., 1997). The reaction involves for the production of itaconic acid from succinic acid, mono and di-methyl esters and succinic anhydride. The reaction involves the formation of intermediate compound citraconic anhydride as shown in figure 1.3.1




F1.3.1 A Overall reaction for Itaconic acid formation from succinates and formaldehydes.




F1.3.1 B The process flow sheet for itaconic acid production.

The present invention relates to a process for the preparation of itaconic acid. The chemicals formaldehyde, succinic acid and citraconic acid were prepared. Reacting excess amount of formaldehyde with dimethyl succinates with the catalyst. The catalyst is $TiO_2$ The temperature maintained at 320-440°C and pressure 20 - 400 Psi. The reaction is processed until Citraconic anhydride (CAN) is formed. Hydrolyzing the citraconic anhydride to citraconic acid and dimethyl succinate to succinic acid at elevated temperatures in water, the methanol is distilled from the reaction mixture. Oxidizing methanol again to form formalin and separating citraconic acid and succinic acid from the reaction mixture. The effluent from the condensation reactor gives a product mixture containing CAN, succinic anhydride (SAN), monomethyl esters (MMC and MMS), dimethyl esters (DMC and DMS), methanol (MeOH), and unreacted formaldehyde. This mixture is first hydrolyzed along with simultaneous methanol and formaldehyde removal to give an aqueous solution containing essentially CA and SA.

The further processing steps for formation and recovery of IA from this CA/SA solution:

(1) Separation and recovery of SA from the mixture,

(2) Isomerization of CA to IA with byproduct formation,

(3) Separation and purification of IA from the isomerized products, and

(4) Re-isomerization of byproducts from step 2 back to CA.

The purity of IA crystals formed depends on the SA concentration in solution (which can be controlled by the temperature of the SA crystallization step).

Itaconic acid can be recovered in high yields from a mixed aqueous solution of CA and SA. SA can be crystallized out of solution selectively because of its low solubility relative to CA. Citraconic acid can then be isomerized to IA with 87% selectivity at approximately 60% conversion. The IA formed can be recovered by crystallization, with product purity depending primarily on SA concentration in solution.

### *1.3.2 Production of Itaconic Acid using Pseudozyma Anartica NRRLY-7808*

The production of itaconic acid by the fermentation process has overcome the synthetic process. Since, the catalytic process requires huge chemicals, energy and discharges hazardous chemicals. The organism most often used for IA production is *Aspergilluss terreus,* grown under phosphate-limited conditions (Willke T, Vorlop K.,D.,2001) although some species of the plant pathogenic fungal genus *Ustilago*, a basiodiomycete, are also known to produce IA during fermentation. The sensitivity of *A. terreus* fermentations to metal concentrations (Peppler, H., J., 1979) and difficulties working with filamentous organisms in bioreactors has led to the testing of yeasts for possible IA production conditions. *Pseudozyma antarctica* NRRL (National Center for Agricultural Utilization Research, Peoria, Illinois) Y-7808 to produce itaconic acid from glucose and other sugars under nitrogen-limited growth conditions. Species *of Pseudozyma* are basidiomycetes and are believed to be closely related *Ustilago* Yeast strains screened were from the ARS culture collection. Initial screening for organic acid production under nitrogen-limited growth conditions was carried out in a medium with the following composition (g/L):

Glucose or glycerol, 80; (NH4)2SO4, 0.5; KH2PO4, 1.7; Na2HPO4, 12; MgSO4·7H2O, 1.4; CaCl2, 0.02; ZnSO4·7H2O, 0.02; FeSO4·7H2O, 0.05; MnSO4·H2O, 0.02; Thiamine hydrochloride, 0.006; yeast extract, 0.5. Initial pH was 6.0 and sterile bromocresol purple was added post-autoclave as a pH indicator. Temperature was maintained at 28 ◦C. Sugar concentrations were assayed by the Anthrone/sulfuric acid method. *Pseudozyma Antarctica* NRRLY-7808 was found to produce itaconic acid from glucose and other sugars under nitrogen-limited growth conditions. Glucose and fructose were the most efficiently utilized substrates, followed by sucrose and maltose.

### *1.3.3 Production of Itaconic Acid using Corn starch with Aspergillus terreus SKR10*

Itaconic acid producing strain, Aspergillus terreus SKR10, was isolated from horticulture waste. Market refuse, apple and banana, were explored as novel substrates for itaconic acid production. The yield is about 31g/l were obtained with acid and a-amylase hydrolyzed corn starch.

The efficiency of itaconic acid production by this wild type strain was improved by ultraviolet, chemical and mixed mutagenic treatments (Reddy, C., S.,K, 2002) Year after year there has been an increasing use of organic acids particularly itaconic,

gluconic, lactic, fumaric and kojic acids. Itaconic acid (C5H6O4) is an unsaturated dicarboxylic acid, crystalline, relatively non-toxic with a melting point of 167–168 °C

The property that makes itaconic acid a uniquely valuable compound is the conjunction of the two carboxyl groups and the methylene group. The methylene group is able to take part in addition polymerization giving rise to polymers with many free carboxyl groups that confer advantageous properties.

Synthesis of itaconic acid has proven to be uneconomical because of high substrate costs and/or relatively low yields. Itaconic acid is known to be produced by Aspergillus terreus and Aspergillus itaconicus (Milsom, P.,.E., 1985). A. terreus SKR10 was isolated from horticulture waste, A. terreus was grown and maintained on Czapek Dox agar medium at 34 _C for 6–8 days. Briefly, the market refuse apple and banana were individually washed and mashed into a coarse pulp and the juice was extracted in water at 90 _C, in a four to five step extraction procedure. The extracts were referred to as 'banana waste extract' and 'apple waste extract' respectively. The total sugars were estimated by routine methods and the extract was suitably diluted for use as substrate. Corn starch was hydrolyzed by acid and enzyme hydrolysis methods. Acid hydrolysis of corn starch was carried out at 140 _C using nitric acid at pH 2.0. Strain improvement was done by mutagenic treatments to improve the yields of itaconic acid. Mutagenic treatment of A. terreus SKR10 was done by exposure to ultraviolet radiations (UV), N-methyl-N0-nitro-N-nitrosoguanidine (NTG), colchicines and sodium azide.

Screening for high itaconic acid producers was done by the gradient plating method (Yahiro, K., et al, 1995). The fruit wastes and corn starch were suitably processed and the physico-chemical and biological parameters were optimized for the production of itaconic acid. The mutagenic treatment which gives a yield of 46g/l of itaconic acid with acid and amylase hydrolyzed corn starch. The present study signifies the use of corn starch and fruit wastes as potential substrates for itaconic acid fermentation.

### *1.3.4 Production of Itaconic Acid using Aspergillus terreus TN484-M1*

Itaconic acid, or methylene succinic acid, is an unsaturated acid with conjugated double bonds and two carboxyl groups. Because of its unique structure and characteristics, itaconic acid and its ester are useful materials for the bio industry. It is used for the synthesis of fiber, resin, plastic, rubber, paints, surfactant, ion-exchange resins and lubricants. Roher reported itaconic acid production on an industrial scale using sugar molasses or glucose by Aspergillus terreus (Roher, M., 1996). Itaconic acid production using raw starchy materials that replace molasses or glucose have been reported, but the utilization of sago starch in itaconic acid production is still limited.

Sago starch was hydrolyzed using either chemical agents, or enzymes. The hydrolyzing enzymes used were a-amylase, glucoamylase and crude cellulase enzyme from Acremonium sp. A. terreus TN484-M1 was used, the ingredient concentration in

the production medium was used to optimize the medium composition. The chosen hydrolysis agent or enzyme and the optimized medium composition were used in itaconic acid production using a 3-l jar fermentor. Itaconic acid production in a 3-l jar fermentor using the optimum medium containing hydrolysate from sago starch was carried out. Dissolved oxygen (DO) concentration during fermentation decreased with cell growth and reached 3% even though the agitation rate was increased. The recovered products from sago starch and glucose fermentation were analyzed for purity.

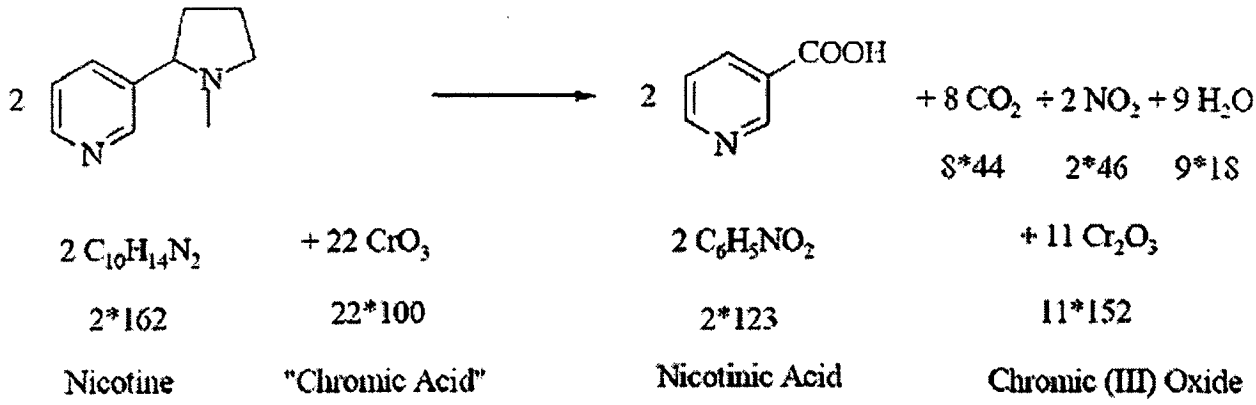
Sago starch was hydrolyzed either by a chemical (using hydrochloric or nitric acids) or enzymatic (using glucoamylase or a-amylase) process. Enzymatic hydrolysis is a cost-intensive expensive process; nitric acid is still the best hydrolyzing agent.

## 1.4 PRODUCTION METHODS FOR NICOTINIC ACID

The industrialization of the world is irrevocably leading to an increase in ecological problems such as pollution, global warming and possible irreversible effects of the earth's stratosphere. Today, belatedly, more emphasis is being made to minimize such effects at the research and development stages of new processes. Armor (1999) defines green chemistry as the design of chemical products and processes which reduces or eliminates the generation of hazardous substances. These principles include not only the obvious features such as avoidance of waste production, high carbon efficiency (low carbon dioxide waste!), and low energy consumption, but also rather more subtle features. Thus a feedstock which is environmentally benign, may involve ecologically or energetically unfavorable processes to manufacture it in the first place. He quotes $H_2O_2$ and ammonia as examples of very energy-intensive feedstock, and how research should be directed at the total energy demand of a given process. A vital part of any new chemical process development will involve the design, manufacture and utilization of catalysts, which of course they will be subject to the same screening as the chemical process itself.

### *1.4.1 Liquid-phase oxidation using permanganate, chromic acid or other metal oxides*

The classic method of preparing nicotinic acid was by oxidizing nicotine with potassium dichromate. The reaction is as follows




F1.4.1 Chromic acid oxidation of Nicotine to Nicotinic acid

Chromic acid ($CrO_3$) is carcinogenic and environmentally threatening. Chromic (III) oxide, on the other hand, is extensively used in the tanning industry, and has a higher present value on the market than its precursor. Assuming an ideal chemical reaction (100% yield!), Thus almost 9 tonnes of side product is produced for 1 ton of desired product.

The above reaction gives the following figures of nicotinic acid produced in table T3

| Chemicals produced | Tonnes |
|---|---|
| Nicotinic acid | 1.32 |
| Chromic acid | 9.02 |
| $CO_2$ produced | 1.43 |
| NOx (Calculated as $No_2$) | 0.37 |
| Chromic oxide | 6.80 |

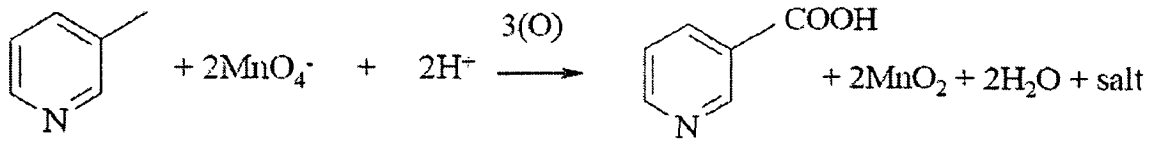
Table T3: Production of nicotinic acid in tonnes

*1.4.2 Liquid-phase oxidation of 3-picoline with permanganate, chromic acid, or nitric acid*

From the chemical standpoint, 3-Picoline is the ideal starting-material for Nicotinic acid or amide: the Methyl group can be selectively and readily oxidized to the carboxyl derivative with few side-products or pollutants. High selectivity coupled with the low molecular weight compared to the end-product make picoline an attractive industrial starting-material for the production of nicotinic derivatives.

3-Picoline is obtained, typically in 1:2 ratio along with the main product pyridine, by the gas-phase reaction of acetaldehyde, formaldehyde and ammonia. The lack of

selectivity of this reaction to either pyridine or picoline has meant that the economy of the major product (pyridine) has determined the price and availability of picoline. The oxidation of picoline with permanganate or chromic acid suffers from the same drawbacks, albeit in a lesser form, as nicotine. The following reaction of 3-Pcoline with permanganate and in presence of sulphuric acid to obtain niacin




3-Picoline (as $KMnO_4$) (as $H_2SO_4$) Nicotinic Acid

F1.4.2 The permanganate Oxidation of 3-Picoline

For 1 tonne of nicotinic acid, 2.8 tonnes of inorganic material are produced as waste. With chromium trioxide (neglecting any inorganic acid involved to produce the required chromic acid), 1.24 tonnes of $Cr_2O_3$ are produced/tonne of nicotinic acid. This assumes stoichiometric quantities of permanganate and quantitative yields, both of which in practice are unrealistic. A stoichiometric excess of 50 to 100% oxidant is usual, and molar yields of 80-90% are generally not exceeded. Thus the inorganic waste for the permanganate process would probably lie around 4 tonnes/tonne of niacin produced, and for chromium between 1.7 and 2.0 tonnes/tonne. Clearly from an ecological standpoint, this situation is untenable. Even though chromium (III) sulphate can be utilized in the leather industry as a tanning agent (4), there are several factors which argue against this type of process, even if the process appears on the surface to be economically attractive:

(a). The combining of two economies in one process requires that both end products (here chromic oxide and nicotinic acid) can be sold. Thus the success of the process is dependent on the demand for both products being sustained.

(b). The energy required for the production of chromic acid (or permanganate) is considerable. (Chromate ore is roasted with sodium carbonate at temperatures around 1000°C to produce the common starting-material for most chromium compounds, namely sodium chromate)

(c). Niacin is used as a feed and food additive. The presence of even small quantities of chromium, however beneficial this may be in practice (chromium is an essential trace metal in the human metabolism), is not likely to be accepted by either today's stringent legislation, nor by buyers who are geared to high-quality supplies. Removal of last

traces of impurity is possible by recrystallisation, but this increases the number of unit operations, is therefore expensive and energy consuming, and the problem remains as to what to do with the chromium-containing mother liquors.

The liquid-phase oxidation of picoline with nitric acid at atmospheric pressures (usually with sulphuric acid to ensure sufficiently high temperatures) has been the basis of some back-yard processes, but again has many disadvantages:

(a). Safety: Batch processes with large quantities of nitric acid and organic material are intrinsically hazardous and corrosive, and stringent precautions are necessary to avoid runaway reactions and explosions.

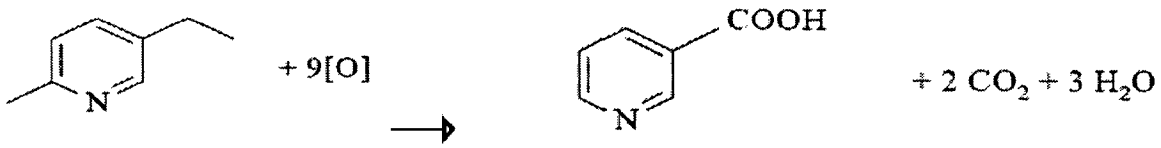
(b). Quality; Nitric acid is not only an oxidant, but is also a nitrating agent. Depending on reaction conditions, considerable quantities of nitrated pyridines can be produced, which can only be separated with expensive crystallisation techniques.

(c). Ecology: The inevitable generation of large quantities of toxic NOx fumes requires a well-planned containment and recuperation system. This is expensive, and unless great care and considerable expense is undertaken, NOx waste-gas will be released to the atmosphere, causing potential pollution problems.

*1.4.3 Liquid-phase Oxidation of MEP with Nitric acid*

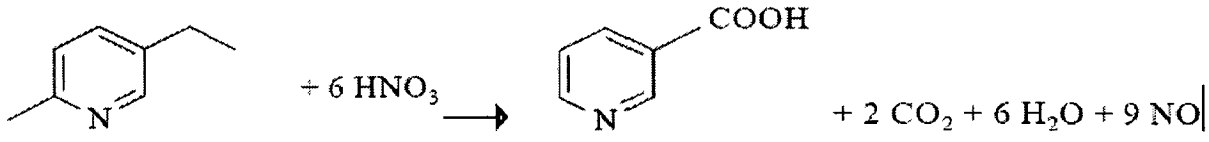
To avoid the above problem of picoline sourcing, non-pyridine producers have used methyl-ethyl-pyridine as an alternative for niacin. The liquid-phase oxidation with nitric acid is surprisingly selective, and has been used since 1965 by Lonza to produce up to 15000 tonnes/year of niacin. The reaction can be approximately represented as follows:

1. Oxidation of MEP to Niacin /Nicotinic acid

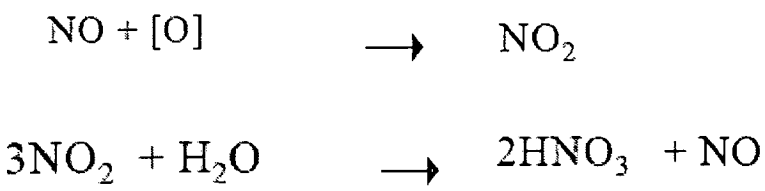



2-methyl-5-ethylpyridine Nicotinic acid

2. Oxidation with MEP with Nitric Acid



3. Regeneration of Nitric Acid



F 1.4.3 Oxidation of MEP with Nitric acid

Methyl ethyl pyridine (MEP) is itself produced by the liquid-phase condensation of paraldehyde and ammonia. Again this complex reaction proceeds surprisingly selectively (>70%) and is the main reason why this material offers itself as an alternative to the simpler molecule picoline. Continuous development and improvement of this process over the years have led to a high-quality product, and to Lonza's ability to maintain their position as the world leader in niacin manufacture. But however many improvements and developments have been made to this process, it intrinsically holds some disadvantages, when considered from the "green" stand-point:

(a). Safety: using nitric acid at high temperatures and pressures requires a well-conceived and continually executed safety concept, using advanced reaction technology.

(b). Ecology (carbon dioxide and nitric oxides): although nitric oxide fumes can be largely regenerated to nitric acid, some nitric oxide (NO) is invariably present in the off-gases, which then have to be catalytically treated to remove the last traces of NOx. Carbon dioxide, however, cannot readily be recycled, and this is vented to the atmosphere. In today's process (including deep oxidation of the starting-material), as can be readily calculated from the reaction equation, over 1 tonne of $CO_2$ is produced per tonne of niacin.

(c). Down-stream processing: in order to produce a product quality acceptable to today's standards, extensive processing in the form of recrystallisation and decolorizing is necessary. As mentioned above, recrystallisation is an energy and labour intensive process.

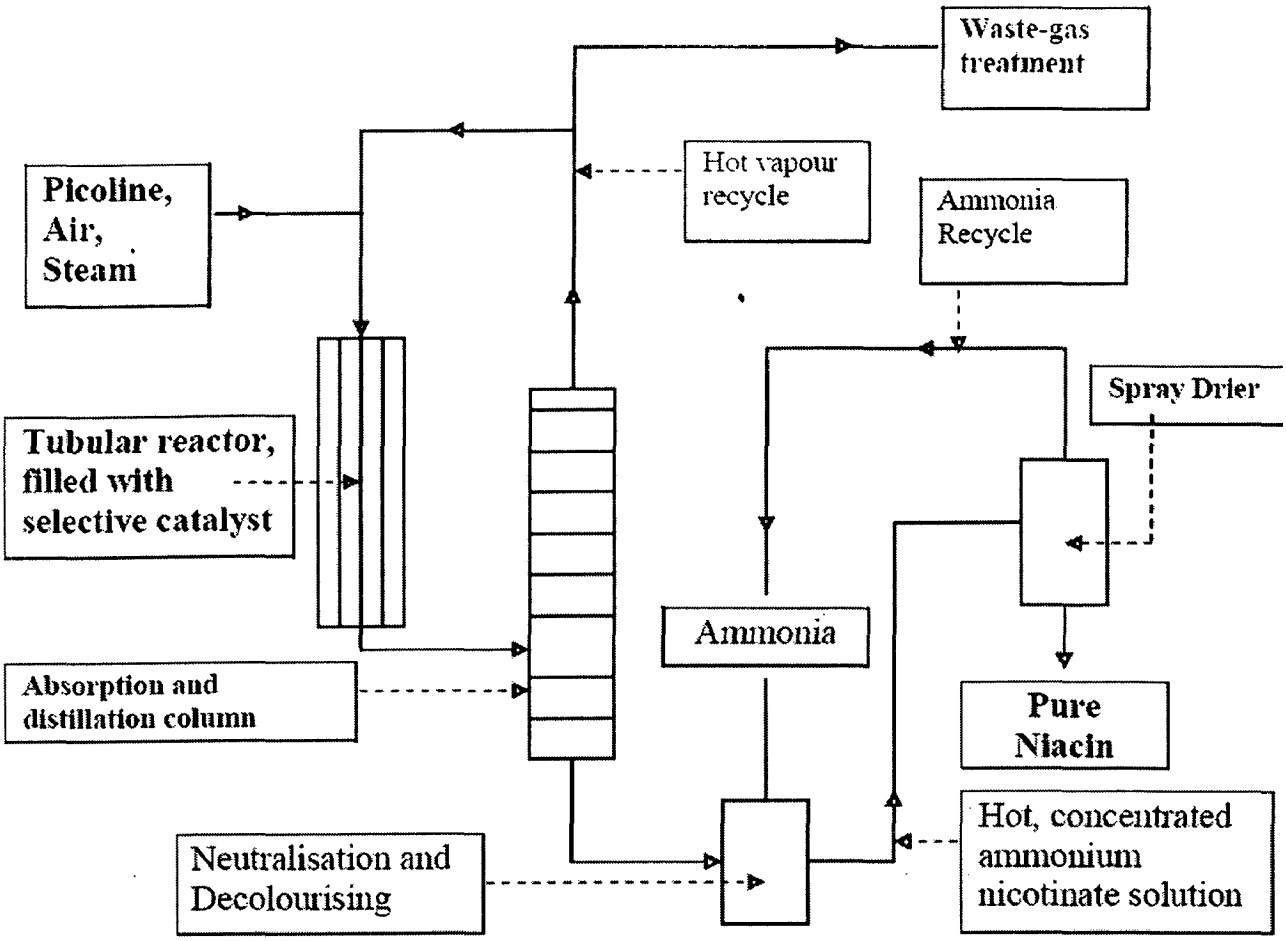
(d). Starting-material: although MEP is produced from cheap starting-materials (ammonia and paraldehyde), the process itself produces considerable quantities of side-products and/or waste material, which have to be separated and suitably treated to avoid environmental pollution.

*1.4.4 Lonza's Direct Oxidation Process*

The manufacture of niacin based on the catalytic gas-phase oxidation of picoline. The technology is based on spray drying of a highly concentrated solution of ammonium nicotinate. This method takes advantage of the fact that under Lonza's reaction conditions, ammonia is produced as a side-product in the total or deep oxidation. The classical oxidizing agents such as chromium or manganese lose one or more oxygen atoms to effect the oxidation of an organic material, a catalyst component such as molybdenum, vanadium or niobium is reduced by the organic material, and is practically simultaneously re-oxidized by oxygen in the air Andruschkevich .T (1999).

The identification of vanadium oxide as one of the most suitable. This material is normally used with a support, typically an oxide of titanium, aluminum or silicon, or a mixture of these. The accessibility for the substrate to enter and react on the catalyst surface, and for the product to be removed, are governed by factors such as physical form, pore size, pore distribution, and surface area. Lonza (1998)

Picoline vapour is selectively and almost quantitatively converted into nicotinic acid in the reactor. Nicotinic acid is transported from the reactor by the hot air and water vapour. These vapours are partially condensed in an absorption and distillation column. Niacin and water condense to form a solution, whereas unconverted picoline, pyridine carboxaldehyde, water vapour and gases leave the top of the column still in the vapour phase. Most of these vapours can be recycled. A small purge is necessary to remove the waste products formed in the reaction. This waste stream can either be condensed and the liquid subsequently incinerated, or the hot vapours can be catalytically oxidized and de-nitrified by standard procedures The solubility of niacin in water, even at 100°C, is fairly low, so that large quantities of water are necessary for total dissolution. This is a disadvantage in a green process, since large amounts of energy are required to remove excess water in an evaporation or crystallization process. In solution, ammonium nicotinate is highly stable and can be refluxed without decomposition. However, Lonza utilizes the fact that ammonium nicotinate decomposes into its separate constituents when water is removed at temperature over 160°C.




F1.4.4: Schematic Layout of the Lonza Niacin Air Oxidation Process

The following advantages are simultaneously incorporated:

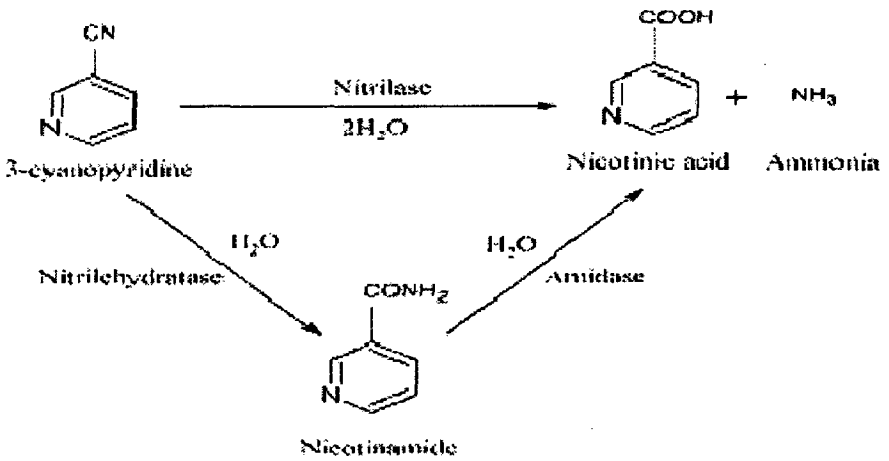
- The amount of water to be removed is drastically reduced, thus saving energy.
- The physical form of the spray-dried product is very uniform
- The niacin obtained is very pure
- Ammonia liberated from the spray-drier can be recycled into the process
- No mother liquor is produced, avoiding additional work-up, recycling or possible waste.

1.4.5 Production Of Nicotinic Acid Using Bacillus Pallidus Dac521

A thermostable nitrilase produced by the thermophilic bacterium Bacillus pallidus Dac521 catalyzed the direct hydrolysis of 3-cyanopyridine to nicotinic acid without detectable formation of nicotinamide. The reaction conditions for nicotinic acid production were optimized by using free bacterial cells. Temperature and pH optima were 60°C and 8.0, respectively, with no detectable mass transfer limitation at the highest cell loading. Under optimized conditions, 100% of the 3-cyanopyridine substrate could be converted to nicotinic acid at a conversion rate of 76 mol/min/mg dry cell

weight. Free bacterial cells were effective in converting 3-cyanopyridine at concentrations of up to 0.3 M and the intracellular 3-cyanopyridinase stability was increased in the presence of the substrate at concentrations of 0.2 and 0.3 M. Both 3-cyanopyridine and nicotinic acid inhibited the hydrolysis of 3-cyanopyridine at concentrations greater than 0.2 M.

Nitriles can be converted to the corresponding carboxylic acids plus ammonia by a single enzyme, nitrilase (EC 3.5.5.1), without the formation of a stable amide intermediate. Microbial nitrilases have been identified in a number of mesophilic bacterial species including *Acinetobacter* Yamamoto. K (1991*) Arthrobacter Bandyopadhyay. A. K* et.al *(1986), Alcaligenes* Nagaswa . T et.al (1990), *Comamonas* Levy–Schil et.al *(1995), Klebsiella*. Stalker D.M (1987)*Rhodococcus* M. Kobayashi, et.al(1989) *and Nocardia*. Harper .D.B et.al(1976) However, only one thermophilic nitrilase-producing bacterium—*Bacillus pallidus Cramp.R* et.al(1997) is currently known. Many of these enzymes have broad substrate specificity's, but with a preference for aromatic or heterocyclic substrates such as benzonitrile or the cyanopyridines, the nicotinic acid precursors. Nicotinic acid is currently produced by chemical synthesis involving the oxidation of 2-methyl-5-ethylpyridine or the hydrolysis of 3-cyanopyridine at high temperatures (330°C) and pressures (290 atm). Alternatively, nicotinic acid can be produced under mild conditions by the bioconversion of 3-cyanopyridine with microbial nitrilases Mathew . C. D et.al(1988).The microbial enzymes (nitrilase or nitrile hydratase and amidase) that hydrolyse 3-cyanopyridine to nicotinic acid. Conversion of 3-cyanopyridine to nicotinic acid is shown in the Figure 1.4.5




F1.4.5: Conversion of 3-cyanopyridine to Nicotinic acid

The conversion of 3-cyanopyridine to nicotinic acid previously assumed from the release of ammonia during incubations and the absence of detectable amide

intermediates with a variety of substrates. Induction of nitrilase activity in *B. pallidus* Dac521 by benzonitrile was found to generate high levels of 3-cyanopyridinase activity. The bioconversion of 3-cyanopyridine to nicotinic acid by *B. pallidus* Dac521 was inhibited by both nicotinic acid and the use of high concentrations of substrate. Microbial hydrolysis of 3-cyanopyridine by using mesophilic micro-organisms such as Rhodococcus rhodochrous and Nocardia rhodochrous Vaughan P.A. et.al (1989) proceeds quantitatively, whereas chemical hydrolysis is hampered by moderate yields and high cost. Carboxylic acids are important chemicals of commerce. They are among the most attractive products for manufacture from biomass, such as corn starch fermentation.

## 1.5 RECOVERY METHODS

Carboxylic acids are also stable oxidation products and therefore frequently appear as by-products or in aqueous waste streams. Carboxylic acids have many commercial applications such as:

- Raw material for manufacturing nylon and biodegradable plastics
- Builders in detergents
- Acidulents and buffers in food
- Chemical intermediates for the pharmaceutical industry

ADVANTAGES

- Recovers low-volatility and low- to moderate-solubility carboxylic acids, such as adipic and succinic acids.
- Works simply, inexpensively, and with low energy consumption.
- Removes co-extracted water by stripping.
- Lessens the solubilities of carboxylic acids, allowing precipitation and recovery of most of the dissolved acid.
- Successful with commonly used solvents, such as ketones, esters, alcohols, and ethers.
- Recovers carboxylic acids from fermentation broths and other industrial streams.
- Effectively removes and recovers carboxylic acids from effluent streams.

### *1.5.1 Solvent Extraction*

Carboxylic acids are important commercial products. The requirements of carboxylic acids (lactic acid, citric acid, propionic acid etc.) are increasing every year. Therefore, it is important to have an efficient recovery method following the production of carboxylic acid. At present most of the manufacturers use the conventional method of recovery, which is the calcium hydroxide precipitation method. This method of

recovery is expensive and unfriendly to the environment as it consumes lime and sulphuric acid and also produces a large quantity of calcium sulphate sludge as solid waste. It is, therefore, reasonable to look for other methods of recovery for carboxylic acid. Lactic acid is used in food, chemical and pharmaceutical fields, and a raw material for the production of biodegradable polylactic acid, both, substitutes for conventional plastic materials and new materials of specific uses, such as controlled drug delivery or artificial prostheses. This short review focuses on the developments of recovery of lactic acid from fermentation broth ( Wasewar, K. L., 2005)

Many of the solvent extraction-distillation schemes described in the literature only operate effectively at relatively high concentration of acids (>20%) from aqueous solution and are not really applicable to concentration of acids found in fermentation liquors. The major reason is the partition coefficient diminishes as the acid concentration in the aqueous solution becomes lower. Tetrahydrofuran and its derivatives act in the reverse way (Guinot and Chassaing, 1948) and are thus potentially useful additives to extraction solvent such as benzene and toluene. The hydrophobic solvent and water boiled off first, propionic acid second, trialkyl phosphate last. Trialkyl phosphate increased the partition coefficient, but did have to be distilled. This system enabled a large volume of solvent to be used without increasing distillation costs.

The choice of solvent system is very critical and has to be tailored to the acid being extracted. It is a compromise between a high partition coefficient for the acid and solubility of water in the solvent. On these grounds dichloromethane has been claimed to be good solvent for acid extraction

*1.5.2 Ion Exchange*

The method of removing carboxylic acids from effluent streams comprising the steps of pretreatment which may include chemical conditioning, clarification and filtering the effluent stream to remove suspended solid particles to provide a filtered stream. The filtered stream is subjected to membrane filtration to remove organic compounds having a molecular weight of greater than 150 while simultaneously permitting permeation of the membrane by the carboxylic acids to provide a membrane filtered stream. A reverse osmosis membrane is provided having a high pressure side and a low pressure side, and the membrane filtered stream is introduced to the high pressure side of the reverse osmosis membrane. The carboxylic acids are concentrated in the high pressure side of the reverse osmosis membrane. In a preferred embodiment, purified liquid (permeate) is neutralized and passed to the high pressure side of a second pass reverse osmosis membrane, producing a high-purity final permeate for plant reuse or discharge to surface water (Al-samadi, Riad A. 1997).

Removal of organic pollutants from the aquatic environment has received increasing attention. The use of synthetic resins as polymeric adsorbents for this purpose is important not only in the protection of the environment from pollution but also in the effective we of raw materials, because the resins can be regenerated and the organic pollutants can be recovered without chemical change. Carboxylic acids are important materials in use by chemical industries. They are often obtained as aqueous solutions. Isolation of them is an important process in chemical industry, but it is not always easy due to the high solubility in water, especially in the aliphatic carboxylic acids of low molecular weight. On the other hand, they are important organic pollutants which increase the COD value of industrial waste water.

Synthetic resins such as styrene-di-vinylbenzene resin, strong base anion exchange resin, and strong and weak acid cation-exchange have been used to adsorb carboxylic acids in aqueous solution.

*1.5.3 Calcium Hydroxide Precipitation Method*

A novel method for recovering carboxylic acid from a waste water stream is described. The method involves first neutralizing the carboxylic acid in the waste water with CaO or $Ca(OH)_2$ to form calcium carboxylate. The resulting calcium carboxylate is then reacted with sulfite or sulfate to regenerate the carboxylic acid. The resulting waste water typically has a carboxylic acid content of at least 25-wt %. (Fan, M. and Brown, R., C., 2005. The process is simple and reliable but, suffers from

1. Consumption of large quantities of reagent
2. Huge amount of waste per ton of acid produced.
3. Disposal problem of waste.

*1.5.4 Membrane Technique*

Membrane science and technology had an impressive growth, confirming their solutions of crucial problems and to sustainable industrial development. Molecular separation species based on polymeric, ceramic and liquid membranes have been studied and applied in wider spectrum of areas. Selective removal of products through yields effective conversions with product –inhibited or thermodynamically unfavourable reactions.

Carboxylic acids are an important group of additives having extensive uses in the food industries. Such compounds include citric, gluconic, lactic, malic and tartaric acids. Carboxylic acids are traditionally produced in batch fermenters depending upon medium and microorganisms, stirred fermenters (Margaritis and Wilke 1978). Simultaneous membrane based solvent extraction (MBSE) and membrane based solvent stripping (MBSS) of 5-methyl-2-pyrazine carboxylic acid (MPCA) in hollow fiber contactors with solvent. An effective transport of MPCA was achieved. The analysis of mass-transfer resistances showed, that the kinetics of the acid-carrier complexes

formation and/or decomposition should be taken into account. The contribution of the mass-transfer resistances based on reaction kinetics to the overall resistances in MBSE and/or MBSS is from 40 to 80%. The proposed reaction-diffusion model gives a much better fit to the experimental values than a pure diffusion model. Low-ethanol wines and other alcoholic beverages are produced by treating ordinary alcoholic beverages with novel membrane extraction methods. Semi-permeable membranes and extraction fluids comprised either of a non-toxic, water-immiscible organic solvent or an aqueous solution of a low-molecular-weight but membrane-impermeable solute are used under mild conditions to selectively extract ethanol from alcoholic beverages, while leaving substantially intact the complement of other organic constituents that contribute to the color, aroma, and taste of the beverage. The methods disclosed may be adapted to continuous processing of alcohol-containing beverages, in which an ethanol-rich product is continuously recovered from the organic or aqueous extraction fluid and the latter is continuously regenerated and subsequently recycled to the membrane extraction unit.( Matson, Stephen L., 1988)

*1.5.5Electrodialysis*

Electrodialysis is a process where ion exchange membranes are used for removing ions from an aqueous solution under the driving force of electrical field. Electrodialysis is applied to remove salts from solutions or to concentrate ionic substances. A special type of electrodialysis is water-splitting electrodialysis. Instead of anion exchange membranes in desalting, bipolar membranes are used in water-splitting electrodialysis. Water-splitting electrodialysis is applied to electro-conversion of salts to the corresponding acids. There are two different methods for recovery of lactic acid. It is a two stage electrodialysis method in the first case and electrodialysis with double exchange reaction in the second case. In the first step of desalting, sodium lactate is recovered, purified and concentrated, in the water-splitting or acidification step, lactic acid is regenerated from sodium lactate, and sodium hydroxide is recovered and purified.

Electrodialysis (Weier et al, 1992) offers a potential means of concentrating the salts and at the same time selectively removing them from the non ionic components of the broth. Electrolyte used here is sodium sulfate and the feed stream is the fermentation broth containing propionic acid with other organic acids. The concentrate is the propionic acid rich stream. The electrodialysis unit consists of a fixed voltage power supply, a peristaltic pump and a membrane stack. The stack consists of alternating cation and anion exchange membrane.

The electrolyte flows through the channels adjacent to each electrode. The electrolyte and the product stream are always re-circulated. Two fed side modes of operations are used:

- One pass mode, the feed stream makes a single pass through depleting channel. The acid concentration then rises which simulates the concentration that would be achieved in purely countercurrent operation.
- · Recycle mode, feed solution is continuously recycled, I.e., single stage batch recovery.

At the start of the process the product stream volume is low. The feed and the electrolyte stream are high. Now voltage is supplied and conductivity of the product stream is measured. The process terminates once the conductivity stops rising. The ratio of final to initial total acid concentration at pH 7 ranges from 9.2 to 4.1 for the one pass runs and 4.1 to 2.4 for recycle runs, representing an important degree of concentration. In absolute terms, the final concentration is limited by the electro-osmotic water flux.

1.5.6 *Emulsion Liquid Membrane Extraction*

Separation techniques based on immiscible liquid phases have long served as an effective means of separation and purification. Liquid-liquid solvent extraction is a commonly used separation process. Typically, an aqueous feed stream is mixed with an immiscible solvent by means of mechanical agitation.

Packed or agitated columns are sometimes used to enhance the contact between the two streams. The solvent is selected such that the solute has a higher solubility in it versus the original aqueous feed stream; the extraction is achieved as a result of favorable partitioning of the solute into the solvent. In facilitated extraction, extractants (chemical complexing reagents) are added to the solvent to enhance the partitioning, selectivity, or both. The main drawbacks of such approaches are:

(1) A settling stage is usually required after the extraction, making continuous operation more difficult.

(2) The extraction is limited by the equilibrium of partitioning.

More recently, dispersion-free solvent extraction using microporous hollow-fiber contactors (HFC's) has been shown to be an effective alternative to normal dispersed (stirred tank) extraction. HFC's consist of microporous hollow fibers arranged in a shell-and-tube configuration. The fiber material can be either hydrophilic or hydrophobic. When a hydrophobic fiber is used, higher pressure is applied on the aqueous phase. The aqueous phase will not penetrate or wet the hydrophobic membrane. The organic phase is present in the pores but cannot penetrate into the aqueous side because the aqueous phase is at a higher pressure. Thus, a stable aqueous-organic interface is established at the pore openings. The advantage of HFC's lies in their ability to offer a very high surface area/volume ratio without dispersion or mixing of the two phases. The use of hollow-fiber contactors eliminates the need for a settling stage and allows for direct scale-up due to modular design. In addition, the high energy needed in the mechanical dispersion method is eliminated. Naturally, the extent of extraction is still

limited by the equilibrium. To circumvent equilibrium constraints, emulsion liquid membranes (ELM's) combine extraction and stripping into a single operation. ELM's have been successfully used to treat a variety of aqueous streams contaminated with heavy metal ions, like copper, zinc, cadmium, nickel, mercury, lead and chromium. ELM's, first invented by Li, are made by forming an emulsion between two immiscible phases, usually stabilized by surfactants. In this case, an emulsion liquid membrane (ELM) (Wiensek, J. M. and Su, S. Y., 2000) is first prepared by mixing under high shear (a milkshake blender is typically used in the laboratory) a physical mixture of 10 M NaOH and an immiscible organic phase (e.g. toluene). The mixture is a physical mixture + the water and oil do not dissolve into one another; rather the smaller volume phase is dispersed into the larger volume phase ( see Fig. F 1.4.7 A).

Typically, 30%v/v of the dispersion is the internal phase, which in this case is the aqueous NaOH solution. The mechanical action of the blender will form the dispersion or emulsion but the two phases will quickly separate into bulk coalesced phases if there is no stabilizing surfactant present. The ELM cocktail is a mixture of an oil membrane phase, an aqueous stripping phase which is encapsulated in the interior of the oil membrane, and finally a surfactant is added to stabilize the emulsion. Each application requires its own special mixture to obtain optimal results, and other additives may be present which increase the solubility of the solute in the oil membrane phase by some form of chemical complexation. Once the ELM is prepared, it can then be further dispersed into the feed phase containing the organic acids to be separated (see Fig. F 1.4.7 B). The emulsion globules are dispersed into this aqueous feed phase by gentle mixing at 400±500 rpm. Thus, the ELM contains very small droplets of 10MNaOH and this emulsion is further dispersed into the feed phase as 0.1±1 millimeter size globules. The net effect is that an organic phase (or membrane phase) physically separates two aqueous phases. The aqueous feed phase contains the solute to be separated which has a modest partition coefficient into the oil membrane phase. Once in the membrane phase, the organic acid diffuses towards the center of the globule due to a concentration gradient (there is no solute in the center of the globule). Eventually, the organic acid will encounter an internal droplet containing the NaOH and partition into that droplet where a fast, irreversible acid base reaction will ionize the organic acid. Ionized organic acids have essentially zero solubility in the oil membrane phase so that once this reaction occurs; the organic acid is trapped within the aqueous internal phase and will not be able to diffuse back out of the emulsion.

The ELM extraction in a stirred contactor as described above has two main disadvantages:

(1) On prolonged contact with the feed stream, the emulsion swells with water, increasing the internal-phase volume. Water uptake (or swell) causes a reduction in the stripping reagent concentration in the internal phase, which in turn reduces the stripping efficiency. Furthermore, the solute that has been

concentrated in the internal phase is also diluted, resulting in lower separation efficiency of the liquid membrane.

(2) Leakage of the internal-phase contents into the feed stream because of membrane rupture. Leakage, like swell, also reduces the efficiency of separation. Leakage can be minimized by making a more stable emulsion with optimized surfactant, but this makes the subsequent demulsification and product recovery steps more difficult. Lower shear rates also minimize leakage, but mass transfer resistances then become significant (i.e., very slow rates of separation).

### *1.5.7 Supported Emulsion Liquid Membrane*

Supported emulsion liquid membranes (SELM's) (Wiensek, J. M. and Su, S. Y., 2000) combine the advantages of emulsion liquid membrane separation and dispersion-free solvent extraction. In this design, an ELM carries out simultaneous extraction and stripping from the feed stream by a liquid-liquid, dispersion-free contacting in an HFC. The membrane pores are not wetted by the internal aqueous droplets, so the stripping phase is never in the proximity of the external aqueous feed phase. This wettability effect as well as the absence of high shear rates, which are encountered in agitated dispersion, eliminates leakage of the internal stripping phase. In addition, since the internal aqueous droplets cannot directly contact the feed aqueous phase due to the intervening hydrophobic membrane, the amount of surfactant required in the system is minimal (in fact, no surfactant should be needed). Swell is primarily caused by the surfactant which is readily hydrated in the low ionic strength environment of the feed phase. This hydrated surfactant then diffuses in toward the center of the emulsion globule until it encounters an internal phase droplet at high ionic strength where it is quickly stripped of its waters of hydration. Thus, minimizing the surfactant in the system also limits the swell.

SELM extraction offers superior performance over ELM extraction in stirred tank contactors. The leakage of internal-phase contents into the feed phase is 0.02 % for the SELM, while it is as high as 8%for the stirred contactor. This reduced leakage accounts for the improved extraction by SELM's.

### 1.5.8 *Distillation*

The distillation technique is one of the methods for recovering carboxylic acids. The recovery of acetic acid from its dilute aqueous solutions is a major problem in both petrochemical and fine chemical industries. The conventional methods of recovery are azeotropic distillation, simple distillation and liquid-liquid extraction. Physical separations such as distillation and extraction suffer from several drawbacks. The esterification of an aqueous solution (30%) of acetic acid with n-butanol/ iso-amyl alcohol is a reversible reaction. As excess of water is present in the reaction mixture,

the conversion is greatly restricted by the equilibrium limitations. The esters of acetic acid, namely, n-ethyl acetate and iso-amyl acetate, have a wide range of applications (Sahab, 2000). In view of the appreciable value of these esters, this work was directed towards recovery of 30% acetic acid by reaction with n-butanol and iso-amyl alcohol in a reactive distillation column (RDC) using macroporous ion-exchange resin, Indion 130, as a catalyst bed, confined in stainless steel wire cages. The effect of various parameters, e.g. total feed flow rate, length of catalytic section, reflux ratio, mole ratio of the reactants, location of feed points and effect of recycle of water were studied.

The distillation method is advantage: well-established/reliable technology. The drawbacks are consumption of energy, formation of high-boiling internal esters, dimers, and polymers of propionic acid during distillation .

1.5.9 *Reverse Osmosis*

Reverse osmosis has also studied for recovering lactic acid from fermentation broths (Smith et al., 1977; Schlicher and Cheryan, 1990). They concluded that the reverse osmosis could effectively concentrate lactic acid from 10 to 120 g $dm^{-3}$ at a 6.9 MPa transmembrane pressure at energy use lower than multiple effect evaporators.

A method for recovering carboxylic acids from a dilute aqueous solution thereof having a concentration below about ten percent (10%) by weight, which includes passing the dilute acid solution through a reverse osmosis separator, thereby producing a permeate substantially free of acid and a retentate having an acid concentration above about ten percent (10%) by weight. The retentate is contacted with a liquid extractant for acids to produce an acid-rich extractat and an acid-free raffinate. The acid is then recovered. Reverse osmosis has also studied for recovering acrylic acid from process or waste water streams in which the stream is vaporized and contacted with a liquid high boiling solvent for acrylic acid, thereby absorbing acrylic acid into the solvent. Mixed trialkylphosphine oxides are a preferred solvent. Acrylic acid is stripped from the solvent with heat and, optionally, stripping gas. It may be separated from any accompanying materials to produce acrylic acid of high purity.(Fu-ming, L., Gualy, R., G., 2001).

1.5.10 *Reactive Extraction*

Reactive extraction with specified extractant giving a higher distribution coefficient has been proposed as a promising technique for the recovery of acid. Some the advantages include increased reactor productivity, ease in reactor pH control without requiring of base addition, and use of high concentration substrate as the process feed to reduce process waste and production costs. This method may also allow the process to produce and recover the product in one continuous step and reduce the down stream processing load and the recovery costs.

Aliphatic tertiary amines dissolved in different diluents are powerful extracting reagents for carboxylic acids. The amine binds the acid in an organic phase through a reversible complexation.

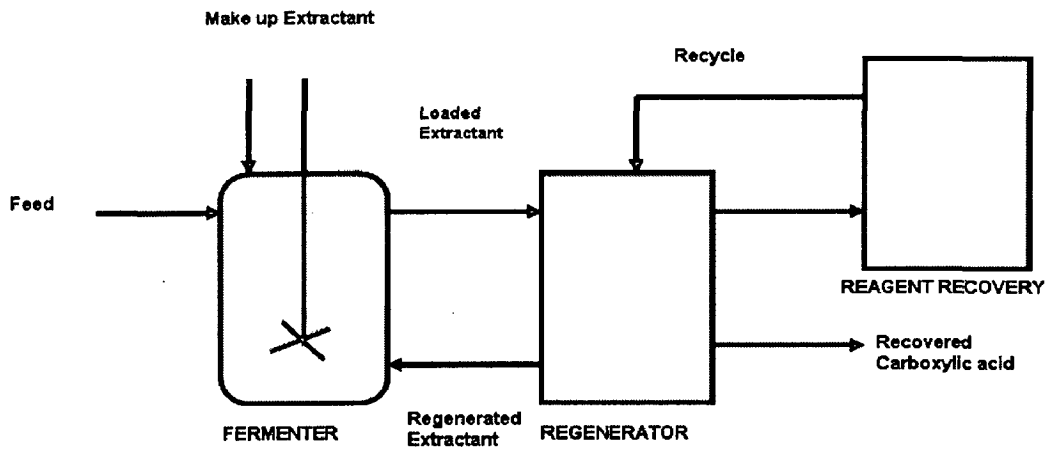
The method is described by a simple complexation reaction with equilibrium of the form:

Solute + n Extractant ↔ Complex

The equilibrium is described by an equilibrium constant $K_E$

$$K_E = \frac{[Complex]}{[Solute][Extrac\tan t]^n} \qquad (1.5.10.1)$$

Since, the concentration of itaconic and nicotinic acid is low, the separations by reactive extraction tend to be more attractive. The method can be described by a simple flow diagram (see Fig. F 1.4.10).




F 1.4.10 Flow Diagram of Reactive Extraction

The extractant used can be broadly classified into three categories based on the functional group:

1. Conventional oxygen-bearing hydrocarbon extractants [methyl isobutyl ketone (MIBK), octanol, decanol, etc].
2. Phosphorus-bonded oxygen-bearing extractants (tributyl phosphate, etc.)
3. High molecular weight aliphatic amines (Aliquat, Alamine, etc).

The advantage of extractant is high distribution coefficient but the only disadvantage is viscous and slow to disengage when used neat. To improve the physical properties and increase the extraction power of extractant diluents are used as a second component. The diluent are of three types based on functional group attached:

1.Active diluent containing chlorine atoms (methylenechloride, 1-chlorobutane, chlorobenzene, chloroform).

2. Carbon bonded oxygen donor active diluents (MIBK, 1-octanol, ethyl acetate).

3. Phosphorous- bonded oxygen donor active diluents (tri-butyl phosphate).

In some cases, the solute –extractant adduct separates from the diluent to form third phase. The solution for this kind of problem is either control solvent loading or adds a modifier (third component) to solvent mixture. The reactive equilibrium description of the system can be written as a set of equilibliria involving the dissociation of acid in water and formation of complex with acid and extractant by ion pair association or hydrogen-bonding. It assumes that the reactive extraction between acid and extractant takes place at the organic-aqueous interface and two types of complexes, HAS and $HAS_2$ form in stepwise manner.

The distribution coefficient $K_D$, can be defined as the total molar concentration of acid in (all forms) in the organic phase, divided by that in the aqueous phase.

$$K_D = \frac{C_{org}}{C_{aq}} = \frac{[HA]_{org} + [BHA]_{org} + [B_2HA]_{org}}{[HA]^*_{aq}} = \frac{\phi m + K_{11}[B]_{org} + K_{11}K_{12}[B]^2_{org}}{1 + 10^{pH-pKa}} \qquad (1.5.10.2)$$

The equilibrium constants $K_{11}$ and $K_{12}$ can be calculated from loading factor Z.

$$Z = \frac{[BHA]_{org}}{[B]_{i,org}} \qquad (1.5.10.3)$$

$$\frac{Z}{(1-Z)} = K_{11}[HA]_{aq} \qquad (1.5.10.4)$$

$$\frac{Z}{(2-Z)} = K_{12}[HA]^2_{aq} \qquad (1.5.10.5)$$

# CHAPTER 2

# REACTIVE EXTRACTION

## 2.1. Reactive Extraction of Carboxylic acids

The demand for carboxylic acids is growing tremendously. The carboxylic acids are commercially produced by fermentation. Fermentation route is one of the oldest known routes for the production of organic acids. With the development of petrochemical industry and increase in demand of organic acids fermentation was replaced by organic synthesis. Mainly the mono carboxylic acids acetic, lactic, di-carboxylic acids like succinic, itaconic acids etc and tri-carboxylic acids like citric acid were produced. Recently with the rise in petroleum costs and development of new biotechnology, the fermentation route is of interest again.

At present, the acids are recovered from the microbes and precipitated as insoluble calcium salts. The salts are treated by sulfuric acid to convert them to free organic acids. Since, this recovery method is a complex process, solvent extraction processes have been proposed as an alternative method to the existing conventional process. Application of liquid membrane processes to the fermentated broth is also proposed. The extraction technique has the advantage of continuously removing the acid from the broth and keeping the acids concentration in the broth to a low level. This is effective in suppressing product inhibition and increasing reactor efficiency.

### *2.1.1. Reactive Extraction of Nicotinic and Itaconic acid*

Research done on reactive extraction of nicotinic and itaconic acids is very less compared to that with simple aliphatic monoacids. The presence of a functional group on a carbon atom of acid molecule deviates the two acids from their corresponding structure. They show low degree of extraction and low equilibrium compared to their corresponding aliphatic carboxylic acids. The degree of extraction of the acids depends on the acidity, electronegativity and hydrophobicity of the acids.

### *2.1.2. Effect of Extractants and Diluents*

In case of quartenary amines like Aliquat 336 and tertiary amines like Alamine 300 is a mixture containing mainly tri-n-octylamine(>93% ). The influence of diluents and the acid and amine concentrations on the extraction degree of nicotinic acid were performed using polar (1,2-dichloroethane, 1,2-DCE), protic (cyclopentanol), proton accepting (methyl isobutyl ketone, MIBK) and inert (n-heptane) diluents. Nicotinic acid is directly proportional to the extractant concentration for a fixed equilibrium acid concentration in the aqueous phase. The noticeably low extraction

degree of nicotinic acid in polar diluents, e.g., 1,2-dichlorobenzene. This is due to the intramolecular hydrogen bonding of the second proton accepting group in the pyridine ring. Aprotic ketones, dibenzyl ether and benzyl acetate solvents as well as protic 1-octanol, containing an oxygenated functional group, regarding to the solvent polarity and hydrogenbonding ability. The highest strength of the complex solvation was found for 1,2-dichloroethane, chloroform and nitrobenzene promoting probably (1,1) acid-amine complex formation related to the highest sf factors (modified separation factor for amine/diluent mixture) and at least 20 times larger D as compared to the pure diluent. The synergistic extraction power of amine/alcohol and amine/ketone systems is noticeably larger yielding D and Zt greater than 1, except for MIBK due to the simultaneous effect of the physical extraction and the diluent-complex interaction through hydrogen bonding (Senol, 2002).

Itaconic acid forms (1, 1) and (1, 2) type acid – amine complex with Quartenary amine Aliquat 336. This phenomenon is in contrast to the extraction rules that more the hydrophobic and acidic in nature the greater degree of extraction is obtained. This may be due to extra association with extractant and itaconic acid or less steric hindrance for phosphorus bonded oxygen containing extractants.

In case of Tri-octyl Amine in Ethyl acetate the degree of extraction for both the acids increases with increase in the extractant concentration but is not directly proportional to the extractant concentration for a fixed equilibrium acid concentration in the aqueous phase. This fact ascertains that the polar diluents provide additional solvating power that allows higher levels of polar acid – amine complexes to stay in the organic phase. Both the acids form (1, 1) and (1, 2) type of complex with Tri-octyl Amine. Itaconic acid shows higher degree of extraction compared to Nicotinic acid with Tri-octyl Amine in Ethyl acetate. The extraction equilibria of itaconic acid with tri-n-octylamine (TOA) and/or tri-n-butyl phosphate (TBP) were measured. The solvation numbers of the acids were the same as the numbers of the carboxyl groups on each acid molecule in the extraction with TOA or TBP alone. The extraction equilibrium constants were roughly correlated with the hydrophobicity of the acid. In the case of using the mixed extractant of TBP and TOA, the synergism was observed in the extraction of the acid investigated. Specialty, the extractions of itaconic acid gave a remarkable synergism (Matsumoto. ,M. , Otono, T. , Kondo. K. , 2001)

*2.1.3. Effect of Temperature*

Water immiscible amines are observed to be selective and powerful extractants for separation of carboxylic acids from their dilute solutions. The distribution coefficient in the extraction of citric acid by amine based extractants is higher, by 1 or 2 magnitudes, compared to those by extraction with other solvents, such as ketones, alcohols, esters, amides, and organic alkyl phosphates (Yu-Ming et al, 1983). This

enables high separation yield, using less stages and low phase ratio. However, this conflicts with the recovery of the acid from the extractant.

A solution to this problem was suggested by Baniel et al., who found that the distribution coefficient for the extraction of citric acid by tertiary amines decreases when temperature increased. They developed and implemented a new process for recovery of citric acid from its fermentation broth, called temperature swing. The acid is extracted from the solution by a tertiary amine (Tridodecyl amine) in a suitable diluent at approximately ambient temperature and then back extracted at an elevated temperature of 80 - 140°C.

Wennersten (Wennersten, 1983) examined extraction of citric acid using $C_8$ – $C_{10}$ tertiary amine (Alamine 336) in various diluents at 25 and 60°C. He concluded that the formation of acid – amine complex is strongly dependent on temperature.

Tamada and others (Tamada et al, 1989; Tamada and King, 1990) showed that on increasing the temperature there is a decrease in extraction of succinic and lactic acid by Alamine 304 in MIBK or in chloroform. Based on Van'tHoff's equation, they calculated enthalpy and entropy for the association in these extraction systems. Tamada research concluded that molar complexation of 1:1 acid – amine ratio is much more exothermic and involves much greater loss of entropy than the formation of 2:1 and 3:1 complexes.

The Van't Hoff equation is derived from the free energy expression

$$\Delta G = \Delta H - T\Delta S = -RT\ln(K_E) \qquad (2.1.3.1)$$

Hence, $$\ln(K_E) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (2.1.3.2)$$

On differentiating above equation

$$d\left(\frac{\ln(K_E)}{dT}\right) = \frac{\Delta H}{RT^2} - \frac{d\Delta H}{dt}RT + \frac{d\Delta S}{R}dt \qquad (2.1.3.3)$$

For relatively small changes in temperature, it can be assumed that the enthalpy and entropy are independent of temperature. Thus,

$$\frac{d(\ln K_E)}{d(1/T)} = -\frac{\Delta H}{R} \qquad (2.1.3.4)$$

Eyal (Eyal et al., 1991) examined the effect of temperature on the extraction of mineral acids by tertiary amines in kerosene and octanol. They concluded that the temperature effect increases as the branching of amine, with its dilution, increases and as the polarity of the diluent decreases.

Sadaka and Garcia (Sadaka and Garcia, 1998) tested the extraction of shikimic and guinic acid by Alamine 304 in Heptanol at various temperature. Ratios of 2-3 were observed between the distribution coefficients at 5°C and those at 60°C. They proposed extracting the acids at low temperatures and recovering them at high temperatures. In

addition they suggested adding a "displacer" (oleic acid) to the organic phase in the back extraction stage.

Eyal and co-workers proposed a temperature swing process for the recovery of ascorbic acid (Eyal and Hazan, 2000) or erythorbic acid (Eyal et al., 2001) from their fermentation liquors, using secondary and tertiary alkyl amine in a diluent. Particularly high temperature effects were observed for these acids. This phenomenon is utilized to generate concentrated back extracts from dilute fermentation liquors.

Eyal and Canari (Eyal and Canari, 1995; Canari and Eyal, 2003 ) developed a theory dividing the extraction mechanism of acids with amine based extractants into two main categories:

i. Ion pair formation
ii. Hydrogen bonding and Solvation

The ion pair Mechanism is the dominant mechanism for those cases where the amine extractant has an apparent basicity greater than that of the anion of the extracted acid (The amine's apparent basicity is determined by Grinstead's method (Grinstead, 1966) as the pH of Half neutralization ($pH_{hn}$) of the extractant). On the other hand, in cases of relatively weak extractants compared to the anion of the extracted acid ($pH_{hn}<pK_a$), extraction is conducted either through hydrogen bonding or through salvation interactions. In these latter mechanisms, the degree of extraction is mainly determined by the concentration of the undissociated fraction of acid and thus, is dependent strongly on the $pK_a$ value of the acid. This theory successfully explains the extraction of monoprotic (Canari and Eyal, 2003a) and diprotic acids (Canari and Eyal, 2003b), the selectivity in the acids' extraction from multi acid systems (Canari and Eyal, 2003c; Canari and Eyal, 2003d) and the effect of anion concentration in the aqueous phase (Canari and Eyal, 2003e).

Perrin calculated the effect of temperature on the pKa values of acids based on the following equation

$$-\frac{d(pK_a)}{dT} = \frac{pK_a + 0.052\Delta S^0}{T} \qquad (2.1.3.5)$$

They concluded that the $pK_a$ values on common carboxylic acids decrease only slightly when the temperature is increased. Similarly, $pK_a$ measurements (Perrin, 1981) for the carboxylic acids exhibit a small decrease in $pK_a$ when the temperature is increased but, only up to a given point. Above it, the $pK_a$ value increases.

Another parameter affected by the temperature is the solubility of the acid in aqueous phase and the extract diluents. The solubility of oxalic, malonic, succinic, adipic, malic, maleic, citric and tartaric acids in water increases when temperature is increased from 278.15 K to 338.15 K (Apelblat and Manzulora, 1987).

*2.1.4. Kinetics*

The reactions involving two phase (liquid-liquid) reactions where reaction occurs in one of the liquid phase have mass transfer included with simple reaction kinetics. To understand the reaction better and for convenience the system is classified into four regimes:

i. Regime 1: Very slow reactions
ii. Regime 2: Slow reactions
iii. Regime 3: Fast reactions
iv. Regime 4: Instantaneous reactions

In the regime 1, the rate of reaction is very much slower than the rate of mass transfer. Consequently, the phase (where the reaction takes place) is saturated with the reactant (A) at any moment of time and rate of formation of product will be determined by the kinetics of the homogeneous chemical reaction. The diffusion factors are unimportant in this regime. The rate of mass transfer ($R_A a$ in mol/cm$^3$.sec), is given by

$$R_A a = lk_{mn}[A^*]^m[B_0]^n \qquad (2.1.4.1)$$

The condition for the validity of this mechanism can be expressed as

$$k_L a[A^*] >> lk_{mn}[A^*]^m[B_0]^n \qquad (2.1.4.2)$$

The left hand side of expression 2 gives the volumetric rate of mass transfer and the right hand side gives the rate of homogeneous chemical reaction.

In the regime 2, the rate of reaction is faster than the rate of mass transfer. The reaction then occurs uniformly throughout the phase, but the rate is controlled by the rate of mass transfer. The concentration of dissolved reactant in the phase is zero. According to Higbie's theory, the specific rates of mass transfer ($R_A$ in mol/cm$^2$.sec), can be expressed as

$$R_A = 2\left(\frac{D_A}{\pi t_E}\right)^{1/2}\left([A^*]-[A_0]\right) \qquad (2.1.4.3)$$

The condition to be satisfied for this mechanism is given by

$$k_L a[A^*] << lk_{mn}[A^*]^m[B_o]^n \qquad (2.1.4.4)$$

Under this condition, it is likely that the value of $[A_0]$ is negligible, then the equation (3) changes to

$$R_A = k_L[A^*] \qquad (2.1.4.5)$$

In the regime 3, the physical picture of the problem is based on film theory, the treatment of the problem is based on the penetration theory.

According to film theory, under certain conditions the reaction occurs while the solute diffusing in the film; that is the reaction and diffusion occur simultaneously.

The condition under which the reaction occurs entirely in the film is given by the following expression

$$\sqrt{M} = \frac{\sqrt{\frac{2}{m+1} D_A k_{mn} [A^*]^{m-1} [B_0]^n}}{k_L} >> 1 \qquad (2.1.4.6)$$

In fact, it can be shown that the left-handed side of the expression represents the ratio of the amount of reactant (A) reacting in the film to that reacting in the bulk. Further, under certain conditions the interfacial concentration of species B is practically the same as that in the bulk liquid phase; that is, there is no depletion of the species B in the film. The condition under which no depletion would occur is given by

$$\frac{\sqrt{\frac{2}{m+1} D_A k_{mn} [A^*]^{m-1} [B_0]^n}}{k_L} << \frac{[B_0]}{Z[A^*]} \sqrt{\frac{D_B}{D_A}} \qquad (2.1.4.7)$$

The differential equation for the simultaneous diffusion and reaction in the film can now be written as

$$D_A \frac{d^2[A]}{dx^2} k_{mn} [B_0]^n [A]^m = k_m [A]^m \qquad (2.1.4.8)$$

The boundary conditions are

$$x = 0, \quad [A] = [A^*], \quad \frac{d[B]}{dx} = 0 \qquad (2.1.4.9)$$

$$x = \delta, \quad [A] = 0 \quad \frac{d[A]}{dx} = 0 \qquad (2.1.4.10)$$

The specific rate of transfer of reactant (A) is given by the flux at the interface

$$R_A = -D_A\left(\frac{d[A]}{dx}\right)_{x=0} = -D_A(\Psi)_{x=0} \qquad (2.1.4.11)$$

Hence from equation (8) and (11) and integrating equation (8)

$$\frac{\Psi^2}{2} = \frac{k_m[A]^{m+1}}{D_A(m+1)} + C \qquad (2.1.4.12)$$

Applying boundary conditions

$$R_A = D_A\sqrt{\frac{2k_m[A^*]^{m+1}}{D_A(m+1)}} \qquad (2.1.4.13)$$

Taking the negative value of the square root of the right-hand side of equation (12) at x = 0

$$R_A = [A^*]\sqrt{\frac{2}{m+1}D_A k_m[A^*]^{m-1}} = [A^*]\sqrt{\frac{2}{m+1}D_A k_{mn}[A^*]^{m-1}[B_0]^n} \qquad (2.1.4.14)$$

Table T 2.1.4. A gives the equation for $R_A$ for various values of m and n along with the relevant conditions.

In the regime 4, the reaction is potentially so fast that the solute and the reactant cannot coexist. At a certain distance from the interface, a reaction plane is formed in which both the solute and the reactant are instantaneously consumed by the reaction. The rate of mass transfer in this case will be governed by the rate at which dissolved A and reactant B are supplied to the reaction plane from the interface and bulk, respectively. The necessary condition for the validity of this regime is given by

$$\frac{\sqrt{\frac{2}{m+1}D_A k_{mn}[A^*]^{m-1}[B_0]^n}}{k_l} >> \frac{[B_0]}{Z[A^*]}\sqrt{\frac{D_B}{D_A}} \qquad (2.1.4.15)$$

The different regimes described above for kinetics of two phase reaction can only be used if the interface between the two phases is not disturbed.

For the study of kinetics for reactive extraction of carboxylic acids the interface is not disturbed if is carried out in stirred cell. The stirred cell has low rotation speeds

and so the interfacial area is undisturbed. The study can broadly be classified into following:

i. Effect of speed of agitation

ii. Effect of phase volume

iii. Order with respect to carboxylic acid

iv. Order with respect to extractant

The reactive extraction of carboxylic acids is a fast pseudo mth order reaction and so falls in regime 3. Once the above mentioned effects are calculated the appropriate rate equation is selected and rate constants are evaluated.

For the extraction of Phenyl Acetic acid with Alamine 336 in kerosene (H. K. Gaidhani et al, 2002) the rate was independent of agitation speed and phase volume. The order with respect to acid and alamine were found to be unity (m=1) and zero (n=0) respectively, by applying equation 14. For m=1 and n=0, from table T 2.1.4 A rate equation was obtained and first order rate constant, $k_1$ was calculated as 0.9 $s^{-1}$ with 99% fit.

| Order with respect to | | Equation for Specific rate | Conditions to be satified | |
|---|---|---|---|---|
| Solute (m) | Reactant (n) | of Mass transfer (mol/cm$^2$ sec) | Condition 1 | Condion 2 |
| 0 | 0 | $R_A = \sqrt{2D_A k_0 [A^*]}$ | $\frac{\sqrt{2D_A k_0 /[A^*]}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $\frac{2D_A k_0}{[A^*]} >> k_L^2$ |
| 0 | 1 | $R_A = \sqrt{2D_A k_1 [A^*][B_0]}$ | $\frac{\sqrt{2D_A k_1 [B_0]/[A^*]}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $\frac{2D_A k_1 [B_0]}{[A^*]} >> k_L^2$ |
| 0 | 2 | $R_A = \sqrt{2D_A k_1 [A^*][B_0]^2}$ | $\frac{\sqrt{2D_A k_1 [B_0]^2/[A^*]}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $\frac{2D_A k_1 [B_0]^2}{[A^*]} >> k_L^2$ |
| 1 | 0 | $R_A = [A^*]\sqrt{D_A k_1}$ | $\frac{\sqrt{D_A k_1}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $D_A k_1 >> k_L^2$ |
| 1 | 1 | $R_A = [A^*]\sqrt{D_A k_2 [B_0]}$ | $\frac{\sqrt{D_A k_2 [B_0]}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $D_A k_2 [B_0] >> k_L^2$ |
| 1 | 2 | $R_A = [A^*]\sqrt{D_A k_3 [B_0]^2}$ | $\frac{\sqrt{D_A k_3 [B_0]^2}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $D_A k_3 [B_0]^2 >> k_L^2$ |
| 2 | 0 | $R_A = [A^*]\sqrt{\frac{2}{3} D_A k_2 [A^*]}$ | $\frac{\sqrt{\frac{2}{3} D_A k_2 [A^*]}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $\frac{2}{3} D_A k_2 [A^*] >> k_L^2$ |
| 2 | 1 | $R_A = [A^*]\sqrt{\frac{2}{3} D_A k_3 [A^*][B_0]}$ | $\frac{\sqrt{\frac{2}{3} D_A k_3 [A^*][B_0]}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $\frac{2}{3} D_A k_3 [A^*][B_0] >> k_L^2$ |
| 2 | 2 | $R_A = [A^*]\sqrt{\frac{2}{3} D_A k_4 [A^*][B_0]^2}$ | $\frac{\sqrt{\frac{2}{3} D_A k_4 [A^*][B_0]^2}}{k_L} << \frac{[B_0]}{Z[A^*]}$ | $\frac{2}{3} D_A k_4 [A^*][B_0]^2 >> k_L^2$ |

T 2.1.4 A Mass Transfer accompanied by a Fast Pseudo mth-Order Reaction (Regime 3)

For the extraction of Lactic acid with Alamine 336 in decanol (Wasewar et al, 2002) the rate was independent of agitation speed and phase volume. The order with respect to acid and alamine were found to be unity (m=1) and zero (n=0) respectively, by applying equation 14. For m=1 and n=0, from table T 2.1.4 A rate equation was obtained and first order rate constant, $k_1$ was calculated as 0.21 $s^{-1}$.

For the extraction of Citric acid with Alamine 336 in MIBK (Nikhade et al, 2004) the rate was independent of agitation speed and phase volume. The order with respect to both, carboxylic acid and alamine was found to be unity (m=n=1) respectively. For m=1 and n=1 rate equation was

$$R_A = lK_2[A^*][B_0] \qquad (2.1.4.16)$$

*2.1.5 Toxicity of Extractants*

The use of extractant causes the broth to go toxic for the bacteria. The toxicity caused is of two types:

i. Molecular toxicity: Dissolution in the aqueous broth

ii. Phase toxicity: Direct contact of the cell with the water-immiscible solvent phase

In phase toxicity the site of action of organic solvent is the cell membrane. The cytoplasmic membrane of bacterial cells, a phosphor-lipid bi-layer, is a matrix in which various enzymes and transport proteins are embedded. It plays a vital role in solute transport, maintaining the energy status of the cell, regulation of the intracellular environment, pressure, signal transduction and energy transducing processes. Solvents partition into and disrupt the lipid bilayer, thus compromising cell viability (Inoue and Horikoshi, 1989; Sikkema et al., 1994; Sikkema et al., 1995;) . It has been proved that it is not the chemical structure of the solvent, but the concentration to which it accumulates in the cell membrane that plays a crucial role in determining toxicity (De Bont, 1998; Isken and De Bont, 1998; Sardesai and Bhosle, 2002).

Physiological investigation of microbes has revealed a correlation between solvent toxicity and its log*P* value. The parameter log*P* is defined as the partition coefficient of the given solvent in an equimolar mixture of octanol and water [18]. The greater is the polarity; the lower is the log*P* value and the greater toxicity of the solvent. Generally, solvents with log*P* values below 4 are considered extremely toxic as their degree of partitioning into the aqueous layer (which contains cells) and from there into the lipid membrane bilayer is high. Greater is the degree of accumulation of the solvent in the membrane, higher is its toxicity (De Bont, 1998; Isken and De Bont, 1998; Sardesai and Bhosle, 2002). This toxicity can be solved by two ways:

1. Replace of the toxic solvent component with a non toxic one.

2. Add of an immiscible, biocompatible component (oils) to the medium to entrap any toxic solvent dissolving into the aqueous medium phase.

*2.1.6. Back Extraction*

Once the acid is extracted from the aqueous phase it is regenerated from the organic phase and the organic phase is recycled for further acid extraction. The various methods (King et al, 1990) used for regeneration are:

1. Acid-Base treatment
2. Distillation
3. Temperature swing
4. Diluent swing
5. Gas Anti-solvent Induced

In acid – base treatment first the acid is precipitated in form salt by addition of base and then filtered from the organic phase. The filtered salt is then treated with acid and organic acid regenerated.

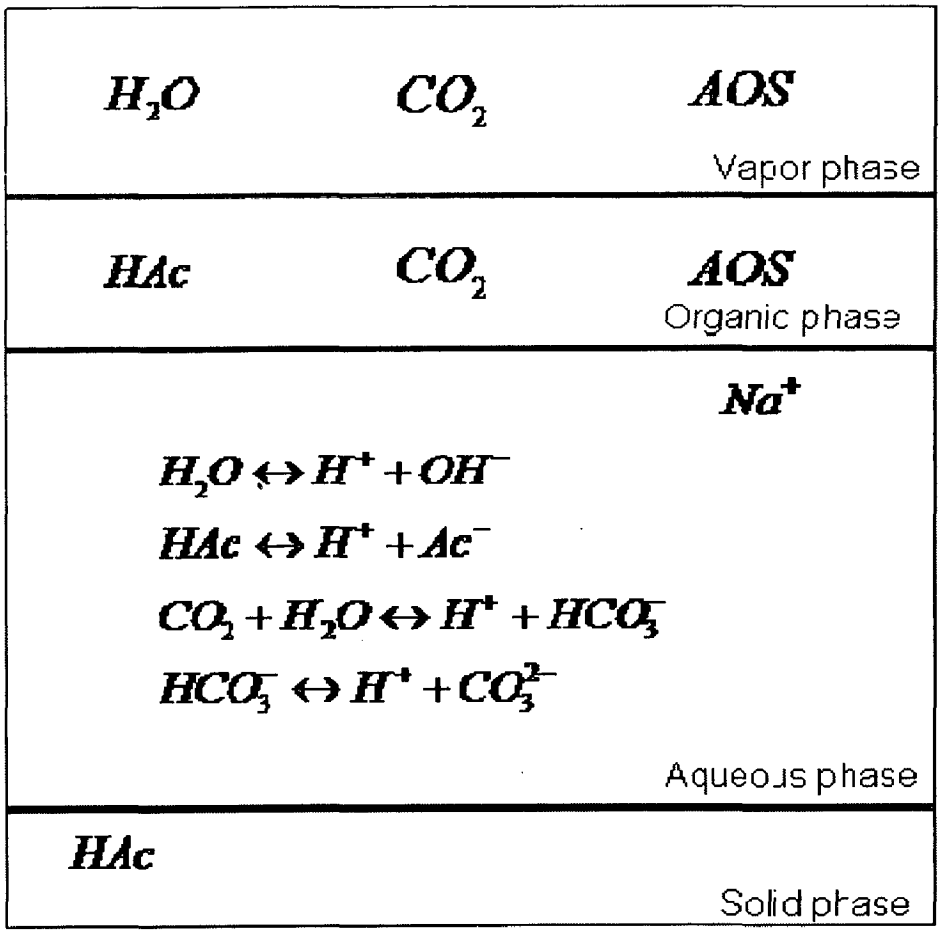
In distillation the acid is recovered from the organic phase removing the diluent in form of top product and the extractant - acid complex is the bottom product. The organic phase free from acid is recycled.

In temperature swing method, the extraction is carried out at low temperature, producing acid loaded organic extract and aqueous raffinate waste stream containing unwanted feed components. During regeneration, the extract is contacted with fresh aqueous stream at higher temperature. At this elevated temperature acid – extractant complex breaks up and the acid is released into the aqueous stream producing acid free organic phase.

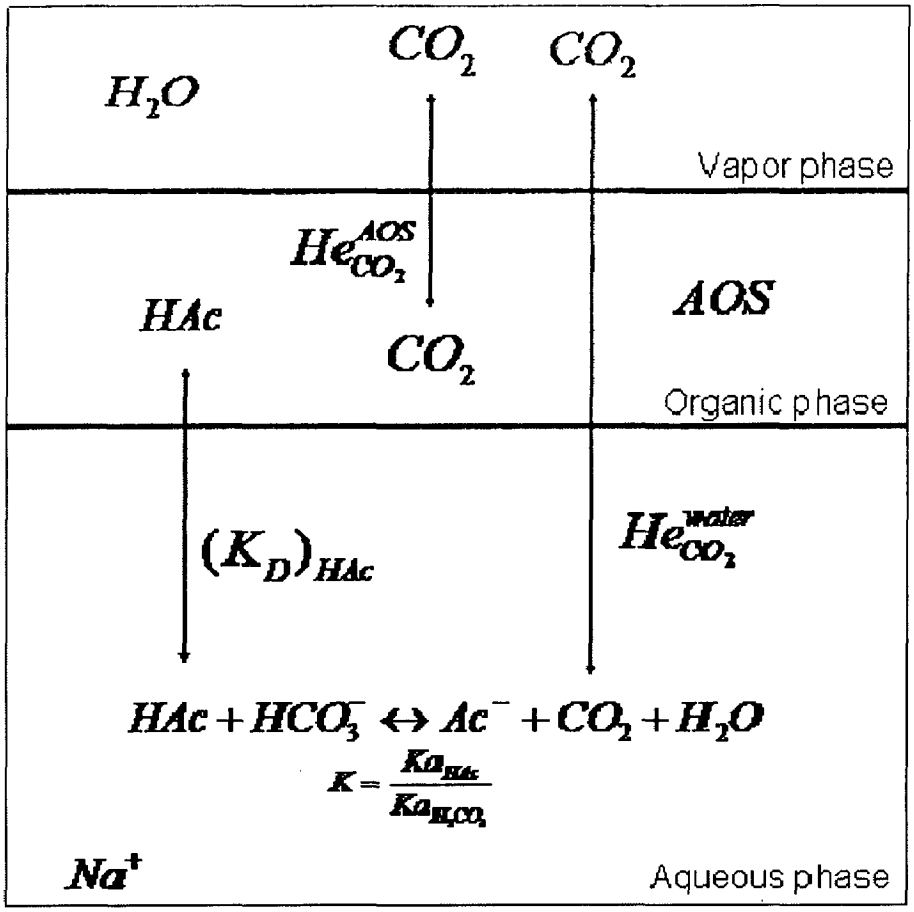
Diluent swing regeneration method is based on change in diluent composition. In this process the extraction is carried out in a solvent composed of the extractant and diluent that promotes distribution of acid in the organic phase. The composition of acid – laden organic phase leaving the extractor is then altered, by either removal of the diluent or addition of another diluent to produce a solvent system that promotes distribution of the acid to the aqueous phase. this altered organic phase is contacted with fresh aqueous stream in the regenerator to produce the acid – laden aqueous product and the acid depleted solvent for recycle to the extractor.

After extraction of the carboxylic acids from the organic phase, the carboxylate is required to be converted back into the acid. Commonly, this is done by introducing a strong mineral acid and performing back – extraction into an apolar organic solvent from which the acid is subsequently distilled. As a large scale example of such recovery, the fermentative production of lactic and citric acids can be mentioned. Although feasible, a major disadvantage of this recovery process is generation of salt which is to be removed to allow recycle of the aqueous solution in the extraction section. In the Gas Anti - solvent induced mechanism , an aqueous solution of

bicarbonate is used for the extraction of carboxylic acids, followed by back recovery of extracted acid using carbon di-oxide under pressure (Kuzmanovic, B. et al, 2005). In the extraction step, the bicarbonate salt causes dissociation of the acid where carbon di-oxide and water are formed (Fig. F 2.1.6 A), whereas in the back recovery, carbon di-oxide under shifts the carboxylic acid equilibrium towards the undissociated form generating only bicarbonate ion (Fig. F 2.1.6 B). in this way no new salts are formed, but only carbon di-oxide in the extraction and bicarbonate in the back recovery step, which can be recycled to the next recovery or extraction cycle, respectively.




F 2.1.6 A Four-phase equilibrium involving 10 species and 4 chemical equilibrium reactions in the back recovery of benzoic acid by back extraction if capacity of back extraction solvent is exceeded




F 2.1.6 B Considered equilibria in the extraction of carboxylic acids

# CHAPTER 3

## MATERIALS AND METHODS

### 3.1. Materials

Itaconic acid (HIMEDIA, India) was chemically pure laboratory grade chemical with minimum assay 99.0%. Nicotinic acid (HIMEDIA, India) was laboratory grade chemical with minimum assay 99.0%. Aliquat 336 (HIMEDIA, India) was chemically pure solution with minimum assay 80.0%. The molecular weight is 404.17 and density of 0.888gm/cm$^3$ and Tri-butyl Phosphate (HIMEDIA, India) is chemically pure solution with 99.0%. Ethyl Acetate (RANBAXY, India) is reagent grade chemical with purity 99.0%. For titrating NaOH was obtained from (S. d. fine Chemicals, India), phenolphthalein solution (pH range 8.2-10.0) was used as a indicator.

### 3.2. Experiment

The extraction experiments were carried out in 100 ml conical flasks with stopper which were placed in a temperature controlled water bath shaker (METREX SCIENTIFIC INSTRUMENTS, India). All the experiments were conducted at 305 K except for the temperature study. The ingredients of these flasks were separated using retorts after extraction was complete.

The analysis of the aqueous phase before and after extraction was performed by titrating the sample against fixed concentration of sodium hydroxide solution in duplicate. A fresh sodium hydroxide solution was prepared for every extraction experiment. The error in titration due to carbon dioxide in atmosphere was eliminated.

### 3.2. Experimental Procedure

*3.2.1. Preparation of Nicotinic and Itaconic acids Stock Solutions*

Itaconic acid obtained was in dimmer form. The acid is a dibasic acid so to prepare the acid solutions of concentrations 0.05 kmol/m3 to 0.40kmol/m$^3$, it is weighed based on its molecular weight for known volume of solutions and then verified using sodium hydroxide solution. The solutions were stored in standard flasks as stock solution.

Nicotinic acid obtained was aqueous solution with 70% concentration. The concentration was calculated in kmol/m$^3$ and then it was diluted to prepare various concentration of acid from 0.05kmol/m$^3$ to 0.140kmol/m$^3$ and verified using sodium hydroxide solution. The solutions were stored in standard flasks as stock solution.

*3.2.2. Preparation of Aqueous phase for Extraction*

The acid stock solutions were used as aqueous phase directly without any further treatment.

*3.2.3. Preparation of Organic phase for Extraction*

Organic phase of desired concentrations was prepared by well mixing the extractant with the diluents. In some of the experiments pure diluents were used alone as the organic phase.

*3.2.4. Extraction Experiment*

Equilibrium investigations were carried out by adding equal volumes (20 ml) of aqueous and organic solutions of various concentrations in the conical flasks and placed in the temperature controlled water bath shaker. The experiment was run for 6 h at 305 K and then left for attaining equilibrium for 2 h. The mixture is the transferred to retorts for separation of two phases. When a clear separation of the two phases was achieved, the lower aqueous phase was carefully pipette out and analyzed for acid concentration by titrating against standard sodium hydroxide solution. The concentration of acid in the organic phase was calculated by mass balance.

# CHAPTER 4

## RESULT AND DISCUSSION

The results of the experiments performed to describe the equilibria for acid extraction from aqueous solutions are presented and discussed in this section.

Known concentrations of aqueous and organic phases were equilibrated at constant temperature. The acid concentration in aqueous phase after extraction was analyzed and that in the organic phase was calculated. The success of extraction was quantified in terms of degree of extraction (D) defined as:

$$D = \frac{[HA]_{i,aq} - [HA]_{aq}}{[HA]_{i,aq}} x100 = \frac{[BHA]_{org}}{[HA]_{i,aq}} x100 \qquad (4.1)$$

Degree of extraction is defined in terms of concentrations since the volumes of the aqueous and organic phases are equal and assuming that they do not change after extraction, else number of moles of acid can be used. Instead of degree of extraction, fraction extracted, which is defined as the ratio of substance extracted to the total mass of substance initially present (Rice et al., 2000) can also be used.

A higher degree of extraction means that more carboxylic acid is transferred from the aqueous phase to the organic phase, which implies a successful forward extraction

The distribution coefficient, $K_D$, which is defined as the ratio of the concentrations of the carboxylic acids in the two phases, is also a measure of degree of extraction. Degree of extraction can also be calculated by distribution coefficient. The distribution coefficients are also calculated and tabulated for the experiments.

$$K_D = \frac{[BHA]_{org}}{[HA]_{aq}} \qquad (4.2)$$

$$D = \frac{K_D}{1 + K_D} x100 \qquad (4.3)$$

The loading of the extractant, Z, was defined as ratio of the total concentration of acid (in all forms) in the organic phase to the total concentration of extractant (in all forms) in the organic phase.

In the case of itaconic acid and nicotinic acid extraction from their aqueous solutions by Aliquat 336 and TBP, the loading of the extractant can be calculated as the ratio of the concentration of the acids that was calculated to be present in the organic phase

to the total concentration of extractant (Aliquat 336, TBP) in the organic phase. Loading value for all the extractions with extractants are calculated and listed in the tables together with degree of extraction and $K_D$ values.

## 4.1. Physical Extraction with pure diluents

Diluents are simple hydrocarbons that can be broadly classified into two types, inert diluents with no active functional group and active diluents with a functional group. Diluents can also be categorized based on type of functional group, into alkanes, alkenes, alcohols, ethers, esters, aromatics, alkyl-substituted aromatics, halogenated aromatics. They are generally used as second component in the reactive extraction of carboxylic acid to improve the physical properties and the extraction power of extractants. This is because the extractants are highly viscous and resist flow. Different types of diluents give large difference in the value of distribution coefficient for same acid. This is found for compounds containing the ethoxy group. Presence of more number of electronegative ethoxy groups decrease the electron donating ability of the carbonyl oxygen and diminish its lewis basicity, this serve a decrease in distribution coefficient (Wardell and King, 1978).

### *4.1.1. Diluents with functional group*

The extraction experiments were carried out by contacting organic phases composed of pure ethyl acetate aqueous phases containing itaconic acid, the concentration of itaconic acid were 0.05 – 0.4 kmol/$m^3$.The results of these experiments are given in the table T 4.1.1 A, B, C and D, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acid before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction (D) and distribution coefficient ($K_D$) are calculated from equation 4.1, 4.2. Similarly, the aqueous phases containing nicotinic acid, the concentration of nicotinic acids were 0.05 – 0.14 kmol/$m^3$.The results of these experiments are given in the table T 4.1.1 A, B, C, D and E and T 4.1.2 A, B, C, D and E which show the variation in the concentration of aqueous phase for the different initial concentrations of nicotinic acid before and after extraction.

These results are plotted in figure F 4.1.1 A, F 4.1.2 A different concentrations in aqueous phases, to observe the variation of the degree of extraction. From the plot it can be seen that degree of extraction with ethyl acetate, toluene, hexane, kerosene oil and sunflower oil. It is observed that the ethyl acetate giving higher degree of extraction as compared with toluene, hexane, kerosene oil and sunflower oil. This is in consistent with the previous literature which explains it based on the functional group of the diluent. The toluene gives less degree of extraction, since it is having a benzene ring structure. The alkyl group present in toluene is having more electronegativity, the

distribution coefficient decreases (Ketest, A. S., 1986). The hexane and kerosene are the inert compounds. The hexane is a straight chain aliphatic compound and kerosene is a mixture of carbon atoms ($C_9 - C_{16}$). These compounds are having the low tendency for degree of extraction and distribution coefficient compared to ethyl acetate. Sunflower oil is mixture of fatty acids (lenoleic, oleic, palmitic, stearic, alpha lenoleic acids) and fatty acids have alkoxy group so, has higher electronegetivity compared to kerosene, which is mixture of alkanes. This is in consistent with the previous literature which explains it based on the number of alkoxy groups the diluent.

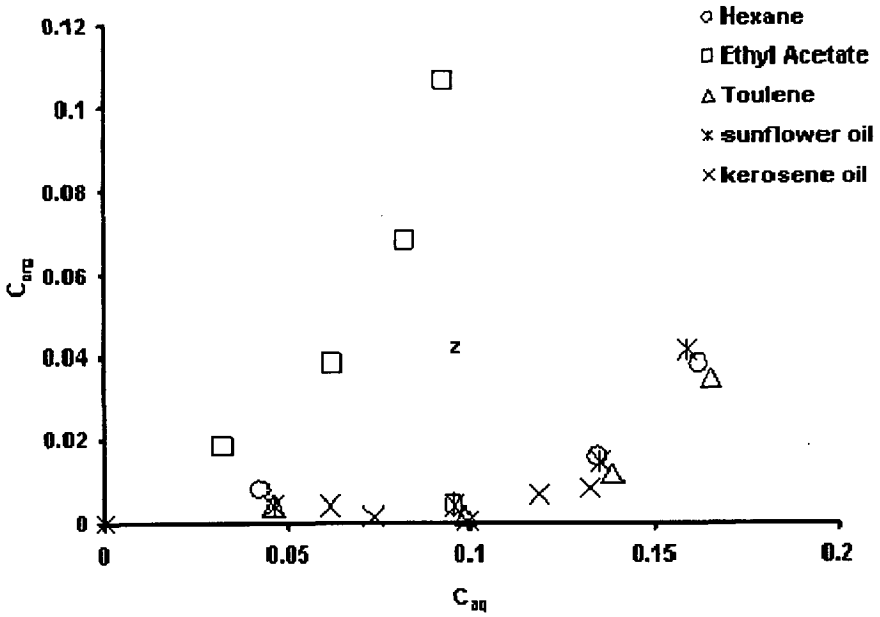



Fig. F 4.1.1 A: Equilibrium isotherm of Itaconic acid in pure diluents

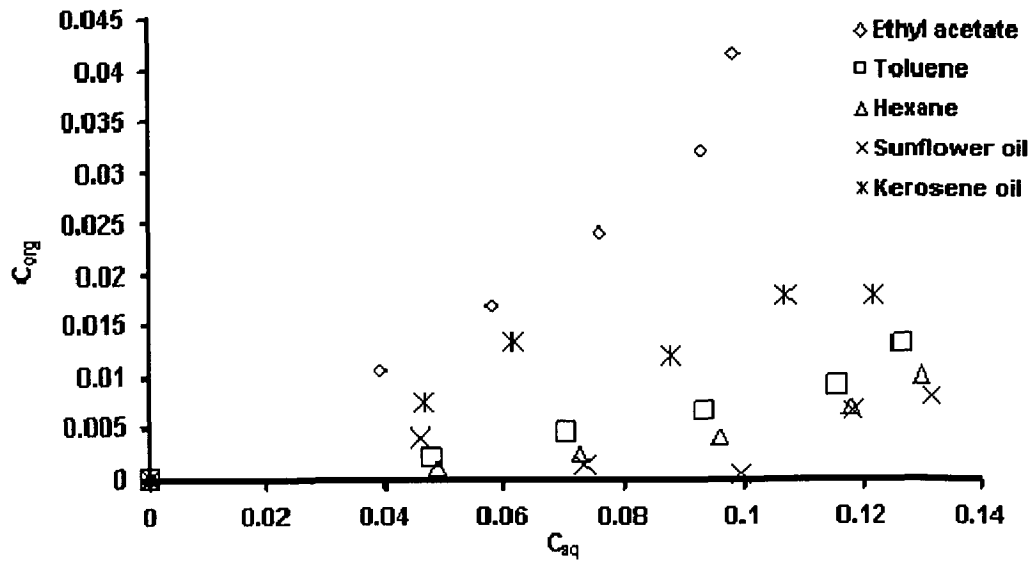



Fig. F 4.1.2 A: Equilibrium isotherm of Nicotinic acid s in pure diluents

4.2. Chemical Extraction with Aliquat 336 dissolved in diluents

Extraction of proton baring organic and inorganic compounds from aqueous media by long chain aliphatic amines dissolved in water immiscible organic solvents is one of the new developments in separation technology. The extractability of acids, in contrast to that of anionic acidic metal complexes, depends more on the composition of the organic phase, amine, and the diluent than on the aqueous phase conditions. The requirements for practical extraction applications are rather general for both weak and strong acids and are fairly well described in the chemical literature.

The fundamental difference between oxygen and nitrogen bearing basic extractants as far as the acid extraction is concerned is the behavior of acid proton during the transfer from an aqueous phase into an organic solution. In case of systems with oxygen-bearing solvents, whether carbon, phosphorus, or sulfur bond, the acid strength in the aqueous solution and that of the hydrogen bond in the organic solution are the measures of extractability. On the other hand, the acid extracted into an amine containing in the organic phase is no longer regarded as an acid but an ammonium salt. It is thus the extent of ion pair association between the alkyl-ammonium cation and the acid radical that is the measure of extractability, or more precisely, the stability of the organic phase species.

Thus the extraction process is based on an acid-base reaction between the alkylamine, R, and the acid, HA:

$$HA_{(w)} + R_{(o)} \leftrightarrow RHA_{(o)} \qquad (4.2.1)$$

$$K_E = \frac{[RHA]_{(o)}}{[HA]_{(w)}[R]_{(o)}} \qquad (4.2.2)$$

Where $[HA]_{(w)}$ is calculated from $C_{HA(w)}$ and the dissociation constant of the acid. Because of the usually high extractability of the acids by all alkylamine extractants, the equilibrium constant $K_E$ depends on the nature of the diluent more than the other extraction systems.

A striking behavior of acid-amine extraction systems is that the organic phase is capable of taking up acid in excess of that necessary for the stoichiometric neutralization of the amine base. This has been shown to be the case of some of the monocarboxylic, but not dicarboxylic, acids under consideration. Though the exact nature of chemistry involved in the uptake of extra acid is not known, and in spite of the obvious non ideality of the organic phase under these conditions, distribution data have been interpreted in terms of simple mass action equations of the type

$$RHA_{(o)} + nHA_{(w)} \leftrightarrow RHA(HA)_{n(o)}$$

$$K_{En} = \frac{[RHA(HA)_{n(o)}]}{[RHA]_{(o)}[HA]^{n}_{(w)}} \qquad (4.2.3)$$

The extent to which the organic phase can be loaded with acid is expressed as the loading factor Z. When the diluent used has an acid interaction functional group or a solvent that dissolves the acid to a considerable extent, $C_{HA(w)}$ should be corrected for the acid extracted into the diluent alone. The value of Z depends on extractability of the acid (strength of acid-base interaction) and its aqueous phase concentration and is independent of amine content in an inert diluent. If the organic phase is not highly concentrated (Z<0.5), the constant $K_s$ can be expressed via the experimental accessible loading ratio

$$\frac{Z}{(1-Z)} = K_E[HA]_{(w)} \qquad (4.2.4)$$

and the quasi-ideal behavior of the system can be demonstrated by a linear plot of Z/(1-Z) against $[HA]_{(w)}$, the slope yielding $K_E$.

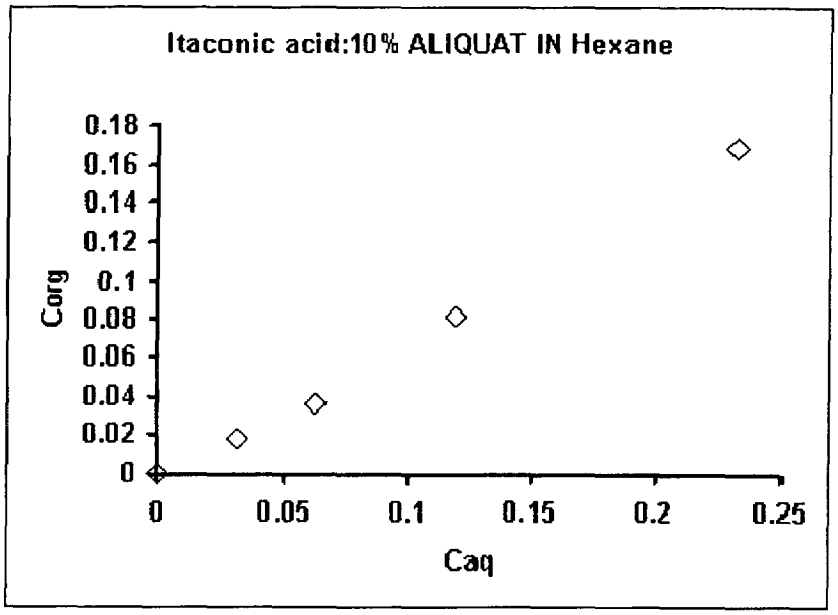
*4.2.1 Extraction with Aliquat 336 dissolved in Hexane*

The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in Hexane at various concentrations; with aqueous phases containing itaconic acid at concentration 0.05 – 0.4 kmol/$m^3$ and nicotinic acid at 0.05-14 kmol/$m^3$. The results of these experiments are given in the table T 4.2.1 A and T 4.2.1 B which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic and nicotinic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 4.2.4

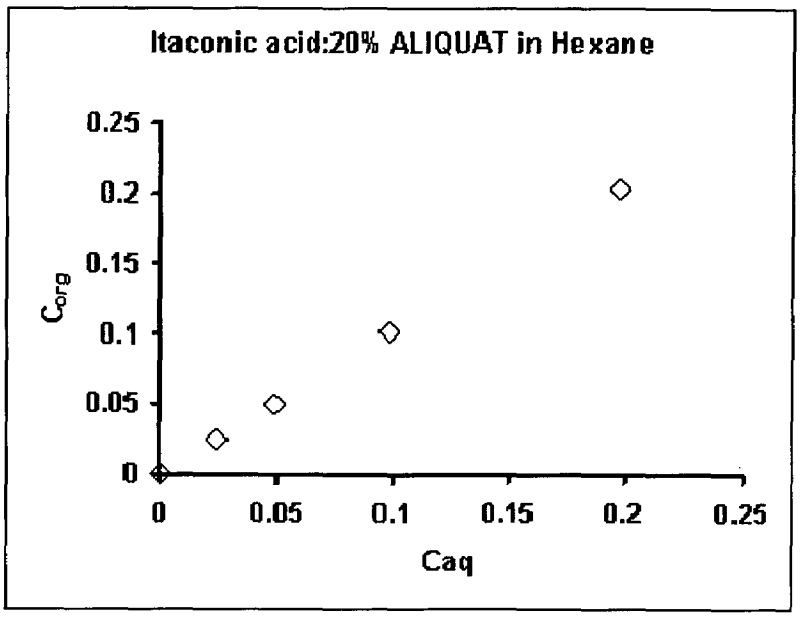
These results are plotted in figure F 4.2.1 A, B, C,D and F 4.2.2 A, B, C,D different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that on increase in extractant concentration there is a decrease in degree of extraction for both the acids. In the extraction of itaconic and nicotinic acids it can be observed that the loading factor reduces with increase in extractant concentration for a particular acid concentration. Systems that include diluent specifically in the complex stoichiometry show this kind of behavior (Tamada et al. 1990a). In case of both the acids, when the acid concentration is increased there is decrease in degree of extraction. The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of Z/(1-Z) Vs. $C_{aq}$ was

obtained by fitting a straight line through origin according to the equation 4.2.4. The $K_{11}$ for itaconic and nicotinic acids are 4.1833 and 0.6562 respectively.

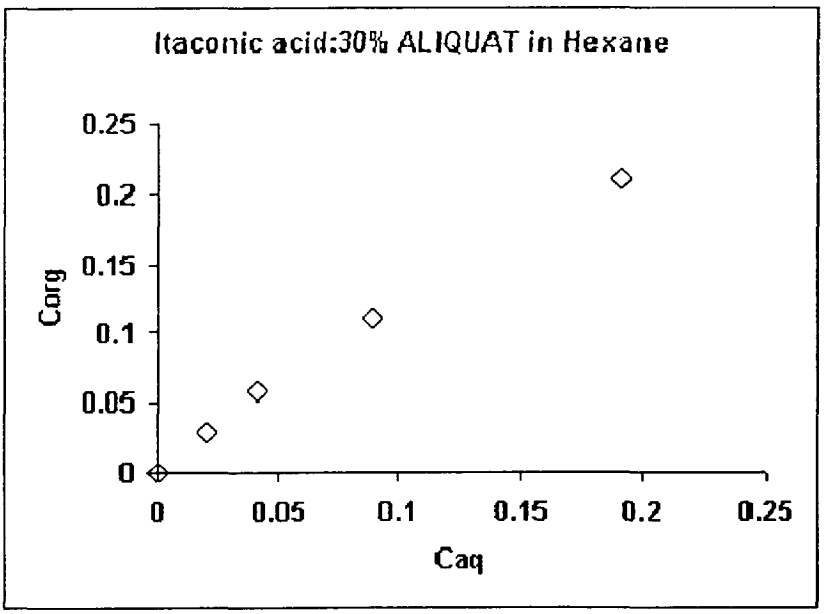
Plots for Itaconic acids



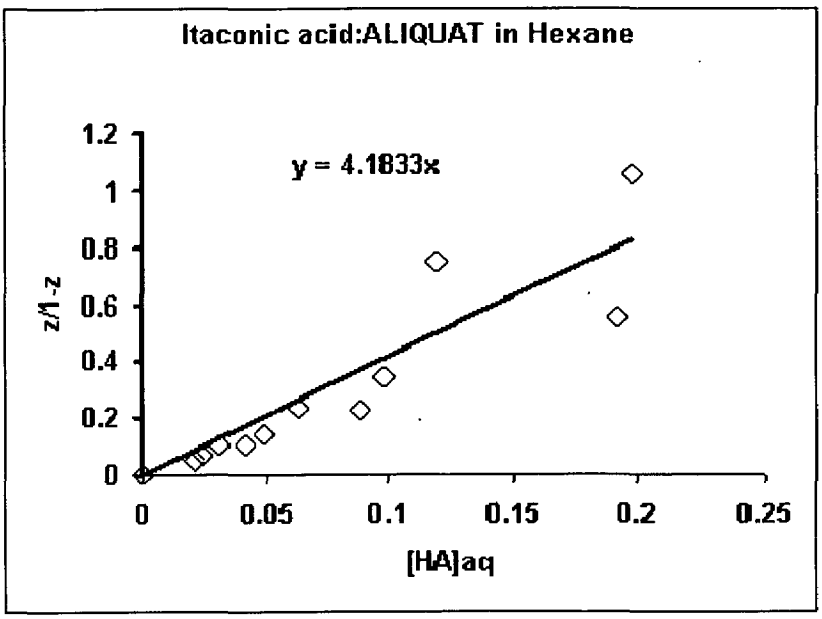

F 4.2.1 A Equilibrium isotherm of Itaconic acid with 10% Aliquat 336 in Hexane




F 4.2.1 B Equilibrium isotherm of with Itaconic acid 20% Aliquat 336 in Hexane

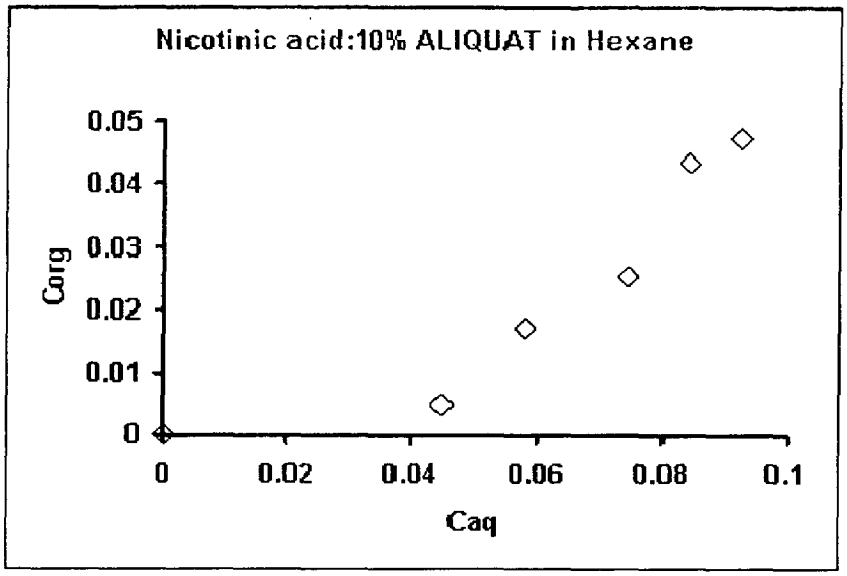



F 4.2.1 C Equilibrium isotherm of with Itaconic acid 30% Aliquat 336 in Hexane

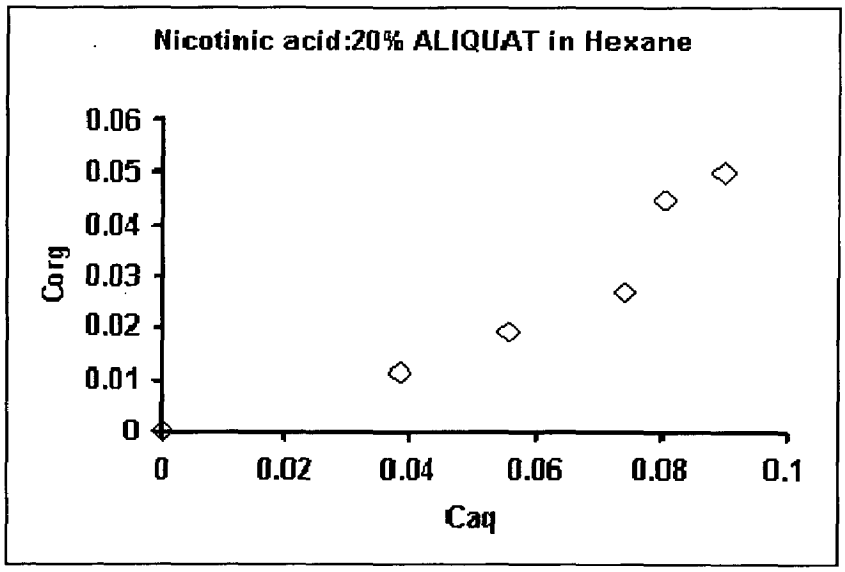



F 4.2.1 D Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with Hexane as the diluent

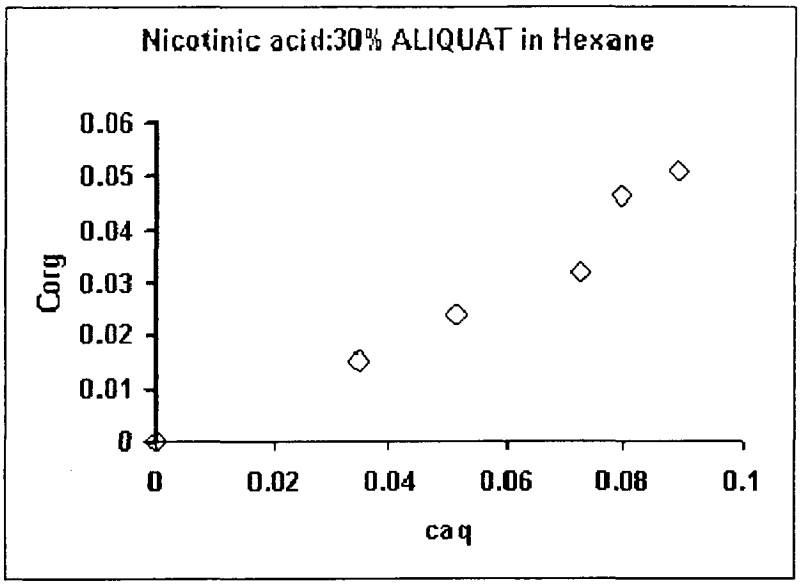
Plots for Nicotinic acid



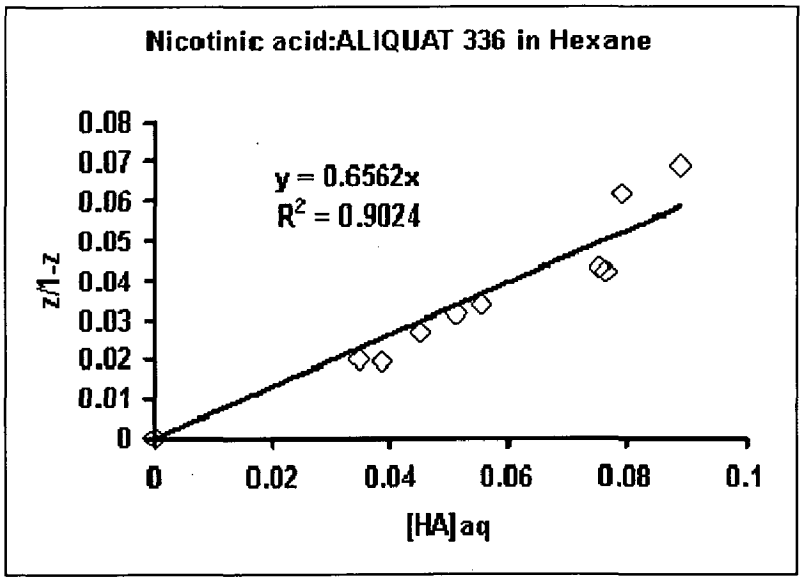

F 4.2.2 A Equilibrium isotherm of Nicotinic acid with 10% Aliquat 336 in Hexane




F 4.2.2 B Equilibrium isotherm of Nicotinic acid with 20% Aliquat 336 in Hexane




F 4.2.2 C Equilibrium isotherm of Nicotinic acid with 30% Aliquat 336 in Hexane



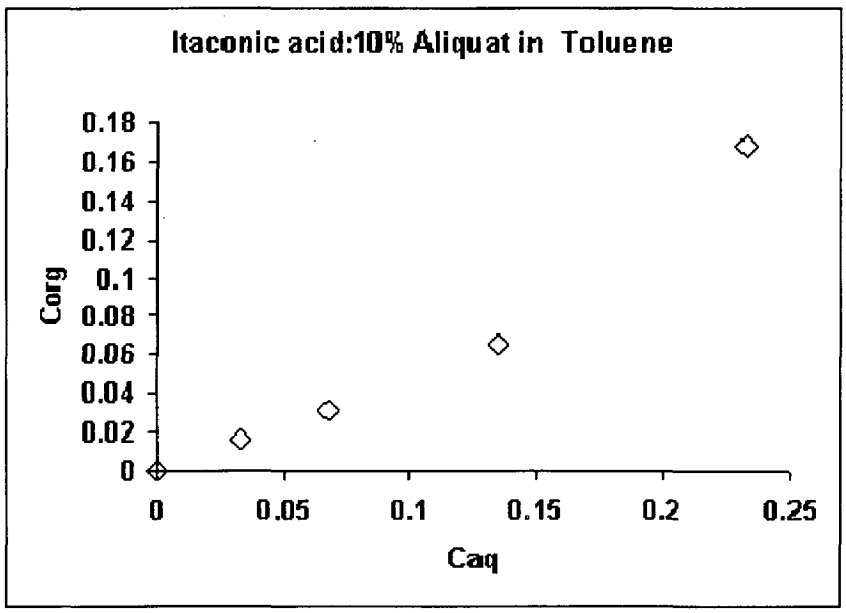

F 4.2.2 D Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with Hexane as the diluent

*4.2.3 Extraction with Aliquat 336 dissolved in Toluene*

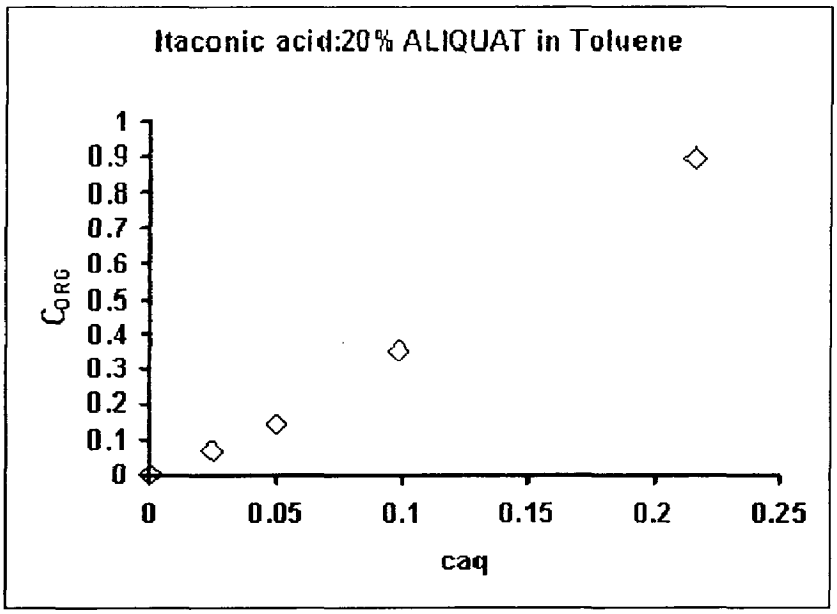
The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in oleyl alcohol at various concentrations; with aqueous phases containing itaconic acid and nicotinic acids at concentration 0.05 – 0.4 kmol/$m^3$. The results of these experiments are given in the table T 4.2.2 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acid and nicotinic acids

before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 4.2.4

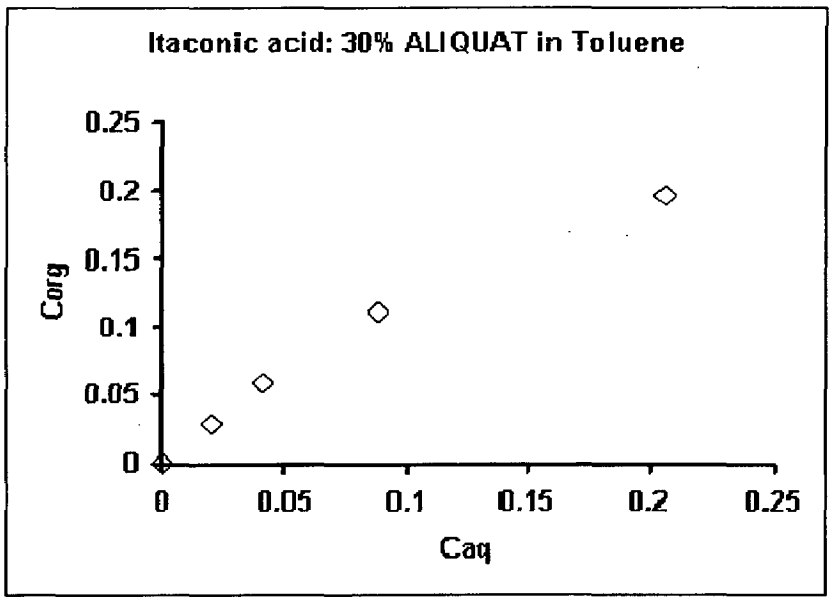
These results are plotted in figure F 4.2.2 A, B and C different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for itaconic acid on increase in extractant concentration there is a low increase in degree of extraction but is converse for nicotinic acid. The toluene is alkylated aromatic group. The extraction for both the acids is low, since it has pi bonds, due to this the electronegativity increases, the extraction decreases. In the extraction of itaconic acid and nicotinic acids it can be observed that the loading factor reduces with increase in extractant concentration for a particular acid concentration. Systems that include diluent specifically in the complex stoichiometry show this kind of behavior (Tamada et al. 1990a). In case of both the acids, when the acid concentration is increased there is an increase in degree of extraction. The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of Z/(1-Z) Vs. $C_{aq}$ was obtained by fitting a straight line through origin according to the equation 4.2.4. The $K_{11}$ for itaconic acid and nicotinic acid are 3.3456 and 0.9415 respectively.



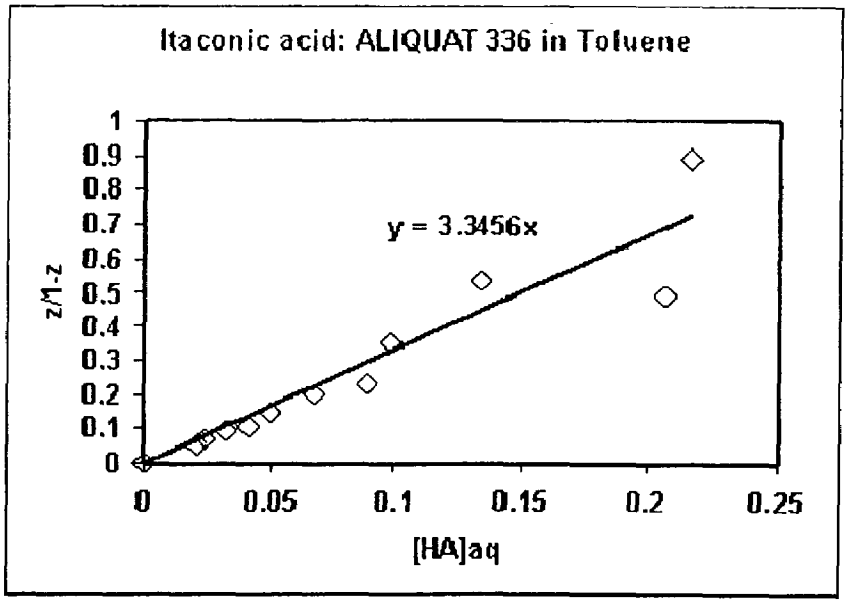

F 4.2.3 A Equilibrium isotherm of Itaconic acid with 10% Aliquat 336 in Toluene



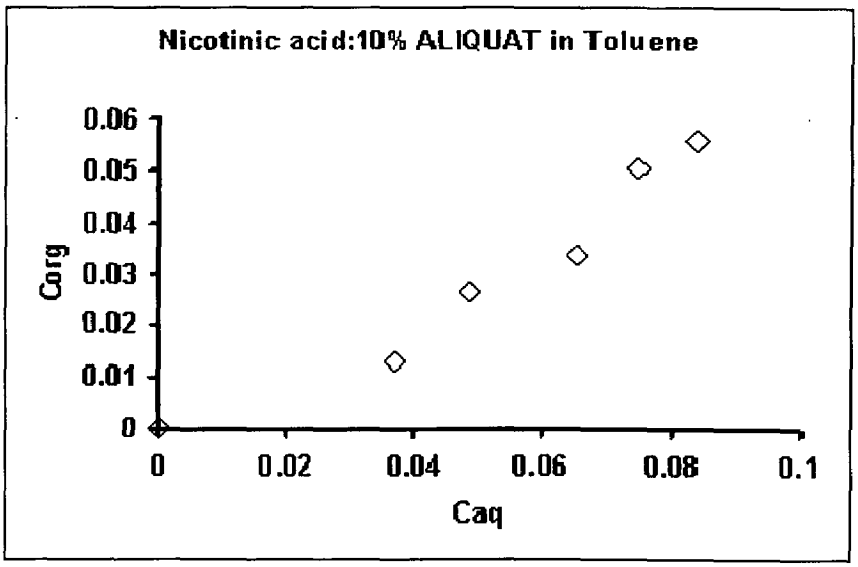

F 4.2.3 B Equilibrium isotherm of Itaconic acid with 20% Aliquat 336 in Toluene



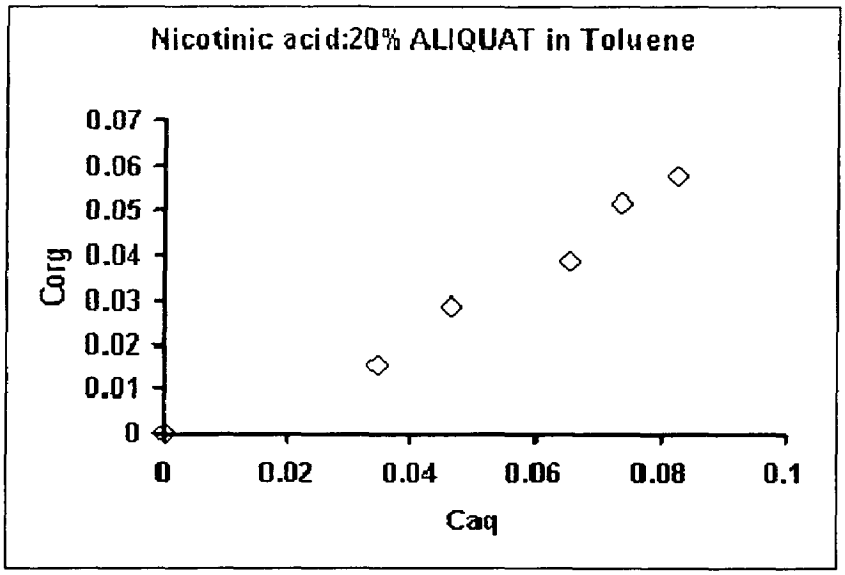

F 4.2.3 C Equilibrium isotherm of Itaconic acid with 30% Aliquat 336 in Toluene



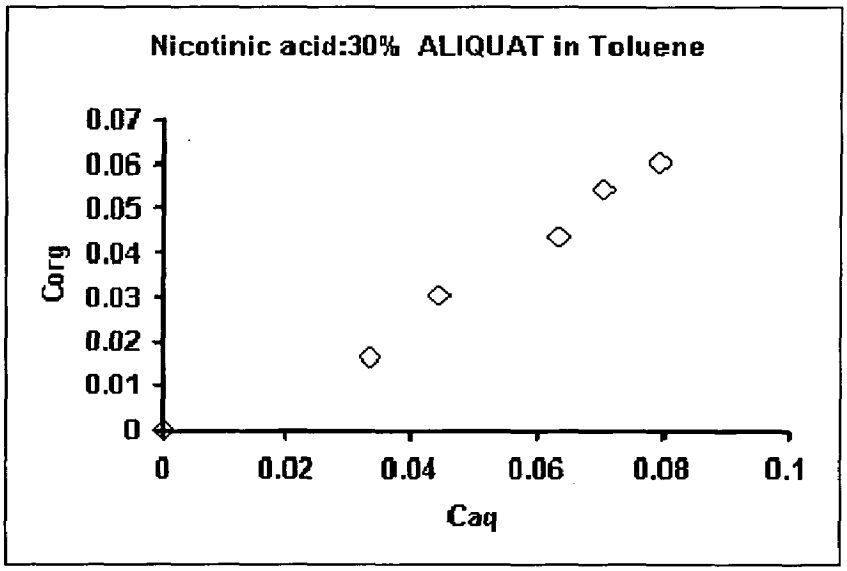

F 4.2.3 D Plot of $Z/(1-Z)$ versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with Toluene as the diluent



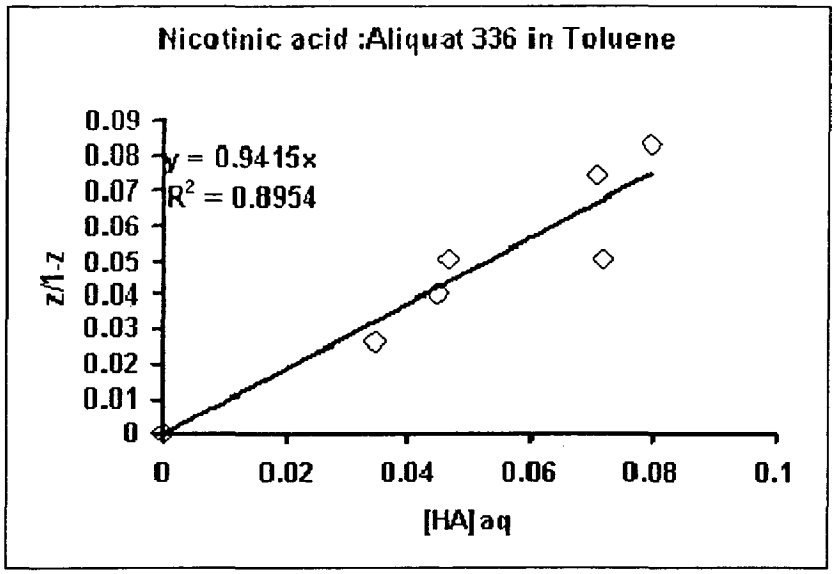

F 4.2.3 A Equilibrium isotherm of Nicotinic acid with 10% Aliquat 336 in Toluene




F 4.2.4 B Equilibrium isotherm of Nicotinic acid with 20% Aliquat 336 in Toluene




F 4.2.4 C Equilibrium isotherm of Nicotinic acid with 30% Aliquat 336 in Toluene



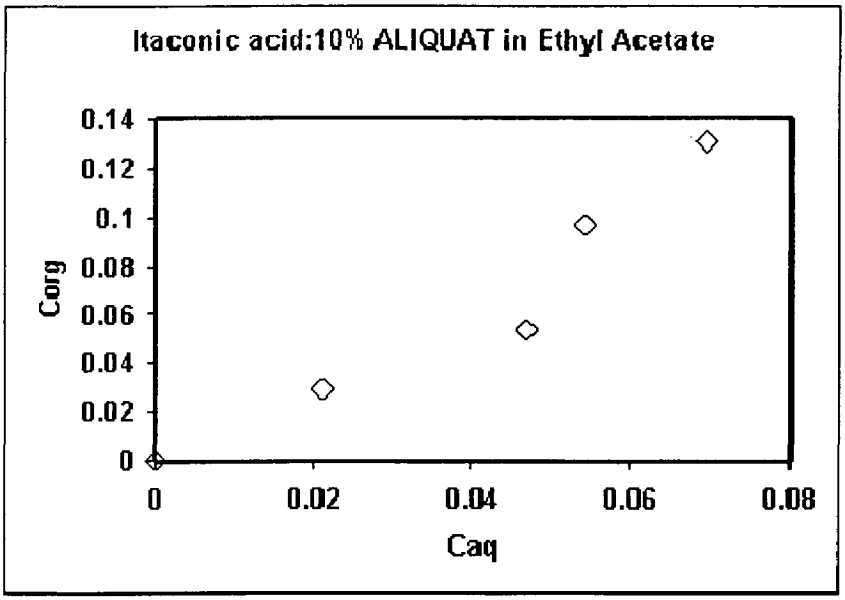

F 4.2.4 D Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with Toluene as the diluent

*4.2.3 Extraction with Aliquat 336 dissolved in Ethyl acetate*

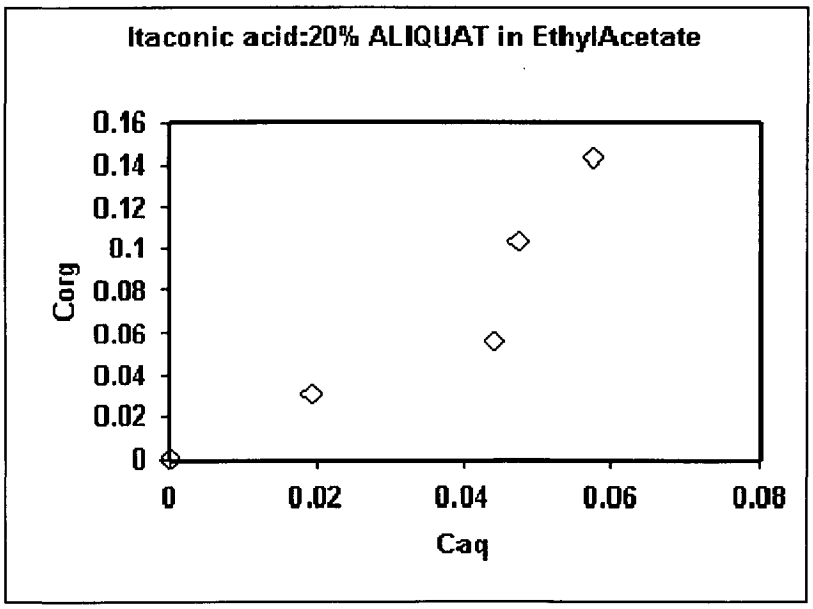
The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in ethyl acetate at various concentrations; with aqueous phases containing itaconic acid and nicotinic acids at concentration 0.05 – 0.4 kmol/$m^3$. The results of these experiments are given in the table T 4.2.3 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acidand nicotinic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 4.2.4

These results are plotted in figure F 4.2.3 A, B, C and D different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for itaconic acid and nicotinic acid on increase in extractant concentration there is an increase in degree of extraction. In the extraction of itaconic acid and nicotinic acids it can be observed that the loading factor reduces with increase in extractant concentration for a particular acid concentration. Systems that include diluent specifically in the complex stoichiometry show this kind of behavior (Tamada et al. 1990a). In case of both the acids, when the acid concentration is increased there is a decrease in degree of extraction. The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of Z/(1-Z) Vs. $C_{aq}$ was obtained by fitting a straight line through origin according to the

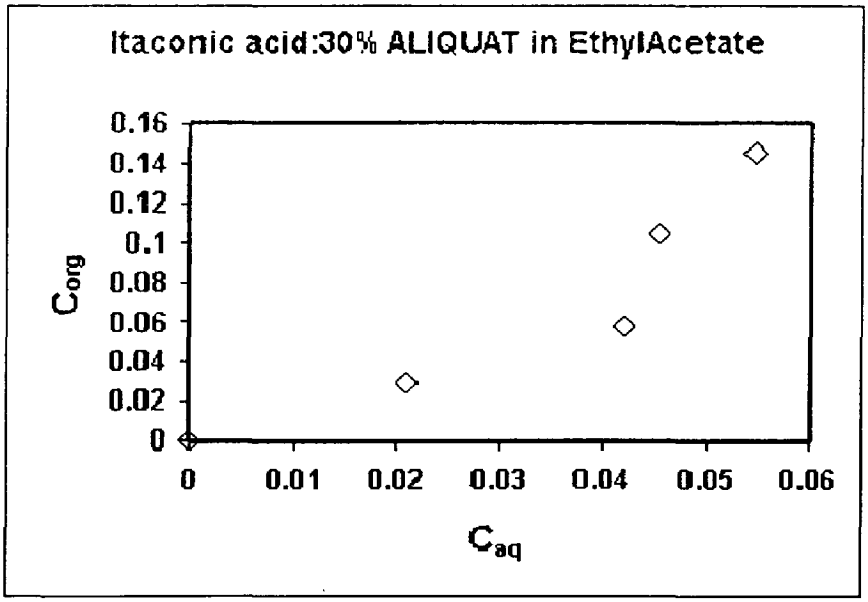
equation 4.2.4. The $K_{11}$ for itaconic acid and nicotinic acid are 5.4866 and 5.8792 respectively.



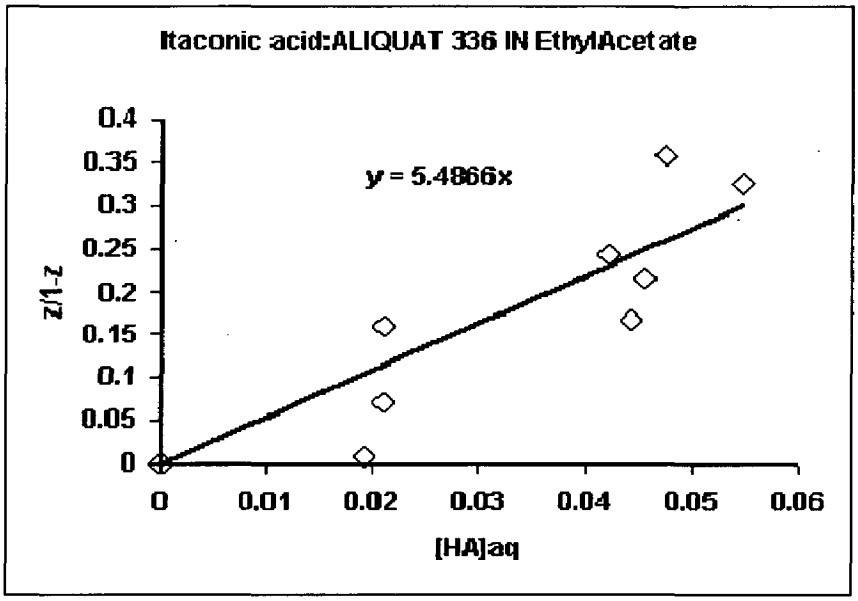

F 4.2.3 A Equilibrium isotherm of Itaconic acid with 10% Aliquat 336 in ethyl acetate



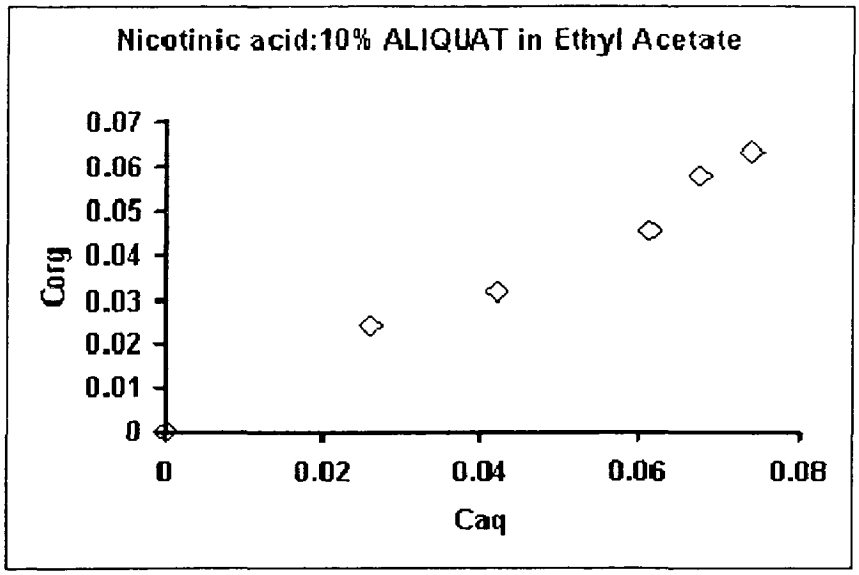

F 4.2.3 B Equilibrium isotherm of Itaconic acid with 20% Aliquat 336 in ethyl acetate



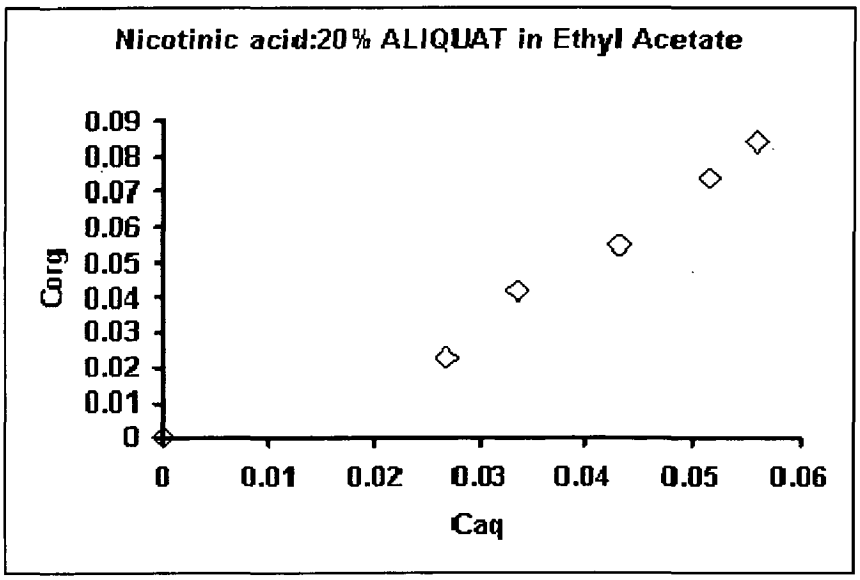

F 4.2.3 C Equilibrium isotherm of Itaconic acid with 30% Aliquat 336 in ethyl acetate



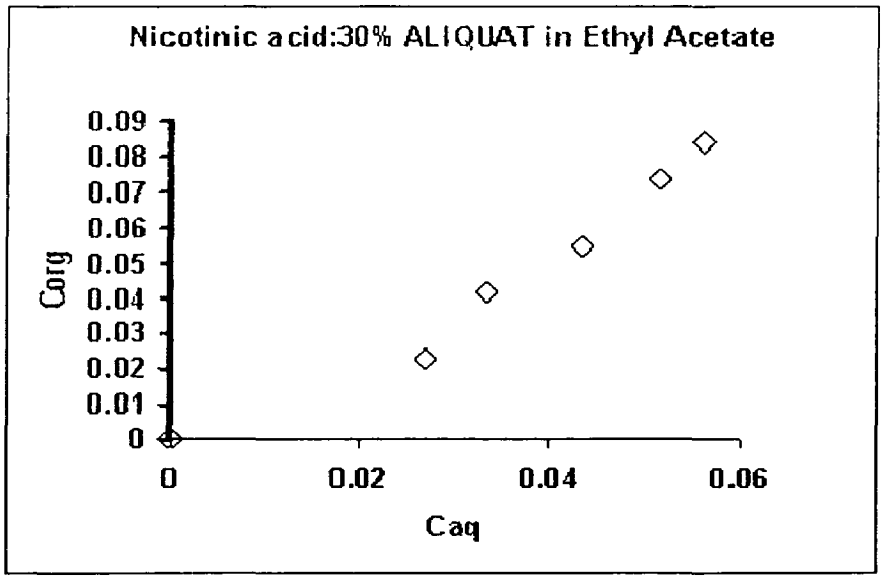

F 4.2.3 D Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with ethyl acetate as the diluent



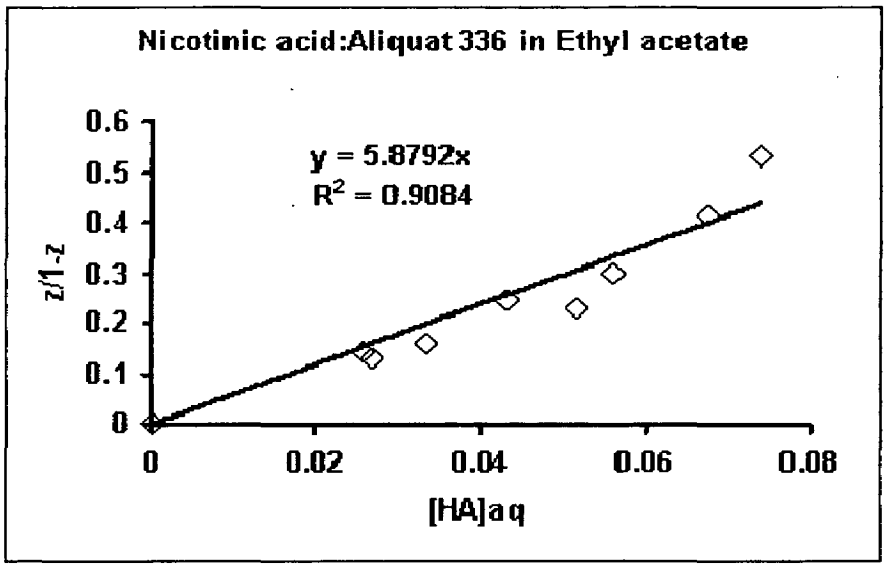

F 4.2.3 E Equilibrium isotherm of Nicotinic acid with 10% Aliquat 336 in ethyl acetate




F 4.2.3 F Equilibrium isotherm of Nicotinic acid with 20% Aliquat 336 in ethyl acetate




F 4.2.3 G Equilibrium isotherm of Nicotinic acid with 30% Aliquat 336 in ethyl acetate




F 4.2.3 H Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with ethyl acetate as the diluent

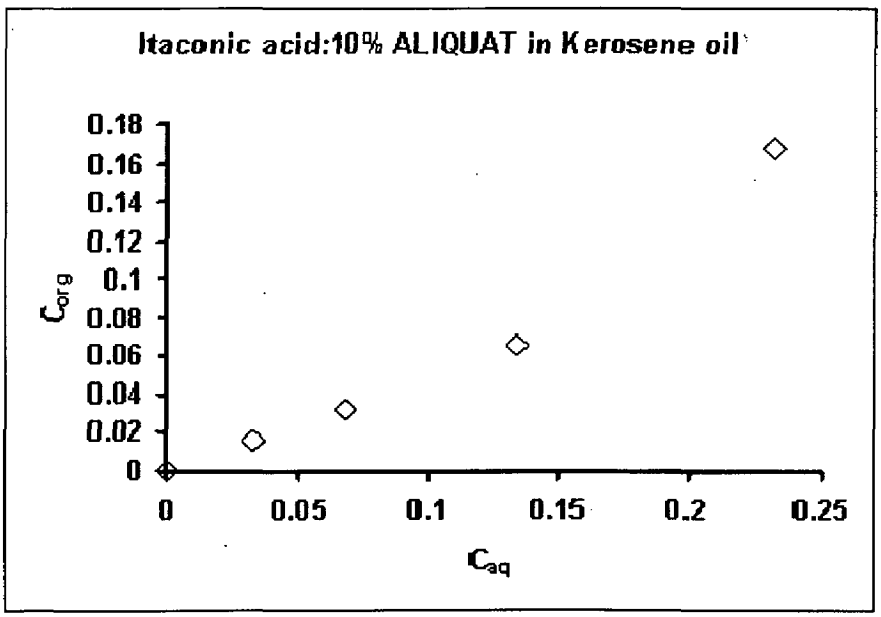
*4.2.4 Extraction with Aliquat 336 dissolved in kerosene oil*

The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in kerosene at various concentrations; with aqueous phases containing itaconic acid and nicotinic acids at concentration 0.05 – 0.4 kmol/$m^3$. The results of these experiments are given in the table T 4.2.4 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acid and nicotinic acids before and after extraction. The difference between the two is calculated to be the organic

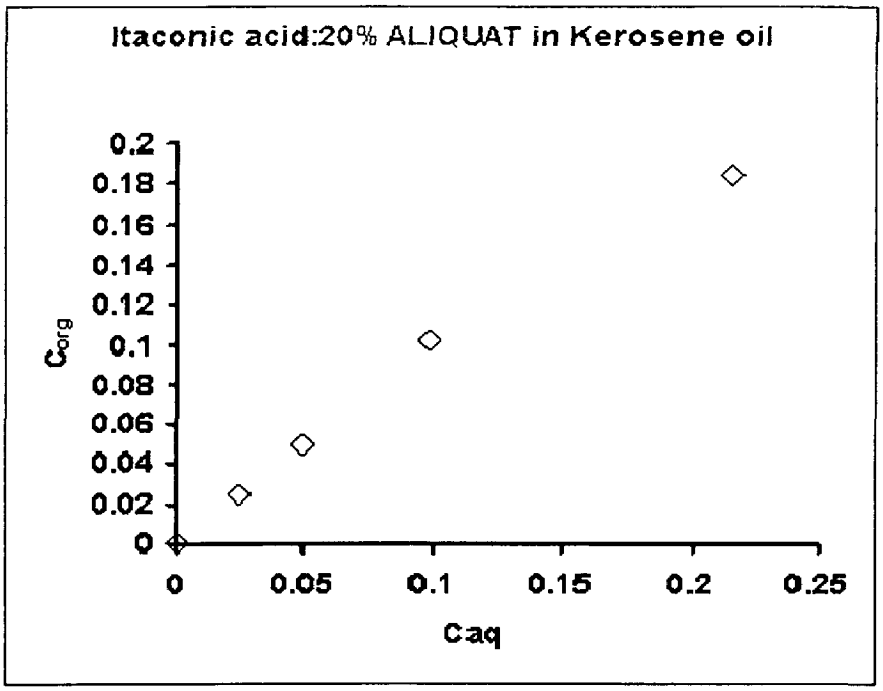
phase acid concentration, from the mass balance. The degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 4.2.4

These results are plotted in figure F 4.2.4 A, B, C and D different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for itaconic acid and nicotinic acid on increase in extractant concentration there is an increase in degree of extraction. In the extraction of itaconic acid and nicotinic acids it can be observed that the loading factor reduces with increase in extractant concentration for a particular acid concentration. Systems that include diluent specifically in the complex stoichiometry show this kind of behavior (Tamada et al. 1990a). In case of both the acids, when the acid concentration is increased there is no regular pattern in degree of extraction. The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of Z/(1-Z) Vs. $C_{aq}$ was obtained by fitting a straight line through origin according to the equation 4.2.4

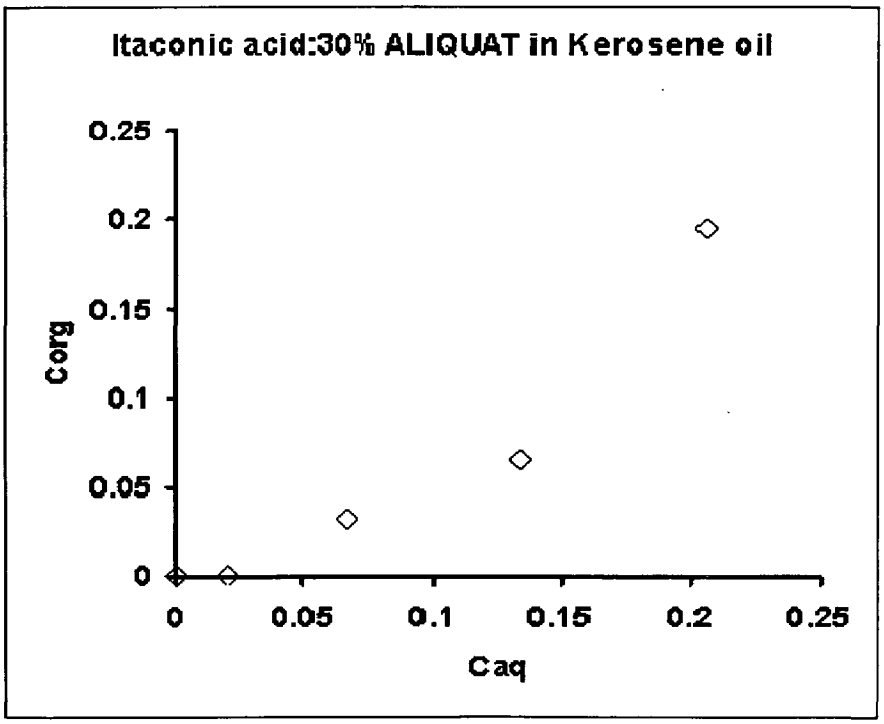
The $K_{11}$ for itaconic acid and nicotinic acid are 3.022 and 0.6666 respectively.



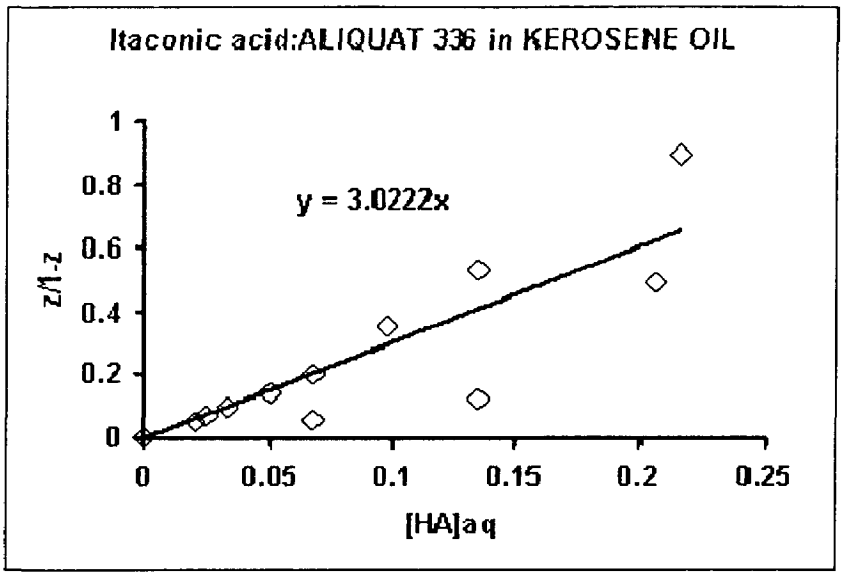

F 4.2.4 A Equilibrium isotherm of Itaconic acid with 10% Aliquat 336 in kerosene oil



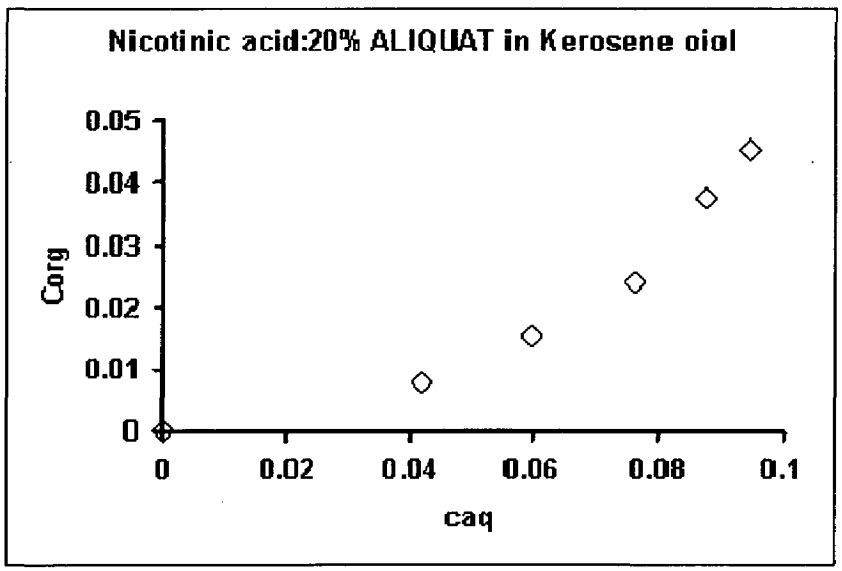

F 4.2.4 B Equilibrium isotherm of Itaconic acids with 20% Aliquat 336 in kerosene oil



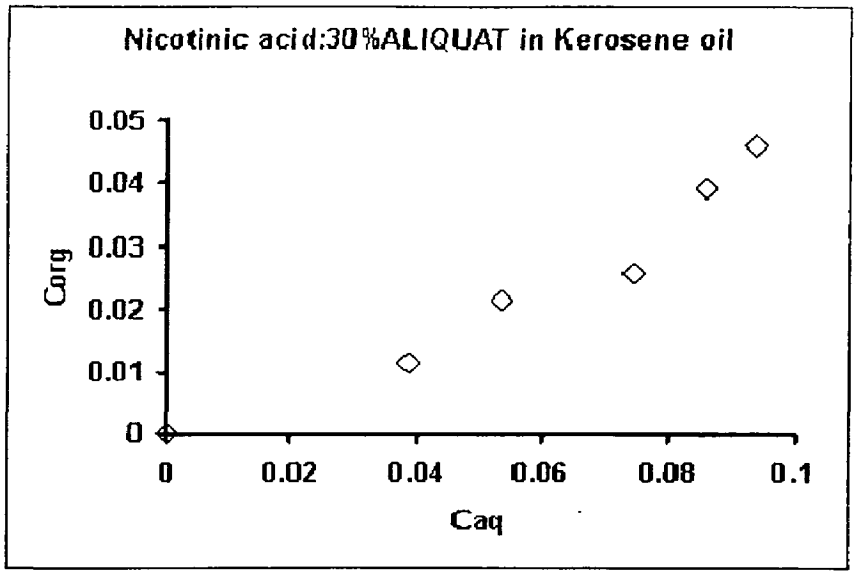

F 4.2.4 C Equilibrium isotherm of Itaconic acid with 30% Aliquat 336 in kerosene oil



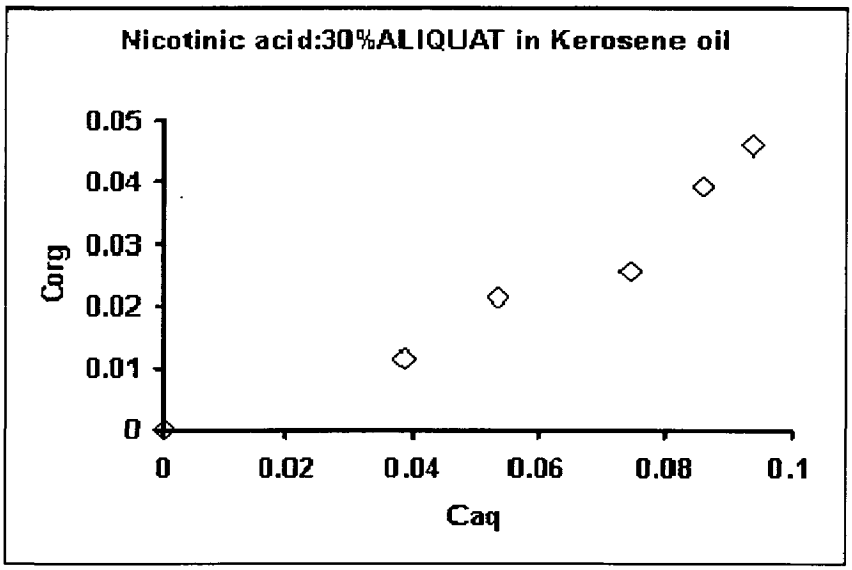

F 4.2.4 D Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with kerosene oil as the diluent



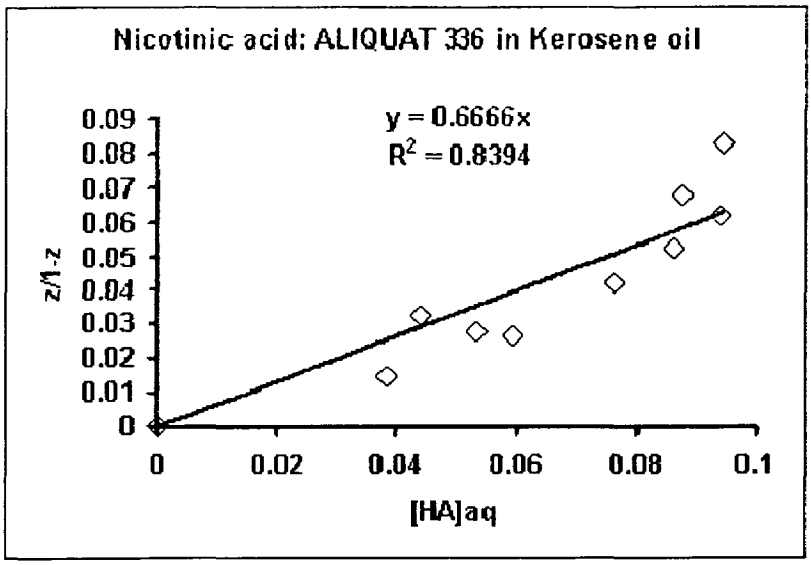

F 4.2.4 E Equilibrium isotherm of Nicotinic acid with 10% Aliquat 336 in kerosene oil




F 4.2.4 F Equilibrium isotherm of Nicotinic acid with 20% Aliquat 336 in kerosene oil




F 4.2.4 G Equilibrium isotherm of Nicotinic acid with 30% Aliquat 336 in kerosene oil



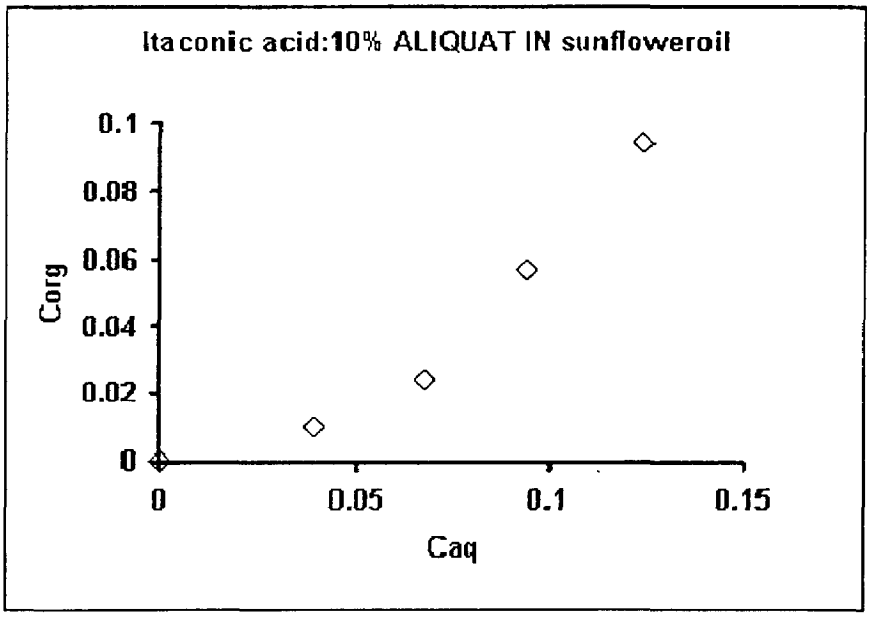

F 4.2.4 H Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with kerosene oil as the diluent

*4.2.5 Extraction with Aliquat 336 dissolved in sunflower oil*

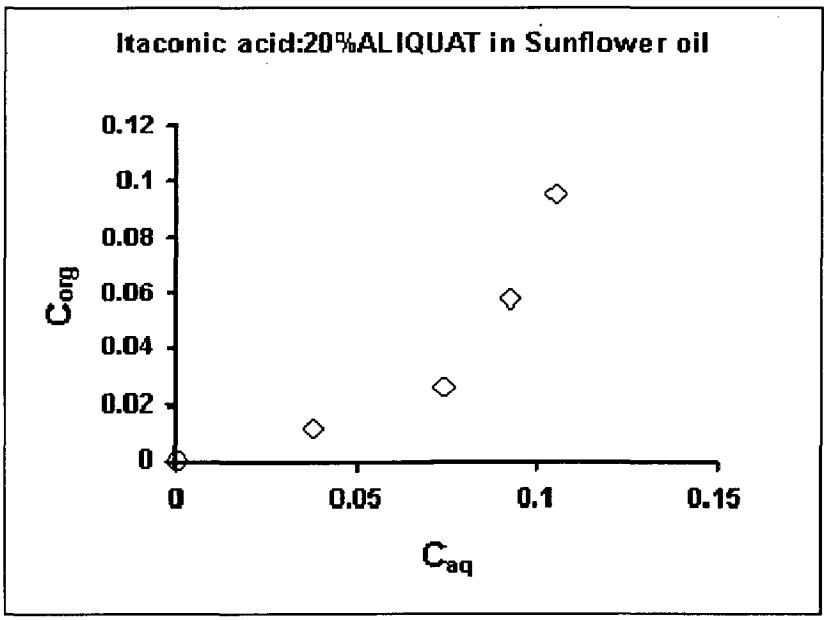
The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in sunflower oil at various concentrations; with aqueous phases containing itaconic acid and nicotinic acids at concentration 0.05 – 0.4 kmol/$m^3$. The results of these experiments are given in the table T 4.2.5 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acid and nicotinic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 4.2.4

These results are plotted in figure F 4.2.5 A, B and C different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for itaconic acid on increase in extractant concentration there is an increase in degree of extraction and decrease in loading factor but in case nicotinic acid both, degree of extraction and loading factor, decrease from this it can be concluded that for extracting itaconic acid and nicotinic acid mixture use of high aliquat 336 concentration is favorable. Systems that include diluent specifically in the complex stoichiometry show decrease in loading factor with amine extractant concentration (Tamada et al. 1990a). In case itaconic acid when the acid concentration is increased there is a decrease in degree of extraction but, for nicotinic acid its increases initially and then decreases. The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of Z/(1-Z) Vs. $C_{aq}$ was obtained by fitting

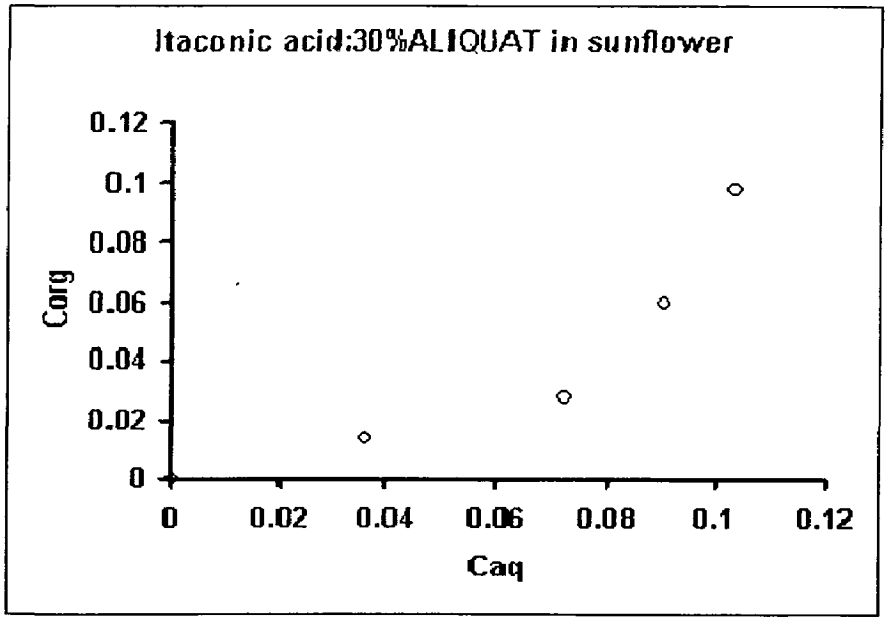
a straight line through origin according to the equation 4.2.4.The $K_{11}$ for itaconic acid and nicotinic acid are 2.9734 and 0.9465 respectively.



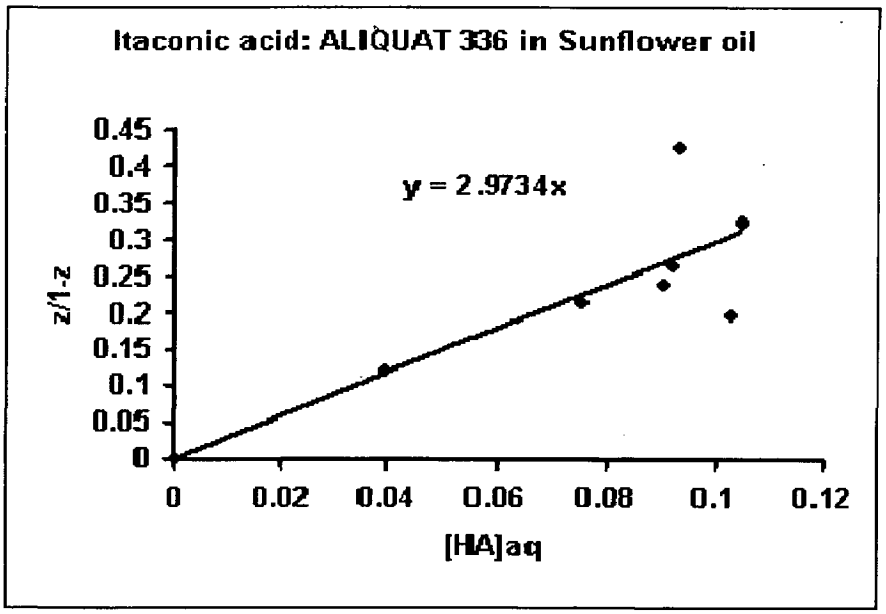

F 4.2.5 A Equilibrium isotherm of Itaconic acid with 10% Aliquat 336 in sunflower oil



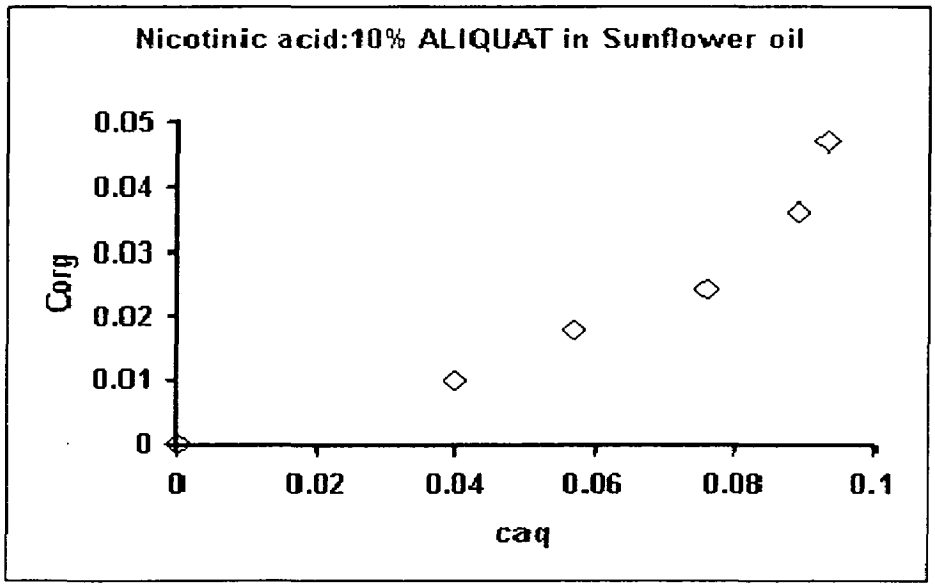

F 4.2.5 B Equilibrium isotherm of Itaconic acid with 20% Aliquat 336 in sunflower oil



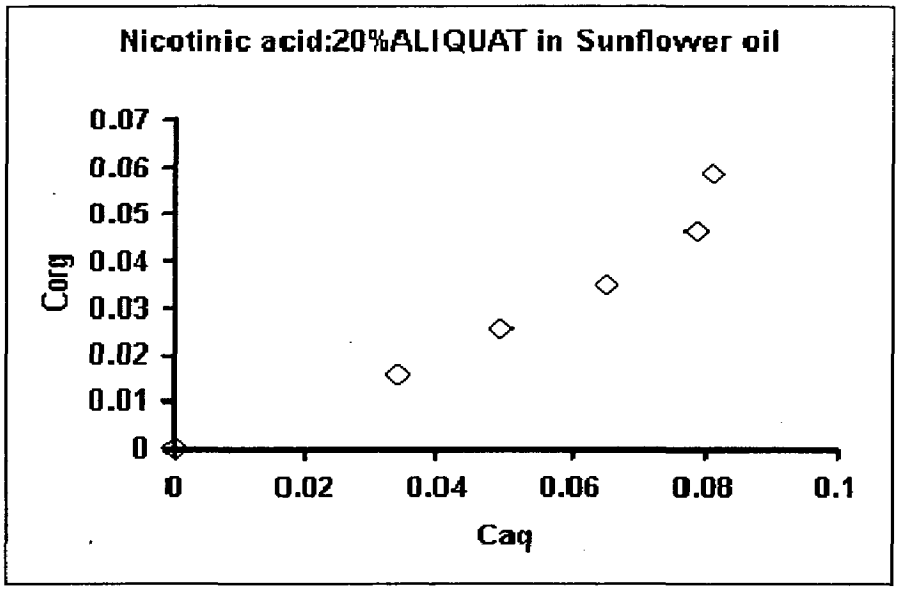

F 4.2.5 C Equilibrium isotherm of Itaconic acid with 30% Aliquat 336 in sunflower oil



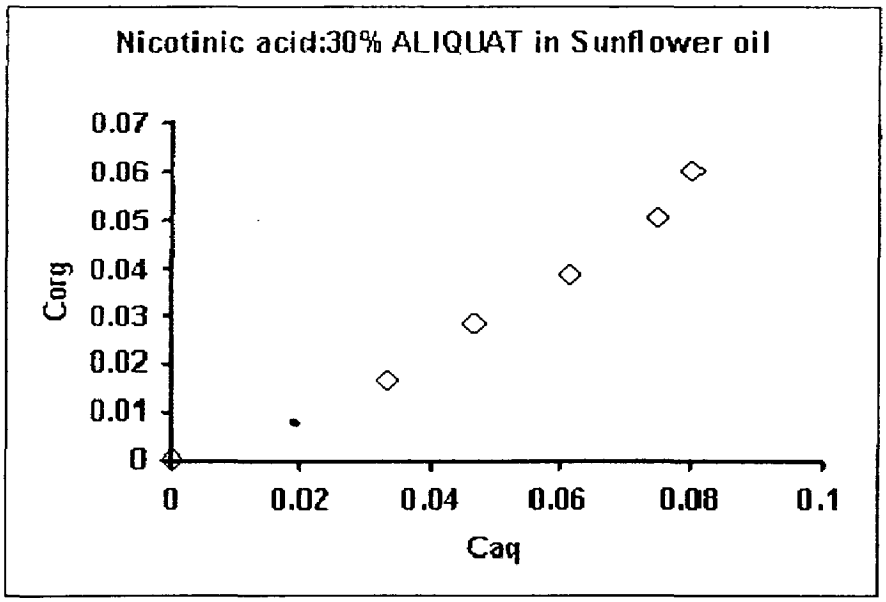

F 4.2.5 D Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with sunflower oil as the diluent



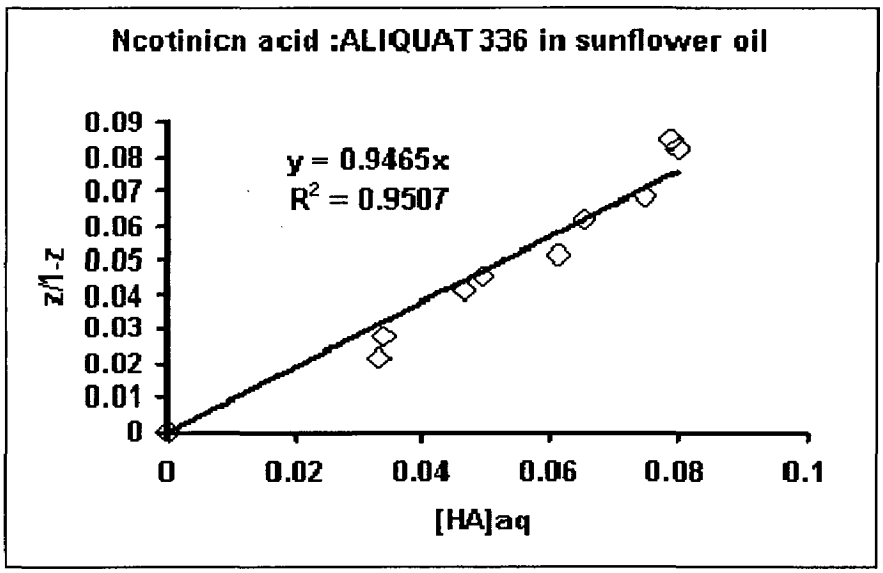

F 4.2.5 E Equilibrium isotherm of Nicotinic acid with 10% Aliquat 336 in sunflower oil




F 4.2.5 F Equilibrium isotherm of Nicotinic acid with 20% Aliquat 336 in sunflower oil




F 4.2.5 G Equilibrium isotherm of Nicotinic acid with 30% Aliquat 336 in sunflower oil




F 4.2.5 H Plot of Z/(1-Z) versus $C_{aq}$ for estimation of (1,1) acid – Aliquat 336 equilibrium constants with sunflower oil as the diluent

4.3. Chemical Extraction with TBP dissolved in diluents

Generally, weak organic acids extracted by organo-phosphorus compounds have a significantly higher distribution ratio than by carbon-bonded oxygen donor extracts under comparable experimental conditions and their extractability is higher than that of mineral acids.

In describing the equililibria involved in the extraction of weak monocarboxylic acids by strong solvating extractants, such as organo-phosphorus compounds and sulfoxides, the pertinent steps of the heterogeneous process are the dissociation of the acid in the aqueous phase.

$$HA \leftrightarrow H^+ + A^-$$

$$K_{HA} = \frac{[H^+][A^-]}{[HA]} \qquad (4.3.1)$$

The formation of the acid solvates in the organic phase,

$$HA_{(w)} + pS_{(o)} \leftrightarrow HA \cdot S_{p(o)}$$

$$K_E = \frac{[HA \cdot S_p]_{(o)}}{[HA]_{(w)}[S]^p_{(o)}} \qquad (4.3.2)$$

The experimentally accessible distribution coefficient $K_D$ on a molar concentration scale and expressed in terms of the total concentration of acid in aqueous phase (in all forms) and in the organic phase (in all forms) is given by

$$K_D = \frac{C_{HA(o)}}{C_{HA(w)}} = \frac{[HA \cdot S_p]_{(o)}}{[HA]_{(w)} + [A^-]_{(w)}} = \frac{K_E[HA]_{(w)}[S]^p_{(o)}}{[HA]_{(w)} + \frac{K_{HA}[HA]_{(w)}}{[H^+]_{(w)}}} = \frac{K_E[S]^p_{(o)}}{1 + \frac{K_{HA}}{[H^+]_{(w)}}} = \frac{K_E[S]^p_{(o)}}{1 + 10^{pH - pKa}}$$

(4.3.3)

$$[S]_{(o)} = C_s - p[HA]_{(o)} \qquad (4.3.4)$$

If the ratio $K_{HA}/[H^+]_{(w)}$ has a negligibly small value, the salvation number p can be obtained by partial differentiation of $K_D$ with respect to $[S]_{(o)}$, a plot of

$$\log K_D = \log K_E + p \log([S]_{(o)}) \qquad (4.3.5)$$

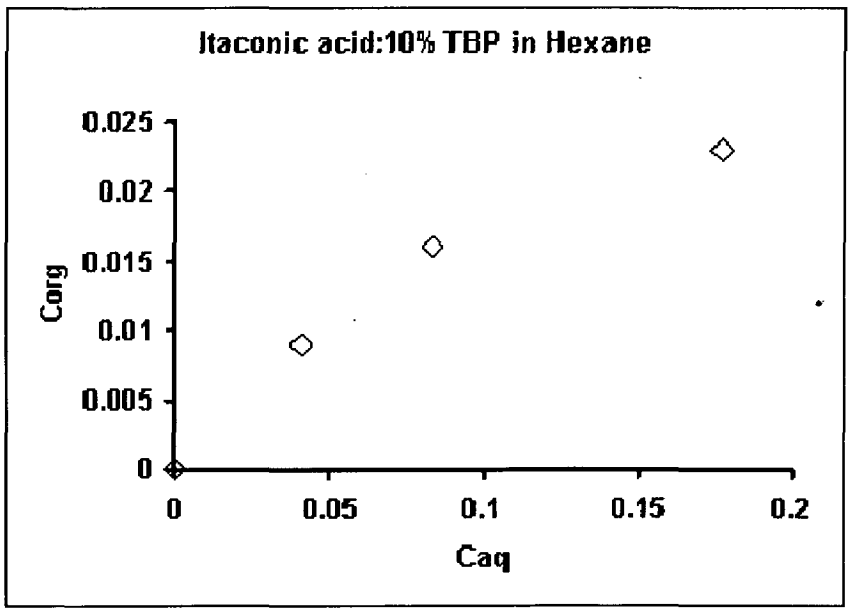
Yielding slope p and intercept $K_E$. Both o these quantities are dependent on the solute and extractant concentration however, remain constant over some range. At high solute concentration, as an appreciable fraction of extractant molecule becomes bound to acid, lower values of p will predominate, and the plot of equation 4.3.5 will deviate from straight line requirement.

*4.3.1 Extraction with TBP dissolved in Hexane*

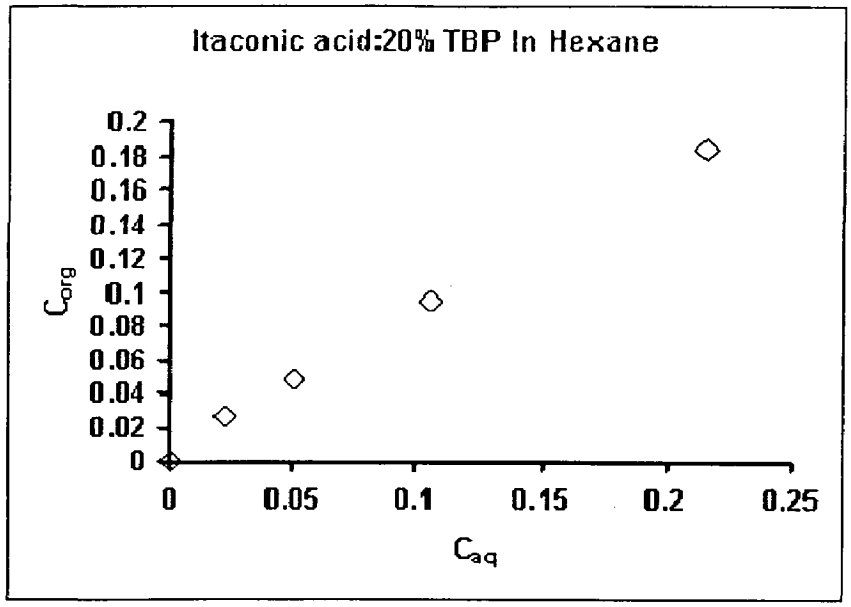
The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in sunflower oil at various

concentrations; with aqueous phases containing itaconic acid with concentration 0.05 – 0.4 kmol/$m^3$ and nicotinic acid at concentration 0.05 – 0.14kmol/$m^3$. The results of these experiments are given in the table T 4.3.4 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acid and nicotinic acid before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction is calculated from equation 4.1.

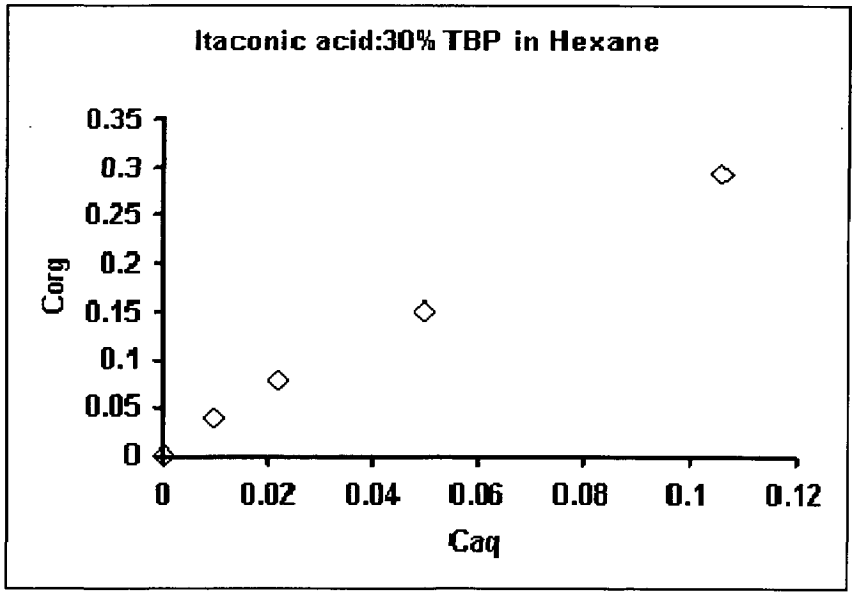
These results are plotted in figure F 4.3.1 A, B, C, D, E, F at different concentrations in aqueous phases, to observe the variation of the degree of extraction. From the plots it can be analyzed that for itaconic acid on increase in extractant concentration there is an increase in degree of extraction but, for nicotinic acid degree of extraction decreases. In case itaconic acid, when the acid concentration is increased there is an increase and then decrease in degree of extraction but, for nicotinic acid, very less pattern in degree of extraction. The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of log ($K_D$) Vs $\log([B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The $K_{11}$ for itaconic acid and nicotinic acid are respectively.



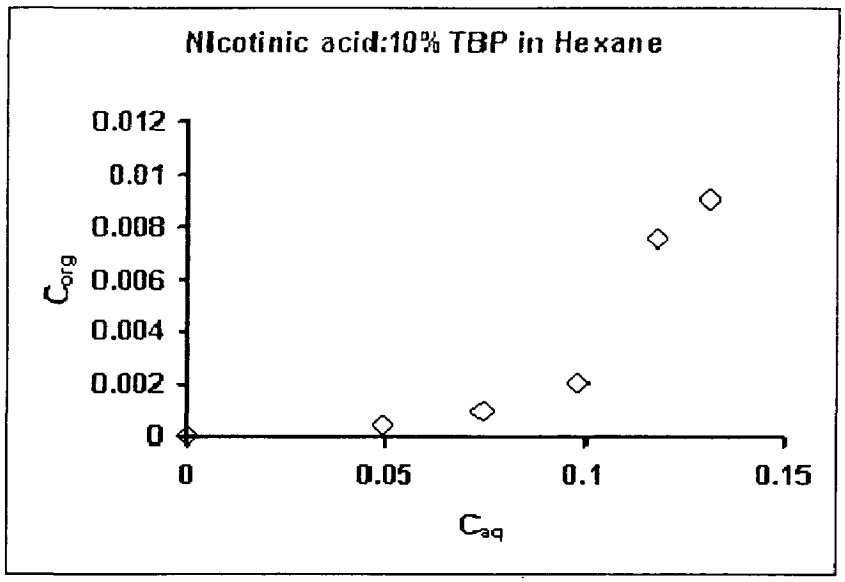

F 4.3.1 A Equilibrium isotherm of Itaconic acid with 10% TBP in Hexane



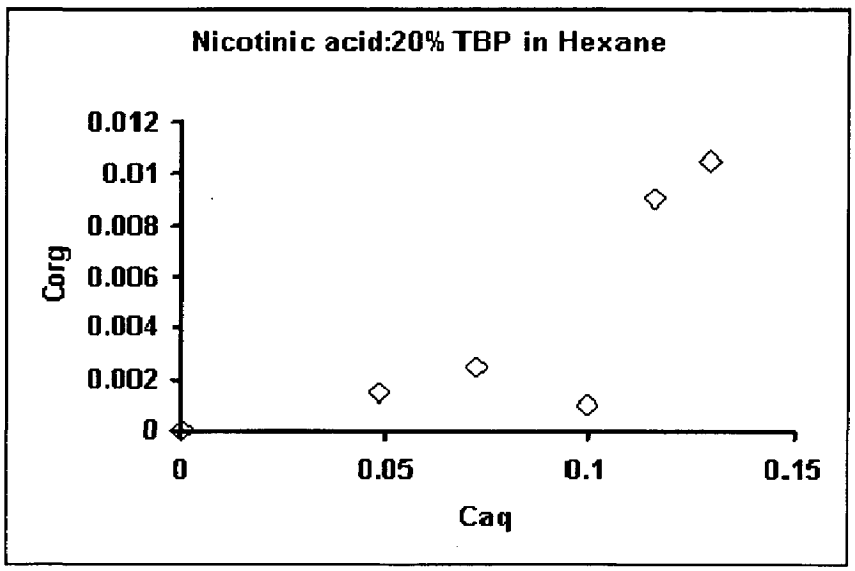

F 4.3.1 B Equilibrium isotherm of Itaconic acid with 20% TBP in Hexane



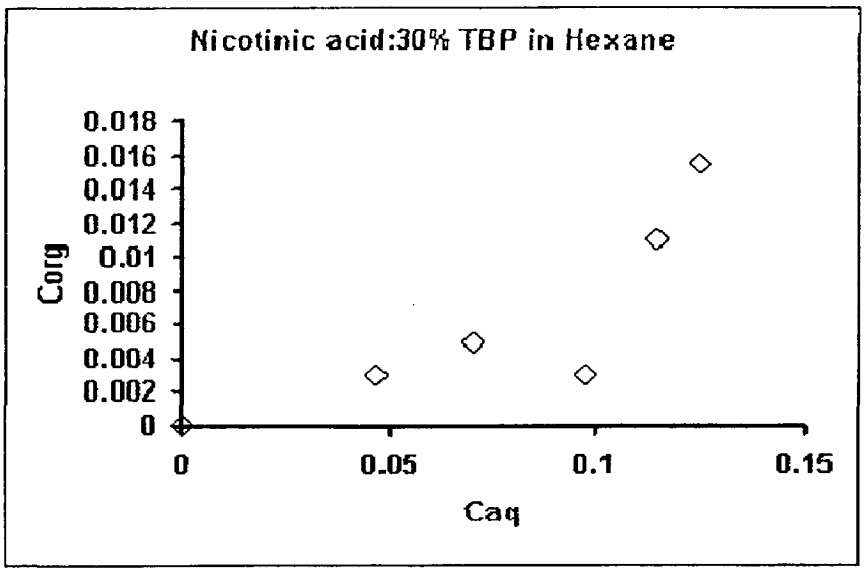

F 4.3.1 C Equilibrium isotherm of Itaconic acid with 30% TBP in Hexane




F 4.3.1 D Equilibrium isotherm of Nicotinic acid with 10% TBP in Hexane




F 4.3.1 E Equilibrium isotherm of Nicotinic acid with 20% TBP in Hexane

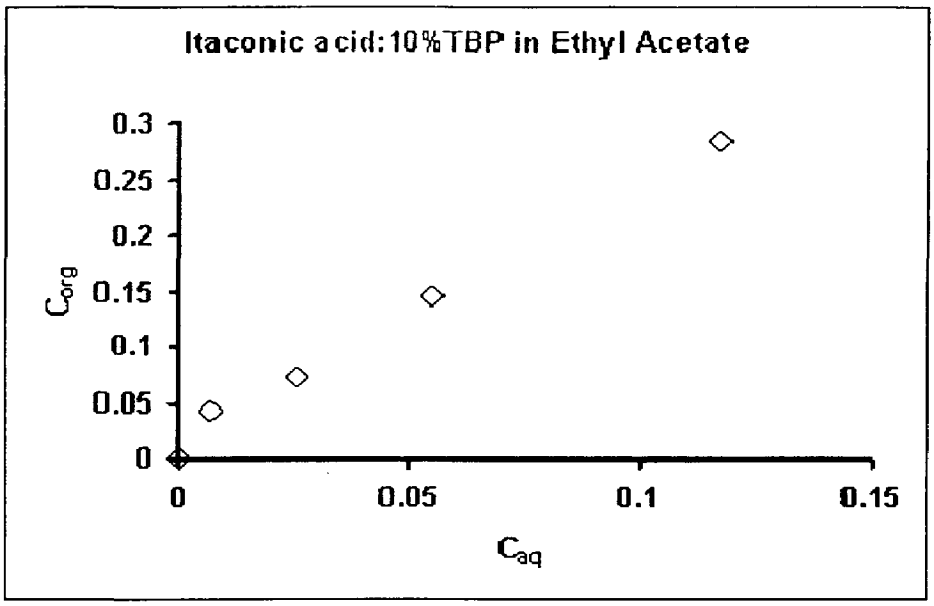



F 4.3.1 F Equilibrium isotherm of Nicotinic acid with 30% TBP in Hexane

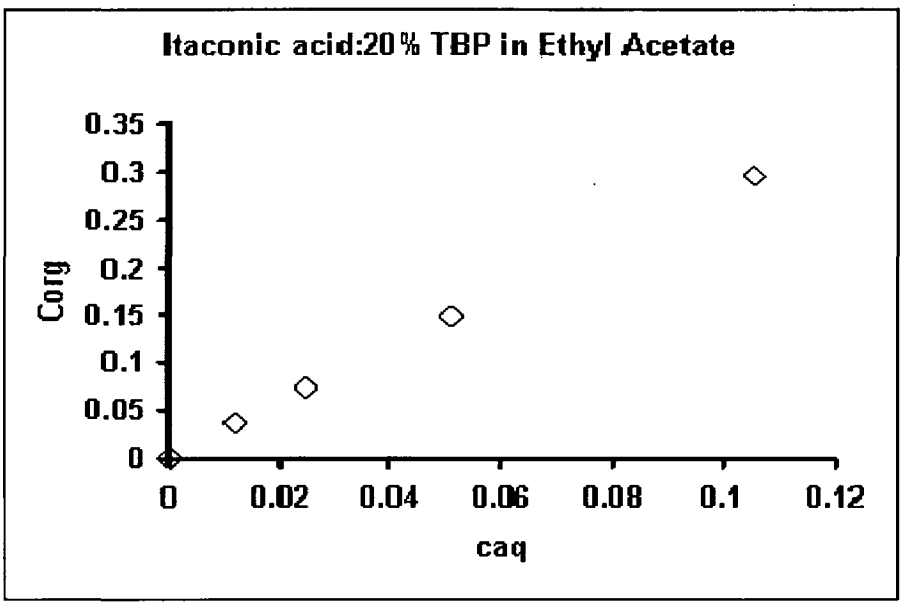
*4.3.2 Extraction with TBP dissolved in Ethyl acetate*

The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in ethyl acetate at various concentrations; with aqueous phases containing itaconic acid with concentration 0.05 – 0.4 kmol/$m^3$ and nicotinic acid at concentration 0.05 – 0.14kmol/$m^3$. The results of these experiments are given in the table T 4.3.4 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acid and nicotinic acid before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction is calculated from equation 4.1.

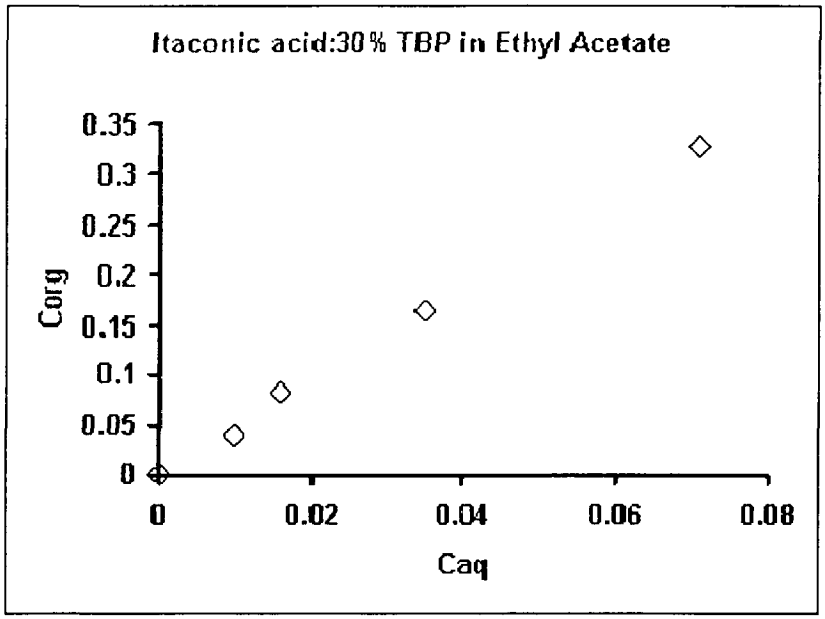
These results are plotted in figure F 4.3.2 A, B, C, D, E, F at different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for itaconic acid and nicotinic acid on increase in extractant concentration there is an increase in degree of extraction In case nicotinic acid, when the acid concentration is increased there is an increase in degree of extraction and then decrease in degree of extraction. The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of log ($K_D$) Vs $\log([B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The $K_{11}$ for itaconic acid and nicotinic acid are respectively.



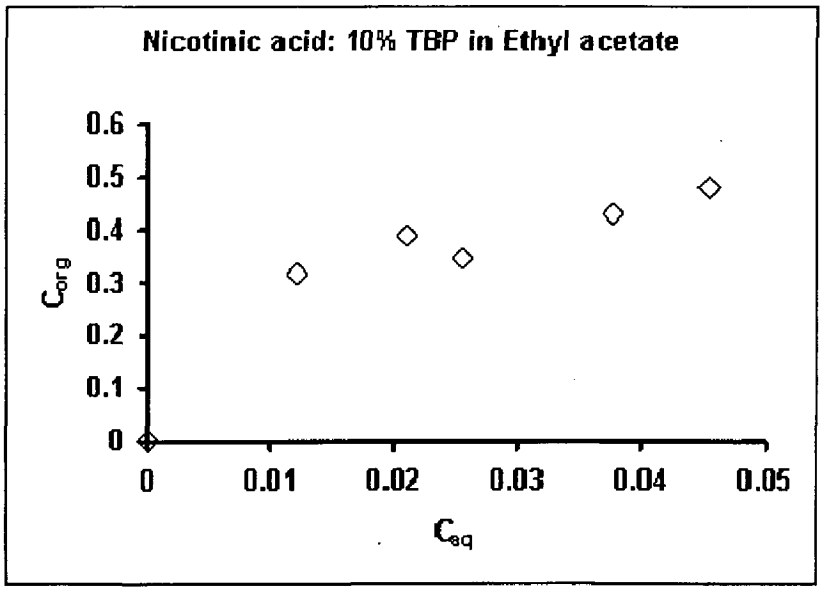

F 4.3.2 A Equilibrium isotherm of Itaconic acid with 10% TBP in Ethyl I acetate



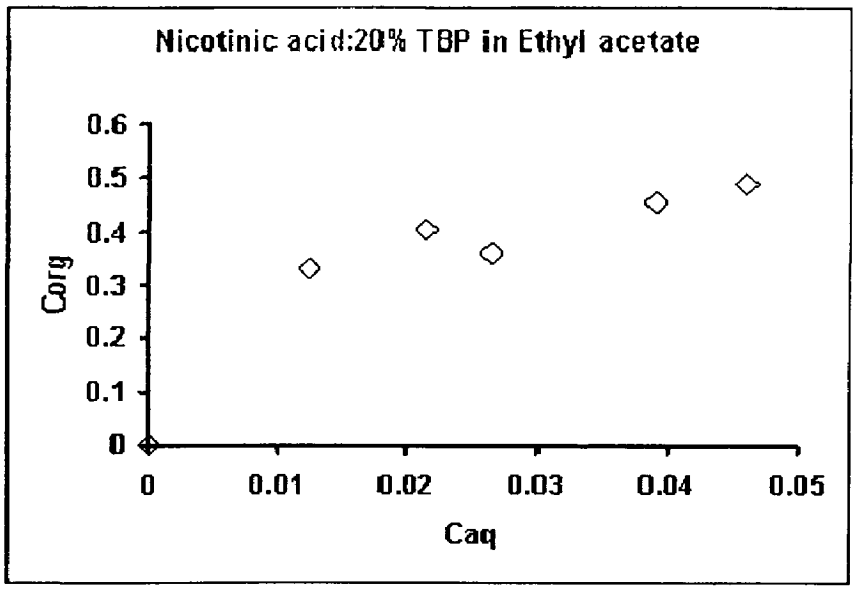

F 4.3.2 B Equilibrium isotherm of Itaconic acid with 20% TBP in Ethyl Acetate



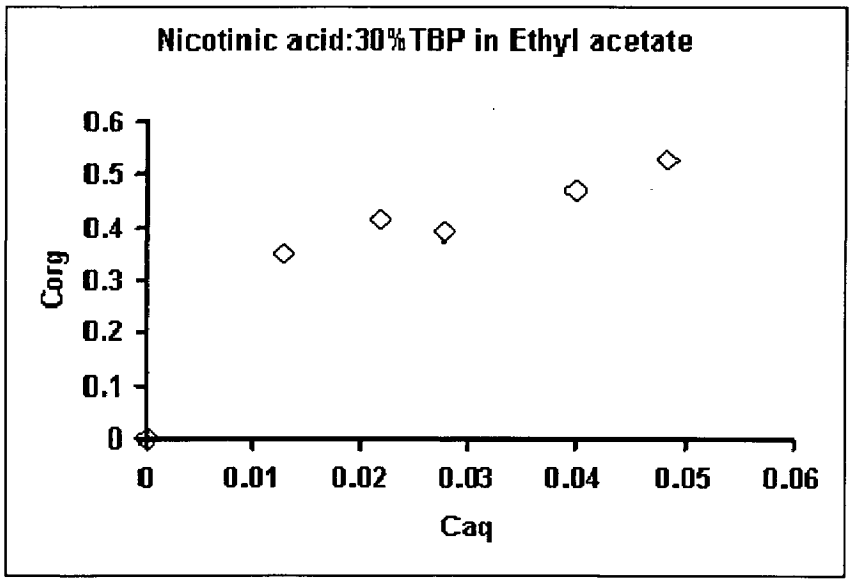

F 4.3.2 C Equilibrium isotherm of Itaconic acid with 30% TBP in Ethyl I acetate




F 4.3.2 D Equilibrium isotherm of Nicotinic acid with 10% TBP in Ethyl acetate




F 4.3.2 E Equilibrium isotherm of Nicotinic acid with 20% TBP in Ethyl acetate



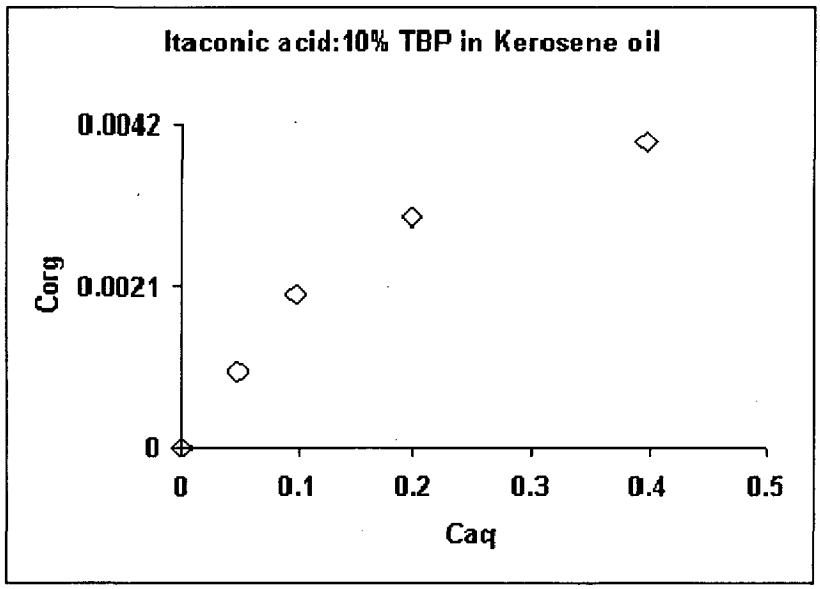

F 4.3.2 F Equilibrium isotherm of Nicotinic acid with 30% TBP in Ethyl I acetate

*4.3.3 Extraction with TBP dissolved in kerosene oil*

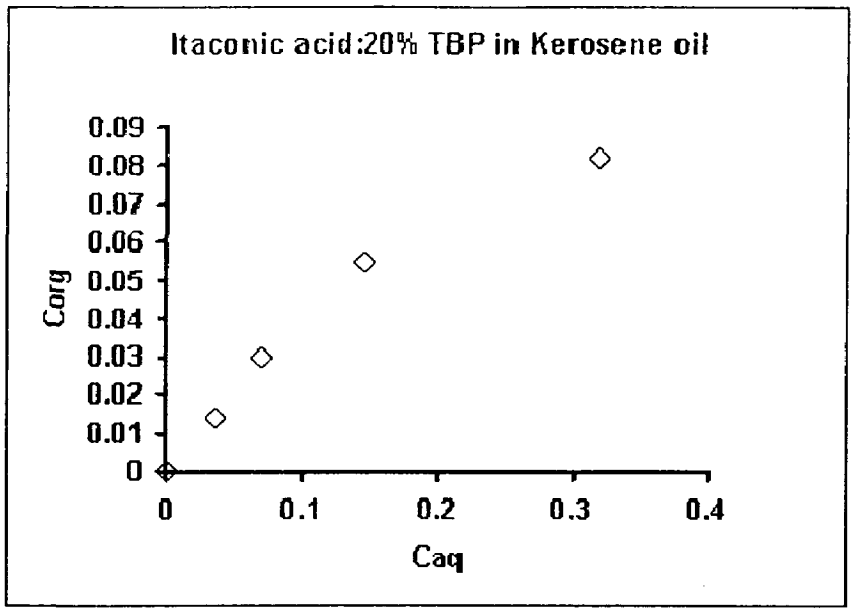
The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in sunflower oil at various concentrations; with aqueous phases containing itaconic acid with concentration 0.05 – 0.4 kmol/$m^3$ and nicotinic acid at concentration 0.05 – 0.14kmol/$m^3$. The results of these experiments are given in the table T 4.3.4 A and B, which show the variation in the concentration of aqueous phase for the different initial

concentrations of itaconic acid and nicotinic acid before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction is calculated from equation 4.1.

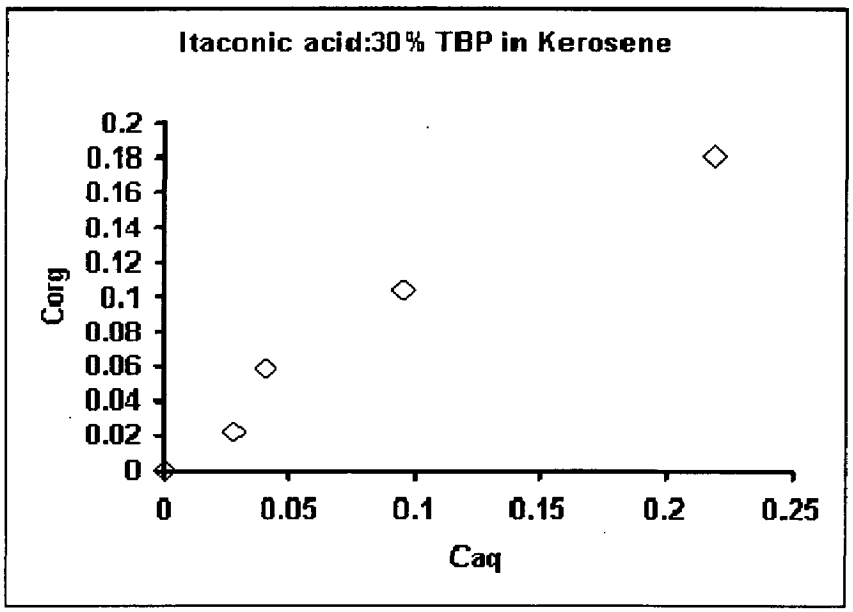
These results are plotted in figure F 4.3.3 A, B, C, D, E, F at different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for itaconic acid on increase in extractant concentration there is an increase in degree of extraction but, in case of nicotinic acid poor degree of extraction. In case itaconic acid, when the acid concentration is increased there is a decrease in degree of extraction similarly for nicotinic acid, there is less change in degree of extraction. This is due to the inerts .since kerosene is a mixture of alkanes, the carbon atoms present from $C_9$-$C_{16}$.the absorbance of the acid is low in case of kerosene oil.The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of log ($K_D$) Vs $\log([B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The $K_{11}$ for itaconic acid and nicotinic acid are .....respectively.



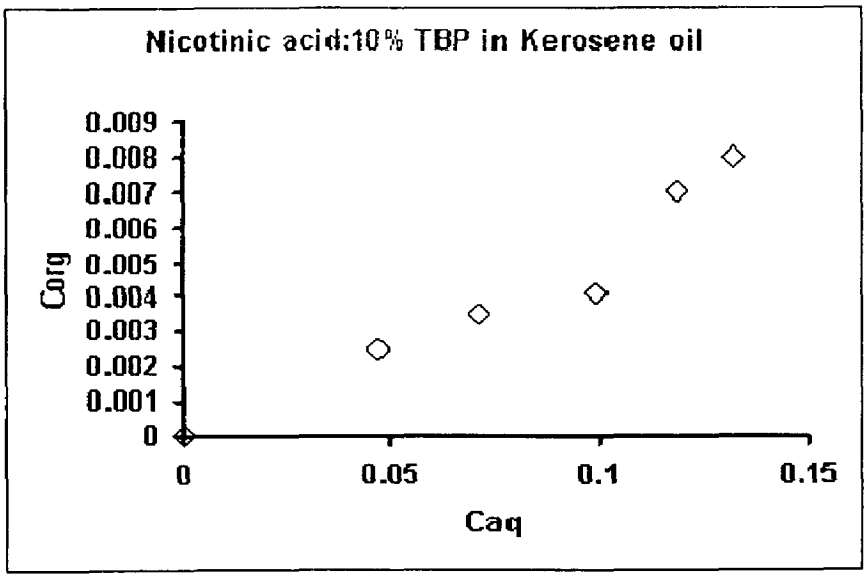

F 4.3.3.A Equilibrium isotherm of Itaconic acid with 10% TBP in Kerosene oil



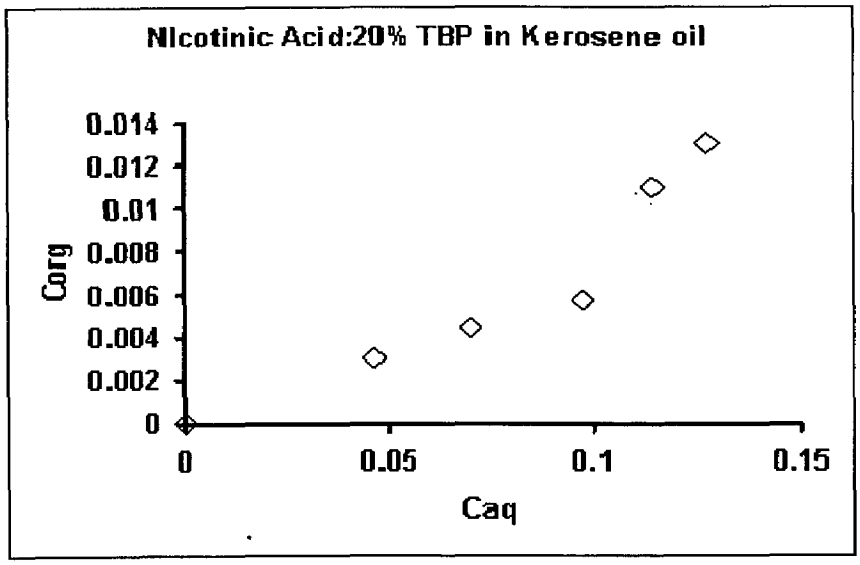

F 4.3.3 B Equilibrium isotherm of Itaconic acid with 20% TBP in Kerosene oil



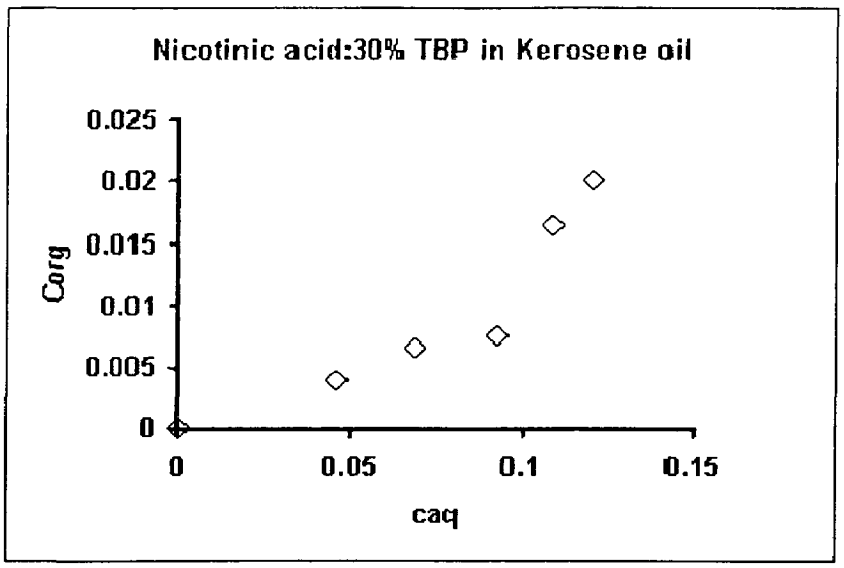

F 4.3.3.C Equilibrium isotherm of Itaconic acid with 30% TBP in Kerosene oil




F 4.3.3.D Equilibrium isotherm of Nicotinic acid with 10% TBP in Kerosene oil




F 4.3.3.E Equilibrium isotherm of Nicotinic acid with 20% TBP in Kerosene oil

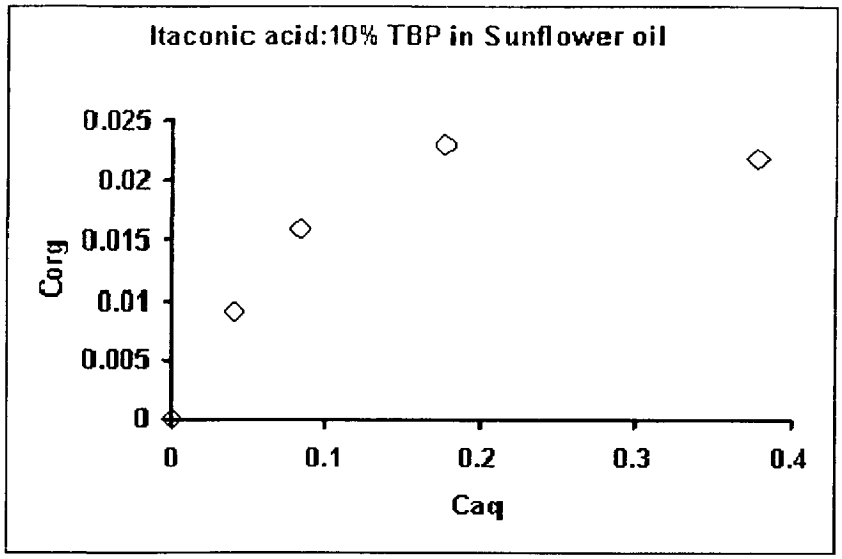



F 4.3.3.F Equilibrium isotherm of Nicotinic acid with 30% TBP in Kerosene oil

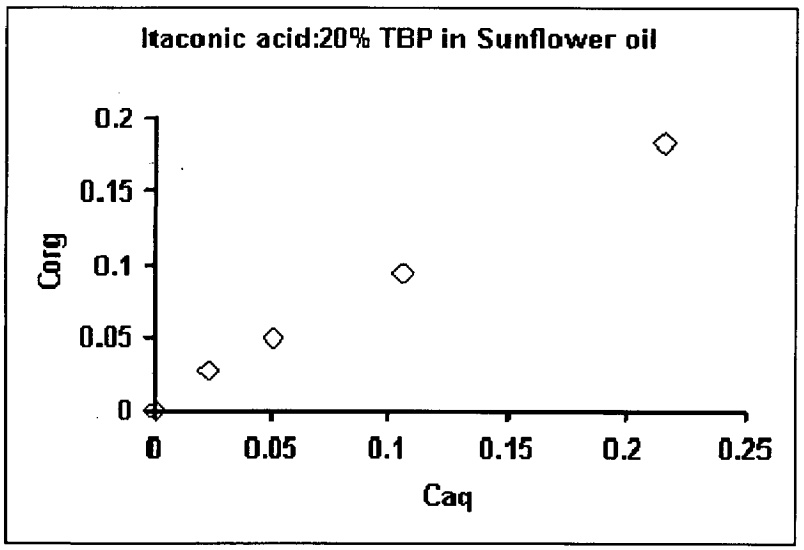
*4.3.4 Extraction with TBP dissolved in sunflower oil*

The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in sunflower oil at various concentrations; with aqueous phases containing itaconic acid with concentration 0.05 – 0.4 kmol/$m^3$ and nicotinic acid at concentration 0.05 – 0.14kmol/$m^3$. The results of these experiments are given in the table T 4.3.4 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acid and nicotinic acid before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction is calculated from equation 4.1.

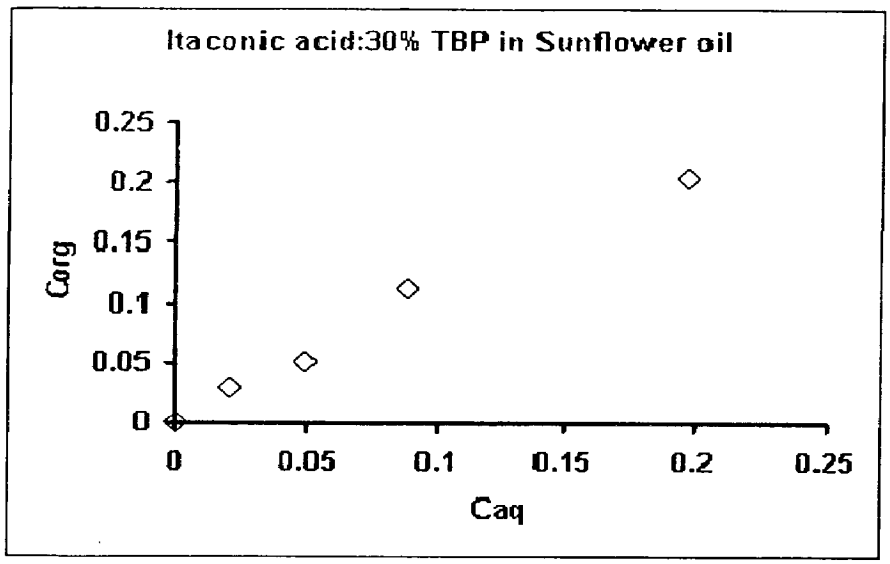
These results are plotted in figure F 4.3.4 A, B, C, D, E, F at different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for itaconic acid and nicotinic acid on increase in extractant concentration there is an increase in degree of extraction but, in case nicotinic acid degree of extraction decreases. In case of itaconic acid, when the acid concentration is increased there is an increase in degree of extraction but, for nicotinic acid, there is a decrease in degree of extraction. The sunflower oil is a mixture of higher fatty acids, the attraction of acid ions is less in case of sunflower oil.The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of log ($K_D$) Vs log($[B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The $K_{11}$ for itaconic acid and nicotinic acid are .....respectively.



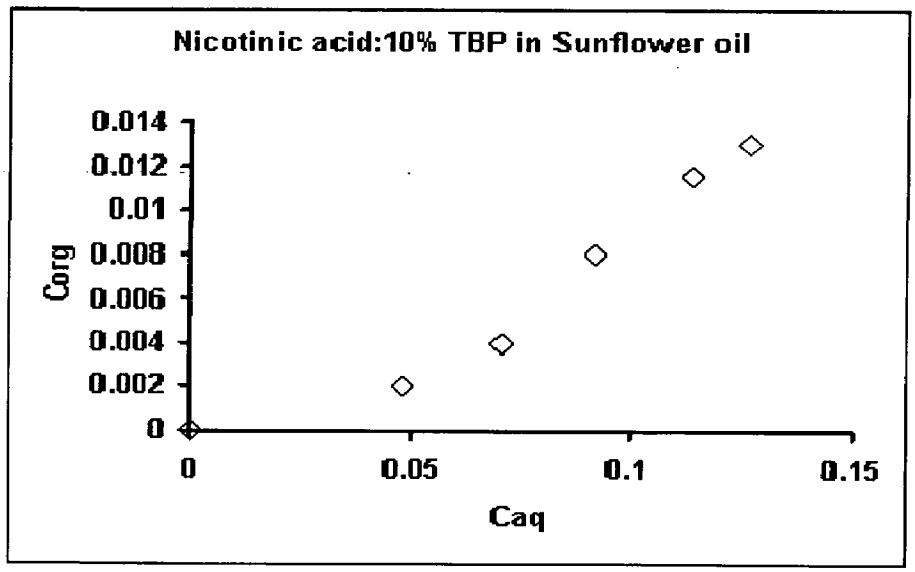

F 4.3.4 A Equilibrium isotherm of Itaconic acid with 10% TBP in sunflower oil



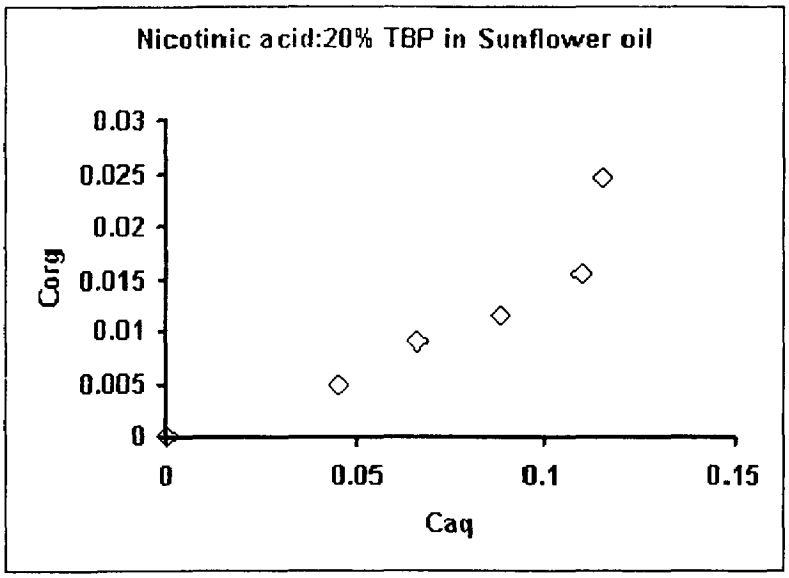

F 4.3.4 B Equilibrium isotherm of Itaconic acid with 20% TBP in Sunflower oil



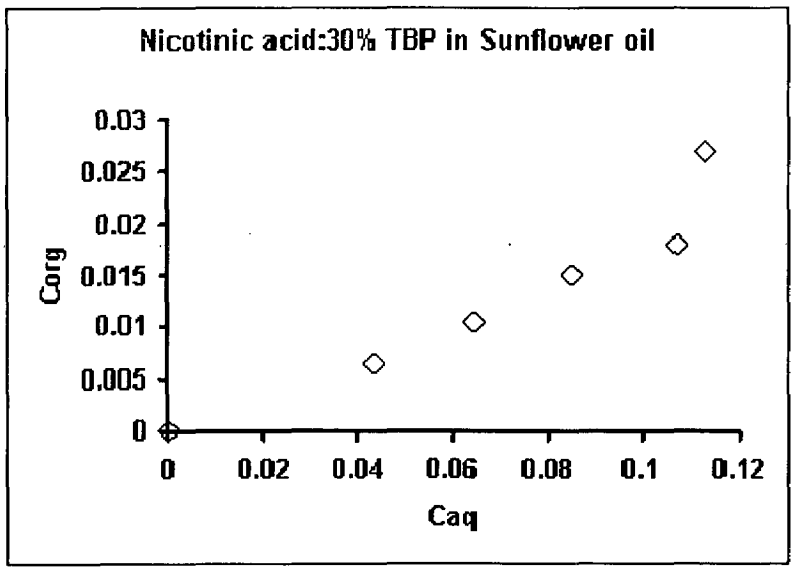

F 4.3.4CEquilibrium isotherm of Itaconic acid with 30% TBP in Sunflower oil




F 4.3.4 D Equilibrium isotherm of Nicotinic acid with 10% TBP in sunflower oil




F 4.3.4 E Equilibrium isotherm of Nicotinic acid with 20% TBP in Sunflower oil

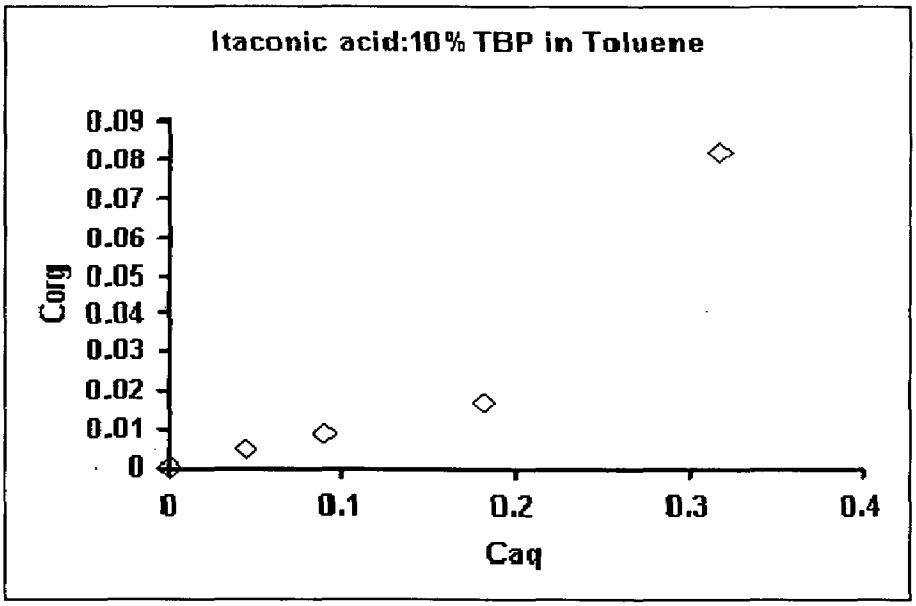



F 4.3.4FEquilibrium isotherm of Nicotinic acid with 30% TBP in Sunflower

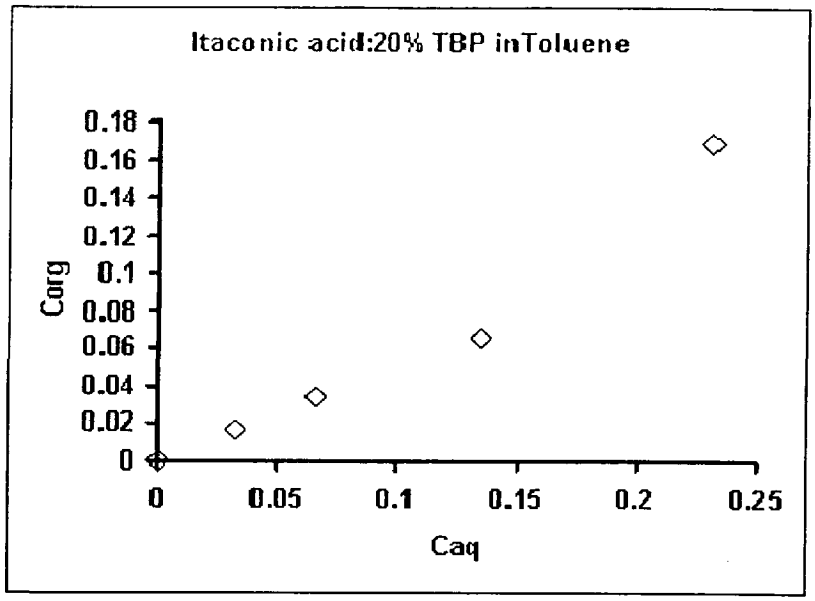
*4.3.4 Extraction with TBP dissolved in Toluene*

The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in Toluene at various concentrations; with aqueous phases containing itaconic acid with concentration 0.05 – 0.4 kmol/$m^3$ and nicotinic acid at concentration 0.05 – 0.14kmol/$m^3$. The results of these experiments are given in the table T 4.3.4 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of itaconic acid and nicotinic acid before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction is calculated from equation 4.1

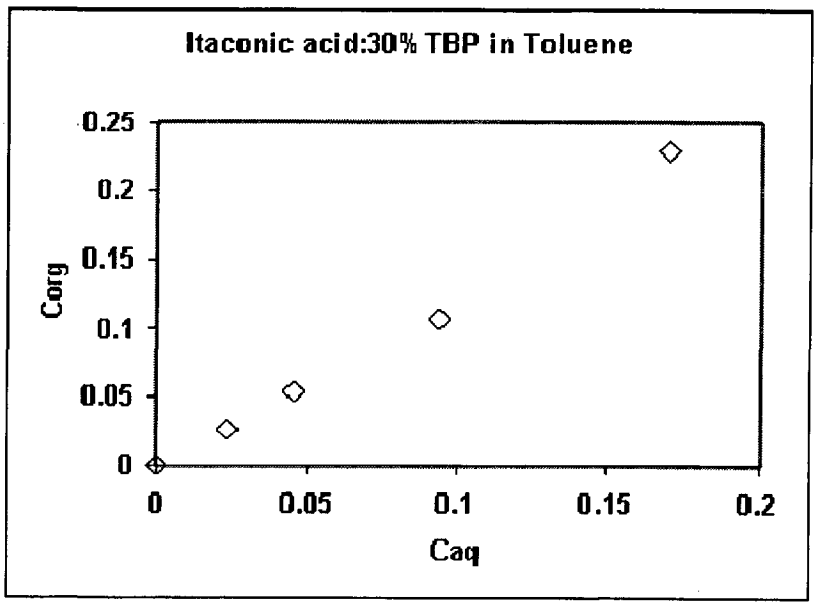
These results are plotted in figure F 4.3.5 A, B, C, D, E, F at different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for itaconic acid and nicotinic acid on increase in extractant concentration there is an increase in degree of extraction .similarly for nicotinic acid degree of extraction increases.. In case of itaconic acid, when the acid concentration is increased there is an increase in degree of extraction. The toluene is an alkyl aromatic belonging to the benzene ring structure, the electronegativity increases in case of toluene so the degree of extraction decreases. The values of equilibrium constant ($K_{11}$) for both the acids, from the plot of log ($K_D$) Vs $\log([B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The $K_{11}$ for itaconic acid and nicotinic acid are .....respectively.



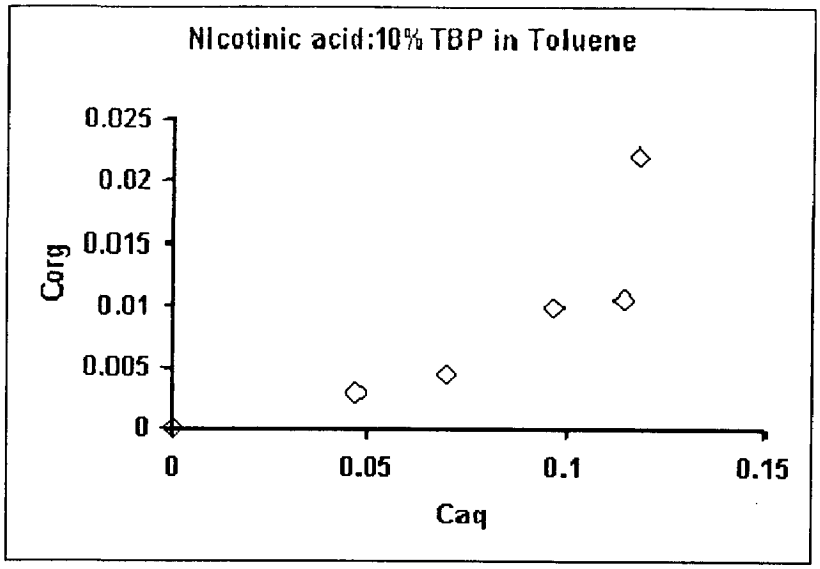

F 4.3.4 A Equilibrium isotherm of Itaconic acid with 10% TBP in Toluene



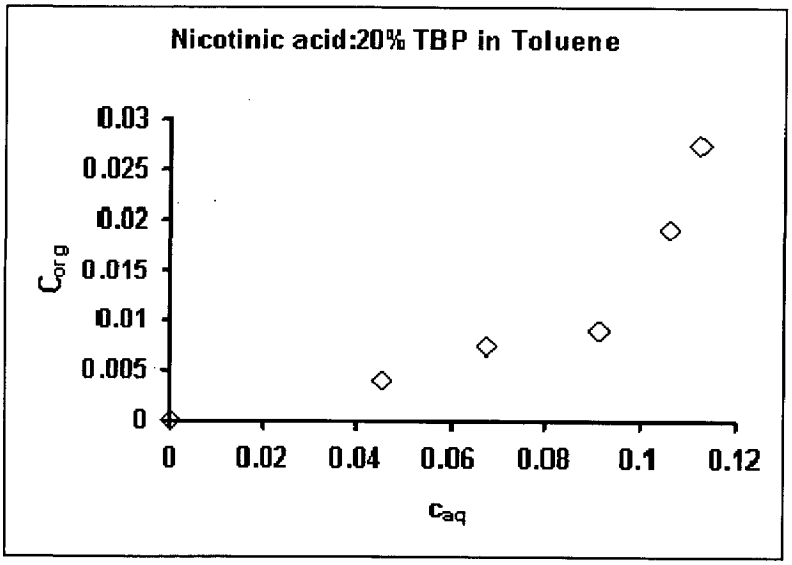

F 4.3.4 B Equilibrium isotherm of Itaconic acid with 20% TBP in Toluene



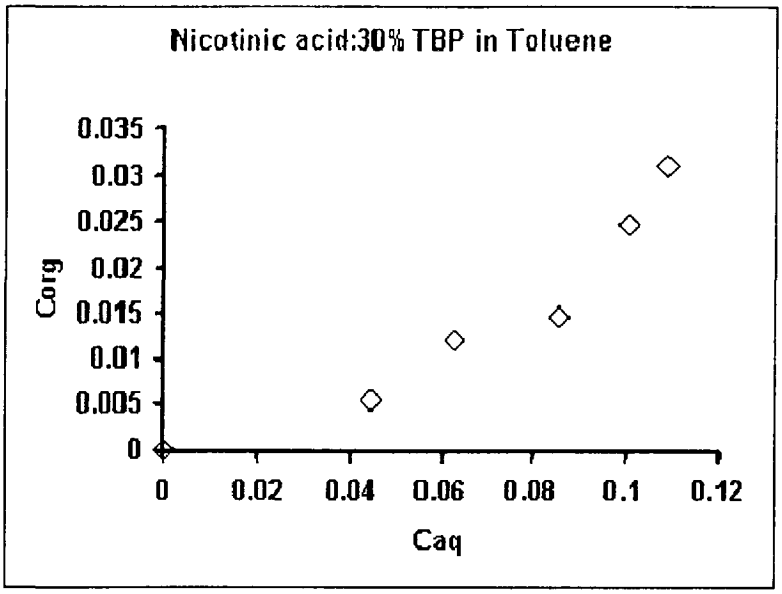

F 4.3.4 C Equilibrium isotherm of Itaconic acid with 30% TBP in Toluene




F 4.3.4 D Equilibrium isotherm of Nicotinic acid with 10% TBP in Toluene




F 4.3.4 E Equilibrium isotherm of Nicotinic acid with 20% TBP in Toluene



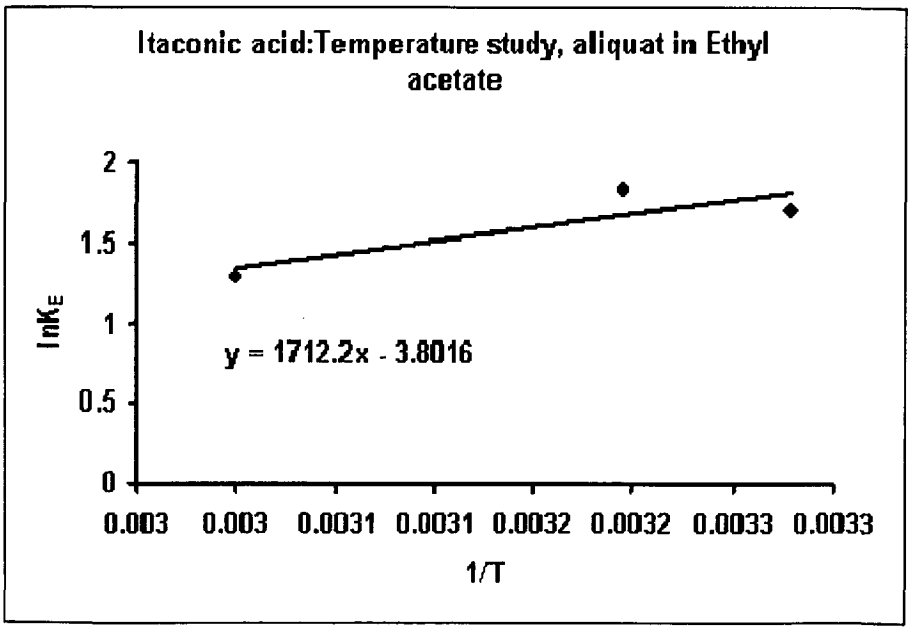

F 4.3.4 F Equilibrium isotherm of Nicotinic acid with 30% TBP in Toluene

4.4. Effect of Temperature

*4.4.1 Extraction of Itaconic acid with Aliquat 336 in Ethyl acetate*

For the temperature study, the extraction of Itaconic acid using Aliquat-336 dissolved in Ethyl acetate. The concentrations for itaconic acid were 0.05 -0.4 kmol/$m^3$. The Aliquat 336 (tri-capryl methyl ammonium chloride) is a salt of quaternary amine. The results of these experiments are given in the table T 4.4.1 A, B, C and D, which shows the equilibrium data of extraction at temperatures 305.15 K, 313.15 K, 323.15 K and 333 K respectively. The enthalpy and entropy are calculated from equation 2.1.3.2 and plotting a graph 1/T (K) Vs. ln($K_E$)

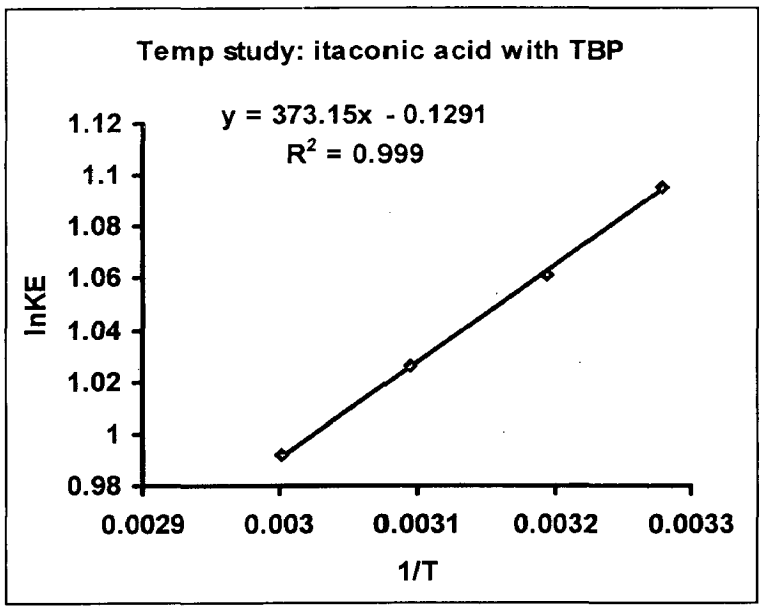
The enthalpy and entropy are -14.325 KJ/mol and -31.606 J/mol K.




F 4.4.1 Plot of $K_{11}$ versus 1/T for estimation of enthalpy and entropy of Itaconic acid – Aliquat 336 with Ethyl acetate

*4.4.2 Extraction of Itaconic acid with TBP in Ethyl acetate*

The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in *Ethyl acetate* at various concentrations; with aqueous phases containing itaconic acid at concentration varying from 0.05 to 0.4 kmol/$m^3$. The results of these experiments are given in the table T 4.4.2 A, B, C and D, which show the equilibrium data of extraction at temperatures 305.15 K, 313.15 K, 323.15 K and 333 K respectively. The enthalpy and entropy are calculated from equation 2.1.3.2. The enthalpy and entropy for itaconic acid with TBP in ethyl acetate are 3.1023 KJ/mol and 1.0733 J/mol K.




F 4.4.2 Plot of $K_{11}$ versus 1/T for estimation of enthalpy and entropy of itaconic acid – TBP with Ethyl acetate

*4.4.3 Extraction of Nicotinic acid with Aliquat 336 in Ethyl acetate*

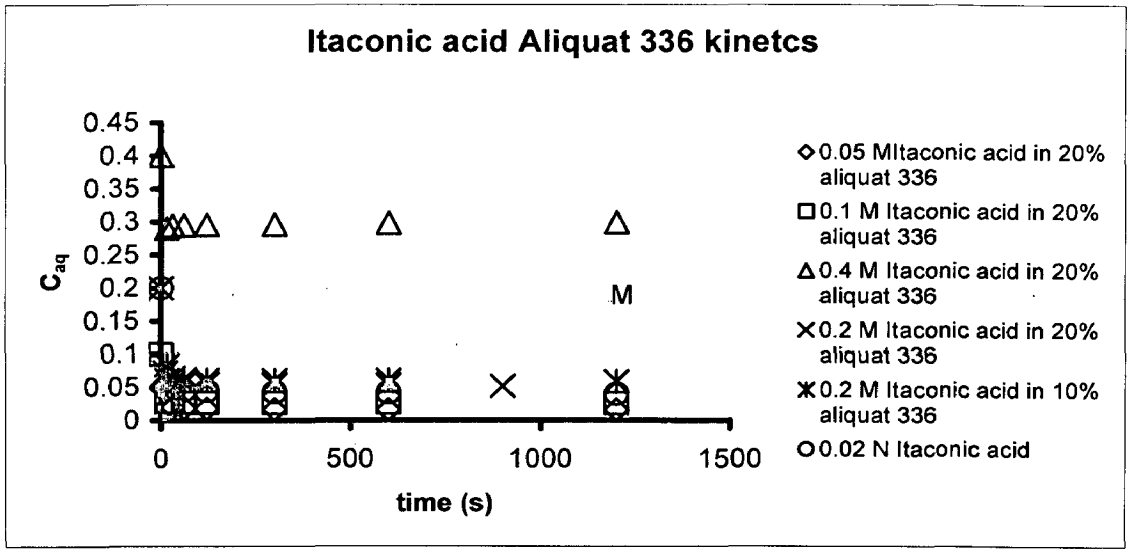
The extraction experiments were carried out by contacting organic phase composed of Aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in ethyl acetate at various concentrations; with aqueous phases containing nicotinic acid at concentration varying from 0.05 to 0.14 kmol/$m^3$. The results of these experiments are given in the table T 4.4.3 A, B, C which show the equilibrium data of extraction at temperatures 313.15 K, 323.15 K and 333 K respectively. The enthalpy and entropy are calculated from equation 2.1.3.2. The enthalpy and entropy are -26 KJ/mol and -71.876 J/mol K.

4.5 Kinetics Study

*4.5.1 Extraction of Itaconic acid with Aliquat 336 in Ethyl acetate*

The extraction experiment was carried out in agitated disc contactor taking equal volumes (100 ml) of aqueous and organic phases. The container was a beaker of size 55 mm inner diameter and 100 mm height. The experiment was run at an agitation speed of 550 RPM. Aqueous phase was pipetted out at different times (15 sec, 30 sec, 1 min, 2 min, 5 min, 10 min, 15 min, 20 min) and analyzed for the concentration in aqueous phase. The organic phase concentration was calculated by component mass balance. The equilibrium aqueous phase concentration was plotted again

$$-r_A = k_1 C_{aq}^{\alpha} B_{org}^{\beta} - k_2 C_{org}^{\gamma} \qquad \text{and} \qquad K_E = \frac{k_1}{k_2} \qquad (4.5.1)$$

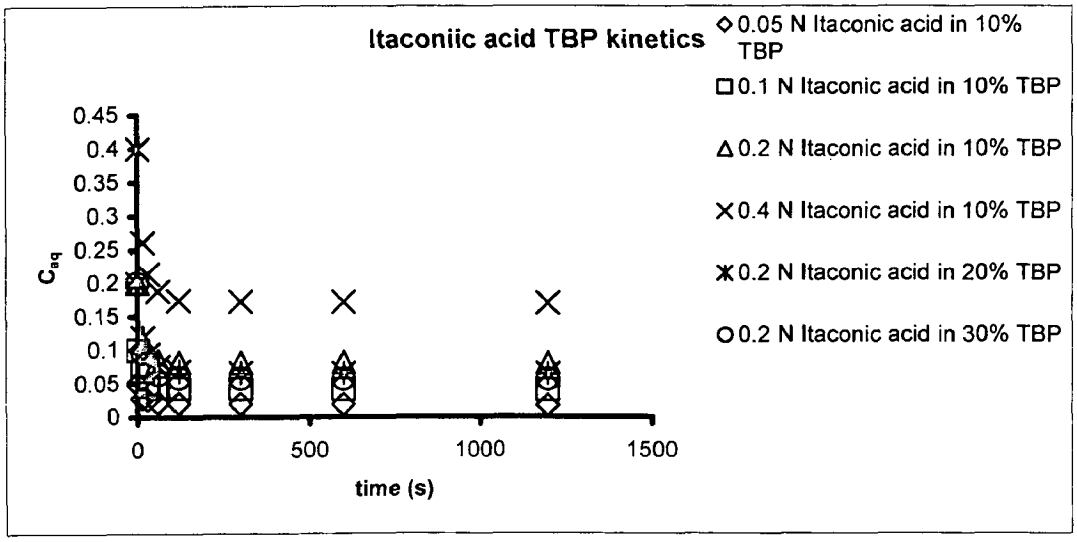



F 4.5.1 Kinetics curves of itaconic acid with Aliquat 336 in ethyl acetate

*4.5.2 Extraction Itaconic acid with TBP in ethyl acetate*

The extraction experiment was carried out in agitated disc contactor taking equal volumes (50 ml) of aqueous and organic phases. The container was a beaker of size 55 mm inner diameter and 100 mm height. The experiment was run at an agitation speed of 550 RPM. Aqueous phase was pipette out at different times (15 sec, 30 sec, 1 min, 2 min, 5 min, 10 min, 15 min, 20 min) and analyzed for the concentration in aqueous phase. The organic phase concentration was calculated by component mass balance. The equilibrium aqueous phase concentration was plotted against time (F 4.5.2) to calculate rate of reaction from the slope of the curve. The data was then fit in general equation of reversible reaction (4.5.1) and the constants were calculated. The constants are tabulated in table T 4.5.R.

$$-r_A = k_1 C_{aq}^{\alpha} B_{org}^{\beta} - k_2 C_{org}^{\gamma} \qquad \text{and} \qquad K_E = \frac{k_1}{k_2} \qquad (4.5.1)$$

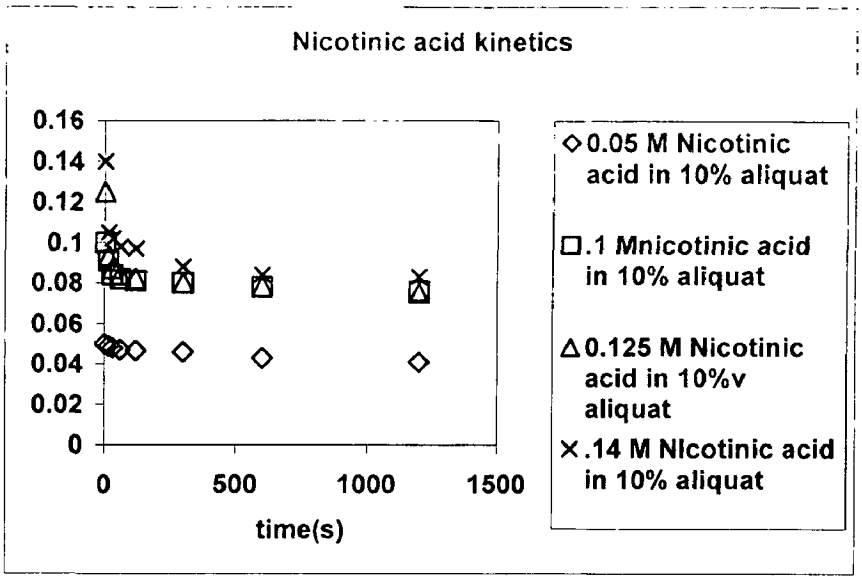



F 4.5.2 Kinetics curves of itaconic acid with TBP in ethyl acetate

*4.5.3 Extraction of Nicotinic acid with Aliquat 336 in ethyl acetate*

The extraction experiment was carried out in agitated disc contactor taking equal volumes (100 ml) of aqueous and organic phases. The container was a beaker of size 55 mm inner diameter and 100 mm height. The experiment was run at an agitation speed of 550 RPM. Aqueous phase was pipette out at different times (15 sec, 30 sec, 1 min, 2 min, 5 min, 10 min, 15 min, 20 min) and analyzed for the concentration in aqueous phase. The organic phase concentration was calculated by component mass balance. The equilibrium aqueous phase concentration was plotted against time (F 4.5.3) to calculate rate of reaction from the slope of the curve. The data was then fit in general equation of reversible reaction (4.5.1) and the constants were calculated. The constants are tabulated in table T 4.5.R.

$$-r_A = k_1 C_{aq}^{\alpha} B_{org}^{\beta} - k_2 C_{org}^{\gamma} \qquad \text{and} \qquad K_E = \frac{k_1}{k_2} \qquad (4.5.1)$$

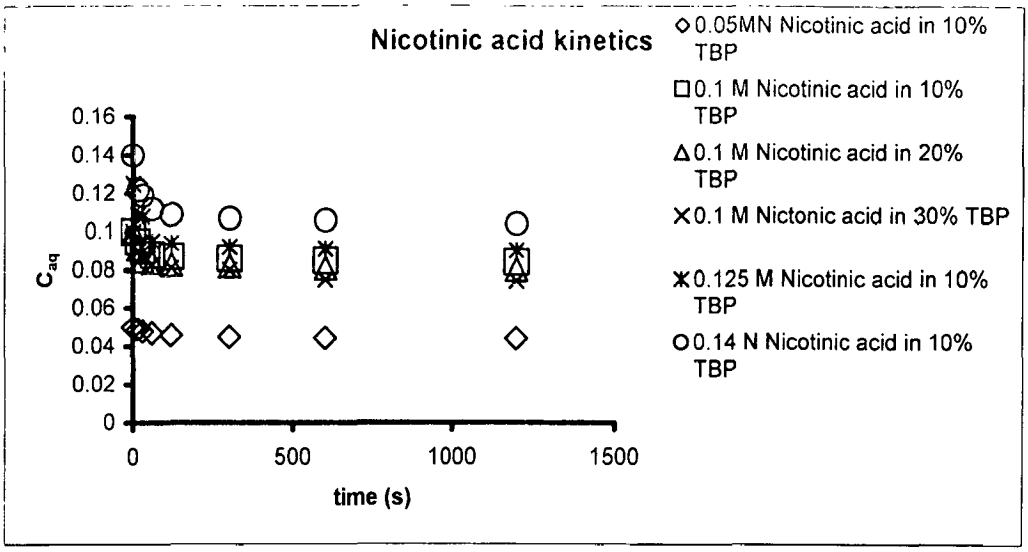



F 4.5.3 Kinetics curves of nicotinic acid with Aliquat 336 in ethyl acetate

*4.5.4 Extraction Nicotinic acid with TBP in ethyl acetate*

The extraction experiment was carried out in agitated disc contactor taking equal volumes (50 ml) of aqueous and organic phases. The container was a beaker of size 55 mm inner diameter and 100 mm height. The experiment was run at an agitation speed of 550 RPM. Aqueous phase was pipetted out at different times (15 sec, 30 sec, 1 min, 2 min, 5 min, 10 min, 15 min, 20 min) and analyzed for the concentration in aqueous phase. The organic phase concentration was calculated by component mass balance. The equilibrium aqueous phase concentration was plotted against time (F 4.5.4) to calculate rate of reaction from the slope of the curve. The data was then fit in general equation of reversible reaction (4.5.1) and the constants were calculated. The constants are tabulated in table T 4.5.R.

$$-r_A = k_1 C_{aq}^{\alpha} B_{org}^{\beta} - k_2 C_{org}^{\gamma} \qquad \text{and} \qquad K_E = \frac{k_1}{k_2} \qquad (4.5.1)$$




F 4.5.4 Kinetics curves of nicotinic acid with TBP in ethyl acetate time (F 4.5.1) to calculate rate of reaction from the slope of the curve.

The data was then fit in general equation of reversible reaction (4.5.1) and the constants were calculated. The constants are tabulated in table T 4.5.R.

# CHAPTER 5

## CONCLUSIONS AND RECOMMENDATIONS

The Itaconic acid is a valuable carboxylic acid. It is widely used acid for making resins, binding agents. it is the third monomer of acrylic group. Equilibrium investigations on the reactive extraction of itaconic acid and nicotinic acids from their aqueous phases at different concentrations and temperatures were conducted by contacting and equilibrating the aqueous phases with organic phases which contain tri-butyl phosphate (TBP) or Aliquat 336 (tri-capryl methyl ammonium chloride) as extractants in various diluents.

According to the extraction results of itaconic acid and nicotinic acid, following conclusions were made:

1. Degree of extraction is higher for quaternary amines than phosphorus bonded oxygen extractants when dissolved in any type of diluent.
2. Ethyl acetate as diluent has the higher solvating power than other functional group diluents. Better extraction was obtained for Aliquat 336 dissolved in ethyl acetate. It also has better solvating power towards the acid-amine complex.
3. Degree of extraction is high for Aliquat 336 dissolved in functional group baring diluents and it decreases on concentrating the organic phase in contrast to inert diluents like kerosene oil, sunflower oil.
4. Degree of extraction increases with increase in acid concentration for all organic phase of Aliquat 336 and TBP.
5. The extraction is low for organic phase of Aliquat 336 and TBP dissolved in Toluene, kerosene oil and sunflower oil.
6. Degree of extraction is high for pure tri-butyl phosphate and it decreases on dilution of the organic phase with any of the diluent.
7. Degree of extraction increases upto an acid concentration of 0.1 – 0.40 $kmol/m^3$ for itaconic acid.
8. Enthalpy for the reactive extraction with aliquat 336 in ethyl acetate is negetive, this shows that the formation of acid - amine complex is exothermic in nature.
9. Enthalpy for the reactive extraction with tri-butyl phosphate in kerosene is positive, this shows that the formation of acid - TBP complex is endothermic in nature.
10. The acid - extractant complexation reaction is a mass transferred accompanied fast pseudo mth order reaction falling in regime 3.

According to the extraction results of nicotinic acid, following conclusions were made:

Nicotinic acid or niacin is mainly used in pharmaceutical industries.

1. Ethyl Acetate as diluent has the higher solvating power than other functional group diluents. Better extraction was obtained extraction was obtained for Aliquat 336 dissolved in ethyl acetate and TBP dissolved in ethyl acetate than other functional group diluents. It also has better solvating power towards the acid-amine complex.
2. Degree of extraction is higher for quaternary amines than phosphorus bonded oxygen extractants when dissolved in any type of diluent.
3. Degree of extraction is high for Aliquat 336 dissolved in functional group baring diluents and it decreases on diluting the organic phase in contrast to Ethyl alcohol and sunflower oil.
4. Degree of extraction decreases with increase in acid concentration for all organic phase of Aliquat 336
5. Degree of extraction is high for pure tri-butyl phosphate and it decreases on dilution of the organic phase except for sunflower oil.
6. The acid - extractant complexation reaction is a mass tansfered accompanied fast pseudo mth order reaction falling in regime 3.
7. Degree of extraction slowly increases for organic phases of tri-butyl phosphate for Toluene, kerosene oil and sunflower oil as diluent,
8. Enthalpy for the reactive extraction with aliquat 336 in ethyl acetate is negetive, this shows that the formation of acid - amine complex is exothermic in nature.
9. Enthalpy for the reactive extraction with tri-butyl phosphate in ethyl acetate is negative and more than that with aliquat 336 in ethyl acetate, this shows that the formation of acid - TBP complex is exothermic in nature and evolves more heat than in aliquat 336 in ethyl acetate.

The reactive extraction is an emerging technology, it is successful when the acid concentration is low it is to be recovered. The reactive extraction is also useful in mining to recover the metals. Effect of dissolved salts (calcium salts), pH and back extraction technique can be carried as next step, in the design of industrial reactive extraction process that is going to attempt forward and backward extraction of itaconic acid and nicotinic acid simultaneously to achieve continuous product recovery.

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# ANNEXURE

## A. PHYSICAL EXTRACTION WITH PURE DILUENTS

T 4.1.1 A Equilibrium data of itaconic acid in pure Hexane

| $C_{aq}$ initial | $C_{aq}$ final | $C_{org}$ | $K_D$ |
|---|---|---|---|
| 0.05 | 0.042667 | 0.007333 | 0.171875 |
| 0.1 | 0.096 | 0.004 | 0.041667 |
| 0.15 | 0.134667 | 0.015333 | 0.113861 |
| 0.2 | 0.162 | 0.038 | 0.234568 |

T 4.1.1 B Equilibrium data of itaconic acid in pure Toluene

| $C_{aq}$ initial | $C_{aq}$ final | $C_{org}$ | $K_D$ |
|---|---|---|---|
| 0.05 | 0.046 | 0.004 | 0.086957 |
| 0.1 | 0.098667 | 0.001333 | 0.013514 |
| 0.15 | 0.138667 | 0.011333 | 0.081731 |
| 0.2 | 0.165333 | 0.034667 | 0.209677 |

T 4.1.1 C Equilibrium data of itaconic acid id in pure Kerosene oil

| C aq initial | C aq final | C org | KD |
|---|---|---|---|
| 0.05 | 0 | 0 | |
| 0.1 | 0.042667 | 0.007333 | 0.171875 |
| 0.15 | 0.096 | 0.004 | 0.041667 |
| 0.2 | 0.134667 | 0.015333 | 0.113861 |
| | 0.162 | 0.038 | 0.234568 |

T 4.1.1 D Equilibrium data of itaconic acid in pure Sunflower oil

| $C_{aq}$ initial | $C_{aq}$ final | $C_{org}$ | $K_D$ |
|---|---|---|---|
| 0.05 | 0.046 | 0.004 | 0.086957 |
| 0.1 | 0.096 | 0.004 | 0.041667 |
| 0.15 | 0.135333 | 0.014667 | 0.108374 |
| 0.2 | 0.158667 | 0.041333 | 0.260504 |

T 4.1.1 E Equilibrium data of itaconic acid in pure Ethyl acetate

| $C_{aq}$ initial | $C_{aq}$ final | $C_{org}$ | $K_D$ |
|---|---|---|---|
| 0.05 | 0.032 | 0.018 | 0.5625 |
| 0.1 | 0.062 | 0.038 | 0.612903 |
| 0.15 | 0.082 | 0.068 | 0.829268 |
| 0.2 | 0.093333 | 0.106667 | 1.142857 |

T 4.1.2 A Equilibrium data of Nicotinic acid in pure Hexane

| C aq initial | C aq final | C org | KD |
|---|---|---|---|
| 0.05 | 0.049 | 0.001 | 0.020408 |
| 0.075 | 0.0725 | 0.0025 | 0.034483 |
| 0.1 | 0.096 | 0.004 | 0.041667 |
| 0.125 | 0.118 | 0.007 | 0.059322 |
| 0.14 | 0.13 | 0.01 | 0.076923 |

T 4.1.2 B Equilibrium data of Nicotinic acid in pure Toluene

| C aq initial | C aq final | C org | KD |
|---|---|---|---|
| 0.05 | 0.048 | 0.002 | 0.041667 |
| 0.075 | 0.0705 | 0.0045 | 0.06383 |
| 0.1 | 0.0935 | 0.0065 | 0.069519 |
| 0.125 | 0.116 | 0.009 | 0.077586 |
| 0.14 | 0.127 | 0.013 | 0.102362 |

T 4.1.2 C Equilibrium data of Nicotinic acid in pure Kerosene oil

| C aq initial | C aq final | C org | KD |
|---|---|---|---|
| 0.05 | 0.0435 | 0.0065 | 0.149425 |
| 0.075 | 0.0615 | 0.0135 | 0.219512 |
| 0.1 | 0.088 | 0.012 | 0.136364 |
| 0.125 | 0.107 | 0.018 | 0.168224 |
| 0.14 | 0.122 | 0.018 | 0.147541 |

T 4.1.2 D Equilibrium data of Nicotinic acid in pure Sunflower oil

| C aq initial | C aq final | C org | KD |
|---|---|---|---|
| 0.05 | 0.046 | 0.004 | 0.086957 |
| 0.075 | 0.0735 | 0.0015 | 0.020408 |
| 0.1 | 0.0995 | 0.0005 | 0.005025 |
| 0.125 | 0.1185 | 0.0065 | 0.054852 |
| 0.14 | 0.132 | 0.008 | 0.060606 |

T 4.1.2 E Equilibrium data of Nicotinic acid in pure Ethyl acetate

| C aq initial | C aq final | C org | KD |
|---|---|---|---|
| 0.05 | 0.0395 | 0.0105 | 0.265823 |
| 0.075 | 0.058 | 0.017 | 0.293103 |
| 0.1 | 0.076 | 0.024 | 0.315789 |
| 0.125 | 0.093 | 0.032 | 0.344086 |
| 0.14 | 0.0985 | 0.0415 | 0.42132 |

T 4.2.1 A Equilibrium data of itaconic acid with Aliquat 336 in Hexane

| 10% Aliquat | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C aq initial | %NaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | Σ | z1/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 4.7 | 0.03733 | 0.01866 | 0.56574 | 0.19 | 0.01866 | 0.17133 | 0.09824 | 0.10894 | -0.76618 | -0.22494 | 37.33333 |
| 0.1 | 9.5 | 0.06333 | 0.03666 | 0.57894 | 0.19 | 0.03666 | 0.16333 | 0.25982 | 0.22913 | -0.87493 | -0.23761 | 36.66667 |
| 0.2 | 17.8 | 0.11866 | 0.08133 | 0.68533 | 0.19 | 0.08133 | 0.10866 | 0.42807 | 0.74846 | -0.98396 | -0.16406 | 40.66667 |
| 0.4 | 34.8 | 0.232 | 0.168 | 0.72414 | 0.19 | 0.168 | 0.022 | 0.88421 | 7.63636 | -1.65717 | -0.14017 | 42 |
| | | | | | | | | | | | | |
| 20% Aliquat | | | | | | | | | | | | |
| C aq initial | %NaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | Σ | z1/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 3.7 | 0.02466 | 0.02533 | 1.02702 | 0.395 | 0.02533 | 0.39666 | 0.06413 | 0.06853 | -0.4321 | 0.01158 | 50.66667 |
| 0.1 | 7.4 | 0.04933 | 0.05066 | 1.02702 | 0.395 | 0.05066 | 0.34433 | 0.12827 | 0.14714 | -0.4633 | 0.01158 | 50.66667 |
| 0.2 | 14.7 | 0.098 | 0.102 | 1.04081 | 0.395 | 0.102 | 0.293 | 0.25822 | 0.34812 | -0.5331 | 0.01737 | 51 |
| 0.4 | 29.6 | 0.19733 | 0.20266 | 1.02702 | 0.395 | 0.20266 | 0.19233 | 0.51308 | 1.05272 | -0.7759 | 0.01158 | 50.66667 |
| | | | | | | | | | | | | |
| 30% Aliquat | | | | | | | | | | | | |
| C aq initial | %NaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | Σ | z1/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 3.1 | 0.02066 | 0.02933 | 1.41935 | 0.59 | 0.02933 | 0.56066 | 0.04971 | 0.05235 | -0.2825 | 0.15209 | 58.66667 |
| 0.1 | 6.2 | 0.04133 | 0.05866 | 1.41935 | 0.59 | 0.05866 | 0.53133 | 0.09943 | 0.11042 | -0.2746 | 0.15209 | 58.66667 |
| 0.2 | 13.3 | 0.08866 | 0.11133 | 1.25629 | 0.59 | 0.11133 | 0.47866 | 0.18701 | 0.22991 | -0.3199 | 0.09885 | 55.66667 |
| 0.4 | 26.6 | 0.19066 | 0.20933 | 1.09702 | 0.59 | 0.20933 | 0.38066 | 0.36948 | 0.58512 | -0.4196 | 0.04059 | 52.33333 |

T 4.2.1 B Equilibrium data of Nicotinic acid with Alquat 336 in Hexane

| 10% Alquat | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C aq initial | VNaOH | C aq final | C org | KD | [Bi org | [BHA] org | [B] org | z | z\(1-z) | Log(KD) | Log([B]org) | D |
| 0.05 | 9 | 0.045 | 0.005 | 0.111111 | 0.19 | 0.005 | 0.185 | 0.025816 | 0.027027 | -0.95424 | -0.73284 | 10 |
| 0.075 | 11.6 | 0.058 | 0.017 | 0.293103 | 0.19 | 0.017 | 0.173 | 0.089474 | 0.098266 | -0.53297 | -0.76954 | 22.66667 |
| 0.1 | 15.7 | 0.078 | 0.022 | 0.273885 | 0.19 | 0.025 | 0.168 | 0.117158 | 0.132696 | -0.56243 | -0.7734 | 21.5 |
| 0.125 | 16.3 | 0.0815 | 0.043 | 0.533742 | 0.19 | 0.043 | 0.148 | 0.229047 | 0.297068 | -0.27259 | -0.83476 | 34.8 |
| 0.14 | 18.5 | 0.0925 | 0.047 | 0.513514 | 0.19 | 0.047 | 0.142 | 0.25 | 0.333333 | -0.28944 | -0.84618 | 33.92857 |
| | | | | | | | | | | | | |
| 30%alquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [Bi org | [BHA] org | [B] org | z | z\(1-z) | Log(KD) | Log([B]org) | D |
| 0.05 | 7.7 | 0.0385 | 0.0115 | 0.298701 | 0.595 | 0.0115 | 0.585 | 0.019728 | 0.019709 | -0.52476 | -0.23295 | 23 |
| 0.075 | 11.1 | 0.0555 | 0.0195 | 0.351351 | 0.595 | 0.0195 | 0.575 | 0.032773 | 0.033884 | -0.45458 | -0.23995 | 29 |
| 0.1 | 15.3 | 0.0765 | 0.0235 | 0.307189 | 0.595 | 0.0235 | 0.571 | 0.039496 | 0.041112 | -0.51294 | -0.24298 | 23.5 |
| 0.125 | 16.1 | 0.0805 | 0.0445 | 0.552795 | 0.595 | 0.0445 | 0.505 | 0.074179 | 0.080839 | -0.25743 | -0.25243 | 35.6 |
| 0.14 | 18 | 0.09 | 0.05 | 0.555556 | 0.595 | 0.05 | 0.545 | 0.084034 | 0.091743 | -0.25573 | -0.26303 | 35.71429 |
| | | | | | | | | | | | | |
| 40%alquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [Bi org | [BHA] org | [B] org | z | z\(1-z) | Log(KD) | Log([B]org) | D |
| 0.05 | 6.9 | 0.0345 | 0.0155 | 0.449275 | 0.79 | 0.0155 | 0.745 | 0.019652 | 0.020013 | -0.34748 | -0.11079 | 31 |
| 0.075 | 10.2 | 0.051 | 0.024 | 0.470588 | 0.79 | 0.024 | 0.766 | 0.030538 | 0.031332 | -0.32736 | -0.11771 | 32 |
| 0.1 | 15.1 | 0.0755 | 0.0245 | 0.324503 | 0.79 | 0.0245 | 0.765 | 0.031013 | 0.032005 | -0.48878 | -0.11605 | 24.5 |
| 0.125 | 15.8 | 0.079 | 0.046 | 0.582278 | 0.79 | 0.046 | 0.744 | 0.058228 | 0.061824 | -0.23488 | -0.12427 | 36.8 |
| 0.14 | 17.8 | 0.089 | 0.051 | 0.573034 | 0.79 | 0.051 | 0.739 | 0.069057 | 0.074157 | -0.24182 | -0.13156 | 36.42857 |

T 4.2.2 A Equilibrium data of Itaconic acid with Aliquat 336 in Toluene

| 10% Aliquat | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 5 | 0.033333 | 0.016667 | 0.5 | 0.19 | 0.016667 | 0.173333 | 0.087719 | 0.096154 | -0.761118 | -0.30103 | 33.33333 |
| 0.1 | 10.2 | 0.068 | 0.032 | 0.470588 | 0.19 | 0.032 | 0.158 | 0.168421 | 0.202532 | -0.801343 | -0.327359 | 32 |
| 0.2 | 20.1 | 0.134 | 0.066 | 0.492537 | 0.19 | 0.066 | 0.124 | 0.347368 | 0.532258 | -0.906578 | -0.307561 | 33 |
| 0.4 | 34.8 | 0.232 | 0.168 | 0.724138 | 0.19 | 0.168 | 0.022 | 0.884211 | 7.636364 | -1.657577 | -0.140179 | 42 |
| | | | | | | | | | | | | |
| 20% Aliquat | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 3.7 | 0.024667 | 0.025333 | 1.027027 | 0.39 | 0.025333 | 0.364667 | 0.064957 | 0.06947 | -0.438104 | 0.011582 | 50.66667 |
| 0.1 | 7.5 | 0.05 | 0.05 | 1 | 0.39 | 0.05 | 0.34 | 0.128205 | 0.147059 | -0.468521 | 9.64E-17 | 50 |
| 0.2 | 14.7 | 0.098 | 0.102 | 1.040816 | 0.39 | 0.102 | 0.288 | 0.261538 | 0.354167 | -0.540608 | 0.017374 | 51 |
| 0.4 | 32.4 | 0.216 | 0.184 | 0.851852 | 0.39 | 0.184 | 0.206 | 0.471795 | 0.893204 | -0.686133 | -0.069636 | 46 |
| | | | | | | | | | | | | |
| 30%Aliquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 3.1 | 0.020667 | 0.029333 | 1.419355 | 0.59 | 0.029333 | 0.560667 | 0.049718 | 0.052319 | -0.251295 | 0.152091 | 58.66667 |
| 0.1 | 6.2 | 0.041333 | 0.058667 | 1.419355 | 0.59 | 0.058667 | 0.531333 | 0.099435 | 0.110414 | -0.274633 | 0.152091 | 58.66667 |
| 0.2 | 13.3 | 0.088667 | 0.111333 | 1.255639 | 0.59 | 0.111333 | 0.478667 | 0.188701 | 0.232591 | -0.319967 | 0.098865 | 55.66667 |
| 0.4 | 30.8 | 0.205333 | 0.194667 | 0.948052 | 0.59 | 0.194667 | 0.395333 | 0.329944 | 0.492411 | -0.403037 | -0.023168 | 48.66667 |

T 4.2.2 B Equilibrium data of Nicotinic acid with Aliquat 336 in Toluene

| 10% aliquat | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 7.4 | 0.037 | 0.013 | 0.351351 | 0.19 | 0.013 | 0.177 | 0.068421 | 0.073446 | -0.752027 | -0.454258 | 26 |
| 0.075 | 9.7 | 0.0485 | 0.0265 | 0.546392 | 0.19 | 0.0265 | 0.1635 | 0.139474 | 0.16208 | -0.786482 | -0.262496 | 35.33333 |
| 0.1 | 14.6 | 0.073 | 0.027 | 0.369863 | 0.19 | 0.027 | 0.163 | 0.142105 | 0.165644 | -0.787812 | -0.431959 | 27 |
| 0.125 | 14.9 | 0.0745 | 0.0505 | 0.677852 | 0.19 | 0.0505 | 0.1395 | 0.265789 | 0.362007 | -0.855426 | -0.168865 | 40.4 |
| 0.14 | 16.8 | 0.084 | 0.056 | 0.666667 | 0.19 | 0.056 | 0.134 | 0.294737 | 0.41791 | -0.872895 | -0.176091 | 40 |
| | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| 30%aliquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 6.9 | 0.0345 | 0.0155 | 0.449275 | 0.595 | 0.0155 | 0.5795 | 0.02605 | 0.026747 | -0.236947 | -0.347487 | 31 |
| 0.075 | 9.3 | 0.0465 | 0.0285 | 0.612903 | 0.595 | 0.0285 | 0.5665 | 0.047899 | 0.050309 | -0.2468 | -0.212608 | 38 |
| 0.1 | 14.3 | 0.0715 | 0.0285 | 0.398601 | 0.595 | 0.0285 | 0.5665 | 0.047899 | 0.050309 | -0.2468 | -0.399461 | 28.5 |
| 0.125 | 14.7 | 0.0735 | 0.0515 | 0.70068 | 0.595 | 0.0515 | 0.5435 | 0.086555 | 0.094756 | -0.2648 | -0.15448 | 41.2 |
| 0.14 | 16.5 | 0.0825 | 0.0575 | 0.69697 | 0.595 | 0.0575 | 0.5375 | 0.096639 | 0.106977 | -0.269622 | -0.156786 | 41.07143 |
| | | | | | | | | | | | | |
| 40%aliquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 6.7 | 0.0335 | 0.0165 | 0.492537 | 0.79 | 0.0165 | 0.7735 | 0.020886 | 0.021332 | -0.11154 | -0.307561 | 33 |
| 0.075 | 8.9 | 0.0445 | 0.0305 | 0.685393 | 0.79 | 0.0305 | 0.7595 | 0.038608 | 0.040158 | -0.119472 | -0.16406 | 40.66667 |
| 0.1 | 13.7 | 0.0685 | 0.0315 | 0.459854 | 0.79 | 0.0315 | 0.7585 | 0.039873 | 0.041529 | -0.120044 | -0.33738 | 31.5 |
| 0.125 | 14.1 | 0.0705 | 0.0545 | 0.77305 | 0.79 | 0.0545 | 0.7355 | 0.068987 | 0.074099 | -0.133417 | -0.111793 | 43.6 |
| 0.14 | 15.9 | 0.0795 | 0.0605 | 0.761006 | 0.79 | 0.0605 | 0.7295 | 0.076582 | 0.082934 | -0.136975 | -0.118612 | 43.21429 |

T 4.2.3 A Equilibrium data of Itaconic acid with Aliquat 336 in Ethyl acetate

| 10% Aliquat | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| | | 0 | 0 | | | | | | | | | |
| 0.05 | 3.15 | 0.021 | 0.029 | 1.380952 | 0.19 | 0.029 | 0.161 | 0.152632 | 0.161 | -0.793174 | 0.140179 | 58 |
| 0.1 | 7 | 0.046667 | 0.053333 | 1.142857 | 0.19 | 0.053333 | 0.136667 | 0.280702 | 0.390244 | -0.864337 | 0.057992 | 53.33333 |
| 0.15 | 8.1 | 0.054 | 0.096 | 1.777778 | 0.19 | 0.096 | 0.094 | 0.505263 | 1.021277 | -1.026872 | 0.249877 | 64 |
| 0.2 | 10.4 | 0.069333 | 0.130667 | 1.884615 | 0.19 | 0.130667 | 0.059333 | 0.687719 | 2.202247 | -1.226701 | 0.275223 | 65.33333 |
| | | | | | | | | | | | | |
| 20% Aliquat | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| | | | | | | | | | | | | |
| 0.05 | 2.9 | 0.019333 | 0.030667 | 1.586207 | 0.39 | 0.030667 | 0.359333 | 0.078632 | 0.085343 | -0.444502 | 0.20036 | 61.33333 |
| 0.1 | 6.6 | 0.044 | 0.056 | 1.272727 | 0.39 | 0.056 | 0.334 | 0.14359 | 0.167665 | -0.476254 | 0.104735 | 56 |
| 0.15 | 7.1 | 0.047333 | 0.102667 | 2.169014 | 0.39 | 0.102667 | 0.287333 | 0.263248 | 0.357309 | -0.541614 | 0.336262 | 68.44444 |
| 0.2 | 8.6 | 0.057333 | 0.142667 | 2.488372 | 0.39 | 0.142667 | 0.247333 | 0.365812 | 0.576819 | -0.606717 | 0.395915 | 71.33333 |
| | | | | | | | | | | | | |
| 30% Aliquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 2.3 | 0.021 | 0.029 | 1.380952 | 0.59 | 0.029 | 0.561 | 0.049153 | 0.051693 | -0.251037 | 0.140179 | 58 |
| 0.1 | 6.3 | 0.042 | 0.058 | 1.380952 | 0.59 | 0.058 | 0.532 | 0.098305 | 0.109023 | -0.274088 | 0.140179 | 58 |
| 0.15 | 6.8 | 0.045333 | 0.104667 | 2.308824 | 0.59 | 0.104667 | 0.485333 | 0.177401 | 0.215659 | -0.31396 | 0.363391 | 69.77778 |
| 0.2 | 8.2 | 0.054667 | 0.145333 | 2.658537 | 0.59 | 0.145333 | 0.444667 | 0.246328 | 0.326837 | -0.351965 | 0.424643 | 72.66667 |

T 4.2.3 B Equilibrium data of Nicotinic acid with Aliquat 336 in Ethyl acetate

| 10% Aliquat | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 5.2 | 0.026 | 0.024 | 0.923077 | 0.19 | 0.024 | 0.166 | 0.126316 | 0.144578 | -0.779892 | -0.034762 | 48 |
| 0.075 | 6.5 | 0.043333 | 0.031667 | 0.730769 | 0.19 | 0.031667 | 0.158333 | 0.166667 | 0.2 | -0.800428 | -0.13622 | 42.22222 |
| 0.1 | 9.5 | 0.063333 | 0.036667 | 0.578947 | 0.19 | 0.036667 | 0.153333 | 0.192982 | 0.23913 | -0.814363 | -0.237361 | 36.66667 |
| 0.125 | 10.1 | 0.067333 | 0.057667 | 0.856436 | 0.19 | 0.057667 | 0.132333 | 0.303509 | 0.435768 | -0.878331 | -0.067305 | 46.13333 |
| 0.14 | 11.1 | 0.074 | 0.066 | 0.891892 | 0.19 | 0.066 | 0.124 | 0.347368 | 0.532258 | -0.906578 | -0.049688 | 47.14286 |
| | | | | | | | | | | | | |
| 20% Aliquat | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 5.4 | 0.027 | 0.023 | 0.851852 | 0.395 | 0.023 | 0.372 | 0.058228 | 0.061828 | -0.429457 | -0.069636 | 46 |
| 0.075 | 6.7 | 0.0335 | 0.0415 | 1.238806 | 0.395 | 0.0415 | 0.3535 | 0.105063 | 0.117397 | -0.451611 | 0.093003 | 55.33333 |
| 0.1 | 9.8 | 0.049 | 0.051 | 1.040816 | 0.395 | 0.051 | 0.344 | 0.129114 | 0.148256 | -0.463442 | 0.017374 | 51 |
| 0.125 | 10.3 | 0.0515 | 0.0735 | 1.427184 | 0.395 | 0.0735 | 0.3215 | 0.186076 | 0.228616 | -0.492819 | 0.15448 | 58.8 |
| 0.14 | 11.2 | 0.056 | 0.084 | 1.5 | 0.395 | 0.084 | 0.311 | 0.212658 | 0.270096 | -0.50724 | 0.176091 | 60 |
| | | | | | | | | | | | | |
| 30% Aliquat | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 5.6 | 0.028 | 0.022 | 0.785714 | 0.595 | 0.022 | 0.573 | 0.036975 | 0.038394 | -0.241845 | -0.104735 | 44 |
| 0.075 | 6.8 | 0.034 | 0.041 | 1.205882 | 0.595 | 0.041 | 0.554 | 0.068908 | 0.074007 | -0.25649 | 0.081305 | 54.66667 |

T 4.2.4 A Equilibrium data of Itaconic acid with Aliquat 336 in kerosene oil

| 10% Aliquat | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 5 | 0.033333 | 0.016667 | 0.5 | 0.19 | 0.016667 | 0.173333 | 0.087719 | 0.096154 | -0.761118 | -0.30103 | 33.33333 |
| 0.1 | 10.2 | 0.068 | 0.032 | 0.470588 | 0.19 | 0.032 | 0.158 | 0.168421 | 0.202532 | -0.801343 | -0.327359 | 32 |
| 0.2 | 20.1 | 0.134 | 0.066 | 0.492537 | 0.19 | 0.066 | 0.124 | 0.347368 | 0.532258 | -0.906578 | -0.307561 | 33 |
| 0.4 | 34.8 | 0.232 | 0.168 | 0.724138 | 0.19 | 0.168 | 0.022 | 0.884211 | 7.636364 | -1.657577 | -0.140179 | 42 |
| | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| 20% Aliquat | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 3.7 | 0.024667 | 0.025333 | 1.027027 | 0.39 | 0.025333 | 0.364667 | 0.064957 | 0.06947 | -0.438104 | 0.011582 | 50.66667 |
| 0.1 | 7.5 | 0.05 | 0.05 | 1 | 0.39 | 0.05 | 0.34 | 0.128205 | 0.147059 | -0.468521 | 9.64E-17 | 50 |
| 0.2 | 14.7 | 0.098 | 0.102 | 1.040816 | 0.39 | 0.102 | 0.288 | 0.261538 | 0.354167 | -0.540608 | 0.017374 | 51 |
| 0.4 | 32.4 | 0.216 | 0.184 | 0.851852 | 0.39 | 0.184 | 0.206 | 0.471795 | 0.893204 | -0.686133 | -0.069636 | 46 |
| | | | | | | | | | | | | |
| )0% Aliquat | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 3.1 | 0.020667 | 0.029333 | 1.419355 | 0.59 | 0.029333 | 0.560667 | 0.049718 | 0.052319 | -0.251295 | 0.152091 | 58.66667 |
| 0.1 | 10.2 | 0.068 | 0.032 | 0.470588 | 0.59 | 0.032 | 0.558 | 0.054237 | 0.057348 | -0.253366 | -0.327359 | 32 |
| 0.2 | 20.1 | 0.134 | 0.066 | 0.492537 | 0.59 | 0.066 | 0.524 | 0.111864 | 0.125954 | -0.280669 | -0.307561 | 33 |
| 0.4 | 30.8 | 0.205333 | 0.194667 | 0.948052 | 0.59 | 0.194667 | 0.395333 | 0.329944 | 0.492411 | -0.403037 | -0.023168 | 48.66667 |

T 4.2.4 B Equilibrium data of Nicotinic acid with Aliquat 336 in kerosene oil

| 10% Aliquat | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 8.8 | 0.044 | 0.006 | 0.136364 | 0.19 | 0.006 | 0.184 | 0.031579 | 0.032609 | -0.735182 | -0.865301 | 12 |
| 0.075 | 12.1 | 0.0605 | 0.0145 | 0.239669 | 0.19 | 0.0145 | 0.1755 | 0.076316 | 0.082621 | -0.755723 | -0.620387 | 19.33333 |
| 0.1 | 15.8 | 0.079 | 0.021 | 0.265823 | 0.19 | 0.021 | 0.169 | 0.110526 | 0.12426 | -0.772113 | -0.575408 | 21 |
| 0.125 | 19.1 | 0.0955 | 0.0295 | 0.308901 | 0.19 | 0.0295 | 0.1605 | 0.155263 | 0.183801 | -0.794525 | -0.510181 | 23.6 |
| 0.14 | 21.2 | 0.106 | 0.034 | 0.320755 | 0.19 | 0.034 | 0.156 | 0.178947 | 0.217949 | -0.806875 | -0.493827 | 24.28571 |
| | | | | | | | | | | | | |
| 30% Aliquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 8.4 | 0.042 | 0.008 | 0.190476 | 0.595 | 0.008 | 0.587 | 0.013445 | 0.013629 | -0.231362 | -0.720159 | 16 |
| 0.075 | 11.9 | 0.0595 | 0.0155 | 0.260504 | 0.595 | 0.0155 | 0.5795 | 0.02605 | 0.026747 | -0.236947 | -0.584185 | 20.66667 |
| 0.1 | 15.2 | 0.076 | 0.024 | 0.315789 | 0.595 | 0.024 | 0.571 | 0.040336 | 0.042032 | -0.243364 | -0.500602 | 24 |
| 0.125 | 17.5 | 0.0875 | 0.0375 | 0.428571 | 0.595 | 0.0375 | 0.5575 | 0.063025 | 0.067265 | -0.253755 | -0.367977 | 30 |
| 0.14 | 18.9 | 0.0945 | 0.0455 | 0.481481 | 0.595 | 0.0455 | 0.5495 | 0.076471 | 0.082803 | -0.260032 | -0.31742 | 32.5 |
| | | | | | | | | | | | | |
| 40% Aliquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org) | Log(KD) | D |
| 0.05 | 7.7 | 0.0385 | 0.0115 | 0.298701 | 0.79 | 0.0115 | 0.7785 | 0.014557 | 0.014772 | -0.108741 | -0.524763 | 23 |
| 0.075 | 10.7 | 0.0535 | 0.0215 | 0.401869 | 0.79 | 0.0215 | 0.7685 | 0.027215 | 0.027977 | -0.114356 | -0.395915 | 28.66667 |
| 0.1 | 14.9 | 0.0745 | 0.0255 | 0.342282 | 0.79 | 0.0255 | 0.7645 | 0.032278 | 0.033355 | -0.116623 | -0.465616 | 25.5 |
| 0.125 | 17.2 | 0.086 | 0.039 | 0.453488 | 0.79 | 0.039 | 0.751 | 0.049367 | 0.051931 | -0.12436 | -0.343434 | 31.2 |
| 0.14 | 18.8 | 0.094 | 0.046 | 0.489362 | 0.79 | 0.046 | 0.744 | 0.058228 | 0.061828 | -0.128427 | -0.31037 | 32.85714 |

T 4.2.5 A Equilibrium data of Itaconic acid with Aliquat 336 in sunflower oil

| 10% Aliquat | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 5.9 | 0.039333 | 0.010667 | 0.271186 | 0.19 | 0.010667 | 0.179333 | 0.05614 | 0.12 | -0.746339 | -0.566732 | 21.33333 |
| 0.1 | 11.3 | 0.075333 | 0.024667 | 0.327434 | 0.19 | 0.024667 | 0.165333 | 0.129825 | 0.149194 | -0.78164 | -0.484877 | 24.66667 |
| 0.15 | 14 | 0.093333 | 0.056667 | 0.607143 | 0.19 | 0.056667 | 0.133333 | 0.298246 | 0.425 | -0.875061 | -0.216709 | 37.77778 |
| 0.2 | 15.9 | 0.106 | 0.094 | 0.886792 | 0.19 | 0.094 | 0.096 | 0.494737 | 0.979167 | -1.017729 | -0.052178 | 47 |
| 20% Aliquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 5.7 | 0.038 | 0.012 | 0.315789 | 0.39 | 0.012 | 0.378 | 0.030769 | 0.031746 | -0.422508 | -0.500602 | 24 |
| 0.1 | 11.1 | 0.074 | 0.026 | 0.351351 | 0.39 | 0.026 | 0.364 | 0.066667 | 0.071429 | -0.438899 | -0.454258 | 26 |
| 0.15 | 13.8 | 0.092 | 0.058 | 0.630435 | 0.39 | 0.058 | 0.332 | 0.148718 | 0.174699 | -0.478862 | -0.20036 | 38.66667 |
| 0.2 | 15.7 | 0.104667 | 0.095333 | 0.910828 | 0.39 | 0.095333 | 0.294667 | 0.244444 | 0.323529 | -0.530669 | -0.040564 | 47.66667 |
| 30% Aliquat | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | [BA] org | z | z/(1-z) | Log([BA]or | Log(KD) | D |
| 0.05 | 5.4 | 0.036 | 0.014 | 0.388889 | 0.59 | 0.014 | 0.576 | 0.023729 | 0.024306 | -0.239578 | -0.410174 | 28 |
| 0.1 | 10.8 | 0.072 | 0.028 | 0.388889 | 0.59 | 0.028 | 0.562 | 0.047458 | 0.049822 | -0.250264 | -0.410174 | 28 |
| 0.15 | 13.5 | 0.09 | 0.06 | 0.666667 | 0.59 | 0.06 | 0.53 | 0.101695 | 0.113208 | -0.275724 | -0.176091 | 40 |
| 0.2 | 15.4 | 0.102667 | 0.097333 | 0.948052 | 0.59 | 0.097333 | 0.492667 | 0.164972 | 0.197564 | -0.307447 | -0.023168 | 48.66667 |

T 4.2.5 B Equilibrium data of Nicotinic acid with Aliquat 336 in sunflower oil

| 10% aliquat | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org | Log(KD) | D |
| 0.05 | 8 | 0.04 | 0.01 | 0.25 | 0.19 | 0.01 | 0.18 | 0.052632 | 0.055556 | -0.744727 | -0.60206 | 20 |
| 0.075 | 11.4 | 0.057 | 0.018 | 0.315789 | 0.19 | 0.018 | 0.172 | 0.094737 | 0.104651 | -0.764472 | -0.500602 | 24 |
| 0.1 | 15.2 | 0.076 | 0.024 | 0.315789 | 0.19 | 0.024 | 0.166 | 0.126316 | 0.144578 | -0.779892 | -0.500602 | 24 |
| 0.125 | 17.8 | 0.089 | 0.036 | 0.404494 | 0.19 | 0.036 | 0.154 | 0.189474 | 0.233766 | -0.812479 | -0.393088 | 28.8 |
| 0.14 | 18.6 | 0.093 | 0.047 | 0.505376 | 0.19 | 0.047 | 0.143 | 0.247368 | 0.328671 | -0.844664 | -0.296385 | 33.57143 |
| | | | | | | | | | | | | |
| 30%aliquat | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org | Log(KD) | D |
| 0.05 | 5.1 | 0.034 | 0.016 | 0.470588 | 0.595 | 0.016 | 0.579 | 0.026891 | 0.027634 | -0.237321 | -0.327359 | 32 |
| 0.075 | 7.4 | 0.049333 | 0.025667 | 0.52027 | 0.595 | 0.025667 | 0.569333 | 0.043137 | 0.045082 | -0.244633 | -0.283771 | 34.22222 |
| 0.1 | 9.8 | 0.065333 | 0.034667 | 0.530612 | 0.595 | 0.034667 | 0.560333 | 0.058263 | 0.061868 | -0.251554 | -0.275223 | 34.66667 |
| 0.125 | 11.8 | 0.078667 | 0.046333 | 0.588983 | 0.595 | 0.046333 | 0.548667 | 0.077871 | 0.084447 | -0.260691 | -0.229897 | 37.06667 |
| 0.14 | 12.2 | 0.081333 | 0.058667 | 0.721311 | 0.595 | 0.058667 | 0.536333 | 0.098599 | 0.109385 | -0.270565 | -0.141877 | 41.90476 |
| | | | | | | | | | | | | |
| 40%aliquat | | | | | | | | | | | | |
| | | | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [BHA] org | [B] org | z | z/(1-z) | Log([B]org | Log(KD) | D |
| 0.05 | 5 | 0.033333 | 0.016667 | 0.5 | 0.79 | 0.016667 | 0.773333 | 0.021097 | 0.021552 | -0.111633 | -0.30103 | 33.33333 |
| 0.075 | 7 | 0.046667 | 0.028333 | 0.607143 | 0.79 | 0.028333 | 0.761667 | 0.035865 | 0.037199 | -0.118235 | -0.216709 | 37.77778 |
| 0.1 | 9.2 | 0.061333 | 0.038667 | 0.630435 | 0.79 | 0.038667 | 0.751333 | 0.048945 | 0.051464 | -0.124167 | -0.20036 | 38.66667 |
| 0.125 | 11.2 | 0.074667 | 0.050333 | 0.674107 | 0.79 | 0.050333 | 0.739667 | 0.063713 | 0.068049 | -0.130964 | -0.171271 | 40.26667 |
| 0.14 | 12 | 0.08 | 0.06 | 0.75 | 0.79 | 0.06 | 0.73 | 0.075949 | 0.082192 | -0.136677 | -0.124939 | 42.85714 |

C. CHEMICAL EXTRACTION WITH TBP IN DILUENTS

T 4.3.1 A Equilibrium data of Itaconic acid with TBP in Hexane

| 10% TBP | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 1.5 | 0.015 | 0.035 | 2.333333 | 0.37 | 0.035 | 3.85 | 3.7 | 0.367977 | 70 |
| 0.1 | 2.9 | 0.029 | 0.071 | 2.448276 | 0.37 | 0.071 | 3.85 | 3.61 | 0.38886 | 71 |
| 0.2 | 4.5 | 0.045 | 0.155 | 3.444444 | 0.37 | 0.155 | 3.85 | 3.55 | 0.537119 | 77.5 |
| 0.4 | 9.5 | 0.095 | 0.305 | 3.210526 | 0.37 | 0.305 | 3.85 | 3.3 | 0.506576 | 76.25 |
| | | | | | | | | | | |
| 20% tbp | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 2.1 | 0.021 | 0.029 | 1.380952 | 0.74 | 0.029 | 3.85 | 3.7 | 0.140179 | 58 |
| 0.1 | 4.4 | 0.044 | 0.056 | 1.272727 | 0.74 | 0.056 | 3.85 | 3.61 | 0.104735 | 56 |
| 0.2 | 9.2 | 0.092 | 0.108 | 1.173913 | 0.74 | 0.108 | 3.85 | 3.55 | 0.069636 | 54 |
| 0.4 | 19.3 | 0.193 | 0.207 | 1.072539 | 0.74 | 0.207 | 3.85 | 3.3 | 0.030413 | 51.75 |
| | | | | | | | | | | |
| 30% TBP | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 0.9 | 0.009 | 0.041 | 4.555556 | 1.1 | 0.041 | 3.85 | 3.7 | 0.658541 | 82 |
| 0.1 | 1.2 | 0.012 | 0.088 | 7.333333 | 1.1 | 0.088 | 3.85 | 3.61 | 0.865301 | 88 |
| 0.2 | 3.3 | 0.033 | 0.167 | 5.060606 | 1.1 | 0.167 | 3.85 | 3.55 | 0.704203 | 83.5 |
| 0.4 | 7.5 | 0.075 | 0.325 | 4.333333 | 1.1 | 0.325 | 3.85 | 3.3 | 0.636822 | 81.25 |

T 4.3.1 B Equilibrium data of Nicotinic acid with TBP in Hexane

| 10% TBP | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.0495 | 0.0005 | 0.010101 | 0.37 | 0.0005 | 4.85 | 4.574078 | 1 |
| 0.075 | 0.074 | 0.001 | 0.013514 | 0.37 | 0.001 | 4.85 | 4.407192 | 1.333333 |
| 0.1 | 0.098 | 0.002 | 0.020408 | 0.37 | 0.002 | 4.85 | 4.286816 | 2 |
| 0.125 | 0.1175 | 0.0075 | 0.06383 | 0.37 | 0.0075 | 4.85 | 4.220422 | 6 |
| 0.14 | 0.131 | 0.009 | 0.068702 | 0.37 | 0.009 | 4.85 | 4.190954 | 6.428571 |
| | | | | | | | | |
| 20% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.0485 | 0.0015 | 0.030928 | 0.74 | 0.0015 | 4.85 | 4.581834 | 3 |
| 0.075 | 0.0725 | 0.0025 | 0.034483 | 0.74 | 0.0025 | 4.85 | 4.416132 | 3.333333 |
| 0.1 | 0.099 | 0.001 | 0.010101 | 0.74 | 0.001 | 4.85 | 4.282726 | 1 |
| 0.125 | 0.116 | 0.009 | 0.077586 | 0.74 | 0.009 | 4.85 | 4.224529 | 7.2 |
| 0.14 | 0.1295 | 0.0105 | 0.081081 | 0.74 | 0.0105 | 4.85 | 4.193562 | 7.5 |
| | | | | | | | | |
| 30% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.047 | 0.003 | 0.06383 | 1.1 | 0.003 | 4.85 | 4.593606 | 6 |
| 0.075 | 0.07 | 0.005 | 0.071429 | 1.1 | 0.005 | 4.85 | 4.431402 | 6.666667 |
| 0.1 | 0.097 | 0.003 | 0.030928 | 1.1 | 0.003 | 4.85 | 4.29098 | 3 |
| 0.125 | 0.114 | 0.011 | 0.096491 | 1.1 | 0.011 | 4.85 | 4.230265 | 8.8 |
| 0.14 | 0.1245 | 0.0155 | 0.124498 | 1.1 | 0.0155 | 4.85 | 4.203457 | 11.07143 |

T 4.3.2 A Equilibrium data of Itaconic acid with TBP in Toluene

| 10% TBP | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 4.5 | 0.045 | 0.005 | 0.111111 | 0.37 | 0.005 | 3.85 | 3.7 | -0.954243 | 10 |
| 0.1 | 9.1 | 0.091 | 0.009 | 0.098901 | 0.37 | 0.009 | 3.85 | 3.61 | -1.004799 | 9 |
| 0.2 | 18.3 | 0.183 | 0.017 | 0.092896 | 0.37 | 0.017 | 3.85 | 3.55 | -1.032002 | 8.5 |
| 0.4 | 31.8 | 0.318 | 0.082 | 0.257862 | 0.37 | 0.082 | 3.85 | 3.3 | -0.588613 | 20.5 |
| | | | | | | | | | | |
| | | | | | | | | | | |
| 20% TBP | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 3.3 | 0.033 | 0.017 | 0.515152 | 0.74 | 0.017 | 3.85 | 3.7 | -0.288065 | 34 |
| 0.1 | 6.6 | 0.066 | 0.034 | 0.515152 | 0.74 | 0.034 | 3.85 | 3.61 | -0.288065 | 34 |
| 0.2 | 13.4 | 0.134 | 0.066 | 0.492537 | 0.74 | 0.066 | 3.85 | 3.55 | -0.307561 | 33 |
| 0.4 | 23.1 | 0.231 | 0.169 | 0.731602 | 0.74 | 0.169 | 3.85 | 3.3 | -0.135725 | 42.25 |
| | | | | | | | | | | |
| | | | | | | | | | | |
| 30% TBP | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 2.4 | 0.024 | 0.026 | 1.083333 | 1.1 | 0.026 | 3.85 | 3.7 | 0.034762 | 52 |
| 0.1 | 4.6 | 0.046 | 0.054 | 1.173913 | 1.1 | 0.054 | 3.85 | 3.61 | 0.069636 | 54 |
| 0.2 | 9.4 | 0.094 | 0.106 | 1.12766 | 1.1 | 0.106 | 3.85 | 3.55 | 0.052178 | 53 |
| 0.4 | 17 | 0.17 | 0.23 | 1.352941 | 1.1 | 0.23 | 3.85 | 3.3 | 0.131279 | 57.5 |

T 4.3.2 B Equilibrium data of Nicotinic acid with TBP in Toluene

| 10% TBP | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | |
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.047 | 0.003 | 0.06383 | 0.37 | 0.003 | 3.85 | 3.7 | 6 |
| 0.1 | | 0.097 | 0.003 | 0.030928 | 0.37 | 0.003 | 3.85 | 3.61 | 3 |
| 0.125 | | 0.1145 | 0.0105 | 0.091703 | 0.37 | 0.0105 | 3.85 | 3.55 | 8.4 |
| 0.14 | | 0.118 | 0.022 | 0.186441 | 0.37 | 0.022 | 3.85 | 3.33 | 15.71429 |
| | | | | | | | | | |
| 20% TBP | | | | | | | | | |
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.046 | 0.004 | 0.086957 | 0.74 | 0.004 | 3.85 | 3.7 | 8 |
| 0.1 | | 0.091 | 0.009 | 0.098901 | 0.74 | 0.009 | 3.85 | 3.61 | 9 |
| 0.125 | | 0.106 | 0.019 | 0.179245 | 0.74 | 0.019 | 3.85 | 3.55 | 15.2 |
| 0.14 | | 0.1125 | 0.0275 | 0.244444 | 0.74 | 0.0275 | 3.85 | 3.33 | 19.64286 |
| | | | | | | | | | |
| 30%TBP | | | | | | | | | |
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.0445 | 0.0055 | 0.123596 | 1.1 | 0.0055 | 3.85 | 3.7 | 11 |
| 0.1 | | 0.0855 | 0.0145 | 0.169591 | 1.1 | 0.0145 | 3.85 | 3.61 | 14.5 |
| 0.125 | | 0.1005 | 0.0245 | 0.243781 | 1.1 | 0.0245 | 3.85 | 3.55 | 19.6 |
| 0.14 | | 0.109 | 0.031 | 0.284404 | 1.1 | 0.031 | 3.85 | 3.33 | 22.14286 |

T 4.3.3 A Equilibrium data of Itaconic acid with TBP in Ethyl acetate

| 10% TBP | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 0.7 | 0.007 | 0.043 | 6.142857 | 0.37 | 0.043 | 3.85 | 3.7 | 0.78837 | 86 |
| 0.1 | 2.6 | 0.026 | 0.074 | 2.846154 | 0.37 | 0.074 | 3.85 | 3.61 | 0.454258 | 74 |
| 0.2 | 5.5 | 0.055 | 0.145 | 2.636364 | 0.37 | 0.145 | 3.85 | 3.55 | 0.421005 | 72.5 |
| 0.4 | 11.7 | 0.117 | 0.283 | 2.418803 | 0.37 | 0.283 | 3.85 | 3.3 | 0.383601 | 70.75 |
| | | | | | | | | | | |
| 20% TBP | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 1.2 | 0.012 | 0.038 | 3.166667 | 0.74 | 0.038 | 3.85 | 3.7 | 0.500602 | 76 |
| 0.1 | 2.5 | 0.025 | 0.075 | 3 | 0.74 | 0.075 | 3.85 | 3.61 | 0.477121 | 75 |
| 0.2 | 5.1 | 0.051 | 0.149 | 2.921569 | 0.74 | 0.149 | 3.85 | 3.55 | 0.465616 | 74.5 |
| 0.4 | 10.5 | 0.105 | 0.295 | 2.809524 | 0.74 | 0.295 | 3.85 | 3.3 | 0.448633 | 73.75 |
| | | | | | | | | | | |
| 30% TBP | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 1 | 0.01 | 0.04 | 4 | 1.1 | 0.04 | 3.85 | 3.7 | 0.60206 | 80 |
| 0.1 | 1.6 | 0.016 | 0.084 | 5.25 | 1.1 | 0.084 | 3.85 | 3.61 | 0.720159 | 84 |
| 0.2 | 3.5 | 0.035 | 0.165 | 4.714286 | 1.1 | 0.165 | 3.85 | 3.55 | 0.673416 | 82.5 |
| 0.4 | 7.1 | 0.071 | 0.329 | 4.633803 | 1.1 | 0.329 | 3.85 | 3.3 | 0.665938 | 82.25 |

T 4.3.3 B Equilibrium data of Nicotinic acid with TBP in Ethyl acetate

| 0.1 | ethyl acetate in TBP | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.038 | 0.012 | 0.315789 | 0.37 | 0.012 | 3.85 | 3.7 | 24 |
| 0.1 | | 0.0745 | 0.0255 | 0.342282 | 0.37 | 0.0255 | 3.85 | 3.61 | 25.5 |
| 0.125 | | 0.0875 | 0.0375 | 0.428571 | 0.37 | 0.0375 | 3.85 | 3.61 | 30 |
| 0.14 | | 0.0945 | 0.0455 | 0.481481 | 0.37 | 0.0455 | 3.85 | 3.61 | 32.5 |
| | | | | | | | | | |
| 0.2 | | | | | | | | | |
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.0375 | 0.0125 | 0.333333 | 0.74 | 0.0125 | 3.85 | 3.7 | 25 |
| 0.1 | | 0.0735 | 0.0265 | 0.360544 | 0.74 | 0.0265 | 3.85 | 3.61 | 26.5 |
| 0.125 | | 0.086 | 0.039 | 0.453488 | 0.74 | 0.039 | 3.85 | 3.61 | 31.2 |
| 0.14 | | 0.094 | 0.046 | 0.489362 | 0.74 | 0.046 | 3.85 | 3.61 | 32.85714 |
| | | | | | | | | | |
| 0.3 | | | | | | | | | |
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.037 | 0.013 | 0.351351 | 1.1 | 0.013 | 3.85 | 3.7 | 26 |
| 0.1 | | 0.072 | 0.028 | 0.388889 | 1.1 | 0.028 | 3.85 | 3.61 | 28 |
| 0.125 | | 0.085 | 0.04 | 0.470588 | 1.1 | 0.04 | 3.85 | 3.61 | 32 |
| 0.14 | | 0.0915 | 0.0485 | 0.530055 | 1.1 | 0.0485 | 3.85 | 3.61 | 34.64286 |

T 4.3.4 A Equilibrium data of Itaconic acid with TBP in Kerosene oil

| 10% TBP | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 4.8 | 0.048 | 0.002 | 0.041667 | 0.37 | 0.002 | 3.85 | 3.7 | -1.380211 | 4 |
| 0.1 | 9.8 | 0.098 | 0.002 | 0.020408 | 0.37 | 0.002 | 3.85 | 3.61 | -1.690196 | 2 |
| 0.2 | 19.7 | 0.197 | 0.003 | 0.015228 | 0.37 | 0.003 | 3.85 | 3.55 | -1.817345 | 1.5 |
| 0.4 | 39.6 | 0.396 | 0.004 | 0.010101 | 0.37 | 0.004 | 3.85 | 3.3 | -1.995635 | 1 |
| | | | | | | | | | | |
| | | | | | | | | | | |
| 20% TBP | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 3.6 | 0.036 | 0.014 | 0.388889 | 0.74 | 0.014 | 3.85 | 3.7 | -0.410174 | 28 |
| 0.1 | 7 | 0.07 | 0.03 | 0.428571 | 0.74 | 0.03 | 3.85 | 3.61 | -0.367977 | 30 |
| 0.2 | 14.5 | 0.145 | 0.055 | 0.37931 | 0.74 | 0.055 | 3.85 | 3.55 | -0.421005 | 27.5 |
| 0.4 | 31.8 | 0.318 | 0.082 | 0.257862 | 0.74 | 0.082 | 3.85 | 3.3 | -0.588613 | 20.5 |
| | | | | | | | | | | |
| | | | | | | | | | | |
| 30% TBP | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 2.8 | 0.028 | 0.022 | 0.785714 | 1.1 | 0.022 | 3.85 | 3.7 | -0.104735 | 44 |
| 0.1 | 4.1 | 0.041 | 0.059 | 1.439024 | 1.1 | 0.059 | 3.85 | 3.61 | 0.158068 | 59 |
| 0.2 | 9.6 | 0.096 | 0.104 | 1.083333 | 1.1 | 0.104 | 3.85 | 3.55 | 0.034762 | 52 |
| 0.4 | 21.9 | 0.219 | 0.181 | 0.826484 | 1.1 | 0.181 | 3.85 | 3.3 | -0.082766 | 45.25 |

T 4.3.4 B Equilibrium data of Nicotinic acid with TBP in Kerosene oil

| 0.1 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [HA] org | pKa | pH | D |
| 0.05 | 9.5 | 0.0475 | 0.0025 | 0.052632 | 0.37 | 0.0025 | 3.85 | 3.7 | 5 |
| 0.1 | 19.8 | 0.099 | 0.001 | 0.010101 | 0.37 | 0.001 | 3.85 | 3.61 | 1 |
| 0.125 | 23.6 | 0.118 | 0.007 | 0.059322 | 0.37 | 0.007 | 3.85 | 3.55 | 5.6 |
| 0.14 | 26.4 | 0.132 | 0.008 | 0.060606 | 0.37 | 0.008 | 3.85 | 3.33 | 5.714286 |
| | | | | | | | | | |
| | | | | | | | | | |
| 0.2 | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [HA] org | pKa | pH | D |
| 0.05 | 9.4 | 0.047 | 0.003 | 0.06383 | 0.74 | 0.003 | 3.85 | 3.7 | 6 |
| 0.1 | 19.4 | 0.097 | 0.003 | 0.030928 | 0.74 | 0.003 | 3.85 | 3.61 | 3 |
| 0.125 | 22.8 | 0.114 | 0.011 | 0.096491 | 0.74 | 0.011 | 3.85 | 3.55 | 8.8 |
| 0.14 | 25.4 | 0.127 | 0.013 | 0.102362 | 0.74 | 0.013 | 3.85 | 3.33 | 9.285714 |
| | | | | | | | | | |
| 0.3 | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [B]i org | [HA] org | pKa | pH | D |
| 0.05 | 9.2 | 0.046 | 0.004 | 0.086957 | 1.1 | 0.004 | 3.85 | 3.7 | 8 |
| 0.1 | 18.5 | 0.0925 | 0.0075 | 0.081081 | 1.1 | 0.0075 | 3.85 | 3.61 | 7.5 |
| 0.125 | 21.7 | 0.1085 | 0.0165 | 0.152074 | 1.1 | 0.0165 | 3.85 | 3.55 | 13.2 |
| 0.14 | 24 | 0.12 | 0.02 | 0.166667 | 1.1 | 0.02 | 3.85 | 3.33 | 14.28571 |

T 4.3.5 A Equilibrium data of Itaconic acid with TBP in Sunflower oil

| 10% TBP | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 4.1 | 0.041 | 0.009 | 0.219512 | 0.37 | 0.009 | 3.85 | 3.7 | -0.658541 | 18 |
| 0.1 | 8.4 | 0.084 | 0.016 | 0.190476 | 0.37 | 0.016 | 3.85 | 3.61 | -0.720159 | 16 |
| 0.2 | 17.7 | 0.177 | 0.023 | 0.129944 | 0.37 | 0.023 | 3.85 | 3.55 | -0.886245 | 11.5 |
| 0.4 | 37.8 | 0.378 | 0.022 | 0.058201 | 0.37 | 0.022 | 3.85 | 3.3 | -1.235069 | 5.5 |
| | | | | | | | | | | |
| 20% tbp | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 2.3 | 0.023 | 0.027 | 1.173913 | 0.74 | 0.027 | 3.85 | 3.7 | 0.069636 | 54 |
| 0.1 | 5.1 | 0.051 | 0.049 | 0.960784 | 0.74 | 0.049 | 3.85 | 3.61 | -0.017374 | 49 |
| 0.2 | 10.6 | 0.106 | 0.094 | 0.886792 | 0.74 | 0.094 | 3.85 | 3.55 | -0.052178 | 47 |
| 0.4 | 21.6 | 0.216 | 0.184 | 0.851852 | 0.74 | 0.184 | 3.85 | 3.3 | -0.069636 | 46 |
| | | | | | | | | | | |
| 30% TBP | | | | | | | | | | |
| | | | | | | | | | | |
| C aq initial | VNaOH | C aq final | C org | KD | [BA]i org | [BHA] org | pKa | pH | Log(KD) | D |
| 0.05 | 2.1 | 0.021 | 0.029 | 1.380952 | 1.1 | 0.029 | 3.85 | 3.7 | 0.140179 | 58 |
| 0.1 | 4.9 | 0.049 | 0.051 | 1.040816 | 1.1 | 0.051 | 3.85 | 3.61 | 0.017374 | 51 |
| 0.2 | 8.9 | 0.089 | 0.111 | 1.247191 | 1.1 | 0.111 | 3.85 | 3.55 | 0.095933 | 55.5 |
| 0.4 | 19.6 | 0.196 | 0.204 | 1.040816 | 1.1 | 0.204 | 3.85 | 3.3 | 0.017374 | 51 |

T 4.3.5 B Equilibrium data of Nicotinic acid with TBP in Sunflower oil

| 10%TBP | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.048 | 0.002 | 0.041667 | | 0.37 | 0.002 | 3.85 | 3.7 | 4 |
| 0.1 | 0.092 | 0.008 | 0.086957 | | 0.37 | 0.008 | 3.85 | 3.61 | 8 |
| 0.125 | 0.1135 | 0.0115 | 0.101322 | | 0.37 | 0.0115 | 3.85 | 3.55 | 9.2 |
| 0.14 | 0.127 | 0.013 | 0.102362 | | 0.37 | 0.013 | 3.85 | 3.33 | 9.285714 |
| | | | | | | | | | |
| 20%TBP | | | | | | | | | |
| C aq initial | C aq final | C org | KD | | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.045 | 0.005 | 0.111111 | | 0.74 | 0.005 | 3.85 | 3.7 | 10 |
| 0.1 | 0.0885 | 0.0115 | 0.129944 | | 0.74 | 0.0115 | 3.85 | 3.61 | 11.5 |
| 0.125 | 0.1095 | 0.0155 | 0.141553 | | 0.74 | 0.0155 | 3.85 | 3.55 | 12.4 |
| 0.14 | 0.1155 | 0.0245 | 0.212121 | | 0.74 | 0.0245 | 3.85 | 3.33 | 17.5 |
| | | | | | | | | | |
| 0.3 | | | | | | | | | |
| C aq initial | C aq final | C org | KD | | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.0435 | 0.0065 | 0.149425 | | 1.1 | 0.0065 | 3.85 | 3.7 | 13 |
| 0.1 | 0.085 | 0.015 | 0.176471 | | 1.1 | 0.015 | 3.85 | 3.61 | 15 |
| 0.125 | 0.107 | 0.018 | 0.168224 | | 1.1 | 0.018 | 3.85 | 3.55 | 14.4 |
| 0.14 | C aq final | C org | KD | | 1.1 | 0.027 | 3.85 | 3.33 | 19.28571 |

T 4.3.R Equilibrium constant $K_{11}$ and salvation number p for chemical extraction with TBP in diluents

| | Itaconic acid | | Nicotinic acid | |
|---|---|---|---|---|
| | p | K11 | p | K11 |
| Ethyl acetate | 2.2 | 2.991 | 3.6 | 2.7657 |
| Hexane | 0.95 | 1.7641 | 3.2 | 1.5 |
| Toluene | 1.05 | 1.079 | 3.5 | 1.85 |
| Kerosene oil | 1.11 | 1.958 | 2.85 | 2.617 |
| Sunflower oil | 1.05 | 1.2792 | 6.25 | 1.165 |

D. EFFECT OF TEMPERATURE ON REACTIVE EXTACTION

T 4.6.1 A Equilibrium data of Itaconic acid with Aliquat 336 in Ethyl acetate at 313 K

| 10% Aliquat | | | | | | | |
|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.024747 | 0.025253 | 1.020474 | 0.19 | 0.132912 | 0.153286 | 50.50667 |
| 0.1 | 0.033707 | 0.066293 | 1.966772 | 0.19 | 0.348912 | 0.535891 | 66.29333 |
| 0.2 | 0.062293 | 0.137707 | 2.210616 | 0.19 | 0.724772 | 2.63335 | 68.85333 |
| 0.4 | 0.09984 | 0.30016 | 3.00641 | 0.19 | 1.579789 | 3.759519 | 75.04 |
| | | | | | | | |
| | | | | | | | |
| 20% Aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.021333 | 0.028667 | 1.34375 | 0.39 | 0.073504 | 0.079336 | 57.33333 |
| 0.1 | 0.029013 | 0.070987 | 2.446691 | 0.39 | 0.182017 | 0.222519 | 70.98667 |
| 0.2 | 0.055893 | 0.144107 | 2.578244 | 0.39 | 0.369504 | 0.586054 | 72.05333 |
| 0.4 | 0.084053 | 0.315947 | 3.758883 | 0.39 | 0.81012 | 4.266475 | 78.98667 |
| | | | | | | | |
| | | | | | | | |
| 30% aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.019627 | 0.030373 | 1.547554 | 0.79 | 0.038447 | 0.039985 | 60.74667 |
| 0.1 | 0.02688 | 0.07312 | 2.720238 | 0.79 | 0.092557 | 0.101998 | 73.12 |
| 0.2 | 0.054187 | 0.145813 | 2.690945 | 0.79 | 0.184574 | 0.226353 | 72.90667 |
| 0.4 | 0.081493 | 0.318507 | 3.908377 | 0.79 | 0.403173 | 0.675527 | 79.62667 |

T 4.6.2 B Equilibrium data of Itaconic acid with Aliquat 336 in Ethyl acetate at 323 K

| 10% Aliquat | | | | | | | |
|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.023893 | 0.026107 | 1.092634 | 0.19 | 0.137404 | 0.159291 | 52.21333 |
| 0.1 | 0.03328 | 0.06672 | 2.004808 | 0.19 | 0.351158 | 0.541207 | 66.72 |
| 0.2 | 0.058027 | 0.141973 | 2.446691 | 0.19 | 0.747228 | 2.956135 | 70.98667 |
| 0.4 | 0.09984 | 0.30016 | 3.00641 | 0.19 | 1.579789 | -2.724764 | 75.04 |
| | | | | | | | |
| | | | | | | | |
| 20% Aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.019627 | 0.030373 | 1.547554 | 0.39 | 0.07788 | 0.084458 | 60.74667 |
| 0.1 | 0.026027 | 0.073973 | 2.842213 | 0.39 | 0.189675 | 0.234073 | 73.97333 |
| 0.2 | 0.04352 | 0.15648 | 3.595588 | 0.39 | 0.401231 | 0.670092 | 78.24 |
| 0.4 | 0.08064 | 0.31936 | 3.960317 | 0.39 | 0.818872 | 4.520951 | 79.84 |
| | | | | | | | |
| | | | | | | | |
| 30% aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.017067 | 0.032933 | 1.929688 | 0.79 | 0.041688 | 0.043501 | 65.86667 |
| 0.1 | 0.025173 | 0.074827 | 2.972458 | 0.79 | 0.094717 | 0.104627 | 74.82667 |
| 0.2 | 0.041387 | 0.158613 | 3.832474 | 0.79 | 0.200776 | 0.251214 | 79.30667 |
| 0.4 | 0.077227 | 0.322773 | 4.179558 | 0.79 | 0.408574 | 0.690828 | 80.69333 |

T 4.6.3 C Equilibrium data of Itaconic acid with Aliquat 336 in Ethyl acetate at 333 K

| 10% Aliquat | | | | | | | |
|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.034987 | 0.015013 | 0.429116 | 0.19 | 0.079018 | 0.085797 | 30.02667 |
| 0.1 | 0.053333 | 0.046667 | 0.875 | 0.19 | 0.245614 | 0.325581 | 46.66667 |
| 0.2 | 0.092587 | 0.107413 | 1.160138 | 0.19 | 0.565333 | 1.300613 | 53.70667 |
| 0.4 | 0.154027 | 0.245973 | 1.596953 | 0.19 | 1.294596 | -4.394474 | 61.49333 |
| | | | | | | | |
| | | | | | | | |
| 20% Aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.03328 | 0.01672 | 0.502404 | 0.39 | 0.042872 | 0.044792 | 33.44 |
| 0.1 | 0.049493 | 0.050507 | 1.020474 | 0.39 | 0.129504 | 0.148771 | 50.50667 |
| 0.2 | 0.083627 | 0.116373 | 1.391582 | 0.39 | 0.298393 | 0.4253 | 58.18667 |
| 0.4 | 0.13824 | 0.26176 | 1.893519 | 0.39 | 0.671179 | 2.041173 | 65.44 |
| | | | | | | | |
| | | | | | | | |
| 30% aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.023893 | 0.026107 | 1.092634 | 0.79 | 0.033046 | 0.034176 | 52.21333 |
| 0.1 | 0.03968 | 0.06032 | 1.520161 | 0.79 | 0.076354 | 0.082666 | 60.32 |
| 0.2 | 0.06784 | 0.13216 | 1.948113 | 0.79 | 0.167291 | 0.2009 | 66.08 |
| 0.4 | 0.12288 | 0.27712 | 2.255208 | 0.79 | 0.350785 | 0.540321 | 69.28 |

T 4.6.2 A Equilibrium data of Itaconic acid with TBP in Ethyl acetate at 313 K

| 10% TBP | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.016213 | 0.033787 | 2.083882 | 0.37 | 0.033787 | 3.85 | 3.708965 | 67.57333 |
| 0.1 | 0.020907 | 0.079093 | 3.783163 | 0.37 | 0.079093 | 3.85 | 3.659169 | 79.09333 |
| 0.2 | 0.039253 | 0.160747 | 4.095109 | 0.37 | 0.160747 | 3.85 | 3.569423 | 80.37333 |
| 0.4 | 0.077653 | 0.322347 | 4.151099 | 0.37 | 0.322347 | 3.85 | 3.391809 | 80.58667 |
| | | | | | | | | |
| | | | | | | | | |
| 20% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.014933 | 0.035067 | 2.348214 | 0.74 | 0.035067 | 3.85 | 3.707558 | 70.13333 |
| 0.1 | 0.019627 | 0.080373 | 4.095109 | 0.74 | 0.080373 | 3.85 | 3.657762 | 80.37333 |
| 0.2 | 0.036693 | 0.163307 | 4.450581 | 0.74 | 0.163307 | 3.85 | 3.56661 | 81.65333 |
| 0.4 | 0.06528 | 0.33472 | 5.127451 | 0.74 | 0.33472 | 3.85 | 3.378209 | 83.68 |
| | | | | | | | | |
| 30% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.01408 | 0.03592 | 2.551136 | 1.1 | 0.03592 | 3.85 | 3.70662 | 71.84 |
| 0.1 | 0.018773 | 0.081227 | 4.326705 | 1.1 | 0.081227 | 3.85 | 3.656824 | 81.22667 |
| 0.2 | 0.03072 | 0.16928 | 5.510417 | 1.1 | 0.16928 | 3.85 | 3.560044 | 84.64 |
| 0.4 | 0.05504 | 0.34496 | 6.267442 | 1.1 | 0.34496 | 3.85 | 3.366954 | 86.24 |

T 4.6.2 B Equilibrium data of Itaconic acid with TBP in Ethyl acetate at 323 K

| 10% TBP | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.016213 | 0.033787 | 2.083882 | 0.37 | 0.033787 | 3.85 | 3.708965 | 67.57333 |
| 0.1 | 0.02688 | 0.07312 | 2.720238 | 0.37 | 0.07312 | 3.85 | 3.665734 | 73.12 |
| 0.2 | 0.04608 | 0.15392 | 3.340278 | 0.37 | 0.15392 | 3.85 | 3.576927 | 76.96 |
| 0.4 | 0.088747 | 0.311253 | 3.507212 | 0.37 | 0.311253 | 3.85 | 3.404001 | 77.81333 |
| | | | | | | | | |
| | | | | | | | | |
| 20% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.01792 | 0.03208 | 1.790179 | 0.74 | 0.03208 | 3.85 | 3.710841 | 64.16 |
| 0.1 | 0.024747 | 0.075253 | 3.040948 | 0.74 | 0.075253 | 3.85 | 3.663389 | 75.25333 |
| 0.2 | 0.037547 | 0.162453 | 4.326705 | 0.74 | 0.162453 | 3.85 | 3.567548 | 81.22667 |
| 0.4 | 0.066987 | 0.333013 | 4.971338 | 0.74 | 0.333013 | 3.85 | 3.380085 | 83.25333 |
| | | | | | | | | |
| 30% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.0192 | 0.0308 | 1.604167 | 1.1 | 0.0308 | 3.85 | 3.712248 | 61.6 |
| 0.1 | 0.02432 | 0.07568 | 3.111842 | 1.1 | 0.07568 | 3.85 | 3.66292 | 75.68 |
| 0.2 | 0.036693 | 0.163307 | 4.450581 | 1.1 | 0.163307 | 3.85 | 3.56661 | 81.65333 |
| 0.4 | 0.061013 | 0.338987 | 5.555944 | 1.1 | 0.338987 | 3.85 | 3.37352 | 84.74667 |

T 4.6.2 C Equilibrium data of Itaconic acid with TBP in Ethyl acetate at 333 K

| 10% TBP | C aq final | C org | KD | [B]i org | pKa | pH | D |
|---|---|---|---|---|---|---|---|
| C aq initial | 0.0256 | 0.0244 | 0.953125 | 0.37 | 3.85 | 3.717963 | 48.8 |
| 0.05 | 0.037547 | 0.062453 | 1.663352 | 0.37 | 3.85 | 3.704832 | 62.45333 |
| 0.1 | 0.06016 | 0.13984 | 2.324468 | 0.37 | 3.85 | 3.679978 | 69.92 |
| 0.2 | 0.09088 | 0.30912 | 3.401408 | 0.37 | 3.85 | 3.646214 | 77.28 |
| 0.4 | | | | | | | |
| | | | | | | | |
| 20% TBP | C aq final | C org | KD | [B]i org | | | D |
| C aq initial | 0.032853 | 0.017147 | 0.521916 | 0.74 | pKa | pH | 34.29333 |
| 0.05 | 0.036267 | 0.063733 | 1.757353 | 0.74 | 3.85 | 3.706239 | 63.73333 |
| 0.1 | 0.0576 | 0.1424 | 2.472222 | 0.74 | 3.85 | 3.682792 | 71.2 |
| 0.2 | 0.09984 | 0.30016 | 3.00641 | 0.74 | 3.85 | 3.636366 | 75.04 |
| 0.4 | | | | | 3.85 | 3.7461 | |
| | | | | | | | |
| 30% TBP | C aq final | C org | KD | [B]i org | | | D |
| C aq initial | 0.034987 | 0.015013 | 0.429116 | 1.1 | pKa | pH | 30.02667 |
| 0.05 | 0.0384 | 0.0616 | 1.604167 | 1.1 | 3.85 | 3.703895 | 61.6 |
| 0.1 | 0.052907 | 0.147093 | 2.780242 | 1.1 | 3.85 | 3.68795 | 73.54667 |
| 0.2 | 0.06656 | 0.33344 | 5.009615 | 1.1 | 3.85 | 3.672944 | 83.36 |
| | 0.06656 | 0.33344 | 5.009615 | 1.1 | 0.33344 | 0.76656 | 0.303127 |

T 4.6.3 A Equilibrium data of Nicotinic acid with Aliquat 336 in Ethyl acetate at 313 K

| 10% Aliquat | | | | | | | |
|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.031573 | 0.018427 | 0.583615 | 0.19 | 0.096982 | 0.107398 | 36.85333 |
| 0.1 | 0.05376 | 0.04624 | 0.860119 | 0.19 | 0.243368 | 0.321647 | 46.24 |
| 0.125 | 0.061867 | 0.063133 | 1.020474 | 0.19 | 0.332281 | 0.497635 | 50.50667 |
| 0.14 | 0.06912 | 0.07088 | 1.025463 | 0.19 | 0.373053 | 0.59503 | 50.62857 |
| | | | | | | | |
| 20% aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.029867 | 0.020133 | 0.674107 | 0.39 | 0.051624 | 0.054434 | 40.26667 |
| 0.1 | 0.052053 | 0.047947 | 0.921107 | 0.39 | 0.12294 | 0.140173 | 47.94667 |
| 0.125 | 0.060587 | 0.064413 | 1.06316 | 0.39 | 0.165162 | 0.197838 | 51.53067 |
| 0.14 | 0.066987 | 0.073013 | 1.089968 | 0.39 | 0.187214 | 0.230336 | 52.15238 |
| | | | | | | | |
| 30% Aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.028587 | 0.021413 | 0.749067 | 0.59 | 0.036294 | 0.037661 | 42.82667 |
| 0.1 | 0.050773 | 0.049227 | 0.969538 | 0.79 | 0.062312 | 0.066453 | 49.22667 |
| 0.125 | 0.058027 | 0.066973 | 1.154182 | 0.79 | 0.084776 | 0.092629 | 53.57867 |
| 0.14 | 0.064427 | 0.075573 | 1.173013 | 0.79 | 0.095662 | 0.105782 | 53.98095 |

T 4.6.3 B Equilibrium data of Nicotinic acid with Aliquat 336 in Ethyl acetate at 323 K

| 10% Aliquat | | | | | | | |
|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.030293 | 0.019707 | 0.650528 | 0.19 | 0.103719 | 0.115722 | 39.41333 |
| 0.1 | 0.0576 | 0.0424 | 0.736111 | 0.19 | 0.223158 | 0.287263 | 42.4 |
| 0.125 | 0.064427 | 0.060573 | 0.94019 | 0.19 | 0.318807 | 0.468013 | 48.45867 |
| 0.14 | 0.069973 | 0.070027 | 1.000762 | 0.19 | 0.368561 | 0.583685 | 50.01905 |
| | | | | | | | |
| 20% aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.029013 | 0.020987 | 0.723346 | 0.39 | 0.053812 | 0.056872 | 41.97333 |
| 0.1 | 0.05632 | 0.04368 | 0.775568 | 0.39 | 0.112 | 0.126126 | 43.68 |
| 0.125 | 0.06272 | 0.06228 | 0.992985 | 0.39 | 0.159692 | 0.19004 | 49.824 |
| 0.14 | 0.068693 | 0.071307 | 1.038043 | 0.39 | 0.182838 | 0.223747 | 50.93333 |
| | | | | | | | |
| 30% Aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.02816 | 0.02184 | 0.775568 | 0.59 | 0.037017 | 0.03844 | 43.68 |
| 0.1 | 0.05504 | 0.04496 | 0.81686 | 0.59 | 0.076203 | 0.082489 | 44.96 |
| 0.125 | 0.061013 | 0.063987 | 1.048733 | 0.59 | 0.108452 | 0.121645 | 51.18933 |
| 0.14 | 0.06656 | 0.07344 | 1.103365 | 0.59 | 0.124475 | 0.142171 | 52.45714 |

T 4.6.3 C Equilibrium data of Nicotinic acid with Aliquat 336 in Ethyl acetate at 333 K

| 10% Aliquat | | | | | | | |
|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.03456 | 0.01544 | 0.446759 | 0.19 | 0.081263 | 0.088451 | 30.88 |
| 0.1 | 0.059733 | 0.040267 | 0.674107 | 0.19 | 0.21193 | 0.268923 | 40.26667 |
| 0.125 | 0.06272 | 0.06228 | 0.992985 | 0.19 | 0.327789 | 0.487629 | 49.824 |
| 0.14 | 0.068267 | 0.071733 | 1.050781 | 0.19 | 0.377544 | 0.606539 | 51.2381 |
| | | | | | | | |
| 20% aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.032853 | 0.017147 | 0.521916 | 0.39 | 0.043966 | 0.045988 | 34.29333 |
| 0.1 | 0.056747 | 0.043253 | 0.762218 | 0.39 | 0.110906 | 0.12474 | 43.25333 |
| 0.125 | 0.061867 | 0.063133 | 1.020474 | 0.39 | 0.16188 | 0.193147 | 50.50667 |
| 0.14 | 0.066987 | 0.073013 | 1.089968 | 0.39 | 0.187214 | 0.230336 | 52.15238 |
| | | | | | | | |
| | | | | | | | |
| 30% Aliquat | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | z | z/(1-z) | D |
| 0.05 | 0.03072 | 0.01928 | 0.627604 | 0.59 | 0.032678 | 0.033782 | 38.56 |
| 0.1 | 0.054613 | 0.045387 | 0.831055 | 0.59 | 0.076927 | 0.083337 | 45.38667 |
| 0.125 | 0.059733 | 0.065267 | 1.092634 | 0.59 | 0.110621 | 0.124381 | 52.21333 |
| 0.14 | 0.064427 | 0.075573 | 1.173013 | 0.59 | 0.12809 | 0.146908 | 53.98095 |

T 4.6.4 A Equilibrium data of Nicotinic acid with TBP in Ethyl acetate at 313 K

| 10% TBP | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.03 | 0.02 | 0.666667 | 0.37 | 0.02 | 3.85 | 3.724118 | 40 |
| 0.075 | 0.043333 | 0.031667 | 0.730769 | 0.37 | 0.031667 | 3.85 | 3.711295 | 42.22222 |
| 0.1 | 0.05 | 0.05 | 1 | 0.37 | 0.05 | 3.85 | 3.691145 | 50 |
| 0.125 | 0.054 | 0.071 | 1.314815 | 0.37 | 0.071 | 3.85 | 3.668064 | 56.8 |
| 0.14 | 0.06 | 0.08 | 1.333333 | 0.37 | 0.08 | 3.85 | 3.658172 | 57.14286 |
| | | | | | | | | |
| 20% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.029333 | 0.020667 | 0.704545 | 0.74 | 0.020667 | 3.85 | 3.723385 | 41.33333 |
| 0.075 | 0.044 | 0.031 | 0.704545 | 0.74 | 0.031 | 3.85 | 3.712028 | 41.33333 |
| 0.1 | 0.05 | 0.05 | 1 | 0.74 | 0.05 | 3.85 | 3.691145 | 50 |
| 0.125 | 0.052 | 0.073 | 1.403846 | 0.74 | 0.073 | 3.85 | 3.665866 | 58.4 |
| 0.14 | 0.062667 | 0.077333 | 1.234043 | 0.74 | 0.077333 | 3.85 | 3.661103 | 55.2381 |
| | | | | | | | | |
| 30% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.02816 | 0.02184 | 0.775568 | 1.1 | 0.02184 | 3.85 | 3.722096 | 43.68 |
| 0.075 | 0.041813 | 0.033187 | 0.793686 | 1.1 | 0.033187 | 3.85 | 3.709625 | 44.24889 |
| 0.1 | 0.045227 | 0.054773 | 1.211085 | 1.1 | 0.054773 | 3.85 | 3.685899 | 54.77333 |
| 0.125 | 0.046507 | 0.078493 | 1.687787 | 1.1 | 0.078493 | 3.85 | 3.659828 | 62.79467 |
| 0.14 | 0.05376 | 0.08624 | 1.604167 | 1.1 | 0.08624 | 3.85 | 3.651314 | 61.6 |

T 4.6.4 B Equilibrium data of Nicotinic acid with TBP in Ethyl acetate at 323 K

| 10% TBP | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.02688 | 0.02312 | 0.860119 | 0.37 | 0.02312 | 3.85 | 3.720689 | 46.24 |
| 0.075 | 0.041387 | 0.033613 | 0.812178 | 0.37 | 0.033613 | 3.85 | 3.709156 | 44.81778 |
| 0.1 | 0.04736 | 0.05264 | 1.111486 | 0.37 | 0.05264 | 3.85 | 3.688243 | 52.64 |
| 0.125 | 0.051627 | 0.073373 | 1.421229 | 0.37 | 0.073373 | 3.85 | 3.665455 | 58.69867 |
| 0.14 | 0.058027 | 0.081973 | 1.412684 | 0.37 | 0.081973 | 3.85 | 3.656003 | 58.55238 |
| | | | | | | | | |
| 20% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.043333 | 0.006667 | 0.153846 | 0.74 | 0.006667 | 3.85 | 3.738773 | 13.33333 |
| 0.075 | 0.065333 | 0.009667 | 0.147959 | 0.74 | 0.009667 | 3.85 | 3.735475 | 12.88889 |
| 0.1 | 0.076 | 0.024 | 0.315789 | 0.74 | 0.024 | 3.85 | 3.719722 | 24 |
| 0.125 | 0.081333 | 0.043667 | 0.536885 | 0.74 | 0.043667 | 3.85 | 3.698106 | 34.93333 |
| 0.14 | 0.093333 | 0.046667 | 0.5 | 0.74 | 0.046667 | 3.85 | 3.694809 | 33.33333 |
| | | | | | | | | |
| 30% TBP | | | | | | | | |
| C aq initial | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | 0.03072 | 0.01928 | 0.627604 | 1.1 | 0.01928 | 3.85 | 3.724909 | 38.56 |
| 0.075 | 0.04224 | 0.03276 | 0.775568 | 1.1 | 0.03276 | 3.85 | 3.710093 | 43.68 |
| 0.1 | 0.049067 | 0.050933 | 1.038043 | 1.1 | 0.050933 | 3.85 | 3.690119 | 50.93333 |
| 0.125 | 0.05248 | 0.07252 | 1.38186 | 1.1 | 0.07252 | 3.85 | 3.666393 | 58.016 |
| 0.14 | 0.063147 | 0.076853 | 1.217061 | 1.1 | 0.076853 | 3.85 | 3.661631 | 54.89524 |

T 4.6.4 C Equilibrium data of Nicotinic acid with TBP in Ethyl acetate at 333 K

| 10% TBP | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.026453 | 0.023547 | 0.890121 | 0.37 | 0.023547 | 3.85 | 3.72022 | 47.0933 |
| 0.075 | | 0.037973 | 0.037027 | 0.97507 | 0.37 | 0.037027 | 3.85 | 3.705404 | 49.3688 |
| 0.1 | | 0.038827 | 0.061173 | 1.575549 | 0.37 | 0.061173 | 3.85 | 3.678864 | 61.1733 |
| 0.125 | | 0.040107 | 0.084893 | 2.116689 | 0.37 | 0.084893 | 3.85 | 3.652794 | 67.9146 |
| 0.14 | | 0.047787 | 0.092213 | 1.929688 | 0.37 | 0.092213 | 3.85 | 3.644748 | 65.8666 |
| | | | | | | | | | |
| 20% TBP | | | | | | | | | |
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.042 | 0.008 | 0.190476 | 0.74 | 0.008 | 3.85 | 3.737307 | 1 |
| 0.075 | | 0.06 | 0.015 | 0.25 | 0.74 | 0.015 | 3.85 | 3.729614 | 2 |
| 0.1 | | 0.061333 | 0.038667 | 0.630435 | 0.74 | 0.038667 | 3.85 | 3.703601 | 38.6666 |
| 0.125 | | 0.063333 | 0.061667 | 0.973684 | 0.74 | 0.061667 | 3.85 | 3.678322 | 49.3333 |
| 0.14 | | 0.075333 | 0.064667 | 0.858407 | 0.74 | 0.064667 | 3.85 | 3.675025 | 46.1904 |
| | | | | | | | | | |
| 30% TBP | | | | | | | | | |
| C aq initial | | C aq final | C org | KD | [B]i org | [BHA] org | pKa | pH | D |
| 0.05 | | 0.027307 | 0.022693 | 0.831055 | 1.1 | 0.022693 | 3.85 | 3.721158 | 45.3866 |
| 0.075 | | 0.038827 | 0.036173 | 0.931662 | 1.1 | 0.036173 | 3.85 | 3.706342 | 48.2311 |
| 0.1 | | 0.03968 | 0.06032 | 1.520161 | 1.1 | 0.06032 | 3.85 | 3.679802 | 60.3 |
| 0.125 | | 0.04096 | 0.08404 | 2.051758 | 1.1 | 0.08404 | 3.85 | 3.653732 | 67.23 |
| 0.14 | | 0.04864 | 0.09136 | 1.878289 | 1.1 | 0.09136 | 3.85 | 3.645686 | 65.2571 |

E. KINETCS OF REACTIVE EXTRACTION

T 4.7.1 A Kinetics data of 0.05M itaconic acid with 20% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | | 0.05 | 0.27 | 0.27 | 0 | |
| 15 | 0.05 | 0.021 | 0.27 | 0.241 | 0.029 | -0.0005 |
| 30 | 0.05 | 0.02 | 0.27 | 0.24 | 0.03 | -0.00006222 |
| 60 | 0.05 | 0.019 | 0.27 | 0.239 | 0.031 | -0.00001515 |
| 120 | 0.05 | 0.018 | 0.27 | 0.238 | 0.032 | -0.00000711 |
| 300 | 0.05 | 0.017 | 0.27 | 0.237 | 0.033 | -0.000005797 |
| 600 | 0.05 | 0.016 | 0.27 | 0.236 | 0.034 | -0.000001904 |
| 1200 | 0.05 | 0.016 | 0.27 | 0.236 | 0.034 | -0.000001568 |

T 4.7.1 B Kinetics data of 0.10 M itaconic acid acid with 20% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | | 0.1 | 0.27 | 0.27 | 0 | -0.00177 |
| 15 | 0.1 | 0.028 | 0.27 | 0.198 | 0.072 | -0.0008 |
| 30 | 0.1 | 0.0275 | 0.27 | 0.1975 | 0.0725 | -0.0000666 |
| 60 | 0.1 | 0.0273 | 0.27 | 0.1973 | 0.0727 | -0.0000533 |
| 120 | 0.1 | 0.0271 | 0.27 | 0.1971 | 0.0729 | -0.0000266 |
| 300 | 0.1 | 0.0265 | 0.27 | 0.1965 | 0.0735 | -0.00000888 |
| 600 | 0.1 | 0.026 | 0.27 | 0.196 | 0.074 | -0.000005925 |
| 1200 | 0.1 | 0.0256 | 0.27 | 0.1956 | 0.0744 | -0.00000484 |

T 4.7.1 C Kinetics data of 0.40M itaconic acid with 20% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | | 0.4 | 0.27 | 0.27 | 0 | |
| 15 | 0.4 | 0.29 | 0.27 | 0.16 | 0.11 | -0.000333 |
| 30 | 0.4 | 0.294 | 0.27 | 0.164 | 0.106 | -0.00015 |
| 60 | 0.4 | 0.295 | 0.27 | 0.165 | 0.105 | -0.0000888 |
| 120 | 0.4 | 0.2955 | 0.27 | 0.1655 | 0.1045 | -0.0000533 |
| 300 | 0.4 | 0.296 | 0.27 | 0.166 | 0.104 | -0.0000222 |
| 600 | 0.4 | 0.298 | 0.27 | 0.168 | 0.102 | -0.00001333 |
| 1200 | 0.4 | 0.299 | 0.27 | 0.169 | 0.101 | -0.000007843 |

T 4.7.1 D Kinetics data of 0.2M itaconic acid with 20% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | | 0.2 | 0.27 | 0.27 | 0 | |
| 10 | 0.2 | 0.073 | 0.27 | 0.143 | 0.127 | -0.00333 |
| 15 | 0.2 | 0.062 | 0.27 | 0.132 | 0.138 | -0.00155 |
| 30 | 0.2 | 0.058 | 0.27 | 0.128 | 0.142 | -0.000333 |
| 60 | 0.2 | 0.057 | 0.27 | 0.127 | 0.143 | -0.00010416 |
| 120 | 0.2 | 0.056 | 0.27 | 0.126 | 0.144 | -0.0000666 |
| 300 | 0.2 | 0.055 | 0.27 | 0.125 | 0.145 | -0.0000533 |
| 600 | 0.2 | 0.054 | 0.27 | 0.124 | 0.146 | -0.00001818 |
| 900 | 0.2 | 0.052 | 0.27 | 0.122 | 0.148 | -0.0000177 |

T 4.7.1 E Kinetics data of 0.2M itaconic acid with 10% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | | 0.2 | | 0.19 | 0 | |
| 15 | 0.2 | 0.084 | 0.19 | 0.074 | 0.116 | -0.004166 |
| 30 | 0.2 | 0.065 | 0.19 | 0.055 | 0.135 | -0.0009523 |
| 60 | 0.2 | 0.063 | 0.19 | 0.053 | 0.137 | -0.0003111 |
| 120 | 0.2 | 0.062 | 0.19 | 0.052 | 0.138 | -0.0001142 |
| 300 | 0.2 | 0.0615 | 0.19 | 0.0515 | 0.1385 | -0.00004761 |
| 600 | 0.2 | 0.061 | 0.19 | 0.051 | 0.139 | -0.00001333 |
| 1200 | 0.2 | 0.059 | 0.19 | 0.049 | 0.141 | -0.000003703 |

T 4.7.1 F Kinetics data of 0.2M itaconic acid with 30% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | | 0.2 | | 0.19 | 0 | |
| 15 | 0.2 | 0.048 | 0.19 | 0.038 | 0.152 | -0.0000476 |
| 30 | 0.2 | 0.047 | 0.19 | 0.037 | 0.153 | -0.0000428 |
| 60 | 0.2 | 0.046 | 0.19 | 0.036 | 0.154 | -0.0000386 |
| 120 | 0.2 | 0.045 | 0.19 | 0.035 | 0.155 | -0.00001568 |
| 300 | 0.2 | 0.043 | 0.19 | 0.033 | 0.157 | -0.00001511 |
| 600 | 0.2 | 0.042 | 0.19 | 0.032 | 0.158 | -0.00001204 |
| 1200 | 0.2 | 0.04 | 0.19 | 0.03 | 0.16 | -1.17647E-05 |

T 4.7.2 A Kinetics data of .05M itaconic acid with 10% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.05 | 0.05 | 0.37 | 0.37 | 0 | |
| 15 | 0.05 | 0.028 | 0.37 | 0.348 | 0.022 | -0.0002933 |
| 30 | 0.05 | 0.026 | 0.37 | 0.346 | 0.024 | -0.0001777 |
| 60 | 0.05 | 0.022 | 0.37 | 0.342 | 0.028 | -0.0000944 |
| 120 | 0.05 | 0.021 | 0.37 | 0.341 | 0.029 | -0.00000444 |
| 300 | 0.05 | 0.02 | 0.37 | 0.34 | 0.03 | -0.000003137 |
| 600 | 0.05 | 0.019 | 0.37 | 0.339 | 0.031 | -0.000002424 |
| 1200 | 0.05 | 0.017 | 0.37 | 0.337 | 0.033 | -0.00000127 |

T 4.7.2 B Kinetics data of 0.1M itaconic acid with 10% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.1 | 0.1 | 0.37 | 0.37 | | |
| 15 | 0.1 | 0.069 | 0.37 | 0.339 | 0.031 | -0.0022 |
| 30 | 0.1 | 0.046 | 0.37 | 0.316 | 0.054 | -0.000133 |
| 60 | 0.1 | 0.044 | 0.37 | 0.314 | 0.056 | -0.00003809 |
| 120 | 0.1 | 0.043 | 0.37 | 0.313 | 0.057 | -0.0000133 |
| 300 | 0.1 | 0.042 | 0.37 | 0.312 | 0.058 | -0.0000044 |
| 600 | 0.1 | 0.041 | 0.37 | 0.311 | 0.059 | -0.00000363 |
| 1200 | 0.1 | 0.04 | 0.37 | 0.31 | 0.06 | -0.00000355 |

T 4.7.2 C Kinetics data of 0.20M itaconic acid with 10% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.2 | 0.2 | 0.37 | 0.37 | | |
| 15 | 0.2 | 0.112 | 0.37 | 0.282 | 0.088 | -0.00048 |
| 30 | 0.2 | 0.098 | 0.37 | 0.268 | 0.102 | -0.001636 |
| 60 | 0.2 | 0.084 | 0.37 | 0.254 | 0.116 | -0.0006969 |
| 120 | 0.2 | 0.082 | 0.37 | 0.252 | 0.118 | -0.000048 |
| 300 | 0.2 | 0.081 | 0.37 | 0.251 | 0.119 | -0.0000222 |
| 600 | 0.2 | 0.0815 | 0.37 | 0.2515 | 0.1185 | -0.00001818 |
| 1200 | 0.2 | 0.08 | 0.37 | 0.25 | 0.12 | -0.000016 |

T 4.7.2 D Kinetics data of 0.4 M itaconic acid with 10% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.4 | 0.4 | 0.37 | 0.37 | | |
| 15 | 0.4 | 0.261 | 0.37 | 0.231 | 0.139 | -0.01066 |
| 30 | 0.4 | 0.214 | 0.37 | 0.184 | 0.186 | -0.00136 |
| 60 | 0.4 | 0.188 | 0.37 | 0.158 | 0.212 | -0.0006222 |
| 120 | 0.4 | 0.174 | 0.37 | 0.144 | 0.226 | -0.00005185 |
| 300 | 0.4 | 0.172 | 0.37 | 0.142 | 0.228 | -0.00003733 |
| 600 | 0.4 | 0.171 | 0.37 | 0.141 | 0.229 | -0.00001296 |
| 1200 | 0.4 | 0.169 | 0.37 | 0.139 | 0.231 | -0.000007407 |

T 4.7.2 E Kinetics data of 0.2M itaconic acid with 30% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.2 | 0.2 | 1.1 | 0.37 | | |
| 15 | 0.2 | 0.096 | 1.1 | 0.996 | 0.104 | -0.0133 |
| 30 | 0.2 | 0.074 | 1.1 | 0.974 | 0.126 | -0.001555 |
| 60 | 0.2 | 0.064 | 1.1 | 0.964 | 0.136 | -0.0002325 |
| 120 | 0.2 | 0.059 | 1.1 | 0.959 | 0.141 | -0.00002857 |
| 300 | 0.2 | 0.058 | 1.1 | 0.958 | 0.142 | -0.00001666 |
| 600 | 0.2 | 0.057 | 1.1 | 0.957 | 0.143 | -0.00001481 |
| 1200 | 0.2 | 0.056 | 1.1 | 0.956 | 0.144 | -0.0000074 |

T 4.7.2 E Kinetics data of 0.2M itaconic acid with 20% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.2 | 0.2 | 0.74 | 0.74 | | |
| 15 | 0.2 | 0.119 | 0.74 | 0.659 | 0.081 | -0.0033 |
| 30 | 0.2 | 0.094 | 0.74 | 0.634 | 0.106 | -0.0008 |
| 60 | 0.2 | 0.076 | 0.74 | 0.616 | 0.124 | -0.0002133 |
| 120 | 0.2 | 0.069 | 0.74 | 0.609 | 0.131 | -0.0000555 |
| 300 | 0.2 | 0.066 | 0.74 | 0.606 | 0.134 | -0.00004 |
| 600 | 0.2 | 0.065 | 0.74 | 0.605 | 0.135 | -0.0000277 |
| 1200 | 0.2 | 0.064 | 0.74 | 0.604 | 0.136 | -0.00001851 |

T 4.7.2 F Kinetics data of 0.05M Nicotinic acid with 10% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.05 | 0.05 | 0.37 | 0.37 | | |
| 15 | 0.05 | 0.049 | 0.37 | 0.369 | 0.001 | -0.0008985 |
| 30 | 0.05 | 0.048 | 0.37 | 0.368 | 0.002 | -0.000866 |
| 60 | 0.05 | 0.047 | 0.37 | 0.367 | 0.003 | -0.000777 |
| 120 | 0.05 | 0.046 | 0.37 | 0.366 | 0.004 | -0.0003619 |
| 300 | 0.05 | 0.045 | 0.37 | 0.365 | 0.005 | -0.00008571 |
| 600 | 0.05 | 0.0445 | 0.37 | 0.3645 | 0.0055 | -0.0000222 |
| 1200 | 0.05 | 0.044 | 0.37 | 0.364 | 0.006 | -0.000007407 |

T 4.7.2 G Kinetics data of 0.1M Nicotinic acid with 10% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.1 | 0.1 | 0.37 | 0.37 | | |
| 15 | 0.1 | 0.095 | 0.37 | 0.365 | 0.005 | -0.0004166 |
| 30 | 0.1 | 0.09 | 0.37 | 0.36 | 0.01 | -0.0002724 |
| 60 | 0.1 | 0.088 | 0.37 | 0.358 | 0.012 | -0.0000586 |
| 120 | 0.1 | 0.087 | 0.37 | 0.357 | 0.013 | -0.0000133 |
| 300 | 0.1 | 0.086 | 0.37 | 0.356 | 0.014 | -0.00001 |
| 600 | 0.1 | 0.085 | 0.37 | 0.355 | 0.015 | -0.00000583 |
| 1200 | 0.1 | 0.084 | 0.37 | 0.354 | 0.016 | -0.00000307 |

T 4.7.3 H Kinetics data of 0.125M nicotinic acid with 20% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.1 | 0.1 | 0.74 | 0.74 | | |
| 15 | 0.1 | 0.091 | 0.74 | 0.731 | 0.009 | -0.000606 |
| 30 | 0.1 | 0.085 | 0.74 | 0.725 | 0.015 | -0.000106 |
| 60 | 0.1 | 0.084 | 0.74 | 0.724 | 0.016 | -0.0000635 |
| 120 | 0.1 | 0.083 | 0.74 | 0.723 | 0.017 | -0.000016 |
| 300 | 0.1 | 0.082 | 0.74 | 0.722 | 0.018 | -0.000008 |
| 600 | 0.1 | 0.081 | 0.74 | 0.721 | 0.019 | -0.000006 |
| 1200 | 0.1 | 0.08 | 0.74 | 0.72 | 0.02 | -0.0000053 |

T 4.7.3 H Kinetics data of 0.1 nicotinic acid with 30% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.1 | 0.1 | 1.1 | 1.1 | | |
| 15 | 0.1 | 0.09 | 1.1 | 1.09 | 0.01 | -0.0002506 |
| 30 | 0.1 | 0.087 | 1.1 | 1.087 | 0.013 | -0.00016 |
| 60 | 0.1 | 0.083 | 1.1 | 1.083 | 0.017 | -0.0001 |
| 120 | 0.1 | 0.081 | 1.1 | 1.081 | 0.019 | -0.00005185 |
| 300 | 0.1 | 0.08 | 1.1 | 1.08 | 0.02 | -0.00003358 |
| 600 | 0.1 | 0.075 | 1.1 | 1.075 | 0.025 | -0.00001435 |
| 1200 | 0.1 | 0.074 | 1.1 | 1.074 | 0.026 | -0.0000133 |

T 4.7.3 A Kinetics data of 0.05M nicotinic acid with 10% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.1 | 0.1 | 0.37 | 0.37 | | |
| 15 | 0.1 | 0.095 | 0.37 | 0.365 | 0.005 | -0.0004166 |
| 30 | 0.1 | 0.09 | 0.37 | 0.36 | 0.01 | -0.0002724 |
| 60 | 0.1 | 0.088 | 0.37 | 0.358 | 0.012 | -0.0000586 |
| 120 | 0.1 | 0.087 | 0.37 | 0.357 | 0.013 | -0.0000133 |
| 300 | 0.1 | 0.086 | 0.37 | 0.356 | 0.014 | -0.00001 |

T 4.7.3 B Kinetics data of 0.1M nicotinic acid with 10% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.1 | 0.1 | 0.19 | 0.19 | | |
| 15 | 0.1 | 0.091 | 0.19 | 0.181 | 0.009 | -0.0003 |
| 30 | 0.1 | 0.084 | 0.19 | 0.174 | 0.016 | -0.00017 |
| 60 | 0.1 | 0.082 | 0.19 | 0.172 | 0.018 | -0.000133 |
| 120 | 0.1 | 0.081 | 0.19 | 0.171 | 0.019 | -0.000053 |
| 300 | 0.1 | 0.08 | 0.19 | 0.17 | 0.02 | -0.000017 |
| 600 | 0.1 | 0.078 | 0.19 | 0.168 | 0.022 | -0.000012 |
| 1200 | 0.1 | 0.076 | 0.19 | 0.166 | 0.024 | -0.000037 |

T 4.7.3 C Kinetics data of 0.125M nicotinic acid with 10% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.125 | 0.125 | 0.19 | 0.19 | | |
| 15 | 0.125 | 0.093 | 0.19 | 0.158 | 0.032 | -0.00000133 |
| 30 | 0.125 | 0.087 | 0.19 | 0.152 | 0.038 | -0.00006 |
| 60 | 0.125 | 0.084 | 0.19 | 0.149 | 0.041 | -0.00006333 |
| 120 | 0.125 | 0.082 | 0.19 | 0.147 | 0.043 | -0.00004222 |
| 300 | 0.125 | 0.08 | 0.19 | 0.145 | 0.045 | -0.000015 |
| 600 | 0.125 | 0.078 | 0.19 | 0.143 | 0.047 | -0.000141666 |
| 1200 | 0.125 | 0.075 | 0.19 | 0.14 | 0.05 | -0.000007017 |

T 4.7.3 D Kinetics data of 0.14M nicotinic acid with 10% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $[B]_{iorg}$ | $[B]_{org}$ | $[BHA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|
| 0 | 0.14 | 0.14 | 0.19 | 0.19 | | |
| 15 | 0.14 | 0.105 | 0.19 | 0.155 | 0.035 | -0.000075 |
| 30 | 0.14 | 0.102 | 0.19 | 0.152 | 0.038 | -0.00008333 |
| 60 | 0.14 | 0.098 | 0.19 | 0.148 | 0.042 | -0.0000733 |
| 120 | 0.14 | 0.097 | 0.19 | 0.147 | 0.043 | -0.00003667 |
| 300 | 0.14 | 0.088 | 0.19 | 0.138 | 0.052 | -0.000015833 |
| 600 | 0.14 | 0.084 | 0.19 | 0.134 | 0.056 | -0.00000625 |
| 1200 | 0.14 | 0.083 | 0.19 | 0.133 | 0.057 | -0.000004285 |

T 4.7.3 E Kinetics data of 0.1Mnicotinic acid with 20% Aliquat 336 in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $C_{org}$ | $K_D$ | $[B]_{i\,org}$ | $[B]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.20 | 0.2 | 0.00 | | 0.37 | 0.37 | |
| 15 | 0.20 | 0.199 | 0.001 | 0.005025 | 0.37 | 0.369 | -5.25776E-05 |
| 30 | 0.20 | 0.198 | 0.002 | 0.010101 | 0.37 | 0.368 | -2.67987E-05 |
| 60 | 0.20 | 0.198 | 0.002 | 0.010101 | 0.37 | 0.368 | -2.11654E-05 |
| 120 | 0.20 | 0.197 | 0.003 | 0.015228 | 0.37 | 0.367 | -8.75E-05 |
| 300 | 0.20 | 0.195 | 0.005 | 0.025641 | 0.37 | 0.365 | 0.0001982 |
| 600 | 0.20 | 0.19 | 0.01 | 0.052632 | 0.37 | 0.36 | 0.0015224 |
| 1200 | 0.20 | 0.181 | 0.019 | 0.104972 | 0.37 | 0.351 | 0.0662168 |

T 4.7.4 F Kinetics data of 0.1Micotinic acid with 30% Aliquat 336 in ethyl acetat

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $C_{org}$ | $K_D$ | $[B]_{i\,org}$ | $[BA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.20 | 0 | 0.2 | | 0.74 | 0.74 | |
| 15 | 0.20 | 0.198 | 0.002 | 0.010101 | 0.74 | 0.738 | 0.005395031 |
| 30 | 0.20 | 0.196 | 0.004 | 0.020408 | 0.74 | 0.736 | -0.001400021 |
| 60 | 0.20 | 0.192 | 0.008 | 0.041667 | 0.74 | 0.732 | -0.007476659 |
| 120 | 0.20 | 0.189 | 0.011 | 0.058201 | 0.74 | 0.729 | -0.000329094 |
| 300 | 0.20 | 0.186 | 0.014 | 0.075269 | 0.74 | 0.726 | 0.21344 |
| 600 | 0.20 | 0.179 | 0.021 | 0.117318 | 0.74 | 0.719 | 3.82958 |
| 1200 | 0.20 | 0.173 | 0.027 | 0.156069 | 0.74 | 0.713 | 45.74606 |

T 4.7.4 B Kinetics data of 0.20 N nicotinic acid with 20% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $C_{org}$ | $K_D$ | $[B]_{i\,org}$ | $[BA]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.20 | 0 | 0.2 | | 0.74 | 0.74 | |
| 15 | 0.20 | 0.198 | 0.002 | 0.010101 | 0.74 | 0.738 | 0.005395031 |
| 30 | 0.20 | 0.196 | 0.004 | 0.020408 | 0.74 | 0.736 | -0.001400021 |
| 60 | 0.20 | 0.192 | 0.008 | 0.041667 | 0.74 | 0.732 | -0.007476659 |
| 120 | 0.20 | 0.189 | 0.011 | 0.058201 | 0.74 | 0.729 | -0.000329094 |
| 300 | 0.20 | 0.186 | 0.014 | 0.075269 | 0.74 | 0.726 | 0.21344 |
| 600 | 0.20 | 0.179 | 0.021 | 0.117318 | 0.74 | 0.719 | 3.82958 |
| 1200 | 0.20 | 0.173 | 0.027 | 0.156069 | 0.74 | 0.713 | 45.74606 |

T 4.7.4 C Kinetics data of 0.20 N nicotinic acid with 30% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $C_{org}$ | $K_D$ | $[B]_{i\,org}$ | $[B]_{org}$ | $(-)r_{HA}$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.20 | 0.2 | 0.00 | | | | |
| 15 | 0.20 | 0.199 | 0.001 | 0.005025 | 1.1 | 1.099 | -3.6732E-05 |
| 30 | 0.20 | 0.198 | 0.002 | 0.010101 | 1.1 | 1.098 | -5.73478E-05 |
| 60 | 0.20 | 0.197 | 0.003 | 0.015228 | 1.1 | 1.097 | -8.26528E-05 |
| 120 | 0.20 | 0.191 | 0.009 | 0.04712 | 1.1 | 1.091 | -8.51488E-05 |
| 300 | 0.20 | 0.188 | 0.012 | 0.06383 | 1.1 | 1.088 | 3.8E-05 |
| 600 | 0.20 | 0.185 | 0.015 | 0.081081 | 1.1 | 1.085 | -0.00013 |
| 1200 | 0.20 | 0.178 | 0.022 | 0.123596 | 1.1 | 1.078 | 0.005366 |

T 4.7.4 D Kinetics data of 0.20 N nicotinic acid with 40% TBP in ethyl acetate

| time (s) | $C_{i\,aq}$ | $C_{aq}$ | $C_{org}$ | $K_D$ | $[B]_{i\,org}$ | $[B]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.20 | 0.2 | 0.00 | | 1.48 | 1.48 | |
| 15 | 0.20 | 0.19548 | 0.00452 | 0.023123 | 1.48 | 1.47548 | -0.00014393 |
| 30 | 0.20 | 0.1944 | 0.0056 | 0.028807 | 1.48 | 1.4744 | -9.52442E-05 |
| 60 | 0.20 | 0.19116 | 0.00884 | 0.046244 | 1.48 | 1.47116 | -1.72832E-05 |
| 120 | 0.20 | 0.189 | 0.011 | 0.058201 | 1.48 | 1.469 | 7.88608E-05 |
| 300 | 0.20 | 0.18576 | 0.01424 | 0.076658 | 1.48 | 1.46576 | 0.00019 |
| 600 | 0.20 | 0.17604 | 0.02396 | 0.136105 | 1.48 | 1.45604 | 0.000904 |
| 1200 | 0.20 | 0.16632 | 0.03368 | 0.202501 | 1.48 | 1.44632 | -0.000584 |

T 4.7.4 E Kinetics data of 0.05 N nicotinic acid with 30% TBP in ethyl acetate

| time (s) | $C_{i\ aq}$ | $C_{aq}$ | $C_{org}$ | $K_D$ | $[BA]_{i\ org}$ | $[B]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|---|
| | 0.05 | 0.05 | 0 | | 1.1 | 1.1 | |
| 15 | 0.05 | 0.0495 | 0.0005 | 0.010101 | 1.1 | 1.0995 | -4.63232E-05 |
| 30 | 0.05 | 0.049 | 0.001 | 0.020408 | 1.1 | 1.099 | -3.51876E-05 |
| 60 | 0.05 | 0.0485 | 0.0015 | 0.030928 | 1.1 | 1.0985 | -1.99303E-05 |
| 120 | 0.05 | 0.048 | 0.002 | 0.041667 | 1.1 | 1.098 | -1.35091E-05 |
| 300 | 0.05 | 0.0475 | 0.0025 | 0.052632 | 1.1 | 1.0975 | -0.00012045 |
| 600 | 0.05 | 0.047 | 0.003 | 0.06383 | 1.1 | 1.097 | -0.0004752 |
| 1200 | 0.05 | 0.0465 | 0.0035 | 0.075269 | 1.1 | 1.0965 | -0.0030072 |

T 4.7.4 F Kinetics data of 0.10 N nicotinic acid with 30% TBP in ethyl acetate

| time (s) | $C_{i\ aq}$ | $C_{aq}$ | $C_{org}$ | $K_D$ | $[B]_{i\ org}$ | $[B]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.10 | 0.1 | 0.00 | | 1.1 | 1.1 | |
| 15 | 0.10 | 0.097 | 0.003 | 0.030928 | 1.1 | 1.097 | -0.000101703 |
| 30 | 0.10 | 0.096 | 0.004 | 0.041667 | 1.1 | 1.096 | -0.000101024 |
| 60 | 0.10 | 0.094 | 0.006 | 0.06383 | 1.1 | 1.094 | -9.37264E-05 |
| 120 | 0.10 | 0.088 | 0.012 | 0.136364 | 1.1 | 1.088 | -6.31744E-05 |
| 300 | 0.10 | 0.087 | 0.013 | 0.149425 | 1.1 | 1.087 | 0.000029 |
| 600 | 0.10 | 0.086 | 0.014 | 0.162791 | 1.1 | 1.086 | -0.00022 |
| 1200 | 0.10 | 0.085 | 0.015 | 0.176471 | 1.1 | 1.085 | 0.001388 |

T 4.7.4 G Kinetics data of 0.40 N nicotinic acid with 30% TBP in ethyl acetate

| time (s) | $C_{i\ aq}$ | $C_{aq}$ | $C_{org}$ | $K_D$ | $[B]_{i\ org}$ | $[B]_{org}$ | $(-)r_A$ |
|---|---|---|---|---|---|---|---|
| 0 | 0.40 | 0.4 | 0.00 | | 1.1 | 1.1 | |
| 15 | 0.40 | 0.396 | 0.004 | 0.010101 | 1.1 | 1.096 | -0.000172633 |
| 30 | 0.40 | 0.396 | 0.004 | 0.010101 | 1.1 | 1.096 | -0.000150268 |
| 60 | 0.40 | 0.394 | 0.006 | 0.015228 | 1.1 | 1.094 | -0.00011901 |
| 120 | 0.40 | 0.392 | 0.008 | 0.020408 | 1.1 | 1.092 | -0.000100314 |
| 300 | 0.40 | 0.39 | 0.01 | 0.025641 | 1.1 | 1.09 | -0.000221 |
| 600 | 0.40 | 0.38 | 0.02 | 0.052632 | 1.1 | 1.08 | -0.000296 |
| 1200 | 0.40 | 0.33 | 0.07 | 0.212121 | 1.1 | 1.03 | -0.001256 |

T 4.5.R Rate constants and order for the kinetics of complexation reaction

| | | Aliquat 336 in ethyl acetate | TBP in ethyl acetate |
|---|---|---|---|
| Itaconic acid | $k_1$ | 1.18 | 0.09406 |
| | $k_2$ | 0.0215 | 0.3145 |
| | α | 0.7 | 1 |
| | β | 2.5 | 2.2 |
| | γ | 1 | 1 |
| Nicotinic acid | $k_1$ | 0.934 | 0.6115 |
| | $k_2$ | 0.159 | 0.221 |
| | α | 0.95 | 0.91 |
| | β | 1 | 3.5 |
| | γ | 1 | 1 |