Intensification of Recovery of Carboxylic Acids using Reactive Extraction

THESIS
Submitted in partial fulfillment
of the requirements for the degree of
DOCTOR OF PHILOSOPHY

By

SUSHIL KUMAR

Under the supervision of
Prof B V Babu

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE (BITS)
PILANI (RAJASTHAN) INDIA
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CERTIFICATE

This is to certify that the thesis entitled **"Intensification of Recovery of Carboxylic Acids using Reactive Extraction"** and submitted by **Sushil Kumar** ID. No. **2005PHXF001P** for the award of Ph.D. Degree of the Institute embodies the original work done by him under my supervision.

Signature in full of the Supervisor	____________________
Name in capital block letters	**Prof B V BABU**

Designation Dean,
Educational Hardware Division
Professor, Chemical Engineering Group
BITS Pilani, India

Date:

DEDICATED

TO

MY DEAR PARENTS
&
BELOVED Wife

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ABSTRACT

It is essential to replace the petroleum based feedstocks by renewable resources for the sustainable development of industrial sector. Commercial production of carboxylic acids is mainly carried out by chemical synthesis from petroleum feedstocks. However, fermentation technology is also an attractive alternative to produce carboxylic acids from renewable sources. In order to make the fermentation route economically viable, it is necessary to develop novel fermentation processes that use highly efficient separation techniques. Among various available alternatives for recovery of carboxylic acids from fermentation broth, reactive extraction with a chemical (acid and extractant reaction) phenomenon is a promising technique. It can also be used for separation of acids from various aqueous waste streams. Organophosphorus-based and long-chain aliphatic amine-based extractants along with the diluents are effective for separation of carboxylic acids from dilute aqueous solution.

The existing literature suggests that great strides have been made in the separation of lactic acid from aqueous solution using reactive extraction. The experimental study of reactive extraction is limited to other carboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid and nicotinic acid. Nicotinic acid and Butyric acid have huge potential as building-block chemicals in various pharmaceutical industries to produce many medicines. Propionic acid and acetic acid are widely used in food industry as a preservative. The study on the reactive extraction of propionic- and nicotinic acid using extractant in a mixture of an inert diluent and a modifier is limited. The reactive extraction study for recovery of propionic acid and nicotinic acid from fermentation broth using biocompatible mixture of diluents is also not reported in the literature.

In the present study, the recovery of various carboxylic acids from aqueous solution using organophosphorus-based [tri-n-butylphosphate (TBP) and tri-n-octylphosphine oxide (TOPO) in the range of 0.55 – 3.65 mol.L^{-1} and 0.10 – 0.71 mol.L^{-1} respectively] as well as long-chain aliphatic amine-based extractants [tri-n-octylamine (TOA), tri-n-dodecylamine (TDA) and methyltrioctylammonium chloride (Aliquat 336) in the range of 0.23 – 1.37 mol.L^{-1}, 0.08 – 0.39 mol.L^{-1} and 0.33 – 1.33 mol.L^{-1} respectively] is carried out. To improve the efficiency of reactive extraction, the use of extractant in a modifier with an inert diluent is proposed. The extraction of propionic acid (0.0675 – 1.35 mol.L^{-1}) is carried out using TBP, TOA and Aliquat 336 dissolved in inert diluents and modifiers. The effect of modifiers (1-octanol and 1-decanol) in the inert diluents (n-decane, kerosene, cyclohexane, toluene and n-dodecane) on distribution coefficient is derived. Equilibrium studies are also carried out by using biocompatible extractant/diluent systems for the extraction of propionic- and nicotinic acid. To find the equilibrium constant and stoichiometry of the reaction, the model is proposed based on mass action law (chemodel). The values of equilibrium extraction constant (K_E) and the number of acid molecule (m) and reacting extractant molecules (n) are also estimated for the various systems studied in the present work. An objective function is formulated based on the model predicted value of distribution coefficient (K_D) and experimental data. A population based search algorithm called differential evolution (DE) and graphical methods are employed. The linear salvation energy relation (LSER), and a model based on the values of dipole moment (μ) and E_T (a parameter based on the absorption spectrum of pyridinium-N-phenolbetaine) are proposed and used to quantify the effect of diluent on the values of K_D and K_E respectively.

The equilibrium experimental results for recovery of carboxylic acids using pure diluents are presented to determine the effect of diluent, effect of type of acid and acid concentration on the extraction efficiency. Active diluents (MIBK, 1-octanol and 1-decanol) show the maximum values of partition coefficient (P) and minimum values of dimerization coefficient (D) in the extraction of all acids. The equilibrium experiments for the extraction of propionic acid are carried out using TBP and TOA dissolved in an inert diluent (n-decane, kerosene, cyclohexane, toluene and n-dodecane) and a modifier (1-decanol). It is found that the degree of extraction (%) of propionic acid increases with an increase in the concentration of 1-decanol. In the extraction of propionic acid using TBP in inert diluent-1-decanol (1:1 v/v), 1:1 complexes between acid and TBP are formed. The highest strength of the complex solvation ($K_E = 77.52$) is found using TOA in toluene (inert diluent) and 1-decanol (1:1 v/v). The equilibrium experiments are carried out for extraction of mono-carboxylic acids (formic, acetic, propionic and butyric acid) using TOA in 6 different diluents. The extraction power of amine and diluent system increases in the order of chloroform ≥ 1-decanol > MIBK > benzene > decane+1-decanol (3:1 v/v) > decane. Simultaneous formation of 1:1, 2:1 and 3:1 complexes between acid and TOA are found. The maximum extraction is found for butyric acid.

The extraction of nicotinic acid is studied using TOPO and TOA in different diluents. In case of TOPO, it is found that 1:1 complexes are formed between nicotinic acid and TOPO. The strength of the complex solvation is found to be in the order of toluene < 4-MIBK < dichloromethane < kerosene < *n*-octane < 1-decanol. In all the tested diluents, toluene is the best solvating agent for acid-TOPO complexation yielding a value of 5.04 for K_E. While using TOA, it is found that the highest strength of the complex solvation is obtained for MIBK giving a maximum loading ratio ($Z = 0.42$). The degree of extraction using Aliquat 336 (extractant) in different diluents is found to be insignificant. TOA in n-decane-1-decanol (1:1 v/v) is used for the extraction of nicotinic acid and yields a value of $K_{E1} = 31.38$. Equilibrium experiments, for the extraction of nicotinic acid, are also carried out using TDA with non-toxic diluents [*n*-dodecane and oleyl alcohol (2:1 v/v)]. Based on the estimated values of loading ratios, it is found that 1:1 complexes of nicotinic acid and TDA are formed.

To study the effect of temperature on the extraction of propionic acid and nicotinic acid, the experiments are carried out at various temperatures. It is found that the recovery of acid decreases as temperature increases. The apparent enthalpies and entropies of reactive extraction of propionic acid with TBP and reactive extraction of nicotinic acid with TDA are estimated. The kinetic study is carried out for the extraction of nicotinic and propionic acid and kinetic parameters are determined by formulating an elementary kinetic model.

Keywords: *Carboxylic acids; Fermentation broths; Aqueous waste streams; Intensification; Recovery; Reactive Extraction; Physical equilibrium; Chemical equilibrium; Extractants; Diluents; Modifiers; Chemodel; LSER model; Equilibrium constants; Stoichiometry; Kinetic parameters; Temperature; Differential Evaluation.*

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NOMENCLATURE

A_C	Mass transfer area (m^2)
$[A]^-$	Dissociated concentrations of acid (mol.L^{-1})
$[A^-]_{(aq)}$	Dissociated concentrations of acid in aqueous phase (mol.L^{-1})
$\overline{C}_{HA}$	Total concentration of acid in organic phase (mol.L^{-1})
C_{HA}	Total concentration of propionic acid in aqueous phase, (mol.L^{-1})
C^*_{org}	Equilibrium acid concentration (mol.L^{-1})
C_{org}	Organic phase acid concentration (mol.L^{-1})
C_{11}	Concentration of (1:1) complex between acid and extractant (mol.L^{-1})
C_{12}	Concentration of (1:2) complex between acid and extractant (mol.L^{-1})
C_{21}	Concentration of (2:1) complex between acid and extractant (mol.L^{-1})
C_{R_3N}	Concentration of free TOA in organic phase (mol.L^{-1})
$C_{(R_3N)_{in}}$	Initial concentration of TOA in organic phase (mol.L^{-1})
D	Dimerization coefficient (mol^{-1}.L)
E	Degree of extraction, extracted acid/initial acid (%)
$[E \cdot HA]_{org}$	Concentration of acid-extractant complex in organic phase (mol.L^{-1})
E_{T}	Diluent parameter (-)
F	DE parameter (-)
$[HA]$	Non-dissociated concentrations of acid (mol.L^{-1})
$\{\mathrm{HA}\}$	Activity of acid in aqueous phase (mol.L^{-1})
HA_{aq}	Concentration of acid in aqueous phase (mol.L^{-1})
HA_{org}	Concentration of acid in organic phase (mol.L^{-1})
$[H^+]$	Hydrogen ion concentration in aqueous solution (mol.L^{-1})
r_A	Reaction rate (mol.L^{-1}.s^{-1})
$\{\overline{S}\}$	Activity of extractant in organic phase (mol.L^{-1})
$[\overline{S}]$	Concentration of extractant in organic phase (mol.L^{-1})
$[\overline{S}]_{in}$	Initial concentration of extractant in organic phase (mol.L^{-1})
k_1, k_2	Reaction rate constants
K_{11}, K_{12}, K_{21}, K_{31}	Equilibrium constants for 1:1, 1:2, 2:1 and 3:1 complexes between acid and extractant, respectively
K_a	Dissociation constant (mol^{-1}.L)
K_D	Distribution coefficient (-)
K_{D}^0	Distribution coefficients for an ideal inert diluent (-)
K_E	Apparent equilibrium extraction constant (mol^{-1}·L)
$K_{E,true}$	True equilibrium constants
K_{Ea}	Equilibrium constant for formation of (a:1) complex, mol^{-1}·L
k_{L}	Mass transfer coefficient

m	Number of acid molecules involved in complex (-)
N	Speed of agitation (rpm)
n	Number of extractant molecules involved in complex (-)
NP	Number of population in differential evaluation algorithm (-)
P	Partition coefficient (-)
p, s, d, b, a	Regression coefficients for LSER model (-)
R^2	Coefficient of determination (-)
R_3N	Tertiary amine (-)
S	Molecules of extractant (-)
SP_1	Solvatochromic parameters of first solvent in solvent mixtures (-)
SP_2	Solvatochromic parameters of second solvent in solvent mixtures (-)
t	Time (sec)
X_1	Mole fraction of the first solvent in solvent mixture (-)
XYZ	LSER property in terms of solvent properties (solvatochromic parameters) (-)
Z	Loading ratio, acid extracted/total extractant in organic phase (-)
$Z_{\max}$	Maximum loading of amine (-)
Z_t	The overall loading factor of amine (-)
ΔH	Change in enthalpy (kJ.mol^{-1})
ΔS	Change in entropy (J.mol^{-1}.K^{-1})

Greek Symbols

α	Solvatochromic parameter (HBA) of the diluents (-)
α'	Order of kinetic reaction wrt. concentration of acid (-)
β	Solvatochromic parameter (HBD) of the diluents (-)
β'	Order of kinetic reaction wrt. concentration of free amine (-)
γ'	Order of kinetic reaction wrt. concentration of acid:amine complex (-)
π^*	Solvatochromic parameter (solvent dipolarity) of the diluents (-)
μ	Dipole moment (debye)
δ	Solvatochromic parameter (polarizability correction) of the diluents (-)
δ_h	Hildebrand's solubility parameter (-)
Δ	Change (-)

Subscripts

T	Total
0	Ideal
in	Initial
aq	Aqueous
org	Organic

Abbreviations

Alamine 336	Tri-n-(octyl-decyl)-amine
CAS #	Chemical abstracts service number
CHEMODEL	Chemical equilibrium model
CR	Cross over frequency in differential evaluation algorithm
FTIR	Fourier transform infrared analysis

HA	Carboxylic acid
HBA	Hydrogen-bond acceptor
HBD	Hydrogen-bond donor
HF	Formic acid
HP	Propionic acid
HB	Butyric acid
HNc	Nicotinic acid
HL	Lactic acid
IUPAC	International Union of Pure and Applied Chemistry
LSER	Linear solvation energy relationship
MIBK	Methyl isobutyle ketone
TBP	Tri-butyl phosphate
TDA	Tri-n-decylamine
TOA	Tri-n-octylamine
TOPO	Tri-octylphosphine oxide
v/v	Volume/volume

CHAPTER – 1

INTRODUCTION

For the sustainable development of chemical industry, the dependence on petroleum feedstock to produce various chemicals should be reduced to a great extent. It can be achieved by adapting the biotechnology based processes, which uses renewable resources. The market share of biotechnological processes for the production of various chemical products is increasing and expected to rise from the current level of 5% to 20% by 2010 (Hatti-Kaul *et al.,* 2007). The greenhouse gas emissions can be also be reduced by avoiding the petroleum feedstock. From a chemical and economic point of view, these processes are favorable. Organic acids constitute a key group among the building-block chemicals that can be produced by microbial processes. Consequently, the field that investigates microbial organic acid production is growing rapidly (Sauer *et al.*, 2008). For example, the worldwide market growth for lactic acid is increasing every year and the production in 2006 was about 68,000 tons per year. The worldwide market growth is expected to be between 10% and 15% per year (Vijayakumar *et al.,* 2008). Specific applications of propionic acid also draw attention toward a better synthesis process using microbial fermentation, which will increase the productivity and reduce the overall production cost. Its U.S. market is estimated at 235 million pounds per year and is growing at 4% annually (Wasewar and Pangarkar, 2006). In the following sections, the overview of production, separation (conventional techniques and reactive extraction) and back-extraction of carboxylic acids is made.

1.1 Carboxylic Acids

Carboxylic acids are the organic acids characterized by the presence of a carboxyl group comprised of a hydroxyl group bonded to a carbonyl group. Carboxylic acids are polar in nature, and also form hydrogen bonds with each other. Lower carboxylic acids (1 to 4 carbons) are miscible with water, whereas higher carboxylic acids (more than 4 carbons) are very much less-soluble due to the increasing hydrophobic nature of the alkyl chain. They tend to be rather soluble in less-polar solvents such as ethers and alcohols (Marrison and Boyd, 1992). Carboxylic acids are widespread in nature and typically weak acids. These acids partially dissociate into H^+ cations and $RCOO^-$ anions in aqueous solution. Both dissociate and nondissociate forms exist at equilibrium as given by Eq. (1.1):

$$RCOOH \leftrightarrow RCOO^- + H^+ \tag{1.1}$$

Carboxylic acids can be chemically synthesized by oxidation of primary alcohols or aldehydes. Alkyl group on a benzene ring will be fully oxidized to produce a carboxylic acid, regardless of its chain length. Some of the organic acids (acetic acid, propionic acid, butyric acid, lactic acid, itaconic acid, tartaric acid, and citric acid) can also be obtained by the fermentation of glucose via the glycolytic pathway and glyoxylate bypass. The aerobic fermentation process leading to the formation of organic acids is one of the best established microbial conversion pathways (Atkinson and Mavituna, 1983). Pyruvic acid is also oxidized in a cyclic manner to yield a number of di- and tricarboxylic aliphatic acids of four to six carbon atoms. Out of various carboxylic acids obtained by fermentation processes based on the importance and wide applications, the details on acetic acid, propionic acid, butyric acid, nicotinic acid and lactic acid are given in the Table 1.1.

Table - 1.1. Various carboxylic acids obtained by fermentation process

S. No	Name of acid	Source	Fermentation system	Usage	References
1.	Acetic acid	Vinegar	*Acetobacter*	used as food additives, descaling agents and chemical industries	Yanoda *et al.*, 2001; Sim *et al.,* 2007
2.	Propionic acid	milk (Gk. protus prion)	*P. acidipropionici* bacterium	used as a preservative and to make pesticides, pharmaceuticals etc.	Playne, 1985; Jin and Yang, 1998
3.	Butyric acid	butter (L. butyrum)	*Clostridium tyrobutyricum*	manufacture of plastics, agricultural applications	Dziedzak, 1986; Wo and Yang, 2003
4.	Nicotinic acid	grains vegetables, meat and poultry beef	*Nitrilases* enzymes	used in pharmaceuticals and medicines	O'Reilly and Turner, 2003; Chuck, 2005
5.	Lactic acid	whey, potatoes, and cornstarch	*Lactobacillus delbrueckii*	used in biopolymer, as a food additive, sweets, and soft drinks etc.	Akerberg *et al.,* 1998; Vijayakumar *et al.,* (2008)

Fermentation technology for the production of organic acids in particular has been known for more than a century and acids have been produced in the form of aqueous solutions. The carboxylic acid fermentation is inhibited by acidic pH and acids are the major fermentation product (Hsu and Yang, 1991; Blanc and Goma, 1987b). The conventional fermentation technology for the production of carboxylic acid salts such as propionate, butyrate, and succinate, etc., is thus limited by low fermentation rate and low product concentration. Consequently, the conventional fermentation route for the production of carboxylic acid is inefficient and it can not compete with the petrochemical routes. In order to make the fermentation route economically viable, it is necessary to develop novel fermentation processes that use highly efficient bioreactors and separation techniques.

Separation of mono-carboxylic acids such as formic acid, acetic acid or propionic acid from aqueous waste streams (industrial effluents) has also been important and essential from the industrial and pollution control points of view (Helsel, 1977). Processing in petrochemical plants and wood pulping mills often generate aqueous effluent streams containing carboxylic acids, particularly formic acid and acetic acid (Technical Bulletin, 1999). An aspect of high environmental importance is the recycling of acids from effluents rather than their neutralization to form sludge for disposal.

1.2 Separation of Carboxylic Acid from Aqueous Solutions

The growing importance of biological production, expressed with new routes and increasing production rates, asks for adapted downstream processing for product separation. The following separation methods have been employed for the separation of carboxylic acids from the fermentation broths and aqueous stream:

- precipitation (Shreve and Brink, 1977; Pazouki and Panda, 1998)
- electro-dialysis (Hong *et al.*, 1986; Boyaval *et al.*, 1987; Nomura *et al.*, 1987; Lee *et al.*, 1998),
- anion exchange (Cao *et al.*, 2002),
- adsorption (Dai and King, 1996),
- direct distillation (Helsel, 1977; Cockrem and Johnson, 1991),
- ultra filtration (Boyaval *et al.*, 1987),
- reverse osmosis (Timmer *et al.*, 1994),
- liquid surfactant membrane extraction (Sirman *et al.*, 1991), and
- liquid extraction (Wardell and King, 1978; Baniel, 1982; Hauer and Marr, 1994), etc..

In conventional processes, carboxylic acids have been recovered from the fermentation broth by precipitation of calcium salt with calcium hydroxide. In this recovery scheme, calcium salt of acid is precipitated, recovered by filtration, and then converted to acid by the addition of sulfuric acid. The diluted acid product is then sequentially purified using activated carbon, evaporation, and crystallization. In the calcium precipitation process, the separation and final purification stages account for up to 50% of the production costs (Shreve and Brink, 1977). Since, it consumes lime and sulfuric acid and produces a large quantity of calcium sulfate sludge as solid waste (Chaudhuri and Pyle, 1992; Eyal and Bressler, 1993), this method of recovery is expensive and unfriendly to the environment. Because of the detrimental effect of low pH, reactor productivities are low and the products are obtained in a dilute form.

Electro-dialysis is a recovery process where ion-exchange membranes are used for removing ions from an aqueous solution under the driving force of electrical field. Electro-dialysis and dialysis have the problem of membrane fouling, which requires frequent cleaning of the dialyzer. Moreover, large-volume dialysis units, even greater than the volume of the fermentor vessel, would be required in a commercial-scale unit. Electro-dialysis gives a higher extent of lactic acid separation but with increased power and energy consumption (Litchfield, 1996).

Carboxylic acids may be recovered by adsorption on solid adsorbent. Kawabata *et al.* (1982) separated carboxylic acid by using a polymer adsorbent of pyridine skeletal structure and a cross-linked structure. The polymer adsorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts. The selected elutants are aliphatic alcohol, aliphatic ketones and carboxylic esters. But the cost associated with regeneration of commercial adsorbents and ion-exchange resins makes adsorption operation very expensive. Chen and Ju (2002) studied the coupled fermentation and adsorption to prevent the product concentration to reach inhibitory levels.

During direct distillation, high-boiling internal esters as dimmers and polymers can be formed. As an alternative to fractionation, to reduce energy consumption, azeotropic dehydration can be employed with addition of another liquid. In this technique, the entrainer carries the water overhead in the distillation column with the mixture being phase separated after condensation and entrainer being returned to the column. It is effective only for high concentration of acids.

Reverse Osmosis could effectively concentrate the acid from 10 to120 gdm^{-3} at a 6.9 MPa trans-membrane pressure (lesser energy than that used in multiple effect evaporators). Liquid surfactant membrane extraction exhibits a high complexity of operation due to swelling of the membranes in liquid surfactants. Supported liquid membranes often suffer from membrane instability (Zihao and Kenfeng, 1995).

The integrated fermentation-separation systems have been successfully used to reduce end-product inhibition and, thus, to improve the overall process efficiency (Roffler *et al.*, 1984; Daugulis, 1988; Meynial-Salles *et al.,* 2008).

1.3 Intensification for Carboxylic Acid Separation: Reactive Extraction

Among various available alternatives for simultaneous removal of the product, extraction is often the most suitable (Freeman *et al.,* 1993; Schugeri, 1994; Weilnhammer and Blass, 1994; Jaquet *et al.,* 1996). Fermentation processes involving *in-situ* extraction or extractive fermentation has been receiving growing attention because they are capable of relieving end-product inhibition and bringing about high productivity. The complete processes to produce carboxylic acids via microbial route have the following common steps: (1) fermentation, (2) reactive extraction, and (3) back-extraction for regeneration and recycle of the reactive extractant by different techniques as shown in Figure 1.1. In the complete processes to produce carboxylic acids via microbial route, the extraction process is attached to the fermentation and back-extraction processes as shown in Figure 1.1

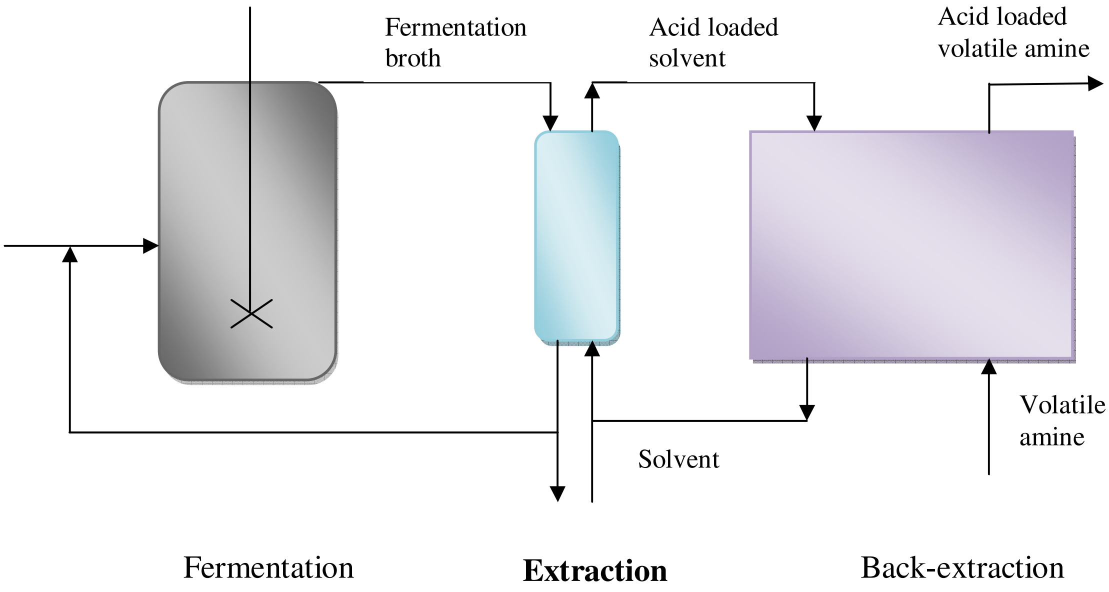

Figure 1.1. Schematic representation of the combined microbial production, extraction and back-extraction system

It will be useful to define some terms here for the understanding of liquid-liquid extraction (solvent extraction) at this stage, which are also applicable to reactive extraction (Rice *et al.,* 2000):

Extractant: The active component(s) primarily responsible for transfer of a solute from aqueous phase to the organic (solvent) phase. The extractant is sometimes called reactant or carrier.

Extract: The separated phase (often but not necessarily organic) that contains the carboxylic acid extracted from the other phase.

Diluent: The liquid or homogeneous mixture of liquids in which extractant(s) and possible modifier(s) may be dissolved to form the solvent phase.

Solvent: The term applied to the whole initial organic phase containing the extractant. The solvent may contain only extractant or it may be a composite homogeneous mixture of extractant(s) with diluent(s) and also sometimes modifiers and accelerators.

Modifier: A substance added to the solvent to improve its properties, e.g., by increasing the solubility of an extractant and changing interfacial parameters.

Reactive extraction is developed to intensify separation by solvent extraction and represents a connection between chemical (solute and extractant reaction) and physical phenomena (diffusion and solubilization of the system components). Therefore, a reactive extraction method has been proposed to be an effective primary separation step for the recovery of bio-products from a dilute fermentation process (Wennersten, 1983; Hartl and Marr, 1993; Cascaval and Galaction, 2004; Wasewar *et al.,* 2004). Some of the advantages are increased reactor productivity and easy control in reactor pH without adding base. The use of a high-concentration substrate as the process feed reduces process wastes and production costs. This method may also allow the process to produce and recover the fermentation products in one continuous step and reduce the downstream processing load and recovery costs. Reactive extraction strongly depends on various parameters such as the distribution coefficient, degree of extraction, loading ratio, complexation equilibrium constant, types of complexes (1:1, 2:1, etc.), rate constant of carboxylic acid-extractant reaction, properties of the solvent (extractant and diluent), type of solvent, temperature, pH, acid concentration, etc. (Kertes and King, 1986; Kahya *et al.,* 2001).

The extraction of carboxylic acids is categorized into three groups: (i) acid extraction by solvation with carbon-bonded oxygen-bearing extractants (also inert aliphatic and aromatic hydrocarbons and some of their substituted homologs); (ii) acid extraction by solvation with phosphorus-bonded oxygen-bearing extractants; and (iii) acid extraction by proton transfer or by ion pair formation, the extractant being high-molecular weight aliphatic amines. The distribution coefficients of carboxylic acids between the aqueous phases and organic phases with only first categorized solvents are very low, contributing by physical extraction. Compared to physical liquid-liquid extraction, the selectivity of separation is remarkably enhanced in reactive extraction using second and third categorized solvents, because the reactant present in the organic phase promotes the transfer of carboxylic acid to the organic phase (Kertes and King, 1986).

Organophosphoric derivatives and long-chain aliphatic amines as given in Table 1.1 are effective extractants for separation of carboxylic acids from dilute aqueous solution. Phosphorus-bonded, oxygen-containing extractants have a phosphoryl group and a stronger Lewis basicity than those of carbon-bonded, oxygen-containing extractants. The chemical stability of organophosphorous compounds plays an important role in the possibility of its use as an efficient extractant with good separation efficiency. When organophosphorus extractants are used, the solvation has a higher specificity. Phosphorus-bonded, oxygen-containing extractants can only co-extract small amounts of water, and show low solubilities in water. With the long-chain, aliphatic amines-based extractants, the specific chemical interactions between amine and acid molecules in the organic phase allow more acid to be extracted from the aqueous phase. Among various categories of amines; (1) primary amines are characterized by a large mutual solubility of the aqueous and organic phase, (2) secondary amines have the highest reported distribution coefficient, but tend to form amides in the downstream regeneration by distillation (Ricker *et al.,* 1979), (3) The specific affinity of long-chain tertiary amines for carboxylic acid gives high selectivity for this type of solute with respect to water and eventually non-acidic species in the mixture (King and Poole, 1991) and (4) Quaternary amines extract carboxylic acid at both acidic and basic pH via an anion exchange mechanism (Yang *et al.*, 1991), but are difficult to regenerate by back extraction. Generally, these extractants are dissolved in a diluent. It controls the viscosity and density of the solvent phase. However, the chemical structure of a diluent may have various effects connected with the formation of acid-amine complexes in the organic phase. The mass action law based modeling is used to find the stoichiometry of reactive extraction and apparent equilibrium constants in the formation of different complexes between acid and extractant (Kertes and King, 1986).

Table 1.2. Some important phosphorus- and amine-based extractants

Extractant category	**Extractants**
Phosphorus-bonded oxygen-bearing extractants	tributyl phosphate (TBP)
	tributyl phosphine oxide (TBPO)
	trioctyl phosphine oxide (TOPO)
	Cyanex@923, mixture of four trialkyl phosphine oxide
	di-(2-ethylhexyl)-phosphoric acid (D2EHPA)
High-molecular mass aliphatic amine based extractants	lauryl-trialkylmethylamine (Amberlite LA-2)
	tri-n-octylamine (Alamine 300)
	tri-iso-octylamine (HOSTAREX A 324)
	tri-n-(octyl-decyl)-amine (Alamine 336)
	quaternary alkylammonium salt (Aliquat 336)
	tri-n-dodeocylamine

1.4 Back-extraction of Carboxylic Acids

The back-extraction process is used to regenerate and recycle the extractant-diluent from a loaded organic phase (Figure 1.1). Tamada and King (1990c) considered two approaches thorough (1) a swing of temperature and (2) a swing of diluent composition. Yabannavar and Wang (1991) suggested two methods for recovery of lactic acid from a loaded organic phase: (1) using NaOH and (2) using HCl. Poole and King (1991) suggested a reactive extraction process in which an aqueous solution of a low molecular weight amine is used for back-extraction.

It is important to generate the equilibrium and kinetic extraction data for the recovery of carboxylic acids from aqueous solutions to enhance the biological production of carboxylic acids (acetic, propionic, butyric and nicotinic acids). The different modeling and simulation approaches can be used to determine the associated extraction mechanisms between extractant-diluent and acid.

1.5 Objectives

Thus, the following objectives of the present study are formulated based on the background on this subject:

1. To understand the physical and chemical aspects of reactive extraction over other recovery processes for carboxylic acids.
2. To carry out detailed experimental studies on:
    a. Physical and Chemical Equilibrium
    b. Effect of Temperature, diluents, extractant, type of carboxylic acid used, aqueous phase composition, organic phase composition, etc. on extraction efficiency.

   c. Extraction Kinetics

3. To estimate the extraction efficiency in terms of distribution coefficient, degree of extraction and loading ratio.
4. To develop and simulate mathematical models (equilibrium and kinetic) for describing the extraction mechanism and for estimating stoichiometric coefficients, equilibrium complexation constant and kinetic parameters.

1.6 Organization of Thesis

The above mentioned experimental and theoretical study is initialized by carrying out an exhaustive literature survey for industrial applications, production processes and intensification of purification process (reactive extraction) for carboxylic acids with modeling and simulation approach, which is given in Chapter-2. To obtain the equilibrium data on reactive extraction of carboxylic acids, experiments (physical, chemical and kinetics) are carried out with different type of extractants dissolved in different diluents. The detail of experimental setup and its procedures is elaborated in Chapter-3. On the basis of experimental data, improvements in existing mathematical models with simulation methodology for determination equilibrium constants and stoichiometry, and for quantifying the effect of diluents on reactive extraction are proposed in Chapter-4. The obtained experimental data are discussed and analyzed in detail in Chapter-5. It also includes the determination of equilibrium constants, stoichiometry coefficients and kinetic constants from the obtained experimental data using proposed mathematical models. Chapter-6 deals with the summary of the work, major contributions and important conclusions drawn from the present study.

CHAPTER – 2

LITERATURE REVIEW

Various studies reported in literature on microbial production (fermentation processes), extractive fermentation and the recovery of carboxylic acids using reactive extraction [experimental (equilibrium and kinetic) and theoretical investigations] are discussed in detail in section 2.1 to 2.2 of this chapter. Main focus is given to the reactive extraction of carboxylic acids (acetic-, propionic-, butyric-, nicotinic- and lactic acid) from aqueous solutions.

2.1 Microbial Production and Extractive Fermentation of Carboxylic Acids

In recent years, the application of enzymes to organic chemical processing has attracted the attention of researchers world over. Strains of the genus *Propionibacterium* are used in several industrial processes because of their ability to convert lactate and carbohydrates to propionic acid, acetic acid, and carbon dioxide. Propionic acid bacteria are widely used in the dairy industry. Nitrilases enzymes are also gaining popularity as biocatalysts for the mild and selective hydrolysis of nitriles. Several studies (Table 2.1) on bioproduction of nicotinic acid, mono-carboxylic acids (acetic, propionic and butyric acid) and lactic acid catalyzed by enzymes are carried out. An extractive fermentation process is successfully employed for microbial production with simultaneous removal of different acids (Table 2.2).

Table 2.1 Microbial production of carboxylic acids using renewable sources

S. No.	Reference	Carboxylic acid	Major contribution
1.	Peter *et al.,* 1989	Nicotinic acid	They suggested the process to convert 3-cyanopyridine to nicotinic acid using *Nocardia rhodochrous* LL100-21 immobilized in calcium alginate beads
2.	Barbirato *et al.,* 1997; Himmi *et al.,* 2000	Propionic acid	The greater production of propionic acid by *Propionibacteria* was obtained with glycerol as carbon source
3.	Huang *et al.,* (2002)	Acetic, propionic, and butyric acids	Corn meal hydrolyzed with amylases was used as the carbon source for producing the acids via anaerobic fermentations.
4.	Suwannakham and Yang (2005)	Propionic acid	Fed-batch fermentations of glucose by *P. acidipropionici* ATCC 4875 in free-cell suspension culture and immobilized in a fibrous-bed bioreactor (FBB) are studied
5.	Kaplan *et al.,* (2006)	Nicotinic acid	Biotransformation of 3-cyanopyridine into nicotinic acid by fungal nitrilases is carried out
6.	Cantarella *et al.,* (2008)	Nicotinic acid	They performed amidase-catalyzed (*Microbacterium imperiale* CBS 498–74) production of nicotinic acid in batch and continuous stirred membrane reactors.
7.	Coral *et al.,* (2008)	Propionic acid	It is produced by Propionibacterium acidipropionici ATCC 4965 using a basal medium with sugarcane molasses (BMSM), glycerol or lactate (BML) in small batch fermentation at 30 and 36 °C
8.	Wee and Ryu (2009)	Lactic acid	They carried out continuous fermentations using lignocellulosic hydrolyzates and corn steep liquor as inexpensive raw materials
9.	Jiang *et al.,* (2009)	Butyric acid	Butyrate fermentation by immobilized *Clostridium tyrobutyricum* is carried out in a fibrous bed bioreactor using cane molasses

Table 2.2 Extractive fermentation of carboxylic acids

S. No.	Refer-ences	Acids	Fermentation system	Extraction system	Major contribution
1	Lewis and Yang (1992)	Propionic acid	Lactose medium and *Propionibacterium acidipropionici* bacterium	Tertiary amine (Alamine 336) in 2-octanol	It includes better pH control (by removing acid products) and a purer product
2.	Ozadali *et al.* (1996)	Propionic acid and acetic acid	Glucose and corn steep liquor mediums and *Propionibacterium*	liquid membranes or hollow-fiber membrane extraction	About 35 $g.L^{-1}$ propionic acid and 12 $g.L^{-1}$ acetic acid were produced. 25% acetic acid and 44.5% of the propionic acid, respectively is extracted
3.	Zhong *et al.,* (1998)	Propionic acid	Glucose medium and five strains of *Propionibacteria* (*P. acidipropionici* P9, P68, and P200910 and *P. thoenii* P20 and P127)	Alamine 304 (trilaurylamine) in 2-octanol, 1-dodecanol, and Witcohol 85 NF	The solvent containing 2-octanol exhibited the highest partition coefficient in acid extraction
4.	Jin and Yang (1998)	Propionic acid	Lactose medium and *Propionibacterium acidipropionici* bacterium	Ditridecylamine in oleyl alcohol	The higher product concentration (75 $g.L^{-1}$ or higher), and higher product purity (90%) is found.
5.	Wu and Yang (2003)	Butyric acid	Glucose medium and *Clostridium tyrobutyricum* immobilized cells in a fibrous bed bioreactor	10% (v/v) Alamine 336(a tertiary amine) in oleyl alcohol	The higher reactor productivity (7.37 $g.L^{-1}.h^{-1}$) and butyric acid yield (0.45 $g.g^{-1}$) is found.
6.	Wasewar *et al.,* (2004)	Lactic acid	Glucose medium and *Lactobacillus delbrueckii*	Different extractant and diluent systems	They presented a review on fermentation of glucose to lactic acid coupled with reactive extraction

Table 2.2 Continued

S. No.	**References**	**Acids**	**Fermentation system**	**Extraction system**	**Major contribution**
7.	Yang *et al.*, (2007)	Carboxylic acids	Different mediums	Different extractant and diluent systems	They reviewed on extractive fermentation for the production of carboxylic acids such as acetic-, propionic-, butyric-, fumaric-, malic-, acrylic- citric-, gluconic- and itaconic acids
8.	Grzenia *et al.*, (2008)	Acetic acid	Sulphuric acid pretreated corn stover hydrolysate	Alamine 336 and Aliquat 336 (a quaternary amine) in 1-octanol	The results indicate more than 60% removal of acetic acid using Alamine 336. Extraction rates are much slower for Aliquat 336
9.	Gao *et al.*, (2009)	lactic acid	A recombinant yeast	Tri-n-decylamine (TDA)	Extractive fermentation with TDA provide high L-lactic acid production relative to fermentation with extraction
10.	Alkaya *et al.*, (2009)	Acetic, butyric, propionic and valeric acids	anaerobic acidification of sugar beet processing wastes	[trioctylphosphine oxide (TOPO) in kerosene	At this pH = 2.5, percent recovery of acids is changed from 43% to 98%, depending on the type of the acid extracted and the concentration of TOPO in kerosene (5–20%)

2.2 Reactive Extraction of Carboxylic Acids

Many studies are reported in the literature on reactive extraction of carboxylic acids. These studies focus on various aspects such as chemical interactions involved in the complexation of carboxylic acid with extractants, possible reaction mechanisms, solvent selection, effects of temperature, pH, aqueous and organic phase compositions on extraction, effects of modifiers, in-situ product recovery, kinetics of extraction, acid recovery from organic phase by back extraction, etc.. Among various fermentation product carboxylic acids, the most commonly investigated ones are acetic-, butyric-, citric-, formic-, fumaric-, lactic-, maleic-, propionic-, pyruvic-, succinic- and tartaric acids (Wardell, 1978; Kertes, 1985; Prochazka, 1994; Poposka, 2000; Tamada, 1990). The studies on extraction of these acids are discussed and summarized in two sections (2.2.1 & 2.2.2): 1. Equilibrium studies, and 2. Kinetic studies.

2.2.1 Equilibrium Studies

Various aspects of reactive extraction of carboxylic acids were investigated in a number of equilibrium studies in the literature.

The pioneering studies on reactive extraction of carboxylic acids were carried out by King, and his group. Kertes and King, (1986) reviewed the extraction chemistry of fermentation product (carboxylic acids) aiming to improve the existing extractive recovery technology. They pointed out that conventional extraction systems, which use alcohols, ketones or ethers as solvents were inefficient for acid recovery from dilute solutions. In their work, they identified novel, more powerful extractants such as organophosphorus and aliphatic amine extractants, which can recover organic acids more efficiently from a wide variety of aqueous solutions.

King and his co-workers (Tamada *et al.,* 1990a-c) then studied the extraction of carboxylic acids with amine extractants, more specifically a commercially available tertiary amine, Alamine 336 which has 8-10 carbon length aliphatic chains. Tamada *et al.,* (1990a) studied the extraction of several carboxylic acids including lactic-, acetic-, succinic-, malonic-, fumaric-, and maleic acids by a tertiary amine extractant (Alamine 336) in a variety of diluents and compared the equilibrium behaviors of different systems. The diluent-complex interactions were found to affect the stoichiometry of reaction and magnitude of the corresponding equilibrium constants using mass action law modeling. Common behavior was the formation of complexes with more than one acid per amine for monocarboxylic acids. As far as the degree of extraction is concerned, more acid is extracted by increasing pK_a of the acids. They observed that for most of the acids studied, the solubility of the complex by the diluent decreases in the order of alcohol ≥ nitrobenzene ≥ proton donating halogenated hydrocarbon > ketone > halogenated aromatic > benzene > alkyl aromatic > aliphatic hydrocarbon. The mass action law description of a system as a series of stoichiometric reactions were referred to as chemical modeling. An equilibrium description of the system was given as a set of reactions of p molecule of acid (A), molecules and q molecule of amine (B), molecules to form various *(p,q)* complexes, with corresponding equilibrium constants as given by Eqs. (2.1) and (2.2).

$$pA + qB \Leftrightarrow \overline{A_p B_q} \qquad (2.1)$$

$$\beta = \frac{[A_p B_q]}{[A]^p [B]^q} \tag{2.2}$$

With appropriate material balances, Z was determined for a given set of stoichiometries and used for finding the equilibrium, complexation constants.

$$Z = \frac{C_{A,org}}{C_{B,tot}} = \frac{\sum p\beta_{pq}[A]^p[B]^q}{C_{B,tot}} \tag{2.3}$$

In the subsequent study of Tamada *et al.,* (1990b), the results of mass action law analysis of the previous study were combined with the results from spectroscopic studies to analyze the chemical interactions involved in the complexation of carboxylic acids with amine extractants using various diluents. These results indicate that the formation of the (1,1) complex involves ion-pair or hydrogen-bond formation between the acid and the amine, while (2,1) complex formation involves hydrogen bonding between the carboxyl group of the second acid and the carboxylate group of the first. In the last part of their work, they (Tamada *et al.,* 1990c) studied the co-extraction of water during the extraction of succinic acid by Alamine 336 in different diluents and found out that the amounts of coextracted water increases as the solubilities of water in the pure diluents increases.

Hartl and Marr (1993) investigated a three-phase extraction process, for its applicability in the separation of organic acids from fermentation broth and compared it with other processes. Principal consideration was given to the extraction of lactic acid, gluconic acid, citric acid, and L-leucine. Apart from the already proven reactive extraction, liquid membrane permeation did not show advantages over extraction when dealing with fermentation broth with high acid concentrations. The three-phase extraction process gained high enrichment for most of the investigated acids. But, this technique showed limited extraction rates.

Distribution of citric acid between water and trialkylamine (C_7-C_9) dissolved in 7 various diluents (pxylene. toluene, benzene, MIBK, I-octanol, methylene chloride and chloroform) was studied by Bizek *et al.,* (1993). The estimated values of overall extraction constants, K_{11}, K_{12} and K_{23} using a chemical modeling approach for acid:amine complexes, were correlated with solvatochromic parameters of the diluents according to the linear solvation energy relationship (LSER) as given by Eq.(2.8). Using this correlation the extractability of citric acid can be predicted for a wide range of diluents or their mixtures.

$$\ln K_{ij} = \ln K_{ij}{}^{0} + s_{ij}(\pi^* + d_{ij}\delta) + b_{ij}\beta + a_{ij}\alpha \tag{2.8}$$

Yoshizawa *et al.,* (1994) studied the equilibrium between propionic acid (HA) in an aqueous solution with trioctylamine ($\overline{\mathrm{B}}$) in dodecane at 303 K. Propionic acid was found to be extracted into the organic solution as $\overline{(\mathrm{HA})_n\mathrm{B}}$ (*n* = 1, 2, 3 and 4) complexes when the propionic acid concentration in aqueous solution was less than 1.0 mole.dm^{-3}. However, at concentrations above 1.0 mol.dm^{-3}, the consecutive reaction between complexes proceeded simultaneously with the extraction reaction between the complexes and propionic acid.

Eyal and Canari (1995) investigated the pH dependence of carboxylic and mineral acid extraction by amine based extractants and the effects of pK_a, amine basicity, and diluent properties. The degree of extraction was most sensitive to pH for extraction through ion-pair formation. Extraction by H-bonding, however, was most sensitive at about the pK_a value of the acid. Polar and protic diluents were found to enhance extraction through ion-pair formation, but had no effect on H-bonding or even hinder it. Extraction through ion-pair formation was preferred stronger acids at low pH while H-bonding extracted weaker acids more efficiently.

San-Martin *et al.,* (1996) studied the extraction of lactic acid (HL) from aqueous solutions by Alamine 336 (B) dissolved in toluene. They carried out the experiments in the temperature range of 25 – 60 °C and for two amine concentrations of 20 and 40% (v/v) in toluene. The extent to which the organic phase (amine + toluene) may be loaded with lactic acid was expressed as a loading ratio, $Z = C_{\overline{HL}}/C_B$. The values of *Z* were independent of the amine concentration and, hence, the extracted complex contains only one molecule of amine. *Z* decreased with increasing temperature. The extraction equilibrium results also indicated consecutive formation of three acid-amine species with stoichiometric ratios of 1: 1, 2: 1 and 3: 1.

Studies were also carried out to observe the synergistic extraction of carboxylic acids. The presence of more than one acid in the aqueous phase affects the extraction characteristics. Juang *et al.,* (1997a) conducted equilibrium experiments for lactic and citric acids with tri-n-octylamine (TOA) in the temperature range of 293 – 323 K. Simultaneous formation of lactic acid-TOA complexes (1,1) , (1,2), and (3,1) was proposed in the organic phase when TOA was used as extractant alone. It was shown that the dominant complex was (1, 1) at low $[HA]_{in}$ and becomes (3, 1) at higher $[HA]_{in}$. In the presence of D2EHPA, a synergistic effect was present at $[HA]_{in} > 0.02$ mol/dm^3 for the described conditions ($[TOA]_{in} = 0.1$ mol/dm^3).

Malmary *et al.,* (1998) conducted liquid-liquid equilibrium experiments for the extraction of five individual carboxylic acids (aconitic-, citric-, lactic-, malic-, and oxalic acid) using a tertiary amine (triisooctylamine) as extractant. Triisooctylamine was dissolved in various diluents such as chloroform, 1-octanol and a mixture of heptane (50 vol %) & 1-hexanol (modifier, 50 vol %). They showed that the partition coefficient for a specific acid reaches a maximum for a concentration of tertiary amine in a binary mixture of amine [25% (vol/vol)] and 1-octanol [75% (vol/vol)].

The effects of organic phase extractant concentration and aqueous phase pH on the lactic acid extraction with two extractants, trioctyl amine (TOA) and Aliquat 336, in three diluents [methylisobutyl ketone (MIBK), octanol and paraffin liquid] were examined by Choudhury *et al.,* (1998). Among the extractants, TOA was found to be a better extractant than Aliquat 336 in all the diluents. MIBK had a profound effect on the extraction behaviour of TOA in comparison with octanol and paraffin liquid while none of the diluents affected the extraction with Aliquat 336. The extraction of lactic acid was favoured at low pH. While TOA was found to be highly toxic at the molecular and the phase level, the paraffin liquid was totally non-toxic.

Hong and Hong (1999) used the mixture of tripropylamine (TPA) and trioctylamine (TOA) dissolved in 1-octanol/n-heptane in the reactive extraction of (L+) lactic acid in aqueous solution. Maximum distribution coefficients were obtained in the range from 6:4 to 8:2 weight ratios of TPA/TOA at 5% (w/w) lactic acid in aqueous phase and their extraction efficiencies were above 90%. By introducing TPA into TOA, the third phase formation could be overcome, thereby; the settling time is shorter than that in the case of TOA alone.

Senol (1999) investigated the distribution of formic-, levulinic- and acetic acids between water and Alamine 336 dissolved in various diluents, and compared the results with the extraction equilibria of pure diluent alone studied at 25 °C. He correlated the experimental results using a modified linear solvation energy relation (LSER) and various versions of the mass action law, namely, a chemical modeling approach and a modified version of the Langmuir equilibrium model comprising one or two acid-amine complex formations. Finally, the reliability of the proposed extraction models was analyzed statistically on the basis of the overall loading factor of amine, Z_t, using a log-ratio objective function.

Frieling and Schügerl (1999) also investigated the effect of temperature on the equilibrium distribution of lactic acid between the aqueous phase and the organic phase containing Hostarex A327 and isodecanol in kerosene. They observed that the loading of the organic phase decreased with increasing the temperature. The temperature dependence of loading of the Cyanex 923 in kerosene system was less significant.

Kahya *et al.,* (2000) conducted a study on optimization of process parameters for reactive lactic acid extraction using Alamine 336 diluted with oleyl alcohol. The distribution coefficient was found to be increasing with increasing stirring rate, extraction time, amount of Alamine 336 and V_{org}/V_{aq}, and decreasing with increasing temperature and initial lactic acid concentration. The optimum conditions were found by using the Linear Box-Wilson experimental design method and reported as initial lactic acid concentration = 21 g/L, pH = 2.0, temperature = 32 $^{\circ}$C, stirring rate = 120 rpm, amount of Alamine 336 in oleyl alcohol = 41% and V_{org}/V_{aq} = 1/1.

Dinculescu *et al.,* (2000) proposed reactive extraction of citric acid with trioctylamine with solvent recycling as an alternative to the classical method. Octanol, cyclohexanol, iso-butyl alcohol and paraffin oil were used as organic solvents in this study. The removal efficiency was enhanced when the reactive extraction was accompanied by back-extraction using sodium carbonate as stripping agent.

Cai *et al.,* (2001) studied the extraction equilibria of formic and acetic acid with kerosene solutions of such phosphate-containing extractants as trialkylphosphine oxide (TRPO) and tributyl phosphate (TBP). For dilute acids, TRPO provided higher distribution coefficients than TBP, whereas for high acid concentration, the differences became very small. A mathematic model considering both (2:1) and (1:1) acid- extractant complexes was proposed.

Wang *et al.,* (2001) investigated the extraction equilibria of aqueous solutions of formic acid, acetic acid, propionic acid, butyric acid, caproic acid, monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, and lactic acid with trialkylphosphine oxide in kerosene. By using mass action law, and suitable assumptions, the extraction equilibrium constant, K_{11}, was evaluated by a least-squares regression method. It was found that distribution ratios increase with the increase of trialkylphosphine oxide concentration and decrease with the increase of the acid concentration in the aqueous phase.

Koparan *et al.,* (2001) investigated the reactive extraction of citric acid at atmospheric and supercritical conditions using tertiary amines (Hostarex A 327 and Alamine 336) and eight different diluents. The distribution coefficient values obtained with Hostarex A 327 were higher than those of Alamine 336. Separation yields of citric acid were obtained in the temperature range of 308 – 328 K and in the pressure range of 80 to 180 bars in a supercritical extraction system which is continuous in terms of CO_2. It was found that the separation yield decreased with increasing extraction pressure at all investigated temperatures. The highest separation yield (28%) was obtained at the critical pressure.

Malmary *et al.,* (2001) studied the liquid-liquid equilibria between the solvent system [triisooctylamine + 1-octanol (modifier) + n-heptane] and an aqueous solution of an individual carboxylic acid such as citric-, lactic- and malic acids. The experimental data showed that the partition coefficient for a particular organic acid depends on the kind of solute, notably when the acid concentration in the aqueous phase is low. A mathematical model, where both chemical association and physical distribution are taken into consideration, was proposed.

The distribution of nicotinic acid between water and Alamine 300 (tri-*n*-octylamine), dissolved in various polar and non-polar diluents, was studied at 298 K using a phase volume ratio of ψ = 1:1 by Senol (2001, 2002). The cyclic alcohol/amine system yielded the highest synergistic extraction efficiency. The strength of complex solvation was found to be reasonably high for halogenated aliphatic hydrocarbons and nitrobenzene, activating mainly the formation of probably (1,1) acid-amine complex. Physical solubility of nicotinic acid in pure diluent alone is remarkably low with a distribution coefficient for cyclopentanol of 0.92 and less for others. The results were correlated using versions of the mass action law, i.e., a modified Langmuir equilibrium model and a CHEMODEL modeling approach comprising one or two acid-amine complex formation.

The fraction of ion-pair association between trioctylamine (TOA) and propionic acid in the organic phase (n-octanol as diluent) was quantitatively determined by Zhenyu *et al.,* (2002) using Fourier transform infrared (FTIR) analysis. The apparent reactive extraction equilibrium constant (K_{11}), was calculated using the quantitative FTIR spectrum and the equilibrium data. The results proved that the fraction of ion-pair association depends on diluent concentration, complex dissolution for propionic acid, and association between TOA and propionic acid. The values of K_{11} based on quantitative FTIR showed the same loading trend as that from the equilibrium data.

Another synergistic extraction system was developed by Matsumoto *et al.,* (2001). The extraction equilibria of acetic-, glycolic-, propionic-, lactic-, succinic-, fumaric-, L-malic- and itaconic acids with tri-n-octylamine (TOA) and/or tri-n-butylphosphate (TBP) used as extractants was analyzed. Synergism was observed in the extraction of all of the acids\ investigated, when a mixed extractant of TOA and TBP was used. Several stoichiometries were also proposed for the coupling of the acids with the extractants, those being, one to one complexes of the acid with either TOA or TBP and the 1:2:1 complex of acid, TBP and TOA respectively. They (Matsumoto *et al.,*, 2003) also performed the synergistic extraction of lactic acid with tri-*n*-butylphosphate (TBP) and alkylamines to find an optimum synergistic extraction system and found that extractability with alkylamines increases in order from tertiary>secondary>primary. Extractability increased with increasing alkyl chain length in trialkylamine; tri-*n*-octylamine (TOA) enabled the best extractability, however, further increases in chain length resulted in a decrease in extractability. The diluent effect was small due to a high concentration of TBP. It was found that the synergistic extractions of lactic and succinic acids with TOA and TBP are exothermic processes.

Canari and Eyal (2003a,b) studied the extraction selectivity and its dependence on pH in binary mixtures of monocarboxylic acids, and lactic-, glutaric-, malic-, and maleic acids using extractants containing Primene JMT. Selectivity was found to depend strongly on pH. The study showed that the stronger acid is selectively extracted through ion-pair formation, in cases where the extractant is a stronger base than the anions of both acids. However, the weaker acid is preferably extracted by H-bond interactions with the formed ion-pair. Upon pH elevation, the selectivity to the stronger acid decreases in the above-stoichiometric range but increases in the range where loading factor, $Z < 1$.

Li *et al.,* (2003) found the liquid-liquid extraction based on reversible chemical complexation as a novel separation technique that is highly effective and selective for the separation of polar organic solutes from aqueous solutions. They studied equilibria of aqueous solutions of glyoxylic acid, glycolic acid, acrylic acid, and benzoic acid with trialkylphosphine oxide (TRPO) in kerosene with different complexing agent concentrations and initial acid concentrations at 298 K. Models for describing the extraction equilibrium of monocarboxylic acids were proposed. The model parameters, K_{11} (maximum value of K_{11} for benzoic acid = 160.8 $L{\cdot}mol^{-1}$) were obtained by experimental data regression.

Qin *et al.,* (2003a) studied the extraction of glycolic acid and glyoxylic acid from aqueous solution by trialkylphosphine oxide in methyl isobutyl ketone and trioctylamine in 1-octanol with different concentrations of extractant and acid. The degree of extraction for glycolic acid with trialkylphosphine oxide is higher than that for glyoxylic acid; this is in contrast with the fact that the degree of extraction for glycolic acid with amine is much lower than that for glyoxylic acid. Thus, trialkylphosphine oxide could be used to remove glycolic acid from the mixture of glycolic acid and glyoxylic acid. They (Qin *et al.,* 2003b) also determined liquid-liquid equilibria for aqueous solutions of carboxylic acids such as formic-, acetic-, propionic-, butyric-, valeric-, monochloroacetic-, dichloroacetic-, trichloroacetic-, glyoxylic-, glycolic-, and lactic acids, with trioctylamine (TOA) in various diluents (1-octanol, chloroform, methyl isobutyl ketone (MIBK), tetrachloromethane, and hexane). By using the mass action law and suitable assumptions, an expression for extraction equilibrium was derived, and apparent extraction equilibrium constants were evaluated. The apparent extraction equilibrium constants were found to be dependent on the hydrophobicity and pK_a of the carboxylic acid, as well as the specific basicity of the extractant.

Canari and Eyal (2004) observed stronger temperature effects in cases where, (1) the alkyl amine was relatively weak ($pH_{hn} < 5$), (2) the alkyl amine was highly substituted, (3) the carboxylic acid was relatively weak ($pK_a > 3$), (4) polycarboxylic acid was extracted, (5) the concentration of the amine and/or the carboxylic acid in the organic phase was low, (6) the amine and/or acid were bulky, and (7) the diluent of the amine had low polarity.

Senol (2004) studied the distribution of acetic acid between water and Alamine 308 (triisooctylamine) dissolved in various diluents of proton-donating and -accepting (benzyl alcohol, chloroform, methylisobutyl ketone), polar (1,2-dichloroethane), and inert (xylene) types, as well as a comparison with the extraction equilibria of pure diluent alone (1-octanol) at 298K. The highest synergistic extraction efficiency was found for an amine/cyclic alcohol system, and halogenated aliphatic hydrocarbons exhibited the largest strength of the complex solvation, promoting probably (1, 1) acid-amine complexation. The results are correlated using a linear solvation energy relation (SERAS) and different versions of the mass action law, i.e., a chemodel approach and a modified Langmuir equilibrium model comprising the formation of one or two acid-amine complexes.

Yankov *et al.,* (2004) reported the recovery of lactic acid from aqueous solutions and simulated fermentation broth by TOA dissolved in a binary diluent. As less toxic for the bacteria producing lactic acid, 1-decanol was selected as a modifier and *n*-dodecane as an inert diluent. A detailed study on the effect of the organic phase composition on distribution coefficient of lactic acid was carried out. The extraction equilibrium constants were determined and a strong influence of diluents was observed on the values of determined extraction constant and the number of extractant molecules in the acid–amine complex.

A novel method for the extraction of lactic acid by means of a modified extractant was proposed by Kyuchoukov *et al.,* (2004). A quaternary ammonium salt (Aliquat 336), dissolved in 1-decanol and *n*-dodecane, and was treated successively with different concentrations of ammonium carbonate for replacement of the chloride anion with a carbonate one. A comparison between the modified extractant and its classical form was established. It was concluded from the obtained results that the carbonate form of Aliquat 336 was more efficient than the classical chloride.

Hong and Hong (2004) studied the reactive extraction of succinic acid from aqueous solutions with various tertiary amines dissolved in 1-octanol and in n-heptane as a function of the chain length of the tertiary amine. With the tertiary amine extractants in 1-octanol, the extractabilities of tertiary amines were proportional to their chain length. But, in n-heptane, the extractabilities of tertiary amines decreased with their chain length. From IR spectroscopy, it was found that the difference of extractability in 1-octanol and in n-heptane was mainly due to the different degree of intramolecular hydrogen bonding of succinic acid with the polarity of diluents.

Marinova *et al.,* (2005) derived the effect of the modifier 1-decanol on the extraction of tartaric acid by the extractants tri-*n*octylamine (TOA), quaternary ammonium chloride (Aliquat 336), or their mixture in the diluent (*n*-dodecane) at different pH values. The effect of the modifier was examined as a function of the initial pH value of the aqueous solution for the three extractants mentioned above. At low pH values, the increase in the modifier concentration did not significantly affect the extraction of tartaric acid with Aliquat 336, but favored the distribution coefficient with TOA as an extractant, and manifested a very strong positive effect in the case of the mixed extractant. At high pH values, the extraction with Aliquat 336 decreased at the higher modifier concentration and the same trend was observed for the mixed extractant as well. The extraction of tartaric acid with TOA does not depend on the modifier concentration.

Wisniewski and Pierzchalska (2005) examined the use of the organophosphine oxides (Cyanex$^{®}$921 and Cyanex$^{®}$923) for the extraction of monocarboxylic acids (formic-, acetic- and propionic acids) from aqueous solutions and the stripping of monocarboxylic acids with water from the loaded extractants. Cyanex$^{®}$921 extracted carboxylic acids slightly better than Cyanex$^{®}$923 with 1:1 complexes formed by both extractants with the acids during extraction. Extraction efficiency increased as the concentration of acid decreased and, also, as the temperature is increased, the amount of acid extracted found to decrease. The apparent enthalpy and entropy of the extraction reaction were determined. Distribution ratios were found to be increasing as the concentration of NaCl in the aqueous solution increased at 293K.

Kyuchoukov *et al.,* (2005) investigated the mechanism for extraction of lactic acid with Aliquat 336 dissolved in dodecane and decanol at various experimental conditions. The ratio between the extracted anions and whole (undissociated) molecules was calculated with the treatment of experimental results and found to be dependent strongly on pH and lactic acid concentration. The overall distribution coefficient increased or decreased with the pH increase in dependence on lactic acid concentration. The obtained linear dependence, of the acid molecules concentration in the organic phase on their concentration in the aqueous phase, was a strong argument to the presence of physical extraction by Aliquat 336.

Extraction of succinic acid and acetic acid by tri-*n*-octylamine (TOA) was studied with various pH values of their aqueous solutions by Hong and Hong (2005). In the extraction of acetic acid, a sharp decrease in loading values (*Z*) with increasing pH began at higher values than that of succinic acid extraction due to its higher pK_a value. Based on the difference in extractability of succinic acid and acetic acid with pH, the selective removal of acetic acid from the aqueous mixture of succinic acid and acetic acid was carried out. After three successive extractions using 0.25 mol/kg TOA dissolved in 1-octanol at pH 5.1, a large amount of acetic acid from aqueous acid mixture was removed.

Inci and Uslu (2005a) investigated the extraction equilibria of glycolic acid in aqueous solutions by trioctyl methylammonium chloride (Aliquat 336) in mixtures of three individual diluting solvents and two solvent mixtures at a temperature of 298.15 K. In this study, the maximum removal of glycolic acid was 49% with 1.76 $mol \cdot L^{-1}$ initial concentration of Aliquat 336 in propanol. The maximum extraction efficiencies for diluents and their mixtures at maximum Aliquat 336 were found to be the following order: propanol > MIBK-propanol > ethyl acetate > MIBK > propanol-toluene > MIBK-toluene > cyclohexane > butanol > toluene > isooctane.

Inci and Uslu (2005b) also investigated the effect of diluent on extraction of citric acid. The experiments were carried out using mixtures of trioctyl methylammonium chloride (Aliquat 336) and organic diluent (cyclohexane, 2,2,4-trimethyl pentane, 1-butanol, toluene, methyl isobutyl ketone, and ethyl acetate) at 298.15 K. The maximum extraction efficiency of citric acid was found to be 57% with 2,2,4-trimethyl pentane and methyl isobutyl ketone for an initial concentration of Aliquat 336 of 1.74 mol/L.

Shan *et al.,* (2006) described the extraction of monocarboxylic acids using five types of mixed solvents such as trioctylamine (TOA)/1-octanol, TOA/methyl *iso*-butyl ketone (MIBK), TOA/tetrachloromethane (CCl4), trialkylphosphine oxide (TRPO)/1-octanol and TRPO/kerosene and 12 monocarboxylic acids (formic-, acetic-, propionic-, butyric-, valeric-, caproic-, monochloroacetic-, dichloroacetic-, trichloroacetic-, glycolic-, glyoxylic-, and lactic acids). From the results of these experiments, a new mathematical model, including a new definition of extractant's basicity (p$K_{a,BS}$), was developed and validated. The results showed that the values of p$K_{a,BS}$ depended on the extractant and diluent type, extractant concentration and the type of solute. In this paper, the relative basicity of the extractant to the solute *(*p$K_{a,BS}$*)* was defined as follows:

$$E \cdot HA_{(org)} \xleftrightarrow{K_{a,BS}} E_{(org)} + H^{+}_{(aq)} + A^{+}_{(aq)} \tag{2.4}$$

$$K_{a,BS} = {[E]_{(org)}[H^{+}]_{(aq)}[A^{-}]_{(aq)}} \Big/ {[E \cdot HA]_{org}} \tag{2.5}$$

where E and HA stand for extractant and carboxylic acid, respectively.

It was assumed to form 1:1 complex between extractant and carboxylic acid. Equilibrium extraction constant was given by Eq. (2.6) or Eq. (2.7)

$$K_{11} = {[H^+]_{(aq)}[A^-]_{(aq)}} \Big/ {K_{a,BS}[HA]_{(aq)}} \tag{2.6}$$

$$K_{11} = {K_a} \Big/ {K_{a,BS}} \quad \text{or} \quad \log K_{11} = pK_{a,BS} - pK_a \tag{2.7}$$

Wasewar and Pangarkar (2006) determined equilibria for propionic acid extraction by trioctyl amine in various solvents (hexanol, butyl acetate, petroleum ether). The extraction equilibrium was interpreted as a result of consecutive formation of two acid-amine complexes with stoichiometries of 1:1 and 2:1. Equilibrium complexation constants for (1:1) and (2:1) were estimated. They also presented the effects of diluent on the extraction equilibrium.

Bilgin *et al.,* (2006) studied the distribution of butyric acid between water and trioctylamine dissolved in 17 different solvents and 4 vegetable oils at a temperature of 298.15K. The highest distribution coefficient for butyric acid was found with trioctylamine dissolved in isoamyl alcohol. As the molar mass of the alcohol is increased, the value of the distribution coefficient found to be decreased. In this extraction, it was observed that in comparison with the use pure diluents as extractant, the use of trioctylamine dissolved in alcohol increased the value of distribution coefficient (K_D) by 6 – 7 times; dissolving in ketones increased K_D by 3 – 5 times; dissolving in esters increased by 4 – 9 times; dissolving in *tert-b*utyl methyl ether increased by 2.3 times; dissolving in hydrocarbons increased by 10 – 18 times; and dissolving in vegetable oils increased by 12.5 times.

Uslu (2006) conducted kinetic and equilibrium studies for the extraction of propionic acid from aqueous solution with Alamine 336 diluted in toluene at 298.15 K. The equilibrium data were interpreted by a proposed mechanism of three reactions of complexation by which 1:1, 2:1 and 3:1 acid-amine complexes are formed. The results of the liquid-liquid equilibrium measurements were correlated by a linear salvation energy relationship (LSER) model as given by Eq. (2.8), which takes into account of the physical interactions. From the regression coefficients of LSER model (Eq. 2.9), information on the solvent-solute interaction was obtained.

$$\ln K_D = \ln {K_D}^0 + s(\pi^* + d\delta) + b\beta + a\alpha \tag{2.8}$$

$$\ln K_D = 5.004 + 114.1392(\pi^* - 0.461\delta) + 105.3173\beta + 0\alpha \tag{2.9}$$

The extraction of propionic acid with Aliquat 336 dissolved in five single solvents (cyclohexane, hexane, toluene, methyl isobutyl ketone, and ethyl acetate) and binary solvents (hexane + MIBK, hexane + toluene, and MIBK + toluene) was investigated at temperature of 298.15 K by Uslu and Inci (2007). The obtained results and the observed phenomena were discussed by taking into consideration the mechanism of extraction and the concentration of interaction product in the aqueous phase.

Uslu *et al.,* (2007) also reported on the extraction of citric acid by trioctyl methyl ammonium chloride (TOMAC in the range of 0.362 to 1.775 mol/L) dissolved in 1-propanol, 1-octanol, 1-decanol (active solvents), and their mixtures (1:1 volume ratio) at two different temperatures (298.15 K and 303.15 K). The maximum extraction efficiencies for diluents at maximum TOMAC were found as: 1-propanol >> 1-octanol > 1-decanol > (1-propanol + 1-octanol) > (1-propanol + 1-decanol) > (1-octanol + 1-decanol). The results of the liquid-liquid equilibrium measurements were correlated by a linear solvation energy relationship (LSER) model using solvatochromic parameters obtained from the literature. The resulting LSER regression was given by Eq. (2.12):

$$\ln K_{\mathrm{D}} = 0.4372 + 1.8789(\Pi^{*} + 0\delta) + 1.2316\beta + 2.6531\alpha \tag{2.12}$$

Inci (2007) reported equilibrium studies for the extraction of succinic acid from aqueous solution with tridodecylamine diluted in MIBK at 298.15 K. The equilibrium data were also interpreted by a proposed mechanism of three reactions of complexation by which (1:1) and (2:1) acid-amine complexes are formed. The results of the liquid-liquid equilibrium measurements were correlated by a linear solvation energy relationship (LSER) model, which takes into account the physical interactions. From the regression coefficients, information on the solvent-solute interaction was obtained and the solvation models were proposed. The resulting LSER regression equation (2.10) was used to predict ln K_{D} for the organic solutes

$$\ln K_{\mathrm{D}} = -2.789 + 1736.73(\Pi^{*} - 2221.68\delta) + 0\alpha - 0\beta \tag{2.10}$$

Maisuria and Hossain (2007) carried out equilibrium studies on the extraction of lactic acid in various organic phases and its re-extraction into aqueous solutions characterized by using distribution coefficient for the respective processes. The values of the distribution coefficients were obtained by varying the operating conditions (i) for extraction: feed solution pH, types of carrier and its concentrations (trioctylamine, trihexylamine, and tridodecylamine), solvent and its concentration in the organic phase; and (ii) for re-extraction: the type, pH, and concentration of recovery solution. It was found that 20 wt % of trioctylamine (an ionic carrier) dissolved in tributyl phosphate (an active solvent) was found to be the best extracting phase. For re-extraction, an aqueous solution of sodium carbonate gave the best recovery from the organic phase.

Cascaval *et al.,* (2007) presented the comparative study of the reactive extraction of nicotinic acid with Amberlite LA-2 (lauryl-trialkyl-methylamine) and di-(2-ethylhexyl)-phosphoric acid (D2EHPA). Compared to D2EHPA, the use of Amberlite LA-2 allows the possibility of reaching higher extraction efficiency, the extraction degree being supplementally increased by increasing the solvent polarity. The highest value of the extraction constant was obtained for reactive extraction with Amberlite LA-2 dissolved in dichloromethane. The suggested mechanism of reactive extraction with D2EHPA involved the formation of a salt as the product of the interfacial reaction between one molecule of each reactant in all cases.

Li *et al.,* (2007) recovered fumaric acid from wastewater having low concentration of organic acid using chemical extraction (trialkyl amine, N_{7301} as an extractant) and stripping (NaOH as stripping agent). The heat effect of the extraction process, the formation of acid-amine complexes, and the corresponding equilibrium constant were determined. In the optimum condition, kerosene/N_{7301}/n-octanol was 2:2:1, pH was 0.5, and the temperature was 303K, through chemical extraction. The extractant was regenerated by a stripping process with 2% NaOH, and the stripping rate almost arrived at 100%. It was suggested that after extraction, the fumaric acid wastewater can be further treated by oxidation or biodegradation to environmentally acceptable levels.

Maisuria and Hossain (2007) carried out the equilibrium studies on the extraction of lactic acid in various organic phases and its re-extraction into aqueous solutions with variable pH. Beyond the pH range of 2 to 3, the value of distribution coefficients decreased sharply to very low values at pH = 5. This could be due to the effect of available concentration of undissociated lactic acid, which decreases considerably with the increase in pH.

Keshav *et al.,* (2008a) studied reactive extraction of propionic acid from aqueous solution (0.05 to 0.4 mol.L^{-1}) using different extractants, tri *n*-butylphosphate (TBP, organophosphorous compound), tri-*n*-octylamine (TOA, tertiary amine), and Aliquat 336 (quaternary amine) in 1-octanol. The order of extraction power was found to be TOA > Aliquat 336 > TBP. The highest value of equilibrium complexation constant (25.67 m^3/kmol) and distribution coefficient (14.09) of TOA suggested it to be the best extractant among the three. In all the extractions (1:1), acid-extractant complexes were formed with loading ratios less than 0.5, except in Aliquat where values higher than 0.5 were also obtained.

Keshav *et al.,* (2008b) also studied the recovery of propionic acid from aqueous phase by reactive extraction using tri-*n*-butyl phosphate (TBP) in petroleum ether. Using the mixture of extractant (TBP)-diluent (petroleum ether), the extraction was significantly improved. Results were presented in terms of distribution coefficient, equilibrium complexation constant, loading ratio and extraction efficiency. Propionic acid and TBP were found to form ($\gamma = 1:1$) complex with no overloading.

Keshav *et al.,* (2008c) also reported equilibrium of propionic acid with tri *n*-butylphosphate (TBP) in eight different diluents. Since the loading ratio was less than 0.5 in most of the cases, no overloading was obtained and only a (1:1) acid-TBP complex was formed. The extraction constants were correlated with the physical constants of diluents (dipole moment and E_T parameter).

$$K_S = 1.2\text{X}10^{-6}\mu^{-0.02266}E_T^{4.14} \qquad (2.11)$$

Uslu (2008) studied the reactive extraction of levulinic acid using tripropylamine (TPA) in toluene solution. Equilibrium studies for the extraction of levulinic acid from aqueous solution were carried out at 298.15 K. The equilibrium data were also interpreted by a proposed mechanism of complexation by which (1:1) and (2:1) acid-amine complexes formed. Kinetic parameters of extraction of levulinic acid by TPA in toluene were also determined. The results of the liquid-liquid equilibrium measurements were correlated by a linear solvation energy relationship (LSER) as given by Eq. (2.12).

$$\ln K_{\mathrm{D}} = -3.748 + 95.104(\Pi^{*} - 1.748\delta) + 0\alpha - 107.418\beta \tag{2.12}$$

Uslu and Kirbalsar (2008) reported equilibrium experiments on the extraction of levulinic acid by trioctylamine (TOA) dissolved in different ester solvents (ethyl propionate, dimethyl phthalate, hexyl acetate, cyclohexyl acetate, dimethyl adipate, propyl acetate, dimethyl glutarate, dimethyl fumarate, diethyl sebacate, and diethyl carbonate), as well as single solvents. The diethyl carbonate was found to be the most effective solvent with a maximum distribution coefficient of 5.75. Maximum values of possible equilibrium complexation constants (K_{11} and K_{21}) with diethyl carbonate for (1:1), and (2:1) molecule ratios of acid-amine, were reported as 3.32 and 32.59 respectively.

The extraction of dicarboxylic acids (itaconic-, maleic-, malic-, oxalic-, tartaric-, and succinic acid) from aqueous solutions with tributylphosphate dissolved in dodecane was studied at different volume phase ratios by Kyuchoukov *et al.,* (2008). Considering the mass action law, two complexes (one molecule of dicarboxylic acid interacting with one or two molecules of extractant) were assumed to exist in the organic phase, and the corresponding extraction constants were evaluated. It was shown that the number of interacting molecules of the extractant and hence the overall extraction constant strongly depend on the composition of the extraction system.

Uslu *et al.,* (2009a,b) studied the reactive extraction of formic acid and levulinic acid by Amberlite LA-2 dissolved in five different esters, five different alcohols and two different ketones at isothermal conditions (298.15 K). The comparison between physical and reactive extraction was made. The isoamyl alcohol was found to be the most effective solvent with a maximum distribution coefficient value of 19.223 for formic acid and 68.017 for levulinic acid. Furthermore, the linear solvation energy relationship (LSER) model equation was obtained to calculate the distribution coefficients for alcohols with a coefficient of determination (R^2) value of 0.976 in case of formic acid extraction, and loading factors (T_T) for the alcohols with a R^2 value of 0.98 in case of levulinic acid extraction.

The effects of temperature on the partition (P) and dimerization (D) coefficients in reactive extractions of acrylic, propionic, and butyric acids using Aliquat 336 in oleyl alcohol were evaluated by Keshav *et al.,* (2009a), and it was found that P decreases with increasing temperature, whereas the effect of temperature on D varied with no specific trend. Chemical extraction using Aliquat 336 in oleyl alcohol at temperatures ranging from 305 to 333 K showed an increase in K_E values with temperature up to 313 K for acrylic and propionic acids but a decrease with increasing temperature for butyric acid over the range studied. The enthalpy (ΔH) and entropy (ΔS) of reaction were evaluated at different temperatures.

Keshav *et al.,* (2009b) performed the reactive extraction of acrylic acid from aqueous solutions using tri-n-butyl phosphate (TBP) in different diluents (paraffin liquid, toluene, and butyl acetate). Comparison was made on the basis of different physical properties of the solvents like molecular weight, dipole moment, dielectric constant, and E_T parameter. Results show that higher values of distribution coefficients by chemical extraction were obtained for TBP in inert diluents (paraffin liquid and toluene).

2.2.2 Kinetic Study

Juang and Haung (1997b) performed the kinetic study for the rates and mechanism of the liquid-liquid extraction of lactic acid with tri-n-octylamine (TOA) in xylene using a microporous membrane-based stirred cell. It was shown that this operation could give intrinsic rate equations for the formation and dissociation of the acid-amine complexes. A possible reaction mechanism was also proposed. In addition, the effect of temperature on the reaction rates was studied and the activation energies (43.6 and 62.1 kJ mol^{-1}) were obtained. The proposed mechanism indicated that the formation and dissociation of the 1:1 lactic acid-TOA complex, were rate-controlling.

Popaska *et al.,* (1998) carried out kinetic measurements for the extraction of citric acid from aqueous solutions with trioctylamine in isodecanol/*n*-paraffins mixture in a highly agitated system (750 min^{-1}) at 25 ^{o}C. The kinetic data were interpreted by (1) a formal elementary kinetic model, and (2) a proposed mechanism of two reactions of complexation by which (1, 1) and (1, 2) acid-amine complexes are formed. In both cases, very good fits between the experimental kinetic curves and calculated ones were obtained. The formal elementary kinetic model with the rate of the forward reaction being of the order of 0.73 with respect to the concentration of citric acid in the aqueous phase and of first order with respect to the amine concentration., and the rate of the backword reaction as first order with respect to the concentration of the acid-amine complex, could be suitable for the analysis and design of the process in dynamic conditions.

Popaska *et al.,* (2000) studied the equilibrium and kinetics of tartaric acid extraction from aqueous solutions with HOSTAREX A 324 (commercial tri-*iso*-octylamine) in *iso*-decanol/low aromatic kerosene mixtures, as a function of acid, amine and *iso*-decanol concentrations at 298 K. For interpretation of the equilibrium data the modified Langmuir isotherm was used. The equilibrium data were also interpreted by a proposed mechanism of three reactions by which (1,1), (1,2) and (2,1) acid-amine complexes are formed. The kinetic data were interpreted (1) by a formal elementary kinetic model, and (2) by using the proposed reaction mechanism. In both cases, very good fits between the experimental and calculated kinetic curves were obtained. The formal elementary kinetic model with the rate of the forward reaction being of the order of 0.7 with respect to acid concentration in the aqueous phase and of 1.5 order with respect to the amine concentration, and the rate of the reverse reaction as first order with respect to the concentration of the acid–amine complex, could be suitable for the analysis and design of the process in dynamic conditions.

Schlosser *et al.,* (2005) presented an overview on various possibilities of the application of membrane-based solvent extraction (MBSE) and pertraction in recovery and separation of organic acids, and in biotransformations. The factors that were considered in the development of MBSE application, Hybrid processes employing MBSE and mass-transfer characteristics of hollow fiber contactors for MBSE of organic acids were presented. A case study on recovery of 5-methyl-2-pyrazinecarboxylic acid

(MPCA), by simultaneous MBSE and membrane-based solvent stripping, showed potential of this process.

Uslu (2006) conducted kinetic studies for the extraction of propionic acid from aqueous solution with Alamine 336 diluted in toluene at 298.15 K using a stirred cell. The physical mass transfer coefficient, k_L, was obtained by conducting physical extraction (diluent only) of the propionic acid from water using Eq. (2.13).

$$k_L = \frac{V_{org}}{A_C} \int \frac{dC_{org}}{C^*_{org} - C_{org}} \tag{2.13}$$

The value of k_L was evaluated using Eq (2.13) for different speeds of agitation. The regression relation between the mass-transfer coefficient and the speed of agitation obtained by a statistical analysis data was given by Eq. (2.14).

$$k_L = 1.76 \times 10^{-4} N^{4.1} \tag{2.14}$$

Inci (2007) reported kinetic studies for the extraction of succinic acid from aqueous solution with tridodecylamine diluted in MIBK at 298.15 K. Kinetic studies were carried out using a stirred cell. In this case, mass-transfer coefficient found to be dependent on the speed of agitation by a statistical analysis data as given by Eq. (2.15).

$$k_L = 1.55 \times 10^{-4} N^{4.4} \tag{2.15}$$

Very recently, Uslu (2008) studied the reactive extraction of levulinic acid using tripropylamine (TPA) in toluene solution. Kinetic parameters (mass-transfer coefficient) of extraction of levulinic acid by TPA in toluene were also determined and found to be dependent on the speed of agitation with a relationship as given by Eq. (2.16).

$$k_L = 1.312 \times 10^{-3} N^{3.9} \tag{2.16}$$

2.3 Gaps in Existing Literature

There is a resurgence of interest in the industrial society for large-scale production of fermentation chemicals with the use of renewable resources due to the sharp increase in petroleum cost in the recent past. Consequently, the field that investigates microbial organic acid production is currently moving very fast. It is also important for carboxylic acid production of biological origin, as used in foods and pharmaceuticals. The growing importance of biological production, expressed with new routes and increasing production rates, asks for adapted downstream processing for product separation. The existing literature on carboxylic acids suggests that great strides have been made in the separation of lactic acid from aqueous solution using reactive extraction to enhance the microbial production (90%) of lactic acid. Other carboxylic acids such as propionic acid and nicotinic acid (despite the fact that a feasible industrial bio-process has not yet been developed) have huge potential as a building-block chemical used in various industries. Data on reactive extraction for the recovery of nicotinic acid, propionic acid and butyric acid from aqueous solution for intensification of microbial production are still scarce. Various extractants and diluents can be used for reactive extraction of these acids to provide optimum combination of extractants and diluents according to reaction conditions. With different types of extractant-diluent systems for extraction of mainly, nicotinic acid and propionic acid, there is a need to propose mathematical models for determination of the reaction mechanism, and equilibrium & kinetic parameters. In the past study, the graphical and conventional optimization methods, used for the estimation of equilibrium parameters, do not guarantee the global optimum values. Still, an evolutionary based optimization routine [differential evolution (DE)] is not used to estimate the equilibrium parameters. The reactive extraction data can also be utilized in the design of extraction processes for the separation of carboxylic acids from fermentation broths and the aqueous waste industrial stream. Linear solvation energy relationship (LSER) enables to estimate the distribution coefficients for a wide range of diluents using solvatochromic parameters. This quantification of diluent effect is limited to some carboxylic acids with specific extractants only. There is a lot of scope to generate the reactive extraction data with less toxic or non-toxic extractant/diluent system to prepare the biocompatible mixture for extraction of propionic acid and nicotinic acid. Reactive extraction using aminic and phosphoric extractants is an emerging prospective method for the recovery of nicotinic acid.

2.4 Scope of the Work

Since all conventional separation techniques require high energy and material consumptions. Reactive extraction with a specified extractant giving a higher distribution coefficient proposed as a promising technique for the nicotinic acid separation in terms of intensification of the nicotinic acid and propionic production (biological). The design of an industrial reactive extraction process relies on the knowledge of the following four major steps:

- Reactive phase equilibria
- Kinetic parameters
- Apparatus selection and design

The present study aims to accomplish the first one of the above mentioned steps that is to obtain equilibrium data for a specific reactive extraction system for recovery of nicotinic acid, propionic acid, acetic acid, and butyric acid. The study is also carried out to obtain kinetic data for reactive extraction of propionic- and nicotinic acids. These data will later be useful in the design of a reactive extraction unit that is to be coupled with the fermentation system to achieve in-situ recovery and purification of the product. The separation unit that is going to be designed in the future will attempt to perform extraction and back extraction of carboxylic acids simultaneously in a single separation unit in a continuous or semi-continuous mode. Reactive extraction will also be used an efficient, economical, and environmental friendly method for separation of formic, acetic and propionic acids from waste water streams.

In the present study, extraction of carboxylic acids from its aqueous solutions is performed to obtain the equilibrium data and to determine the optimum conditions for the intensification of recovery of carboxylic acids. The effects of various parameters on the extraction are investigated with the intention of implementing the data obtained to a future industrial separation unit. The equilibrium investigations are carried out in shaking flasks of 100 mL in which the aqueous and organic phases are contacted until the equilibrium is attained. Long chain aliphatic amines such quaternary ammonium salts (Aliquat 336), tri-n-octyl amine (TOA) and tri-n-dodecyl amine (TDA), and organophosphorus based derivatives such as tri-n-butyl phosphate (TBP) and tri-n-octyl phosphine oxide (TOPO) dissolved in different inert diluents (n-hexane, n-heptane, n-octane, n-decane, n-dodecane, kerosene, benzene, toluene, diethyl ether and dichloromethane) with or without active diluents, also known as modifiers (1-octanol, 1-decanol, MIBK and oleyl alcohol) are used as the organic phases. The effects of initial aqueous phase acid concentration, organic phase extractant concentration and modifier composition on the extraction efficiency are studied. The equilibrium investigations are carried out by using biocompatible extractant-diluent systems such as TOA/Aliquat 336 in n-dodecane and 1-decanol for the extraction of propionic acid and nicotinic acid, and TDA in n-dodecane and oleyl alcohol for the extraction of nicotinic acid. The equilibrium constants and stoichiometry of the reaction through a proposed model (based on mass action law) are estimated for the various systems studied in the present work. A population based search algorithm called differential evolution (DE) and graphical methods are employed. Attempts have been made to quantify the effect of diluents on extraction efficiency (in terms of distribution coefficient) of extractant (TOA) using LSER model for the extraction of formic acid, acetic acid, propionic acid and butyric acid. The effect of diluents on extraction efficiency (distribution coefficient) of extractant (TOPO) is also quantified using a model comprised of dipole moment/E_T parameter for the extraction of nicotinic acid. The state-of-the-art reviews have been made on fermentation production, recovery from fermentation broths and applications of lactic acid in biopolymers, recent development in manufacturing processes (chemical and enzymatic) of nicotinic acid and most efficient separation technique, the reactive extraction, and on intensification of recovery of carboxylic acids from aqueous solution using reactive extraction.

CHAPTER – 3

EXPERIMENTAL

The experimental methodology that is followed to obtain the equilibrium extraction data for the extraction of carboxylic acids from its aqueous solutions is described in this chapter. Since the aim of this study is to understand the effects of various factors on the equilibrium and kinetic extraction characteristics, the variables to be studied are first identified. For the extraction systems used in the present study, various variables such as aqueous phase carboxylic acid concentration, type of carboxylic acid, organic phase extractant concentration, type of extractant, type of diluent, modifier composition, temperature and stirring speed. Different carboxylic acid-extractant-diluent systems with the concentration ranges applied to extraction experiments (equilibrium and kinetic) carried out are listed in Table 3.1 – 3.3.

The ranges of variables used in this study are determined to simulate the conditions of an actual fermentation broth and industrial waste water streams, and a potential reactive extraction system that could be coupled with the fermentor.

Table 3.1 Different carboxylic acid-extractant-diluent systems with concentration range applied to equilibrium extraction experiments

S. No.	Carboxylic acid		Extractant		Diluents
	Name	Range (mol.L^{-1})	Name	Range (mol.L^{-1})	
1.	Formic acid	0.265 – 1.32	-	-	*n*-decane, benzene, dichloromethane (DCM), methyl isobutyl ketone (MIBK), 1-decanol and *n*-decane + 1-decanol (1:1 v/v)
2.	Acetic acid	0.05 – 0.26			
3.	Propionic acid	0.068 – 0.408			
4.	Butyric acid	0.095 – 0.567			
5.	Nicotinic acid	0.025 – 0.12	-	-	*n*-heptane, benzene, kerosene, diethyl ether, MIBK and 1-octanol
6.	Propionic acid	0.135 – 0.675	tri-n-butyl phosphate (TBP)	0.55 – 2.92	*n*-decane + 1-decanol and kerosene + 1-decanol
7.	Nicotinic acid	0.02 – 0.13	TBP	0.73 – 3.65	MIBK, 1-decanol, *n*-decane and kerosene
8.	Nicotinic acid	0.02 – 0.12	tri-n-octyl phosphine oxide (TOPO)	0.10 – 0.71	kerosene + 1-octanol (2:1 v/v), heptane + 1-octanol (2:1 v/v), *n*-octane, toluene, MIBK, DCM, kerosene and 1-decanol
9.	Formic acid	0.265 – 1.32	tri-n-octylamine (TOA)	0.46	*n*-decane, benzene, dichloromethane (DCM), methyl isobutyl ketone (MIBK), 1-decanol and *n*-decane + 1-decanol (1:1 v/v)
10.	Acetic acid	0.05 – 0.26			
11.	Propionic acid	0.068 – 0.408			
12.	Butyric acid	0.095 – 0.567			

(Table 3.1 Continued…).

13.	Propionic acid	0.0675 – 0.675	TOA	0.22 – 1.14	toluene + 1-decanol, cyclohexane + 1-decanol and kerosene + 1-decanol
14.	Propionic acid	0.0675 – 0.675	TOA	0.46 – 1.14	*n*-dodecane + 1-decanol
15.	Propionic acid	0.0675 – 1.35	Aliquat 336 (a quaternary amine)	0.22 – 1.32	1-octanol and *n*-dodecane + 1-decanol
16.	Nicotinic acid	0.02 – 0.12	TOA	0.28 – 1.38	*n*-dodecane, butyl acetate, toluene and MIBK
17.	Nicotinic acid	0.025 – 0.10	Aliquat 336	0.55	*n*-decane, 1-decanol, toluene and MIBK
18.	Nicotinic acid	0.02 – 0.12	TOA	0.11 – 0.57	toluene + 1-decanol, *n*-decane + 1-decanol, kerosene + 1-decanol, cyclohexane + 1-octanol and *n*-decane + 1-octanol
19.	Nicotinic acid	0.023 – 0.122	tri-n-dodecylamine (TDA)	0.08 – 0.39	*n*-dodecane + oleyl alcohol

Table 3.2 Different carboxylic acid-extractant-diluent systems applied to study the influence of temperature on extraction efficiency

S. No.	**Carboxylic acid**	**Extractant**	**Diluents**	**Temperature range (K)**
1.	Propionic acid (0.405 mol.L^{-1})	TBP (0.91 – 1.46 mol.L^{-1})	n-decane + 1-decanol (1:1 v/v) and kerosene + 1-decanol (1:1 v/v)	298 – 334
2.	Nicotinic acid (0.122 mol.L^{-1})	TDA (0.08 – 0.39 mol.L^{-1})	*n*-dodecane + oleyl alcohol (2:1 v/v)	298 – 333

Table 3.3 Different carboxylic acid-extractant-diluent systems applied to study extraction kinetics

S. No.	**Carboxylic acid**	**Extractant**	**Diluents**	**Stirring speed (rpm)**
1.	Nicotinic acid (0.02 – 0.12 mol.L^{-1})	TOA (0.23 mol.L^{-1})	MIBK	250 - 500
2.	Propionic acid (0.27 – 0.54 mol.L^{-1})	TOA (0.46 mol.L^{-1})	cyclohexane + 1-decanol (1:1 v/v)	350

Recently, extractive recovery of carboxylic acids by phosphorus- and amine- based systems from aqueous solutions (fermentation broth and wastewater), including lower than 10 % (w/w) acid concentrations, has received increasing interest. These concentration values (Table 3.1-3.3) of different acids (formic acid, acetic acid, propionic acid, butyric acid and nicotinic acid) in the aqueous phase solutions are taken according to the concentration range of these carboxylic acids found in the actual fermentation broths as well as in waste water streams (Kertes and King, 1986; Senol, 2002; Senol, 2004; Senol, 2005). These concentration values should be low enough due to the product inhibition and toxic effect towards the carboxylic acid producing microbes.

The organic phase extractant (TBP) concentration is varied between 0.55 mol.L^{-1} (15% v/v) and 3.65 mol.L^{-1} (pure TBP) and dissolved in various inert and active diluents. Other organic phase extractants (TOPO, TOA, TDA and Aliquat 336) are also dissolved in diluents as per the physical properties of the extractant and its toxic effect. TOA, TDA and Aliquat 336 are highly viscous in nature, so it is very difficult to handle and use them directly in liquid extraction in their pure form. Higher range concentration of TOPO (solid powdered material) in diluents may form highly viscous solution that may take longer time to reach equilibrium. Therefore these have to be diluted with a suitable organic solvent prior to their use in extraction. It is found that higher concentration of extractant results in more acid extraction and less product inhibition (Tong, 1998). However, in the extraction experiments, maximum concentration of extractant in the diluent can not be beyond certain value in order to suppress its toxic effect and to obtain an organic phase that can be more easily handled and mixed with the aqueous phase to provide better mass transfer. Since, the temperature in the fermentation process for the production of carboxylic acids may encounter in the range of 298 to 333 K, the effect of temperature has been investigated at a particular aqueous phase concentrations of propionic acid and nicotinic acid and different organic phase concentrations of extractant. Additional experiments are conducted to observe the effects of different diluents on the extraction behavior when pure extractant or pure diluent is used as the organic phase. Some sets of experiments are repeated twice to check the reproducibility of the experiments and the average of the two results was taken as the final value.

3.1 Equipment

The equilibrium extraction experiments are carried out in the conical flasks (Borosil Glassware, India) of 100 mL which are placed in a temperature controlled reciprocal shaking water bath (HS 250 basic REMI labs, India). Temperature was maintained constant in the shaking bath by a water thermostat. The ingredients of these flasks are separated by using a separating funnel (Borosil Glassware, India) of 100 mL after the extraction is complete.

The analysis of the aqueous phases before and after extraction, are performed by using potentiometric titration with fresh sodium hydroxide filled in a burette of 50 mL, and also using an UV spectrophotometer (Systronics, 119 model, 262 nm, India).

The initial and equilibrium pH values of aqueous solutions are measured using a digital pH-meter of ArmField Instruments (PCT 40, Basic Process Module, UK).

3.2 Materials

The materials used in this study are various carboxylic acids, extractants (phosphorus based and amine based) and diluents (inert and modifier), which are listed in Table 3.4.

3.2.1 Other Reagents

De-ionized water, used to prepare the aqueous solutions of various concentrations of carboxylic acids, is procured from S. D. Fine-Chem Ltd., India. Sodium hydroxide, used for titration is of analytical grade with a purity of 98% and supplied by Merck Pvt. Ltd., Germany. For the standardization of NaOH solution, oxalic acid with a purity of 99.8% is obtained from S. D. Fine-Chem Ltd., India. Phenolphthalein solution (pH range of 8.2 to 10.0), used as an indicator for titration, is obtained from CDH Pvt. Ltd., India.

The physical characteristics with CAS # and IUPAC name of all reagents used in the extraction equilibrium experiments are given in Table 3.4. IUPAC nomenclature is a system of naming chemical compounds and of describing the science of chemistry in general it becomes necessary to ensure that each compound has a unique name. This requires the addition of extra rules to the standard IUPAC system (the CAS system is the most commonly used in this context). CAS registry numbers (CAS #s) are unique numerical identifiers for chemical elements, compounds, polymers, biological sequences, mixtures and alloys. Chemical Abstracts Service (CAS), a division of the American Chemical Society, assigns these identifiers to every chemical that has been described in the literature.

Table 3.4 Physical characteristics of acids, extractants, diluents and modifiers

S. No.	Reagents	IUPAC name	CAS #	Suppliers	Purity (% C)	Mol. Wt., $g.mol^{-1}$	Specific gravity, $g.cm^{-3}$	Viscosity (cP)
1.	Formic acid	Methanoic acid	64-18-6	HIMEDIA, India.	99	46.03	1.22	1.57 (26^0C)
2.	Acetic acid	Ethanoic acid	64-19-7	HIMEDIA, India.	99	60.05	1.049	1.22 (25^0C)
3.	Propionic acid	Propionic acid	79-09-4	Sigma-Aldrich Co. USA	98	74.08	0.99	10 (25^0C)
4.	Butyric acid	Butanoic acid	107-92-6	BDH Pvt. Ltd, India.	98	88.11	0.96	1.56 (20°C)
5.	Nicotinic acid	pyridine-3-carboxylic acid,	59-67-6	HIMEDIA, India.	99.5	123.10	1.473	-
6.	TBP	Tri-n-butyl phophate	126-73-8	Spectrochem. Pvt. Ltd., India	98	266.32	0.973	3.4 (25 ^{0}C)
7.	TOPO	1-Dioctylphosphoryl octane	78-50-2	Sigma-Aldrich Co. USA	99	386.65	-	-
8.	TOA	N,N-dioctyloctan-1-amine	1116-76-3	Fluka, USA.	98	353.68	0.809	-
9.	TDA	-	-	Fluka, USA.	95	519.92	0.811	-
10.	Aliquat 336	*N*-Methyl-*N*,*N*-dioctyloctan-1-ammonium chloride	63393-96-4	Spectrochem. Pvt. Ltd., India	97	404.16	0.884	$1.5x10^6$ (30^0C)
11.	n-Hexane	Hexane	110-54-3	S. D. Fine-Chem Ltd., India	99	86.18	0.6548	0.294 (25^0C)
12.	Cyclohexane	Cyclohexane	110-82-7	S. D. Fine-Chem Ltd., India	99	84.16	0.779	0.98 (25^0C)
13.	n-Heptane	Heptane	142-82-5	S. D. Fine-Chem Ltd., India	99	100.21	0.684	0.386 (25^0C)

Table 3.4 continued

14.	n-Octane	Octane	111-65-9	S. D. Fine-Chem Ltd., India	99.7	114.23	0.701	0.54 (20^{0}C)
15.	n-Decane	Decane	124-18-5	Spectrochem. Pvt. Ltd., India	99.5	142.29	0.73	0.92 (20^{0}C)
16.	n-Dodecane	Dodecane	112-40-3	Spectrochem. Pvt. Ltd., India	98	170.34	0.75	1.34 (25°C)
17.	Diethyl ether	Ethoxyethane	60-29-7	BDH Pvt. Ltd., India	98	74.12	0.7134	0.224 (25 °C)
18.	Dichloro methane	Dichloro methane	75-09-2	S. D. Fine-Chem Ltd., India	99	84.93	1.326	0.406 (25°C)
19.	Chloroform	Tri chloro methane	67-66-3	S. D. Fine-Chem Ltd., India	99	119.38	1.48	0.54 (25 °C)
20.	MIBK	4-Methylpentan-2-one	108-10-1	Spectrochem. Pvt. Ltd., India	99.8	100.16	0.801	0.58 (20 °C)
21.	Kerosene	-	8008-20-6	Commercial grade	-	170	0.78-0.81	2.17 (20 °C)
22.	Toluene	Methyl benzene	108-88-3	SISCO Res. Lab. Pvt. Ltd. India	99.7	92.14	0.867	0.557 (25°C)
23.	Benzene	Benzene	71-43-2	SISCO Res. Lab. Pvt. Ltd. India	99.5	78.11	0.8786	0.652 (20 °C)
24.	1-Octanol (modifier)	Octane-1-ol	111-87-5	Spectrochem. Pvt. Ltd., India	99	130.23	0.822	8.4 (20 °C)
25.	1-Decanol (modifier)	Decane-1-ol	112-30-1	Spectrochem. Pvt. Ltd., India	98	158.28	0.830	34 (22°C)
26.	Butyl acetate	Butyl ethanoate	123-86-4	S. D. Fine-Chem Ltd., India	98	116.16	0.88	0.74 (20 °C)
27.	Oleyl alcohol (modifier)	Octadec-9-en-1-ol	143-28-2	Sigma-Aldrich Co. USA	60	268.48	0.85	-

3.3 Experimental Procedure

3.3.1 Preparation of Carboxylic Acids Stock Solutions

To minimize experimental error in aqueous phase acid solutions, stock solutions of the carboxylic acids with following concentrations are prepared by diluting them with deionized water: nicotinic acid – 0.13 $mol.L^{-1}$, formic acid – 1.32 $mol.L^{-1}$, acetic acid – 0.26 $mol.L^{-1}$, propionic acid – 1.35 $mol.L^{-1}$ and butyric acid – 0.57 $mol.L^{-1}$. The stock solutions are then analyzed for their acid content by titrating them with 0.05 N NaOH solution.

3.3.2 Preparation of the Aqueous Phase for Extraction

The stock aqueous solutions of the all acids are diluted to the desired concentrations (for nicotinic acid, in the range of 0.02 - 0.13 $mol.L^{-1}$; for acetic acid, in the range of 0.05 - 0.26 $mol.L^{-1}$, for propionic acid, in the range of 0.0675 - 1.35 $mol.L^{-1}$; for butyric acid, in the range of 0.095 - 0.57 $mol.L^{-1}$ and for formic acid, in the range of 0.26 - 1.32 $mol.L^{-1}$) using de-ionized water. The pH values of these initial aqueous solutions are measured by a pH meter (PCT 40, Basic Process Module, UK).

3.3.3 Preparation of the Organic Phase for Extraction

Organic phases are prepared by mixing the extractant (amine-based and phosphorus-based) thoroughly in the diluents given in Tables 3.1 - 3.3. Pure diluents are also used alone as the organic phase to study physical extraction equilibrium. The organic solutions of 1.37 M TOA, 0.39 M TDA and 1.33 M Aliquat 336 in diluents are first prepared, and then they are diluted to the desired sub-levels with a suitable diluent. Phosphorous based extractant, tri-n-butyl phosphate (TBP) is diluted in the range of 15-80% TBP (v/v) with various diluents. 0.71 M organic solution of TOPO is used to prepare the desired sub-level concentrations in the diluents. In some of the experiments pure TBP is also used as an organic phase.

3.3.4 Equilibrium Studies

The extraction equilibrium experiments are carried out at constant temperature (298 K) with equal volumes (12 cm^3, 16 cm^3 and 25 $cm^3$of each phase) of the aqueous and organic solutions shaken at 100 rpm for 8 hours in conical flasks of 100 mL on a temperature controlled reciprocal shaking machine (HS 250 basic REMI labs, India). To study the effect of temperature on reactive extraction, the equilibrium experiments are carried out at four different temperatures (298 – 334 K). The schematic diagram of equilibrium extraction setup is shown in Fig. 3.1 and the photographs are shown in Plates – 3.1 to 3.2. This mixing time of 8 hrs is chosen as the appropriate time for attaining equilibrium based on our preliminary studies. After attaining equilibrium, the mixture is allowed to settle for 4 hrs in the separating funnels of 125 mL at constant temperature (298 K) bath operated at atmospheric pressure (Plate 3.3). After settling the organic and aqueous phases are separated. The aqueous phase is carefully pipetted out and analyzed for residual aqueous phase acid concentration by titration (discussed in section 3.4). The initial and equilibrium pH values of aqueous solutions are measured using a digital pH-meter of ArmField Instruments (PCT 40, Basic Process Module, UK) as shown in Plate 3.4.

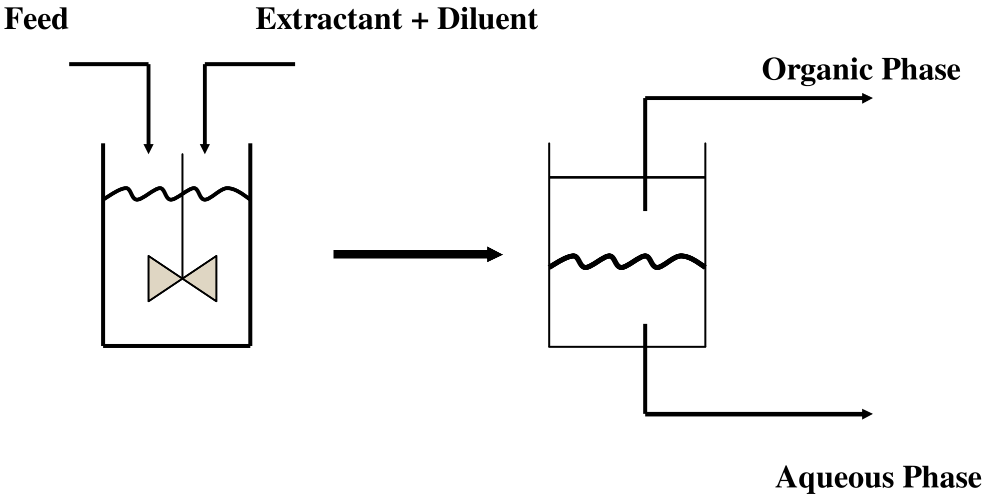

Figure 3.1 Schematic diagram of equilibrium extraction set-up

Plate 3.1 Photograph of equilibrium experimental setup at room temperature

Plate 3.2 Photograph of equilibrium experimental setup with controlled temperature

Plate 3.3 Photograph of experimental setup for the separation of organic and aqueous phases

Plate 3.4 Photograph of a digital pH-meter of ArmField instruments (PCT 40, Basic Process Module, UK)

3.3.5 Kinetics Studies

The stirring vessel for kinetic measurements used in this work is cylindrical glass, 5.0 cm in diameter and 10.0 cm high, with a flat bottom. An aqueous solution of propionic acid and nicotinic acid of known concentration (0.405 $mol{\cdot}L^{-1}$ and 0.10 $mol{\cdot}L^{-1}$ respectively) with a volume of 25 cm^3 are first placed in the vessel. The four-blade paddle with stirrer is used for agitation. The position of the turbine stirrer is adjusted to 1.0 cm below the interface. An equal volume of extraction mixture is then added, and the mixture is stirred thoroughly. The entire vessel is immersed in a thermostat controlled at a room temperature of 298 K. One sample is used for collecting data to determine the acid concentration in aqueous phase (potentiometric titration with 0.02 N NaOH using phenolphthalein as the indicator). The concentration of nicotinic acid and propionic acid in the organic phase is determined by mass balance. To ensure that the concentration corresponds to the time when the sample is taken, the separation of the phases is carried out quickly and successively in three separating funnels of 125 mL.

3.4 Analytical Methods

The concentration of acid in the aqueous phase is determined by taking a sample volume of 2 cm^3 using potentiometric titration with fresh sodium hydroxide solution of 0.01 N (for extraction of nicotinic acid and acetic acid) and 0.02 N (for extraction of formic acid, propionic acid and butyric acid) with phenolphthalein as an indicator. The concentration of nicotinic acid in the aqueous phase is also determined using an UV spectrophotometer (Systronics, 119 model, 262 nm, India). The acid concentration in the organic phase is calculated by mass balance. The reproducibility is checked by carrying out the experiments twice and mean value is used for subsequent calculations. The results are found to be reproducible within ±5%.

A calibration curve (Figure 3.3) is drawn with the standard solutions of known concentration of nicotinic acid using UV spectrophotometer. The absorbance can be detected at very low concentrations and its variation with concentration is linear for very dilute solutions. For obtaining the calibration curve, a stock solution of nicotinic acid (0.75 $mmol.L^{-1}$) is prepared. From this stock solution, nine samples of aqueous solution are prepared in the concentration range of 0.015 – 0.75 $mmol.L^{-1}$ and the corresponding absorbance is determined using UV Spectrophotometer. Since working in the linear region gives more reliable results, all samples for analysis are diluted in various ratios to fit their concentrations in this low concentration linear region of the calibration curve. Some samples are diluted 10- fold while some others are diluted 50- fold before putting them into the spectrophotometer to get the absorbance of solution within the range of UV spectrophotometer reading. The concentrations of the samples are then found by using the calibration curve as shown in Figure 3.2. The photograph of the UV spectrophotometer is shown in the plate 3.5.

The extraction process is analyzed by means of the degree of extraction and distribution coefficient. The distribution coefficient, K_D, is calculated using Eq. 3.1.

$$K_{\mathrm{D}} = \frac{\overline{C}_{\mathrm{HA}}}{C_{\mathrm{HA}}} \qquad (3.1)$$

where, $\overline{C}_{\mathrm{HA}}$ is the total concentration of carboxylic acid in organic phase and C_{HA} is the total acid concentration (dissociated and un-dissociated) in aqueous phase at equilibrium.

The degree of extraction is defined as the ratio of acid concentration in the extracted phase to the initial acid concentration in aqueous solution by assuming no change in volume at equilibrium as given by Eq. 3.2.

$$E = \frac{K_{\mathrm{D}}}{1 + K_{\mathrm{D}}} \times 100 \qquad (3.2)$$

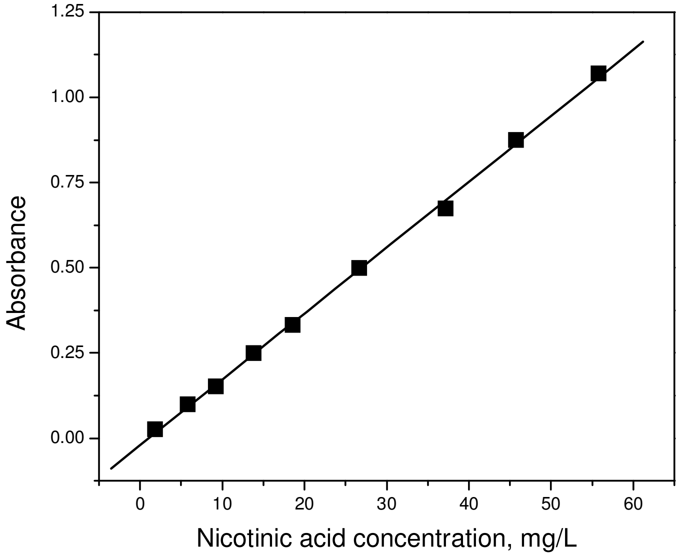

Figure 3.2 Calibration curve for analysis of aqueous phase nicotinic acid concentration

Plate-3.5 Photograph of UV-VIS spectrometer (Systronics, 119 model India)

CHAPTER – 4

MATHEMATICAL MODELING AND SIMULATION

Modeling of reactive extraction for recovery of carboxylic acids implies the representation of chemical and physical phenomena occurring in the process in mathematical form constituting the extractants and/or diluents as the organic system, and acid & water as the aqueous system. In other words, whole process is to be represented as a system of equations which taken together can provide a valuable quantitative information about the entire process. The models of reactive extraction can be broadly categorized into two groups: (1) Equilibrium models, and (2) kinetic models. Equilibrium models are important in order to predict the thermodynamic parameters of chemical reactions and distribution of carboxylic acids between organic solvent and water. The equilibrium model assumes that all the reactions are in thermodynamic equilibrium occurring at the interface of aqueous and organic phases. It determines the stoichiometries (the number of reacting extractant molecules, n) and the values of equilibrium extraction constant (K_E) of reactive extraction. It is observed that most of the equilibrium models developed so far assumes the apparent equilibrium extraction constants, expressed in terms of species concentrations (Kertes and King, 1986; Tamada *et al.,* 1990a; Yoshizawa *et al.,* 1994; Juang *et al.,* 1997a; Matsumoto *et al.,* 2001; Yankov *et al.,* 2004; Shan *et al.,* 2006; Cascaval *et al.,* 2007; Keshav *et al.,* 2008a). In the equilibrium study, several diluents can be used with the extractant to provide the data on extraction of carboxylic acids. The recovery of acid from aqueous solution is found to depend on the type of diluent used. The linear solvation energy relationship (LSER) with solvatochromic parameters of the diluents (Bizek *et al.,* 1993; Senol, 2004; Uslu, 2006; Uslu *et al.,* 2007; Inci, 2007) and dipole moment & E_T parameter relationship (Keshav *et al.,* 2008c), are used to predict the extractability of carboxylic acids for a wide range of diluents or their mixtures. In the kinetic study of reactive extraction of carboxylic acids, different models are used to predict the kinetic constants and orders of chemical reaction between the acid molecules and extractant molecules (Popaska *et al.,* 1998; Schlosser *et al.,* 2005; Inci, 2007; Uslu, 2008).

After studying various modeling approaches to equilibrium and kinetic study, a mass action law (chemodel) with and without modifications are employed in the present study to determine the stoichiometries of reaction (the number of reacting extractant molecules, n) and the values of equilibrium extraction constant (K_E) for the new different acid/extractant/diluents system. Effect of diluent on the recovery of mono-carboxylic acids from aqueous solution is derived by both LSER models using solvatochromic parameters of all diluents with different approach, and dipole moment & E_T parameter relationship. Kinetic parameters of reactive extraction are estimated for the nicotinic acid and propionic acid with tri-n-octyl amine dissolved in diluents using Poposka *et al.,* (2000) kinetic model. Equilibrium experimental results are compared with the results predicted by equilibrium model formulated in the present study. The detailed descriptions of these models are presented in Sections 4.1 & 4.2.

4.1 Equilibrium Models

4.1.1 Mass Action Law Model

The basic mass action law represents the equilibria involved in the extraction process between carboxylic acid and solvent system. Different models are used to represent equilibria with phosphoric and aminic extractants. Extraction equilibria with pure diluents are designated as physical extraction, and the extraction equilibria with phosphoric and aminic extractants are designated as chemical extraction. Different mass action law approaches are used to represent the physical and chemical extraction discussed in the Sections 4.1.1.1 and 4.1.1.2 respectively.

4.1.1.1 Physical Extraction Equilibria

In the physical extraction of carboxylic acids, inert non-interacting hydrocarbons, substituted hydrocarbons and oxygen bearing organic solvents (active solvents) are used as organic phase. In spite of the substantial difference in the extractive capacity between the two types of solvents, the same mass action law description of the process applies to both. The distribution of a carboxylic acid between water and a non-polar hydrocarbon is relatively free of complexities and is considered to be a physical distribution. However, the effect of partial dissociation of acid in the aqueous phase and extensive dimerization in the organic phase should be accounted. On the other hand, acids extracted by carbon-bonded oxygen donor solvents (active diluents) are strongly hydrated by varying numbers of water molecules. The exact solvation number of the acid molecules in the organic phase is usually undetermined, but it is known that a large number of solvent molecules are needed for an efficient competition with the water molecules that hydrate the acid at the interface.

The set of mass action equations describing the transfer of a weak mono-carboxylic acid from water into an organic solvent with which the acid does not interact to form specific solvates must take the following three aspects into account:

(i) The ionization of acid in the aqueous solution as given by Eq. (4.1):

$$HA \Leftrightarrow H^{+} + A^{-} \tag{4.1}$$

Dissociation constant (K_a) of acid is defined as

$$K_a = \frac{[H^{+}][A^{-}]}{[HA]} \tag{4.2}$$

(ii) The partition of the un-dissociated molecular acid between the two phases, aqueous and organic is represented as Eq. (4.3):

$$HA_{aq} \Leftrightarrow HA_{org} \tag{4.3}$$

Partition coefficient (P) of above equilibria is calculated by Eq. (4.4)

$$P = \frac{[HA]_{org}}{[HA]_{aq}} \tag{4.4}$$

(iii) The dimerization of the acid in the organic phase and dimerization constant (D) are given by Eq. (4.5) and Eq. (4.6) respectively:

$$2HA_{org} \Leftrightarrow (HA)_{2_{org}} \tag{4.5}$$

$$D = \frac{[HA]_{2_{org}}}{[HA]^{2}{}_{org}} \tag{4.6}$$

The distribution coefficient (K_D) on molar concentration scale is expressed in terms of the total concentration of the acid in all its possible forms in the aqueous phase (C_{HA}) and organic phase, ($\overline{C}_{HA}$) as given by Eqs. (4.7 – 4.10):

$$K_D = \frac{\overline{C}_{HA}}{C_{HA}} = \frac{[HA]_{org} + 2[(HA)_2]_{org}}{[HA]_{aq} + [A^{-}]_{aq}} \tag{4.7}$$

$$\Rightarrow K_D = \frac{[HA]_{aq} P + 2D[HA]^2{}_{org}}{[HA]_{aq} + K_a [HA]_{aq} / [H^+]_{aq}} \tag{4.8}$$

$$\Rightarrow K_D = \frac{[HA]_{aq} P + 2DP^2[HA]^2{}_{aq}}{[HA]_{aq}(1 + K_a / [H^+]_{aq})} \tag{4.9}$$

$$\Rightarrow K_D = \frac{P + 2DP^2[HA]_{aq}}{(1 + K_a / [H^+]_{aq})} \tag{4.10}$$

The terms in square brackets represent the concentration in moles per liter.

For the dilute aqueous solutions, the term $(1 + K_a / [H^+]_{aq})$ is negligible, and hence Eq. (4.10) reduces to Eq. (4.11):

$$K_D = P + 2DP^2[HA]_{aq} \tag{4.11}$$

A plot of K_D versus $[HA]_{aq}$ which in turn is obtained from $C_{HA(aq)}$ via the known dissociation constant (pK_a), yields the values of P and D for different solvents.

4.1.1.2 Chemical Extraction Equilibria (Chemodel)

If chemical interactions between the components (acid and extractant) of the complex are strong compared to the physical interactions in the system, the equilibrium behavior can be modeled effectively by postulating the formation of various stoichiometric complexes of acid and extractant. This mass action law description of a system as a series of stoichiometric reactions will be referred to as chemical modeling.

An equilibrium description of a system can be written as a set of reactions between *m* molecules of acid (*HA*), and n molecules of extractant (S) to form various *(m:n)* complexes, with corresponding equilibrium constants ($K_{E,true}$) as given by Eqs. 4.12 & 4.13.

$$mHA + n\overline{S} \Leftrightarrow \overline{(S)_n(HA)_m} \tag{4.12}$$

$$K_{E,true} = \frac{\left\{\overline{(S)_n (HA)_m}\right\}}{\{HA\}^m \left\{\overline{S}\right\}^n} \tag{4.13}$$

where, the species activities are denoted by braces and the organic-phase species are marked with an overbar.

For practical usage, the activities of the organic phase species are assumed to be proportional to the respective concentration of the species, with the constant of proportionality (the nonidealities) accounted for in the equilibrium constant. The activity of the acid is assumed to be proportional to the concentration of un-dissociated acid in the equilibrium aqueous phase. The differences in properties (e.g., hydrophobicity) among the various acids are incorporated into the equilibrium constant. The apparent equilibrium constant for the overall reaction can be written as

$$K_E = \frac{[\overline{(S)_n (HA)_m}]}{[HA]^m [\overline{S}]^n} \tag{4.14}$$

For simplicity, the apparent equilibrium extraction constants, expressed in terms of species concentrations, are used. The physical extraction of carboxylic acid, acid dimerization and water co-extraction are neglected due to the presence of significantly stronger interactions between acid and extractant molecules. Extraction equilibrium of mono-carboxylic acid using phosphorus bonded oxygen bearing extractants [(tri-*n*-butyl phosphate (TBP) and tri-*n*-octylphosphine oxide (TOPO)] dissolved in the diluent and/or the diluent mixture is represented as:

$$HA + \overline{S} \Leftrightarrow \overline{S : HA} \tag{4.15}$$

The interaction between a mono-carboxylic acid and amine based extractants (tertiary amine and quaternary amine) is realized through hydrogen bonding of non-dissociated acid molecule given by either Eq. (4.15) or by ion-pair formation (Eq. 4.16):

$$\overline{S} + H^{+} + A^{-} \Leftrightarrow \overline{SH^{+}A^{-}} \tag{4.16}$$

where, S = for the extractant.

The prevailing mechanism out of the two possible mechanisms as represented by Eqs. 4.15 & 4.16 respectively depends on (1) the *pH* of the acid solution, (2) the pK_a of the acid, (3) the concentration of acid and extractant and (4) the basicity of the extractant with respect to the acid. The exact mechanism can be revealed only by data from IR spectra. The final mathematical expressions for the distribution coefficient (K_D) are identical in the case of H-bound and ion-pair mechanisms.

Case – 1:

If more than one extractant molecule per acid molecule takes part in the complex formation, the extraction equilibrium is given by Eq. (4.17).

$$HA + n\overline{S} \Leftrightarrow \overline{S_nHA} \tag{4.17}$$

The extraction equilibrium constant, K_E, can be calculated using Eq. (4.18):

$$K_E = \frac{[\overline{(S)_n HA}]}{[HA][\overline{S}]^n} \tag{4.18}$$

Carboxylic acid also dissociates under equilibrium in aqueous phase as given by Eq. (4.19):

$$HA \Leftrightarrow H^{+} + A^{-} \tag{4.19}$$

The non-dissociated acid concentration in the aqueous phase [HA] can be calculated with the relationships as given in Eqs. (4.20 – 4.22) using the total (analytical) concentration, C_{HA} and the dissociation constant (K_a).

$$K_a = \frac{[H^{+}][A^{-}]}{[HA]} \tag{4.20}$$

$$C_{HA} = [HA] + [A^-] \tag{4.21}$$

$$[HA] = \frac{C_{HA}}{(1 + K_a / [H^+])} \tag{4.22}$$

The distribution coefficient (K_D) is defined as a ratio of the total (analytical) acid concentrations in the organic phase ($\overline{C}_{HA}$) and the aqueous phase (C_{HA}) as given by Eq. (4.23):

$$K_D = \frac{\overline{C}_{HA}}{C_{HA}} = \frac{[\overline{(S)_n HA}]}{C_{HA}} \tag{4.23}$$

Substituting the values of $[\overline{(S)_n HA}]$ and C_{HA} from Eqs. (4.18) and (4.22) respectively in Eq. (4.23) results Eq. (4.24).

$$K_D = K_E \frac{[\overline{S}]^n}{(1 + K_a / [H^+])} \tag{4.24}$$

The above equation, represented in logarithmic form, yields the straight line with intercept of log K_E and slope of n.

$$\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right) = \log K_E + n \log\left([\overline{S}]\right) \tag{4.25}$$

where, $[\overline{S}]$ is the free extractant concentration in the organic phase, represented as:

$$[\overline{S}] = [\overline{S}]_{in} - n[\overline{HA(S)_n}] \tag{4.26}$$

Putting the value of $[\overline{S}]$ from Eq. (4.26) in Eq. (4.25) results Eq. (4.27)

$$\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right) = \log K_E + n \log\left([\overline{S}]_{in} - n[\overline{HA(S)_n}]\right) \tag{4.27}$$

Due to apparition of n under logarithm, an optimization procedure for estimation of n and K_E is applied. If $[\bar{S}]_{in} >> n[\overline{HA(S)_n}]$, the initial extractant concentration $[\bar{S}]_{in}$ can also be used to determine n and K_E of Eq. (4.25).

Case – 2:

If m molecules of acid make complex with n molecules of extractant, the extraction equilibrium is represented by Eq. (4.12), and the equilibrium constant is calculated using Eq. (4.28)

$$K_E = \frac{[\overline{(S)_n (HA)_m}]}{[HA]^m [\bar{S}]^n} = \frac{[\overline{(S)_n (HA)_m}](1 + K_a/[H^+])^m}{[\bar{S}]^n C_{HA}^m} \tag{4.28}$$

The distribution coefficient is defined as:

$$K_D = \frac{\bar{C}_{HA}}{C_{HA}} = m\frac{[\overline{(S)_n (HA)_m}]}{C_{HA}} \tag{4.29}$$

Substituting the values of $[\overline{(S)_n (HA)_m}]$ from Eqs. (4.29) in Eq. (4.28) results Eq. (4.30).

$$K_E = \frac{K_D (1 + K_a/[H^+])^m}{m[\bar{S}]^n C_{HA}^{m-1}} \tag{4.30}$$

The free extractant concentration, $[\bar{S}]$ in the organic phase, represented as:

$$[\bar{S}] = [\bar{S}]_{in} - n[\overline{(HA)_m (S)_n}] \tag{4.31}$$

$$\Rightarrow [\bar{S}] = [\bar{S}]_{in} - K_D n C_{HA} / m \tag{4.32}$$

Using the Eqs. 4.30 and 4.32, Eq. 4.33 results in

$$K_D = mK_E \left([\bar{S}]_{in} - K_D n \frac{C_{HP}}{m} \right)^n \frac{C_{HP}{}^{n-1}}{(1 + K_a/[H^+])^m} \tag{4.33}$$

and above equation, in logarithmic form is presented by Eq. (4.34)

$$\log K_D + m\log(1 + K_a/[H^+]) = \log m + \log K_E + n\log\left([\bar{S}]_{in} - K_D n\frac{C_{HP}}{m}\right) + (m-1)\log C_{HP} \tag{4.34}$$

Case – 3: Chemodel for Simultaneous Formation of Various Complexes

The model is based on the loading ratio for formation of various types of complexes (1:1, 2:1 and 3:1) between acid and amine, as an extractant. The extent to which the organic phase (extractant and diluents) may be loaded with acid is expressed by the loading ratio, Z (ratio of total acid concentration in the organic phase to the total extractant concentration) as given by Eq. (4.35)

$$Z = \frac{\bar{C}_{HA}}{[\bar{S}]_{in}} \tag{4.35}$$

The value of Z depends on the extractability of the acid (strength of the acid-base interaction) and its aqueous concentration. The stoichiometry of the overall extraction equilibrium depends on the loading ratio in organic phase (Z). If the organic phase is not highly concentrated by acid, i.e., at very low loading ratios ($Z < 0.5$), 1:1 complex of acid and extractant is formed. A plot of $Z/(1\text{-}Z)$ versus $[HA]$ yields a straight line passing through origin with a slope of complexation constant (K_{11}) as given by Eq. (4.36):

$$\frac{Z}{1-Z} = K_{11}[HA] \tag{4.36}$$

For higher loading ratios (at least, $Z > 0.5$), the acid:extractant (2:1), complexes are formed, and a plot of $Z/(2–Z)$ versus $[HA]^2$ is a straight line whose slope gives the complexation constant, K_{21}, for the (2:1) complex as shown by Eq. (4.37).

$$\frac{Z}{2-Z} = K_{21}[HA]^2 \tag{4.37}$$

If the carboxylic acid concentration is high enough, the (3:1) complex may be formed and a plot of $Z/(3-Z)$ versus $[HA]^3$ should yield a straight line, whose slope gives the complexation constant for the (3:1) complex. K_{31} is obtained from Eq. (4.38).

$$\frac{Z}{3-Z} = K_{31}[HA]^3 \tag{4.38}$$

The different model based on the assumption of simultaneously formation of various types of complexes (m, n) between acid and amine (extractant) is presented. In this study, the formation of three types of complexes, i.e., (1, 2) (1, 1) and (2, 1), are considered. The stoichiometric equations describing the extraction are given by Eqs. (4.39 – 4.41):

$$HA + \overline{R_3N} \Leftrightarrow \overline{HAR_3N} \tag{4.39}$$

$$HA + 2\overline{R_3N} \Leftrightarrow \overline{HA(R_3N)_2} \tag{4.40}$$

$$HA + \overline{HAR_3N} \Leftrightarrow \overline{(HA)_2 R_3N} \tag{4.41}$$

where, HA and R_3N represent the carboxylic acid and the tri-n-alkyl amine respectively. The corresponding extraction constants are calculated using Eqs. (4.42 – 4.44):

$$K_{11} = \frac{\left[\overline{HAR_3N}\right]}{[HA]\left[\overline{R_3N}\right]} \approx \frac{\overline{C}_{11}}{[HA]C_{R_3N}} \tag{4.42}$$

$$K_{12} = \frac{\left[\overline{HA(R_3N)_2}\right]}{[HA]\left[\overline{R_3N}\right]^2} \approx \frac{\overline{C}_{12}}{[HA]C_{R_3N}^2} \tag{4.43}$$

$$K_{21} = \frac{\left[\overline{(HA)_2 R_3N}\right]}{[HA]\left[\overline{HAR_3N}\right]} \approx \frac{\overline{C}_{21}}{[HA]C_{11}} \tag{4.44}$$

$\overline{C}_{11}$, $\overline{C}_{12}$, and $\overline{C}_{21}$ are the concentrations of the complexes of (1,1) (1,2) and (2,1) respectively. The acid concentration and free amine concentration in the organic phase are given by Eq. 4.45 and Eq. (4.46) respectively.

$$\overline{C}_{HA} = \overline{C}_{11} + \overline{C}_{12} + 2\overline{C}_{21} = K_{11}[HA]C_{R_3N} + K_{12}[HA]C_{R_3N}^2 + 2K_{21}[HA]\overline{C}_{11} \qquad (4.45)$$

$$C_{R_3N} = C_{R_3N_{in}} - (\overline{C}_{11} + 2\overline{C}_{12} + \overline{C}_{21}) = C_{R_3N_{in}} - (K_{11}[HA]C_{R_3N} + 2K_{12}[HA]C_{R_3N}^2 + K_{21}[HA]\overline{C}_{11}) \qquad (4.46)$$

From experimental results based on the total acid concentration in equilibrium in the aqueous phase, and by applying the mass action law, the values of the equilibrium constants K_{11}, K_{12} and K_{21} and the concentration of complex $\overline{C}_{11}$, $\overline{C}_{12}$, and $\overline{C}_{21}$ can be calculated.

4.1.1.3 Modified Langmuir Equilibrium Model

The distribution of the undissociated acid between aqueous and organic phases, where the acid is bound to the amine molecules, is described by the overall stoichiometry of reactions of complex formation as given by Eq. (4.47)

$$aHA + \overline{R_3N} \Leftrightarrow \overline{R_3N(HA)_a} \quad , \qquad (4.47)$$

The extraction equilibrium constant, K_E, can be calculated using Eq. (4.48):

$$K_E = \frac{[\overline{R_3N(HA)_a}]}{[HA]^a[\overline{R_3N}]} \qquad (4.48)$$

In contrast to Eq. (4.12), representing the formation reaction of an individual complex, Eq. (4.47) is conceived as an overall reaction, representing several parallel reactions. Therefore, the stoichiometric coefficients *m*, *n* are now defined as rational numbers and *a* = *m*/*n*.

Poposka *et al.,* (2000) and Senol (2004) described the shape of isotherms $[\overline{C}_{HA} = f(C_{HA})]$ using modified Langmuir equilibrium model (Eq. 4.49) assuming an overall acid:amine complexation with an associated number (*z*) related to the maximum loading of amine ($z = Z_{\max}$), where the undissociated acid molecules are regarded as adsorbate.

$$\frac{\overline{C}_{HA}}{(\overline{C}_{HA})_{\max}} = \frac{Z}{Z_{\max}} = \frac{K_E (C_{HA})^a}{1 + K_E (C_{HA})^a} \tag{4.49}$$

It can be found that for a maximum loading of the extractant, $z = Z_{\max} = m/n = a$.

4.1.2 Linear Solvation Energy Relation (LSER)

According to Kamlet *et al.,* (1983), the linear solvation energy relationship (LSER) that measures property XYZ, in terms of solvent properties (solvatochromic parameters), is represented by Eq. (4.50)

$$XYZ = XYZ^0 + \frac{P(\delta_h)^2}{100} + s(\pi^* + d\delta) + b\beta + a\alpha + e\xi \tag{4.50}$$

where δ_h is the Hildebrand's solubility parameter, a measure of the solvent/solvent interactions that are interrupted in creating a cavity for the solute. π^* is the solvatochromic parameter that measure the solute + solvent interactions, and δ is the solvatochromic parameter that measure dipole + dipole, and dipole + induced dipole interactions. The π^* scale is an index of solvent dipolarity/polarizability, which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. δ parameter is a polarizability correction term equal to 0.0 for nonchlorinated aliphatic solvents, 0.5 for polychlorinated aliphatics, and 1.0 for aromatic solvents. Solvatochromic parameter *β,* representing scale of solvent HBD (hydrogen-bond donor) acidities, describes the ability of solvent to donate a proton in a solvent-to-solute hydrogen bond. The α scale of HBA (hydrogen-bond acceptor) basicities provides a measure of the solvent's ability to accept a proton (donate an electron pair) in a solute-to-solvent hydrogen bond. The ξ parameter, a measure of coordinate covalency, equals to -0.20 for P=O bases, 0.0 for C=O, S=O, and N=O bases, 0.20 for single-bonded oxygen bases, 0.60 for pyridine bases, and 1.00 for sp^3-hybridized amine bases. This parameter (ξ) is very useful in correlating certain types of basicity properties. The coefficients *p*, *s*, *e, d*, *a*, and *b* represent the properties of solute, and are also the regression coefficients. Equation 4.51 is adopted to describe the effect of diluents on the values of distribution coefficients (K_D):

$$\ln K_D = \ln K_D{}^0 + \frac{P(\delta_h)^2}{100} + s(\pi^* + d\delta) + b\beta + a\alpha + e\xi \tag{4.51}$$

where the parameters π^*, δ, β and α refer to the diluents, and $K_D{}^0$ represents the distribution coefficient for an ideal inert diluent. The second term of Eq. (4.51), which contains the solubility parameter δ_h, does not affect the values of the objective function ($\ln K_D$) significantly and the value of ξ is 0 values for the diluents used in this study. Thus, Eq. (4.51), results in Eq. (4.52)

$$\ln K_D = \ln K_D{}^0 + s(\pi^* + d\delta) + b\beta + a\alpha \tag{4.52}$$

In case, a mixture of diluents is used with the extractant, the solvatochromic parameters of the solvent mixtures are calculated using Eq. (4.53) (Bizek *et al.,* 1993).

$$SP_{12} = X_1 SP_1 + (1 - X_1) SP_2 \tag{4.53}$$

where, X_1 is the mole fraction of the first solvent and $X_2 = 1 - X_1$, is the mole fraction of the second solvent. SP_1 is the solvatochromic parameter of the first solvent and SP_2 is the solvatochromic parameter of the second solvent in solvent mixtures.

4.1.3 Two Parameters (μ and E_T) Model

Different approaches have been used to quantify the effect of diluents on 1:1 complexation. Both partition and self-association constants strongly depend on the nature of the diluents. The thermodynamic activity of the species taking part in the organic phase equilibrium changes with the diluent type. Attempts have been made to correlate the extraction efficiency in terms of K_E values with solvent properties such as molecular mass, boiling point, density, refractive index, dielectric constant, dipole moment, and E_T parameter (Dimroth *et al.,* 1963). E_T is an empirical parameter that gives an assessment of solvation energy of the solute and is based on the absorption spectrum of pyridinium-N-phenolbetaine. It provides anion solvation by ion-dipole and ioninduced dipole forces. In the carboxylic acid extraction with extractant, K_E values can be correlated well with the solvent dipole moment μ and the E_T parameter using the following relationship (Eq. 4.54).

$$K_E = a_1 \mu^{a_2} E_T^{\ a_3} \tag{4.54}$$

However, for similar type diluents such as inerts (hexane and heptane) or aromatics (benzene and toluene), the dependence on molar mass, boiling point, and specific gravity can also be made. An increase in molar mass, boiling point, and specific gravity hinders the dissolution of the acid-extractant complex and hence lowers the equilibrium extraction coefficient. Hence, the correlation of K_E (Eq. 4.54) in terms of the solvent dipole moment (μ) and the absorption spectrum parameter (E_T) is very useful to quantify the effect of diluents on the extraction of carboxylic acid.

4.2 Kinetic Model

On the basis of the kinetic and equilibrium data obtained from a vigorously agitated system (as discussed in Section 3.3.5) allows the elimination of transport effects on the overall process. A formal elementary kinetic model is used for the evaluation of the chemical kinetic parameters.

4.2.1 An Elementary Kinetic Model

Chemical reaction between acid molecules and amine molecules is represented by Eq. (4.55)

$$mHA + \overline{R_3N} = \overline{(R_3N)(HA)_m} \qquad (4.55)$$

By analogy with the true elementary reaction, the rate equation may be written as:

$$-r_A = -\frac{dC_{HA}}{dt} = k_1 C_{HA}^{\alpha'} C_S^{\beta'} - k_2 C_C^{\gamma'} \qquad (4.56)$$

where, the individual orders α', β' and γ' are to be determined from the experimental kinetic data. The concentrations of all the components in the rate expression (4.56) can be derived from Eq. (4.55) taking the acid concentration in the aqueous phase as a basis for calculations.

4.3 Numerical Solution and Simulation

The mathematical equilibrium (physical and chemical) model [Eqs. (4.1-4.41)] is simulated to predict the stoichiometry of reaction and equilibrium constants. The mathematical model described by Eqs. (4.42-4.46) is solved to derive the effect of diluents on the extraction of acid. Kinetics of reactive extraction is estimated using the simulation of Eqs. (4.56). The models, described in Sections (4.1 & 4.2), are simulated as discussed in this Section.

The physical equilibrium model (Eqs. 4.1 – 4.11) is solved graphically by plotting distribution coefficient (K_D) on y-axis and undissociated acid concentration ($[HA]$) on x-axis to calculate the partition coefficients and dimerization constants for different carboxylic acids (formic acid, acetic acid, propionic acid, butyric acid and nicotinic acid) using different diluents.

The chemical equilibrium model (Section 4.1.1.2) is solved to estimate the stoichiometry (m and n) of reactive extraction reaction between acid and extractant and equilibrium constants (K_E) by minimizing the square of the error between experimental and model predicted data. Minimization of the square of the error is accomplished by two approaches: (1) using graphical method (best fit line), and (2) developing code in MATLAB (v 7.0.1) and in C language. In the graphical method, a plot of equation (4.27) by taking, $\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right)$ on y-axis and log $[\overline{S}]_{in}$ on x-axis assuming $[\overline{S}]_{in} >> n[\overline{HA(S)_n}]$ is employed to estimate n and K_E. The same model equation is also plotted with an assumption of 1:1 complex between acid and extractant. The model equations (4.36-4.38) are employed to estimate the equilibrium constants for (1:1), (2:1) and (3:1) complexes of acid and extractant by plotting $Z/(1\text{-}Z)$ versus $[HA]$, $Z/(2\text{-}Z)$ versus $[HA]^2$ and $Z/(3\text{-}Z)$ versus $[HA]^3$ respectively.

The objective functions [Eqs. (4.24 & 27) and Eqs. (4.33 & 34)] are highly nonlinear and complex in nature, may have local optima (non-concave). Most of the traditional optimization algorithms based on gradient methods have the possibility of getting trapped at local optimum depending upon the degree of non-linearity and initial guess (Babu, 2004). In the recent past, nontraditional search and optimization techniques (evolutionary computation) based on natural phenomenon such as genetic algorithms (GAs), differential evolution (DE), etc. (Price and Storn, 1997; Babu and Sastry, 1999; Ownubolu and Babu, 2004) have been developed to overcome these problems. So, a population based search algorithm called differential evolution (DE), which is simple and robust and has a proven successful record [Babu and Sastry, 1999; Ownubolu and Babu, 2004; Angira and Babu, 2006; Babu and Munavar, 2007] is also employed in the present study. Differential evolution approach is used to solve the model equations (4.24, 4.27, 4.33 and 4.34) for estimation of extraction equilibrium constants (K_E), the number of reacting extractant molecules (n) and the number of reacting acid molecules (m). An objective function based on least square error between experimental and predicted value of K_D and $\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right)$ for Eqs. (4.24 & 4.27) respectively, and K_D and $\log K_D$ for Eqs. (4.33 & 4.34) repectively, have been minimized. The key parameters of control in DE are: NP- the population size, CR-the cross over constant, and F the weight applied to random differential (scaling factor). These parameters are problem dependent. However, certain guidelines and heuristics are available for the choice of these parameters (Babu, 2004; Price and Storn, 1997). Based on these heuristics, the values of DE key parameters for the present problem are set as NP = 20, 30; CR = 0.9; F = 0.5.

Nonlinear modified Langmuir isotherms [Eq. (4.49)] are fitted using a professional graphics software package ORIGIN (version 6.0) to estimate the equilibrium constants (K_E) and number of reacting acid molecules (a) in acid:extractant complexes.

Equilibrium model equations (4.52 and 4.54) are solved using the linear regression method to find the model parameters for the estimation of diluent effect on the recovery of acid from aqueous solution.

Computer programme on MATLAB 7.0.1 is used for experimental kinetic data fitting. In this simulation, the best pair of rate constants for a given particular set of individual orders - α', β' and γ' in the rate expression (4.56) is determined.

CHAPTER – 5

RESULTS AND DISCUSSION

This chapter presents the experimental (equilibrium and kinetic) and simulation results obtained for the intensification of recovery of carboxylic acids using reactive extraction. The extraction of acids is carried out using (1) pure diluents, (2) phosphorus based extractants such as tri-*n*-butylphosphate (TBP) and tri-*n*-octylphosphine oxide (TOPO), and (3) amine based extractants such as tri-*n*-octylamine (TOA), tri-*n*-dodecylamine (TDA) and tri-*n*-octylmethylammonium chloride (Aliquat 336). The extraction efficiency in terms of distribution coefficient (K_D), degrees of extraction and loading ratio is calculated using experimental data. Based on the mathematical models as described in chapter 4, (1) partition coefficient (P) and dimerization constant (D) for extraction of acids using pure diluents, and (2) equilibrium constant (K_E), stoichiometry of reaction and kinetic parameters for extraction of acids using different extractants are determined. The effects of type of carboxylic acid, diluent and temperature on extraction efficiency are also studied. The results of this study on physical extraction using pure diluents, reactive extraction (equilibrium) using phosphorus-based extractants and reactive extraction (equilibrium & kinetics) using amine-based extractants are discussed in Sections 5.1 – 5.3 respectively.

5.1 Physical Extraction with Pure Diluents

The extraction of carboxylic acids into inert (non-interacting) hydrocarbons, substituted hydrocarbons and oxygen bearing organic diluents is studied. The distribution of the acid between water and the hydrocarbon is relatively free of complexities. The acids extracted by carbon-bonded oxygen donor solvents are strongly hydrated by varying number of water molecules. The exact solvation number of the acid molecules in the organic phase usually can not be determined. A large number of solvent molecules are needed for an efficient competition with the water molecules that hydrate the acid at the interface (Kertes and King, 1986). The extraction of acid with pure diluents (without extractant) is regarded as physical extraction. Physical equilibrium results of experimental and modeling & simulation studies are described in Sections 5.1.1 and 5.1.2.

5.1.1 Experimental Study

The equilibrium isotherms for the extraction of carboxylic acids (formic acid, acetic acid, propionic acid, butyric acid and nicotinic acid) using different inert diluents (*n*-heptane, *n*-decane, benzene and kerosene) and active diluents (diethyl ether, chloroform, MIBK, 1-octanol and 1-decanol) are presented in Figures 5.1 – 5.5. For a low range of acid concentration, there is a linear relationship between acid concentration in the aqueous and organic phase, and nonlinearity exist for the higher acid concentrations. It may be noted that for the low concentrations of acid, the Henry's law type isotherm is valid. For higher concentrations, non-ideal behavior can prevail causing a deviation from Henry's law. Due to the low concentration range of nicotinic, acetic, propionic and butyric acids used in physical extraction, almost a linear relationship is found between the concentrations of acids in aqueous and organic phase (Figure 5.2 – 5.5). In the following sections (5.1.1.1 – 5.1.1.3), the parametric studies carried out to determine their influence on extraction efficiency are discussed.

5.1.1.1 Effect of Type of Carboxylic Acid

The important factors associated with the characteristics of acids which affect their extractability are the number of carboxylic groups, their acid strength (pK_a), the nature and number of additional functional groups (keto, hydroxo, pyridine, etc.) on the molecules, and the size & hydration of the anion. The nature of the extracted acid [hydrophobicity (log P^a = distribution coefficient with 1-octanol as the extractant in log form) and acidity] is one of the most important factors affecting the degree of extraction. The extraction is expected to increase with an increase in acidity and hydrophobicity of the acid. To examine the quantitative and independent contribution of the hydrophobicity and acidity of acid on the extraction equilibrium, the physical extraction of formic acid (pK_a = 3.75, log P^a = -0.538), acetic acid (pK_a = 4.74, log P^a = -0.313), propionic acid (pK_a = 4.87, log P^a = 0.290), butyric acid (pK_a = 4.81, log P^a = 0.802) and nicotinic acid (pK_a = 4.75, log P^a = unavailable) using several inert and active diluents is performed.

The results of physical extraction are presented in Tables 5.1 – 5.5. The extraction efficiency as given by distribution coefficient (K_D) and degree of extraction (E) using different diluents is found to increase by increasing both the pK_a values (3.75 to 4.87) and hydrophobicity (-0.538 to 0.802) for the extraction of formic-, acetic- and propionic acid. In the extraction of propionic and butyric acid (having almost similar acid strength), the extraction efficiency depends strongly on hydrophobicity of acids and found to increase with an increased hydrophobicity. The hydrophilicity of the acid radical is increased by the presence of hydroxo-, keto-, or nitro- functional groups due to which considerable difference in the values of K_D are obtained. The extractability of nicotinic acid using MIBK (K_D = 0.18) is found to be low as compared to that of other acids (K_D = 0.46 for acetic acid, K_D = 1.96 for propionic acid and K_D = 5.92 for butyric acid) having almost similar acid strength. Even, mono-carboxylic acids are more extractable than di- or polybasic acids with an equal number of carbon atoms due to an increased affinity for the aqueous solution of acids with two or more functional groups (Kertes and King, 1986).

5.1.1.2 Effect of Diluent

The physical solubility of formic-, acetic-, propionic- and nicotinic acids in pure diluents alone is remarkably small. The extraction of acids from aqueous solution using pure diluents is found to be very low: (1) a maximum K_D of 0.54 for 1-decanol, 0.63 for MIBK, and ranging from 0.01 to 0.22 for other inert diluents such as *n*-decane, chloroform and benzene (Table 5.1) in case of formic acid, (2) a maximum K_D of 0.42 for 1-decanol, 0.47 for MIBK, and ranging from 0.006 to 0.07 for other inert diluents such as *n*-decane, chloroform and benzene (Table 5.2) in case of acetic acid, (3) a maximum K_D of 1.60 for 1-decanol, 1.97 for methyl isobutyl ketone (MIBK), and ranging from 0.02 to 0.34 for other inert diluents such as *n*-decane, chloroform and benzene (Table 5.3) in case of propionic acid and (4) a maximum K_D of 0.34 for 1-octanol, 0.18 for MIBK, and ranging from 0.01 to 0.06 for other inert diluents such as diethyl ether, *n*-heptane, kerosene and benzene (Table 5.5) for nicotinic acid. Due to high hydrobhobicity, butyric acid shows reasonable physical extraction with a maximum K_D of 5.5 for 1-decanol, 6.5 for MIBK, 3.4 for chloroform, 2.1 for benzene and 0.5 for *n*-decane (Table 5.4). The aliphatic and aromatic solvents, including substituted hydrocarbon (n-heptane, *n*-decane, benzene, kerosene, and chloroform) are characterized by a low degree of acid extractability. On the other hand, acids extracted by carbon-bonded oxygen donor solvents (MIBK, 1-octanol and 1-decanol) are strongly hydrated by varying the number of water molecules. Ketone, diethyl ether and protic 1-octanol, 1-decanol containing an oxygenated functional group yield higher and different K_D values depending upon the solvent polarity and the hydrogen bonding ability.

5.1.1.3 Effect of Initial Acid Concentration

The initial concentration of organic acid affects the extraction efficiency as shown in Tables 5.1–5.5. The extraction efficiency (in terms of K_{D} and E) is found to increase almost 60 times for *n*-decane, 19 times for benzene and 7 times for chloroform, with an increase in the concentration of formic acid from 0.26 to 1.32 $\mathrm{mol.L^{-1}}$. Similarly trend has been found for other acids (acetic-, propionic-, butyric-, and nicotinic acid). The values of K_{D} and E remain almost independent of acid concentration (formic acid is an exception) when 1-decanol, 1-octanol and MIBK are used as solvents. Due to the higher initial concentration of formic acid, K_{D} increased 2.5 times for 1-decanol and 2 times for MIBK, with an increase in the concentration of acid from 0.26 to 1.32 $\mathrm{mol.L^{-1}}$. In inert solvents, the solvation sheath around the functional group(s) in high acid concentration may consist of a mixture of water and solvent molecules, due to which the possibility for the solvation of solute species with organic solvent increases.

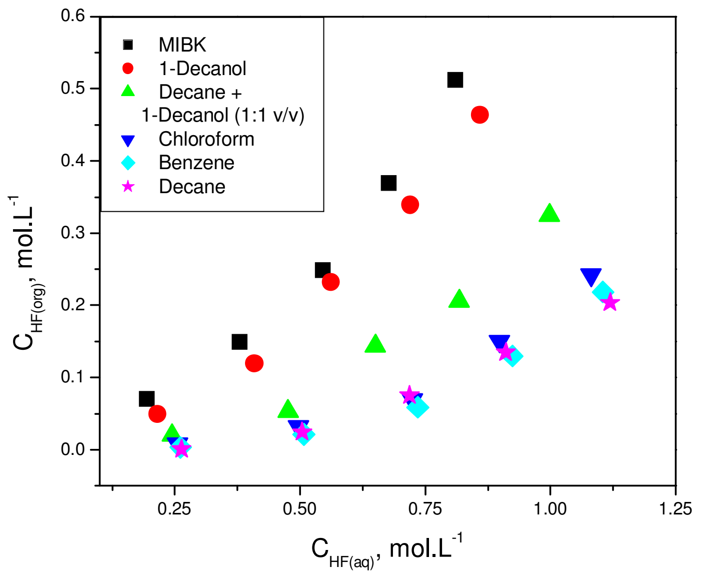

Figure 5.1. Extraction equilibrium isotherms of formic acid (HF) with different diluents

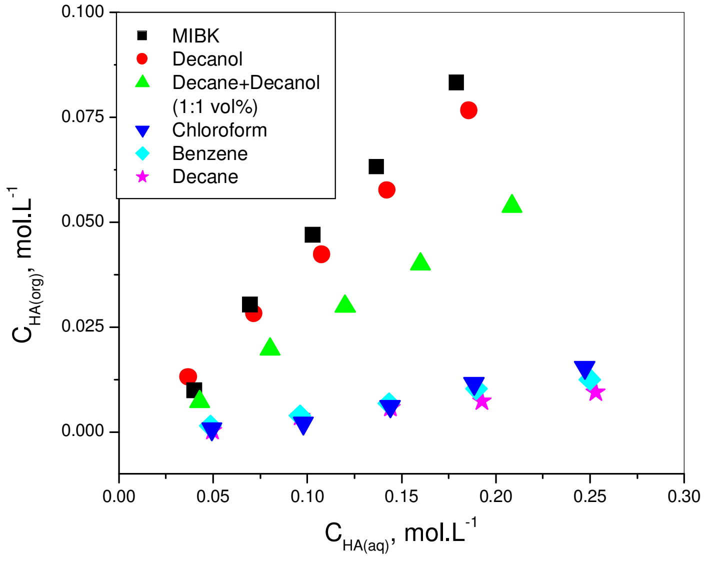

Figure 5.2. Extraction equilibrium isotherms of acetic acid (HA) with different diluents

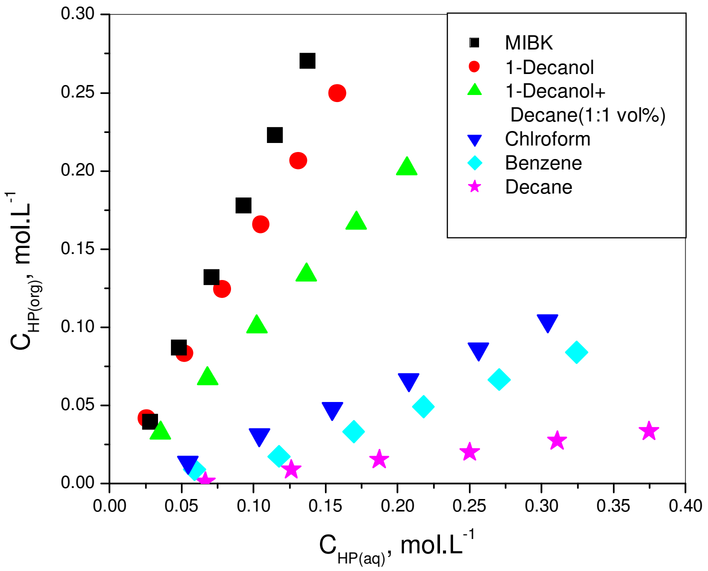

Figure 5.3. Extraction equilibrium isotherms of propionic acid (HP) with different diluents

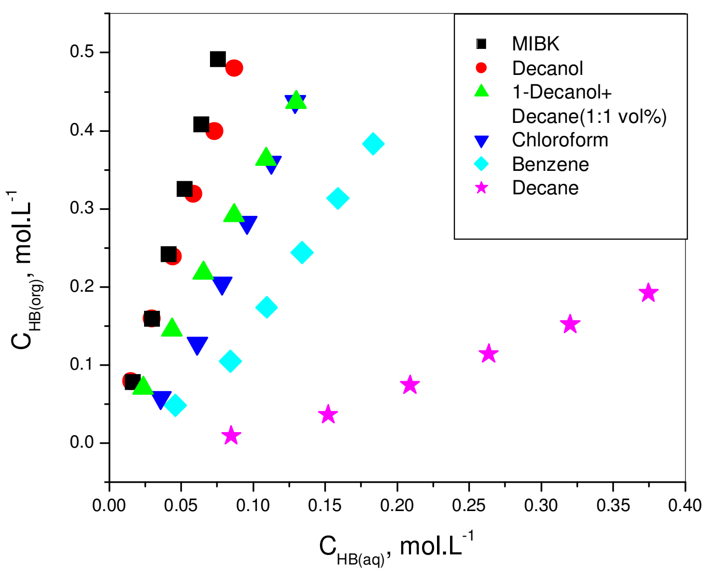

Figure 5.4. Extraction equilibrium isotherms of butyric acid (HB) with different diluents

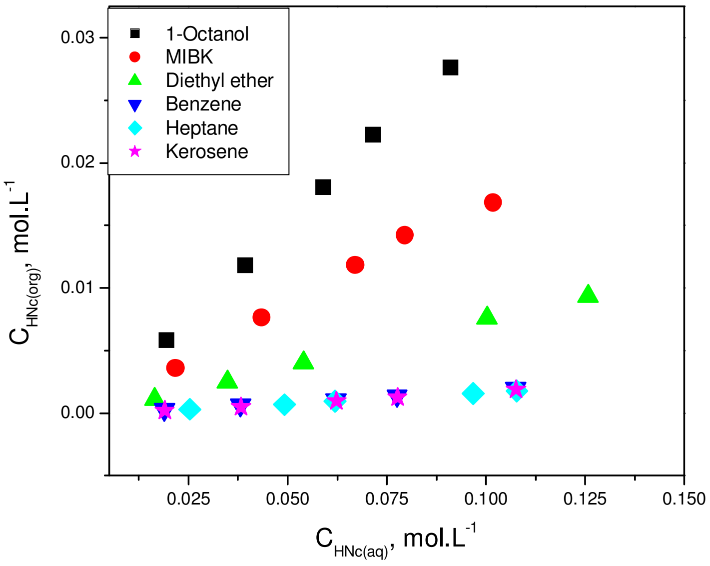

Figure 5.5. Extraction equilibrium isotherms of nicotinic acid (HNc) with different diluents

Table 5.1. Physical equilibria of formic acid extraction using different diluents

Diluent	C_{in} mol.L^{-1}	C_{HF} mol.L^{-1}	$\overline{C}_{HF}$ mol.L^{-1}	K_D	E
1-Decanol	0.26	0.2155	0.0491	0.23	18.56
	0.53	0.4096	0.1196	0.29	22.6
	0.79	0.5620	0.2318	0.41	30.11
	1.06	0.7200	0.3390	0.47	32.35
	1.32	0.8592	0.4638	0.54	36.53
n-Decane	0.26	0.2638	0.0008	0.003	3.21
	0.53	0.5046	0.0246	0.05	4.65
	0.79	0.7186	0.0752	0.10	10.43
	1.05	0.9110	0.1350	0.15	12.86
	1.32	1.1192	0.2038	0.19	15.4
Benzene	0.26	0.2615	0.0031	0.01	4.02
	0.53	0.5079	0.0213	0.04	6.06
	0.79	0.7349	0.0589	0.08	10.62
	1.05	0.9238	0.1300	0.14	12.93
	1.32	1.10453	0.21847	0.20	16.51
Chloroform	0.26	0.25614	0.00846	0.03	4.02
	0.53	0.49715	0.03206	0.06	4.83
	0.79	0.7241	0.0697	0.10	11.62
	1.05	0.8982	0.1505	0.17	13.79
	1.32	1.0807	0.2423	0.22	17.49
MIBK	0.26	0.1947	0.0699	0.36	26.41
	0.53	0.3803	0.1489	0.39	27.61
	0.79	0.5458	0.2480	0.45	33.5
	1.05	0.6773	0.3687	0.54	35.48
	1.32	0.8109	0.5121	0.63	38.7
n-Decane + 1-Decanol (1:1 v/v)	0.26	0.245	0.02	0.08	7.54
	0.53	0.476284	0.052917	0.11	10
	0.79	0.65	0.1438	0.22	18.12
	1.05	0.82	0.21	0.26	20.39
	1.32	0.9984	0.3246	0.33	24.53

Table 5.2. Physical equilibria of acetic acid extraction using different diluents

Diluent	C_{in} **mol.L^{-1}**	C_{HA} **mol.L^{-1}**	$\overline{C}_{\mathrm{HA}}$ **mol.L^{-1}**	K_D	P
1-Decanol	0.05	0.0370	0.0130	0.352	26.05
	0.10	0.0718	0.0282	0.392	28.17
	0.15	0.1077	0.0423	0.392	28.17
	0.20	0.1424	0.0576	0.404	28.79
	0.2625	0.1859	0.0766	0.412	29.17
n-Decane	0.05	0.0497	0.0003	0.006	0.62
	0.10	0.0979	0.0021	0.022	2.14
	0.15	0.1460	0.0040	0.027	2.65
	0.20	0.1942	0.0058	0.03	2.91
	0.2625	0.2530	0.0095	0.037	3.6
Benzene	0.05	0.0486	0.0014	0.029	2.81
	0.1	0.0961	0.0039	0.04	3.87
	0.15	0.1432	0.0068	0.047	4.5
	0.2	0.1897	0.0103	0.054	5.15
	0.2625	0.2482	0.0143	0.057	5.43
Chloroform	0.05	0.0493	0.0007	0.014	1.41
	0.1	0.0979	0.0021	0.022	2.11
	0.15	0.1439	0.0061	0.042	4.06
	0.2	0.1906	0.0094	0.049	4.7
	0.2625	0.2472	0.0153	0.062	5.83
MIBK	0.05	0.0401	0.0099	0.246	19.72
	0.1	0.0697	0.0303	0.434	30.28
	0.15	0.1030	0.0470	0.456	31.32
	0.2	0.1369	0.0632	0.462	31.59
	0.2625	0.1792	0.0833	0.465	31.72
n-Decane + 1-Decanol (1:1 v/v)	0.05	0.0428	0.0072	0.168	14.38
	0.1	0.0803	0.0197	0.246	19.73
	0.15	0.1201	0.0299	0.249	19.93
	0.2	0.1596	0.0404	0.253	20.2
	0.2625	0.2088	0.0538	0.258	20.49

Table 5.3. Physical equilibria of propionic acid extraction using different diluents

Diluent	C_{in} **mol.L^{-1}**	C_{HP} **mol.L^{-1}**	$\overline{C}_{HP}$ **mol.L^{-1}**	K_D	E
1-Decanol	0.068	0.0260	0.0416	1.601	61.55
	0.135	0.0520	0.0830	1.597	61.49
	0.203	0.0781	0.1244	1.592	61.41
	0.270	0.1052	0.1656	1.575	61.33
	0.338	0.1311	0.2064	1.575	61.07
	0.408	0.1583	0.2498	1.578	61.21
n-Decane	0.068	0.0665	0.0011	0.016	1.61
	0.135	0.1261	0.0089	0.07	6.56
	0.203	0.1872	0.0153	0.082	7.55
	0.270	0.2501	0.0199	0.08	7.39
	0.338	0.3107	0.0273	0.088	8.07
	0.408	0.3749	0.03	0.089	8.19
Benzene	0.068	0.0589	0.0087	0.148	3.23
	0.135	0.1177	0.0173	0.147	12.79
	0.203	0.1695	0.0330	0.195	16.31
	0.27	0.2179	0.0492	0.226	18.21
	0.338	0.2705	0.0664	0.246	19.65
	0.408	0.3241	0.0839	0.259	20.55
Chloroform	0.068	0.0543	0.0133	0.245	19.7
	0.135	0.1040	0.0310	0.298	22.98
	0.203	0.1547	0.0478	0.309	23.61
	0.27	0.2077	0.0661	0.318	24.47
	0.338	0.2562	0.0861	0.336	25.47
	0.408	0.3043	0.1037	0.341	25.42
MIBK	0.068	0.0283	0.0393	1.39	58.16
	0.135	0.0482	0.0868	1.803	64.32
	0.203	0.0709	0.1316	1.856	64.99
	0.27	0.0932	0.1778	1.908	65.85
	0.338	0.1151	0.2228	1.936	65.91
	0.408	0.1376	0.2704	1.965	66.27
n-Decane + 1-Decanol (1:1 v/v)	0.068	0.0352	0.0324	0.92	47.98
	0.135	0.0680	0.0670	0.98	49.6
	0.203	0.1022	0.1004	0.98	49.55
	0.27	0.1367	0.1333	0.97	49.36
	0.338	0.1713	0.1667	0.97	49.31
	0.408	0.2064	0.2016	0.98	49.41

Table 5.4. Physical equilibria of butyric acid extraction using different diluents

Diluent	C_{in} **mol.L^{-1}**	C_{HB} **mol.L^{-1}**	$\overline{C}_{\mathrm{HB}}$ **mol.L^{-1}**	K_{D}	E
1-Decanol	0.0945	0.0153	0.0792	5.181	83.82
	0.189	0.0298	0.1592	5.339	84.22
	0.2835	0.0444	0.2391	5.387	84.34
	0.378	0.0585	0.3190	5.454	84.37
	0.4725	0.0734	0.3991	5.441	84.48
	0.567	0.0872	0.4798	5.506	84.63
n-Decane	0.0945	0.0849	0.0096	0.114	10.2
	0.189	0.1521	0.0369	0.242	19.51
	0.2835	0.2089	0.0746	0.357	26.3
	0.378	0.2635	0.1145	0.434	30.28
	0.4725	0.3202	0.1523	0.476	32.24
	0.567	0.3746	0.1924	0.514	33.93
Benzene	0.0945	0.0459	0.0486	1.06	51.46
	0.189	0.0841	0.1049	1.247	55.51
	0.2835	0.1094	0.1742	1.593	61.43
	0.378	0.1339	0.2441	1.823	64.57
	0.4725	0.1590	0.3135	1.972	66.36
	0.567	0.1835	0.3835	2.09	67.64
Chloroform	0.0945	0.0359	0.0586	1.63	61.98
	0.189	0.0612	0.1278	2.09	67.64
	0.2835	0.0783	0.2052	2.619	72.37
	0.378	0.0956	0.2824	2.954	74.71
	0.4725	0.1125	0.3600	3.2	76.19
	0.567	0.1292	0.4378	3.389	77.21
MIBK	0.0945	0.0169	0.0777	4.619	82.2
	0.189	0.0298	0.1592	5.339	84.22
	0.2835	0.0416	0.2419	5.816	85.33
	0.378	0.0527	0.3253	6.176	86.06
	0.4725	0.06431	0.4082	6.347	86.39
	0.567	0.0757	0.4913	6.492	86.65
n-Decane + 1-Decanol (1:1 v/v)	0.0945	0.0237	0.0708	2.987	74.92
	0.189	0.0436	0.1454	3.337	76.94
	0.2835	0.0654	0.2182	3.34	76.96
	0.378	0.0867	0.2913	3.36	77.06
	0.4725	0.1090	0.3635	3.337	76.94
	0.567	0.1300	0.4370	3.363	77.08

Table 5.5. Physical equilibria of nicotinic acid extraction using different diluents

Diluent	C_{in} **mol.L^{-1}**	C_{HNc} **mol.L^{-1}**	$\overline{C}_{HNc}$ **mol.L^{-1}**	K_D	E
1-Octanol	0.025	0.0196	0.0058	0.293	22.31
	0.051	0.0393	0.0118	0.297	22.69
	0.077	0.0590	0.018	0.300	23.08
	0.094	0.0717	0.0222	0.305	23.16
	0.120	0.0911	0.0276	0.308	23.17
MIBK	0.025	0.0218	0.0036	0.161	13.85
	0.051	0.0435	0.0076	0.171	14.62
	0.077	0.0671	0.0118	0.173	14.75
	0.094	0.0796	0.0142	0.176	14.95
	0.120	0.1018	0.0168	0.181	15
Diethyl ether	0.020	0.0011	0.0189	0.064	5.97
	0.041	0.0025	0.0382	0.069	6.47
	0.062	0.0040	0.0622	0.073	6.78
	0.085	0.0076	0.0776	0.075	6.96
	0.117	0.0094	0.1075	0.080	7.14
Benzene	0.0192	0.0189	0.0003	0.012	1.41
	0.039	0.0382	0.0006	0.014	1.57
	0.063	0.0622	0.0011	0.017	1.66
	0.079	0.0776	0.0014	0.019	1.73
	0.110	0.1075	0.0020	0.023	1.77
Heptane	0.026	0.0253	0.0003	0.012	1.14
	0.050	0.0492	0.0007	0.013	1.3
	0.063	0.0619	0.0010	0.015	1.5
	0.098	0.0968	0.0016	0.018	1.57
	0.110	0.1077	0.0018	0.019	1.6
Kerosene	0.0192	0.0190	0.0002	0.010	1.01
	0.039	0.0383	0.0005	0.012	1.21
	0.063	0.0623	0.0010	0.015	1.48
	0.079	0.0777	0.0013	0.017	1.56
	0.110	0.1076	0.0019	0.019	1.7

5.1.2 Modeling and Simulation Studies

In this section, the values of partition constant (*P*) and dimerization constant (*D*) are determined using experimental results as discussed in section 5.1.1.

5.1.2.1 Estimation of P and D

The numerical values of *P* and *D* are determined by plotting K_D versus $[\mathrm{HA}]_{\mathrm{aq}}$ using Eq. 4.11 (Figures 5.6– 5.10). The values of constants (*P* and *D*) as given in Tables 5.6 for each acid indicate that there is a close relationship between aqueous phase functions (concentration of acid, nature of acid, etc.) and the chemical nature of the solvent. Generally, Alcohols capable of being both acceptors and donors of proton, give the highest values of partition coefficient, followed by the basic solvents such as ethers and ketones (Kertes and King, 1986). In this study, MIBK shows the maximum partition coefficient values for acids as compared with 1-octanol and 1-decanol due to a higher carbon atoms associated with the alcoholic group. Alcohols having lower carbon atoms (higher distribution coefficients) are not used in the present study due to higher mutual solubilities with aqueous phase and more toxic towards microorganism employed for the production of organic acids. The extracted acid molecules dimerize to only a small extent, or not at all, with 1-decanol, 1-octanol and MIBK as the values of *D* is found to be low (Tables 5.6). This is due to a strong donor-acceptor interaction as well as a stronger solute-solvent hydrogen bonding than the solute-solute interaction that leads to the formation of the dimer. So systems (e.g. acetic acid and *n*-decane) with low *P* values (0.004) exhibit high *D* values (4546) and systems (eg. acetic acid and 1-decanol) with high *P* values (0.35) exhibit low *D* values (1.4). The negative values of *P* (due to experimental error) in the extraction of formic acid with inert diluents signify the presence of total acid (organic phase) in the form of dimmer only. The carboxylic acids (formic and acetic acids) with lower carbon atoms have more tendencies to form dimmers in the organic phase (high values of *D* with inert diluents). The results of physical extraction of carboxylic acids are in good agreement with the results obtained by Wasewar & Pangarkar (2006) for the extraction of propionic acid and Keshav *et al.,* (2009b) for the extraction of acrylic acid in different diluents.

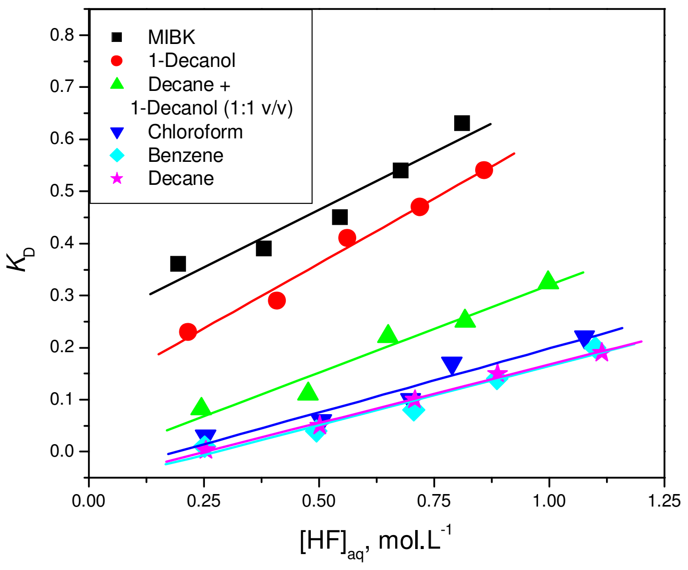

Figure 5.6. K_D versus $[HF]_{aq}$ for determination of *P* and *D* with various diluents in the extraction of formic acid

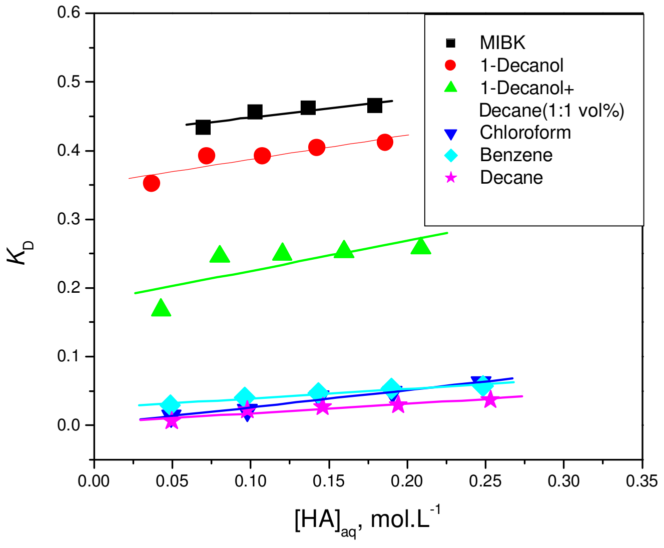

Figure 5.7. K_D versus $[HA]_{aq}$ for determination of *P* and *D* with various diluents in the extraction of acetic acid

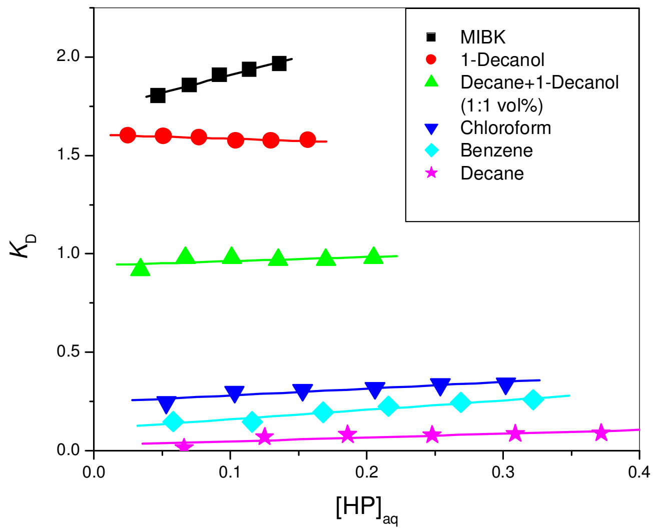

Figure 5.8. K_D versus $[HP]_{aq}$ for determination of P and D with various diluents in the extraction of propionic acid

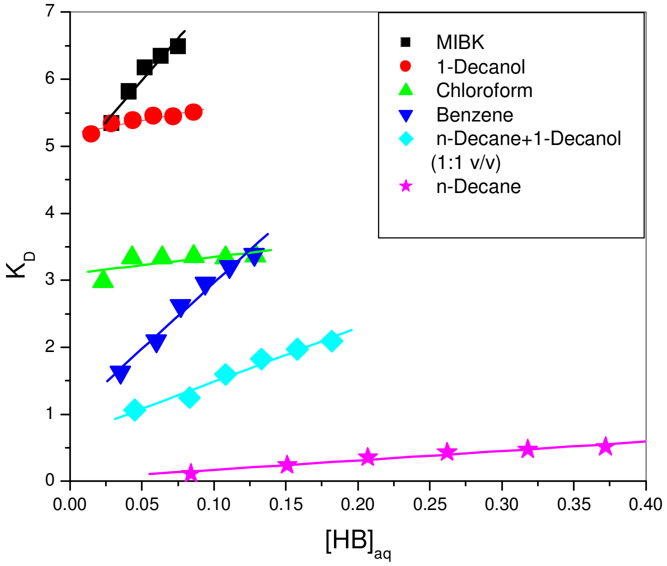

Figure 5.9. K_D versus $[HB]_{aq}$ for determination of P and D with various diluents in the extraction of butyric acid

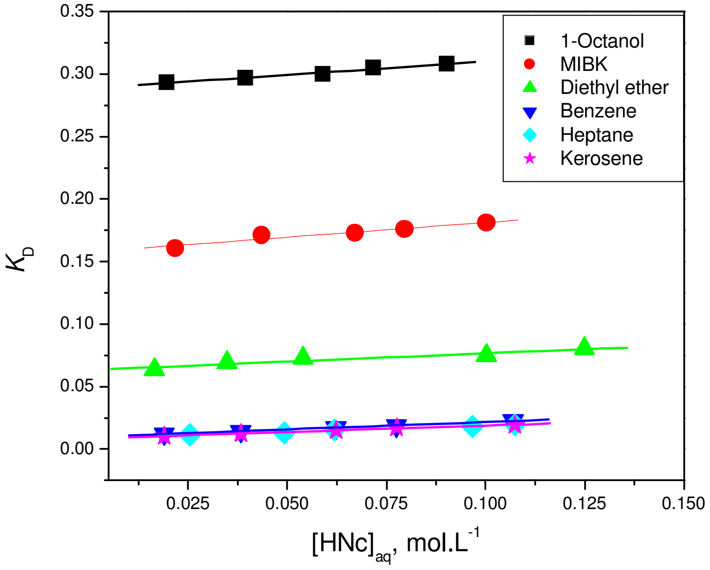

Figure 5.10. K_D **versus** $[HA]_{aq}$ **for determination of** P **and** D **with various diluents in the extraction of nicotinic acid**

Table 5.6. The values of *P* and *D* for extraction of carboxylic acids using pure diluents

Diluents	Formic acid		Acetic acid		Propionic acid		Butyric acid		Nicotinic acid	
	P	***D***	***P***	***D***	***P***	***D***	***P***	***D***	***P***	***D***
1-Decanol	0.112	19.8	0.35	1.40	1.61	0.01	5.18	0.07	-	-
n-Decane	-0.047	53.3	0.004	4546	0.03	117	0.03	738	-	-
Benzene	-0.065	26.6	0.025	112	0.11	19.41	0.68	8.77	0.010	621
Chloroform	-0.05	47	0.002	31250	0.25	2.84	0.99	10.06	-	-
MIBK	0.24	3.7	0.42	0.75	1.46	1.01	4.74	0.55	0.16	4.75
n-Decane + 1-Decanol (1:1 v/v)	-0.016	644	0.18	6.71	0.94	10.22	3.1	0.13	-	-
1-Octanol	-	-	-	-	-	-	-	-	0.29	1.30
Diethyl ether	-	-	-	-	-	-	-	-	0.063	16.41
Heptane	-	-	-	-	-	-	-	-	0.009	610
Kerosene	-	-	-	-	-	-	-	-	0.008	736

5.2 Reactive Extraction using Phosphorus-based Extractants

Organophosphorus compounds, such as TBP and TOPO, are effective extractants for the separation of carboxylic acids from dilute aqueous solution (Kertes and King, 1986). TBP and TOPO (Figure 5.11) have a phosphoryl group (>P=O) which provides a stronger Lewis basicity than those of carbon-bonded oxygen-containing extractants. This leads to a high degree of extraction. The chemical stability of organophosphorous compounds also plays an important role in its use as an efficient extractant with good separation efficiency. When organophosphorus extractants are used, the solvation has a higher specificity. These can only co-extract small amounts of water, and show low solubilities in water. Due to the presence of both electron donor and acceptor groups in =P(O)OH, it undergoes specific interactions like self-association and molecular complex formation with diluents or other solutes. The experimental and simulation results of reactive extraction using these extractants are presented in the sections 5.2.1 and 5.2.2 respectively.

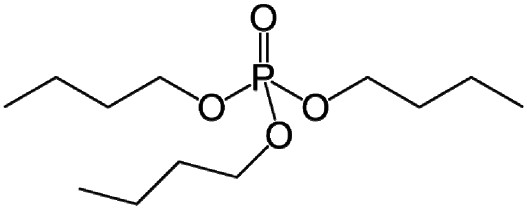

Figure 5.11 (a) Structure of tri-n-butyl phosphate (TBP)

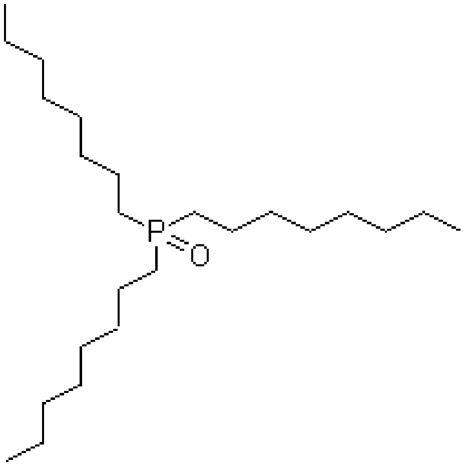

Figure 5.11 (b) Structure of tri-n-octylphosphine oxide (TOPO)

5.2.1 Experimental Studies

In this section, equilibrium experimental results for the reactive extraction of propionic acid and nicotinic acid are presented (Sections 5.2.1.1 and 5.2.1.2).

5.2.1.1 Reactive Extraction of Propionic Acid using TBP

TBP as an extractant is selected because of its low water co-extraction (4.67 % by weight at 20 ^{0}C) and very low solubility in the aqueous phase (0.04 % by weight at 20 ^{0}C). Since TBP has a relatively high viscosity (3.56 x 10^{-3} Pa.s) and density close to unity (0.98 g cm^{-3}), it is used along with diluents. Diluents chosen in the study are *n*-decane and kerosene from inactive chemical class, and 1-decanol as modifier from active chemical class to examine the effect of diluent-complex interactions. The solubility of extracted species increases in the organic phase while using TBP as an extractant in a mixture of an inert diluent and an active diluent (modifier). Hence, the degree of extraction of propionic acid increases with an increase in the concentration of 1-decanol (modifier) in the mixture of TBP and diluents as shown in Figure 5.12. As the viscosity of 1-decanol is high as compared to inactive diluents such as *n*-decane and kerosene, the experiments are performed with the equal volume mixture of *n*-decane and 1-decanol.

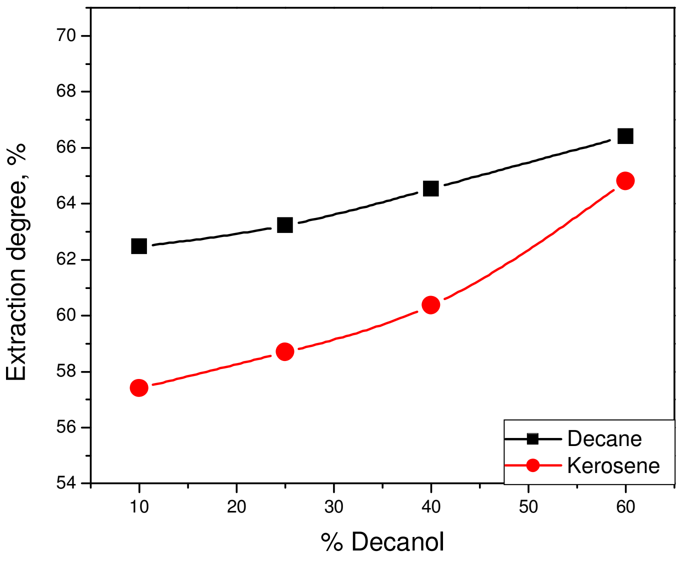

Figure 5.12. Influence of modifier, 1-decanol (10 - 60%) in organic phase on degree of extraction with 25% TBP at 0.405 mol.L^{-1} initial propionic acid concentration

The isotherms for propionic acid using different concentrations of aqueous solution and different concentrations of TBP dissolved in *n*-decane & 1-decanol (1:1 v/v) is shown in Fig. 5.13. Fig. 5.14 shows the isotherms for propionic acid using different concentrations of aqueous solution and different concentrations of kerosene & 1-decanol (1:1 v/v). The equilibrium organic phase acid concentration varies almost linearly with equilibrium aqueous phase acid concentration in both cases. From Figures 5.13 & 5.14, it can be seen that the equilibrium acid concentration in the organic phase increased with increasing TBP concentration. The equilibrium acid concentration in the organic phase also increased with an increase in equilibrium acid concentration in the aqueous phase, for all TBP concentrations in the organic phase. Similar trend for the isotherms was observed in the extraction of propionic acid with TBP in n-dodecane (Flores-Morales *et al.,* 2003).

The experimental data presented in Figures 5.15 and 5.16, show that the degree of extraction (%) significantly increases for an increase in the concentration of TBP. The initial concentration of propionic acid also affects the extraction efficiency of TBP in n-decane/1-decanol (1:1 v/v) (Figures 5.17) and kerosene/1-decanol (1:1 v/v) (Figures 5.18). The degree of extraction (%) significantly decreases when the concentration of propionic acid is increased from 0.135 to 0.676 mol.L^{-1} ~~in~~ for both cases of diluent system. Different concentrations of extractant (TBP) have been used to derive the effect of initial propionic acid concentration on extraction efficiency. The experimental values of equilibrium concentration of propionic acid in aqueous phase are in agreement with the results obtained by Keshav *et al.,* (2008c). They studied the extraction of propionic acid using TBP in different diluents without the use of a modifier.

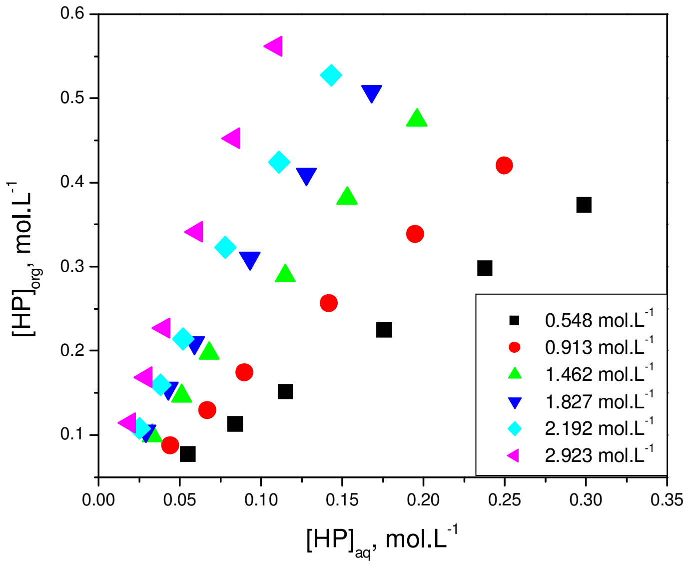

Figure 5.13. Equilibrium isotherms of propionic acid for different TBP concentrations in *n*-decane/1-decanol (1:1 v/v)

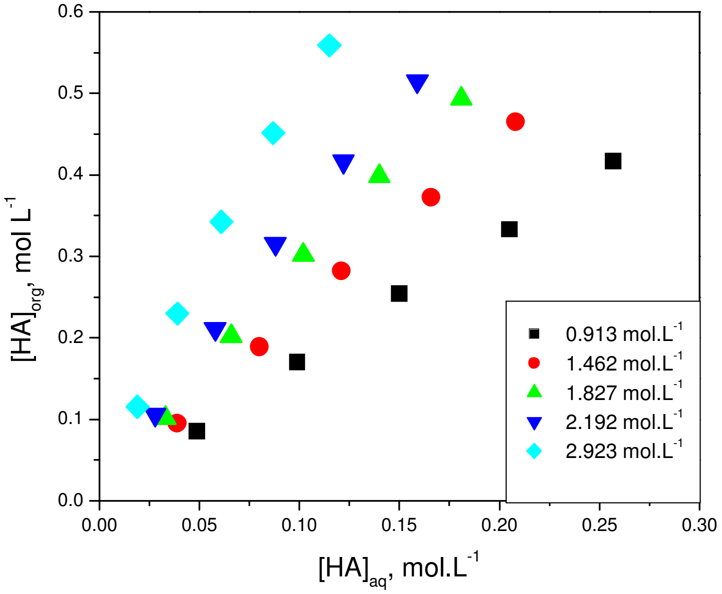

Figure 5.14. Equilibrium isotherms of propionic acid for different TBP concentrations in kerosene/1-decanol (1:1 v/v)

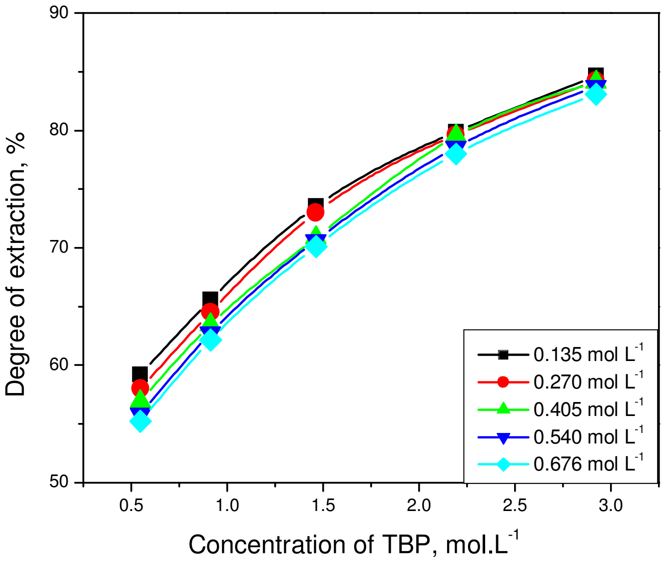

Figure 5.15. Effect of TBP concentration on degree of extraction with different propionic acid concentrations using n-decane/1-decanol (1:1 v/v) as a diluent

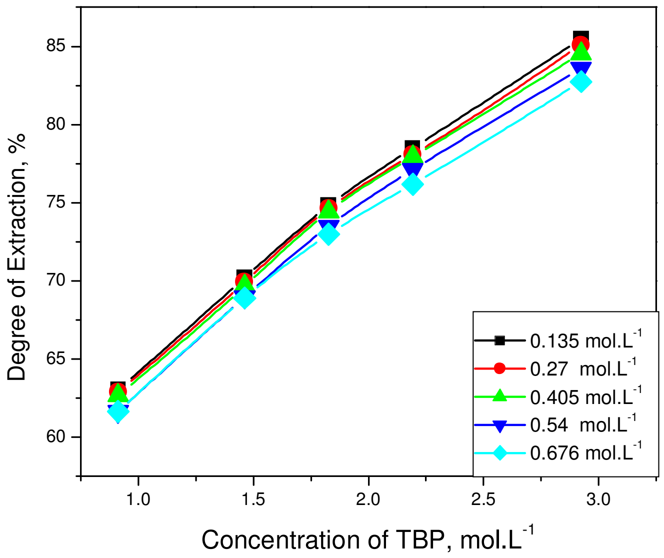

Figure 5.16. Effect of TBP concentration on degree of extraction with different propionic acid concentrations using kerosene/1-decanol (1:1 v/v) as a diluent

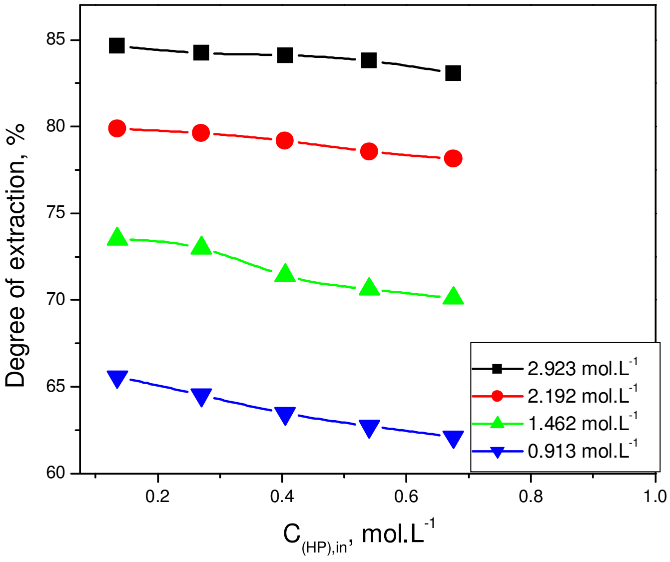

Figure 5.17. Effect of initial propionic acid concentration on degree of extraction with different TBP concentrations in n-decane/1-decanol (1:1 v/v)

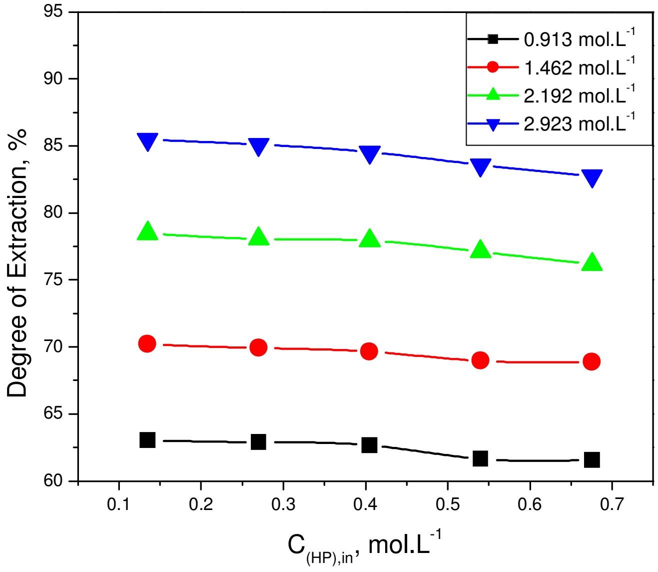

Figure 5.18. Effect of initial propionic acid concentration on degree of extraction with different TBP concentrations in kerosene/1-decanol (1:1 v/v)

Effect of Temperature

The experiments are carried out at four different values (298, 313, 323 and 334 K) of temperature. The effect of temperature on the extraction of propionic acid with TBP (25% and 40%) in *n*-decane/1-decanol (1:1 v/v) and in kerosene/1-decanol (1:1 v/v) are presented in Figures 5.19 and 5.20 respectively. As the temperature increases, the percentage amount of acid extracted decreases. In this concentration range of propionic acid, the increase in the thermal energy disturbs the interaction in the organic phase between TBP and acid, thus decreasing the extraction. However, an improved separation of the phases is observed. From a thermodynamic point of view the molecules of acid in the organic phase are more ordered as they exist as a complex. Thus, acid transfer from the aqueous phase as solvates to the organic phase increases the order and reduces entropy. Generally the transfer of compounds from the aqueous phase to the organic phase is accompanied by a decrease in entropy.

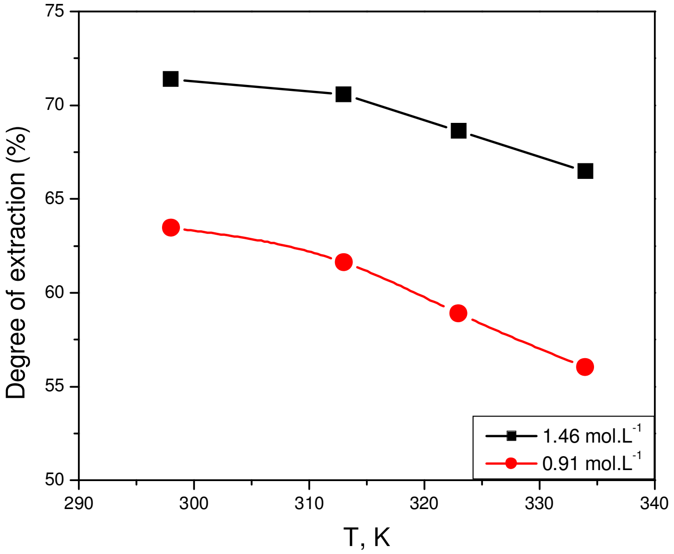

Figure 5.19. Influence of temperature on extraction of propionic acid with TBP (0.913 and 1.462 mol.L^{-1}) in n-decane/1-decanol (1:1 v/v)

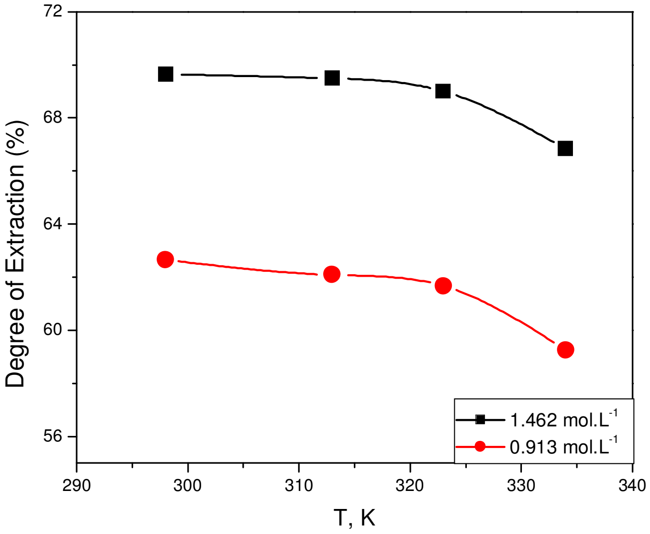

Figure 5.20. Influence of temperature on extraction of propionic acid with TBP (0.913 and 1.462 mol.L^{-1}) in kerosene/1-decanol (1:1 v/v)

5.2.1.2 Reactive Extraction of Nicotinic Acid using TBP and TOPO

Due to the insolubility of nicotinic acid in the organic solvents, its separation by physical extraction with pure diluents is impossible (Table 5.5). It is extracted by phosphorous-bonded oxygen- bearing extractants with a significantly higher distribution ratio than carbon-bonded oxygen-bearing extractants under comparable conditions. TBP and TOPO are used to study the extraction equilibria of nicotinic acid. TOPO is also selected because of its low water co-extraction capacity. TBP is soluble in common organic solvents such as aliphatic, aromatic and chlorinated hydrocarbons, alcohols, esters, ketones, and glycol ethers. Whereas, TOPO is more soluble in aromatics, alcohols and ketones and shows less solubilities in aliphatics and hydrocarbons. In the case of TOPO, the alkoxy groups as found in TBP are substituted by alkyl groups. So, the Lewis basicity is increased through inductive effects. The degree of extraction increases markedly as the number of direct C-P linkages increases.

The reactive phase equilibrium data for the extraction of nicotinic acid using extractant (TBP and TOPO) dissolved in different diluents are presented in Tables 5.7. The data clearly shows that chemical extraction using organophasphorus compounds (TBP and TOPO) is far better than physical extraction as indicated by higher values of K_D. The extraction equilibrium of nicotinic acid is shown in Figure 5.21 using pure TBP as an organic phase. Since a low range of acid concentration is used, a non-linearity is not observed between acid concentrations in the two phases. It can be seen from Figure 5.22 that extraction degree slightly increases with an increase in acid concentration of initial aqueous solution using pure TBP as an extractant. This may be due to the lower range of nicotinic acid concentration used in the initial aqueous solution, and acid concentration is found to be a limiting parameter for the extraction with pure TBP. Generally, for a high initial acid concentration, the distribution coefficient (K_D) may decrease with an increase in the acid concentration in aqueous solution using TBP with diluent. The experimental results given in Figures 5.23 and 5.24 indicate that the extraction efficiency increases with solvent polarity. The effect of diluent on extraction efficiency of TBP is much less marked than that explained on the basis of the diluent effect only. When nicotinic acid is extracted from a 0.10 mol.L^{-1} aqueous solution at 298 K by an organic phase containing 60% v/v of TBP, its distribution coefficient (K_D) is 0.47 with 1-decanol as diluent, 0.45 with *n*-decane as diluent and 0.66 with MIBK as diluent. A stronger effect of diluent is observed when TOPO is used as the extractant (Figure 5.24) rather than TBP (Figure 5.23). The values of K_D are found to be 0.27 and 1.35 using TOPO (with a concentration of 0.39 mol.L^{-1}) dissolved in kerosene/1-decanol (2:1 v/v) and in MIBK respectively.

Table 5.7. Distribution coefficients (K_D) of nicotinic acid (C_{in} = 0.1 mol.L^{-1}) between water and extractant/solvent system

Extractants	Diluents	Extractant Conc. (mol.L^{-1})	K_D	E	pH$_{eq}$
TBP	MIBK	0.73	0.31	23.43	3.18
		1.46	0.48	32.57	3.21
		2.19	0.67	40	3.24
		2.92	0.86	46.29	3.26
	1-Decanol	0.73	0.22	17.71	3.17
		1.46	0.36	26.29	3.19
		2.19	0.47	32	3.21
		2.92	0.72	41.71	3.24
	n-Decane	0.73	0.12	10.86	3.15
		1.46	0.29	22.29	3.18
		2.19	0.45	30.86	3.2
		2.92	0.73	44	3.25
	Kerosene	0.73	0.16	13.86	3.17
		1.46	0.34	25.41	3.20
		2.19	0.46	31.72	3.22
		2.92	0.68	39.07	3.24
TOPO	MIBK	0.56	1.75	63.62	3.36
		0.48	1.58	61.3	3.35
		0.39	1.35	57.43	3.33
		0.28	0.99	49.69	3.29
	Kerosene + 1-octanol (2:1 v/v)	0.56	0.41	29.17	3.22
		0.48	0.33	24.92	3.21
		0.39	0.27	21.05	3.2
		0.28	0.20	17.95	3.19
	n-Heptane + 1-octanol (2:1 v/v)	0.71	0.4	28.75	3.23
		0.57	0.28	21.67	3.21
		0.43	0.19	15.83	3.19
		0.28	0.11	10	3.17

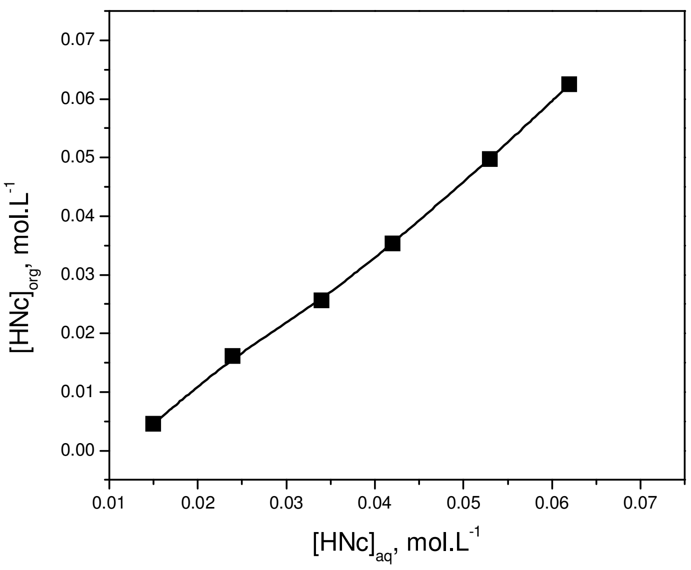

Figure 5.21 Equilibrium isotherms of nicotinic acid using pure TBP

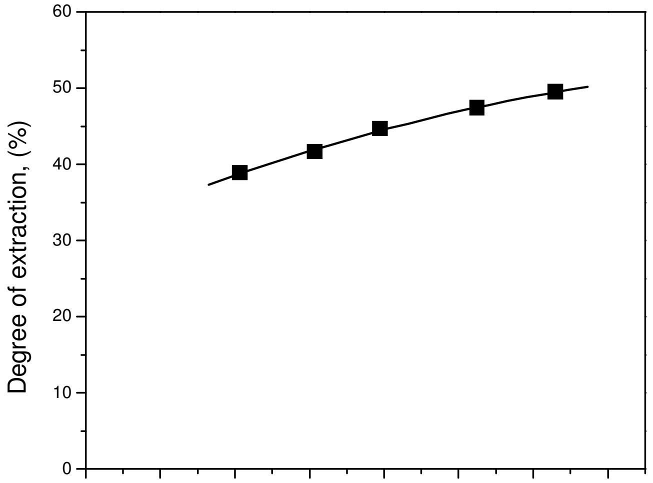

Figure 5.22. Variation in degree of extraction with initial nicotinic acid concentration using pure TBP

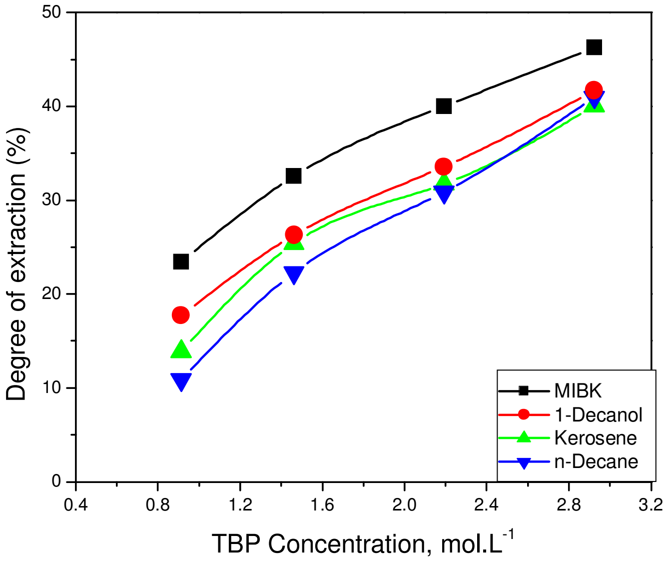

Figure 5.23. Variation in degree of extraction with TBP in various diluents at 0.10 mol.L^{-1} nicotinic acid concentration

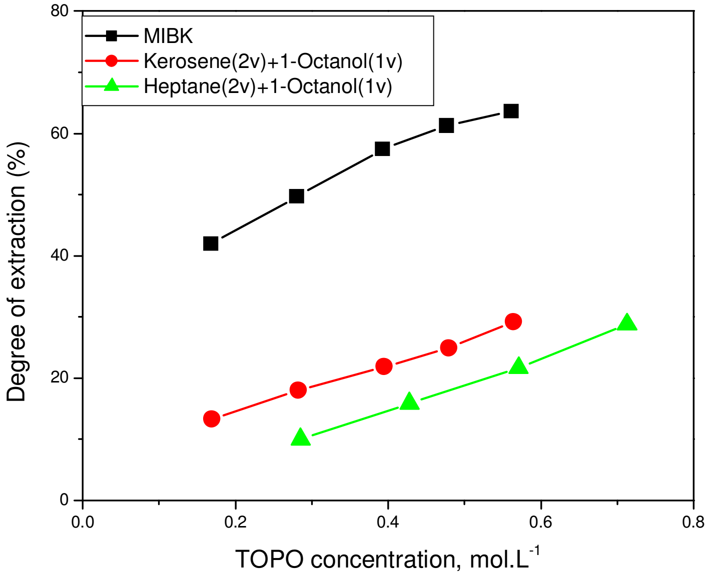

Figure 5.24 Variation in degree of extraction with TOPO in various diluents at 0.10 mol.L^{-1} nicotinic acid concentration

Since, the extraction efficiency with TOPO is more than that with TBP for nicotinic acid, further experiments are carried out using TOPO as an extractant dissolved in six different diluents. The isotherms for nicotinic acid are determined using five different concentrations of aqueous solution and four different concentrations of TOPO dissolved in various diluents, and are shown in Figures 5.25-5.30. For a higher range of TOPO concentration, there is a linear relationship between acid concentration in the two phases, and slightly nonlinear relationship for lower concentrations of TOPO. For low concentrations of acid with respect to higher range of TOPO concentration, Henry's law is valid, whereas at low concentrations of TOPO, non-ideal behavior can prevail causing this deviation.

The distribution coefficients (K_D) and degree of extraction (E) are found to increase with an increase in TOPO concentration in different diluents. However, TOPO is used only in the range of 0.10 to 0.60 mol.L^{-1} in different diluents. Higher concentration range of TOPO in diluents may form highly viscous solution that may take longer time to attain equilibrium. Initial concentration of acid also affects the extraction efficiency as shown in Tables 5.8 to 5.13. The values of K_D and E decrease when the concentration of acid is increased from 0.02 to 0.12 mol.L^{-1}. Different concentrations of TOPO have been used to derive the effect of initial acid concentration on extraction efficiency. The trends in experimental results of this study on equilibrium concentrations of nicotinic acid in aqueous phase are in good agreement with the results reported by Kertes and King (1986). The TOPO/diluent system favors the formation of 'not overloaded' complexes of polar acid-TOPO structures (*m:n*) with the Z factors restricted mainly between 0.02 and 0.40.

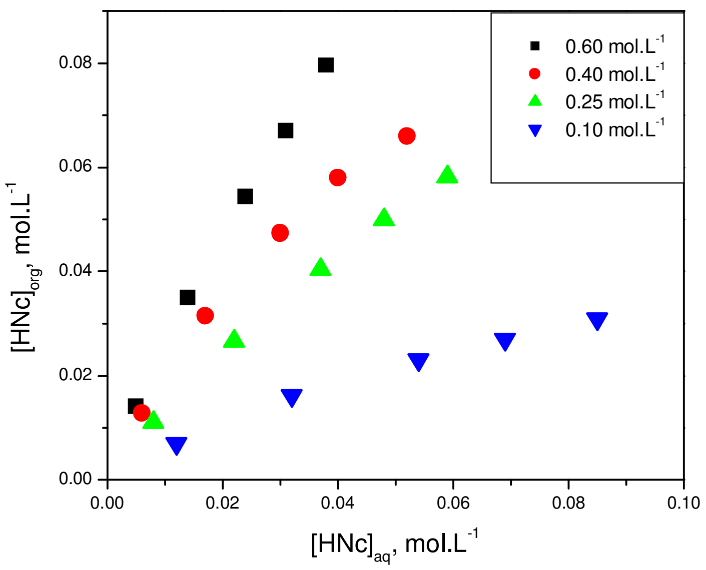

Figure 5.25. Equilibrium isotherms of nicotinic acid for different concentrations of TOPO dissolved in toluene

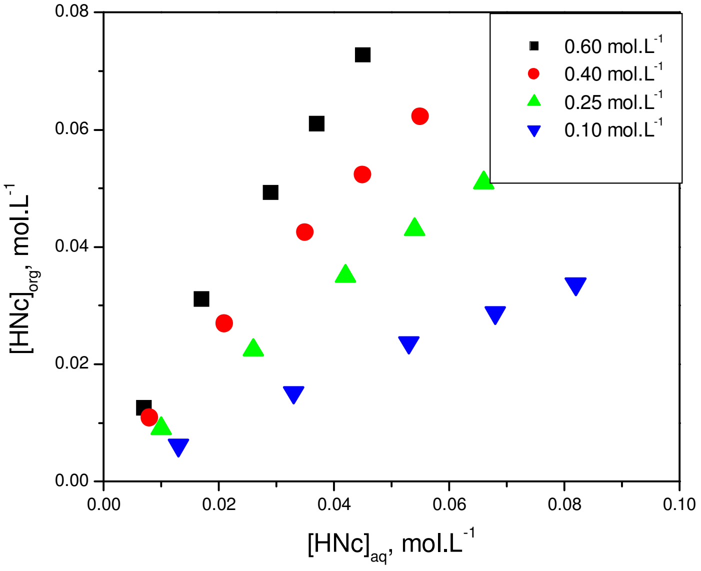

Figure 5.26. Equilibrium isotherms of nicotinic acid for different concentrations of TOPO dissolved in MIBK

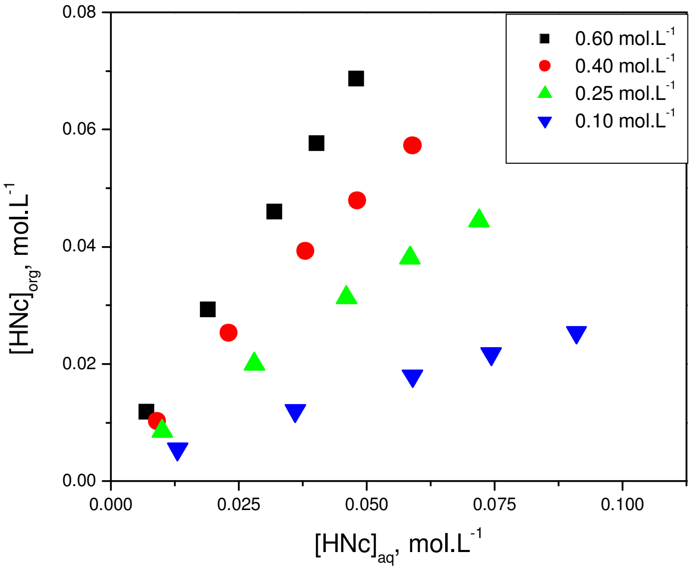

Figure 5.27. Equilibrium isotherms of nicotinic acid for different concentrations of TOPO dissolved in kerosene

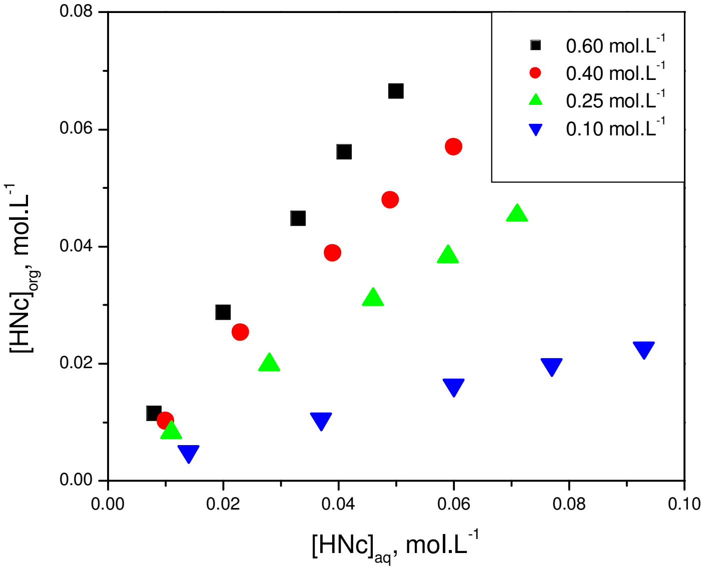

Figure 5.28. Equilibrium isotherms of nicotinic acid for different concentrations of TOPO dissolved in DCM

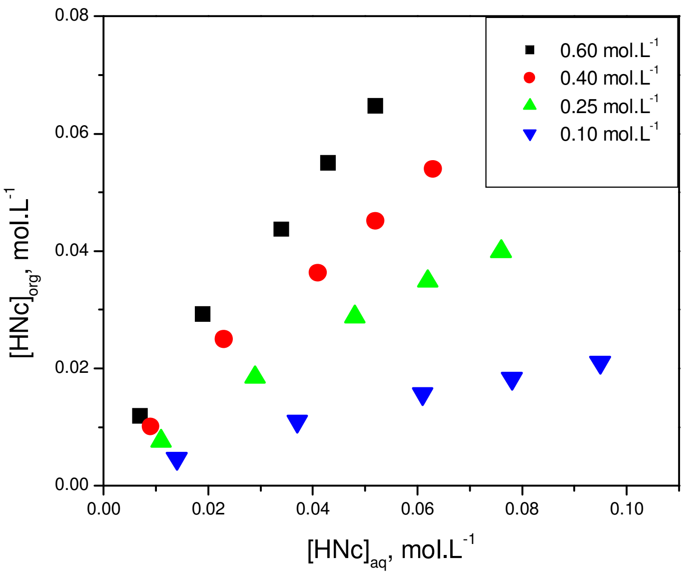

Figure 5.29. Equilibrium isotherms of nicotinic acid for different concentrations of TOPO dissolved in *n*-octane

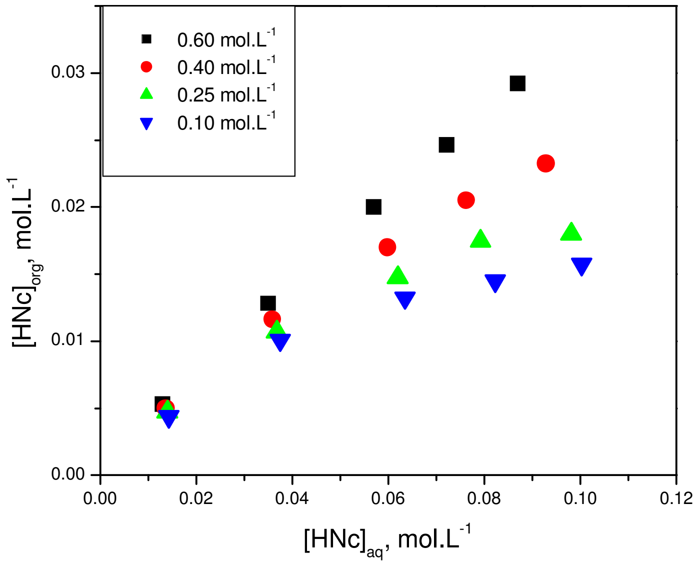

Figure 5.30. Equilibrium isotherms of nicotinic acid for different concentrations of TOPO dissolved in 1-decanol

Table 5.8. Equilibrium results for the extraction of nicotinic acid using TOPO dissolved in toluene at 298 K

C_{in} (mol.L^{-1})	$[S_{\text{org}}]_{\text{in}}$ (mol.L^{-1})	$10^2 \cdot C_{\text{HNc}}$ (mol.L^{-1})	$10^2 \cdot \overline{C}_{\text{HNc}}$ (mol.L^{-1})	K_D	E	Z	$p\text{H}_{\text{eq}}$
0.02	0.10	1.27	0.73	0.57	36.50	0.07	3.87
	0.25	0.89	1.11	1.25	55.50	0.04	3.94
	0.40	0.72	1.28	1.78	64.00	0.03	4.0
	0.60	0.59	1.41	2.39	70.50	0.02	4.02
0.05	0.10	3.38	1.62	0.48	32.40	0.16	3.69
	0.25	2.34	2.66	1.14	53.20	0.11	3.74
	0.40	1.85	3.15	1.70	63.00	0.08	3.75
	0.60	1.53	3.47	2.27	69.40	0.06	3.78
0.08	0.10	5.69	2.31	0.41	28.88	0.23	3.58
	0.25	3.96	4.04	1.02	50.50	0.16	3.65
	0.40	3.26	4.74	1.45	59.25	0.12	3.69
	0.60	2.56	5.44	2.13	68.00	0.09	3.72
0.10	0.10	7.26	2.74	0.38	27.40	0.27	3.53
	0.25	5.03	4.97	0.99	49.70	0.20	3.58
	0.40	4.21	5.79	1.38	57.90	0.15	3.63
	0.60	3.30	6.70	2.03	67.00	0.11	3.69
0.12	0.10	8.91	3.09	0.35	25.75	0.31	3.48
	0.25	6.19	5.81	0.94	48.42	0.23	3.54
	0.40	5.45	6.55	1.20	54.58	0.16	3.58
	0.60	4.04	7.96	1.97	66.33	0.13	3.63

Table 5.9. Equilibrium results for the extraction of nicotinic acid using TOPO dissolved in MIBK at 298 K

C_{in} (mol.L^{-1})	$[S_{\text{org}}]_{\text{in}}$ (mol.L^{-1})	$10^2 \cdot C_{\text{HNc}}$ (mol.L^{-1})	$10^2 \cdot \overline{C}_{\text{HNc}}$ (mol.L^{-1})	K_D	E	Z	$p\text{H}_{\text{eq}}$
0.02	0.10	1.38	0.62	0.45	31.00	0.06	3.84
	0.25	1.10	0.90	0.82	45.00	0.04	3.89
	0.40	0.92	1.08	1.17	54.00	0.03	3.93
	0.60	0.75	1.25	1.67	62.50	0.02	3.96
0.05	0.10	3.48	1.52	0.44	30.40	0.15	3.71
	0.25	2.76	2.24	0.81	44.80	0.09	3.74
	0.40	2.31	2.69	1.16	53.80	0.07	3.78
	0.60	1.89	3.11	1.65	62.20	0.05	3.82
0.08	0.10	5.63	2.37	0.42	29.63	0.24	3.59
	0.25	4.50	3.50	0.78	43.75	0.14	3.65
	0.40	3.75	4.25	1.13	53.13	0.11	3.71
	0.60	3.08	4.92	1.60	61.50	0.08	3.72
0.10	0.10	7.13	2.87	0.40	28.70	0.29	3.57
	0.25	5.70	4.30	0.75	43.00	0.17	3.61
	0.40	4.76	5.24	1.10	52.40	0.13	3.66
	0.60	3.90	6.10	1.56	61.00	0.10	3.68
0.12	0.10	8.63	3.37	0.39	28.08	0.34	3.53
	0.25	6.90	5.10	0.74	42.50	0.20	3.58
	0.40	5.78	6.22	1.08	51.83	0.16	3.61
	0.60	4.73	7.27	1.54	60.58	0.12	3.66

Table 5.10. Equilibrium results for the extraction of nicotinic acid using TOPO dissolved in Dichloromethane (DCM) at 298 K

C_{in} (mol.L^{-1})	$[S_{\text{org}}]_{\text{in}}$ (mol.L^{-1})	$10^2 \cdot C_{\text{HNc}}$ (mol.L^{-1})	$10^2 \cdot \overline{C}_{\text{HNc}}$ (mol.L^{-1})	K_D	E	Z	$p\text{H}_{\text{eq}}$
0.02	0.10	1.50	0.50	0.33	25.00	0.05	3.84
	0.25	1.17	0.83	0.71	41.50	0.03	3.89
	0.40	0.98	1.02	1.04	51.00	0.03	2.91
	0.60	0.84	1.16	1.38	58.00	0.02	3.94
0.05	0.10	3.94	1.06	0.27	21.20	0.11	3.68
	0.25	3.01	1.99	0.66	39.80	0.08	3.77
	0.40	2.47	2.53	1.02	50.60	0.06	3.77
	0.60	2.12	2.88	1.36	57.60	0.05	3.80
0.08	0.10	6.37	1.63	0.26	20.38	0.16	3.60
	0.25	4.90	3.10	0.63	38.75	0.12	3.65
	0.40	4.11	3.89	0.95	48.63	0.10	3.68
	0.60	3.53	4.47	1.27	55.88	0.08	3.70
0.10	0.10	8.01	1.99	0.25	19.90	0.20	3.55
	0.25	6.17	3.83	0.62	38.30	0.15	3.60
	0.40	5.21	4.79	0.92	47.90	0.12	3.64
	0.60	4.38	5.62	1.28	56.20	0.09	3.66
0.12	0.10	9.73	2.27	0.23	18.92	0.23	3.48
	0.25	7.47	4.53	0.61	37.75	0.18	3.56
	0.40	6.30	5.70	0.90	47.50	0.14	3.60
	0.60	5.34	6.66	1.25	55.50	0.11	3.64

Table 5.11. Equilibrium results for the extraction of nicotinic acid using TOPO dissolved in kerosene at 298 K

C_{in} (mol.L^{-1})	$[S_{\text{org}}]_{\text{in}}$ (mol.L^{-1})	$10^2 \cdot C_{\text{HNc}}$ (mol.L^{-1})	$10^2 \cdot \overline{C}_{\text{HNc}}$ (mol.L^{-1})	K_D	E	Z	$p\text{H}_{\text{eq}}$
0.02	0.10	1.45	0.55	0.38	27.5	0.055	3.84
	0.25	1.15	0.85	0.74	42.5	0.034	3.89
	0.40	0.98	1.02	1.04	51	0.026	3.9
	0.60	0.82	1.18	1.44	59	0.02	3.94
0.05	0.10	3.8	1.2	0.32	24	0.12	3.68
	0.25	3.0	2.0	0.67	40	0.08	3.77
	0.40	2.47	2.53	1.02	50.6	0.063	3.79
	0.60	2.07	2.93	1.42	58.6	0.049	3.8
0.08	0.10	6.2	1.8	0.29	22.5	0.18	3.61
	0.25	4.87	3.13	0.64	39.13	0.125	3.65
	0.40	4.07	3.93	0.97	49.13	0.098	3.68
	0.60	3.4	4.6	1.35	57.5	0.077	3.7
0.12	0.10	9.46	2.54	0.27	21.17	0.254	3.49
	0.25	7.56	4.44	0.59	37	0.178	3.56
	0.40	6.27	5.73	0.91	47.75	0.143	3.6
	0.60	5.13	6.87	1.34	57.25	0.115	3.64

Table 5.12. Equilibrium results for the extraction of nicotinic acid using TOPO dissolved in *n*-octane at 298 K

C_{in} (mol.L^{-1})	$[S_{\text{org}}]_{\text{in}}$ (mol.L^{-1})	$10^{2}\cdot C_{\text{HNc}}$ (mol.L^{-1})	$10^{2}\cdot \overline{C}_{\text{HNc}}$ (mol.L^{-1})	K_D	E	Z	$p\text{H}_{\text{eq}}$
0.02	0.10	1.53	0.47	0.31	23.63	0.05	3.84
	0.25	1.24	0.76	0.62	38.25	0.03	3.88
	0.40	0.99	1.01	1.02	50.44	0.03	3.92
	0.60	0.81	1.19	1.46	59.38	0.02	3.96
0.05	0.10	3.90	1.10	0.28	22.00	0.11	3.70
	0.25	3.15	1.85	0.59	36.95	0.07	3.72
	0.40	2.50	2.50	1.00	49.95	0.06	3.75
	0.60	2.08	2.92	1.40	58.4	0.05	3.76
0.08	0.10	6.44	1.56	0.24	19.56	0.16	3.58
	0.25	5.12	2.88	0.56	36.06	0.12	3.65
	0.40	4.37	3.63	0.83	45.34	0.09	3.67
	0.60	3.59	4.41	1.23	55.14	0.07	3.70
0.10	0.10	8.17	1.83	0.22	18.33	0.18	3.53
	0.25	6.52	3.48	0.53	34.83	0.14	3.58
	0.40	5.49	4.51	0.82	45.14	0.11	3.63
	0.60	4.54	5.46	1.20	54.63	0.09	3.67
0.12	0.10	9.90	2.10	0.21	17.50	0.21	3.48
	0.25	8.00	4.00	0.50	33.31	0.16	3.54
	0.40	6.60	5.40	0.82	45	0.14	3.58
	0.60	5.53	6.47	1.17	53.94	0.11	3.63

Table 5.13. Equilibrium results for the extraction of nicotinic acid using TOPO dissolved in 1-Decanol at 298 K

C_{in} (mol.L^{-1})	$[S_{\text{org}}]_{\text{in}}$ (mol.L^{-1})	$10^2 \cdot C_{\text{HNc}}$ (mol.L^{-1})	$10^2 \cdot \overline{C}_{\text{HNc}}$ (mol.L^{-1})	K_D	E	Z	$p\text{H}_{\text{eq}}$
0.02	0.10	1.56	0.44	0.28	22.00	0.04	3.84
	0.25	1.53	0.47	0.31	23.50	0.02	3.84
	0.40	1.50	0.50	0.33	25.00	0.01	3.85
	0.60	1.47	0.53	0.36	26.50	0.01	3.85
0.05	0.10	3.99	1.01	0.25	20.20	0.10	3.68
	0.25	3.93	1.07	0.27	21.40	0.04	3.70
	0.40	3.84	1.16	0.30	23.20	0.03	3.71
	0.60	3.72	1.28	0.34	25.60	0.02	3.72
0.08	0.10	6.68	1.32	0.20	16.50	0.13	3.58
	0.25	6.53	1.47	0.23	18.38	0.06	3.59
	0.40	6.30	1.70	0.27	21.25	0.04	3.59
	0.60	6.00	2.00	0.33	25.00	0.03	3.60
0.10	0.10	8.55	1.45	0.17	14.50	0.16	3.53
	0.25	8.25	1.75	0.21	17.50	0.07	3.54
	0.40	7.95	2.05	0.26	20.50	0.05	3.54
	0.60	7.54	2.46	0.33	24.60	0.04	3.55
0.12	0.10	10.43	1.57	0.15	13.08	0.16	3.46
	0.25	10.20	1.80	0.18	15.00	0.07	3.47
	0.40	9.68	2.32	0.24	19.33	0.06	3.49
	0.60	9.08	2.92	0.32	24.33	0.05	3.51

5.2.2 Modeling and Simulation Studies

The results of theoretical studies (as discussed in Section 4.1) are presented in Sections 5.2.2.1 and 5.2.2.2. The equilibrium constants (K_E) and the number of extractant (TBP and TOPO) molecules per acid molecule (n) based on experimentally determined distribution coefficients (K_D) and loading ratios (Z) are determined. In the section 5.2.2.3, the parameters of μ and E_T model (Section 4.1.3) are estimated to quantify the effect of diluents on the equilibrium extraction of nicotinic acid. The apparent enthalpy (ΔH) and entropy (ΔS) of reactive extraction of propionic acid using TOPO are estimated in Section 5.2.2.4.

5.2.2.1 Estimation of K_E and n based on K_D

For the estimation of equilibrium extraction constant (K_E) and the number of extractant molecules per acid molecule (n), the theoretical study based on mass action law (chemodel) using Equations 4.17 – 4.27 (discussed in chapter 4) has been used. Niitsu and Sekine (1978) reported that the solvation number of the aliphatic carboxylic acids is same as the number of carboxyl groups on each acid. This indicates a stoichiometric association between the individual phosphoryl group and acid group. It displays the effect of acid concentration on the experimentally determined distribution ratio. A plot of equation (4.27), $\log K_D + \log\left(1+\frac{K_a}{[H^+]}\right)$ versus log $[\bar{S}]$ yields a straight line with a slope of n and an intercept of log K_E. This graphical representation is used to estimate the values of K_E and n for different extraction systems as shown in Figures 5.31 – 5.40.

The values of K_E and n are also estimated through the model equation (4.27) using an optimization procedure. A population based search algorithm called differential evolution (DE), which is simple and robust and has a proven successful record is employed in the present study. An objective function based on least square error between experimental data and predicted values of $\log K_D + \log\left(1+\frac{K_a}{[H^+]}\right)$ has been minimized.

The values of K_E and n determined by DE as well as by graphical methods are presented in Table 5.14. Different values of K_E and n are evaluated depending on the initial acid concentration. The graphical methods are used with assumptions of $[\overline{S}]_{in} >> n[\overline{HA(S)_n}]$ in the extraction of acids (propionic- and nicotinic acids) with TBP (0.73 – 2.92 mol.L^{-1}) and $[\overline{S}]_{org} = [\overline{S}]_{in} - \overline{C}_{HA}$ in the extraction of nicotinic acid with TOPO (0.10 – 0.60 mol.L^{-1}). These assumptions are not valid at higher concentrations of acid due to an increased concentration of extractant in the complex form. Hence, the obtained results of K_E and n, for extraction of acids with TBP and TOPO using DE are found to be more accurate than those obtained by graphical methods.

The values of n ($\approx$ 1) estimated by both methods suggest the existence of a stoichiometric association between the individual phosphoryl group and acid group. The values of n deviate from the quasi-ideal behavior, which is probably because of the significant mutual solubility of both the phases. Polar diluents, having higher dielectric constant values also contribute in the extraction of organic acid and results in a value of n less than one. The diluent polarity is an important parameter that controls the extraction degree of ionizable solutes. The dielectric constant may be considered as a characteristic of solvent–solute local interactions, inducing the limitation of solute solvation by solvent or extractant, due to the presence of ionizable groups in the solute chemical structure. Therefore, the solvent polarity controls the extraction constant through its influence on the separation efficiency and mechanism. The high values of coefficient of determination ($R^2 \approx 0.99$) represent good fit of the data with minimum deviation.

The values of K_E and n are also determined for the complete range of nicotinic acid concentrations (0.02 – 0.12 mol.L^{-1}) using TOPO (0.10 – 0.60 mol.L^{-1}) in different diluents as shown in Figure 5.40 and Table 5.15. The strength of the complex solvation is found to be in the decreasing order (toluene < MIBK < dichloromethane < kerosene < *n*-octane < 1-decanol) promoting probably (1,1) acid-TOPO complex formation. In all the tested diluents, toluene containing a benzene ring in the structure is the best solvating agents for acid-TOPO complexation giving a highest value of K_{E} (4.43), which is indicative of the interaction between aromatic π systems at the complexation stage. Extremely low values of equilibrium extraction constant ($K_{\mathrm{E}} = 0.37$) and the number of reacting extractant (TOPO) molecules ($n = 0.26$) with protic 1-decanol are found. It may be possible to have strong interactions between the hydroxyl group of diluent and a phosphoryl group (>P=O) of TOPO or to have adverse effect of pyridine group in the pyridine-3-carboxylic acid structure on the complexes formation with TOPO. Therefore, the dielectric constant and the dipole moments of the diluents control the extraction constant through its influence on separation efficiency and mechanism.

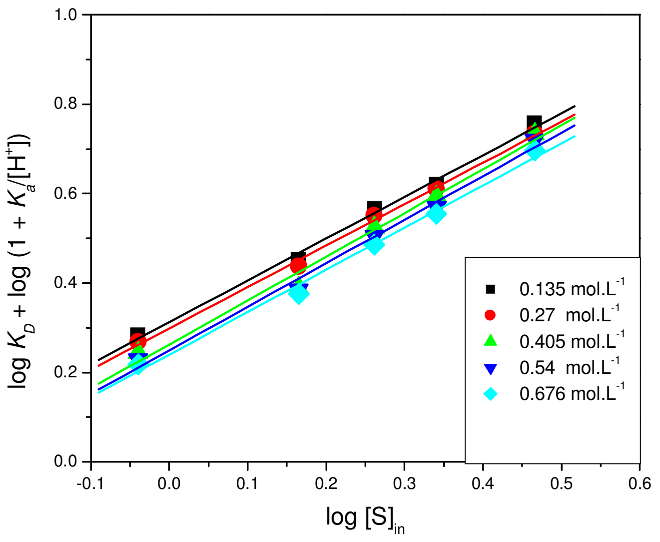

Figure 5.31. Determination of K_E and n using TBP dissolved in n-decane/1-decanol (1:1 v/v) with different initial propionic acid concentration

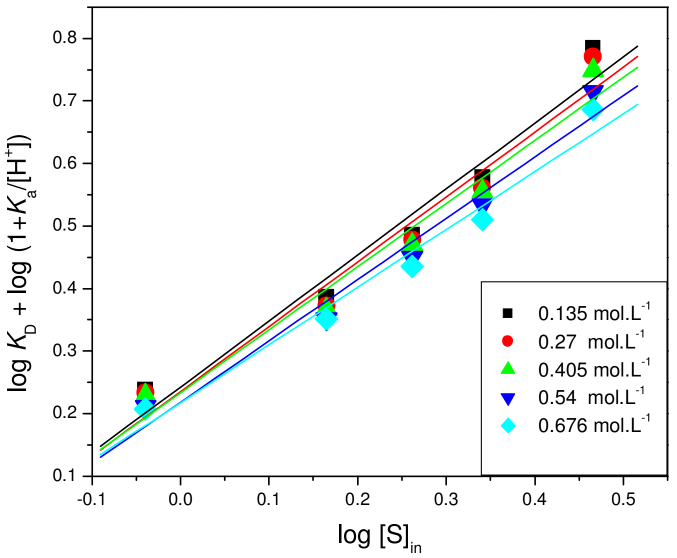

Figure 5.32. Determination of K_E and n using TBP dissolved in kerosene/1-decanol (1:1 v/v) with different initial propionic acid concentration

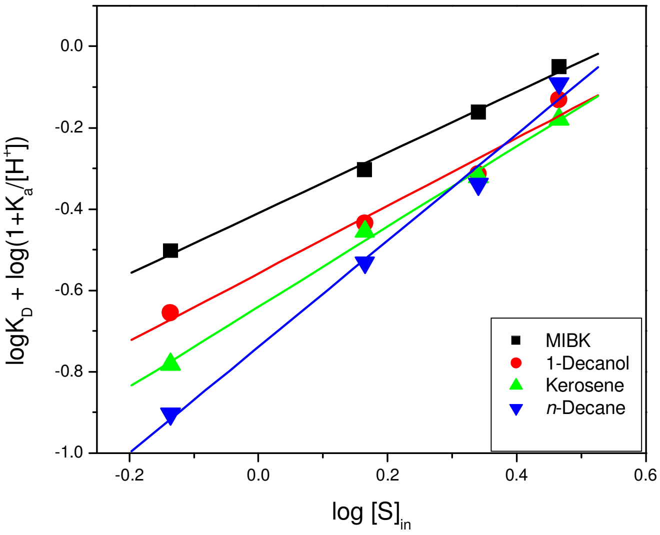

Figure 5.33. Determination of K_E and n using TBP dissolved in different diluents with initial nicotinic acid concentration of 0.10 mol.L^{-1}

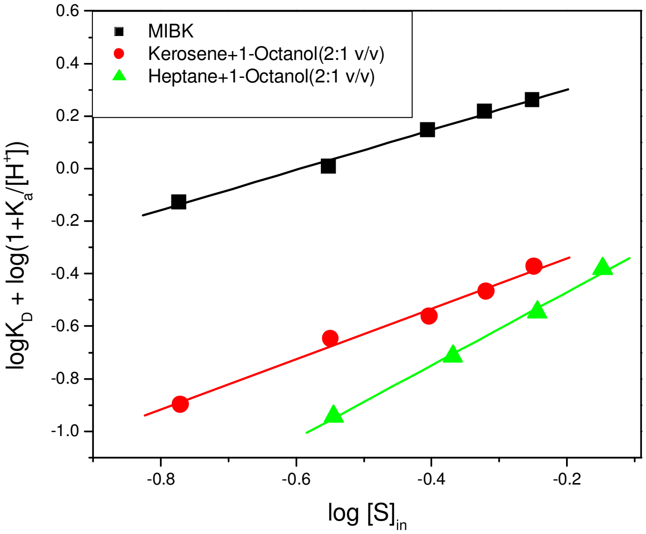

Figure 5.34. Determination of K_E and n using TOPO dissolved in different diluents with initial nicotinic acid concentration of 0.10 mol.L^{-1}

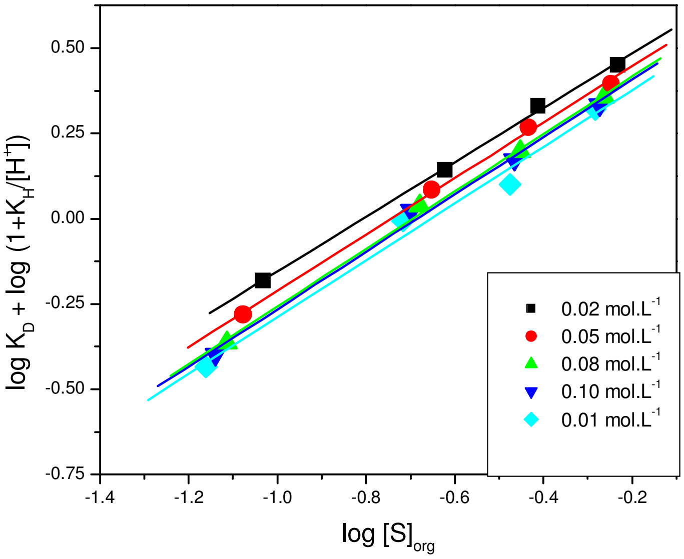

Figure 5.35. Determination of K_E and n using TOPO dissolved in toluene with different initial nicotinic acid concentration

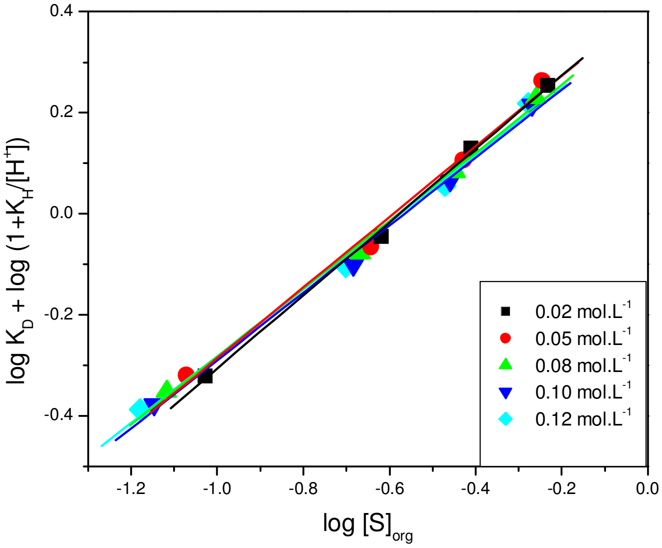

Figure 5.36. Determination of K_E and n using TOPO dissolved in MIBK with different initial nicotinic acid concentration

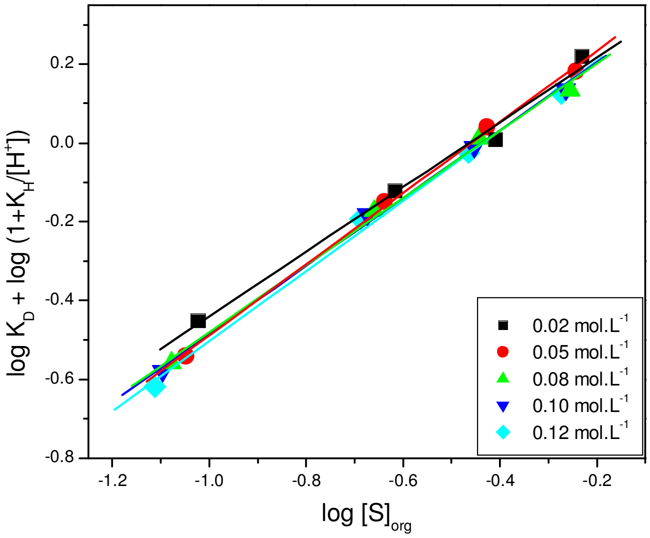

Figure 5.37. Determination of K_E and *n* using TOPO dissolved in DCM with different initial nicotinic acid concentration

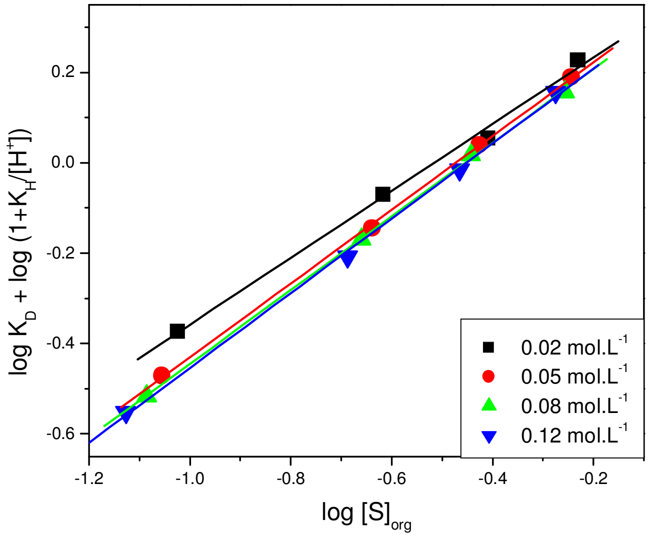

Figure 5.38. Determination of K_E and *n* using TOPO dissolved in kerosene with different initial nicotinic acid concentration

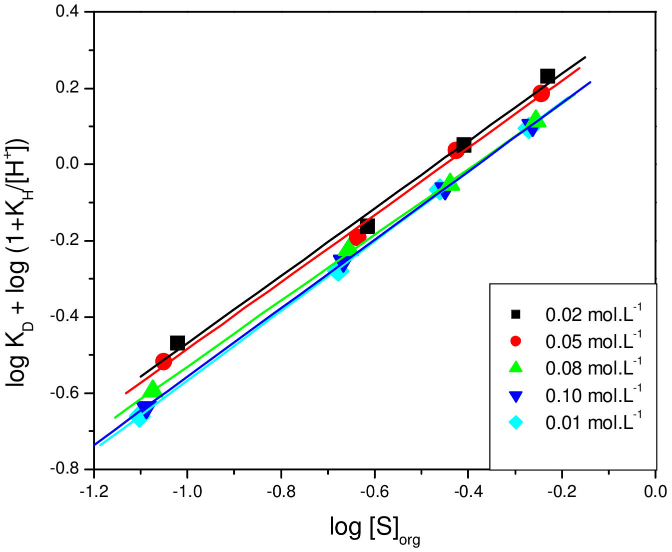

Figure 5.39. Determination of K_E and n using TOPO dissolved in n-octane with different initial nicotinic acid concentration

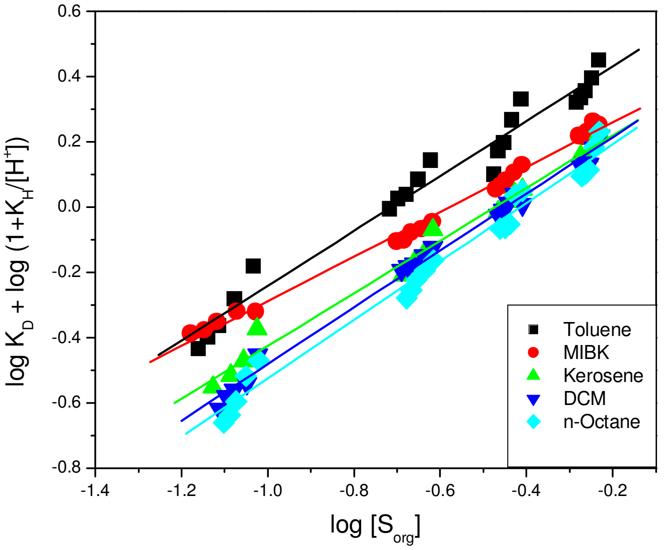

Figure 5.40. Determination of K_E and n with various diluents in the entire range of initial nicotinic acid concentrations and TOPO

Table 5.14. Values of equilibrium extraction constant (K_E) and number of reacting extractant (TBP and TOPO) molecules (*n*) in various diluents at different concentrations of acid

Acids	**Extractants**		**Diluents**	C_{in}	**Using graphical method**			**Using DE**	
	Name	**Range (mol.L^{-1})**		(mol.L^{-1})	K_E	*n*	R^2	K_E	*n*
Propionic acid	TBP	0.91 – 2.92	n-Decane/1-decanol (1:1 v/v)	0.135	2.05	0.93	0.998	2.21	0.85
				0.270	1.99	0.93	0.999	2.27	0.81
				0.405	1.83	0.97	0.993	2.28	0.80
				0.540	1.77	0.97	0.993	2.30	0.76
				0.676	1.74	0.95	0.946	2.33	0.72
			Kerosene/ 1-decanol (1:1 vol%)	0.135	1.75	1.06	0.981	1.98	0.88
				0.270	1.72	1.04	0.979	2.06	0.82
				0.405	1.71	1.01	0.981	2.14	0.77
				0.540	1.65	0.98	0.985	2.14	0.73
				0.676	1.65	0.93	0.986	2.16	0.67
Nicotinic acid	TBP	0.73 – 2.92	MIBK	0.10	0.39	0.75	0.998	-	-
			1-Decanol		0.28	0.83	0.988	-	-
			Kerosene		0.23	0.99	0.998	-	-
			Decane		0.19	1.26	0.995	-	-
	TOPO	0.28 – 0.56	MIBK		2.85	0.76	0.997	-	-
			Kerosene + 1-octanol (2:1 v/v)		0.71	0.96	0.994	-	-
		0.28 – 0.71	Heptane + 1-octanol (2:1 v/v)		0.64	1.39	0.998	-	-
		0.10 – 0.60	*n*-Octane	0.02	2.63	0.88	0.997	2.74	0.95
				0.05	2.51	0.88	0.998	2.71	0.94
				0.08	2.14	0.86	0.999	2.12	0.87
				0.10	2.19	0.89	0.999	2.17	0.90
				0.12	2.24	0.91	0.999	2.16	0.89

Table 5.14 continued……

Nicotinic acid	TOPO	0.10 – 0.60	Toluene	0.02	4.37	0.80	0.999	4.43	0.81
				0.05	4.07	0.82	0.999	4.19	0.84
				0.08	3.89	0.84	0.998	3.81	0.82
				0.10	3.80	0.84	0.997	3.96	0.84
				0.12	3.47	0.83	0.992	2.66	0.64
			MIBK	0.02	2.63	0.73	0.999	2.69	0.77
				0.05	2.57	0.70	0.996	2.64	0.76
				0.08	2.45	0.67	0.998	2.47	0.72
				0.10	2.40	0.67	0.998	2.44	0.73
				0.12	2.40	0.66	0.997	2.40	0.72
			DCM	0.02	2.40	0.82	0.995	2.05	0.75
				0.05	2.63	0.90	0.999	2.55	0.87
				0.08	2.34	0.85	0.998	2.30	0.81
				0.10	2.40	0.86	0.998	2.74	0.99
				0.12	2.45	0.89	0.997	2.19	0.81
			Kerosene	0.02	2.40	0.74	0.998	2.47	0.89
				0.05	2.45	0.82	0.999	2.36	0.82
				0.08	2.34	0.82	0.999	2.53	0.83
				0.12	2.34	0.83	0.999	2.10	0.65
			1-Decanol	0.02	0.42	0.13	0.934	0.42	0.14
				0.05	0.37	0.15	0.938	0.38	0.16
				0.08	0.37	0.25	0.953	0.38	0.27
				0.10	0.39	0.34	0.971	0.40	0.37
				0.12	0.37	0.38	0.948	0.40	0.44

Table 5.15. Values of K_E and n using TOPO (0.10 – 0.60 mol.L^{-1}) in various diluents in the entire range of nicotinic acid concentration (0.02 – 0.12 mol.L^{-1})

Diluents	K_E	n	R^2	SD
n-Octane	2.34	0.90	0.990	0.04
DCM	2.45	0.87	0.996	0.03
Kerosene	2.30	0.85	0.982	0.05
MIBK	2.51	0.69	0.997	0.02
Toluene	3.98	0.84	0.985	0.05

5.2.2.2 Estimation of K_E based on Z

The loading ratio depends on the extractability of the acid (strength of the acid-base interaction) and its concentration in aqueous phase. The stoichiometry of the overall extraction equilibrium is found based on the loading ratio (Z) in the organic phase (Eq. 4.35). If the organic phase is not highly concentrated by acid, i.e., at very low loading ratios ($Z < 0.5$), 1:1 complex of acid and extractant (TBP and TOPO) is formed. Propionic acid (0.135-0.676 mol.L^{-1}) and nicotinic acid (0.02 to 0.12 mol.L^{-1}) are used in the low concentration range with respect to extractant (TBP and TOPO). The loading ratios are found to be very low ($Z < 0.5$), except few values in the extraction of propionic acid at low concentration of TBP. $Z/(1 - Z)$ versus $[HA]$ are plotted to obtain the values of equilibrium constant (K_{11}) for 1:1 complexes of acid and extractant as shown in Figures 5.41 – 5.44. The values of K_{11} at 298 K for the extraction of propionic and nicotinic acids with different concentrations of extractant dissolved in different diluents along with the corresponding values of R^2 and SD are given in Table 5.16. Equilibrium extraction constants (K_{11}) for 1:1 complex of acid and extractant at 298 K with the entire concentration range of extractant in different diluents are also estimated (Figures 5.43 and 5.44) and given in Table 5.16.

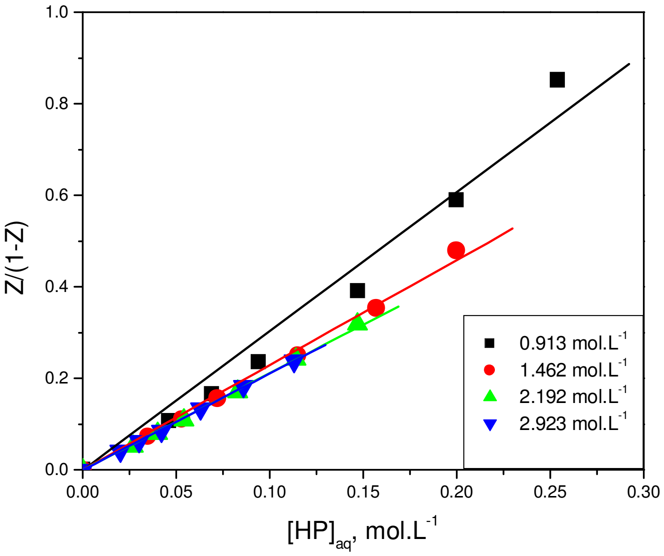

Figure 5.41. Estimation of (1:1) propionic acid-TBP equilibrium constant (K_{E1}) with different TBP concentration in n-decane/1-decanol (1:1 v/v)

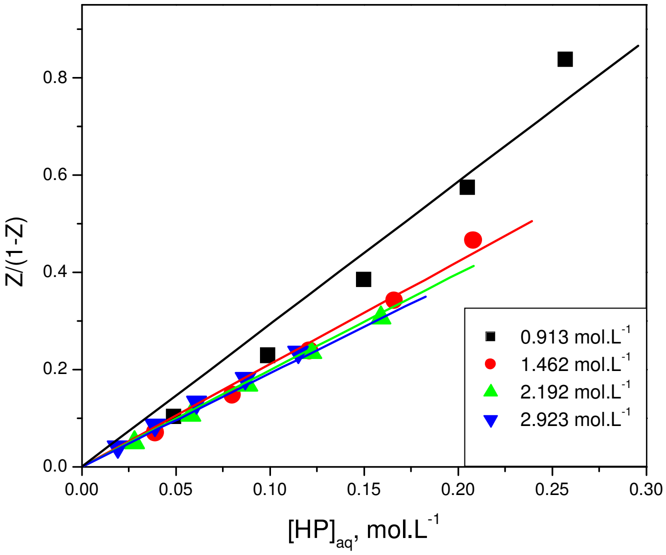

Figure 5.42. Estimation of (1:1) propionic acid-TBP equilibrium constant (K_{E1}) with different TBP concentration in kerosene/1-decanol (1:1 v/v)

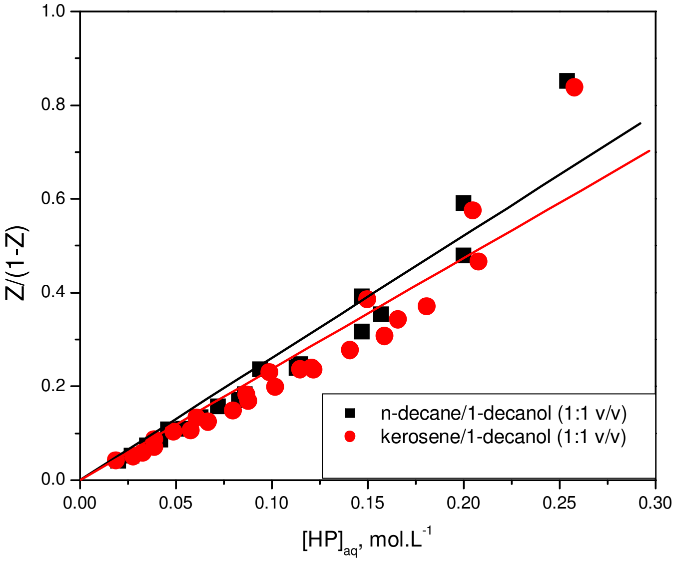

Figure 5.43. Estimation of (1:1) propionic acid-TBP equilibrium constant (K_{E1}) with entire range of TBP concentration in different diluents

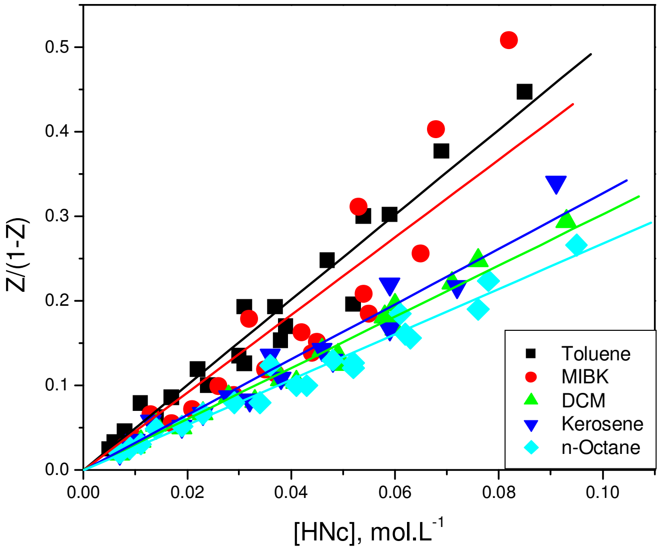

Figure 5.44 Estimation of (1:1) nicotinic acid-TOPO equilibrium complexation constant (K_{E1}) with various diluents in the entire range of TOPO concentration

Table 5.16. Equilibrium extraction constant (K_{11}) for the formation of 1:1 complex of acid and extractant

Acid		Extractant		Diluents	K_{11}	R^2	SD
Name	Conc. (mol.L^{-1})	Name	Conc. (mol.L^{-1})				
Propionic acid	0.135 – 0.675	TBP	0.913	n-Decane/ 1-decanol (1:1 v/v)	3.03	0.991	0.050
			1.462		2.29	0.998	0.010
			2.192		2.11	0.999	0.005
			2.923		2.10	0.999	0.002
			0.913	Kerosene/ 1-decanol (1:1 v/v)	2.93	0.991	0.063
			1.462		2.12	0.997	0.020
			2.192		2.11	0.999	0.000
			2.923		2.09	0.999	0.004
			0.913 – 2.923	n-Decane/ 1-decanol (1:1 v/v)	2.61	0.970	0.060
				Kerosene/ 1-decanol (1:1 v/v)	2.37	0.960	0.060
Nicotinic acid	0.02 – 0.12	TOPO	0.10 – 0.60	n-Octane	2.68	0.982	0.01
				DCM	3.02	0.988	0.01
				Kerosene	3.27	0.975	0.02
				MIBK	4.59	0.921	0.05
				Toluene	5.03	0.976	0.03

5.2.2.3 Estimation of Parameters for Model based on μ and E_T

Different approaches have been used to quantify the effect of diluents on the 1:1 complexation of acid and extractant. Both the partition and self-association constants are strongly depends on the nature of the diluents. The thermodynamic activity of the species taking part in the organic phase equilibrium changes with the type of diluent. Attempts have been made to correlate the extraction efficiency in terms of K_{E} with solvent properties such as molecular mass, boiling point, density, refractive index, dielectric constant, dipole moment, and E_{T} parameter as discussed in section (4.1.4). For the extraction of nicotinic acid with TOPO, the values of K_{E} (Table 5.16) are correlated well with solvent dipole moment μ and the parameter E_{T}, which is based on the absorption spectrum of pyridinium-*N*-phenolbetaine. The available values of μ and E_{T} parameters for toluene (μ = 0.39 Debye; E_{T} = 33.9 kcal.mol^{-1}), octane (μ = 0.02 Debye; E_{T} = 31.1 kcal.mol^{-1}) and dichloromethane (μ = 1.80 Debye; E_{T} = 40.7 kcal.mol^{-1}) (Marcus, 1991) are used to predict the value of K_{E} and resulting correlation is given by Eq. (5.1):

$$K_{\mathrm{E}} = 1.9053\times10^{9}\,\mu^{0.3439}\,E_{\mathrm{T}}^{-5.5776} \qquad (5.1)$$

However, for similar type of diluents such as inerts (hexane and heptane) or aromatics (benzene and toluene), the extraction dependence on molar mass, boiling point, and specific gravity can also be made. An increase in molar mass, boiling point, and specific gravity hinders the dissolution of the acid-TOPO complex and hence lowers the equilibrium extraction coefficient. Hence, the correlation of K_{E} (Eq. 5.1) in terms of the solvent dipole moment (μ) and the absorption spectrum parameter (E_{T}) is very useful to quantify the effect of diluents on the extraction of nicotinic acid.

5.2.2.4 Estimation of ΔH and ΔS

The apparent enthalpy (*ΔH*) and entropy (*ΔS*) are estimated using calculated values of K_E at different temperatures (298, 313, 323 and 334 K) for the reactive extraction of propionic acid using TBP in *n*-decane/1-decanol (1:1 v/v).

The enthalpy and entropy of this process is assumed to be constant over the entire range of temperatures, and their values are estimated using Vant' Hoff Equation (Eq. 5.2) (Tamada and King, 1990c; Wisniewski and Pierzchalska, 2005)

$$\ln K_E = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5.2}$$

The slope and intercept of a plot of ln K_E vs $1/T$ give the apparent enthalpy and entropy of reactive extraction reaction respectively for extraction of propionic acid using TBP as shown in Figure 5.45. The results from Figure 5.45 indicate that the reactive extraction of propionic acid is exothermic as *ΔH* is found to be negative (-5.65 kJ mol^{-1}). Similarly, the entropy of the reaction is found to be -12.37 Jmol^{-1} K^{-1}. Based on Equation (5.1), more the exothermicity of the reaction, the more is the equilibrium sensitivity to temperature. Wisniewski and Pierzchalska (2005) also found the reactive extraction of mono-carboxylic acids using Cyanex$^{®}$921 exothermic in nature. Since the diluent system [n-decane/1-decanol (1:1 v/v)] is found better than that of kerosene/1-decanol (1:1 v/v) system based on equilibrium results, apparent enthalpy and entropy of reactive extraction reaction are calculated only for *n*-decane/1-decanol (1:1 v/v).

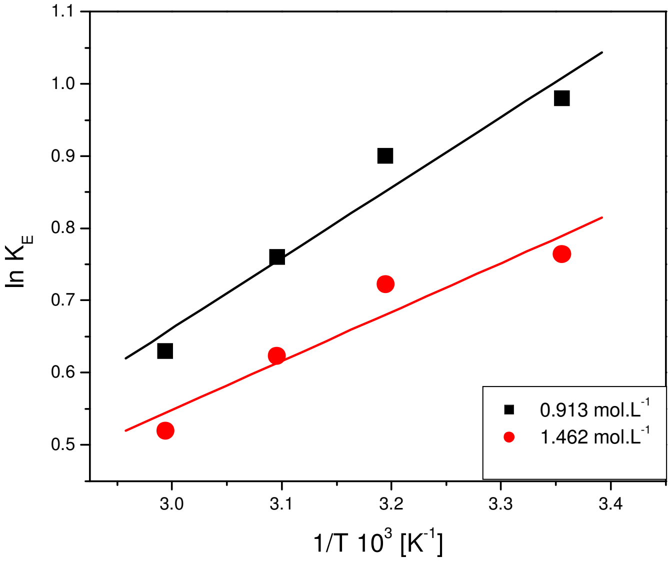

Figure 5.45. Determination of apparent enthalpy and entropy for reactive extraction of propionic acid with TBP (0.913 and 1.462 mol.L^{-1}) in n-decane/1-decanol (1:1 v/v)

5.3 Extraction using Amine-based Extractants

Long-chain aliphatic amines are found to be very effective as extractants for the separation of carboxylic acids from dilute aqueous solution. Compared to physical extraction with the conventional solvents such as alcohols, ketones, and ethers, the specific chemical interactions between amine and acid molecules form acid:amine complexes in the organic phase and allow more acid to be extracted from the aqueous phase. Among various categories of amines, tertiary amines are the most attractive solvents for the extraction of acids, due to their (1) low aqueous solubility, (2) intermediate basicity, (3) reasonable extracting power and (4) good stripping ability (King and Poole, 1991). Generally, these amine extractants are dissolved in a diluent such as ketone, alcohol, hydrocarbon, etc. that dilutes the extractant to desired concentration and also controls the viscosity and density of the organic phase. In the following sections (5.3.1 and 5.3.2), equilibrium and kinetic results (experimental, and simulation & modeling) for the extraction of carboxylic acids using amine-based extractants such as tri-n-octyl amine (TOA), Aliquat 336 and tri-n-dodecyl amine (TDA) dissolved in different diluents are presented.

5.3.1. Experimental Studies

In this study (Sections 5.3.1.1 – 5.3.1.6), the equilibrium experiments results are described for extraction of carboxylic acids (formic-, acetic-, propionic-, butyric- and nicotinic acid) using amine-based extractants (TOA, TDA and Aliquat 336) in different diluents (inert and active). The kinetic data for the extraction of propionic- and nicotinic acid using TOA are presented in Section 5.3.1.7.

5.3.1.1 Reactive Extraction of Mono-carboxylic Acids using TOA Dissolved in Different Diluents

In this section, the results obtained on the extraction equilibrium of C_1-C_4 mono-carboxylic acids (formic, acetic, propionic and butyric acid) from aqueous solutions with TOA are presented. TOA is used with six different diluents [1-decanol, chloroform, methyl isobutyl ketone, n-decane, benzene, and a mixture of 1-decanol and n-decane (1:3 v/v)]. The isotherms for all the acids are determined using different initial concentrations of aqueous solution and a constant concentration of TOA (0.46 mol.L^{-1}) dissolved in various diluents as shown in Figures 5.46-5.49. These isotherms are found to be almost linear with active diluents and slight non-linearity is prevailed with inert diluent (decane). This non ideal behavior (non-linearity in isotherms) is more pronounced in the extraction of formic acid due to higher acid concentrations used.

The equilibrium acid concentration in the organic phase increases with an increase in equilibrium acid concentration in the aqueous phase for the amine concentration (0.46 mol.L^{-1}) in the organic phase (Figures 5.47 – 5.49). As the concentration of the amine in the organic phase becomes lower (0.46 M TOA dissolved in different diluents) relative to formic acid concentrations (0.26 – 1.37 mol.L^{-1}), the organic phase concentration increases slowly with an increase in aqueous phase concentration. This indicates that amine concentration in the organic phase is the limiting reagent for the extraction of acid at its high concentrations in the aqueous phase.

In general, the degree of extraction depends on the type of diluent used. A polar diluent increases the extracting ability of relatively low polar amines (TOA). These provide additional solvating power that allows higher levels of polar-amine complexes to stay in the organic phase. On the other hand, a non-polar diluent does not affect the extraction process with low polar amines (TOA). Dipole moments and dielectric constants of diluents used, are given in Table 5.17. The values of acid strength (pK_a) and hydrophobicity (log P^a) of mono-carboxylic acids are given in Table 5.18. The results obtained for the extraction of formic, acetic, propionic and butyric acids (Tables 5.19-5.22) show that the polar diluents provides a higher extraction efficiency of TOA than the inert diluents. The extraction power of amine/diluent system in terms of loading ratios (Z) or distribution coefficient (K_D) increases in the order of chloroform ≥ 1-decanol > methyl isobutyl ketone > benzene > decane+1-decanol (3:1 v/v) > decane. The synergistic extraction power of amine/alcohol system is remarkably higher due to the simultaneous effect of the physical extraction and chemical interaction through hydrogen bonding. Carboxylic acids are physically more easily extracted by the protic diluent alone (1-decanol) as compared to others (as discussed in section 5.1), whereas the magnitude of the acid-amine complexation is found larger for chlorinated hydrocarbon diluent. Chloroform affects the diluent-complex aggregation more readily through hydrogen bonding and dipole-dipole interaction than the amine-free diluent-acid association. This phenomenon of chloroform is confirmed by a maximum value of loading ratio. However, in the extraction of formic acid, the extraction power of MIBK is found to be the maximum (more than that of 1-decanol and chloroform) at very high concentrations of acid. The values of Z in the range of 0.05 – 0.84 for propionic acid (Table 5.21), and in the range of 0.15 – 1.21 for butyric acid (Table 5.22) suggest simultaneous formation of 1:1 and 2:1 complexes between the acid and amine. The values of Z in the range of 0.0 – 0.5 for acetic acid (Table 5.20) suggest the formation of 1:1 complexes between the acid and amine.

In case of formic acid extraction (Table 5.19), 1:1, 2:1 and 3:1 complexes are possible with high values of loading ratios (0.15 – 2.55).

As indicated by the loading of TOA (Tables 5.20 – 22), the degree of extraction increases in the order of butyric acid > propionic acid > acetic acid. Wang *et al.,* (2001) investigated the same trend for extraction equilibria of aqueous solutions of formic acid, acetic acid, propionic acid, butyric acid with trialkylphosphine oxide in kerosene. Higher chain carboxylic acid has more hydrophobicity (Table 5.18) and can be extracted better. The equilibrium pH is different from the initial pH because of the removal of acid and extractant (amine) dissolved in the aqueous phase. The dependence of pH is not obvious, especially for the acetic, propionic and butyric acid having approximate equal pK_a. The hydrophobicity of the solute is the key aspect because of the similar molecular structures and close pK_a values for the carboxylic acids (acetic, propionic and butyric acid). Since concentrations of formic acid is the higher than those of other acids, the loading of TOA with the same diluents is found to be more even though hydrophobicity of acid is less.

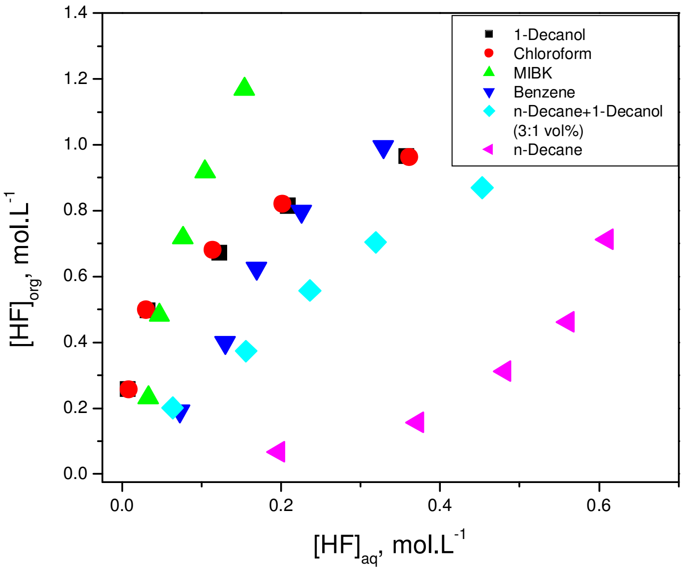

Figure 5.46 Equilibrium isotherms of formic acid for TOA (0.46 mol.L^{-1}) dissolved in different diluents

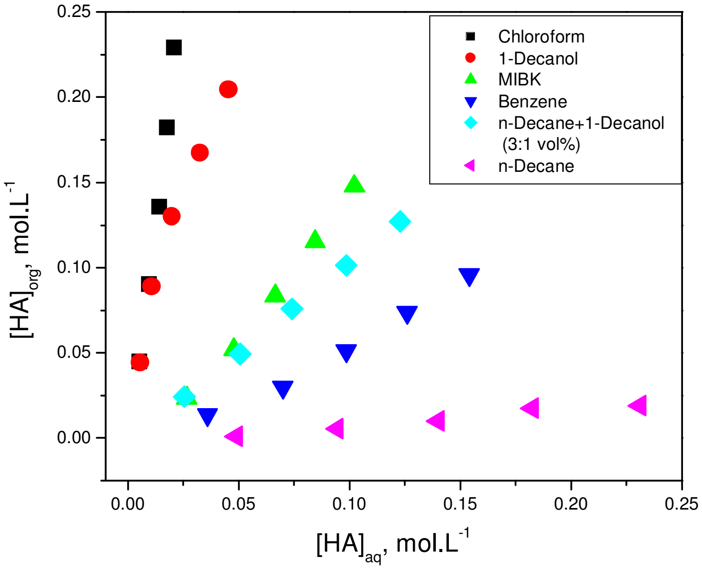

Figure 5.47 Equilibrium isotherms of acetic acid for TOA (0.46 mol.L^{-1}) dissolved in different diluents

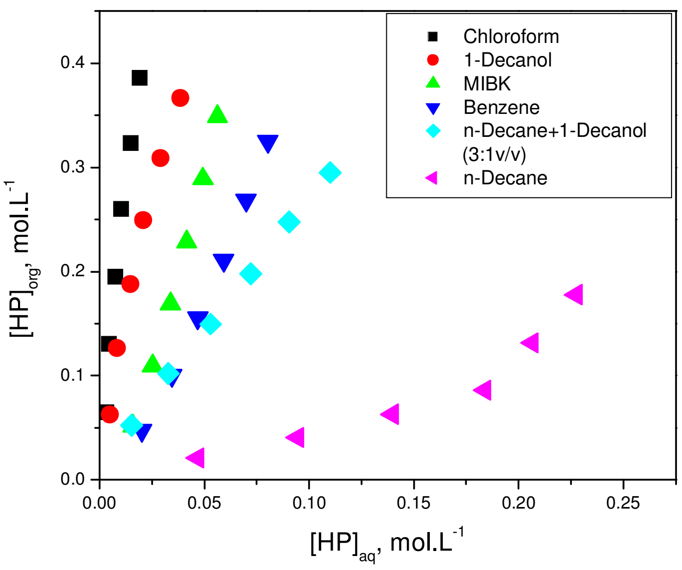

Figure 5.48 Equilibrium isotherms of propionic acid for TOA (0.46 mol.L^{-1}) dissolved in different diluents

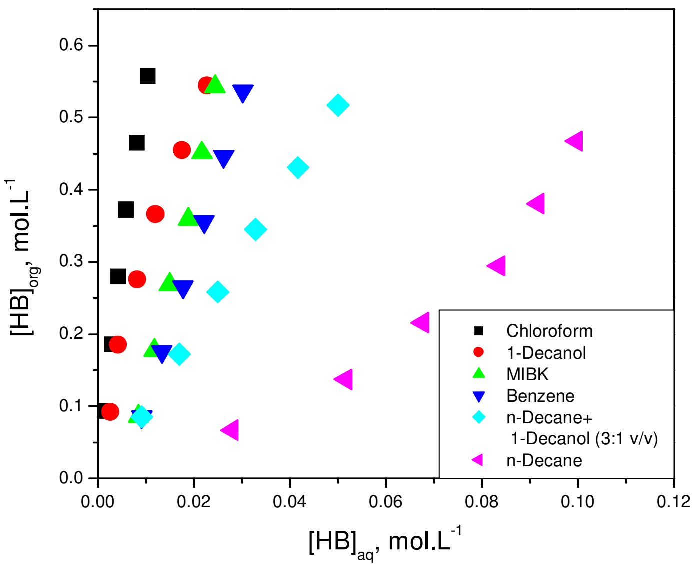

Figure 5.49 Equilibrium isotherms of butyric acid for TOA (0.46 mol.L^{-1}) dissolved in different diluents

Table 5.17. Dielectric constant (ε) and dipole moment (μ) of diluents

S.No.	Component	ε	μ, (D)
1	n-decane	1.90	0.01
2	1-decanol	7.8	2.62
3	Benzene	2.80	0.0
4	MIBK	13.1	2.79
5	chloroform	4.81	1.01

Table 5.18. Physical properties of carboxylic acids

Carboxylic acid	pK_a	Hydrophobicity
Formic acid	3.75	-0.538
Acetic acid	4.74	-0.313
Propionic acid	4.87	0.29
Butyric acid	4.81	0.82

Table 5.19. Equilibrium results for the extraction of formic acid using TOA ($0.46\ \mathrm{mol.L^{-1}}$) dissolved in different diluents at 298 K

Diluent	C_{HF} $\mathrm{mol.L^{-1}}$	$\overline{C}_{\mathrm{HF}}$ $\mathrm{mol.L^{-1}}$	$K_{D,\ exp}$	$K_{D,\ pred}$	E	Z_{exp}	Z_{pred}	$p\mathrm{H_{eq}}$
1-Decanol	0.007	0.257	36	10.59	97.3	0.56	0.16	3.15
	0.032	0.497	15.3	15.01	93.87	1.08	1.06	2.82
	0.123	0.671	5.47	5.98	84.55	1.46	1.6	2.53
	0.209	0.814	3.89	3.63	79.57	1.77	1.65	2.41
	0.358	0.966	2.7	2.15	72.98	2.1	1.67	2.3
Decane	0.197	0.068	0.34	0.19	25.59	0.15	0.08	2.43
	0.372	0.157	0.42	0.5	29.74	0.34	0.41	2.29
	0.482	0.312	0.65	0.68	39.3	0.68	0.71	2.23
	0.561	0.462	0.82	0.78	45.16	1.01	0.95	2.2
	0.611	0.713	1.17	0.82	53.85	1.55	1.1	2.18
Benzene	0.073	0.192	2.64	2.15	72.56	0.42	0.34	2.64
	0.13	0.399	3.08	3.43	75.47	0.87	0.97	2.52
	0.169	0.624	3.69	3.66	78.66	1.36	1.35	2.46
	0.226	0.798	3.54	3.5	77.96	1.74	1.72	2.4
	0.329	0.994	3.02	2.87	75.14	2.17	2.06	2.32
Chloroform	0.009	0.256	29.1	11.43	96.67	0.56	0.22	3.1
	0.031	0.498	16.2	15.37	94.18	1.09	1.03	2.83
	0.114	0.679	5.94	6.52	85.59	1.48	1.63	2.55
	0.202	0.821	4.05	3.83	80.22	1.79	1.69	2.42
	0.362	0.961	2.66	2.18	72.65	2.09	1.72	2.3
MIBK	0.033	0.232	7.02	7.14	87.53	0.5	0.51	2.82
	0.047	0.482	10.2	9.32	91.06	1.05	0.96	2.74
	0.077	0.717	9.31	9.84	90.3	1.56	1.65	2.63
	0.105	0.919	8.79	8.65	89.78	2	1.97	2.57
	0.154	1.169	7.59	6.56	88.36	2.55	2.2	2.48
Decane + 1-Decanol (3:1 v/v)	0.064	0.201	3.15	2.23	75.89	0.44	0.31	2.67
	0.156	0.373	2.39	2.76	70.48	0.81	0.94	2.48
	0.237	0.557	2.36	2.45	70.21	1.21	1.26	2.39
	0.319	0.704	2.21	2.08	68.82	1.53	1.44	2.32
	0.453	0.87	1.92	1.61	65.74	1.89	1.59	2.25

Table 5.20. Equilibrium results for the extraction of acetic acid using TOA ($0.46\ mol.L^{-1}$) dissolved in different diluents at 298 K

Diluent	C_{HA} $mol.L^{-1}$	$\overline{C}_{HA}$ $mol.L^{-1}$	$K_{D, exp}$	$K_{D, pred}$	E	Z_{exp}	Z_{pred}	pH_{eq}
1-Decanol	0.0056	0.0444	7.929	8.4	88.8	0.1	0.1	3.75
	0.01085	0.0892	8.217	7.59	89.2	0.19	0.18	3.6
	0.01995	0.1301	6.519	6.5	86.7	0.28	0.28	3.47
	0.03255	0.1674	5.144	5.43	83.7	0.36	0.39	3.36
	0.0455	0.2045	4.495	4.65	81.8	0.45	0.46	3.29
Decane	0.049	0.001	0.02	0.03	2.0	0	0	3.27
	0.0945	0.0055	0.058	0.05	5.5	0.01	0.01	3.13
	0.14	0.01	0.071	0.07	6.67	0.02	0.02	3.05
	0.18248	0.0175	0.096	0.08	8.76	0.03	0.03	2.99
	0.231	0.019	0.082	0.1	7.6	0.04	0.05	2.94
Benzene	0.03605	0.014	0.387	0.36	27.9	0.03	0.03	3.34
	0.07	0.03	0.429	0.47	30	0.07	0.07	3.2
	0.0987	0.0513	0.52	0.53	34.2	0.11	0.11	3.12
	0.12612	0.0739	0.586	0.57	36.9	0.16	0.16	3.07
	0.154	0.096	0.623	0.6	38.4	0.21	0.2	3.03
Chloroform	0.00525	0.0448	8.524	8.37	89.5	0.1	0.1	3.76
	0.0098	0.0902	9.204	9.63	90.2	0.2	0.21	3.62
	0.01435	0.1357	9.453	10	90.4	0.3	0.31	3.54
	0.01772	0.1823	10.29	9.99	91.1	0.4	0.39	3.5
	0.021	0.229	10.91	9.87	91.6	0.5	0.45	3.46
MIBK	0.0266	0.0234	0.88	0.86	46.8	0.05	0.05	3.41
	0.04795	0.0521	1.086	1.12	52.1	0.11	0.12	3.28
	0.0665	0.0835	1.256	1.26	55.7	0.18	0.18	3.21
	0.08457	0.1154	1.365	1.36	57.7	0.25	0.25	3.16
	0.1022	0.1478	1.446	1.42	59.1	0.32	0.32	3.12
Decane + 1-Decanol (3:1 v/v)	0.02555	0.0245	0.957	0.94	48.9	0.05	0.05	3.42
	0.05075	0.0493	0.97	1.01	49.3	0.11	0.11	3.27
	0.0742	0.0758	1.022	1.02	50.5	0.17	0.17	3.18
	0.09856	0.1014	1.029	1.02	50.7	0.22	0.22	3.12
	0.12285	0.1272	1.04	1.00	50.9	0.28	0.27	3.08

Table 5.21. Equilibrium results for the extraction of propionic acid using TOA ($0.46\ \mathrm{mol.L^{-1}}$) dissolved in different diluents at 298 K

Diluent	C_{HP} mol.L^{-1}	$\overline{C}_{\mathrm{HP}}$ mol.L^{-1}	$K_{D,\,exp}$	$K_{D,\,pred}$	E	Z_{exp}	Z_{pred}	$p\mathrm{H}_{\mathrm{eq}}$
1-Decanol	0.005	0.063	12.87	14.05	92.79	0.14	0.15	3.89
	0.008	0.127	14.98	14.21	93.74	0.28	0.26	3.77
	0.015	0.188	12.74	13.2	92.72	0.41	0.42	3.65
	0.021	0.249	11.98	11.97	92.3	0.54	0.54	3.58
	0.029	0.309	10.55	10.41	91.34	0.67	0.66	3.5
	0.039	0.366	9.472	9	90.45	0.8	0.76	3.44
Decane	0.047	0.021	0.44	0.38	30.77	0.05	0.04	3.4
	0.095	0.04	0.43	0.46	29.94	0.09	0.1	3.25
	0.14	0.063	0.45	0.51	31.07	0.14	0.15	3.16
	0.184	0.086	0.47	0.53	31.87	0.19	0.21	3.1
	0.207	0.131	0.64	0.54	38.9	0.29	0.24	3.08
	0.228	0.178	0.78	0.54	43.83	0.39	0.27	3.06
Benzene	0.02	0.047	2.35	2.21	70.19	0.1	0.1	3.58
	0.034	0.101	2.92	2.98	74.48	0.22	0.22	3.47
	0.047	0.156	3.32	3.39	76.84	0.34	0.35	3.4
	0.059	0.211	3.56	3.63	78.09	0.46	0.47	3.35
	0.07	0.268	3.84	3.73	79.33	0.58	0.57	3.31
	0.08	0.325	4.05	3.77	80.18	0.71	0.66	3.28
Chloroform	0.003	0.064	19.8	24.73	95.19	0.14	0.16	3.98
	0.005	0.13	28.67	26.42	96.63	0.28	0.26	3.91
	0.008	0.195	25.91	26.41	96.28	0.42	0.43	3.8
	0.01	0.26	24.96	25	96.15	0.57	0.57	3.73
	0.015	0.323	21.83	22.31	95.62	0.7	0.72	3.65
	0.019	0.386	20.12	19.82	95.27	0.84	0.83	3.59
MIBK	0.016	0.052	3.24	3.13	76.44	0.11	0.11	3.63
	0.025	0.11	4.33	4.32	81.22	0.24	0.24	3.53
	0.034	0.169	4.99	5.06	83.3	0.37	0.37	3.47
	0.042	0.228	5.49	5.5	84.59	0.5	0.5	3.43
	0.049	0.289	5.86	5.77	85.43	0.63	0.62	3.39
	0.056	0.349	6.2	5.9	86.12	0.76	0.72	3.36
Decane + 1-Decanol (3:1)	0.015	0.052	3.43	3.26	77.4	0.11	0.11	3.64
	0.033	0.102	3.11	3.21	75.69	0.22	0.23	3.48
	0.053	0.15	2.82	3	73.85	0.33	0.35	3.37
	0.072	0.198	2.74	2.77	73.28	0.43	0.44	3.31
	0.091	0.248	2.73	2.56	73.22	0.54	0.51	3.26
	0.11	0.295	2.68	2.37	72.84	0.64	0.57	3.21

Table 5.22. Equilibrium results for the extraction of butyric acid using TOA (0.46 mol.L^{-1}) dissolved in different diluents at 298 K

Diluent	C_{HB} mol.L^{-1}	$\overline{C}_{\mathrm{HB}}$ mol.L^{-1}	$K_{D,\,exp}$	$K_{D,\,pred}$	E	Z_{exp}	Z_{pred}	$p\mathrm{H}_{\mathrm{eq}}$
1-Decanol	0.003	0.092	35.3	37.06	97.25	0.2	0.21	4.0
	0.004	0.185	43.7	39.14	97.76	0.4	0.36	3.89
	0.008	0.275	33.6	35.89	97.11	0.6	0.64	3.75
	0.012	0.366	30.4	31.06	96.82	0.8	0.81	3.66
	0.017	0.455	26	25.28	96.3	0.99	0.96	3.58
	0.023	0.544	23.9	21.17	95.99	1.19	1.05	3.53
Decane	0.028	0.067	2.38	1.81	70.42	0.15	0.11	3.48
	0.052	0.137	2.66	2.93	72.66	0.3	0.33	3.35
	0.068	0.216	3.19	3.42	76.14	0.47	0.5	3.29
	0.084	0.294	3.53	3.71	77.9	0.64	0.68	3.24
	0.092	0.381	4.15	3.8	80.59	0.83	0.76	3.22
	0.1	0.467	4.68	3.85	82.41	1.02	0.84	3.21
Benzene	0.009	0.085	9.38	11.97	90.37	0.19	0.23	3.73
	0.013	0.176	13.2	15.74	92.95	0.38	0.46	3.64
	0.018	0.266	15	17.72	93.76	0.58	0.68	3.58
	0.022	0.356	16.1	18.53	94.15	0.78	0.89	3.53
	0.026	0.446	17	18.55	94.45	0.97	1.06	3.5
	0.03	0.537	17.8	18.19	94.67	1.17	1.2	3.46
Chloroform	0.002	0.093	57.2	54.44	98.28	0.2	0.19	4.1
	0.003	0.186	63.6	65.47	98.45	0.41	0.42	3.97
	0.004	0.279	66.2	67	98.51	0.61	0.62	3.89
	0.006	0.372	63.6	63.68	98.45	0.81	0.81	3.82
	0.008	0.464	57	56.41	98.27	1.01	1	3.75
	0.01	0.557	53.5	49.59	98.17	1.21	1.12	3.7
MIBK	0.008	0.086	10.2	11.45	91.06	0.19	0.21	3.74
	0.012	0.177	15.2	15.35	93.81	0.39	0.39	3.67
	0.015	0.269	18	18.19	94.74	0.59	0.59	3.62
	0.019	0.359	19.1	20.3	95.01	0.78	0.83	3.57
	0.022	0.451	20.8	21.05	95.41	0.98	0.99	3.54
	0.024	0.543	22.3	21.32	95.7	1.18	1.13	3.51
Decane + 1-Decanol (3:1)	0.009	0.085	9.38	8.51	90.37	0.19	0.17	3.73
	0.017	0.172	10.2	10.48	91.06	0.38	0.39	3.59
	0.025	0.259	10.4	10.9	91.19	0.56	0.59	3.51
	0.033	0.345	10.5	10.61	91.32	0.75	0.76	3.45
	0.042	0.431	10.3	9.98	91.18	0.94	0.91	3.39
	0.05	0.517	10.3	9.28	91.17	1.13	1.01	3.36

5.3.1.2 Reactive Extraction of Propionic Acid using TOA Dissolved in Inert Diluent and 1-Decanol (Modifier)

In this section (5.3.1.2), results obtained on extraction of propionic acid with TOA dissolved in an inactive diluent and a modifier, are presented. Diluents chosen in the study are *n*-decane, *n*-dodecane, kerosene and toluene from inactive chemical class, and 1-decanol as a modifier from active chemical class to examine the effect of diluent-complex interactions.

The effect of the concentration of 1-decanol on the degree of extraction of propionic acid (0.405 mol.L^{-1}) is first studied. The organic phase is composed of extractant (TOA), a modifier (1-decanol), and an inert diluent (toluene, kerosene and cyclohexane). The TOA concentration is fixed at 20% v/v (0.46 mol.L^{-1}). Figure 5.50 illustrates the effect of 1-decanol on the extraction of propionic acid with different inert diluents. The higher concentrations of modifier (1-decanol) lead to an increase in the extraction efficiency (degree of extraction) of acid. There is a very strong modifier effect on the degree of extraction, when kerosene or cyclohexane is used as an inert diluent. Toluene used as a diluent show less effect of modifier due to its structure having π aromatic system. No significant change is found in the volumes of organic phase and aqueous phase after their separation. The values of estimated equilibrium constant (K_E) and stoichiometry (n) depends not only on the concentration of modifier in the presence of inert diluent, but also on the volume phase ratio between modifier and diluent (Flores-Morales *et al.,* 2003). The volume phase ratio between modifier and diluent is taken one in this study.

The isotherms for propionic acid are obtained from different aqueous solution concentrations (0.0675 – 0.676 mol.L^{-1}), at a constant concentration of TOA (0.46 mol. L^{-1})

dissolved in toluene & 1-decanol (1:1 v/v), kerosene & 1-decanol (1:1 v/v), and cyclohexane & 1-decanol (1:1 v/v) and the results are presented in Figure 5.51. Almost linear relationship is found between acid concentration in the two phases at equilibirum, and slightly nonlinear relationship for higher concentrations due to Henry's law type isotherm is only valid for low acid concentration range.

Figure 5.52 shows the experimental data for the system having toluene, cyclohexane and kerosene as the inert diluents and 1-decanol as a modifier. There is a significant increase in the degree of extraction (%) for an increase in TOA concentration up to 30 %. For the TOA concentration higher than 30 %, an insignificant increase in extraction efficiency is found with all combinations of inert diluent/1-decanol mixture. From Figure 5.53, the degree of extraction decreases significantly when the concentration of propionic acid is increased from 0.0675 to 0.203 mol.L^{-1} in all cases of inert diluent/1-decanol (1:1 v/v) system. At the higher range concentrations of propionic acid, the concentration of extractant (TOA) may be limiting factor for the extraction of propionic acid.

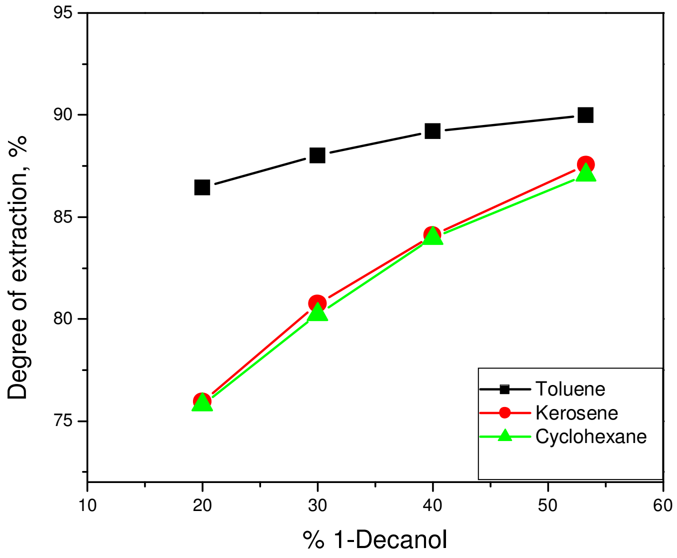

Figure 50. Influence of modifier (1-decanol, %) in the organic phase on degree of extraction with 20% TOA at initial propionic acid concentration of 0.405 mol.L^{-1}.

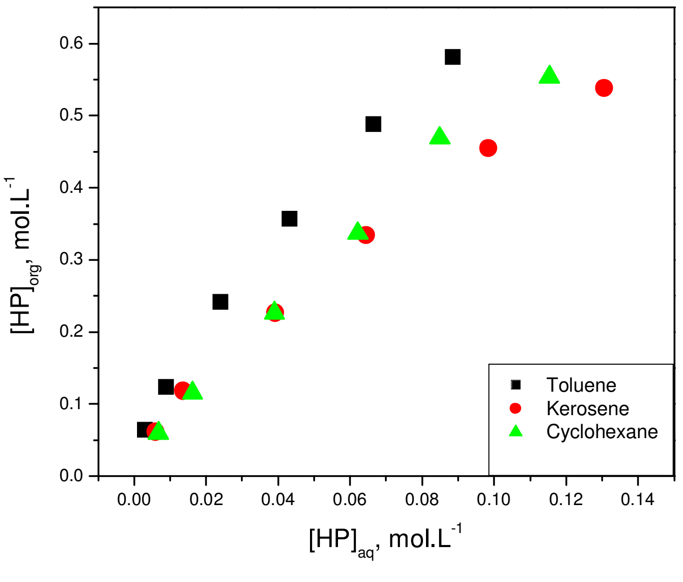

Figure 5.51 Equilibrium isotherms of propionic acid for different inert diluent with 1-decanol (1:1 v/v) at constant TOA concentration (0.46 mol.L^{-1})

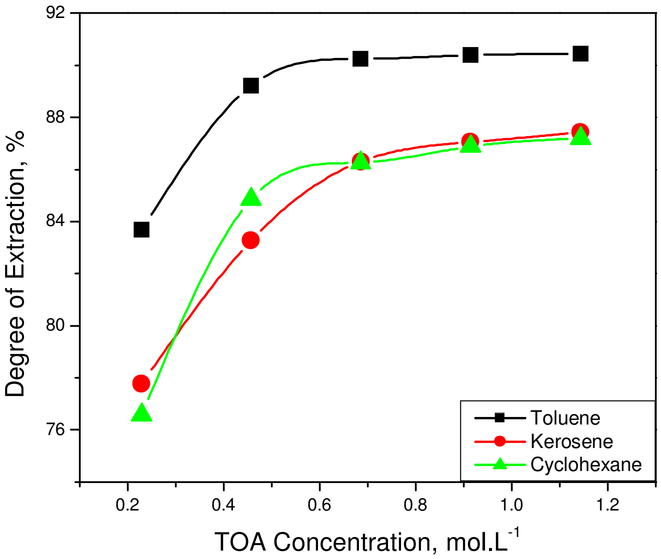

Figure 5.52 Effect of TOA concentrations on degree of extraction for different inert diluent with 1-decanol (1:1 v/v) at constant propionic acid concentration (0.405 mol.L^{-1})

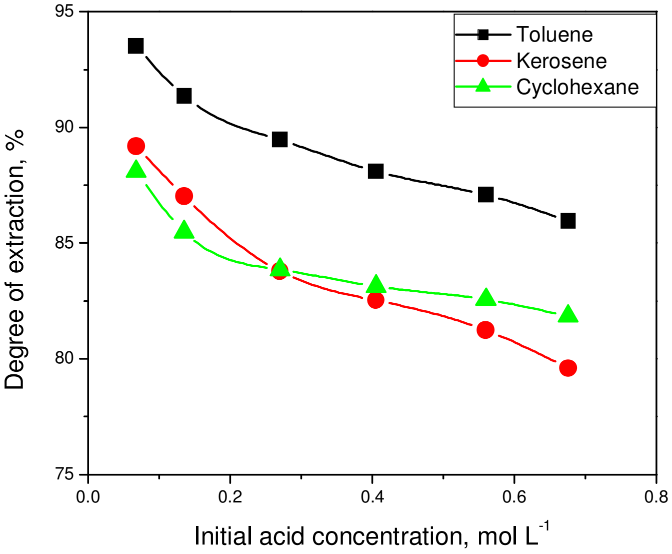

Figure 5.53 Effect of initial acid concentrations on degree of extraction for different inert diluent with 1-decanol (1:1 v/v) at constant TOA concentration (0.46 mol.L^{-1})

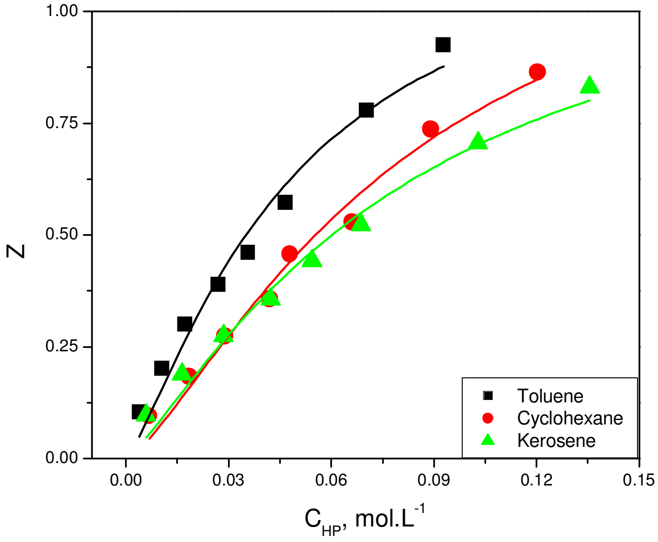

Figure 5.54 Variation of loading ratio with aqueous phase propionic acid concentration, using TOA (0.46 mol.L^{-1}) in different inert diluents/1-decanol (1:1 v/v). (points: experimental results; solid line: modeled results by Eq. 4.49)

The effect of 1-decanol on extraction efficiency is found to be significant with inert diluents. The viscosity of 1-decanol is very high as compared to inactive diluents such as toluene, cyclohexane and kerosene. Hence, the equal volume mixture of inert diluent (toluene, cyclohexane and kerosene) and 1-decanol is used to estimate the equilibrium extraction constant (K_E) and the stoichiometries of extraction reaction. 20% of TOA as an extractant composition is used for the extraction of propionic acid in the range of 0.0675 – 0.676 mol.L^{-1}. The equilibrium results for all diluent systems at constant extractant (TOA) composition of 0.46 mol.L^{-1} are presented in Table 5.23 and Figures 5.51 & 5.54. From Figure 5.54, it is observed that the loading ratio (Z), corresponding to different acid concentrations at constant TOA concentration, reaches towards a plateau. It contemplates a tendency towards the formation of two types of complex structures, i.e., multiple acid per one amine ($n < m$) aggregation, or an equimolar structure ($m = n$). This fact seems to be a common strategy for designing the amine extraction of propionic acid. The effect is more pronounced in the case of toluene used as an inert diluent with 1-decanol, affecting more readily the diluent-complex aggregation through dipole-dipole interaction. The comparably lower solvation degree is found for other tested inert solvents (kerosene and cyclohexane). Hence, the synergistic extraction power (Z) of the amine/diluent system reflects the simultaneous effect of chemical interaction and solvation ability of diluent.

Table 5.23. Equilibrium results for the extraction of propionic acid using TOA (0.46 mol.L^{-1}) dissolved in inert diluent and 1-decanol (1:1 v/v) at 298 K

Diluent system	C_{HP} / mol.L^{-1}	$\overline{C}_{HP}$ / mol.L^{-1}	$K_{D, exp}$	$K_{D, pred}$	E	Z	pH$_{eq}$
Toluene + 1-decanol	0.004	0.063	14.40	11.16	93.51	0.138	3.92
	0.012	0.123	10.60	11.78	91.35	0.27	3.88
	0.028	0.242	8.48	9.70	89.46	0.529	3.63
	0.048	0.357	7.41	7.53	88.1	0.781	3.42
	0.072	0.488	6.75	5.80	87.09	1.067	3.31
	0.095	0.581	6.12	4.74	85.96	1.272	3.22
Kerosene + 1-decanol	0.007	0.060	8.25	6.84	89.19	0.132	4.22
	0.018	0.117	6.71	7.14	87.02	0.257	3.74
	0.044	0.226	5.16	5.95	83.78	0.495	3.43
	0.071	0.334	4.72	4.80	82.52	0.731	3.36
	0.105	0.455	4.33	3.78	81.23	0.995	3.2
	0.138	0.538	3.90	3.12	79.59	1.177	3.12
Cyclohexane + 1-decanol	0.008	0.059	7.41	5.54	88.1	0.13	4.12
	0.02	0.115	5.89	6.44	85.48	0.253	3.68
	0.044	0.226	5.19	6.00	83.85	0.495	3.44
	0.068	0.337	4.93	5.12	83.13	0.737	3.37
	0.091	0.469	5.14	4.42	83.71	1.026	3.24
	0.123	0.553	4.50	3.67	81.83	1.211	3.18

Reactive Extraction of Propionic Acid using TOA Dissolved in n-Dodecane and 1-Decanol

Most organic solvents are toxic to microorganisms to some extent. The presence of an organic solvent can damage the cell membrane, causing membrane rupture and metabolite leakage. For various solvent microorganism combinations, Osborne *et al.,* (1990) found that above a critical solvent concentration in the cell membrane, the cell membrane fluidity is increased and cellular activity is declined. Rapid loss of cellular catalytic activity can also result due to the high surface tension of the solvent (Yabannavar and Wang, 1987). The solvent interacts with the cell by two routes: (1) dissolution in the aqueous broth called molecular toxicity and (2) direct contact of the cell with the water-immiscible solvent phase called phase toxicity (Bassetti and Tramper, 1994). Molecular toxicity usually causes less damage to the cell than the phase toxicity because the former is limited by solvent solubility in the aqueous phase. In phase level toxicity, cell growth is inhibited by the soluble portion of the solvent and the presence of two phase systems. There are two methods to reduce solvent toxicity in an extractive fermentation process. One is replacement of the toxic solvent component with a nontoxic one and the other is addition of an immiscible, biocompatible component to the medium to entrap any toxic solvent dissolved in the aqueous phase (Yabannavar and Wang, 1991b).

It was observed that TOA exhibits symptoms of molecular level toxicity at 10% saturation level and phase level toxicity even at a low phase ratio (aqueous:organic). The toxicity study reveals that n-dodecane (nontoxic) is the most suitable diluent for the simultaneous extraction of propionic acid during fermentation. However 1-decanol could also be used which provides a low phase level toxicity. As mentioned earlier, the selectivity of the solvents for propionic acid is also an important factor in the simultaneous extraction.

The first step in this study of propionic acid extraction is the optimization of the composition of the organic phase which is suitable for extractive fermentation.

Three combinations of extractant-diluent system are prepared: (1) inert diluent (n-dodecane) + TOA, (2) 1-decanol + TOA and (3) n-dodecane + modifier (1-decanol) + TOA. The concentration of propionic acid in the aqueous phase is varied from 0.0675 - 0.675 mol.L^{-1}. The equilibrium extraction experiments are carried out with TOA dissolved in both, n-dodecane and 1-decanol at different concentrations of propionic acid and results are shown in Figures 5.55 and 5.56. The results (Figure 5.55) indicate that the extraction of acid increases with an increase in TOA concentration when it is dissolved in inert diluent (n-dodecane). The degree of extraction first increases and reaches a maximum value, afterwards it decreases with an increase in the concentration of TOA dissolved in 1-decanol (Figure 5.56). Hence, 1-decanol (a protic diluent) may have interactions with TOA:acid complexes and at high acid concentration, TOA concentration is the limiting parameter for a decrease in the degree of extraction. The initial concentration of propionic acid also affects the extraction efficiency of TOA dissolved in both the diluents (Figures 5.55 and 5.56). Since the salvation of acid in the inert diluent (n-dodecane) is increased with an increase in the concentration of propionic acid from 0.135 to 0.405 mol.L^{-1}, degree of extraction (%) significantly increases in case of TOA dissolved in n-dodecane. In case of TOA dissolved in 1-decanol, the degree of extraction (%) is found to significantly decrease for an increase in the concentration of acid. Different concentrations of extractant (TOA) are used to derive the effect of initial acid concentration on extraction efficiency.

The experimental results presented in Figures 5.57 and 5.58, show that the degree of extraction of TOA increases with an increase in the concentration of 1-decanol in the mixture of diluents (n-dodecane and 1-decanol). The effect of 1-decanol on extraction efficiency is found to be more significant with 20% of TOA. Different concentrations of propionic acid are also used to derive the effect of modifier in the diluent mixture. It is obvious that the distribution coefficient or degree of extraction increases with an increase in the polarity of the modifier, while the influence of the inactive diluent is negligible. Although the extraction by the systems with pentanol, hexanol and octanol may be more effective, it is decided to use 1-decanol as a modifier in this study. Pentanol, hexanol and 1-octanol are more toxic for the microorganism. It is known that the toxicity of alcohols to the bacteria decreases with an increase in the length of alkyl chain, and the *n*-alkanes are practically non-toxic (Playne and Smith, 1983; Martak *et al.,* 1997). On the basis of toxicity 20% and 30% of 1-decanol in the organic mixture is used for the extraction of propionic acid with different concentrations of TOA as shown in Figure 5.59. The results presented in Figure 5.59 show that the extraction improves with an increase in the percentage of TOA. This improvement in the extraction efficiency is more significant up to 30% (0.69 mol.L^{-1}) of TOA. Since, n-dodecane is non-toxic for the bacteria in contrast to 1-decanol it is decided to continue with the extraction systems composed of (1) 20% TOA, 20% 1-decanol and 60% n-dodecane, (2) 20% TOA, 30% 1-decanol and 50% n-dodecane, and (3) 30% TOA, 20% 1-decanol and 50% n-dodecane. The isotherms of propionic acid in both phases for these extraction systems are given in Figures 5.60 and 5.61. This system combines a sufficiently low concentration of the modifier with an acceptable value of the distribution coefficient. With these experiments, the loading ratios for the complete range of propionic acid concentration, found in the range of 0.113 – 1.05 (Table 5.26) indicate that 1:1 and 2:1 complexes between acid and TOA are formed simultaneously.

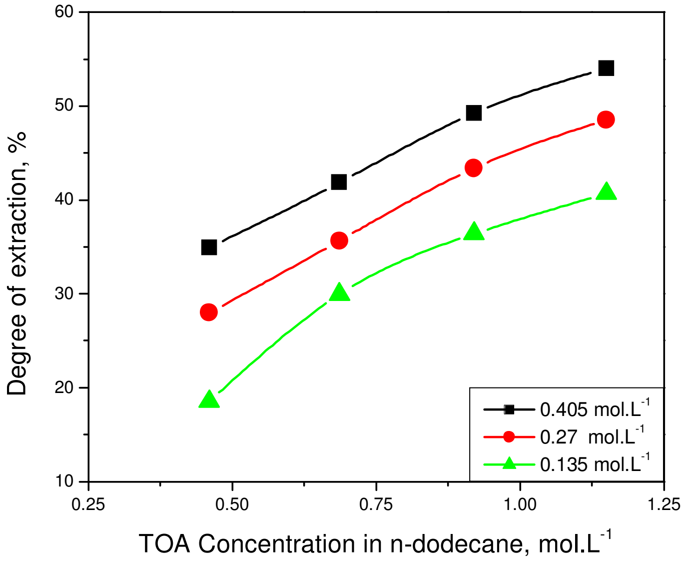

Figure 5.55 Effect of TOA concentration in n-dodecane on degree of extraction at different propionic acid concentration

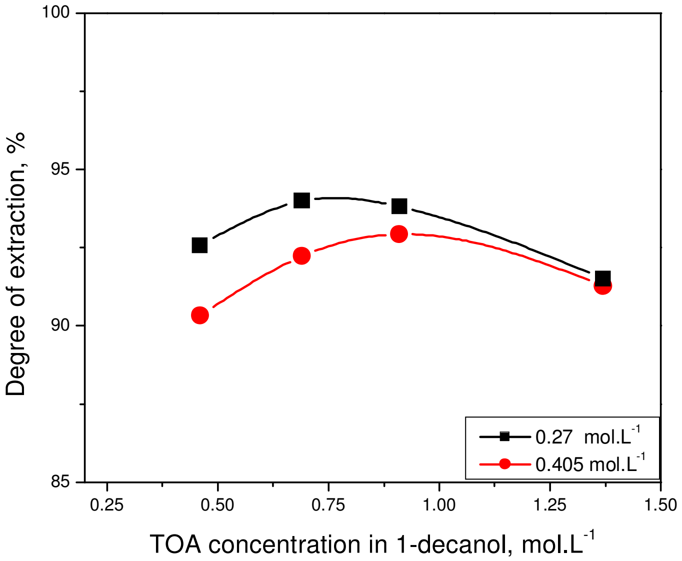

Figure 5.56 Effect of TOA concentration in 1-decanol on degree of extraction at two propionic acid concentration

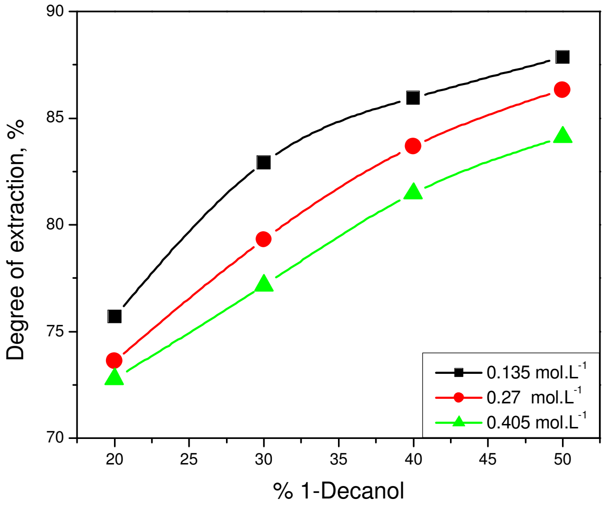

Figure 5.57 Influence of modifier (1-decanol) in organic phase on degree of extraction with 20% of TOA at different concentrations of propionic acid

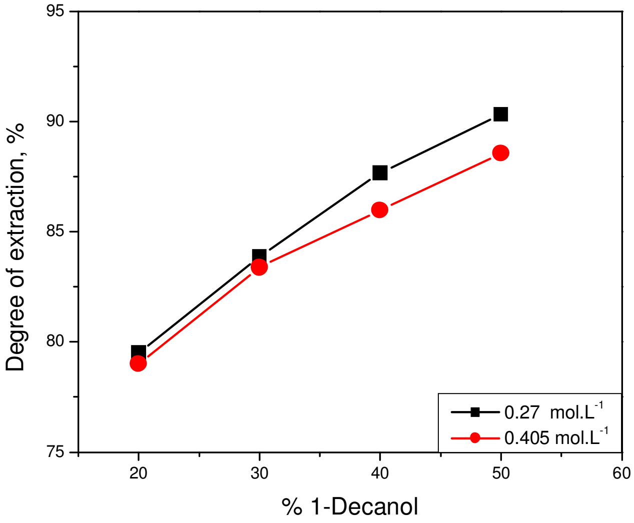

Figure 5.58 Influence of modifier (1-decanol) in organic phase on degree of extraction with 30% of TOA at different concentrations of propionic acid

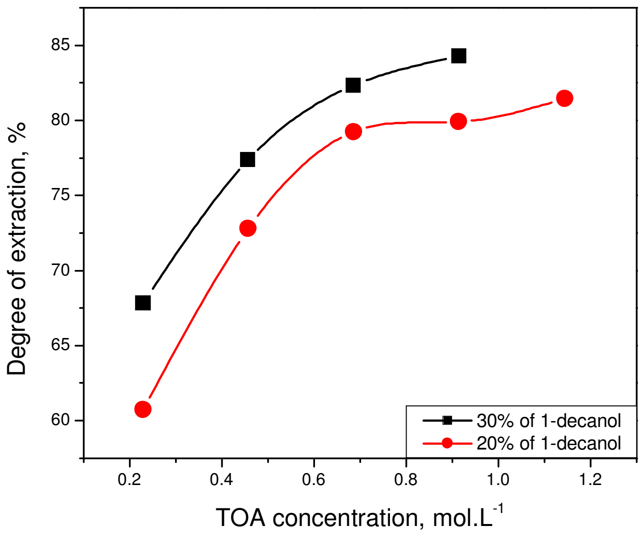

Figure 5.59 Effect of TOA concentrations on the degree of extraction with different concentrations of 1-decanol at propionic acid concentration of 0.405 mol.L^{-1}.

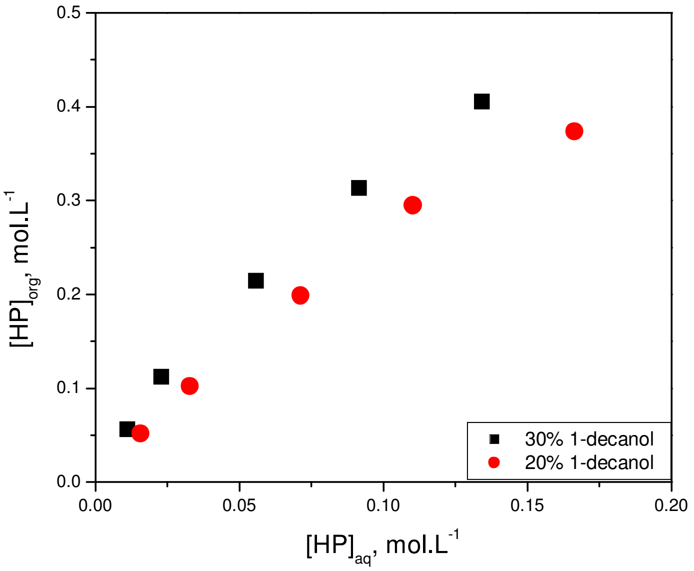

Figure 5.60 Equilibrium isotherms of propionic acid for different concentrations of 1-decanol in mixture of n-dodecane + 1-decanol + TOA (20%)

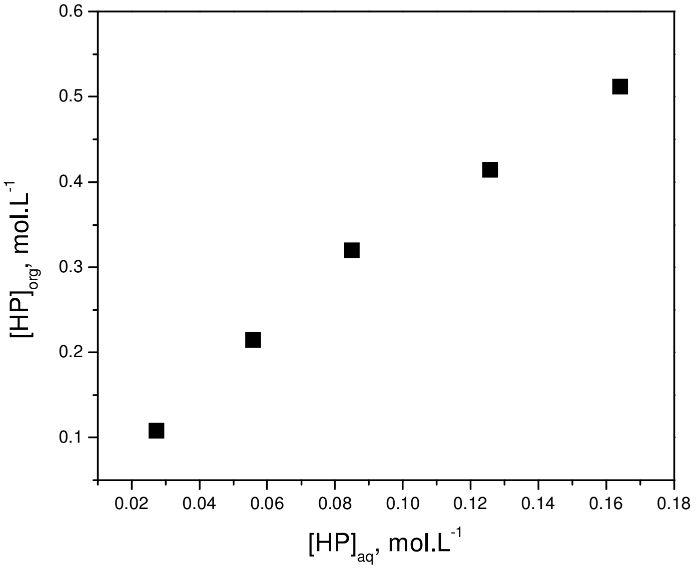

Figure 5.61 Equilibrium isotherms of propionic acid for an extractant/diluent system

[TOA (30%) + n-dodecane (30%) + 1-decanol (20%)]

Table 5.24. Equilibrium results for the extraction of propionic acid using TOA dissolved in n-dodecane and 1-decanol at 298 K

Extractant/Diluent system	C_{HP} **(mol.L^{-1})**	$\overline{C}_{\mathrm{HP}}$ **(mol.L^{-1})**	$K_{D,\ exp}$	$K_{D,\ pred}$	E	Z	$p\mathrm{H}_{\mathrm{eq}}$
TOA (20%) + 1-decanol (20%) + n-dodecane (60%)	0.0157	0.052	3.3	3.029	76.77	0.113	3.59
	0.0328	0.102	3.12	3.242	75.7	0.224	3.43
	0.0712	0.199	2.79	3.005	73.62	0.435	3.26
	0.1103	0.295	2.67	2.623	72.78	0.645	3.16
	0.1665	0.374	2.24	2.157	69.17	0.817	3.07
	0.1956	0.48	2.45	1.964	71.04	1.05	3.04
TOA (20%) + 1-decanol (30%) + n-dodecane (50%)	0.0112	0.011	5.03	4.907	83.41	0.123	3.66
	0.0231	0.022	4.85	4.865	82.92	0.245	3.5
	0.0559	0.054	3.83	4.046	79.31	0.469	3.31
	0.0916	0.09	3.42	3.274	77.38	0.686	3.2
	0.1343	0.132	3.02	2.632	75.13	0.888	3.12
TOA (30%) + 1-decanol (20%) + n-dodecane (50%)	0.0274	0.056	3.92	3.76	79.67	0.157	3.52
	0.0559	0.112	3.83	4.017	79.31	0.312	3.36
	0.085	0.214	3.76	3.753	79.01	0.466	3.27
	0.1258	0.313	3.29	3.247	76.7	0.604	3.18
	0.1643	0.406	3.11	2.818	75.68	0.745	3.13

5.3.1.3 Reactive Extraction of Propionic Acid using Aliquat 336

Since quaternary amines such as Aliquat 336 has the ability to extract carboxylic acid at both acidic and basic pH via an anion exchange mechanism, equilibrium experiments are carried out using Aliquat 336 dissolved in (1) 1-octanol and (2) mixture of n-dodecane and 1-decanol.

Aliquat 336 Dissolved in 1-Octanol

Isotherm of propionic acid (0.0675 to 1.35 mol.L^{-1}) in the aqueous and organic phases using Aliquat 336 (10%) in 1-octanol is presented in Figures 5.62. In the propionic acid extraction with Aliquat 336, the variation of distribution coefficient (K_D) with initial propionic acid concentration is shown in Figure 5.63. With 10% of Aliquat 336 in 1-octanol, K_D is decreased from 2.3 to 2.14 upon increasing the initial concentration of acid from 0.0675 to 1.35 mol.L^{-1}. At higher initial concentration of propionic acid, the amount of Aliquat 336 may be the limiting factor for the amine:acid reaction. Figure 5.63 also presents the comparison of extraction efficiency [distribution coefficient (K_{D})] between pure 1-octanol and 10% of Aliquat 336 in 1-octanol. It can be seen that the recovery of propionic acid from aqueous solution is enhanced with Aliquat 336 dissolved in 1-octanol as compared to pure 1-octanol.

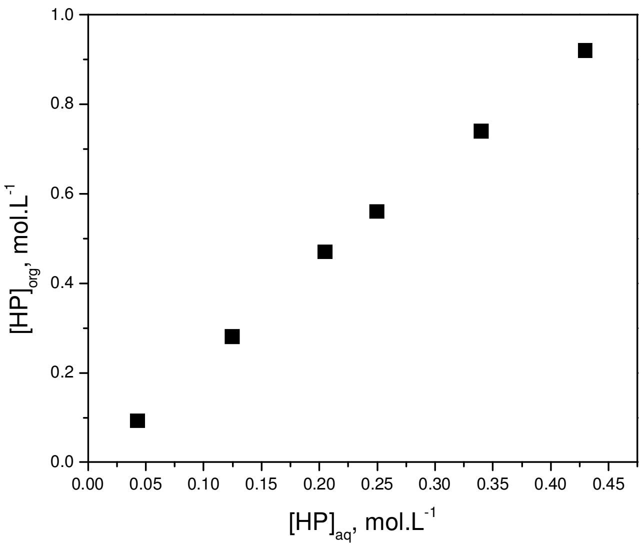

Figure 5.62. Isotherms of propionic acid with Aliquat 336 (10%) in 1-octanol

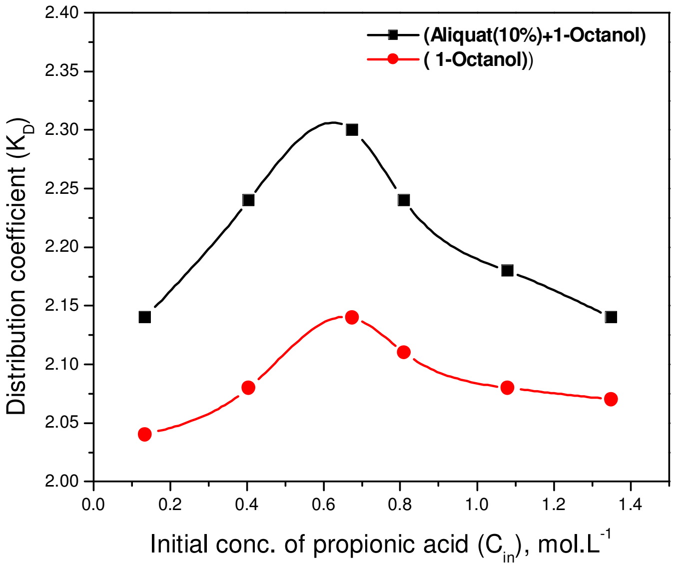

Figure 5.63. Distribution coefficient with initial acid concentration using aliquat 336 (10%) in 1-octanol, and pure 1-octanol

Aliquat 336 Dissolved in n-dodecane (inert) and 1-decanol (modifier)

Since Aliquat 336 is highly viscous and alcoholic diluents (1-octanol and 1-decanol) are more viscous than inert diluents, a mixture of n-dodecane (inert) and 1-decanol (modifier) is used to improve its physical properties. This diluent mixture is also useful to recover propionic acid from fermentation broth at higher pH. The degree of extraction with the variation of 1-decanol in the oragnic mixture is presented in Figure 5.64. The degree of extraction of propionic acid (0.27 mol.L^{-1}) increases markedly with an increase in the concentration of modifier (1-decanol) at a 15% (v/v) and 25% (v/v) of Aliquat 336. When, Aliquat 336 is used as an extractant in a mixture of *n*-dodecane and 1-decanol, the solubility of acid increases in the organic phase. The extraction study is also carried out with various proportions (15 – 60% v/v) of Aliquat 336 dissolved in n-dodecane+1-decanol (2:1 v/v). This study is carried out to understand the influence of the concentration of Aliquat 336. It can be seen from Figure 5.65, the degree of extraction increases with an increase in the concentration of Aliquat 336. In the initial range of amine concentration, the effect is predominant with a tendency to reach a plateau at a higher concentration. The degree of extraction is found to be 87.5% at the highest extractant (Aliquat 336) composition of 60% (v/v). Depending upon the toxicity of the diluents (Section 5.3.1.3), Aliquat 336 (0.55 mol.L^{-1}) is dissolved in n-dodecane + 1-decanol (2:1 v/v) for the extraction of propionic acid (0.0675 – 0.675 mol.L^{-1}) from aqueous solution. The isotherm of propionic acid in both the phases is presented in Figure 5.66 and found to be almost linear.

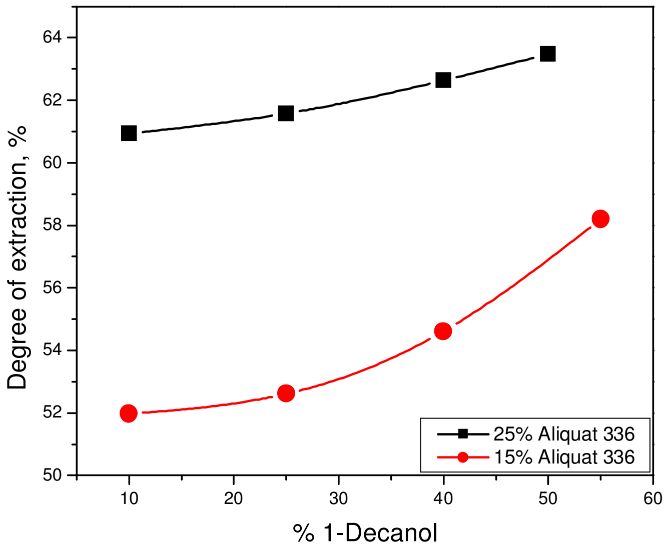

Figure 5.64. Influence of modifier (1-decanol) on degree of extraction with different concentrations of Aliquat 336 at 0.27 mol.L^{-1} of propionic acid

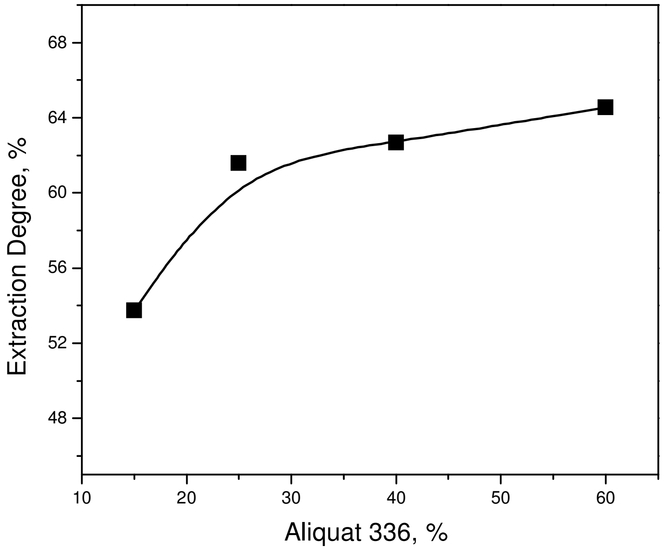

Figure 5.65. Effect of Aliquat 336 dissolved in dodecane and 1-decanol (2:1 v/v) on the degree of extraction at initial propionic acid concentration of 0.27 mol.L^{-1}

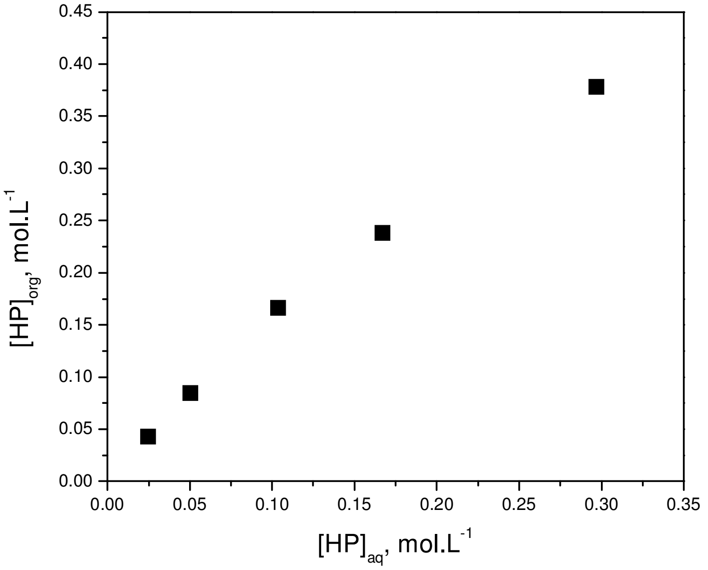

Figure 5.66. Isotherms of propionic acid with Aliquat 336 (25%) in dodecane and 1-decanol (2:1 v/v)

5.3.1.4 Reactive Extraction of Nicotinic Acid using TOA and Aliquat 336 Dissolved in Different Diluents

This section presents the study of the extraction equilibrium of nicotinic acid from aqueous solutions with extractants (TOA and Aliquat 336). Equilibrium data are presented for the extraction of nicotinic acid using TOA in methyl isobutyl ketone, n-decane, toluene and butyl acetate, and Aliquat 336 in methyl isobutyl ketone, n-decane, toluene and 1-decanol. The isotherms for nicotinic acid are determined from four aqueous solution concentrations and four concentrations of TOA dissolved in different diluents as shown in Figure 5.67-5.69. The isotherms for acid are also determined from four different aqueous solution concentrations and a constant concentration (0.55 mol.L^{-1}) of Aliquat 336 as shown in Figure 5.70. Isotherms of nicotinic acid show linearity in the equilibrium concentration of aqueous and organic phases due to low acid concentration (0.02 – 0.12 mol.L^{-1}) with respect to amine concentration. MIBK, as an extractant, yields a maximum value of K_D (0.18) due to polarity and hydrogen bonding ability (Section 5.1.1). Aliphatic hydrocarbon (n-decane) exhibits a low extraction ability with a maximum value of K_D (0.02). The extraction efficiency of n-decane is not significantly improved, when it is used with an extractant (TOA). The highest strength of the complex solvation is found for MIBK with a maximum loading ratio (Z = 0.42) followed by toluene with a maximum loading ratio (Z = 0.154) and butyl acetate (Z = 0.121) as given in Tables (5.25 – 5.27) promoting probably (1,1) acid-TOA complex formation. In all the tested diluents, MIBK (oxygen bonded carbon based compound) with TOA is found to be good solvating agents for nicotinic acid-amine complexation.

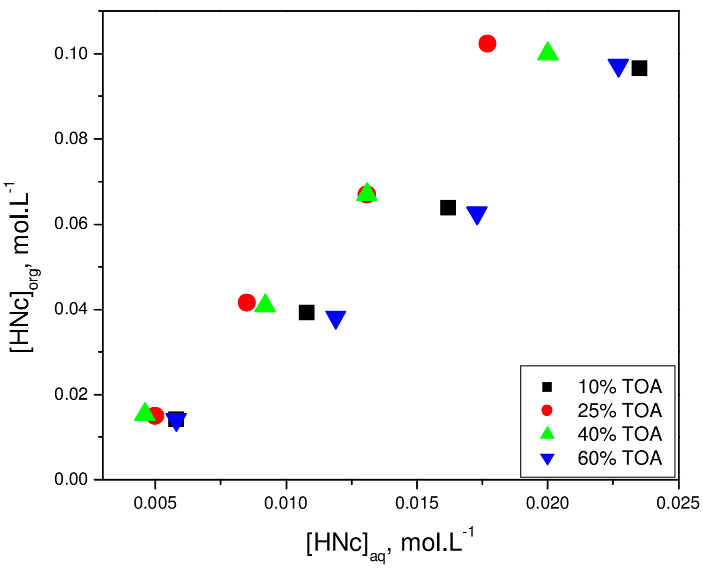

Figure 5.67 Equilibrium isotherms of nicotinic acid for different concentrations of TOA dissolved in MIBK

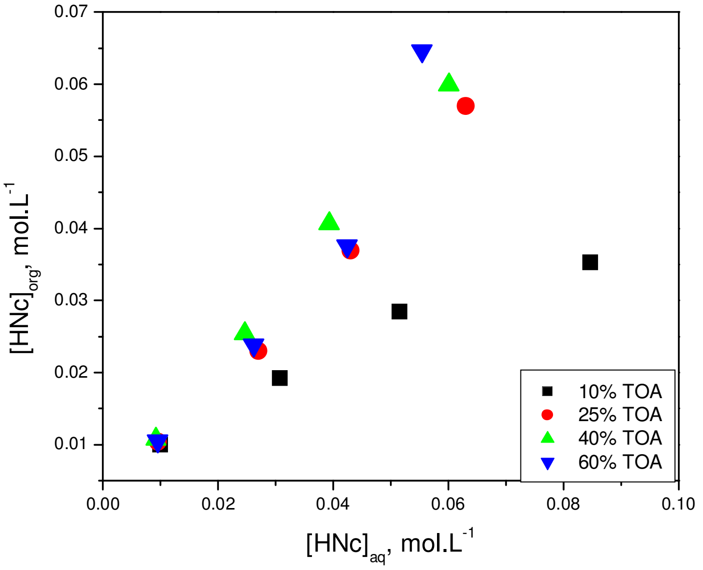

Figure 5.68 Equilibrium isotherms of nicotinic acid for different concentrations of TOA dissolved in toluene

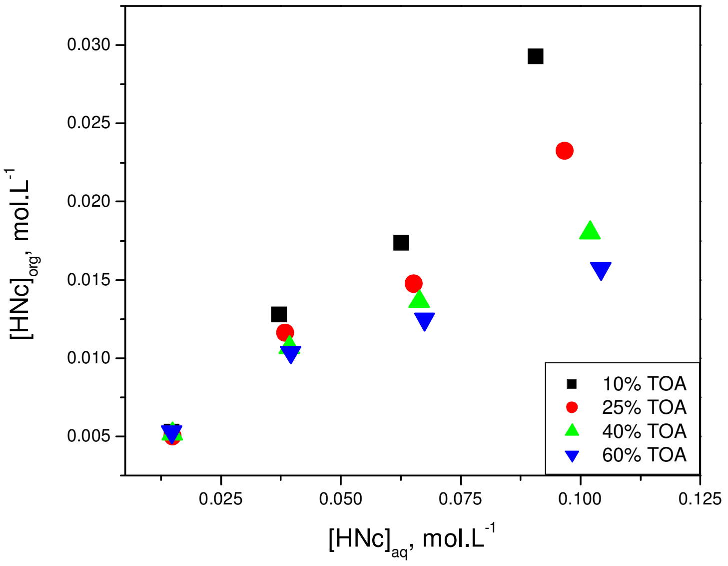

Figure 5.69 Equilibrium isotherms of nicotinic acid for different concentrations of TOA dissolved in butyl acetate

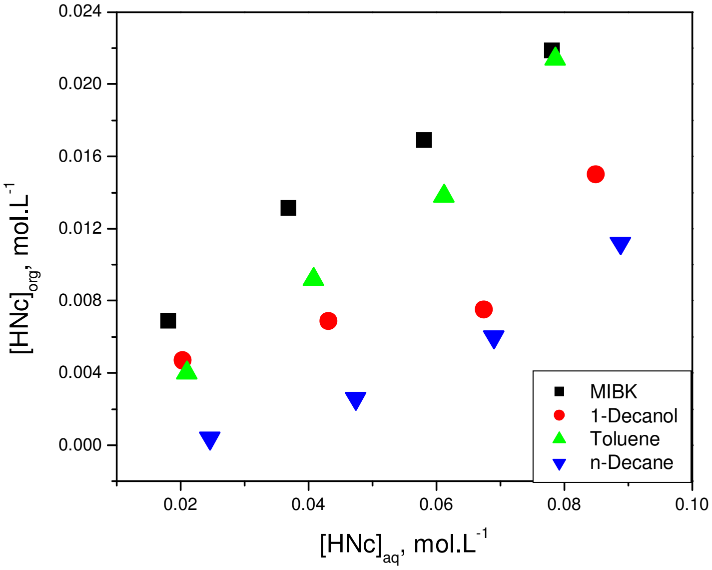

Figure 5.70 Equilibrium isotherms of nicotinic acid for constant concentration of Aliquat 336 (0.55 mol.L^{-1}) in different diluents

The distribution coefficients (K_D) and degree of extraction (E) are found to initially increase, and then decrease with an increase in the concentration of TOA (0.229 – 1.376 mol.L^{-1}) at different concentrations of nicotinic acid (0.02 – 0.12 mol.L^{-1}) in case of MIBK and toluene (as a diluent). Degree of extraction (E) is found to decrease with an increase in the concentration of TOA (0.229 – 1.376 mol.L^{-1}) at different concentrations of nicotinic acid (0.02 – 0.12 mol.L^{-1}) for butyl acetate (as a diluent). The concentration of acid may be the limiting factor for this trend of degree of extraction. Higher concentrations of TOA in diluents may have some interactions with diluents, which leads to decrease in the extraction efficiency. These trends of degree of extraction are also observed for the reactive extraction of propionic acid using TBP dissolved in different diluents by Keshav *et al.,* (2008b). Initial concentration of acid also affects the extraction efficiency as shown in Tables 5.25 – 5.28. Since, low concentrations of nicotinic acid (0.02 to 0.12 mol.L^{-1}) are used as compared to the concentrations of TOA (0.229 – 1.376 mol.L^{-1}), no exact trends are found for the variation in extraction efficiency with initial concentration of acid (Tables 5.25 – 5.28).

The equilibrium results for the extraction of nicotinic acid using Aliquat 336 in different diluents are also presented in Table 5.29. The extraction efficiency of Aliquat 336 due to the presence of ammonium and chloride ions in the chemical structure is found insignificant with all the diluents.

Table 5.25. Equilibrium results for the extraction of nicotinic acid using TOA dissolved in MIBK at 298 K

C_{in} mol.L^{-1}	$[S_{\text{org}}]_{\text{in}}$ mol.L^{-1}	C_{HNc} mol.L^{-1}	$\overline{C}_{\text{HNc}}$ mol.L^{-1}	K_D	E	Z	$p\text{H}_{\text{eq}}$
0.12	0.229	0.0235	0.0965	4.11	80.42	0.421	3.49
	0.573	0.0177	0.1023	5.78	85.25	0.179	3.55
	0.917	0.02	0.1	5	83.33	0.109	3.52
	1.376	0.0227	0.0973	4.29	81.08	0.071	3.5
0.08	0.229	0.0162	0.0638	3.94	79.75	0.279	3.57
	0.573	0.0131	0.0669	5.11	83.63	0.117	3.62
	0.917	0.0131	0.0669	5.11	83.63	0.073	3.62
	1.376	0.0173	0.0627	3.62	78.38	0.046	3.56
0.05	0.229	0.0108	0.0392	3.63	78.4	0.171	3.66
	0.573	0.0085	0.0415	4.88	83	0.072	3.71
	0.917	0.0092	0.0408	4.43	81.6	0.044	3.69
	1.376	0.0119	0.0381	3.2	76.2	0.028	3.64
0.02	0.10	0.0058	0.0142	2.45	71	0.062	3.79
	0.25	0.005	0.015	3	75	0.026	3.83
	0.40	0.0046	0.0154	3.35	77	0.017	3.84
	0.60	0.0058	0.0142	2.45	71	0.01	3.79

Table 5.26. Equilibrium results for the extraction of nicotinic acid using TOA dissolved in toluene at 298 K

C_{in} mol.L^{-1}	$[S_{\text{org}}]_{\text{in}}$ mol.L^{-1}	C_{HNc} mol.L^{-1}	$\overline{C}_{\text{HNc}}$ mol.L^{-1}	K_D	E	Z	$p\text{H}_{\text{eq}}$
0.12	0.229	0.0847	0.0353	0.42	29.42	0.154	3.21
	0.573	0.0631	0.0569	0.9	47.42	0.099	3.28
	0.917	0.0601	0.0599	1	49.92	0.065	3.29
	1.376	0.0554	0.0646	1.17	53.83	0.047	3.3
0.08	0.229	0.0516	0.0284	0.55	35.5	0.124	3.32
	0.573	0.0431	0.0369	0.86	46.13	0.064	3.36
	0.917	0.0393	0.0407	1.04	50.88	0.044	3.38
	1.376	0.0424	0.0376	0.89	47	0.027	3.36
0.05	0.229	0.0339	0.0161	0.47	32.2	0.07	3.41
	0.573	0.027	0.023	0.85	46	0.04	3.46
	0.917	0.0246	0.0254	1.03	50.8	0.028	3.48
	1.376	0.0262	0.0238	0.91	47.6	0.017	3.47
0.02	0.10	0.01	0.01	1	50	0.044	3.68
	0.25	0.0096	0.0104	1.08	52	0.018	3.68
	0.40	0.0092	0.0108	1.17	54	0.012	3.69
	0.60	0.0095	0.0105	1.11	52.5	0.008	3.69

Table 5.27. Equilibrium results for the extraction of nicotinic acid using TOA dissolved in butyl acetate at 298 K

C_{in} **mol.L^{-1}**	$[S_{\text{org}}]_{\text{in}}$ **mol.L^{-1}**	C_{HNc} **mol.L^{-1}**	$\overline{C}_{\text{HNc}}$ **mol.L^{-1}**	K_D	*E*	*Z*	$p\text{H}_{\text{eq}}$
0.12	0.229	0.0908	0.0292	0.32	24.33	0.128	3.2
	0.573	0.0968	0.0232	0.24	19.33	0.04	3.18
	0.917	0.102	0.018	0.18	15	0.02	3.17
	1.376	0.1043	0.0157	0.15	13.08	0.011	3.17
0.08	0.229	0.0626	0.0174	0.28	21.75	0.076	3.28
	0.573	0.0653	0.0147	0.23	18.38	0.026	3.27
	0.917	0.0664	0.0136	0.2	17	0.015	3.26
	1.376	0.0675	0.0125	0.19	15.63	0.009	3.26
0.05	0.229	0.0372	0.0128	0.34	25.6	0.056	3.39
	0.573	0.0384	0.0116	0.3	23.2	0.02	3.38
	0.917	0.0393	0.0107	0.27	21.4	0.012	3.38
	1.376	0.0396	0.0104	0.26	20.8	0.008	3.39
0.02	0.10	0.0147	0.0053	0.36	26.5	0.023	3.58
	0.25	0.015	0.005	0.33	25	0.009	3.59
	0.40	0.0149	0.0051	0.34	25.5	0.006	3.60
	0.60	0.0147	0.0053	0.36	26.5	0.004	3.60

Table 5.28. Equilibrium results for the extraction of nicotinic acid using TOA dissolved in n-dodecane at 298 K

C_{in} / **mol.L^{-1}**	$[S_{\text{org}}]_{\text{in}}$ / **mol.L^{-1}**	C_{HNc} / **mol.L^{-1}**	$\overline{C}_{\text{HNc}}$ / **mol.L^{-1}**	K_D	*E*	*Z*	$p\text{H}_{\text{eq}}$
0.12	0.229	0.117	0.003	0.03	2.47	0.013	3.14
	0.573	0.1124	0.0076	0.07	6.32	0.013	3.15
	0.917	0.1101	0.0099	0.09	8.24	0.011	3.15
	1.376	0.1055	0.0145	0.14	12.09	0.011	3.16
0.08	0.229	0.0785	0.0015	0.02	1.83	0.006	3.23
	0.573	0.077	0.003	0.04	3.75	0.005	3.23
	0.917	0.0747	0.0053	0.07	6.64	0.006	3.24
	1.376	0.0693	0.0107	0.15	13.38	0.008	3.26
0.05	0.229	0.0485	0.0015	0.03	2.98	0.007	3.33
	0.573	0.0477	0.0023	0.05	4.52	0.004	3.34
	0.917	0.0454	0.0046	0.1	9.14	0.005	3.35
	1.376	0.0424	0.0077	0.18	15.3	0.006	3.36

Table 5.29. Equilibrium results for the extraction of nicotinic acid using Aliquat 336 dissolved in different diluents at 298 K

Diluent	C_{in} **mol.L^{-1}**	C_{HNc} **mol.L^{-1}**	$\overline{C}_{\text{HNc}}$ **mol.L^{-1}**	K_D	E	Z	$p\text{H}_{\text{eq}}$
1-Decanol	0.025	0.0203	0.00469	0.23	18.75	0.009	3.47
	0.05	0.0431	0.00688	0.16	13.75	0.013	3.31
	0.075	0.0675	0.0075	0.11	10	0.014	3.21
	0.10	0.085	0.015	0.18	15	0.027	3.16
MIBK	0.025	0.0181	0.00688	0.38	27.5	0.013	3.5
	0.05	0.0369	0.01313	0.36	26.25	0.024	3.34
	0.075	0.0581	0.01688	0.29	22.5	0.031	3.24
	0.10	0.0781	0.02188	0.28	21.88	0.04	3.18
Toluene	0.025	0.021	0.004	0.19	16	0.007	3.46
	0.05	0.0408	0.0092	0.23	18.4	0.017	3.32
	0.075	0.0612	0.0138	0.23	18.4	0.025	3.23
	0.10	0.0786	0.0214	0.27	21.4	0.039	3.18
n-Decane	0.025	0.0246	0.0004	0.02	1.6	0.001	3.43
	0.05	0.0474	0.0026	0.05	5.2	0.005	3.29
	0.075	0.069	0.006	0.09	8	0.011	3.21
	0.10	0.0888	0.0112	0.13	11.2	0.02	3.15

5.3.1.5 Reactive Extraction of Nicotinic Acid using TOA Dissolved in Inert Diluent and Modifier

In this section, the equilibrium experimental results on the extraction of nicotinic acid by TOA in the mixture of an inert diluent and a modifier are presented. Inert diluents chosen in this study are *n*-decane, cyclohexane, kerosene and toluene. 1-octanol and 1-decanol are used as modifiers to examine the effect of modifier on the extraction efficiency of TOA and diluent-complex interactions.

The effect of modifiers (1-decanol and 1-octanol) concentration on the degree of extraction (%) of nicotinic acid extracted by the extractant (TOA) at a constant concentration of the initial aqueous solution (0.10 mol.L^{-1}) is first studied. The organic phase is composed of an extractant (TOA), a modifier, and an inert diluent. The effect of 1-decanol at two different concentrations of TOA [15% and 25% (v/v)] is shown in Figures 5.71 and 5.72. A sharp increase in the degree of extraction is observed when the concentration of 1-decanol is increased from 15% to 35% using 15% of TOA and from 15% to 30% using 25% of TOA. A strong modifier effect on the degree of extraction is found when kerosene and n-decane are used as inert diluents. When toluene is used as an inert diluent, the effect of modifier is found to be less due to higher value of the dielectric constant (π aromatic system). The effect of 1-octanol at two different concentrations of TOA [15% and 25% (v/v)] is shown in Figures 5.73 and 5.74. 1-Octanol as a modifier is found to be more effective as compared to 1-decanol in various inert diluents. The effect of concentration of 1-ocatnol on the degree of extraction is more pronounced than that of 1-decanol, with similar trends (Figures 5.71 – 5.74). Due to the toxicity of alcohols to bacteria, 1-decanol (modifier) and n-decane (inert diluent) with TOA are used for further equilibrium study to determine the values of equilibrium constant (K_E) and stoichiometry of reaction. Based on the results obtained for the influence of 1-decanol (Figures 5.71 and 5.72), an equal volume mixture of n-decane and 1-decanol is used to estimate the values of K_E and the number of acid molecule (m) per amine in the formation of acid:TOA complexes. The effect of TOA composition (5 – 25%) in the organic solutions is also determined using an equal volume mixture of n-decane and 1-decanol (Figure 5.75). The results presented in Figure 5.75 show that the degree of extraction first increases with an increase in the concentration of TOA from 5% to 15% and then decreases for 25 % of TOA concentration.

15% of TOA (0.343 $mol.L^{-1}$) as an extractant composition in the diluents is used for the extraction of nicotinic acid in the range of 0.02 – 0.12 $mol.L^{-1}$. The isotherm for nicotinic acid, determined from different aqueous solution concentrations at constant concentration of TOA dissolved in *n*-decane and 1-decanol (1:1 v/v), is shown in Figure 5.76. The equilibrium organic phase acid concentration varies almost linearly with equilibrium acid concentration in the aqueous phase. The equilibrium acid concentration in the organic phase increases with an increase in equilibrium acid concentration in the aqueous phase. Similar trend in isotherms is observed for all the other systems studied in this work.

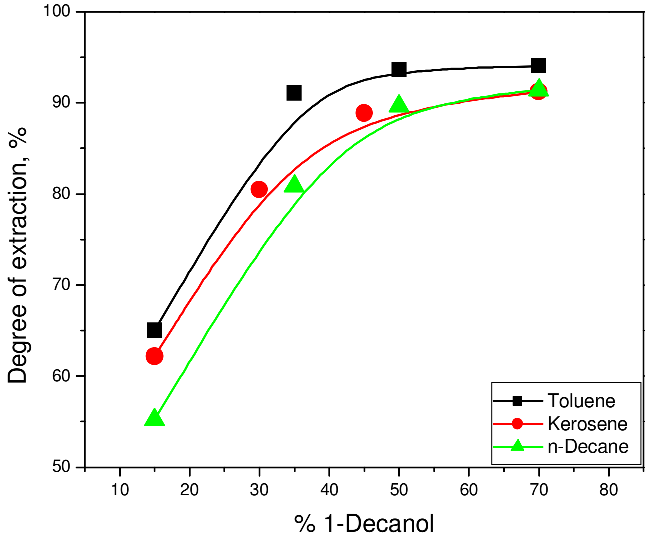

Figure 5.71 Influence of modifier (1-decanol, %) in the mixture of 1-decanol + inert diluent + TOA, on degree of extraction with 15% TOA

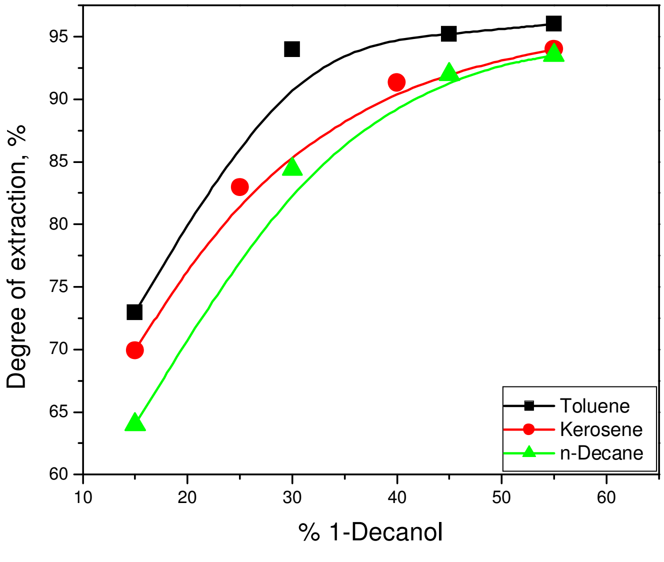

Figure 5.72 Influence of modifier (1-decanol, %) in the mixture of 1-decanol + inert diluent + TOA, on degree of extraction with 25% TOA

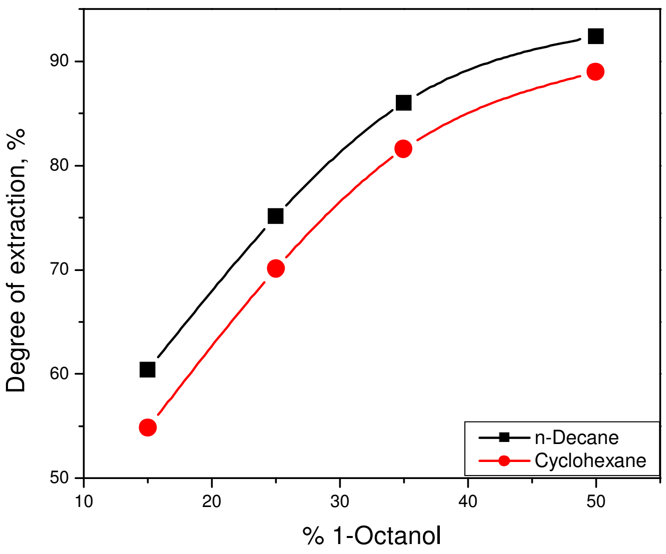

Figure 5.73 Influence of modifier (1-octanol, %) in the mixture of 1-octanol + inert diluent + TOA, on degree of extraction with 15% TOA

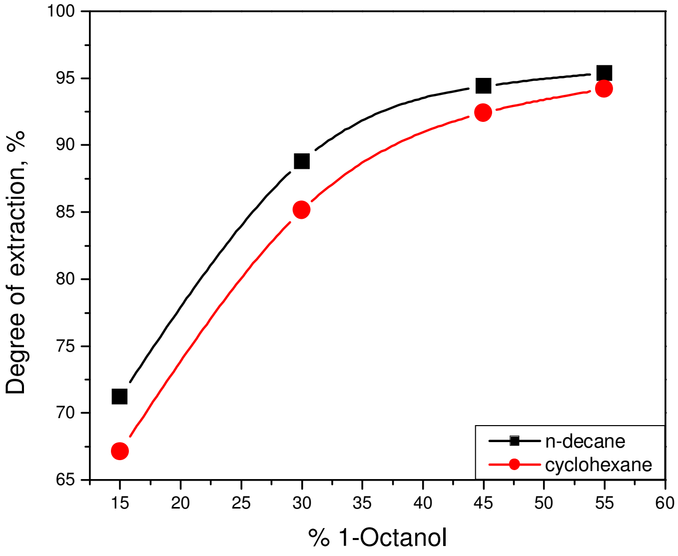

Figure 5.74 Influence of modifier (1-octanol, %) in the mixture of 1-octanol + inert diluent + TOA, on degree of extraction with 25% TOA

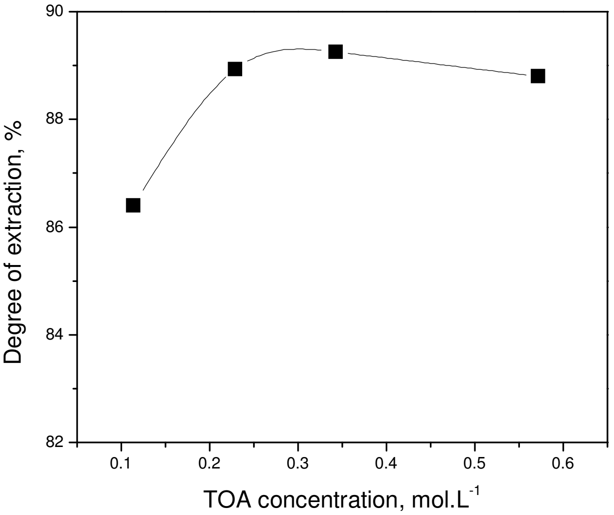

Figure 5.75 Effect of TOA concentrations in the mixture of 1-decanol + n-decane (1:1 v/v) at constant concentration of nicotinic acid (0.10 mol.L^{-1})

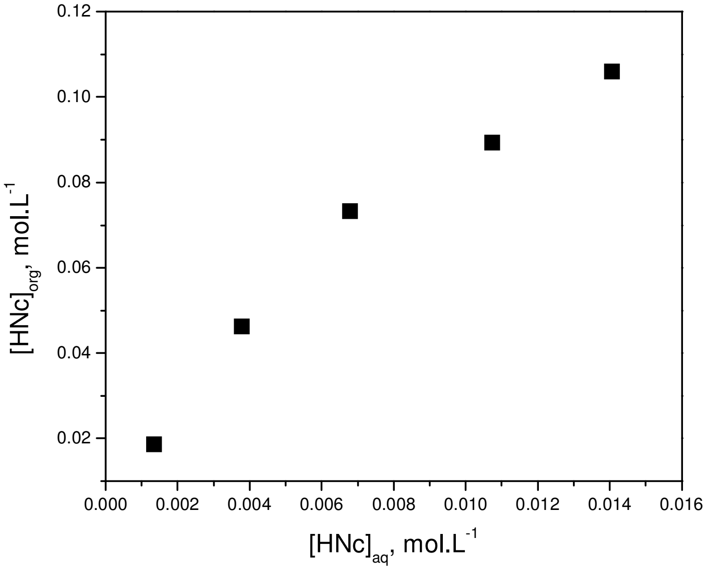

Figure 5.76 Equilibrium isotherms of nicotinic acid with TOA (0.343 mol.L^{-1}) in *n*-decane/1-decanol (1:1 v/v)

5.3.1.6 Reactive Extraction of Nicotinic Acid using TDA Dissolved in n-Dodecane and Oleyl Alcohol

Most organic solvents are toxic to microorganisms to some extent (Section 5.3.1.3). Laane *et al.,* (1985) established a correlation between solvent toxicity and the value of log P^a. log P^a is the logarithm of the distribution ratio of the solvent in a standard octanol-water (two-phase) system and serves as an inverse quantitative measure of the polarity of a solvent. Increased toxicity is associated with increased polarity of the organic solvent (Bruce and Daugulis, 1991). The onset of non-toxicity is reported in the range of log P^a of 4–6. Solvents with the values of log P^a less than 4 are most likely to be toxic to microorganisms. Blending of a toxic solvent (log $P \leq 4$) with a nontoxic one (log $P > 6$) may yield a biocompatible mixture (Yabannavar and Wang, 1991b).

In this section, the extraction of nicotinic acid from aqueous solution is studied using a tri-n-dodecylamine (TDA) as an extractant dissolved in nontoxic diluent system (n-dodecane and oleyl alcohol with log P^a of 6.1 and 7.5 respectively). This extractant and diluent system will be served as a biocompatible mixture for the recovery of nicotinic acid from fermentation broth. With TDA (an extractant), n-dodecane as an inert diluent and oleyl alcohol as a modifier are used. The solubility of extracted species increases in the organic phase with the presence of modifier as discussed in earlier sections. So, degree of extraction of nicotinic acid also increases with an increase in the concentration of oleyl alcohol in organic solution as shown in Figure 5.77. The effect of oleyl alcohol on extraction efficiency is found to be significant with *n*-dodecane. As the viscosity of oleyl alcohol (modifier) is very high as compared to an inactive diluent (*n*-dodecane), the mixture of *n*-dodecane and oleyl alcohol in the volume ratio of 2:1 is used as a diluent. The extraction isotherms for nicotinic acid, determined from four concentrations of aqueous solution and four concentrations of TDA dissolved in *n*-dodecane and oleyl alcohol (2:1 v/v) are shown in Figure 5.78. The experimental data as presented in Figure 5.78 and Table 5.30 show that when the concentration of TDA increases, the values of K_D and E also increase. The initial concentration of nicotinic acid also affects the extraction efficiency (Table 5.30). The values of K_D significantly decrease when the concentration of acid is increased from 0.023 to 0.122 mol.L^{-1}. Different concentrations of TDA are used to understand the effect of initial concentration of acid on the extraction efficiency. The effect of acid concentration on the degree of extraction is more significant with lower concentration of TDA (limiting reagent). In this equilibrium study, a mixture of *n*-dodecane and oleyl alcohol (2:1 v/v) is used with TDA for estimation of K_E and stoichiometry (m, n). Since nicotinic acid used is in the low concentration range of 0.023 to 0.122 mol.L^{-1} as compared to the concentrations of TDA (0.078 - 0.388 mol.L^{-1}), the loading ratio is found to be low ($Z < 0.5$) (Table 5.30). 1:1 complexes of acid and TDA are formed.

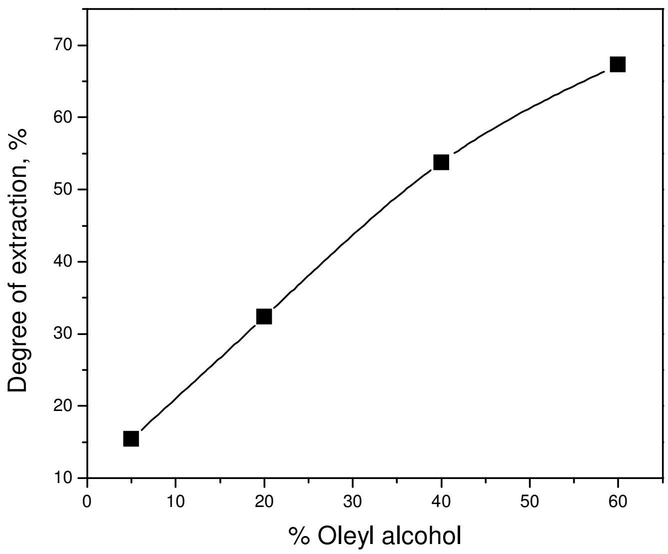

Figure 5.77 Influence of modifier (oleyl alcohol) in the mixture of n-dodecane + oleyl alcohol + TOA, on degree of extraction with 10% TOA

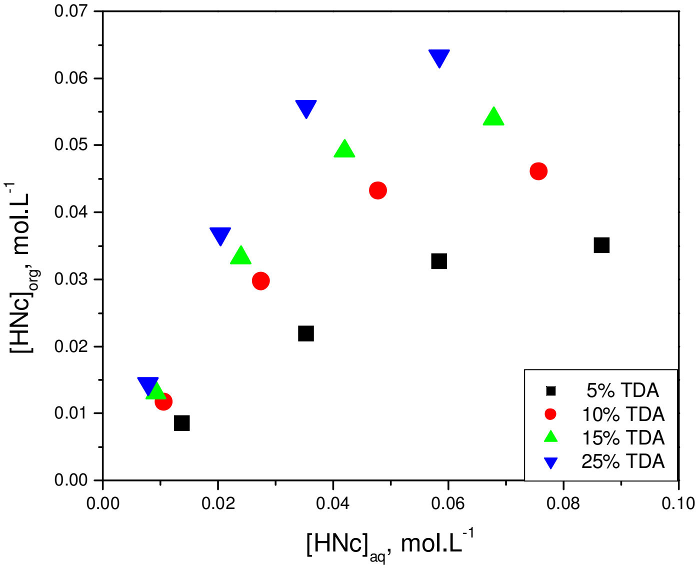

Figure 5.78 Equilibrium isotherms of nicotinic acid for different concentrations of TDA dissolved in n-dodecane + oleyl alcohol (2:1 v/v)

Table 5.30. Equilibrium results for the extraction of nicotinic acid using TDA dissolved in n-dodecane/oleyl alcohol (2:1 v/v) at 301 K

$[\overline{NR}_3]_{\mathrm{in}}$ **mol.L^{-1}**	C_{in} **mol.L^{-1}**	C_{HNc} **mol.L^{-1}**	$\overline{C}_{\mathrm{HNc}}$ **mol.L^{-1}**	K_D	E	Z	$p\mathrm{H}_{\mathrm{eq}}$
0.078	0.022	0.014	0.009	0.62	38.44	0.11	3.14
	0.057	0.035	0.022	0.62	38.28	0.281	3.19
	0.091	0.058	0.033	0.56	35.84	0.419	3.27
	0.122	0.087	0.035	0.41	28.83	0.45	3.35
0.155	0.022	0.011	0.012	1.11	52.51	0.076	3.56
	0.057	0.027	0.03	1.08	52	0.192	3.35
	0.091	0.048	0.043	0.9	47.47	0.279	3.24
	0.122	0.076	0.046	0.61	37.85	0.297	3.16
0.233	0.022	0.009	0.013	1.42	58.66	0.056	3.61
	0.057	0.024	0.033	1.39	58.17	0.143	3.41
	0.091	0.042	0.049	1.17	53.93	0.211	3.29
	0.122	0.068	0.054	0.79	44.29	0.232	3.19
0.388	0.022	0.008	0.014	1.84	64.82	0.037	3.68
	0.057	0.02	0.037	1.8	64.34	0.095	3.47
	0.091	0.035	0.056	1.58	61.25	0.144	3.35
	0.122	0.058	0.063	1.08	52.02	0.163	3.24

Effect of Temperature

The effect of temperature on the extraction of nicotinic acid with TDA (5 – 25%) dissolved in n-dodecane/oleyl alcohol (2:1 v/v) is presented in Figure 5.79. As the temperature increases from 301 to 323 K, the percentage amount of acid extracted decreases for all concentrations of TDA. For the extraction of nicotinic acid, the increase in the thermal energy disturbs the interaction in the organic phase between TDA and acid, thus decreasing the extraction. For a temperature of 333 K, extraction efficiency slightly increased due to the increased interactions between TDA and acid (0.122 mol.L^{-1}) molecules. However, an improved separation of the phases is observed. The variation in the degree of extraction with temperature is in agreement with the results obtained by Keshav *et al.,* (2009). They studied the effect of temperature on the extraction of mono-carboxylic acids using Aliquat 336 dissolved in oleyl alcohol. From a thermodynamic point of view the molecules of acid in the organic phase are more ordered as they exist as a complex. Thus, acid transfer from the aqueous phase as solvates to the organic phase increases the order and reduces the entropy. Generally the transfer of compounds from the aqueous phase to the organic phase is accompanied by a decrease in entropy.

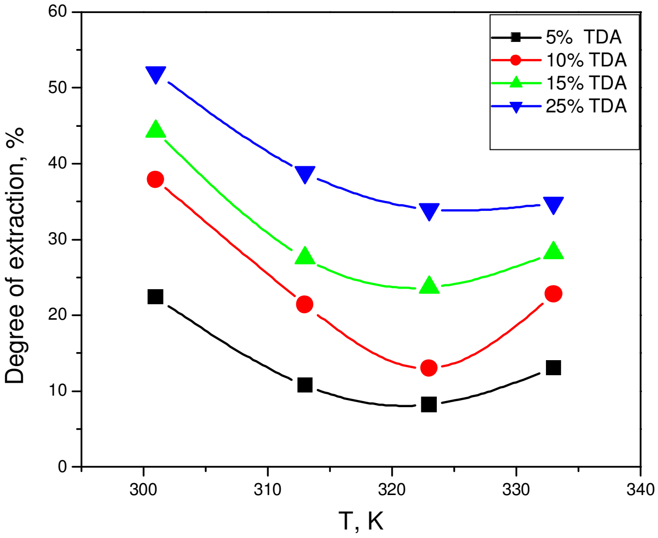

Figure 5.79. Influence of temperature on extraction of nicotinic acid with different concentrations of TDA in n-dodecane/oleyl alcohol (2:1 v/v)

5.3.1.7 Kinetic Study for Reactive Extraction of Propionic- and Nicotinic Acid using TOA

In order to select the stirring condition, preliminary kinetic measurements are performed with the two-phase system of an aqueous phase (an initial nicotinic acid concentration of 0.10 mol.L^{-1}), and an organic phase [TOA in MIBK (0.23 mol.L^{-1})]. For a stirring speed of about 350 rpm, the equilibrium is achieved in 10 min. The shape and the position of the evaluated kinetic curves for stirring speed of 500 rpm is almost the same (Figure 5.80). Hence, according to these preliminary measurements, the selected stirring speed of 350 rpm excludes the influence of the agitation on kinetics. This means that the effect of mass transfer on the overall kinetics is minimized and presumably the interfacial chemical kinetics can be determined from the experimental results according to Poposka and Nikolovski (1995) and Poposka *et. al.,* (1998, 2000). Therefore, the kinetic experiments for the reactive extraction of propionic acid using TOA in a mixture of cyclohexane and 1-decanol (1:1 vol%) and for the reactive extraction of nicotinic acid using TOA in MIBK, are carried out with the stirring speed of 350 rpm and systems are allowed to achieve an equilibrium.

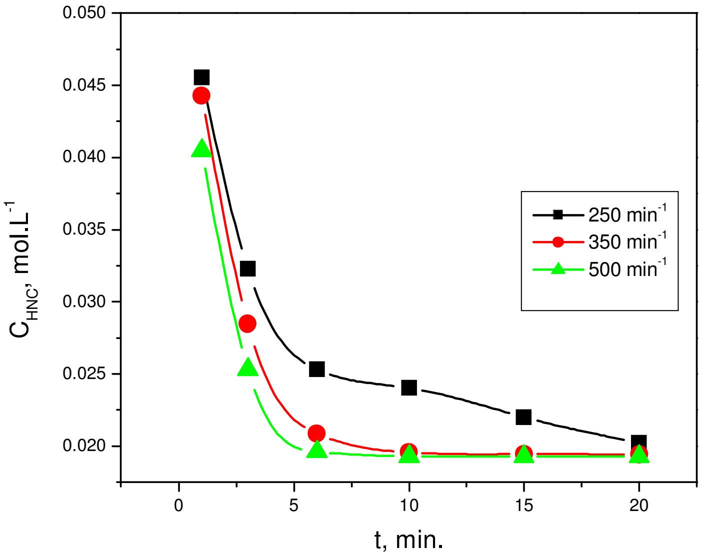

Figure 5.80 Kinetic curves for extraction of nicotinic acid (0.10 mol.L^{-1}) by TOA (0.229 mol.L^{-1}) in MIBK at different stirring speeds

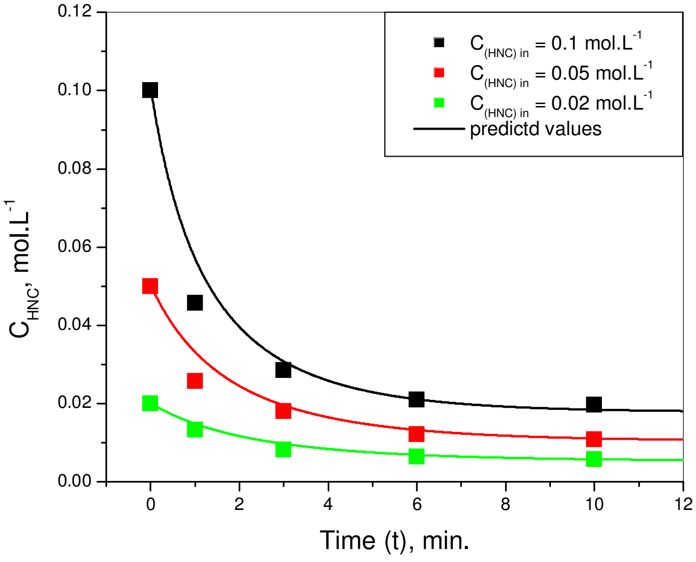

Figure 5.81 Experimental and estimated kinetic curves for extraction of nicotinic acid (0.02 - 0.10 mol.L^{-1}) by TOA (0.229 mol.L^{-1}) in MIBK

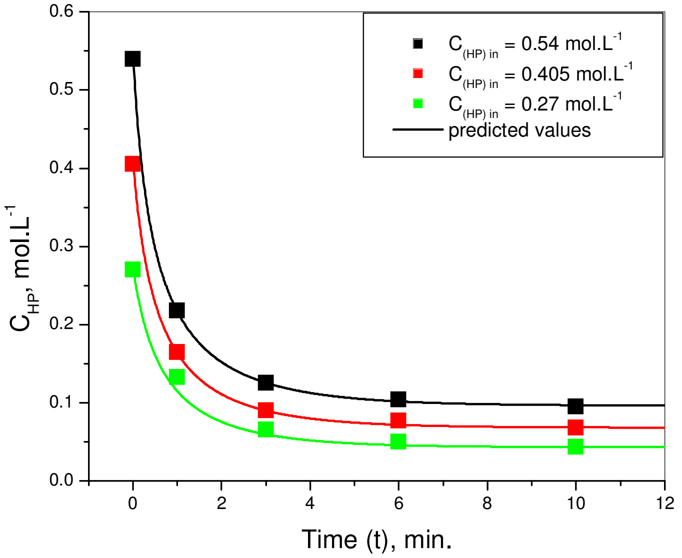

Figure 5.82 Experimental and estimated kinetic curves for extraction of propionic acid (0.27 - 0.54 mol.L^{-1}) by TOA (0.46 mol.L^{-1}) in cyclohexane + 1-decanol (1:1 v/v)

5.3.2 Simulation and Modeling Studies

The results of theoretical studies (discussed in Chapter 4) are presented to determine the various equilibrium and kinetic parameters in the following sections (5.3.2.1 – 5.3.2.6):

5.3.2.1 Estimation of K_E and stoichiometry coefficients (m and n) based on K_D

The graphical method for determining of the number of extractant or acid molecules taking part in the formation of complexes is applicable, when only one type of complex is formed (Yankov *et al.,* 2004). The model equation (4.33) as proposed in Section 4.1.1.2 is solved to determine the values of equilibrium extraction constant (K_E), the number of acid molecule (m) and reacting extractant molecules (n) in the formation of acid:extractant complexes using DE. An objective function based on least square error between experimental and predicted values of K_D is minimized. The estimated values of m and n in the formation of acid:extractant ($m:n$) complexes, and the values of K_E for different acid/extractant/diluent systems are given in Table 5.31.

The predicted values of K_D for each carboxylic acid with different extractant-diluent systems, using this model are comparable with the experimental values of K_D (Section 5.3.1). In the extraction of mono-carboxylic acids (formic-, acetic-, propionic- and butyric acids) with TOA, the predicted and experimental values of K_D at lower acid concentrations are not showing good match (Tables 5.19-22). When equilibrium extraction is carried out with low concentration of acids, Minor errors in the experimental concentration of aqueous phase may lead to high error in the experimental values of K_D ($K_D = \overline{C}_{HA} / C_{HA}$). Therefore the experimental and predicted values of loading ratio ($Z = \overline{C}_{HA} / [NR_3]_{in}$) are found to be more close for all the acid/extractant/diluent systems. In the extraction of mono-carboxylic acids using TOA, the higher strength of the complex solvation is found for chlorinated hydrocarbons (chloroform) promoting probably (1:1) acid-amine complex formation (higher values of K_E and lower values of m). The formation of acid:amine complexes also depends on the nature of diluents, which affect the basicity of the amine and the stability of the ion pair formed in the extract phase (King and Poole, 1991; Canari and Eyal, 2003). When, amine is used as an extractant in a mixture of an inert diluent and an active diluent (modifier) in reactive extraction, the solubility of extracted species increases in the organic phase. The estimated values of K_E and m per amine molecule for the extraction of propionic acid using TOA in n-dodecane and 1-decanol (Table 5.31) indicate that higher concentration of 1-decanol in the organic phase at constant TOA concentration may lead to the more formation of 1:1 complexes between acid and TOA.

In all the tested diluents for the extraction of nicotinic acid, MIBK containing the oxygen bonded carbon in the structure is the best solvating agents for acid-TOA complexation giving (a maximum value of $K_E = 143.81$) due to a high solvation ability. The diluents (MIBK), having higher dielectric constant (13.1) also contribute to the extraction of organic acid and results in a low value of stoichiometry coefficients ($n = 0.70$) per acid molecule. The values of m (near about 1) in the extraction of nicotinic acid using TOA in 1-decanol + n-decane (1:1 v/v) and TDA in oleyl alcohol + n-dodecane (1:2 v/v) indicate 1:1 formation of complexes between acid and amine.

Table 5.31. Values of equilibrium constant (K_E) and number of reacting acid:extractant molecules (m:n) with amine-based extractants using DE

Acid		Extractant		Diluents	*m*	*n*	K_E
Name	**Conc. (mol.L^{-1})**	**Name**	**Conc. (mol.L^{-1})**				
Formic acid	0.265 – 1.32	TOA	0.46	1-decanol	1.69	1	667.83
				decane	2.68	1	2.79
				benzene	2.37	1	100.08
				chloroform	1.73	1	740.46
				MIBK	2.38	1	1203.43
				decane + 1-decanol (3:1 v/v)	1.69	1	667.83
Acetic acid	0.05 – 0.26	TOA	0.46	1-decanol	0.95	1	18.42
				decane	1.77	1	0.40
				benzene	1.42	1	2.41
				chloroform	1.32	1	91.14
				MIBK	1.50	1	8.41
				decane + 1-decanol (3:1 v/v)	1.16	1	3.51
Propionic acid	0.068 – 0.408	TOA	0.46	1-decanol	1.20	1	93.14
				decane	1.34	1	1.86
				benzene	1.67	1	46.39
				chloroform	1.30	1	319.99
				MIBK	1.82	1	131.30
				decane + 1-decanol (3:1 v/v)	1.12	1	12.49
Butyric acid	0.095 – 0.567	TOA	0.46	1-decanol	1.33	1	612.83
				decane	1.95	1	71.24
				benzene	1.92	1	1381.71
				chloroform	1.52	1	3266.14
				MIBK	2.15	1	3516.33
				decane + 1-decanol (3:1 v/v)	1.56	1	208.04
Propionic acid	0.0675 – 0.675	TOA	0.46	toluene + 1-decanol (1:1 v/v)	1.21	1	77.52
				cyclohexane +1-decanol (1:1 v/v)	1.31	1	48.93
				kerosene+1-decanol (1:1 v/v)	1.20	1	40.22

Table 5.31 continued

Propionic acid	0.0675 – 0.676	TOA	0.46	n-dodecane + 1-decanol (3:1 v/v)	1.23	1	16.35
			0.46	n-dodecane + 1-decanol (1.67:1 v/v)	1.20	1	24.88
			0.69	n-dodecane + 1-decanol (2.5:1 v/v)	1.35	1	30.66
		Aliquat 336	0.55	n-dodecane + 1-decanol (2:1 v/v)	1.11	1	4.73
Nicotinic acid	0.02 – 0.12	TOA	0.229	MIBK	1.55	1	143.84
			0.573		1.50	1	65.73
			0.915		1.39	1	24.93
			1.376		1.33	1	8.54
			0.229	toluene	0.67	1	1.60
			0.573		0.84	1	1.16
			0.915		0.91	1	0.99
			1.376		0.84	1	0.48
			0.343	decane + 1-decanol (1:1 v/v)	0.913	1	31.38
	0.023 – 0.122	TDA	0.078	*n*-dodecane and oleyl alcohol (2:1 v/v)	1.15	1	15.69
			0.155		1.01	1	8.84
			0.233		0.98	1	6.62
			0.388		0.96	1	4.68

5.3.2.2 Estimation of K_{11} and K_{21} for the Formation of 1:1 and 2:1 Complexes

The values of loading ratio (*Z*) for the extraction experiments with amine-based extractants are calculated and tabulated in Section 5.3.1. The loading of the extractants for most of the extractions studied in the present work are found to be less than 1. Only those for 0.46 M TOA dissolved in different inert diluent/1-decanol (1:1 v/v) at higher concentration of propionic acid are greater than unity. The organic phases for these sets of experiments are overloaded due to the increase in the extraction capacity of the organic phase at the specific extraction conditions. It is reported by Wasewar *et al.,* (2002) that systems that include the interaction of the diluent with the complex show decreasing loading (*Z*) with increasing amine concentration. This is the case for all the extractions performed in this work. The values of *Z* decreased with an increase in amine concentration for constant initial concentration of aqueous phase (Section 5.3.1). For low loading ratio ($Z < 0.5$), $Z/(1-Z)$ versus $[HA]$ and for higher loading ratios (at least $Z > 0.5$), $Z/(2-Z)$ versus $[HP]^2$ are plotted to obtain the values of K_{11} (formation of 1:1 complexes) and K_{21} (formation of 2:1 complexes) respectively as shown in Figures 5.83 – 5.89 for different extraction systems. The values of K_{11} for 1:1 complex of acid and amine, and K_{21} for 2:1 complex of acid and amine at 298 K for different extraction system are given in Table 5.32. The values of coefficient of determination (R^2) are found near about 0.99 except few values in the extraction of nicotinic acid using TDA.

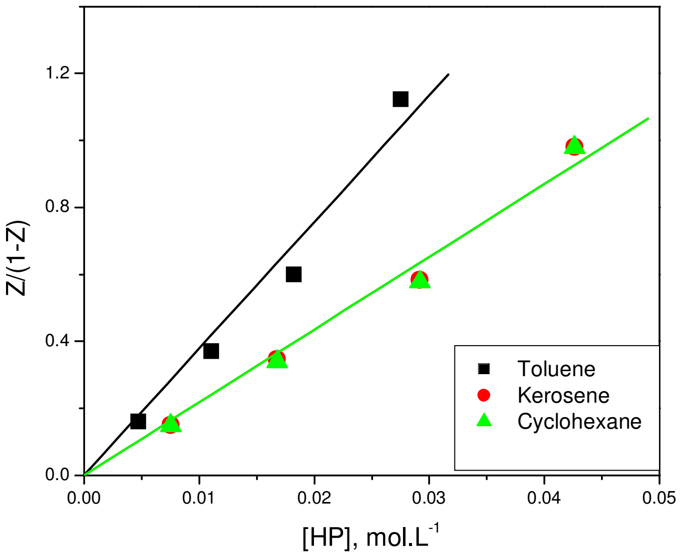

Figure 5.83 Estimation of (1:1) propionic acid-TOA equilibrium constant (K_{E1}) in different inert diluents/1-decanol (1:1 v/v)

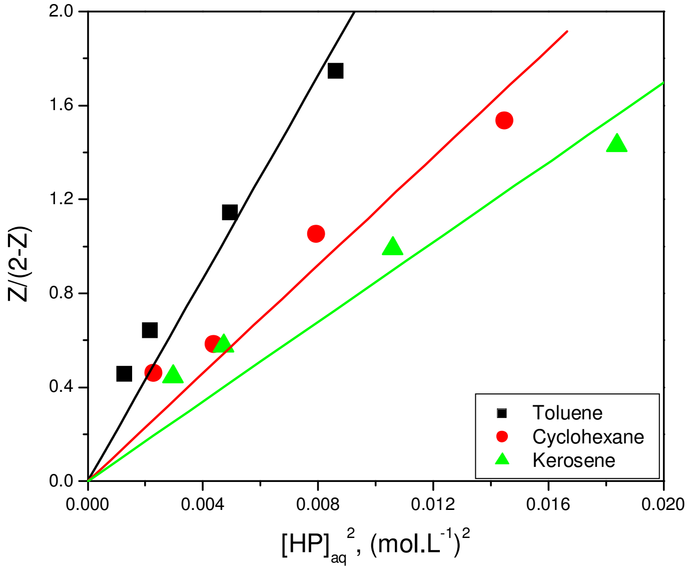

Figure 5.84 Estimation of (2:1) propionic acid-TOA equilibrium constant (K_{E2}) in different inert diluents/1-decanol (1:1 v/v)

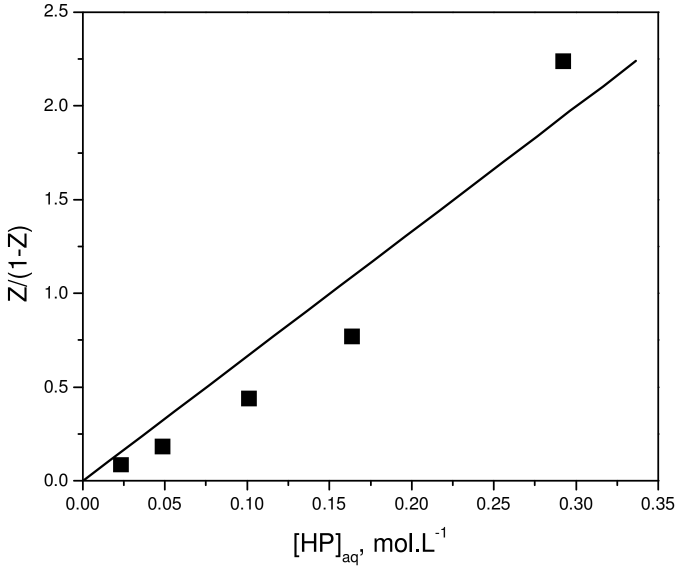

Figure 5.85 Estimation of (1:1) propionic acid-Aliquat 336 equilibrium constant (K_{E1}) in n-dodecane/1-decanol (2:1 v/v)

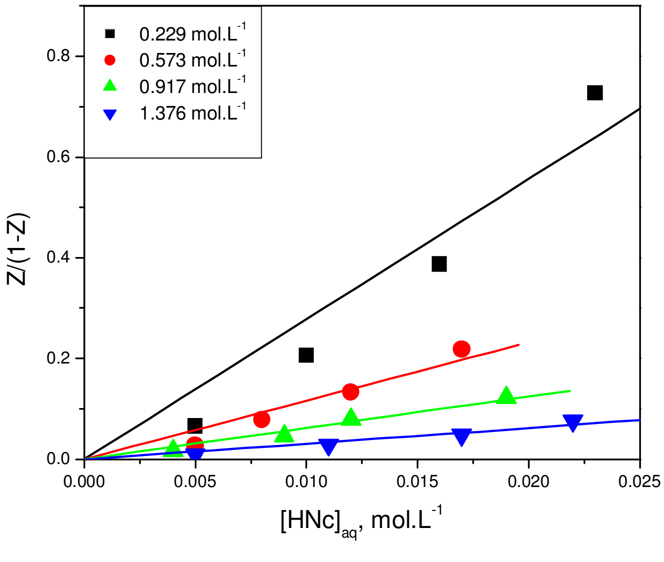

Figure 5.86 Estimation of (1:1) nicotinic acid-TOA equilibrium constant (K_{E1}) with different concentrations of TOA in MIBK

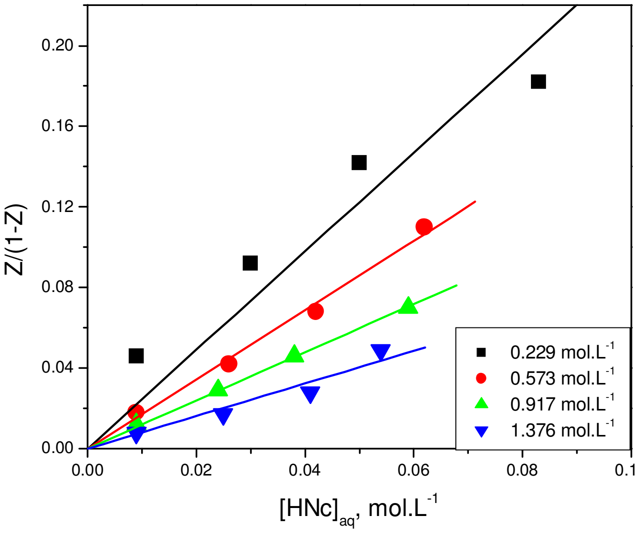

Figure 5.87 Estimation of (1:1) nicotinic acid-TOA equilibrium constant (K_{E1}) with different concentrations of TOA in toluene

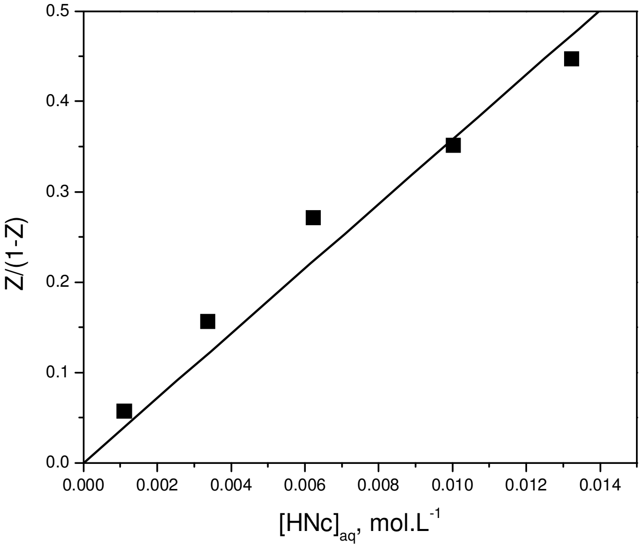

Figure 5.88 Estimation of (1:1) nicotinic acid-TOA equilibrium constant (K_{E1}) with TOA (0.343 mol.L^{-1}) in 1-decanol/n-decane (1:1 v/v)

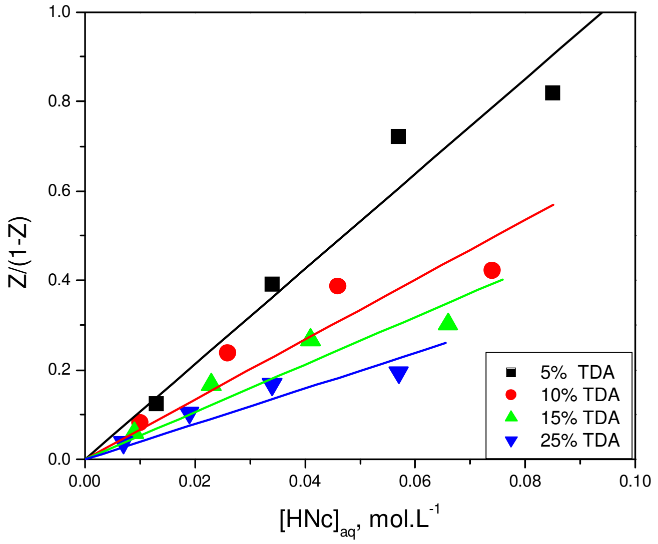

Figure 5.89 Estimation of (1:1) nicotinic acid-TDA equilibrium constant (*K*$_{E1}$) with different concentrations of TDA in n-dodecane/oleyl alcohol (2:1 v/v)

Table 5.32. The values of K_{11} and K_{21} for the formation of 1:1 and 2:1 complexes of acid and extractant respectively

Acid		**Extractant**		**Diluents**	K_{11}	R^2	K_{21}	R^2
Name	**Conc. mol.L^{-1}**	**Name**	**Conc. mol.L^{-1}**					
Propionic acid	0.0675 – 0.675	TOA	0.46	toluene + 1-decacol (1:1 v/v)	37.82	0.989	216	0.999
				cyclohexane + 1-decacol (1:1 v/v)	21.85	0.994	115	0.992
				kerosene + 1-decacol (1:1 v/v)	21.75	0.993	85	0.998
	0.0675 – 0.675	Aliquat 336	0.55	n-dodecane+1-decacol (2:1 v/v)	6.65	0.976	-	-
Nicotinic acid	0.02 – 0.12	TOA	0.229	MIBK	27.81	0.99	-	-
			0.573		11.61	0.999	-	-
			0.915		6.23	0.994	-	-
			1.376		3.11	0.99	-	-
			0.229	toluene	2.45	0.986	-	-
			0.573		1.72	0.995	-	-
			0.915		1.20	0.999	-	-
			1.376		0.81	0.968	-	-
	0.023 – 0.122	TDA	0.078	n-dodecane + oleyl alcohol (2:1 v/v)	10.64	0.967	-	-
			0.155		6.70	0.933	-	-
			0.233		5.30	0.945	-	-
			0.388		3.96	0.947	-	-

5.3.2.3 Estimation of K_E and a = m/n using Modified Langmuir Approach

The experimental results for extraction of propionic acid using TOA in the mixture of inert diluents and 1-decanol (1:1 v/v) are also interpreted in terms of modified Langmuir model (Eq. 4.49). Results of modified Langmuir model approach are plotted as a solid line in Figure 5.53 (Section 5.3.1.2) with an assumption of maximum loading ratio, $Z_{max} = a = m/n$. The best fits of data using for modified Langmuir model provide the values of number of acid molecules per amine molecule (m), which is found to be between one and two for different diluent systems. The values of a show the simultaneous formation of two associated acid:amine (1:1 and 2:1) complexes depending upon the diluent system used. The estimated values of K_E and the number of acid molecules per amine molecule ($a = m$) using modified Langmuir model are presented in Table 5.33. The estimated values of K_E and m using this model show the same qualitative trend as determined by optimization routine DE (Table 5.31). The quantitative difference in the values of K_E and m are found due to assumption ($Z_{max} = a = m/n$) used in Langmuir model (Eq. 4.49).

Table 5.33. Values of K_E and the number of reacting propionic acid molecule per TOA molecule (a =*m/n*) in different diluent systems using modified Langmuir model

Diluents	$C_{in,HP}$ /mol.L^{-1}	TOA /mol.L^{-1}	a	K_E	R^2
Toluene + 1-decanol (1:1 v/v)	0.0675 – 0.676	0.457	1.51	131.50	0.966
Cyclohexane +1-decanol (1:1 v/v)	0.0675 – 0.676	0.457	1.59	79.88	0.978
Kerosene+1-decanol (1:1 v/v)	0.0675 – 0.676	0.457	1.48	58.86	0.976

5.3.2.4 Estimation of LSER parameters

In this study, an LSER model (Eq. 4.52 as discussed in Section 4.1.2) is applied to predict the distribution coefficient for various TOA + diluent systems in the extraction of mono-carboxylic acids (formic-, acetic-, propionic- and butyric acids). The values of the solvatochromic parameters of the diluents used in this study are given in Table 5.34. The solvatochromic parameters for the mixture of decane and 1-decanol are determined using Eq. 4.53 (Section 4.1.2). These parameters for different diluents are fitted to the experimental results. For the estimation of optimum model parameters, a regression-technique-assisted computer program (least square linear regression) is used to minimize the deviation between model predicted and the experimental values of ln K_D. The estimated values of parameters of the model are presented in Table 5.35. The experimental data for the distribution coefficients show a good correlation to the calculated values. Based on the satisfactory results obtained, it is inferred that the distribution coefficients of acids between water and TOA + diluent system can be better described using the LSER model.

Table 5.34. Solvatochromic parameters (hydrogen-bond donor acidities (π^* and δ) and hydrogen-bond acceptor basicities (α and β) for diluents

S.No.	Component	π^*	β	α	δ
1	n-decane	0.03	0	0	0
2	1-decanol	0.40	0.45	0.33	0
3	Benzene	0.59	0.10	0	1.0
4	MIBK	0.63	0.48	0	0
5	chloroform	0.58	0.20	0.10	0.50

Table 5.35. Values of the LSER Model Parameters (*S, d, b, a*), the Coefficient of Linear Regression (R^2)

Type of Acid	$C_{(HA)in}$ /mol.L^{-1}	$\ln K_D^0$	LSER model parameters				R^2
			a	*b*	*S*	*d*	
Formic acid	0.2646	-0.4278	5.8105	-4.6243	5.5452	-0.3535	0.9557
	0.5292	-0.3396	3.4091	-2.7552	4.2381	-0.3297	0.9582
	0.7938	-0.0868	0.602	0.0466	1.6398	-0.1944	0.922
	1.323	0.1245	-1.1478	1.5504	0.0182	10.4122	0.9737
Acetic acid	0.05	-1.4502	7.8578	-6.677	7.2997	-0.3565	0.8648
	0.1	-1.1387	7.2903	-6.8334	7.07	-0.3844	0.9181
	0.15	-1.0558	6.724	-6.7421	6.969	-0.3826	0.9111
	0.25	-1.0051	6.296	-7.2742	7.391	-0.3835	0.9009
Propionic acid	0.0676	-0.28	5.3172	-5.4121	5.3778	-0.3684	0.9043
	0.135	-0.3349	5.5471	-5.9496	6.0743	-0.3604	0.934
	0.27	-0.3071	4.6152	-5.0833	5.5339	-0.3431	0.9423
	0.405	-0.1312	3.596	-4.3025	4.7438	-0.3437	0.965
Butyric acid	0.095	0.3691	4.6603	-4.9496	4.7858	-0.3606	0.9549
	0.189	0.4211	4.1556	-4.0772	4.3137	-0.3334	0.9618
	0.378	0.5291	3.2992	-3.9636	4.2132	-0.3351	0.9627
	0.567	0.6424	2.4114	-3.3065	3.6395	-0.3321	0.9698

5.3.2.5 Estimation of ΔH and ΔS

The apparent enthalpy (*ΔH*) and entropy (*ΔS*) are estimated using calculated values of K_E at different temperatures (301, 313, 323 and 333 K) for the reactive extraction of nicotinic acid using TDA in *n*-dodecane/oleyl alcohol (2:1 v/v). The enthalpy and entropy of this process is assumed to be constant over the temperature range, and their values are estimated using Vant' Hoff equation (Eq. 5.2 as discussed in Section 5.2.2.4).

The slope and intercept of a plot of ln K_E vs $1/T$ give the apparent enthalpy and entropy of reactive extraction reaction respectively. For the estimation of equilibrium constants at each temperature, a plot of equation (4.31) by taking, $\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right)$ on y-axis and log $[\overline{NR_3}]_{in}$ on x-axis yields a straight line with a slope of n and an intercept of log K_E as shown in Figures 5.90. The estimated values of equilibrium constants (K_E) from Figure 5.90 are used to determine the apparent enthalpy and entropy of the reaction as shown in Figure 5.91. The results from Figure 5.91 indicate that the reactive extraction of nicotinic acid is exothermic as *ΔH* is found to be negative (−19.53 kJ mol^{-1}). Similarly, the entropy for the acid is found to be −57.33 Jmol^{-1} K^{-1}. Based on Equation (5.2), the more is the exothermicity of a reaction, the more will be the equilibrium sensitivity to temperature.

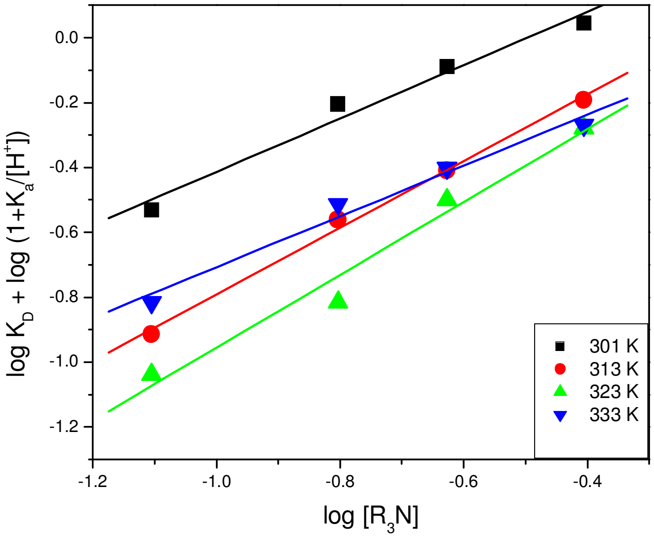

Figure 5.90. Determination of extraction constants (K_E) using TDA (0.079 – 0.393 mol.L^{-1}) in n-dodecane/oleyl alcohol (2:1 v/v) at different temperatures with acid concentration of 0.122 mol.L^{-1}

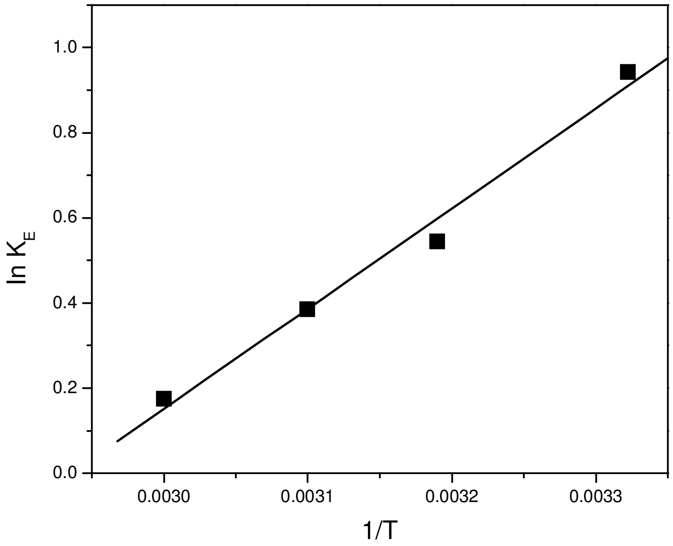

Figure 5.91. Determination of apparent enthalpy and entropy for the extraction of nicotinic acid with TDA in n-dodecane/oleyl alcohol (2:1 v/v)

5.3.2.6 Estimation of Kinetic Parameters

In the kinetic study of reactive extraction of nicotinic and propionic acid using TOA, the best pair of rate constants for a given particular set of individual orders - α', β' and γ' in the rate expression (4.56) are determined. The values of stoichiometric coefficient (*m)* are found to be 1.51 and 1.68 in the extraction of nicotinic acid and propionic acid respectively (estimated by equilibrium study). The different values of individual reaction orders (α', β' and γ') in Eq. (4.56) are considered to obtain the rate constant k_1 and k_2, but different values for the rate constants are found for the given concentration of acid at a constant concentration of TOA. When the experimental kinetic data for the extraction of nicotinic acid are interpreted by a forward reaction rate with α' = 1.52 and β' = 1.0 and the reverse reaction rate with γ' = 1.0, a very good fit is obtained with almost constant values for both the rate constants (k_1 and k_2) for the whole range of acid (0.02 – 0.10 mol.L^{-1}). A good fits of predicted and experimental results with almost constant values for k_1 and k_2 are also obtained, when the reaction rate is used with α' = 1.68 and β' = 1.0 and γ' = 1.0. On the other hand, k_1/k_2 values are independent of the acid concentration and the equilibrium points of these systems lie on the same extraction isotherm. This rate form [α' = 1.52, β' = 1.0, γ' = 1 for nicotinic acid and α' = 1.68, β' = 1.0, γ' = 1 for propionic acid in Eq. (4.56)], describing the net rate of extraction, can be considered as elementary kinetics, which suggests that the chemical complexation of the acid is a multiple reaction mechanism through which several types of acid-amine complexes are formed. The values of the rate constants k_1 and k_2 are presented in Tables 5.36 and 5.37 for extraction of nicotinic acid and propionic acid respectively. The evaluated kinetic curves are shown in Figures 5.81 and 5.82 (Section 5.3.8) as solid lines.

Table 5.36. Values of the rate constants k_1 and k_2 in the rate equation (4.56) for the extraction of nicotinic acid by TOA (0.23 mol.L^{-1}) in MIBK

$\alpha' = 1.52$, $\beta' = 1.0$ and $\gamma' = 1.0$			
C_{in}, mol.L^{-1}	k_1	k_2	k_1/k_2
0.10	10.248	0.0809	126.67
0.05	9.823	0.0776	126.58
0.02	11.004	0.0869	126.63
Average value of $k_1 = 10.36$ and $k_2 = 0.082$			

Table 5.37. Values of the rate constants k_1 and k_2 in the rate equation (4.56) for the extraction of propionic acid by TOA (0.46 mol.L^{-1}) in cyclohexane+1-decanol (1:1 v/v)

$\alpha' = 1.68$, $\beta' = 1.0$ and $\gamma' = 1.0$			
C_{in}, mol.L^{-1}	k_1	k_2	k_1/k_2
0.54	6.332	0.0858	73.80
0.405	6.874	0.0932	73.75
0.27	6.974	0.0945	73.80
Average value of $k_1 = 6.73$ and $k_2 = 0.0912$			

CHAPTER – 6

CONCLUDING REMARKS

Reactive extraction with a specified extractant giving a higher distribution coefficient is proposed as a promising technique for the intensification of recovery of carboxylic acids from fermentation broths as well as aqueous waste streams. In the present study, equilibrium and kinetic experiments are carried out to recover the different carboxylic acids from aqueous solutions. Different combination of extractant and diluent with different compositions are used in the extraction of acids. Various models are developed and used to estimate the equilibrium parameters, stoichiometries of reactive extraction and kinetic parameters. Theoretical study is also performed to predict the effect of diluent on the extraction equilibria of carboxylic acids. These data will be useful in the design of a reactive extraction unit that is to be coupled with the fermentation system to achieve in-situ recovery and purification of the product. This chapter presents a brief summary of the present work followed by conclusions, major contributions and future scope for research in this area.

6.1 Summary

6.1.1. Introduction

The carboxylic acids widely used in the field of food and beverages as an acidulant, in pharmaceutical and chemical industries are important chemicals. Industrial production of carboxylic acids is carried out using the petrochemical feed-stock. These acids are also produced by the biotechnology based processes (fermentation processes), which uses renewable resources. The growing importance of biological production, expressed with new routes and increasing production rates, asks for adapted downstream processing for product separation. In order to make the fermentation route economically viable, it is necessary to develop novel fermentation processes that use highly efficient separation techniques. Separation of mono-carboxylic acids such as formic-, acetic- and propionic acid from aqueous waste stream is also important and essential from the industrial and environmental viewpoint.

Among various available alternatives (liquid extraction, ultra filtration, reverse osmosis, electro-dialysis, direct distillation, liquid surfactant membrane extraction, anion exchange, precipitation and adsorption etc.) for simultaneous removal of the product, extraction is often the most suitable one. Reactive extraction with a chemical (solute and extractant reaction) phenomenon is developed to intensify the separation by solvent extraction. Organophosphorus-based and long-chain aliphatic amine-based extractants are effective for the separation of carboxylic acids from dilute aqueous solution. Generally, these extractants are dissolved in a diluent. It controls the viscosity and density of the solvent phase. However, the chemical structure of a diluent may also have various effects on the formation of acid-amine complexes. The literature related to the fermentation processes for the production of carboxylic acids and the reactive extraction for recovery of the carboxylic acids (lactic acid, citric acid, tartaric acid, acetic acid and propionic acid, etc.) from fermentation broth and aqueous waste stream is extensively reviewed. These studies focus on various aspects such as solvent (extractant and diluent) selection, effects of temperature, pH, aqueous and organic phase compositions on extraction, in-situ product recovery, chemical interactions involved in the complexation of acid with extractant, kinetics of extraction, etc..

6.1.2 Gaps in Existing Literature

It is important for the production of carboxylic acid from the biological origin, as used in foods and pharmaceuticals. The existing literature on carboxylic acids suggests that great strides have been made in the separation of lactic acid from aqueous solution using reactive extraction to enhance the microbial production (90%) of lactic acid. Nicotinic acid and propionic acid (despite the fact that a feasible industrial bio-process has not yet been developed) have huge potential as a building-block chemicals used in various industries. Data on reactive extraction for the recovery of nicotinic acid from aqueous solution for intensification of microbial production are still scarce. The use of active diluent (modifier) with inactive diluent in the extractants is limited. These reactive extraction data can also be utilized in the design of extraction process for the separation of formic acid, acetic acid, propionic acid and butyric acid from the aqueous waste industrial stream. The quantification of diluent effect by LSER model and a model based on μ & E_T parameters is limited to a few carboxylic acids with specific extractant. An evolutionary based optimization routine [differential evolution (DE)] to estimate the equilibrium parameters is not explored. There is a lot of scope to generate the reactive extraction data with less toxic or non-toxic amine/diluent systems for the intensification of propionic- and nicotinic acid production via fermentation route.

6.1.3. Scope of the Work

The present study aims to accomplish the reactive phase equilibria and to obtain the data for the recovery of carboxylic acids. In the present study, extraction of acids from its aqueous solutions is performed to determine the optimum conditions for the recovery of acids from fermentation broth as well as aqueous waste stream. The effects of various parameters on the reactive extraction are investigated with the aim of implementing the data obtained to a future industrial separation unit. Long chain aliphatic amines and organophosphorus based derivatives dissolved in different diluents [inert, active (modifier) and mixture of both] are used as the organic phases for the extraction of acids from aqueous solutions. Since growth of microorganism is inhibited by the toxicity of solvents in the fermentation units, equilibrium studies are also carried out using biocompatible system (extractant/diluent) for the reactive extraction of propionic acid and nicotinic acid. Attempts have been made to quantify the effect of diluents on extraction efficiency (distribution coefficient) of extractant (TOA) using LSER model for the extraction of formic acid, acetic acid, propionic acid and butyric acid. The effect of diluents on extraction efficiency (equilibrium constant) of extractant (TOPO) is quantified using a model based on dipole moment (μ) and E_T parameter for the extraction of nicotinic acid. The solvation strength of complexes is estimated through the mathematical models using an optimization procedure [a population based search algorithm called differential evolution (DE)] and graphical methods. Kinetic study is also carried out to obtain the kinetic data using TOA as an extractant for reactive extraction of propionic- and nicotinic acids.

6.1.4. Experimental Studies

The extraction equilibrium experiments are carried out at constant temperature (298 K) with equal volumes of aqueous and organic solutions shaken at 100 rpm for 8 hours in conical flasks of 100 mL on a temperature controlled reciprocal shaking machine (HS 250 basic REMI labs, India). To study the effect of temperature on reactive extraction, the equilibrium experiments are carried out at four different temperatures (298 – 334 K). Kinetic experiments are carried out in the stirring vessel (cylindrical glass of 5.0 cm in diameter and 10.0 cm in height with a flat bottom). The four-blade paddle adjusted to 1.0 cm below the interface is used for agitation. The aqueous solutions of the carboxylic acids are prepared to the desired concentrations (0.02 - 0.13 mol.L^{-1}for nicotinic acid, 0.05 - 0.25 mol.L^{-1}for acetic acid, 0.0675 - 1.35 mol.L^{-1}for propionic acid, 0.095 - 0.57 mol.L^{-1} for butyric acid and 0.265 - 1.323 mol.L^{-1} for formic acid) using de-ionized water. Organic phases are prepared by different extractants [tri-n-octylphosphine oxide (TOPO), tri-n-butylphosphate (TBP), tri-n-octylamine (TOA), tri-n-dodecylamine (TDA) and methyltrioctylammonium chloride (Aliquat 336)] thoroughly dissolved in different diluents. Pure diluents and pure extractant are also used as organic phase. After attaining the equilibrium, the mixture is allowed to settle for 4 hrs. The aqueous and organic phases of are separated by using a separating funnel of 100 mL. The analysis of the aqueous phases before and after extraction is performed by using potentiometric titration with fresh sodium hydroxide solution, and also using an UV spectrophotometer (Systronics, 119 model, 262 nm, India). The acid concentration in the organic phase is calculated by mass balance. The initial and equilibrium pH values of aqueous solutions are measured using a digital pH-meter of ArmField Instruments (PCT 40, Basic Process Module, UK). The extraction process is analyzed by means of the degree of extraction and distribution coefficient.

6.1.5. Mathematical Modeling and Simulation

Modeling of reactive extraction for recovery of carboxylic acids implies the representation of chemical and physical phenomena occurring in the process in mathematical form constituting the extractants and/or diluents as the organic system, and acid & water as the aqueous system. The models of reactive extraction are broadly categorized into two groups: (1) Equilibrium models and (2) Kinetic models. The equilibrium models assume that all the reactions are in thermodynamic equilibrium at the interface of aqueous and organic phases. The kinetic model is used for predicting kinetic constants and the orders of chemical reaction between the acid molecules and extractant molecules. A mass action law based models for physical extraction (extraction with pure diluent) and for reactive extraction (chemical interactions between the acid and extractant are strong compared to the physical interactions) are employed to determine the stoichiometries of extraction reaction and the values of equilibrium extraction constant (K_E) for different acid/extractant/diluent systems. The model, based on the assumption of simultaneous formation of various types of complexes between acid and amine (extractant), is formulated and solved based on the loading of extractant (Z). The effect of diluent on the recovery of mono-carboxylic acids from the aqueous solution is quantified by the LSER models using solvatochromic parameters of diluents, and a model based on dipole moment (μ) & E_T parameter. Kinetic parameters of reactive extraction are estimated for the nicotinic acid and propionic acid with TOA dissolved in diluents using Poposka *et al.,* (2000) modeling approach. The equilibrium parameters of the proposed models are estimated using a population based search algorithm as optimization routines (Differential Evolution) and by graphical methods.

6.1.6. Results and Discussion

In the following sections, the experimental results obtained in the present study are summarized. The section also discusses the simulated results which are obtained by the proposed mathematical model using the experimental data for the estimation of equilibrium and kinetic parameters.

6.1.6.1. Extraction with Pure Diluents

The equilibrium experimental results for the recovery of carboxylic acids (formic acid, acetic acid, propionic acid, butyric acid and nicotinic acid) using pure diluents [*n*-hexane, *n*-heptane, *n*-decane, *n*-dodecane, toluene, benzene, butyl acetate, diethyl ether, dichloromethane, methyl isobutyl ketone (MIBK), 1-octanol and 1-decanol] are presented to determine the effect of diluent, effect of type of acid and the concentration of acid. In the extraction of acetic-, propionic- and butyric acid having almost similar acid strength (pK_a), the extraction efficiency depends strongly on hydrophobicity of acids and found to be increased with increased hydrophobicity. Due to the presence of functional group in nicotinic acid, the extractability is low (a maximum value of $K_D = 0.18$ in MIBK) as compared to that of other acids having almost similar acid strength. The aliphatic and aromatic solvents, including substituted hydrocarbons (n-heptane, *n*-decane, benzene, kerosene, and chloroform) are characterized by a low degree of acid extractability. However, solvents such as MIBK, diethyl ether and protic 1-octanol and 1-decanol containing an oxygenated functional group yield higher and different values of K_D depending upon the solvent polarity and the hydrogen bonding ability. Extraction efficiency is found to increase with an increase in the concentration of acid in the case of inert diluents but remain almost independent of acid concentration when alcohols and ketones are used. The numerical values of the partition constant (P) and dimerization constant (D) are also estimated using the model.

6.1.6.2. Reactive Extraction using Phosphorus-based Extractants

Equilibrium results are obtained for the reactive extraction of propionic acid and nicotinic acid using TBP and TOPO dissolved in different diluents. When TBP is used in a mixture of an inert diluent (kerosene and n-decane) and modifier (1-decanol) in reactive extraction, the solubility of extracted species is found to increase in the organic phase. The equilibrium isotherms for propionic acid are determined from different concentrations of the aqueous solution and different concentrations of extractant. When the extractant (TBP and TOPO) concentration increases, the degree of extraction (%) also increases. The degree of extraction (%) significantly decreases when the concentration of propionic acid is increased from 0.135 to 0.676 mol.L^{-1}. The effect of temperature on the extraction of propionic acid with 25% and 40% of TBP dissolved in *n*-decane/1-decanol (1:1 v/v) and in kerosene/1-decanol (1:1 v/v) is presented. It is found that as the temperature increases, the percentage amount of acid extracted decreases. The reactive extraction data for nicotinic acid using pure TBP, TBP and TOPO dissolved in different diluents are also presented. A stronger effect of diluent is observed, when TOPO is used as the extractant rather than TBP. The values of $K_D = 0.27$ and 1.35 for the concentration of TOPO (0.39 mol.L^{-1}) dissolved in kerosene + 1-decanol (2:1 v/v) and MIBK respectively are found. The degree of extraction (E) decreases when the concentration of acid is increased from 0.02 to 0.12 mol.L^{-1} and is found to increase with an increase in TOPO concentration. The organic phase is not found to be highly concentrated by acid ($Z < 0.5$), 1:1 complex of acid (propionic- and nicotinic acid) and extractant (TBP and TOPO) is formed. The values of K_E and stoichiometry (n) are estimated using an optimization procedure (DE) as well as graphical method. The estimated values of n indicate a stoichiometric association between the individual phosphoryl and acid group. The diluent, having higher dielectric constant values also contributes in the reactive extraction of acid and results in a low value of stoichiometry coefficients ($n = 0.70$) for MIBK having the dielectric constant value of 13.1. In all the tested diluents, toluene containing a benzene ring in the structure is found to be the best solvating agent for nicotinic acid-TOPO complexation. The reactive extraction of propionic acid using TBP is found exothermic with a negative value of ΔH (–5.65 kJ mol^{-1}).

6.1.6.3. Reactive Extraction using Amine-based Extractants

Equilibrium data are presented for the extraction of mono-carboxylic acids (formic, acetic, propionic and butyric acid) with TOA in 6 different diluents [1-decanol, chloroform, MIBK, n-decane, benzene, and 1-decanol + n-decane (1:3 v/v)]. The extraction power of amine/diluent system in terms of either Z or K_D increases as chloroform ≥ 1-decanol > methyl isobutyl ketone > benzene > decane+1-decanol (3:1 v/v) > decane. LSER model using solvatochromic parameters for the diluents is also applied to predict the distribution coefficient for various TOA + diluent systems on the extraction of mono-carboxylic acid.

Reactive extraction of propionic acid is also carried out with TOA dissolved in an inert diluent (toluene, n-decane, n-dodecane and cyclohexane) and a modifier (1-decanol). The higher modifier concentration leads to an increase in the degree of extraction of propionic acid. Since, n-dodecane is a non-toxic for the bacteria in contrast to 1-decanol and TOA, the extraction systems composed of (1) 20% TOA, 20% 1-decanol and 60% n-dodecane, (2) 20%TOA, 30% 1-decanol and 50% n-dodecane, and (3) 30%TOA, 20% 1-decanol and 50% n-dodecane are used for the extraction of propionic acid (0.0675 – 0.676 $mol.L^{-1}$). Equilibrium experiments are also carried out using Aliquat 336 dissolved in 1-octanol and in the mixture of n-dodecane and 1-decanol for the extraction of propionic acid.

Results of equilibrium concentrations of propionic acid in both the phases are presented in the form of isotherms.

Equilibrium data are presented for the extraction of nicotinic acid using TOA and Aliquat 336 in different diluents (1-decanol, MIBK, n-decane, toluene and butyl acetate). The highest strength of the complex solvation is found for MIBK with a maximum loading ratio ($Z = 0.42$) promoting probably (1,1) acid-amine complex formation. The extraction efficiency of Aliquat 336 is found to be insignificant with all diluents (MIBK, n-decane, toluene and 1-decanol) due to the presence of ammonium and chloride ions. TOA is also used with a mixture of inert diluent (*n*-decane, cyclohexane, kerosene and toluene) and a modifier (1-octanol and 1-decanol). 1-Octanol as a modifier is found to be more effective as compared to 1-decanol in various inert diluents. Due to the toxicity of alcohols towards bacteria, 1-decanol and n-decane with TOA is further used to estimate the value of K_E and stoichiometry of reaction. The extraction of nicotinic acid from aqueous solution is also studied using TDA dissolved in the nontoxic diluent system (n-dodecane and oleyl alcohol with log P of 6.1 and 7.5 respectively). The effect of temperature (301, 313, 323 and 334 K) on the extraction of nicotinic acid with TDA (5 – 25%) in n-dodecane/oleyl alcohol (2:1 v/v) is determined and the percentage amount of acid extracted is found to vary with temperature. The reactive extraction of nicotinic acid with TDA is found to be exothermic with ΔH of -19.53 kJ mol^{-1}. The estimated values of number of acid molecules per amine molecule (m), which is found to be between one and two in the extraction of propionic- and butyric acid show the simultaneous formation of two associated acid:amine (1:1 and 2:1) complexes. The loading ratios for the extraction of acetic- and nicotinic acid found to be low, indicate that 1:1 complexes between acid and extractant. In the extraction of formic acid probably three associated acid:amine (1:1, 2:1 and 3:1) complexes are formed. In the kinetic study of reactive extraction of nicotinic and propionic acid using TOA, the best pair of rate constants (k_1 and k_2) for a given particular set of individual orders - α', β' and γ' are determined.

6.2. Conclusions

Based on the results obtained in the present study, the following conclusions are drawn:

1. Reactive extraction with a specified extractant/diluent system giving a higher distribution coefficient is found to be a promising technique (efficient, economical, and environmental friendly) for the separation of carboxylic acids from fermentation broth and waste water streams.
2. In the extraction (physical) of carboxylic acids, the extraction efficiency depends strongly on the hydrophobicity of acids and is found to be the maximum for butyric acid extraction with the highest value of hydrophobicity.
3. Active diluent (MIBK and 1-decanol) show the maximum partition coefficients for all acids. The extracted acid molecules are found to dimerize to a small extent, or not at all, with 1-decanol and MIBK.
4. The extraction efficiency is found to increase significantly with an increase in the concentration of acid using pure inert diluent, but remains almost independent of acid concentration when 1-decanol and MIBK are used.
5. Organophosphorus compounds (TBP and TOPO) and long-chain amines (TOA and TDA) having stronger basicity than those of pure diluents, are found to be effective extractants for the separation of carboxylic acids from dilute aqueous solution.

6. When an extractant is used as in a mixture of an inert diluent and an active diluent (modifier) in reactive extraction, then the degree of extraction of acids increases with an increase in the concentration of modifier in the organic phase.
7. The degree of extraction (E) is found to increase with an increase in the concentration of extractant (TBP and TOPO) in different diluents and found to decrease when the concentration of acid (propionic- and nicotinic acid) is increased.
8. Since, the loading ratio is found to be low ($Z < 0.5$), 1:1 complexes between propionic acid & TBP, nicotinic acid & TBP, and nicotinic acid & TOPO are formed.
9. The estimated values of equilibrium constant (K_E) and the number of reacting extractant molecules (n) in the extraction of carboxylic acid, using differential evolution (DE), are found to be better than those obtained by graphical method.
10. The strength of the complex solvation is found to be in the decreasing order of toluene < 4-MIBK < dichloromethane < kerosene < *n*-octane < 1-decanol, promoting probably (1,1) nicotinic acid-TOPO complex formation.
11. The approach with the values of μ and E_T parameter of different diluents can be used to quantify the effect of diluents on the 1:1 complexation of nicotinic acid as given by Eq. 5.1.
12. From the equilibrium results for different mono-carboxylic acids using TOA in 6 different diluents, the extraction power of amine and diluent system increases in the order of chloroform ≥ 1-decanol > methyl isobutyl ketone > benzene > decane+1-decanol (3:1 v/v) > decane. The effect of diluent on the values of K_D for different acids can be predicted by LSER model.

13. The values of Z (0.05 – 1.21) for propionic- and butyric acid suggest simultaneous formation of 1:1 and 2:1 complexes between acid and amine. The values of Z (0.0 – 0.5) for acetic acid indicate only 1:1 complexes between acid and amine. In case of formic acid extraction ($Z = 0.15 – 2.55$), 1:1, 2:1 and 3:1 complexes are possible.
14. The predicted values of K_D and Z using DE are comparable with the experimental values of K_D and Z.
15. In the extraction of propionic acid with TOA dissolved in different inert diluents (toluene, kerosene and cyclohexane) and 1-decanol (1:1 v/v), the highest strength of the complex solvation ($K_E = 77.52$ using DE) is found using toluene + 1-decanol (1:1 v/v) with TOA.
16. The extractant/diluent systems comprised of (1) 20%TOA, 20% 1-decanol and 60% n-dodecane, (2) 20%TOA, 30% 1-decanol and 50% n-dodecane and (3) 30%TOA, 20% 1-decanol and 50% n-dodecane are used as biocompatible mixture for the extraction of propionic acid. The loading ratios found in the range of 0.113 – 1.05 indicate that 1:1 and 2:1 complexes between acid and TOA are formed simultaneously. The highest value of $K_E = 33.18$, with 3rd extractant/diluent system, indicate the highest strength of the complex.
17. In the extraction of nicotinic acid using TOA in different diluents (MIBK, toluene, butyl acetate and n-dodecane), the highest strength of the complex solvation is found for MIBK with a maximum loading ratio ($Z = 0.42$). Whereas, the degree of extraction using Aliquat 336 in different diluents (1-decanol, MIBK, toluene and n-decane) is found insignificant.

18. The results for the extraction of nicotinic acid show that the degree of extraction first increases and then decreases with an increase in the concentration of TOA in n-decane/1-decanol (1:1 v/v). 15% of TOA (0.343 mol.L^{-1}) in n-decane/1-decanol (1:1 v/v) used for the extraction of nicotinic acid (0.02 – 0.12 mol.L^{-1}) yields a value of $K_{11} = 31.38$.

19. TDA dissolved in a mixture of nontoxic diluents [*n*-dodecane and oleyl alcohol (2:1 v/v)] is found to be a biocompatible mixture for the recovery of nicotinic acid from fermentation broth. Based on the values of loading ratios ($Z < 0.5$), it is concluded that 1:1 complexes of nicotinic acid and TDA are formed.

20. In the extraction of propionic acid using TBP (25% and 40%) in *n*-decane/1-decanol (1:1 v/v) and kerosene/1-decanol (1:1 v/v), it is found that as the temperature increases, the percentage amount of acid extracted decreases. In the extraction of nicotinic acid with TDA (5–25%) in n-dodecane/oleyl alcohol (2:1 v/v), the degree of extraction is found to decrease with an increases in temperature from 301 to 323 K and slightly increase at a temperature of 333 K.

21. The reactive extraction of propionic acid and nicotinic acid is found to be exothermic with the negative values of ΔH (−5.65 kJ mol^{-1} and −19.53 kJ mol^{-1} respectively). Similarly, the entropy for these acids is found to be −12.37 Jmol^{-1} K^{-1} and −57.33 Jmol^{-1} K^{-1} respectively.

22. In the kinetic study, the extraction of nicotinic acid is interpreted by a forward reaction rate with $\alpha' = 1.52$ and $\beta' = 1.0$ and the reverse reaction rate with $\gamma' = 1.0$ with the corresponding rate constants of $k_1 = 10.36$ and $k_2 = 0.082$. The extraction of propionic acid is interpreted by a forward reaction rate with $\alpha' = 1.68$ and $\beta' = 1.0$ and

the reverse reaction rate with $\gamma' = 1.0$ with the corresponding rate constants of $k_1 = 6.73$ and $k_2 = 0.0912$.

6.3 Major Contributions

1. The diluent systems comprised of an inert diluent and an active diluent (modifier) with extractants (TBP, TOA and TDA) are investigated for the extraction of propionic acid and nicotinic acid.
2. Equilibrium studies are carried out using TOPO as an extractant dissolved in six different diluents (toluene, MIBK, dichloromethane, kerosene, *n*-octane and 1-decanol) to generate the extraction equilibrium data for the recovery of nicotinic acid. The model using the values of μ and E_T parameter of the diluents, are used to quantify the effect of diluents on the extraction of nicotinic acid.
3. The extractant/diluent systems comprised of TOA and Aliquat 336, 1-decanol and n-dodecane (biocompatible mixture) are investigated for the extraction of propionic acid from fermentation broth.
4. The equilibrium study is performed for different mono-carboxylic acids (formic, acetic, propionic and butyric acid) using TOA (extractant) in 6 different diluents [1-decanol, chloroform, methyl isobutyl ketone, n-decane, benzene, and a mixture of 1-decanol and n-decane (1:3 v/v)]. LSER model is proposed to determine the effect of diluent on the values of K_D.
5. The reactive extraction of nicotinic acid using TOA in 4 different diluents (MIBK, toluene, butyl acetate and n-dodecane) is studied.

6. A biocompatible extractant-diluent system of TDA dissolved in the mixture of nontoxic diluents [*n*-dodecane and oleyl alcohol (2:1 v/v] is explored for the recovery of nicotinic acid from fermentation broth.
7. In all the extractant-diluent systems investigated for the extraction of different carboxylic acids, a population based search algorithm called differential evolution (DE), is employed to determine the values of equilibrium extraction constant (K_E) and the stoichiometries of reactive extraction.
8. Kinetic studies are carried out for the extraction of nicotinic acid and propionic acid using TOA in diluents.

6.4 Future Scope of Research

The future scope of this work is enumerated below:

1. The extractant-diluent systems can be investigated for the extraction of propionic acid and nicotinic acid at higher values of p*H* in the range of 4 – 6.
2. The developed mathematical model (chemodel) can be modified for the simultaneous formation of different complexes between acid and extractant based on FTIR analysis of organic phases.
3. Kinetic study on the extraction of propionic and nicotinic acid can be carried out using a porous membrane between aqueous and organic phases.
4. The proposed LSER model can be modified to incorporate the effect of initial acid concentration.
5. Thermodynamic study on LLE can be carried out for quaternary system (carboxylic acid + water + diluent + extractant).

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BIOGRAPHIES

Biography of the Candidate

Sushil Kumar is a Lecturer in Chemical Engineering Department at BITS-Pilani, and currently pursuing his PhD under the supervision of Prof B V Babu. He has completed his B Tech in Chemical Engineering from Harcourt Butler Technological Institute (HBTI), Kanpur (UP) in the year 2000. He obtained his M Tech degree in chemical engineering from Indian Institute of technology (IIT), Kanpur (UP) in 2003. He earlier worked with Central Institute of Plastic Engineering and Technology (CIPET), LUCKNOW (UP), India, from August, 2003 to January, 2005 as Technical Officer. He joined BITS Pilani as an Assistant Lecturer in Chemical Engineering Group in Jan 2005. He has 6 years of teaching experience and has guided 1 Professional Practice –II student and 1 ME dissertation student and around 50 project students. He taught courses such as Biochemical Engineering, Chemical Engineering Thermodynamics, Kinetic Reactor Design, Thermodynamics, Structure and Properties of Materials, Environmental Pollution Control and Measurement Techniques-II and involved in the tutorials of Selected Chemical Engineering Operations, Process Control, Heat Transfer Operations and Chemical Process Technology. His research areas include Process Intensification using Reactive Extraction, Separation Processes in Biotechnology, Biochemical Engineering, Polymer Technology & Biopolymers and Modeling & Simulation. He is associate life member of IIChE.

Biography of Supervisor

Dr B V Babu is Professor of Chemical Engineering and Dean of Educational Hardware Division (EHD) at Birla Institute of Technology and Science (BITS), Pilani. He did his PhD from IIT-Bombay. His biography is included in 2005, 2006 & 2007 editions of Marquis Who's Who in the World, in Thirty-Third Edition of the Dictionary of International Biography in September 2006, in 2000 Outstanding Intellectuals of the 21st Century in 2006, and in First Edition of Marquis Who's Who in Asia in 2007. He is the Coordinator for PETROTECH Society at BITS-Pilani. He is on various academic and administrative committees at BITS Pilani. He is the member of project planning & implementation committees of BITS-Pilani Dubai Campus, BITS-Pilani Goa Campus, and BITS-Pilani Hyderabad Campus. He is external expert member of Board of Studies at Banasthali University and MNIT-Jaipur. He is expert peer committee member of National Assessment and Accreditation Council (NAAC), Bangalore, India. He is also member of Peer Review Committee for The Natural Sciences and Engineering Research Council of Canada (NSERC), Canada; and National Research Foundation (NRF), International Research Grants, South Africa.

He has 24 years of Teaching, Research, Consultancy, and Administrative experience. He guided 5 PhD students, 36 ME Dissertation students and 35 Thesis students and around

200 Project students. He is currently guiding 5 PhD candidates and 2 Thesis students. He is on doctoral advisory committee for 10 PhD students. He currently has 4 research and sponsored projects from MHRD, UGC, DST & KK Birla Academy. He is PhD Examiner for 7 candidates and PhD Thesis Reviewer for 6 Candidates.

His research interests include Evolutionary Computation (Population-based search algorithms for optimization of highly complex and non-linear engineering problems), Environmental Engineering, Biomass Gasification, Energy Integration, Artificial Neural Networks, Nano Technology, and Modeling & Simulation.

He is the recipient of National Technology Day (11th May, 2003) Award given by CSIR, obtained in recognition of the research work done in the area of ‘A New Concept in Differential Evolution (DE) – Nested DE’. His paper entitled "Convective and Radiative Heat Transfer in Pyrolysis of a Biomass Particle" authored by A S Chaurasia, B V Babu, Amanpreet Kaur, and V Thiruchitrambalam, published in Indian Chemical Engineer Journal, Vol. 47 (No. 2), pp. 75-80, April-June, 2005 earned the Kuloor Memorial Award, 2006 awarded for the Best Technical Paper published in the Institute’s Journal “Indian Chemical Engineer” in its issues for 2005.

He is the Life member of Indian Institute of Chemical Engineers (IIChE), Life member of Indian Society for Technical Education (ISTE), Life member of Institution of Engineers (IE), Fellow of International Congress of Chemistry and Environment (ICCE), Life member of Indian Environmental Association (IEA), Life member of Society of Operations Management (SOM), Associate Member of International Society for Structural and Multidisciplinary Optimization (ISSMO), Member of International Institute of Informatics and Systemics (IIIS), Member of International Association of Engineers (IAENG). Nine of his technical papers have been included as successful applications of Differential Evolution (DE: a population based search algorithm for optimization) on their Homepage at http://www.icsi.berkeley.edu/~storn/code.html#appl.

He has around 190 research publications (International & National Journals & Conference Proceedings) to his credit. He completed three consultancy projects successfully and he has been Technical Consultant for Maharashtra Electricity Regulatory Commission (MERC), Mumbai and offering Advisory Services in the “Study relating to Bagasse Based Co-generation”. He also has been invited as a consultant by a Bahrain (Middle East) based company for making a complex of chemical factories. He is a Panel Expert for www.chemicalhouse.com the most vibrant and active site for the Chemical Industry on the net which specializes in exchange of Information in a structured way among the chemical world in more than a Hundred Countries and a Million core chemical manufacturers traders scientists etc. He is Technical Consultant for Sangam (India) Limited Textile Industry at Bhilwara for Removal of Color, BOD, and COD from Effluent Treatment Plant.

He has published five books (1) “Process Plant Simulation”, EDD, BITS-Pilani, 2002, (2)“New Optimization Techniques in Engineering”, Springer-Verlag, Germany, 2004, and (3)”Process Plant Simulation”, Oxford University Press, India, 2004, (4) “Environmental Management Systems”, EDD, BITS-Pilani, 2005, (5) “Chemical Engineering Laboratory Manual”, EDD, BITS-Pilani, 2006. In addition he has written several chapters and invited articles in various books, lecture notes, and International Journals. He was invited to write an editorial and for cover design on Conservation of Natural Resources, for December 2006 Issue of International Research Journal of Chemistry & Environment.

He was the Invited Chief Guest and delivered the Keynote addresses at seven international conferences and workshops (Desert Technology–7, Jodhpur; Life Cycle Assessment, Kaula Lumpur; Indo-US Workshop, IIT-Kanpur; Indo-French Workshop, TERI-New Delhi; Indo-US Workshop, Kolkata; Research tools Workshop, BITS Pilani-Goa Campus; Process Modeling & Simulation Workshop, UPES-Dehradun) and three national seminars. He organized many Seminars & Conferences at BITS-Pilani. He also chaired 20 Technical Sessions at various International & National Conferences. He delivered 43 invited lectures at various IITs and Universities abroad.

He is Editorial Board Member of five International Journals 'Energy Education Science & Technology', 'Research Journal of Chemistry and Environment', 'International Journal of Computer, Mathematical Sciences and Applications', 'Journal on Future Engineering and Technology', and 'International Journal of Applied Evolutionary Computation'. He is the referee & expert reviewer of 59 International Journals. He is also on the Programme Committees at many (around 100) International Conferences. He reviewed five books of McGraw Hill, John Wiley & Science, Elsevier, Oxford University Press, and Tata McGraw Hill publishers.

He is the Organizing Secretary for "National Conference on Environmental Conservation (NCEC-2006)" held at BITS-Pilani during September 1-3, 2006. He is also the Organizing Committee Member (Publicity Chair), and Session Organizer for the Special Session on "Evolutionary Computation" at The Second International Conference on "Computational Intelligence, Robotics, and Autonomous Systems (CIRAS-2003)", National University of Singapore, Singapore, December 15-17, 2003. He is the Session Chair and organized an Invited Session on "Engineering Applications of Evolutionary Computation Techniques" at "The Eighth World Multi-Conference on Systemics, Cybernetics, and Informatics (SCI-2004)", Orlando, Florida, USA, July 18-21, 2004.

APPENDIX I

Code in MatLab for Estimation of the Values of K_E and n

```
function val = rosenbrocksaddle(scale, params)

n  = params.parameter1(1);
Ke = params.parameter2(1);

error = 0;
Ytheo = zeros;

Yexp = [0.653 0.767 0.819 0.87];
CHLbar = [0.223 0.2292 0.232816 0.235952];
R3Nin = [0.328 0.547 0.875 1.312];

for i=1:1:4
   Ytheo(i) = log10(Ke)+n*log10(R3Nin(i)-n*CHLbar(i));
   error = error+((1-Ytheo(i)/Yexp(i))^2);
end

val = scale*(error);
error = 0;
pause(0.1);

function demo1
%DEMO1  Demo for usage of DIFFERENTIALEVOLUTION.
%       DEMO1 starts searching the minimum of Rosenbrock's saddle as a demo.
%       Modify this function for your first optimization.
%
%       Markus Buehren
%       Last modified 03.02.2008
%
%       See also DIFFERENTIALEVOLUTION, ROSENBROCKSADDLE.

optimInfo.title = 'Demo 1 (Rosenbrock''s saddle)';


objFctHandle = @rosenbrocksaddle;

paramDefCell = {
   'parameter1', [0 5], 0.01
   'parameter2', [10 50], 0.1
```

```
};
objFctParams.parameter1 =  2;
objFctParams.parameter2 = 10;

objFctSettings = 100;

DEParams = getdefaultparams;

DEParams.NP = 20;

DEParams.feedSlaveProc = 0;

DEParams.maxiter       = 100;
DEParams.maxtime       = 60;  % in seconds
DEParams.maxclock      = [];

DEParams.refreshiter   = 1;
DEParams.refreshtime   = 10;  % in seconds
DEParams.refreshtime2  = 20;  % in seconds
DEParams.refreshtime3  = 40;  % in seconds

emailParams = [];

rand('state', 1);

 [bestmem, bestval, bestFctParams] = ...
    differentialevolution(DEParams, paramDefCell, objFctHandle, ...
    objFctSettings, objFctParams, emailParams, optimInfo); %#ok

disp(' ');
disp('Best parameter set returned by function differentialevolution:');
disp(bestFctParams);
```

APPENDIX II

Code in 'C' Estimation of the Values of K_E and *m*

```
//For K_E and m
#include<conio.h>
#include<iostream.h>
#include<math.h>
#include<ctype.h>
#include<time.h>
#include<stdlib.h>
#include<stdio.h>

#define NP 30
#define D 2
#define genmax 200


#define F 0.5
#define CR 0.9
FILE *fp;
double funvalue(double aef[]);


#define IM1 2147483563
#define IM2 2147483399

#define AM (1.0/IM1)
#define IMM1 (IM1-1)
#define IA1 40014
#define IA2 40692
#define IQ1 53668
#define IQ2 52774
#define IR1 12211
#define IR2 3791
#define NTAB 32
#define NDIV (1+ IMM1/NTAB)
#define EPS1 1.2e-7
int q,q11;
#define RNMX (1.0-EPS1)
//Random Number Generator Function
double rand_uni(double * );
```

```
double rand_uni(long *idum)
{
   long j,k;
   static long idum2=123456789;
   static long iy=0;
   static long iv[NTAB];
   double temp;
   if(*idum<=0)
     {
           if(-(*idum)<1)
                       *idum=1;
           else
           *idum=-(*idum);
           idum2=(*idum);

           for (j=NTAB+7;j>=0;j--)
           {
             k=(*idum)/IQ1;
             *idum=IA1 * (*idum-k*IQ1)-k*IR1;
             if (*idum<0)
                *idum+=IM1;
             if(j<NTAB)
             iv[j]=*idum;
           }            //End of For loop for j
           iy=iv[0];

}          //End of if
k=(*idum)/IQ1;
*idum=IA1*(*idum-k-IQ1)-k*IR1;
if(*idum<0)
   *idum+=IM1;
   k=idum2/IQ2;
   idum2=IA2*(idum2-k*IQ2)-k*IR2;
   if(idum2<0)
   idum2+=IM2;
   j=iy/NDIV;
   iy=iv[j]-idum2;
   iv[j]=*idum;
//printf(" The Random Number is %4.4f \n %4.4f",temp,RNMX);
           //getch();
   if(iy<1)
     iy+=IMM1;
   if((temp=AM*iy)>RNMX)  {
              return RNMX;
   printf(" The Random Number is RNMX %4.4f \n ",RNMX); getchar();}
   else
```

```
  {
  return temp;
  printf(" The Random Number is %4.4f \n ",temp); getchar();
  } //getch();
} //End Rand Function


main()
{
double ae[NP][D],ae1[NP],aet[NP],aeo[NP],check,aef[NP],newae[NP][D];

int       i,j,k,a,b,c, seed;
double y1,Ft,Fi;

static float ael[2] = {0.5,20.0};
static float aeu[2] = {2.0,150.0};


fp = fopen("E:\\PhD_ Research\\data\\sushil_DE code\\code1\\test31.txt","a+");


printf("Enter the seed for random number\n");

        scanf("%d",&seed);
        long rand_uni_init=seed;

for(i=0;i<NP;i++)
                {

                for(j=0;j<D;j++)
                        {
                        ae[i][j]=ael[j]+(rand_uni(&rand_uni_init))*(aeu[j]-ael[j]);
                        printf("ae[%d][%d]=%e\n",i,j,ae[i][j]);
                        }

                }



        for(k=0;k<genmax;k++)
                {


                        if ((k%10)==0)
                        {
                                printf("k=%d\n",k);
```

```
                fprintf(fp,"k=%d\n",k);
            }

            for(i=0;i<NP;i++)
            {
            do a=(int)((NP)*rand_uni(&rand_uni_init));
                while(a==i);

            do b=(int)((NP)*rand_uni(&rand_uni_init));
                while(b==i || b==a);

            do c=(int)((NP)*rand_uni(&rand_uni_init));
                while( c==i || c==a || c==b);




            for(j=0;j<D;j++)
                {
                    ae1[j] = 0.0;
                    aet[j] = 0.0;
                    ae1[j]= ae[c][j] + F * (ae[a][j] - ae[b][j]);
//Cross over
                    y1 = (rand_uni(&rand_uni_init));




        if ((ae1[j] > aeu[j]) || (ae1[j] < ael[j]))
                    ae1[j]=ael[j]+(rand_uni(&rand_uni_init))*(aeu[j]-
ael[j]);


                        if(y1>CR)
                            aet[j] = ae[i][j];
                        else
                            aet[j] = ae1[j];


                        if(aet[j] <0.0)
                            aet[j] = aet[j] * (-1.0);





                }
```

```
if ((k%10)==0)
                                        {

          for(j=0;j<D;j++)
          fprintf(fp,"%e\t",ae[i][j]);

          for(j=0;j<D;j++)
          fprintf(fp,"%e\t",aet[j]);

                                        }



for(j=0;j<D;j++)
          aef[j] = ae[i][j];




Fi = funvalue(aef);



for(j=0;j<D;j++)
          aef[j] = aet[j];


Ft = funvalue(aef);


if ((k%10)==0)
          {
          fprintf(fp,"Fi = %e\tFt = %e\n",Fi, Ft);
          }


                    if (Ft<Fi)
                              {
                                        for (j=0;j<D;j++)
                                                  newae[i][j]=aet[j];
                              }



          }
```

```
        for(i=0;i<NP;i++)
            {
                for(j=0;j<D;j++)
                    ae[i][j]=newae[i][j];

            }



}

}



double funvalue(double aef[])
{

    int j;
    double Fun,sum, sumsquare;

    double KD[3] = {3.391743522,2.5932447};
    double CHA[3] = {0.011385,0.02783};
    double Sin = 0.115;
    double KAbyH[3] = {0.063095734,0.050118723};


    sum = 0.0;
    sumsquare = 0.0;

    for(j=0;j<1;j++)
        {

    sum = KD[j] - aef[0]*aef[1]*(Sin - ((KD[j] *CHA[j])/ aef[0])) * pow(CHA[j],aef[0]-1)* (1/(pow((1.0 +  KAbyH[j]),aef[0])));


        sumsquare = sumsquare + pow(sum,2.0);
        }


    printf("infunctin F = %f\n",sumsquare);
    //getchar();
    return(sumsquare);

}
```

APPENDIX III

Code in 'MATLAB' for the Kinetic Elementary Model

```
Ca(1) = 0.405;
Cb(1) = 0.457;
Cc(1) = 0;

dt = 0.01;
time = 12;
n = time/dt;

a = 1.69;
b = 1;
y = 1;

A = 1.677;

ke = 73.76;
k1= 6.874;
k2 = k1/ke;

 for i = 1:1:n

    Ca(i+1) = Ca(i) - dt*(k1*Ca(i)^a*Cb(i)^b - k2*Cc(i)^y);
    Cc(i+1) = (Ca(1)- Ca(i+1))/A;
    Cb(i+1) = Cb(1) - Cc(i+1);

 end


 fid = fopen('kinetics.xls','w+'); % opening a file for saving the data in file
 for i=1:n
     fprintf(fid,'%12.8f %12.8f  %12.8f %12.8f \n',i*dt,Ca(i),Cb(i),Cc(i));
 end
fclose(fid);
```