Experimental and Theoretical Studies on Reactive Extraction of Carboxylic Acids

THESIS

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2012

DEDICATED

TO

My Parents,
Wife & Daughter

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE

PILANI (RAJASTHAN) INDIA

CERTIFICATE

This is to certify that the thesis entitled **"Experimental and Theoretical Studies on Reactive Extraction of Carboxylic Acids"** submitted by **Dipaloy Datta,** ID No. **2009PHXF433P** for the award of PhD Degree of the Institute, embodies the original work done by him under my supervision.

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ABSTRACT

The chemical industry has come under increasing pressure to produce chemicals in a more eco-friendly way due to its dependence on non-renewable resources, its non-environmental synthesis route, and its toxic and unwanted byproducts, wastes etc. To overcome the aforesaid problems, scientists have highlighted the potential of bio-based technologies. The production of carboxylic acids from renewable resources using fermentation technology is a promising approach, but still restricted due to the limitations on the recovery of product from fermentation broth. Among several recovery methods available, the reactive extraction is found to be an effective and efficient method for the recovery of bio-products from fermentation broth. This method is also useful to recover carboxylic acids from industrial wastewater streams.

In the present study, the reactive extraction of various carboxylic acids [picolinic (0.01-0.25 mol·L^{-1}), nicotinic (0.02-0.12 mol·L^{-1}), isonicotinic (0.005-0.03 mol·L^{-1}), glycolic (0.01-0.57 mol·L^{-1}), itaconic (0.05-0.25 mol·L^{-1}), formic (0.265-1.323 mol·L^{-1}), and levulinic (0.111-0.541 mol·L^{-1}) acids] from their dilute aqueous solution is carried out. The concentration ranges of carboxylic acids are chosen as to simulate the conditions of an actual fermentation broth and industrial wastewater streams. Different diluents and their mixtures with and without extractants such as organophosphorous- [tri-*n*-butylphosphate (TBP: 0.183-2.192 mol·L^{-1}), trioctylphosphine oxide (TOPO: 0.10-0.50 mol·L^{-1}) and di-2-ethyl hexhyl phosphoric acid (D2EHPA: 0.50 mol·L^{-1})] and amine based extractants [tri-*n*-octylamine (TOA: 0.115-0.648 mol·L^{-1}), tri-dodecylamine (TDDA: 0.079-0.50 mol·L^{-1}) and tri-octylmethylammonium chloride (Aliquat 336: 0.22-0.50 mol·L^{-1})] are used as the extract phase to perform the experiments. The extraction efficiency is described in terms of distribution coefficient (K_D), degree of extraction (*%E*) and loading ratio (*Z*). The effects of initial concentration of acid in the aqueous phase, initial extractant concentration in the organic phase, type of extractant, polarity and toxicity of diluent, mixture of diluents and temperature on the extraction efficiency, are studied. Biocompatible systems for the extraction of nicotinic, isonicotinic and picolinic acids are also investigated using less toxic or non-toxic extractant-diluent system.

Extraction results on carboxylic acids show that active solvents (1-decanol, MIBK, DCM etc.) are found to be better solvating agents compared to inactive ones (hexane, decane, dodecane etc.). The presence of active groups in these diluents enhances the extracting capability of the extractants. It is also observed that the polar diluents solvate acid molecule with less dimer formation in the organic phase, and higher distribution coefficient (K_D), but existence of acid dimer is observed for non-polar diluents. Organophosphorus compounds (TBP, TOPO and D2EHPA) show stronger Lewis basicity than pure diluents (conventional) and better extraction of carboxylic acids from dilute aqueous solution. The specific affinity of long chain aliphatic amines (TOA, TDDA and Aliquat 336) for carboxylic acid gives high selectivity of acid. The optimum values of process design variables (initial acid concentration, initial extractant and modifier composition, and temperature) are determined using response surface

methodology (RSM) and differential evolution (DE) optimization approach for the reactive extraction of glycolic acid using TOA in a mixture of inert diluent (cyclohexane) and modifier (1-decanol). A comprehensive study for the reactive extraction of formic acid is carried out in six different diluents using TOA at 4 different temperatures (298 K, 313 K, 328 K, and 343 K). In this work, the effect of temperature on the reaction stoichiometry, equilibrium constants, and efficiency of reactive extraction is studied in detail. RSM and artificial neuron network (ANN) modeling approach is applied for the reactive extraction of itaconic acid with TOA in a mixture of DCM (modifier) and cyclohexane (inert diluent). The regeneration (back-extraction) of organic phase by pure water at 353 K is carried out for picolinic acid, and 90.5% recovery of acid is achieved.

The mass action law model is applied to estimate stoichiometry (m, n), overall (K_E) and individual equilibrium constants for complex formation. The effect of diluent on K_D is quantified by LSER model using solvatochromic parameters of diluents. Relative basicity model is also proposed to correlate equilibrium constant of 1:1 complex formation (K_{11}) with the basicity of the extractant ($pK_{a,B}$), strength of the acid (pK_a), hydrophobicity of the acid (log P_a) and the nature of the solvent. Modified adsorption models (Langmuir, Freundlich and Temkin) are presented to illustrate the interaction between the molecules of acid (adsorbate) and extractant (adsorbent) at equilibrium.

The intrinsic kinetics of extraction is determined for the extraction of nicotinic acid using TOA dissolved in MIBK. The reaction between nicotinic acid and TOA in MIBK in a stirred cell falls in Regime 1 which is the case of extraction accompanied by a slow chemical reaction (*Hatta* number = 0.12 << 1). The reaction is found to be 0.7 order with respect to acid, and 0.5 order in TOA with a forward and back-ward rate constants of 8.4×10^{-4} (mol m^{-3})$^{-0.2}$$s^{-1}$ and 3.31×10^{-5} (mol m^{-3})$^{-0.2}$$s^{-1}$, respectively.

Keywords: *Carboxylic acids; Separation; Process Intensification; Reactive Extraction; Equilibrium; Diluents; Extractants; Modifiers; Temperature; Kinetics; Back-extraction; Mathematical modeling; Optimization; Differential Evolution; Equilibrium constants; Stoichiometry.*

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NOMENCLATURE

A	Operator at the summing junction in ANN (-)
A_c	Mass transfer area (m^2)
B	Value of bias in ANN (-)
B_T	Constant in Temkin model ($g \cdot g^{-1}$)
CR	Cross over frequency in DE (-)
C_1, C_2	Parameters of relative basicity model (-)
C_e	Solute concentration in aqueous phase at equilibrium ($g \cdot L^{-1}$)
C_{in}	Initial acid concentration in the aqueous phase ($mol \cdot L^{-1}$)
C_{HC}, C_{aq}	Acid concentration of acid in aqueous phase ($mol \cdot L^{-1}$)
C^-	Dissociated acid (-)
$C_{HC}^{diluent}$	Acid concentration in aqueous phase with diluent alone ($mol \cdot L^{-1}$)
$\overline{C}_{11}$, $\overline{C}_{12}$, $\overline{C}_{21}$, $\overline{C}_{31}$	Concentration of 1:1, 1:2, 2:1, and 3:1 acid-extractant complexes, respectively ($mol \cdot L^{-1}$)
$\overline{C}_{HC}$, C_{org}	Acid concentration of acid in organic phase ($mol \cdot L^{-1}$)
$\overline{C}_{HC}^{diluent}$	Acid concentration in organic phase with diluent alone ($mol \cdot L^{-1}$)
C_{org}^*	Acid concentration at equilibrium ($mol \cdot L^{-1}$)
D	Dimerization constant ($mol^{-1} \cdot L$)
D_{HC}	Diffusion coefficient ($m^2 \cdot s^{-1}$)
E	Degree of extraction (%)
E_0	Goal in ANN (-)
f	Freundlich parameter (-)
F	Scaling factor in DE (-)
Ha	Hatta Number (-)
H	Number of neurons in output layer in ANN (-)
ΔH	Change in enthalpy ($J.mol^{-1}$)
HC	Neutral or undissociated acid (-)
[HC]	Undissociated acid concentration ($mol \cdot L^{-1}$)
H_2^+C	Charged cation (-)
H^+	Hydrogen ion (-)
$[H^+]$	Hydrogen ion concentration ($mol \cdot L^{-1}$)
$\overline{HC}$	Undissociated acid in the organic phase (-)
$\overline{(HC)(S)}$, $\overline{H^+C^-S}$, $\overline{(HC)(S)_n}$	Acid-extractant complexes in the organic phase (-)
$[\overline{(HC)(S)_n}]$	Acid-extractant complex concentration ($mol \cdot L^{-1}$)
k	Number of design variables (-)
k_1, k_{-1}	Forward and back-ward reaction rate constants, respectively
$k_{\alpha'\beta'}$	Rate constant of the reaction
k_L	Physical mass transfer coefficient ($m \cdot s^{-1}$)
K_{11}, K_{12}, K_{21}, K_{31}	Equilibrium constants for 1:1, 1:2, 2:1 and 3:1 acid-extractant complexes, respectively
K_{a1}, K_{a2}	Dissociation constants (-)

K_{m1}	Equilibrium constant for *m*:1 acid-extractant complex
K_D	Distribution coefficient (-)
K_E	Equilibrium constant (-)
K_F	Freundlich constant [$(g\cdot g^{-1})\ (L\cdot g^{-1})^{1/n}$]
K_L	Langmuir equilibrium constant ($L\cdot g^{-1}$)
K_T	Equilibrium constant in Freundlich model ($L\cdot g^{-1}$)
$K_{D,\,max}$	Maximum distribution coefficient (-)
K_D^0	Distribution coefficient for an ideal diluent (-)
$K_D^{diluent}$	Distribution coefficient of physical extraction (-)
K_D^{chem}	Distribution coefficient of chemical extraction (-)
K_D^{total}	Overall distribution coefficient (-)
L	Total number of connections (weights and biases) in ANN (-)
m	Number of acid molecules (-)
M	Molecular weight (g/mol)
n	Number of extractant molecules (-)
n_c	Central points in RSM (-)
n_p	Number of inputs in ANN (-)
n_T	Total number of design points in RSM (-)
N	Speed of stirrer (rpm)
NP	Number of population in DE (-)
N_C	Number of the components (-)
N_D	Number of data points (-)
a, b, d, p, s	Regression coefficients of LSER model (-)
pK_a	Acid strength (-)
pK_B	Basicity of the extractant with respect to acid (-)
P	Partition coefficient (-)
q_e	Loading of acid on adsorbate at equilibrium ($g\cdot g^{-1}$)
Q_0	Langmuir constant (g/g)
rmsd	Root mean square deviation (-)
$R_{HC,0}$	Initial specific rate constant ($mol\cdot m^{-2}\cdot s^{-1}$)
R^2	Coefficient of determination (-)
S	Extractant (-)
ΔS	Change in entropy ($J.mol^{-1}.K^{-1}$)
SP_1, SP_2	Solvatochromic parameter of the first and second solvent, respectively, in solvent mixture (-)
$\bar{S}$	Free extractant in the organic phase (-)
$[\bar{S}]$	Free extractant concentration ($mol\cdot L^{-1}$)
$[\bar{S}]_{in}$	Initial extractant concentration ($mol\cdot L^{-1}$)
$[S\cdot HC]_{org}$	Concentration of acid-extractant complex ($mol\cdot L^{-1}$)
t	Time (sec)
T	Temperature (K)
V_{aq}	Volume of aqueous phase (ml)
V_{org}	Volume of organic phase (ml)
w	Weights in ANN (-)
x_i	Normalized value of design variables (-)
X_1, X_2	Mole fraction of the first and second solvent, respectively, in solvent mixture (-)

X_i	Actual value of design variables
XYZ	Solvation property of interest in LSER model in terms of solvatochromic parameters (-)
Y	Response in terms of degree of extraction in RSM (%)
$\hat{Y}$	Predicted value of response in RSM (-)
z	Number of neurons in hidden layer in ANN (-)
Z	Loading ratio (-)

Greek Symbols

α	Solvatochromic parameter (HBA) of the diluent (-)
α'	Order of kinetic reaction with respect to acid (-)
α^*	Distance of axial points in CCOD (-)
β	Solvatochromic parameter (HBD) of the diluent (-)
β_0, β_i, β_{ii}, β_{ij}	Regression coefficients in RSM (-)
β_{OLS}	Vector of regression coefficients (-)
β'	Order of kinetic reaction with respect to extractant (-)
δ	Solvatochromic parameter of the diluent (-)
Δ	Change (-)
ε_r	Relative permittivity or dielectric constant (-)
τ	Temperature (^oC)
μ	Dipole moment (Debye)
η	Viscosity of diluent ($kg \cdot m^{-1} \cdot s^{-1}$)
v	Volume fraction of diluent in the organic phase (-)
Π	Number of the phases (-)
π^*	Solvatochromic parameter (solvent bipolarity) of the diluent (-)
ψ	Diluent association factor (-)
$\forall$	Molar volume of the component ($m^3 \cdot kmol^{-1}$)
Φ	Enhancement factor (-)

Subscripts

0	Ideal
aq	Aqueous
in	Initial
max	Maximum
org	Organic

Abbreviations

Aliquat 336	Tri-octyl methyl ammonium chloride
ANN	Artificial neural network
ANOVA	Analysis of variance
BO	Bio-oil
BP	Back-propagation
CCOD	Central composite orthogonal design
Chemodel	Chemical equilibrium model
D2EHPA	Di-2-ethylhexyl phosphoric acid
DCM	Dichloromethane
DE	Differential evolution
DF	Degrees of freedom
HBA	Hydrogen-bond acceptor
HBD	Hydrogen-bond donor

HL	Hidden layer
LSER	Linear solvation energy relation
MIBK	Methyl isobutyle ketone
MLP	Multi layer perceptron
MS	Mean square
MSE	Mean squared error
OL	Output layer
OLS	Ordinary least squares
RSM	Response surface methodology
SE	Standard error
SD	Standard deviation
SS	Sum of squares
TBP	Tri-*n*-butyl phosphate
TDDA	Tri-dodecylamine
TOA	Tri-*n*-octylamine
TOPO	Tri-octylphosphine oxide
v/v	Volume/volume
wt%	Weight percent

CHAPTER – 1

INTRODUCTION

The chemical industry is under increasing pressure to produce chemicals in a more eco-friendly way due to its reliance on fossil resources, non-environmental synthesis route, and unwanted byproducts and wastes. The sustainability of a chemical industry requires an integrated strategy by taking into account of safety, health and environmental benefits with technological and economical objectives. To overcome the aforesaid problems, scientists have highlighted the potential of bio-based technologies (Bridgwater, 1994; Oasmaa and Kuoppala, 2003; Mahfud *et al*., 2008; Rasrendra *et al*., 2010). The development of bio-refinery (analogous to oil refinery) would provide a chemical feedstock based on renewable resources like biomass.

Carboxylic acids are weak organic acids and extremely useful as starting materials for the production of esters, amides, acid chlorides etc. in the chemical industries. Most of them are produced as intermediates in major metabolic pathways by microorganisms. The acids are generally found in the aqueous streams generated from fermentation broth, industrial wastewater and bio-oil. The production of carboxylic acids from renewable carbon sources by microbial fermentation process is a promising approach, and known for more than a century (Table 1.1). It is noteworthy that the actual market for many organic acids is small, but an economical production process will create new markets and opportunities for the chemical industries (Werpy and Petersen, 2004; Sauer *et al.*, 2008). The efficiency of fermentation process is mainly inhibited by acidic pH due to the production of acid (Hsu and Yang, 1991; Blanc and Goma, 1987). This leads to the low fermentation rate and low concentration of acid in the product stream. Therefore, it is

inefficient and incompetent with the petrochemical route. The process is also restricted due to the limitations on recovery of acid from the dilute aqueous solution (fermentation broth). The aqueous waste streams of industrial (pharmaceutical, polymer, food, leather, textile etc.) effluents often contain carboxylic acids (formic, acetic, propionic etc.) in different forms and concentrations (Wisniewski *et al*., 2005; Kumar and Babu, 2008). Treatment of wastewater using a conventional activated sludge process to meet future water quality standards is not cost effective and produces solid sludge. The recycling of these acids is important from environment point of view rather than discarding them as solid waste. Also, the neutralization these acids may lead to the loss of valuable resource. The increased consumption of fossil fuels in the last decades has created considerable environmental problems (e.g. green house gas emissions), and resulted in a significant increase in the crude oil price. This has encouraged the exploration of renewable resources like biomass for energy generation. Bio-oil (BO) is obtained from lingo-cellulosic biomass using flash pyrolysis technology with a yield up to 70 wt% (Mahfud *et al*., 2008). BO is a complicated mixture of a large number of organic compounds belonging to a wide variety of compound classes (acids, ketones, aldehydes, phenolics etc.). Crude BO is not suitable as a fuel for stationary and non-stationary combustion engines and up-gradation is required. Rather, the acidic nature of BO (pH between 2 and 3) caused by the presence of large amounts of organic acids (formic acid, acetic acid, propionic acid etc.) is considered a critical issue. The acidity limits its application due to extensive corrosion of the metal surfaces of internal combustion engines. The amount of carboxylic acids up to 10.1 wt% is available in the BO, although the actual level of acid depends on the feedstock and processing conditions. Therefore, the extraction of these acids from BO could improve the product properties, and significantly boost the economic attractiveness of BO as fuel (Rasrendra *et al*., 2010).

Table 1.1 Microbial productions of organic acids

SL No.	Organic acids	Microorganisms	Carbon source	Concentration ($mol \cdot L^{-1}$)	Application	References
1.	Acetic	*Propionibacterium acidipropionici*	Glucose	0.152	Acidity regulator, component of vinegar, precursor to solvents and coatings	Woskow and Glatz, 1991
2.	Propionic	*Propionibacterium acidipropionici*	Glucose	0.432	Food preservative, fungicides, herbicides, plasticizers	Woskow and Glatz, 1991
3.	Itaconic	*Aspergillus terreus*	Glucose	0.633	Synthetic resins, coatings, additive in paints	Yahiro *et al.*, 1995
4.	Citric	*Aspergillus niger*	Cane molasse	0.593	Flavoring and preservative in food and beverages	Ikram-ul *et al.*, 2004
5.	Butyric	*Clostridium butyricum*	Glucose	0.190	Food flavors, perfume additives, treating colorectal cancer and hemoglobinopathies	Guo-qing, 2005
6.	Lactic	*Lactobacillus delbrueckii*	Hydrolyzed cane sugar	1.489	Polymer precursor, food, cosmetics	Kadam *et al.*, 2006
7.	Glycolic	*Acidovorax facilis* 72 W	Glycolonitrile	-	Skin care products	Xu *et al.*, 2006
8.	Nicotinic	*Saccharomyces cerevisiaee*	Nicotinamide	0.041 to 0.132	Bio-stimulator, and nutritional supplements	Cantarella *et al.*, 2008
9.	Succinic	*Corynebacterium glutamicum*	Glucose	1.236	Flavoring agent for food, plasticizer, medicines of cancer-curing	Okino *et al.*, 2008
10.	Isonicotinic	*Fusarium solani, Aspergillus niger*	4-cyanopyridine	0.049	Anticorrosion reagent, plating additive, and photosensitive resin stabilizer	Malandra *et al.*, 2009

Several recovery processes are used for the separation of carboxylic acids from their aqueous solutions. Some examples are:

- Ion exchange chromatography (Wang and Liao, 2004; Gao *et al.*, 2009)
- Adsorption (Dai and King, 1996; Husson *et al.*, 1999; Huang *et al.*, 2007)
- Electrodialysis (Hong *et al.*, 1986; Boyaval *et al.*, 1987; Biwer *et al.*, 2005)
- Anion exchange (Mancini *et al.*, 2000; Cao *et al.*, 2002)
- Liquid-liquid extraction (Wardell and King, 1978; Biwer *et al.*, 2005)
- Membrane separation (Moueddeb *et al.*, 1996; Juang *et al.*, 1997)
- Ultra filtration (Boyaval *et al.*, 1987)
- Nano filtration (Timmer *et al.*, 1994)
- Reverse osmosis (Timmer *et al.*, 1994)
- Distillation (Helsel, 1977; Cockrem and Johnson, 1991)
- Precipitation (Shreve and Brink, 1977; Pazouki and Panda, 1998)
- Reactive extraction (Tamada *et al*., 1990; Wasewar *et al*., 2002a)

The conventional method of recovering carboxylic acid from fermentation broth involves the formation of the calcium sulfate which causes a major disposal problem for the environment. Calcium salt of carboxylic acid is formed by the addition of calcium hydroxide into the production medium. It is followed by filtration and addition of sulfuric acid to precipitate calcium sulfate. The dilute solution of carboxylic acid is then purified by activated carbon followed by crystallization. Therefore, the traditional method, because of their high energy requirements and complexity, should be replaced by novel separation technique.

Among these techniques, reactive extraction is found to be a promising method for the recovery of the carboxylic acids from a dilute fermentation broth (Wennersten, 1983; Hartl and Marr, 1993; Cascaval and Galaction, 2004; Wasewar *et al.,* 2004; Kumar

and Babu, 2008). This separation method has advantages such as (i) effective at high concentration of substrate in the extractive fermentation, (ii) the acid can be re-extracted and the solvent can be reused, (iii) better control of pH in the bio-reactor, (iv) better recovery of acid with higher product purity, and (v) reduction of downstream processing load and recovery cost. Reactive extraction represents a reaction between the acid (solute) and extractant molecule at the interface of aqueous and organic phase where transfers of acid molecules take place by the diffusion and solubilization mechanism (Figure 1.1).

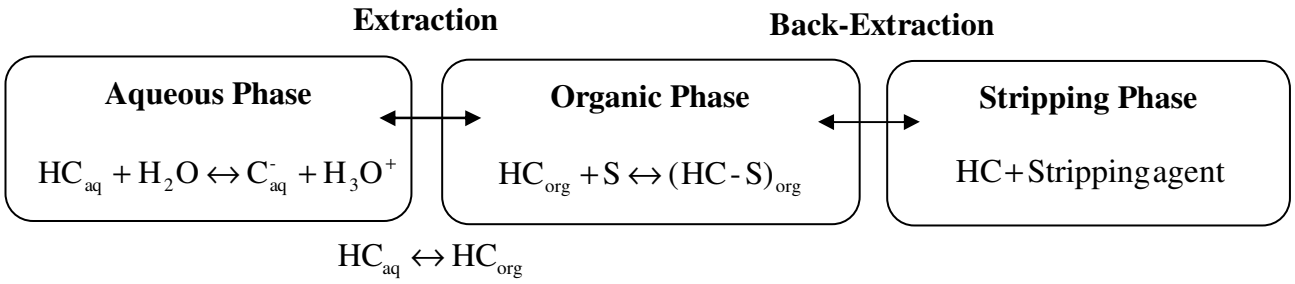


Figure 1.1 Schematic representation of the reactive extraction process (extraction and back-extraction)

Kertes and King (1986) categorize the extractants as three major types:

(i) Carbon bonded oxygen bearing extractants

(ii) Phosphorus bonded oxygen bearing extractants, and

(iii) High molecular weight aliphatic amines

The first two categories are nonreactive in nature and extract the acid molecules by solvation. The distinction between the first two categories is based on the strength of the solvation bonds and the specificity of solvation. The coordinate bonds between carbon bonded oxygen donor extractant and the acid are too weak for a specific solvation but it is significantly more for phosphorus bonded oxygen bearing extractants. The extractants in the second category make the solvation process more specific and the number of solvating molecules per extracted acid molecule can be accessible experimentally. The

aliphatic amines in the third category can react with the carboxylic acid molecule and form acid-amine complexes by proton transfer or by ion pair formation. This causes a significant increase in the distribution coefficient of the carboxylic acid (Wardell and King, 1978). Among aliphatic amines, primary alkyl amines are observed to be excessively soluble in water at room temperature while secondary amines form a gel phase (third phase) at the interface which creates difficulty in phase separation (Kertes and King, 1986). The extractability of tertiary amines is found to be more than that of the primary and secondary amines (Wennersten, 1983). Aliphatic tertiary amines having more than six carbon atoms per chain are found to be effective extractants for the recovery of carboxylic acids (Kertes and King, 1986).

Although a tertiary amine has good extractability, it must always be used with a diluent due to its viscous and corrosive nature. Further, the stability of the formed acid-amine complexes in the reactive extraction is affected by the basicity of the amine which can be manipulated by using different types of diluents. Moreover, use of a diluent controls the physical properties such as density, viscosity, surface tension etc. of the organic phase (Bizek *et al*., 1992).

Diluents can be broadly divided into two groups: (i) active diluents, and (ii) inactive diluents. Generally, the active diluents are polar in nature due to the presence of functional groups. They are good solvating media for an ion-pair such as an acid-amine complex (Tamada and King, 1990). The category includes chlorinated hydrocarbon, ketone, alcohol, and halogenated aromatic solvents. Inactive diluents being non-polar provide very low distribution of the acid and poor solvation of the polar complexes. Alkanes, benzene, alkyl substituted aromatics etc. fall in this category. These diluents limit the formation of the third phase at higher concentrations of acid in the organic phase and are useful in the stripping of acid. The equilibrium curve can be shifted towards the

aqueous phase by increasing the concentration of the inert diluent in the mixture of diluents (Han and Hong, 1996).

Most of the organic solvents used for the separation of carboxylic acids are toxic in nature to the microorganisms to some extent. Even a small quantity of a solvent can inhibit the activity of the microorganisms (biocatalyst) by damaging the cell membrane, causing membrane rupture, and metabolite leakage. Beyond a certain limit (critical solvent concentration) in the cell membrane, the fluidity of cell increases and cellular activity declines (Osborne *et al*., 1990). It is also found that the cell loses its catalytic activity due to the high surface tension developed by the solvent (Yabannavar and Wang, 1987). The solvent interacts with the cell in two ways: (i) by dissolution in the aqueous broth known as molecular toxicity, and (ii) direct contact of the cell with the water-immiscible solvent phase named as phase toxicity (Bassetti and Tramper, 1994). Molecular toxicity usually causes less damage to the cell than does phase toxicity because the former is limited by solvent solubility in the aqueous phase. The biocompatibility of a solvent with microorganism can be predicted based on the values of log P_a of the solvent. log P_a is defined as the logarithm of the distribution coefficient of the solvent in a standard 1-octanol-water two phase system (Laane *et al*., 1985). It is also a measure of the polarity of a solvent as toxicity increases with an increase in the polarity (Bruce and Daugulis, 1991; Barton and Daugulis, 1992). The solvents with the values of log P_a less than 4 are considered to be toxic to microorganisms, and greater than 6 are considered to be nontoxic to the microorganism. For solvents with the values of log P_a between 4 and 6, toxicity depends on the microorganism (Laane *et al*., 1987). The toxicity of a solvent in an extractive fermentation process can be reduced by replacing the toxic solvent with a completely nontoxic one or blending a toxic solvent (log $P_a < 4$) with a nontoxic one (log $P_a > 6$). The addition of a biocompatible solvent to the medium which can entrap any

toxic component dissolved in the aqueous phase will also reduce the toxicity of the medium. This method is tested successfully with *Lactobacillus delbrueckii* for lactic acid production in extractive fermentation (Yabannavar and Wang, 1991 a & b).

In the second stage of reactive extraction, it is necessary to regenerate the organic phase. Tamada and King (1990) have described two approaches for the regeneration of extractant-diluent system: (i) temperature swing regeneration, and (ii) diluent swing regeneration. Yabannavar and Wang (1991) have purified lactic acid from a loaded organic phase using sodium hydroxide (NaOH) and hydrochloric acid (HCl). Poole and King (1991) have used an aqueous solution of low molecular weight amine for complete regeneration of organic phase.

Reactive extraction strongly depends on various parameters such as aqueous phase composition, organic phase composition, types of complexes (1:1, 2:1, etc.) formed, properties of the solvent (extractant and diluent), type of solvent, temperature, pH etc. (Kahya *et al.,* 2001). The purpose should be achieving a high distribution coefficient with higher selectivity. This can be realized by utilizing an appropriate organic phase at optimum conditions.

1.1 Objectives

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

1. To understand the physical and chemical aspects of reactive extraction of carboxylic acids.
2. To carry out the equilibrium and kinetic studies for understanding the effects of the following parameters on the extraction efficiency.
    a. Aqueous phase composition

b. Organic phase composition

c. Type of extractant

d. Type of diluent

e. Type of modifier, and

f. Temperature

3. To formulate and simulate the mathematical models for determination of the equilibrium and kinetic parameters for the reactive extraction of carboxylic acids.

1.2 Organization of Thesis

To fulfill the above objectives, an exhaustive literature survey is initialized for the experimental and theoretical studies on the equilibria and kinetics of recovery of carboxylic acids using reactive extraction, and given in Chapter #2. To obtain the equilibrium (physical and chemical) and kinetic data on reactive extraction of carboxylic acids, experiments are performed with different types of extractants in several diluents. The details of experimental setup and procedure are elaborated in Chapter #3. The mathematical models (theoretical study) for the determination of equilibrium and kinetic parameters are presented in Chapter # 4. This chapter also includes simulation and optimization methodologies for the proposed models. The obtained experimental data are discussed and analyzed in detail in Chapter #5. The stoichiometry coefficients, the equilibrium constants, kinetic parameters and other model parameters determined using experimental data are also included in Chapter #5. In Chapter #6, the summary of the work, important conclusions, major contributions, and future scope of the research are highlighted for the present study.

CHAPTER – 2

LITERATURE REVIEW

Liquid-liquid extraction (LLE) is a process in which a particular solute is removed from a liquid phase (feed phase) by another liquid phase (solvent or extract phase). Application of extraction in life science started in way back to about 3500 BC to recover products from various natural resources. At a Sumerian text dated 2100 BC, production of perfumes, pharmaceutical oils and waxes were documented. In medieval ages extraction was performed with ethanol and was applied in the field of hydrometallurgy by making use of mineral acids (Bart, 2001). With the developments in thermodynamics, particularly the distribution law by Nernst in 1891 and design of an apparatus for extraction, significant improvements were accomplished in the late 19^{th} century. However, it was not until the early 1930's when the first large-scale LLE process was in operation. Lazar Edeleanu (a Romanian Chemist: 1861-1941) removed aromatic and sulphur compounds from liquid kerosene by the LLE process using liquid sulphur dioxide as a solvent at temperature as low as -6 to -12 ^{o}C. This yielded clean kerosene suitable to be used as a fuel for residential lighting. Now a days, besides the extraction of almost all metals in mining industries and environmental applications, extractants are widely used in the extraction of organic and inorganic acids, organic chemistry intermediates and pharmaceuticals for the purposes of separation, purification or enrichment (Marr and Bart, 1982) of the product.

The main difference between reactive extraction and solvent extraction is the reaction between the extractant and the solute in the organic phase. Aliphatic amines and phosphoryl solvents are proposed as effective extractants by earlier researchers (Kertes

and King, 1986). While extractants play the major role in the reaction, diluents also have a significant effect on the level of extraction. Non-aromatic, water immiscible and polar solvents with intermediate molecular weights and high boiling points are commonly preferred for the extraction to have high distribution and selectivity (Holten, 1971). The solvents (diluents) control the physical properties (viscosity, density, surface tension etc.) of the solvent phase and also affect the stability of the complex structure formed between the solute and the extractant.

Various studies reported in the literature on the recovery of carboxylic acids using reactive extraction (experimental and theoretical investigations) are discussed in detail in sections 2.1 (equilibrium) and 2.2 (kinetics) of this chapter.

2.1 Equilibrium Studies on Reactive Extraction of Carboxylic Acids

Several researchers (Kertes and King, 1986; Tamada *et al*., 1990; Tamada and King, 1990a and 1990b; Juang and Huang, 1997; Tong *et al*., 1998; Wasewar *et al*., 2002a-b; Keshav *et al*., 2008a-b; Kumar *et al*., 2009) have studied theoretical and experimental aspects of the recovery of carboxylic acids from their aqueous solutions by reactive extraction. In their work, the investigators have examined the effects of various parameters on the distribution of the acid (solute) between the aqueous and organic phase. Some of these parameters are concentration and composition of both phases, types of the extractants and diluents, pH of the aqueous phase, temperature of the system, and toxicity of the solvent phase to the microorganism (Kertes and King, 1986; Tamada *et al.*, 1990; Gu *et al.*, 1998; Tong *et al.*, 1998; Ma *et al.*, 2006). In addition to these experimental studies, the possible reaction mechanisms are also described and determined using different equilibrium and kinetic models (Poposka *et al.*, 1998 and 2000; Wasewar *et al.* 2002a-b). Some experimental results have showed synergistic and antagonistic effects on

the extraction of the carboxylic acids when there is more than one acid in the aqueous phase or more than one extractant in the organic phase (Juang and Huang, 1997; Kirsch and Maurer, 1997; Canari and Eyal, 2003). Some researchers have tried to recover the carboxylic acids from production medium by extractive fermentation and studied the process conditions affecting recovery during production (Siebold *et al.*, 1995; Tong *et al.*, 1998; Gu *et al.*, 1998; Ma *et al.*, 2006).

King and his group have performed the pioneering studies on the equilibrium of reactive extraction of carboxylic acids. Besides carboxylic acids, they have also studied the extraction of chlorinated hydrocarbons and aromatics (Barbari and King, 1982), ethanol (Munson and King, 1984), ammonia (Mackenzie and King, 1985) and low molecular weight aliphatic alcohols (Kertes and King, 1987) from aqueous solutions. In one of their earlier work, King and co-workers studied the extraction of acetic and formic acids from their aqueous solutions (Wardell and King, 1978) using phosphoryl solvents (tributyl phosphate, dibutyl phosphonate, tributylphosphinoxide and triphenylphosphineoxide) and tertiary amine extractants (tri-*n*-octylamine and tri-iso-octylamine) dissolving in different solvents. High distribution coefficients are achieved with phosphoryl compounds which act as a Lewis base (presence of the phosphoryl bond, P-O). The results indicated that with the increase in the electronegativity, a decrease in the electron-donating ability and disappearance of Lewis basicity were observed. This study also showed the advantage of using long chain amines as extractants in the recovery of carboxylic acids. It was also observed that the extent of the extraction of acetic acid appeared to increase with an increase in the solubility parameter of the diluent besides the polarity.

At the later stage, Kertes and King, in 1986, published a research article in which the authors discussed the improvements in fermentation technology and its need of

commercialization. They have reviewed 11 carboxylic acids (propionic, pyruvic, lactic, succinic, fumaric, maleic, itaconic, tartaric, citric and isocitric) which are obtained by aerobic fermentation of glucose via the glycolytic pathway and glyoxylate bypass. The investigators pointed out that it is the undissociated part of a mono-carboxylic acid which can only be extracted into carbon-bonded and phosphorus-bonded solvent. This revealed that the initial pH of the aqueous solution and the dissociation constant (pK_a) of the acid are two very important and influential parameters in the extraction of particular acid. Mass action law and Nernst distribution law are used in order to evaluate the data. The authors have considered the dimerization of acids in the organic phase and proposed a relation between dimerization constant and partition coefficient. The emphasis is given for the use of aliphatic tertiary amines compared to primary and secondary amines. In particular, mono-carboxylic acids under comparable conditions are noted to be more easily extracted with an appropriate organic phase than di- or tri-carboxylic acids (Kertes and King 1986).

King and his co-workers (Tamada *et al*., 1990, Tamada and King, 1990a-b) continued their studies on reactive extraction of carboxylic acids. In their first study (Tamada *et al*., 1990), they have carried out the extraction equilibrium experiments of carboxylic acids (acetic, lactic, succinic, malonic, fumaric and maleic) with different pK_a values. They have studied the effect of pK_a of the corresponding acid on the extent of extraction. It is found that the acid with higher pK_a value is extracted in more amounts. Furthermore, they have also searched for the effect of functional groups present in acid other than the primary carboxyl group on extraction. The reactive extraction is examined using Alamine 336 dissolved in various diluents (active diluents: 1-octanol, DCM, chloroform, MIBK, nitrobenzene; inert diluent: heptane). These diluents are selected with different chemical characteristics such as electron donating, electron accepting, polar and

non-polar in order to observe the effect of diluent-complex interactions on the equilibrium conditions and the possible formation of acid-amine complexes (1:1, 2:1). They have indicated that solubility of the acid-amine complex in the solvent phase is decreased in the following order: alcohol ≥ nitrobenzene ≥ proton donating halogenated hydrocarbon > ketone > halogenated aromatic > benzene > alkyl aromatic > aromatic hydrocarbon.

In their second study, Tamada and King (1990a) have investigated the chemical interactions between the components by using the results of mass action law analysis and the spectroscopic studies. Organic phase is analyzed by infrared spectroscopy to examine the stoichiometry of the acid-amine complex. They emphasize that there is an ion pair formation between the amine and first acid molecule and there is a hydrogen bond formation between the carboxyl of the second acid molecule and the carboxylate of the first in the formation of 2:1 complex of acid-amine.

In the last part of the study (Tamada and King, 1990b), this group has carried out the co-extraction of water with the acids by Alamine 336 dissolved in various diluents and found that amine had no effect on the co-extraction of water. Water co-extraction was decreased in the order of 1-octanol > MIBK > nitrobenzene > methylene chloride > chloroform > heptane during the extraction of succinic acid. Co-extraction of water for different acids is also compared and it is revealed that mono-carboxylic acids carry less water than dicarboxylic acids. In this study, the effect of the temperature on the reactive extraction of carboxylic acids by Alamine 336 is performed. It is observed that the distribution coefficient decreased with the increase in the temperature of the system as with the formation of the complex, the system became more ordered and entropy decreased. Consequently, the amount of acid extracted decreased with the increase in temperature. Finally, King and his co-workers regenerated the extractant through back-extraction by two approaches: swing temperature and swing diluent methods.

The above studies clearly show that the reaction between the extracted acid and the extractant present in the organic phase is dependent on the corresponding acid and the contents of the organic phase. To explore the possibilities of reactive extraction and its application and commercialization, further studies are carried out with different carboxylic acids using various extractants dissolved in different categories of diluents. A brief review of these extraction studies is summarized in a tabular form and shown in Table 2.1 to have a clear understanding of the various reactive systems used.

Table 2.1 Extractant/diluent system for the recovery of carboxylic acid by reactive extraction: Equilibrium studies

SL No.	Carboxylic acid	Extractant	Diluent	Parameters studied	Findings	References
1.	Different carboxylic acids	Organophosphorous and aliphatic amines	Alcohols, ketones, ethers and hydrocarbons	Various aqueous and organic phase parameters	Reviewed the extraction chemistry of carboxylic acids	Kertes and King, 1986
2.	Acetic, glycolic, propionic, lactic, pyruvic, butyric, succinic, fumaric, maleic, malic, itaconic, tartaric, citric and isocitric	Tri-octyl phosphine oxide (TOPO)	Hexane	Type of acid and initial acid concentration	Hydrophobicity of the acid controls equilibrium constants	Hano *et al*., 1990
3.	Acetic, lactic, succinic, malonic, fumaric and maleic	Tri-alkyl amine (Alamine 336)	Methyl isobutyl ketone (MIBK), n-heptane, dichloromethane (DCM) and nitrobenzene	Effects of diluent-complex interactions	Equilibrium constants, partition coefficient and dimerization constant determined	Tamada *et al*., 1990
4.	Citric	Alamine 336	*p*-Xylene, toluene, benzene, MIBK, 1-octanol, DCM and chloroform	Effect of diluents	K_{11}, K_{12} and K_{23} are correlated with solvatochromic parameters	Bizek *et al*., 1993
5.	Succinic and tartaric	Tri-*n*-octylamine (TOA)	Xylene	Type of acid, temperature, initial acid and TOA concentrations	Reaction stiochiometry	Juang and Huang, 1996
6.	Lactic	TOA	Xylene	Temperature, acid and TOA concentration	(1:1) , (1:2), and (3:1) acid-TOA complexes formed	Juang and Huang, 1997

Table 2.1 Extractant/diluent system for the recovery of carboxylic acid by reactive extraction: Equilibrium studies (continued...)

SL No.	Carboxylic acid	Extractant	Diluent	Parameters studied	Findings	References
7.	(L+) lactic	Tri-propyl amine (TPA) and TOA	1-octanol and heptane	Acid and amine concentration	Mixed tertiary amine of short and long chain can facilitate easy phase separation	Hong *et al*., 1999
8.	Citric, lactic and malic	Tri-iso-octyl amine (TIOA)	1-octanol and heptane	Effect of modifier and type of acid	Extraction mechanism is proposed considering physical and chemical extraction	Malmary *et al*., 2001
9.	Glyoxylic, glycolic, acrylic and benzoic	Tri-alkyl phosphine oxide (TRPO)	Kerosene	Aqueous and organic phase compositions	Equilibrium model for K_{11} is proposed	Li *et al*., 2003
10.	Propionic	Aliquat 336	Cyclohexane, hexane, toluene, MIBK, ethyl acetate, hexane + MIBK, hexane + toluene and MIBK + toluene	Effect of diluent and diluent mixture, acid and amine concentration	Order of extraction: ethyl acetate > MIBK > MIBK + toluene > toluene > hexane + MIBK > toluene + hexane > cyclohexane > hexane	Uslu *et al*., 2007
11.	Propionic	Tri-*n*-butyl phosphate (TBP), TOA and Aliquat 336	1-Octanol	Acid and extractant concentration	Order of extractibility is found to be TOA > Aliquat 336 > TBP, 1:1 complex formed	Keshav *et al*., 2008b
12.	Itaconic, maleic, malic, oxalic, tartaric and succinic	TBP	Do-decane	pH and initial acid concentration	Mechanism of di-carboxylic acids is proposed	Kyuchoukov *et al*., 2008

Table 2.1 Extractant/diluent system for the recovery of carboxylic acid by reactive extraction: Equilibrium studies (continued...)

SL No.	Carboxylic acid	Extractant	Diluent	Parameters studied	Findings	References
13.	Nicotinic	TOPO and TBP	Benzene, heptane, kerosene, 1-octanol, MIBK, diethyl ether, decane, kerosene + 1-octanol and heptane + 1-octanol	Effect of diluent, extractant type, initial acid and extractant concentration	Solvation number and equilibrium extraction constants are determined	Kumar *et al*., 2008
14.	Levulinic	*n*-Lauryl tri-alkyl-methyl amine (Amberlite LA-2)	Dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate, isoamyl alcohol, 1-hexanol, 1-octanol, 1-nonanol, 1-decanol, diisobutyl ketone (DIBK) and MIBK	Diluent effect, and amine concentration	LSER model proposed and K_{11}, K_{21}, and K_{31} are determined	Uslu *et al*., 2009
15.	Formic	Amberlite LA-2	Dimethyl phthalate, dimethyl adipate, dimethyl succinate, dimethyl glutarate, diethyl carbonate, isoamyl alcohol, 1-hexanol, 1-octanol, 1-nonanol, 1-decanol, DIBK and MIBK	Effect of diluent and amine concentration	Extraction constants (K_{51}, K_{61}, and K_{71}) were determined and LSER model proposed	Uslu *et al*., 2009
16.	Nicotinic	Organophosphorous and aliphatic amines	Alcohols, ketones, ethers and hydrocarbons	Various aqueous and organic phase parameters	Reviewed the extraction chemistry of nicotinic acid	Kumar and Babu, 2009
17.	Glycolic	Amberlite LA-2	1-Octanol, cyclohexane, iso-octane, toluene, 2-octanone and MIBK	Solvent type, amine and acid concentration	Order of extraction: MIBK > 2-octanone > 1-octanol > toluene > iso-octane > cyclohexane	Asci *et al*., 2009

Table 2.1 Extractant/diluent system for the recovery of carboxylic acid by reactive extraction: Equilibrium studies (continued...)

SL No.	Carboxylic acid	Extractant	Diluent	Parameters studied	Findings	References
18.	Citric	Tri-dodecylamine (TDDA) and Amberlite LA-2	MIBK, 1-octanol, toluene, cyclohexane, 1-octanol + toluene, 1-octanol + MIBK, MIBK + toluene, 1-octanol + toluene, 1-octanol + MIBK, MIBK + toluene and iso-octane	Diluent effect, amine and acid concentration	1-Octanol proposed to be most effective solvent	Bayazit *et al*., 2009
19.	Isonicotinic	2-Ethylhexylphosphic mono-2-ethyl-hexylester (P507), TBP, and Alamine 336	1-Octanol, tetrachloromethane and kerosene	Diluent effect, amine and acid concentration, pH of aqueous phase	Equilibrium constants and stiochiometries are proposed using FTIR	Li *et al*., 2009
20.	Glutaric	TOA	Isoamyl alcohol, 1-octanol, 1-nonanol, 1-decanol, methyl ethyl ketone (MEK), diisobutyl ketone (DIBK), hexan-2-one, toluene, kerosene, and hexane	Diluent effect, amine and acid concentration	Kerosene is found to be the most effective diluent. Equilibrium constants for 1:1 and 2:1 complex are estimated.	Pehlivanoglu *et al.,* 2009
21.	Lactic	TBP	Dodecane	Acid and solvent composition, change in the phase volumes and pH	Apparent equilibrium constants and the number of reacting extractant molecules	Labbaci *et al*., 2010

Table 2.1 Extractant/diluent system for the recovery of carboxylic acid by reactive extraction: Equilibrium studies (continued...)

SL No.	Carboxylic acid	Extractant	Diluent	Parameters studied	Findings	References
22.	Acrylic	Amberlite LA-2	Cyclohexane, 2-octanone, toluene, MIBK, iso-octane, hexane and 1-octanol	Type of diluent, and amine concentration	1:1 & 1:2 acid-amine complexes for proton-donating diluents and 1:1 & 2:3 for non-proton-donating diluents, overall extraction constants (K_{11}, K_{12} and K_{23})	Asci *et al*., 2010
23.	Formic	TDDA and TBP	Ethyl valerate, diethyl adipate, diethyl sebacate, 1-octanol and heptane	Effect of diluent, acid and amine concentration	Comparative study of physical and chemical extraction, TDDA suggested to be the best extractant	Sahin *et al*., 2010
24.	Penicillin G	Di-*n*-octylamine, TOA, N235 (a mixture of tertiary amines), TBP and di-(2-ethylhexyl) phosphoric acid (D2EHPA)	n-Butyl acetate, MIBK, 2-ethyl hexanol, kerosene and heptane	Initial acid concentration, pH and temperature	Effect of extractant on the stability of penicillin G mainly depends on temperature, degradation of penicillin G in alkali solution is governed by pH, mechanism of degradation discussed	Ren *et al*., 2010
25.	Succinic	Amberlite LA-2	Hexane, cyclohexane, toluene, *iso*-octane, MIBK, 2-octanone and 1-octanol	Initial extractant concentration	Extraction constants (1:1, 1:2 & 2:3) found out, order of extraction of diluents: 1-octanol > 2-octanone > MIBK > toluene > *iso*-octane > hexane > cyclohexane	Asci and Inci, 2010
26.	Itaconic	TBP and Aliquat 336	Sunflower oil	Initial acid and extractant concentration	Non toxic system proposed	Wasewar *et al.,* 2010

Table 2.1 Extractant/diluent system for the recovery of carboxylic acid by reactive extraction: Equilibrium studies (continued...)

SL No.	Carboxylic acid	Extractant	Diluent	Parameters studied	Findings	References
27.	Propionic	TBP	Kerosene and 1-decanol	Aqueous and organic phase compositions, and temperature	Modifier has a strong effect on degree of extraction	Kumar *et al*., 2011
28.	L (+) Tartaric	Amberlite LA-2	1-octanol, cyclohexane, isooctane, hexane, and MIBK	Organic phase compositions	Extractability of acid is high especially with polar solvents (MIBK and 1-octanol)	Inci *et al*., 2011
29.	Caproic	TBP	MIBK and xylene	Phase compositions	MIBK is a better solvent than xylene	Wasewar and Shende, 2011
30.	Acetic	TOA	DCM, butyl acetate, heptanes and 1-octanol	Organic phase compositions and pH	The solvent polarity controls the formed structure of the interfacial acid and TOA compounds	Cascaval *et al.,* 2011
31.	Picolinic	TBP	Sunflower and castor oil	Aqueous and organic phase compositions	Different models are used to represent the equilibrium data	Waghmare *et al*., 2011
32.	Picolinic	Trialkylamine (N235), TBP	Tetrachloromethane, kerosene and 1-octanol	Aqueous and organic phase compositions, and pH	Distribution coefficient highly dependent on pH and the apparent alkalinity of N235/1-octanol	Zhang *et al.,* 2012
33.	Acetic, propionic, butyric and valeric	TBP	Cyclohexane, sulfonated kerosene and 1-octanol	Equilibrium time, temperature and phase ratio	Conditions of extraction and stripping are found	Ren *et al.,* 2012
34.	Citric	TOA	Rice bran oil, sunflower oil, soybean oil, and sesame oil	Aqueous and organic and phase compositions	Overall extraction constants and association numbers	Keshav *et al.*, 2012

2.2 Kinetic Studies on Reactive Extraction of Carboxylic Acids

Kinetic studies are equally essential as equilibrium studies for the complete design of a reactive extraction unit. Lewis type stirred cell (Reschke and Schugerl, 1984), cylindrical stirring vessel with highly agitated system (Poposka *et al*., 1998), stirred cell with a microporous hydrophobic membrane (Jun *et al*., 2005) etc. were used to perform the kinetic studies on the reactive extraction of various carboxylic acids. In these studies, the investigators have described and analyzed the kinetic mechanism of reactive extraction using formal elementary kinetic model, a mechanism of reactions of acid-amine complexes (Poposka *et al*., 1998), theory of extraction accompanied by a chemical reaction (Doraiswamy and Sharma, 1984) etc. The estimation of the intrinsic kinetic parameters such as rate constants (forward and backward) and reaction order were also carried out using experimental data. According to their findings, the reaction between the acid and the extractant not only depends on the composition of the organic and aqueous phases, it also depends on the hydrodynamic parameters (volume ratio of phases, interfacial area and speed of agitation) of the system which also confirmed the region of the (mass transfer controlled or reaction controlled) reaction. In a study by Jun *et al*. in 2007, it was observed that the reaction rates were affected by pH and contamination present in the aqueous phase. At a pH greater than the pK_a of acid, more dissociation took place leading to the reduction in the extraction efficiency. Therefore, it was recommended that to have an effective separation of acid from the production media, the pH of the fermentation broth should be kept at a value less than the pK_a of the acid. Further, a brief review of the kinetic studies on reactive extraction is summarized in Table 2.2 to have an overview of the reactive kinetics of different carboxylic acids.

Table 2.2 Extractant/diluent system for the separation of carboxylic acids by reactive extraction: Kinetic studies

SL No.	Carboxylic acid	Extractant	Diluent	Parameters	Findings	References
1.	Penicillin G	Amberlite LA-2	Kerosene	Agitation speed, interfacial area between two immiscible solutions, pH of aqueous phase, initial carrier and penicillin G concentration	A rate equation for the mass transfer was proposed with the forward and backward rate constants as k_1 = 1.64 L^3 mol^{-2} s^{-1} and $k_2 = 6.56 \times 10^{-5}$ L s^{-1}, respectively	Wang and Lee, 1995
2.	Citric	TOA	iso-Decanol and n-paraffin	Concentrations of acid & amine and speed of agitation	Formal elementary kinetic model proposed and reaction kinetics evaluated	Poposka *et al*., 1998
3.	Penicillin G	Amberlite LA-2	Kerosene and n-butyl acetate	Aqueous and organic phase compositions, pH and temperature	The fractional resistances of aqueous layer diffusion, interfacial chemical reaction and organic layer diffusion were quantitatively determined	Juang and Lin, 1998
4.	Tartaric	TIOA	iso-Decanol, and kerosene	Concentrations of acid, amine and iso-decanol	Modified Langmuir isotherm was proposed and kinetic parameters interpreted by a formal elementary kinetic model	Poposka *et al*., 2000
5.	Lactic	Aliquat 336	Oleyl alcohol	Initial lactate and extractant concentrations in extraction,; initial chloride and extractant-lactate complex concentrations in stripping	Extraction and stripping kinetics were investigated, diffusion through the organic-phase film was determined as the rate-determining step	Hironaka *et al*., 2001
6.	Phenyl acetic	Alamine 336	Kerosene and MIBK	Acid and amine concentration, volume ratio of phases and stirrer speed	Intrinsic kinetics were described; the reaction found to be zero order in Alamine 336 and first order in acid with a rate constant of 0.9 s^{-1}	Gaidhani *et al*., 2002
7.	Penicillin G	Amberlite LA-2	Kerosene	Acid and amine concentration,and pH	Dispersed liquid-liquid extraction system proposed; Danckwert and Biot nos used to determine rate step	Lee, 2004

2.3 Gaps in Existing Literature

The extensive usage of the carboxylic acids in the field of food and pharmaceutical industries opened the path to produce them biochemically. There is a resurgence of interest in the industry for the large-scale production of fermentation chemicals using renewable resources due to the sharp increase in the petroleum cost. The growing importance of biological production also needs downstream processing of products.

Pyridine carboxylic acids (picolinic, nicotinic and isonicotinic acids) and their derivatives are attracting considerable attention for their presence in many natural products. The experimental and theoretical studies are essential to find the best extractant-diluent system, operating conditions and biocompatible system for these acids. The use of modifier is also limited for the extraction of nicotinic and isonicotinic acid. There is no temperature study for the extraction of glycolic, formic, nicotinic and isonicotinic acids. There is limited study to optimize the process variables for reactive extraction using design of experiments and response surface methodology (RSM). These techniques may be useful to find out optimum operating conditions of the reactive extraction system. The differential evolution (DE) optimization technique for the determination of reactive extraction parameters is studied for propionic, acetic, and butyric acids, and still there is need to explore this technique for other acids. Hence, there is a wider scope for the experimental and theoretical investigations on the reactive extraction of carboxylic acids.

2.4 Scope of the Work

The production of carboxylic acids from renewable carbon sources using fermentation process is a promising approach but still restricted due to the limitations on product recovery. The reactive extraction with a specified extractant-diluent system is found to be an effective and efficient method for the recovery of bio-products from the aqueous

solutions. In this thesis, an exhaustive experimental and theoretical studies on the reactive extraction of different carboxylic acids (picolinic, nicotinic, isonicotinic, glycolic, itaconic, formic, and levulinic acids) from their dilute aqueous solutions, is carried out. The extractants are used from the phosphoric [tri-*n*-butyl phosphate (TBP), tri-octyl phosphine oxide (TOPO) and di-2-ethyl hexyl phosphoric acid (D2EHPA)] and aminic [tri-*n*-octyl amine (TOA), tri-dodecyl amine (TDDA) and Aliquat 336] category of extractants. These extractants are dissolved in various inert (hexane, cyclohexane, heptane, decane, dodecane, kerosene, toluene, and benzene), active (DCM, chloroform, MIBK, 1-octanol, 1-decanol, and oleyl alcohol) and non-toxic (sunflower oil, dodecane, and oleyl alcohol) diluents to prepare the organic solutions of different concentrations. The effect of initial concentration of acid in the aqueous phase, initial extractant concentration in the organic phase, type of extractant, polarity and toxicity of diluent, mixture of diluents and temperature is studied on the extraction efficiency.

The physical extraction of picolinic acid using nine different diluents (dodecane, cyclohexane, chlorobenzene, benzene, DCM, MIBK, 1-octanol, 1-decanol and oleyl alcohol), and chemical extraction with 3 phosphoric- (TBP, TOPO and D2EHPA) and 3 aminic (TOA, TDDA and Aliquat 336) extractants dissolved in benzene (inactive) and 1-decanol (active) are carried out. Five different diluents (cyclohexane, chlorobenzene, DCM, MIBK and 1-octanol) are used with TOA to study the effect of diluent on the reactive extraction of picolinic acid. Completely biocompatible system is also used to recover this acid. The back-extraction of picolinic acid is carried out by pure water.

Nicotinic acid is separated from dilute aqueous solution using diluent mixture of 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v) and using TBP, TOPO and TOA dissolved in diluent mixtures. The effect of diluents on reactive extraction of nicotinic acid is studied with TOA dissolved in dodecane, toluene, 1-decanol, MIBK and

chloroform. The organic phase consists of TOA and Aliquat 336 in sunflower oil (a nontoxic diluent) is used to recover this acid.

Extraction of isonicotinic acid using hexane, toluene, DCM, dodecane, and oleyl alcohol alone, and with TBP dissolved in hexane, toluene, and DCM is performed. 1-Decanol and MIBK are also used as modifiers in the reactive extraction of this acid. The recovery of isonicotinic acid is carried out with TOA dissolved in dodecane, toluene, 1-decanol, MIBK, chloroform. Distribution of this acid between water and TDDA dissolved in nontoxic diluents (dodecane and oleyl alcohol) is studied. Experiments are also carried out to analyze the effect of temperature (298, 313, 323 and 333 K) on the extraction efficiency.

The equilibrium study for glycolic acid is carried out using TBP and TOA dissolved in a wide range of diluents [hexane, 1-decanol, hexane + 1-decanol (1:1 v/v), MIBK, benzene, and DCM]. The optimization of process variables to maximize the recovery of glycolic acid is done using experimental design and RSM model. In the reactive extraction of itaconic acid, TOA dissolved in six different diluents (heptane, kerosene, toluene, 1-decanol, MIBK, and DCM) is used as extractant. The work is also done to predict the degree of extraction using RSM and ANN method for itaconic acid reactive extraction. The experiments are performed with TOA in decane, benzene, 1-decanol, decane + 1-decanol (3:1 v/v), MIBK, and chloroform for the recovery of formic acid at 4 different temperatures (298 to 343 K). The physical extraction of levulinic acid using five different diluents (dodecane, benzene, 1-octanol, MIBK and DCM) is carried out. Also, the chemical extraction results are obtained using TBP, TOA, and Aliquat 336 in diluents. The intrinsic kinetics of extraction for nicotinic acid by TOA in MIBK is described and the values of physical mass transfer coefficient, orders of extraction, and rate constants are determined.

CHAPTER – 3

EXPERIMENTAL STUDY

The experimental methodology to obtain the equilibrium and kinetic data for the reactive extraction of carboxylic acids from aqueous solution is described in this chapter. The experimental study is performed to analyze the influence of various parameters on reactive extraction. In the equilibrium study, the parameters selected are: (i) carboxylic acid concentration in the aqueous phase, (ii) type of carboxylic acids, (iii) extractant concentration in the organic phase, (iv) type of extractants, (v) diluent composition in the organic phase, (vi) type of diluents, (vii) temperature, and (viii) toxicity of diluents. In the kinetic study for nicotinic acid, the following parameters are considered: (i) volume ratio of organic to aqueous phase, (ii) speed of stirrer, (iii) aqueous phase composition, and (iv) organic phase composition. The back-extraction of picolinic acid is also carried out using pure water to regenerate the organic phase for different concentrations of acid and extractant. The ranges of these parameters used in the equilibrium, back-extraction, and kinetic experiments are listed in Tables 3.1, 3.2 and 3.3, respectively. These parameters are chosen as to simulate the conditions of an actual fermentation broth and industrial wastewater streams.

3.1 Materials

The materials used in this study are various carboxylic acids, extractants and diluents, and are listed in Tables 3.4 and 3.5 with their physical properties. Deionized water (conductivity < 0.02 $S \cdot m^{-1}$ at 298 K, Millipore, India) is utilized to prepare the aqueous solution of various concentrations of carboxylic acids. Sodium hydroxide (98%; Merck, India) is used for titration, and phenolphthalein solution (pH range of 8.2 to 10.0; CDH, India) as an indicator for titration.

Table 3.1 Ranges of parameters used in the equilibrium experiments

SL No.	Carboxylic acids	Extractants	Diluents	Parameters studied
1.	Picolinic	-	Dodecane, benzene, cyclohexane, chlorobenzene, 1-decanol, oleyl alcohol, DCM, MIBK and 1-octanol	Acid concentration (0.01- 0.25 mol·L^{-1})
				Types of diluents
		TBP, TOPO, Di-2-ethylhexyl phosphoric acid (D2EHPA), TOA, tri-dodecylamine (TDDA) and Aliquat 336	Benzene and 1-decanol	Acid concentration (0.01- 0.25 mol·L^{-1})
				Types of extractants
				Types of diluents
		TOA	Cyclohexane, chlorobenzene, DCM, MIBK and 1-octanol	Acid concentration (0.01- 0.25 mol·L^{-1})
				TOA concentration (0.115-0.459 mol·L^{-1})
				Types of diluents
		TBP and TDDA	Dodecane and oleyl alcohol	Acid concentration (0.01- 0.25 mol·L^{-1})
				TBP concentration (0.365-2.192 mol·L^{-1})
				TDDA concentration (0.079-0.474 mol·L^{-1})
				Types of extractants
				Types of diluents
				Nontoxic diluents
2.	Nicotinic	-	1-Decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v)	Acid concentration (0.02-0.12 mol·L^{-1})
				Mixture of diluents
		TBP, TOPO and TOA	1-Decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v)	Acid concentration (0.02-0.12 mol·L^{-1})
				TBP concentration (0.183 and 0.365 mol·L^{-1})
				TOPO concentration (0.10 to 0.50 mol·L^{-1})
				TOA concentration (0.115 and 0.229 mol·L^{-1})
				Types of extractants
				Mixture of diluents

Table 3.1 Ranges of parameters used in the equilibrium experiments (continued…)

SL No.	Carboxylic acids	Extractants	Diluents	Parameters studied
2.	Nicotinic	TOA	Dodecane, toluene, 1-decanol, MIBK, and chloroform	Acid concentration (0.02-0.12 mol·L^{-1})
				Types of diluents
		TOA and Aliquat 336	Sunflower oil, dodecane and 1-octanol	Acid concentration (0.02-0.12 mol·L^{-1})
				Types of extractants
				Types of diluents
				Nontoxic diluent
				Types of modifier
3.	Isonicotinic	-	Hexane, toluene and DCM	Acid concentration (0.0043-0.0349 mol·L^{-1})
				Types of diluents
		TBP	Hexane, toluene, DCM, 1-decanol and MIBK	Acid concentration (0.0043-0.0349 mol·L^{-1})
				TBP concentration (0.365-1.096 mol·L^{-1})
				Types of diluents
				Types of modifier
		TOA	Dodecane, toluene, 1-decanol, MIBK and chloroform	Acid concentration (0.0043-0.0349 mol·L^{-1})
				Types of diluents
		TDDA	Dodecane and oleyl alcohol	Acid concentration (0.0043-0.0349 mol·L^{-1})
				Types of diluents
				Types of nontoxic diluents
				Temperature (298, 313, 323 and 333 K)
4.	Glycolic	Tri-*n*-butyl phosphate (TBP) and Tri-*n*-octylamine (TOA)	Hexane, 1-decanol, MIBK, benzene, and DCM	Acid concentration (0.10-0.57 mol·L^{-1})
				Types of extractants
				Types of diluents
		TOA	Cyclohexane and 1-decanol	Acid concentration (0.0293-0.1707 mol·L^{-1})
				TOA composition (12.93-27.07 %v/v)
				Modifier composition (16.72-73.28 %v/v)
				Temperature (22.86-51.14 ^{o}C)

Table 3.1 Ranges of parameters used in the equilibrium experiments (continued...)

SL No.	Carboxylic acids	Extractants	Diluents	Parameters studied
5.	Itaconic	TOA	Heptane, kerosene, toluene, 1-decanol, MIBK, and DCM	Acid concentration (0.05 to 0.25 mol·L^{-1})
				TOA concentration (0.115 and 0.229 mol·L^{-1})
				Type of diluents
			Cyclohexane and DCM	Acid concentration (0.02-0.08 mol·L^{-1})
				TOA composition (3.925-16.075 %v/v)
				Modifier composition (13.55-86.45 %v/v)
6.	Formic	TOA	Decane, benzene, 1-decanol, decane + 1-decanol (3:1 v/v), MIBK, and chloroform	Acid concentration (0.265-1.323 mol·L^{-1})
				Types of diluents
				Temperature (313, 328 and 343 K)
7.	Levulinic	TBP, TOA and Aliquat 336	Dodecane, benzene, 1-octanol, MIBK and DCM	Acid concentration (0.111- 0.541 mol·L^{-1})
				TBP concentration (0.365-2.192 mol·L^{-1})
				TOA concentration (0.115-0.689 mol·L^{-1})
				Aliquat 336 concentration (0.109- 0.653 mol·L^{-1})
				Types of extractants
				Types of diluents

Table 3.2 Ranges of parameters used in the back-extraction experiment

Carboxylic acid	Extractant	Diluent	Parameters studied
Picolinic	TDDA	Oleyl alcohol	Acid concentration (0.01 - 0.25 mol·L^{-1})
			TDDA concentration (0.079 and 0.474 mol·L^{-1})

Table 3.3 Ranges of parameters used in the kinetic experiment

Carboxylic acid	Extractant	Diluent	Parameters studied
Nicotinic	TOA	1-Decanol	Acid concentration (0.02 - 0.10 mol·L^{-1})
			TOA concentration (0.115 - 0.46 mol·L^{-1})
			Volume ratio of phases (0.5 - 2)
			Speed of stirrer (30 - 90 rpm)

Table 3.4 Physical characteristics of carboxylic acids used in the experimental study

S. No.	Reagents	IUPAC name	Supplier	Purity (%)	Mol. Wt. /g.mol^{-1}	Specific gravity
1.	Picolinic acid	Pyridine-2-carboxylic acid	CDH, India	98.00	122.12	-
2.	Nicotinic acid	Pyridine-3-carboxylic acid	Himedia, India	99.50	123.11	1.47
3.	Isonicotinic acid	Pyridine-4-carboxylic acid	Himedia, India	99.50	123.11	-
4.	Glycolic acid	2-Hydroxyethanoic acid	Spectrochem, India	98.00	76.05	1.33
5.	Itaconic acid	2-Methylidenebutanedioic acid	Himedia, India	99.50	130.10	1.57
6.	Formic acid	Methanoic acid	Himedia, India	99.00	46.03	1.22
7.	Levulinic acid	4-Oxopentanoic acid	Sigma Aldrich, India	98.00	116.12	1.13

Table 3.5 Physical characteristics of extractants and diluents used in the experimental study

S. No.	Reagents	IUPAC name	Supplier	Purity (%)	Mol. Wt. /g.mol^{-1}	Specific gravity	Viscosity (cP)
Extractants							
1.	TBP	Tri-*n*-butyl phophate	Spectrochem, India	98.00	266.32	0.97	3.4 (25 ^{0}C)
2.	TOPO	1-Dioctylphosphoryl octane	Sigma-Aldrich, India	99.00	386.65	0.88	-
3.	D2EHPA	Di-2-ehylhexyl phosphoric acid	Spectrochem, India	98.00	322.43	0.97	186.92 (30 ^{0}C)
4.	TOA	N, N-dioctyl octan-1-amine	Fluka, India	98.00	353.68	0.81	8.33 (25 ^{0}C)
5.	TDDA	N, N-didodecyl dodecan-1-amine	Fluka, India	95.00	522.00	0.82	-
6.	Aliquat 336	N-methyl-N, N-dioctyloctan-1-ammonium chloride	S. D. Fine, India	80.00	404.17	0.88	1.5 $\times 10^6$ (30 ^{0}C)
Diluents							
7.	n-Hexane	Hexane	CDH, India	99.00	86.18	0.65	0.29 (25^{0}C)
8.	Cyclohexane	Cyclohexane	S. D. Fine, India	99.00	84.16	0.78	0.98 (25^{0}C)
9.	n-Heptane	Heptane	S. D. Fine-Chem	99.00	100.21	0.68	0.39 (25^{0}C)
10.	n-Decane	Decane	Spectrochem, India	99.50	142.29	0.73	0.92 (20^{0}C)
11.	n-Dodecane	Dodecane	Spectrochem, India	95.00	170.33	0.75	1.40 (20°C)
12.	Dichloromethane	Dichloromethane	Fisher Scientific, India	99.00	84.93	1.33	0.41 (25°C)
13.	Chloroform	Tri-chloromethane	CDH, India	99.20	119.38	1.48	0.55 (25 °C)
14.	MIBK	4-Methyl pentan-2-one	Spectrochem, India	99.80	100.16	0.80	0.58 (20 °C)
15.	Kerosene	-	Commercial	-	170.00	0.80	2.17 (20 °C)
16.	Toluene	Methyl benzene	SISCO, India	99.70	92.14	0.87	0.56 (25°C)
17.	Benzene	Benzene	SISCO, India	99.50	78.11	0.88	0.65 (20 °C)
18.	1-Octanol	Octan-1-ol	Spectrochem, India	99.00	130.23	0.82	8.40 (20 °C)
19.	1-Decanol	Decan-1-ol	Spectrochem, India	98.00	158.28	0.83	34.00 (22°C)
20.	Oleyl alcohol	Octadec-9-en-1-ol	Spectrochem, India	98.00	268.48	0.83	-
21.	Sunflower oil	-	Commercial	-	-	0.91	-

3.2 Experimental Procedure

The equilibrium between two phases is constrained by Gibbs' Phase Rule (Eq. 3.1), where *DOF* is the degrees of freedom, N_C is the number of the components, and *Π* is the number of the phases present in the system. This rule is helpful to know the least number of intensive parameters that must be specified in order to describe the system completely (Smith *et al*., 2010).

$$DF = N_C - \Pi + 2 \qquad (3.1)$$

In the reactive extraction experiment, there are four degrees of freedom (temperature, pressure, concentration of the carboxylic acid in the aqueous phase and extractant concentration in the organic phase). Temperature and pressure are kept constant during the experiments, and initial concentrations of acid and extractant in the respective phases are also set accordingly.

The stock solutions of the different carboxylic acids with various concentrations are prepared using deionized water to minimize experimental error as follows: picolinic acid - 0.10 mol·L^{-1}, nicotinic acid - 0.12 mol·L^{-1}, isonicotinic acid - 0.03 mol·L^{-1}, glycolic acid - 0.57 mol·L^{-1}, itaconic acid - 0.25 mol·L^{-1}, formic acid - 1.323 mol·L^{-1} and levulinic acid - 0.5 mol·L^{-1}. These stock solutions are then diluted to the desired concentrations using de-ionized water to perform the equilibrium and kinetic experiments. The pH of initial aqueous solution is measured by a digital pH meter (ArmField Instruments, PCT 40, UK; Figure 3.1). The organic phase is prepared by dissolving different extractants in different diluents at various concentrations. Pure diluents are also used as the organic phase to study physical extraction equilibrium.

Figure 3.1 Digital pH-meter (ArmField instruments, PCT 40, UK)

Figure 3.2 Constant temperature water bath (Remi Labs, HS 250, India)

3.2.1 Equilibrium

Equal volumes (20 ml) of the aqueous and organic solutions are taken in conical flasks (100 ml) and shaken at 100 rpm for 8 hrs on a temperature controlled water bath (Remi Labs, HS 250, India, Figure 3.2) at constant temperature (298 K) and atmospheric pressure. The equilibrium time of 8 hrs is chosen as the appropriate time for attaining equilibrium based on our preliminary studies. After attaining equilibrium, the mixture of aqueous and organic phases is kept for separation in a separating funnel (125 ml) for 4 hrs at 298 K. After separation of phases, the aqueous phase is analyzed to determine the residual concentration of acid. The equilibrium pH of aqueous phase is also measured. In addition, the equilibrium experiments to study the effect of temperature are also carried out at different temperatures (313, 323, 328, 333 and 343 K). The back-extraction study is also carried out using pure water (temperature swing regeneration) at 353 K. The reproducibility of the data is checked by carrying out experiments in some selected cases. The results are found to be reproducible within the error limit of ± 5%. The experimental setup of equilibrium study is shown in Figure 3.3.

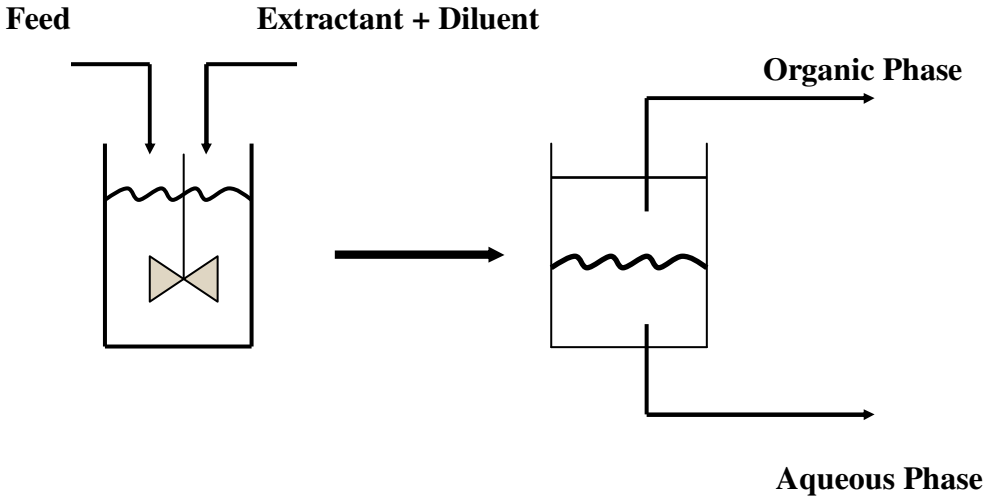


Figure 3.3 Schematic diagram used for the equilibrium experiment

3.2.2 Kinetics

Kinetic experiments are carried out in a cylindrical glass stirred cell (inside diameter = 0.067 m and height = 0.09 m). The vessel is equipped with stainless steel dual flat blade stirrer. The stirred cell is kept in a constant temperature water bath (298 K). Known volumes of aqueous and organic phases (100 ml) are prepared first, and then the aqueous phase is added to the cell. After that, the organic phase is added very slowly and carefully into the stirred cell. It is very critical not to damage the interface while pouring the organic phase. It is followed by setting the speed of the stirrer (30 to 90 rpm), and start of stirring. Proper selection of the speed of agitation is crucial to obtain dependable data. Thus the interface should not be disturbed and the interfacial area should be very close to the geometric area during stirring at the selected stirring speed. Sample of aqueous phase is taken out at definite time intervals (1, 3, 5, 10, 20, 30, 45, and 60 min) until equilibrium is achieved. Kinetic experiments are repeated twice, and average values for the experimental results are used to calculate the kinetic parameters. The experimental setup of kinetic study is shown in Figure 3.4.

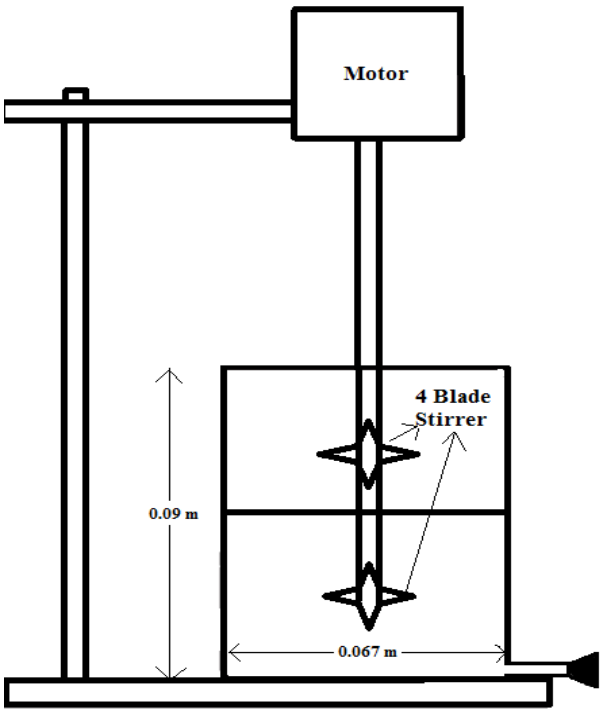


Figure 3.4 Schematic diagram of stirred cell used for the kinetic experiment

3.2.3 Analytical Methods

The concentration of acids (picolinic, nicotinic, isonicotinic, glycolic, itaconic, formic, and levulinic acids) in the aqueous phase is determined by taking samples of 2 ml using titration method with fresh sodium hydroxide solution (0.008, 0.05, and 0.01 N) and phenolphthalein as an indicator. The concentrations of glycolic and nicotinic acids in the aqueous phase are also determined using a UV-VIS spectrophotometer (Evolution 201, Merck, India; Figure 3.5) at 204 nm and 262 nm, respectively. The acid concentration in the organic phase is calculated by mass balance.

The calibration curves for measuring unknown concentrations of glycolic- and nicotinic acids are shown in Figures 3.6 and 3.7, respectively. For the calibration curve, the stock solutions of glycolic acid (0.05 mol·L^{-1}) and nicotinic acid (0.00075 mol·L^{-1}) are prepared. From these stock solutions, samples of aqueous solution are prepared in the concentration range of 0.00625 to 0.05 mol·L^{-1} for glycolic acid and 0.000015 to 0.00075 mol·L^{-1} for nicotinic acid to find out corresponding absorbance and generate calibration curves.

The efficiency of the reactive extraction process is analyzed by calculating the distribution coefficient (K_D), the degree of extraction ($\%E$) and loading ratio (Z). The distribution coefficient is defined as the ratio of total number of moles of acid in the organic phase ($V_{org}\overline{C}_{HC}$) to the total number of moles of acid in the aqueous phase ($V_{aq}C_{HC}$) at equilibrium, and given as follows:

$$K_D = \frac{V_{org}\overline{C}_{HC}}{V_{aq}C_{HC}} \tag{3.2}$$

With the assumption of negligible change in volume of each phase (maximum phase volume of organic phase is found 20.5 ml after reaching equilibrium) at equilibrium the values of K_D are affected only by ± 1%. Therefore, Eq. 3.2 reduces to:

$$K_D = \frac{\overline{C}_{HC}}{C_{HC}} \tag{3.3}$$

The degree of extraction is a ratio of acid concentration in the organic phase at equilibrium to the initial acid concentration in the aqueous phase, and given by Eq. 3.4.

$$E = \frac{\overline{C}_{HC}}{C_{in}} = \frac{K_D}{1+K_D} \times 100 \tag{3.4}$$

The extent to which the organic phase (extractant and diluent) may be loaded with acid is expressed by the loading ratio. It is a ratio of acid concentration in the organic phase at equilibrium to the initial extractant concentration in the organic phase ($[\overline{S}]_{in}$).

$$Z = \frac{\overline{C}_{HC}}{[\overline{S}]_{in}} \tag{3.5}$$

Figure 3.5 UV-VIS spectrophotometer (Evolution 201, Merck, India)

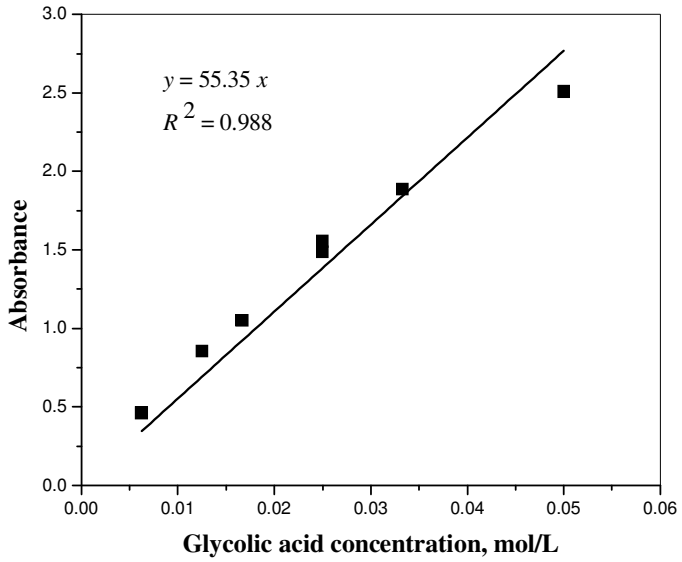


Figure 3.6 Calibration curve for analysis of aqueous phase concentration of glycolic acid at 204 nm using UV-VIS Spectrophotometer

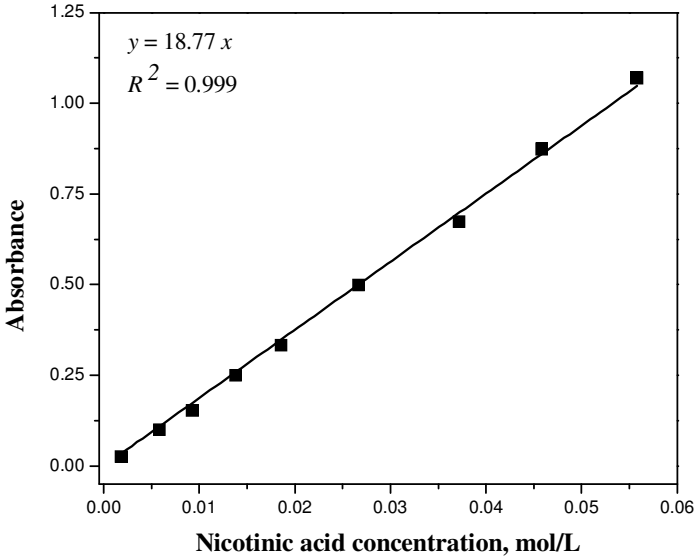


Figure 3.7 Calibration curve for analysis of aqueous phase concentration of nicotinic acid at 262 nm using UV-VIS Spectrophotometer

CHAPTER – 4

THEORETICAL STUDY

The theories of equilibria and kinetics of reactive extraction are explained in Sections 4.1 and 4.2, respectively. These models describe the physical and chemical phenomena occurring in the extraction process in the mathematical forms. They also explain interaction mechanism between the components of aqueous (acid and water) and organic (extractant and/or diluent) phases. In these model equations (equilibrium and kinetic), assumption is made that all the reactions are in thermodynamic equilibrium occurring at the interface of aqueous and organic phases. The sections also describe the techniques for the determination of model parameters. The values of model parameters are useful in providing valuable qualitative and quantitative information about the entire reactive extraction process.

4.1 Equilibrium Models

4.1.1 Mass Action Law Model

Equilibrium data are interpreted by Mass Action Law, which was proposed by Guldberg and Waage in 1864. Kertes and King in 1986 applied Mass Action Law for reactive extraction of carboxylic acids. In the Mass Action Law model, activities of the aqueous and organic phase species are assumed to be proportional to the respective concentration of the species and the equilibrium constant takes care of the constant of proportionality or the non-idealities associated with the reactive system. Therefore, the apparent equilibrium constant (written in terms of species concentration) is used for the development of mathematical model of the reaction equilibrium. This model can be subcategorized in two

types: (i) physical extraction where only diluent (pure form) is used for extraction and (ii) chemical extraction where both extractant (phosphoric and aminic) and diluent take part in the extraction process. These models are discussed in details in the Sections 4.1.1.1 and 4.1.1.2, respectively.

4.1.1.1 Physical Extraction

The process of physical equilibria with pure diluent takes place in three parts: (i) partial dissociation of the acid molecule in aqueous phase, (ii) distribution of the undissociated acid molecule between aqueous and organic phases, and (iii) dimerization of undissociated acid molecule in the organic phase.

(i) Carboxylic acid can exist as undissociated (HC) and dissociated (C^-) forms in the aqueous solution of water. The dissociation of the acid in the aqueous solution depends upon the strength of the acid (pK_a) and is described by Eq. 4.1.

$$HC \leftrightarrow H^+ + C^- \tag{4.1}$$

The dissociation constant (K_a) is calculated using Eq. 4.2.

$$K_a = \frac{[H^+][C^-]}{[HC]} \tag{4.2}$$

The total acid concentration in the aqueous phase (C_{HC}) and undissociated acid ([HC]) concentration can be expressed as Eqs. 4.3 and 4.4, respectively.

$$C_{HC} = [HC] + [C^-] \tag{4.3}$$

$$[HC] = \frac{C_{HC}}{\left(1 + \frac{K_a}{[H^+]}\right)} \tag{4.4}$$

(ii) The distribution of the undissociated acid molecule between aqueous and organic phases is represented by Eq. 4.5 and the corresponding partition coefficient is given by Eq. 4.6.

$$\mathrm{HC} \leftrightarrow \overline{\mathrm{HC}} \tag{4.5}$$

$$P = \frac{[\overline{\mathrm{HC}}]}{[\mathrm{HC}]} \tag{4.6}$$

(iii) The undissociated extracted acid molecules can dimerize in the organic phase due to the strong donor-acceptor interaction. This is due to the solute-solute interaction through hydrogen bond which is stronger than the solute-solvent interaction. The dimerization of the undissociated extracted acid in the organic phase ($\overline{\mathrm{HC}}$) is represented by Eq. 4.7.

$$2\,\overline{\mathrm{HC}} \leftrightarrow (\overline{\mathrm{HC}})_2 \tag{4.7}$$

The dimerization constant (D) is expressed by Eq. 4.8.

$$D = \frac{\overline{(\mathrm{HC})_2}}{\overline{(\mathrm{HC})}^2} \tag{4.8}$$

The extraction efficiency (with pure diluent) of acid is calculated by the physical distribution coefficient, $K_{\mathrm{D}}^{\mathrm{diluent}}$ (Eq. 4.9).

$$K_{\mathrm{D}}^{\mathrm{diluent}} = \frac{\overline{C}_{\mathrm{HC}}^{\mathrm{diluent}}}{C_{\mathrm{HC}}^{\mathrm{diluent}}} \tag{4.9}$$

where $\overline{\mathrm{C}}_{\mathrm{HC}}^{\mathrm{diluent}}$ is the total (undissociated and dimer forms) concentration of acid in the organic phase and $C_{\mathrm{HC}}^{\mathrm{diluent}}$ is the total (dissociated and undissociated) concentration in aqueous phase at equilibrium with pure diluent.

For a dilute concentration of acid (as used in this study), $K_{\mathrm{D}}^{\mathrm{diluent}}$ in terms of dimerization constant (D) and partition coefficient (P) can be represented as (Kertes and King, 1986):

$$K_{\mathrm{D}}^{\mathrm{diluent}} = P + 2DP^2[\mathrm{HC}] \tag{4.10}$$

To estimate the values of physical extraction parameters (*P* and *D*), the plots of $K_D^{diluent}$ versus [HC] can be fitted linearly and value of *P* from the intercept and *D* from the slope can be obtained.

4.1.1.2 Chemical Extraction

The interaction of acid molecule with the extractant molecule in the chemical extraction can occur in two ways: (i) through hydrogen bonding of undissociated acid molecule, Eq. 4.11, and (ii) by ion pair formation, Eq. 4.12 (Yankov *et al.*, 2004).

$$HC + \bar{S} \leftrightarrow \overline{(HC)(S)} \tag{4.11}$$

$$H^+ + C^- + \bar{S} \leftrightarrow \overline{H^+C^-S} \tag{4.12}$$

The extraction mechanism described in Eqs. 4.11 and 4.12 depends on the pH of aqueous solution, pK_a of acid, the acid and extractant concentrations and the basicity of the extractant with respect to the acid (pK_B). The extraction of carboxylic acid by phosphorous based extractants (TBP, TOPO etc.) can be described by Eq. 4.11 and that for amine based extractants (TOA, Aliquat 336 etc.) by both mechanisms (Eqs. 4.11 and 4.12).

An equilibrium extraction process is described as a set of reactions (Eq. 4.13) between *m* molecules of acid (HC) and *n* molecules of extractant (S) to form various (*m*:*n*) complexes with corresponding apparent equilibrium constant (K_E) as given by Eq. 4.14.

$$mHC + n\bar{S} \leftrightarrow \overline{(HC)_m(S)_n} \tag{4.13}$$

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

The distribution coefficient (K_D) can be written as:

$$K_D = \frac{\overline{C}_{HC}}{C_{HC}} = m\frac{[\overline{(HC)_m(S)_n}]}{C_{HC}} \quad (4.15)$$

Substituting the values of [HC] and $[\overline{(HC)_m(S)_n}]$ from Eq. 4.4 and Eq. 4.15, respectively, in Eq. 4.14 results in Eq. 4.16.

$$K_E = \frac{K_D(1+K_a/[H^+])^m}{mC_{HC}^{m-1}[\overline{S}]^n} \quad (4.16)$$

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

$$[S] = [\overline{S}]_{in} - n[\overline{(HC)_m(S)_n}] \quad (4.17)$$

$$[\overline{S}] = [\overline{S}]_{in} - K_D n C_{HC}/m \quad (4.18)$$

Now, putting the value of $[\overline{S}]$ from Eq. 4.18 in Eq. 4.16, Eq. 4.19 is derived.

$$K_D = mK_E\left([\overline{S}]_{in} - K_D n\frac{C_{HC}}{m}\right)^n \frac{C_{HC}^{m-1}}{(1+K_a/[H^+])^m} \quad (4.19)$$

The values of equilibrium extraction constant (K_E) and the stoichiometry (m, n) of the reactive extraction are determined by minimizing the error between the experimental and predicted values of K_D using the following objective function known as root mean square deviation (*rmsd*).

$$rmsd = \left[\frac{\sum\left(K_D^{exp} - K_D^{model}\right)^2}{N_D - 1}\right]^{\frac{1}{2}} \quad (4.20)$$

where N_D is the number of data points.

The equilibrium model for the simultaneous formation of various types of acid-extractant complexes (1:1, 2:1, 3:1, 1:2 etc.) can be represented by a system of equations (Eqs. 4.21 to 4.24) depending upon the type of the acid, extractant and diluent and their concentrations used in the experiment.

$$HC + \overline{S} \leftrightarrow \overline{(HC)(S)} \tag{4.21}$$

$$HC + \overline{(HC)(S)} \leftrightarrow \overline{(HC)_2(S)} \tag{4.22}$$

$$HC + \overline{(HC)_2(S)} \leftrightarrow \overline{(HC)_3(S)} \tag{4.23}$$

$$\overline{(HC)(S)} + \overline{S} \leftrightarrow \overline{(HC)(S)_2} \tag{4.24}$$

The corresponding extraction constants (K_{11}, K_{21}, K_{31} and K_{12}) are calculated using Eqs. 4.25 to 4.28:

$$K_{11} = \frac{\overline{C}_{11}(1 + K_a/[H^+])}{C_{HC}[\overline{S}]} \tag{4.25}$$

$$K_{21} = \frac{\overline{C}_{21}(1 + K_a/[H^+])}{C_{HC}\overline{C}_{11}} \tag{4.26}$$

$$K_{31} = \frac{\overline{C}_{31}(1 + K_a/[H^+])}{C_{HC}\overline{C}_{21}} \tag{4.27}$$

$$K_{12} = \frac{\overline{C}_{12}}{\overline{C}_{11}[\overline{S}]} \tag{4.28}$$

$\overline{C}_{11}, \overline{C}_{21}$, $\overline{C}_{31}$ and $\overline{C}_{12}$ are the concentrations of 1:1, 2:1, 3:1 and 1:2 complexes, respectively, in the organic phase. $\overline{C}_{HC}$ and $[\overline{S}]$ are given by Eqs. 4.29 and 4.30, respectively.

$$\begin{aligned}\overline{C}_{HC} &= \overline{C}_{11} + 2\overline{C}_{21} + 3\overline{C}_{31} + \overline{C}_{12} \\ &= \frac{K_{11}[\overline{S}]C_{HC}}{\left[1 + \frac{K_a}{[H^+]}\right]} + \frac{2K_{11}K_{21}[\overline{S}]C_{HC}^2}{\left[1 + \frac{K_a}{[H^+]}\right]^2} + \frac{3K_{11}K_{21}K_{31}[\overline{S}]C_{HC}^3}{\left[1 + \frac{K_a}{[H^+]}\right]^3} + \frac{K_{11}K_{12}[\overline{S}]^2 C_{HC}}{\left[1 + \frac{K_a}{[H^+]}\right]}\end{aligned} \tag{4.29}$$

$$\begin{aligned}[\overline{S}] &= [\overline{S}]_{in} - (\overline{C}_{11} + \overline{C}_{21} + \overline{C}_{31} + 2\overline{C}_{12}) \\ &= [\overline{S}]_{in} - \left(\frac{K_{11}[\overline{S}]C_{HC}}{\left[1 + \frac{K_a}{[H^+]}\right]} + \frac{K_{11}K_{21}[\overline{S}]C_{HC}^2}{\left[1 + \frac{K_a}{[H^+]}\right]^2} + \frac{K_{11}K_{21}K_{31}[\overline{S}]C_{HC}^3}{\left[1 + \frac{K_a}{[H^+]}\right]^3} + \frac{2K_{11}K_{12}[\overline{S}]^2 C_{HC}}{\left[1 + \frac{K_a}{[H^+]}\right]} \right)\end{aligned} \tag{4.30}$$

Using experimental results and by applying the mass action law, the values of the individual equilibrium constants (K_{11}, K_{21}, K_{31} and K_{12}) and the concentration of complexes ($\overline{C}_{11}, \overline{C}_{21}$, $\overline{C}_{31}$ and $\overline{C}_{12}$) can be estimated. An objective function is defined as Eq. 4.31 and minimizing the error between the experimental and predicted values of $\overline{C}_{HC}$, values of the individual equilibrium constants can be estimated.

$$rmsd = \left[\frac{\sum \left(\overline{C}_{HC}^{exp} - \overline{C}_{HC}^{model} \right)^2}{N_D - 1} \right]^{\frac{1}{2}} \tag{4.31}$$

Now, a model based on the loading ratio (Z) for formation of various types of complexes (1:1, 2:1 etc.) between acid and extractant can also be described. The expression of Z is given by Eq. 3.5. The value of Z depends on the extractability of the acid (strength of the acid-base interaction) and its aqueous concentration, and the stoichiometry of the overall extraction equilibrium. It is found that when the organic phase is not highly concentrated by acid, i.e., at very low loading ratios ($Z < 0.5$), 1:1 acid-extractant complex is formed. A plot of $Z/(1-Z)$ versus [HC] yields a straight line passing through origin with a slope of complexation constant (K_{11}) as given by Eq. 4.32:

$$\frac{Z}{1-Z} = K_{11}[\mathrm{HC}] \tag{4.32}$$

If the carboxylic acid concentration is high enough (at least $Z > 0.5$), this relation can be expressed as shown by Eq. 4.33.

$$\frac{Z}{m-Z} = K_{m1}[\mathrm{HC}]^m \tag{4.33}$$

To account for the extraction only by extractant, a term is defined for the distribution of acid by chemical extraction (K_D^{chem}) as:

$$K_D^{chem} = \frac{\overline{C}_{HC} - \nu \overline{C}_{HC}^{diluent}}{C_{HC}} \tag{4.34}$$

where *v* is the volume fraction of diluent in the organic phase.

Therefore, the overall distribution coefficient (K_D^{total}) by physical and chemical extraction is obtained by adding Eqs. 4.9 and 4.34.

$$K_D^{total} = \nu K_D^{diluent} + K_D^{chem} \tag{4.35}$$

In general the diluent alone also solvates some amount of solute (acid) from aqueous solution by physical extraction which is described in the previous section. Therefore, in such a case, expression for $[\overline{(HC)_m(S)_n}]$ is represented as:

$$[\overline{(HC)_m(S)_n}] = \overline{C}_{HC} - \nu \overline{C}_{HC}^{diluent} \tag{4.36}$$

Therefore, the Eq. 4.36 could be obtained by including the term for physical extraction and rewriting the Eq. 4.33 as:

$$K_{mn}[HC]^m = \frac{\overline{C}_{HC} - \nu \overline{C}_{HC}^{diluent}}{\left[\overline{[S]}_{in} - n(\overline{C}_{HC} - \nu \overline{C}_{HC}^{diluent})\right]^n} \tag{4.37}$$

4.1.2 Linear Solvation Energy Relation (LSER)

A linear solvation energy relationship (LSER) approach has been introduced by Kamlet *et al*. in 1983 and then improved by Abraham (Abraham, 1993). It characterizes solvation effects in terms of nonspecific and H-bonding interactions. Thus, a solvation property of interest (XYZ) for an organic solute is modeled by a linear solvation energy relationship of the form (Abraham *et al*., 2000):

$$XYZ = XYZ^0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H + e\xi \tag{4.38}$$

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^*, an index of solvent dipolarity or polarizability, measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. δ, a polarizability correction term, equals to

0.0 for non-chlorinated 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 H-bond. *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 H-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. The coefficients *p*, *s*, *e, d*, *a*, *h* and *b* are the regression coefficients that measure the relative susceptibilities of XYZ to indicated solvent property scale. Equation 4.38 is adopted to describe the effect of diluents on the values of distribution coefficients (K_D):

$$\log_{10} K_D = \log_{10} K_D{}^0 + s(\pi^* + d\delta) + a\alpha + b\beta + h\delta_H + e\xi \qquad (4.39)$$

where the parameters π^*, δ, β and α refer to the diluents, and $K_D{}^0$ represents the distribution coefficient for an ideal diluent. The fifth term of Eq. (4.39), which contains the solubility parameter δ_H, does not affect the values of the objective function ($\log_{10} K_D$) significantly and the value of $\xi = 0$ is considered for the diluents used in this study. Thus, Eq. 4.39, results in Eq. 4.40.

$$\log_{10} K_D = \log_{10} K_D{}^0 + s(\pi^* + d\delta) + b\beta + a\alpha \qquad (4.40)$$

Eq. 4.40 is adopted to describe the effect of diluents on the values of distribution coefficients (K_D).

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

$$SP_{12} = X_1 SP_1 + (1 - X_1) SP_2 \qquad (4.41)$$

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. The solvatochromic parameters of diluents used in this study are listed in Table 4.1. For the estimation of model parameters, least square regression method is used to minimize the deviation between the experimental and the model predicted values of $\log_{10} K_D$.

Table 4.1 Solvatochromic parameters of diluents (Kamlet *et al.*, 1983)

S. No.	Diluents	π^*	β	α	δ
1.	Hexane	-0.08	0.00	0.00	0.00
2.	1-Decanol	0.40	0.45	0.33	0.00
3.	Benzene	0.59	0.10	0.00	1.00
4.	MIBK	0.63	0.48	0.00	0.00
5.	DCM	0.82	0.10	0.30	0.50
6.	Toluene	0.54	0.11	0.00	1.00
7.	Heptane	-0.08	0.00	0.00	0.00
8.	Dodecane	-0.08	0.00	0.0	0.00
9.	Chloroform	0.58	0.00	0.44	0.50
10.	Decane	0.03	0.00	0.00	0.00
11.	Decane + 1-decanol (3:1 v/v)	0.12	0.11	0.08	0.00
12.	Hexane + 1-decanol (1:1 v/v)	0.16	0.23	0.17	0.00

4.1.3 Modified Langmuir, Freundlich and Temkin Models

Adsorption isotherm describes the interaction between the molecules of acid (adsorbate) and extractant (adsorbent) at equilibrium, and provides information about the optimum use of extractant. These equilibrium isotherms are characterized by certain parameters, and their values state the surface properties and affinity of the adsorbent. The isotherms depend on the specific surface area of an extractant, its composition, the nature of the extractant, the type of acid and the acidity of medium. The acid recovered in the extract phase (in gram) per gram of extractant can be quantitatively described by the modified

Langmuir (Eq. 4.42), modified Freundlich (Eq. 4.43) and modified Temkin (Eq. 4.44) equations at constant temperature (Inci *et al.,* 2011; Gulipalli *et al.,* 2011).

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{4.42}$$

$$q_e = K_F C_e^{\frac{1}{f}} \tag{4.43}$$

$$q_e = B_T \log K_T C_e \tag{4.44}$$

where C_e ($g \cdot L^{-1}$) and q_e ($g \cdot g^{-1}$) are the aqueous phase and organic phase concentrations of solute (adsorbate) at equilibrium, respectively. Q_0 ($g \cdot g^{-1}$) is the monolayer capacity and K_L ($L \cdot g^{-1}$) is the Langmuir equilibrium constant. K_F is the Freundlich constant [($g \cdot g^{-1}$) ($L \cdot g^{-1}$)$^{1/n}$] related to the bonding energy, and f is the heterogeneity factor which is a measure of the deviation from linearity of the adsorption. K_T ($L \cdot g^{-1}$) is the equilibrium binding constant, corresponding to the maximum binding energy, and constant B_T ($g \cdot g^{-1}$) is related to the heat of adsorption for Temkin isotherm. These non-linear isotherms (Langmuir, Freundlich and Temkin) are fitted using a professional software package ORIGIN (*v* 6.0) to estimate the model parameters.

4.1.4 Relative Basicity Model

The basic nature of a compound is defined by its power of accepting hydrogen ion in the aqueous solution. Wasewar *et al*. (2011) have proposed the relative basicity model to correlate 1:1 equilibrium constant (K_{11}) with relative basicity of the extractant. The important factors which influence the equilibrium characteristics of the extraction process are: (i) the nature and strength of the acid (pK_a), (ii) the hydrophobicity of the acid (log P_a), (iii) the nature of the solvent and (iv) the apparent basicity of extractant to acid (p$K_{a,B}$). A model equation is written in the following form to describe the effect of these parameters on K_{11}.

$$\log_{10} K_{11} = C_1 (pK_{a,B} - pK_a + \log P) + C_2 \quad (4.45)$$

K_{11} represents the extraction capacity of the extractant/diluent system and interactions of acid-extractant molecule by ion-pair formation, H-bond and/or solvation at equilibrium. The solvating power is a relatively complicated H-bonding association between the complex and the diluent, which also depends on the nature of the solute, extractant and diluent. Further, p$K_{a,B}$ represents the association of the extractant with acid. Now, to estimate the relative basicity model parameters (C_1 and C_2), the plots of $\log K_{11}$ versus $(pK_{a,B} - pK_a + \log P_a)$ are drawn. A linear trend line is best fitted in ORIGIN (*v* 6.0) software package. The linear fits yield the value of C_1 as a slope and C_2 as an intercept.

4.1.5 Response Surface Methodology (RSM)

The development of an industrial process requires study of the effect of various operating parameters which can be achieved by exhaustive experimentation. The experiments are carried out by varying numerous experimental units to evaluate the performance of the system in terms of single/many output variable (s). These experimental data are useful to draw many valuable results and inferences about the system and the process. Therefore, an experimenter needs to plan and design the experiments, and analyze the results. The approximation of the response function in terms of input variables is called Response Surface Methodology (RSM). RSM is applied for the construction of empirical models based on experimental design and data (Bezerra *et al*, 2008; Montgomery, 2001; Myers and Montgomery, 2002). It is suitable for developing non-parametric simulative models of various processes in real applications (Guan and Yao, 2008; Kılıc *et al*., 2002; Kuscua and Sponza, 2011; Marchitana *et al*., 2010; Oniscu *et al*., 2002; Pathirana and Shahidi, 2005; Rajasimman *et al*., 2009; Silva *et al*., 2007). The developed model is then used to

estimate the optimum of the process variables (parameters) to maximize or minimize the dependent variable or response (Fox *et al*., 2009).

In the RSM modeling, the input variables are normalized to coded levels which usually vary from a minimum level ($-\alpha^*$) up to a maximum level ($+\alpha^*$). In the present study, the value of α^* is selected based on central composite orthogonal design (CCOD) approach and using Eq. 4.46 (Khuri and Cornell, 1987). The experiments are designed considering (i) 2^k factorial CCOD points; (ii) n_c central points (coded as zero value); (iii) two axial points from the central design point at a distance of $\pm\alpha^*$; and (iv) $2k$ star points. k is the total number of design variable. Hence, the total number of experimental design points are become as, $n_T = 2^k + 2k + n_c$.

$$\alpha^* = \left(\frac{\sqrt{n_T \times 2^k} - 2^k}{2} \right)^{\frac{1}{2}} \tag{4.46}$$

The actual values of design variables (X_i) are normalized as x_i (dimensionless) according to the following equation:

$$x_i = \frac{X - \frac{X_{max} + X_{min}}{2}}{\frac{X_{max} - X_{min}}{2}} \tag{4.47}$$

where X_{max} and X_{min} are the maximum and minimum values of a variable for a full factorial design at level 2.

An expression describing a second order RSM model can be written as (Box and Hunter, 1978; Garcia *et al*., 2000):

$$\hat{Y} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i<j}^{k} \beta_{ij} x_i x_j \tag{4.48}$$

where $\hat{Y}$ denotes the predicted response; x_i refers to the design variables in coded form; β_0, β_i, β_{ii}, and β_{ij} are the regression coefficients (offset term, main, quadratic and

interaction effects, respectively); and k is total number of design variables. The regression coefficients are determined using ordinary least squares (OLS) method as (Bowen *et al.*, 2000; El-Hawary, 1993):

$$\beta_{\text{OLS}} = (X^T X)^{-1} X^T Y \tag{4.49}$$

where β_{OLS} is a vector of regression coefficients; X is an extended matrix of the normalized values of the input variables; Y is a column vector of response.

The mathematical design equation (Eq. 4.48) achieved by regression is tested for statistical significance using the analysis of variance (ANOVA). ANOVA compares the variation of regression data about the mean due to the residual. The mathematical correlations for the determination of the ANOVA estimators [i.e. degree of freedom (*DF*), sum of squares (*SS*), mean square (*MS*), *F*-value (from Fischer distribution test), *P*-value (from null hypothesis test), coefficient of determination (R^2), adjusted statistic (R^2_{adj}) etc.] are discussed in the literature for the design of experiments (DoE) and RSM (Bezerra *et al.*, 2008).

4.1.6 Artificial Neural Network (ANN)

An artificial neural network is a mathematical model that is inspired by the structure and functional aspects of biological neural networks. Now a days, neural networks are considered as modeling tool to solve non-linear and multivariate regression problems (Sarkar *et al.*, 2009). An artificial neuron called node is a single computational point which has summing junction and transfer function (Demuth and Beale, 2004). The neurons are connected with weights (w) and biases (B) to pass the information. The operator at the summing junction of a single neuron called argument (A) to be processed is formed using weights and biases, and given as:

$$A = \sum_{i=1}^{n} x_i w_i + B \tag{4.50}$$

The transfer function takes the argument, *A*, and produces the scalar output of a single neuron. The most used transfer functions in ANN are *purelin*, *logsig* and *tansig* (Demuth and Beale, 2004).

$$purelin(A) = A \tag{4.51}$$

$$\log sig(A) = \frac{1}{1+\exp(-A)} \tag{4.52}$$

$$\tan sig(A) = \frac{\exp(A)-\exp(-A)}{\exp(A)+\exp(-A)} \tag{4.53}$$

The pattern in which the inputs and outputs of the neurons are connected is known as architecture of the neural network. The most common neural network architecture used for solving non-linear regression problems is the multi-layer feed-forward neural network or multi-layer perceptron (MLP) (Sadrzadeh *et al*., 2008). It has hidden and output layers consisting of hidden and output neurons, respectively, and the inputs are considered as additional layer. The back-propagation (BP) method is most preferred technique to train the MLP. Training of ANN by means of BP algorithm is an iterative optimization process, and the performance function is minimized by adjusting the weights and biases appropriately. The commonly employed performance function is the mean-squared-error (*MSE*) which is defined as (Desai *et al*., 2008; Curteanu *et al*., 2007):

$$MSE = (Y - \hat{Y})^2 \tag{4.54}$$

where Y and $\hat{Y}$ are the target (experimental response) and output (predicted response), respectively. According to BP algorithm the weights and biases are iteratively updated in the direction in which the performance function MSE decreases most rapidly. Generally, a single iteration of BP algorithm can be written as follows (da Silva and Flauzino, 2008; Erzurumlu and Oktem, 2007).

$$W^{(k+1)} = W^{(k)} - \eta^{(k)} grad^{(k)}(MSE) \tag{4.55}$$

where $W^{(k)}$ is a vector of current weights and biases, $grad^{(k)}(MSE)$ is the current gradient of the performance function MSE and $\eta^{(k)}$ is the learning rate. The flow chart of ANN is shown in Figure 4.1. The Neural Network Toolbox in MATLAB (*v* 7.0.1) mathematical software has been used for construction of ANN model.

After neural network training, the developed ANN model can also be tested for its accuracy using ANOVA. All ANOVA estimators can be calculated in a similar way as RSM model. The calculation of the degree of freedom due to residual and model in case of neural network may be written as:

$$DF_{residual} = n_c - L \tag{4.56}$$

$$DF_{model} = L - 1 \tag{4.57}$$

where n_c is the total number of experiments considered to develop the predictive model, and L is the total number of connections (weights and biases) in the ANN model. For a feed-forward neural network with one hidden layer (HL), the total number of connections is given by:

$$L = z(n_p + H + 1) + H \tag{4.58}$$

where n_p denotes the number of inputs (variables), z is the number of neurons in HL, and H is the number of neurons (nodes) in output layer (OL).

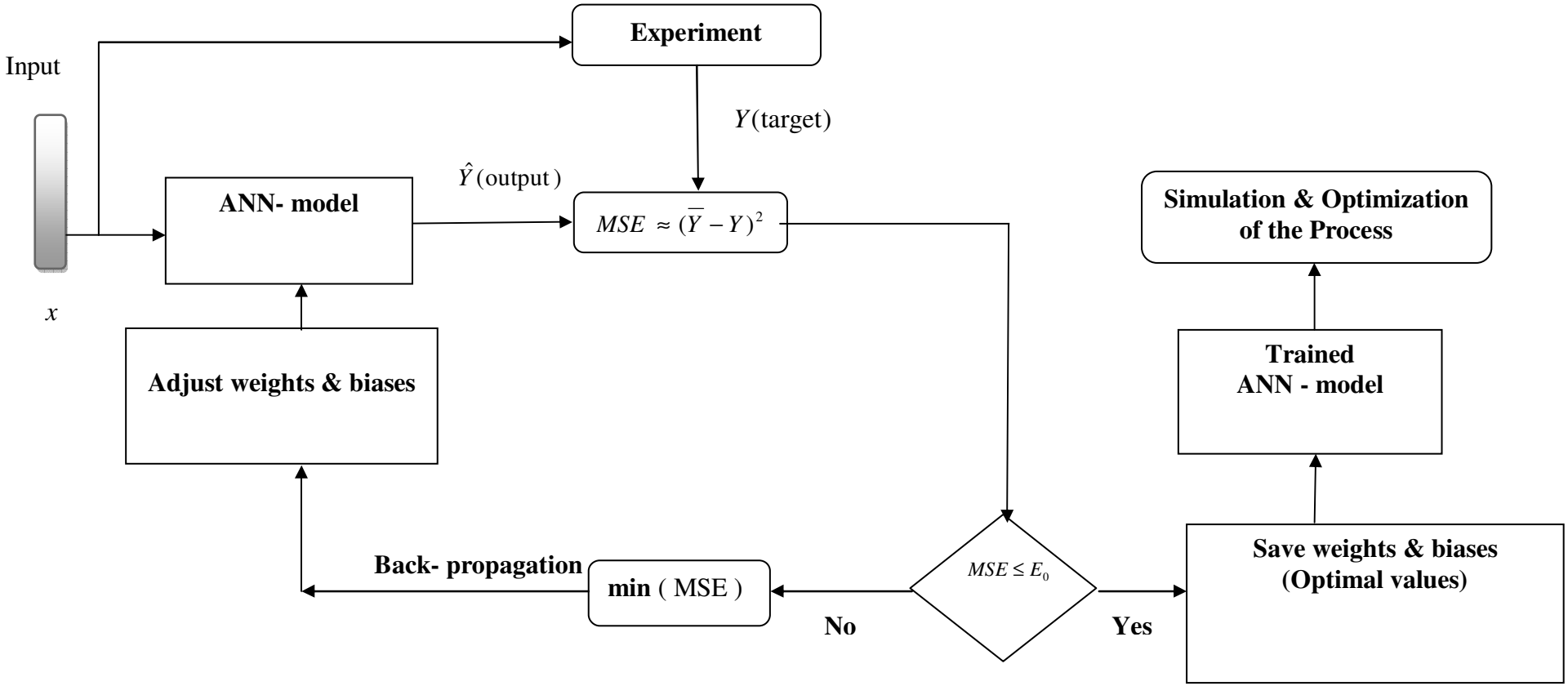


Figure 4.1 The general scheme used for the neural network training using BP method

4.2 Kinetic Model

A comprehensive study on the theory of extraction accompanied with chemical reaction in a stirred cell is proposed by Doraiswamy and Sharma in 1984 to determine the effect of chemical reaction on the specific rate of reaction. With the help of the film and renewal theories with physico-chemical and hydrodynamic parameters, they have classified the reactive system into four reaction regimes (very slow, slow, fast and instantaneous) depending on their relative diffusion and reaction rates (Table 4.2).

Table 4.2 Classical limiting regimes for irreversible reaction in a stirred cell

Regime	**Description**	***Hatta* Number (*Ha*)**	**Effect on the specific rate of extraction ($mol \cdot m^{-2} \cdot s^{-1}$)**			
			$\overline{[HC]}$ $mol \cdot L^{-1}$	$[\bar{S}]$ $mol \cdot L^{-1}$	**Stirrer speed (*N*, rpm)**	**Volume ratio of phases**
1.	Very slow	<< 1	$\alpha[\overline{HC}]^m$	$\alpha[\bar{S}]^n$	None	αV_{org}
2.	Slow		$\alpha[\overline{HC}]$	None	Increases with increase in the speed of stirring	None
3.	Fast	>> 1	$\alpha[\overline{HC}]^{\frac{m+1}{2}}$	$\alpha[\bar{S}]^{\frac{n}{2}}$	None	None
4.	Instantaneous		None	$\alpha[S]$	Increases with increase in the speed of stirring	None

The value of physical mass transfer coefficient (k_L) is required to confirm the regime of reaction. This is obtained by conducting physical extraction of acid from aqueous phase with pure diluent. For a batch process a differential mass balance yields the following equation,

$$V_{aq} \frac{dC_{org}}{dt} = k_L A_c \left(C^*_{org} - C_{org} \right) \qquad (4.59)$$

where A_c is the interfacial area (m^2); V_{aq} is the aqueous phase volume (m^3); C^*_{org} is the equilibrium acid concentration in the organic phase. The time-dependent concentration of acid in the organic phase is obtained by integrating Eq. 4.59 as:

$$\ln\left(\frac{C^*_{org}}{C^*_{org}-C_{org}}\right)=\frac{k_L A_c}{V_{org}}t \tag{4.60}$$

A plot of $\ln\left(\frac{C^*_{org}}{C^*_{org}-C_{org}}\right)$ versus time (t) yields a straight line and the slope is used to evaluate physical mass transfer coefficient (k_L).

The reaction between acid and extractant is reversible. This problem of reversibility can be avoided by measuring the initial specific rate of reaction which is governed only by the forward reaction. Therefore, in this study, the initial specific rate of extraction, $R_{HC,0}$ ($mol\cdot m^{-2}\cdot s^{-1}$) is calculated from experimental data using the following equation:

$$R_{HC,0}=\frac{V_{org}}{A_c}\left(\frac{dC_{HC,org}}{dt}\right)_{t=0} \tag{4.61}$$

$\left(\frac{dC_{HC,org}}{dt}\right)_{t=0}$ is the initial slope of curve which is a representation of the concentration in the organic phase versus time (t). The values of $R_{HC,0}$ are determined with various experimental conditions and used to determine the probable effect of the important variables and to draw an inference on the appropriate kinetics of reactive extraction. In this regard, the effects of the speed of agitation (N) and volume ratio of the phases (V_{org}/V_{aq}) on the initial specific rate of extraction must be examined to determine the reaction regime. Therefore, based on the guidelines provided by Doraiswamy and Sharma, the reactive extraction of acid with extractant in diluent is governed by the following equation:

$$R_{HC,0} = k_{\alpha'\beta'}[\overline{HC}]^{\alpha'}[\overline{S}]^{\beta'} \quad (4.62)$$

where α' and β' are the orders of the reaction with respect to acid and extractant, respectively, and $k_{\alpha'\beta'}$ is the rate constant of the reaction.

For a (α', β') reaction taking place in the organic phase with a rate law shown in Eq. 4.62 and with a high excess of extractant, *Hatta* number (*Ha*) is given by a general expression as:

$$Ha = \frac{\sqrt{\frac{2}{\alpha'+1} k_{\alpha'\beta'}[\overline{HC}]^{\alpha'-1}[\overline{S}]^{\beta'} D_{HC}}}{k_L} \quad (4.63)$$

D_{HC} is the diffusion coefficient of acid into diluent. The value of D_{HC} is estimated using Wilke-Change (1955) and Reddy-Doraiswamy (1967) equations which are given by Eqs. 4.64 and 4.65, respectively.

$$D_{HC} = 7.4\times10^{-12}\frac{T\sqrt{\Psi M}}{\eta(\forall^{acid})^{0.6}} \quad (4.64)$$

$$D_{HC} = 10^{-11}\frac{T\sqrt{M}}{\eta(\forall^{diluent}\forall^{acid})^{\frac{1}{3}}} \quad (4.65)$$

where ψ denotes the diluent association factor; $\forall$ signifies the molar volume of the component; T is temperature (K); M and η represent molecular weight ($kg\cdot kmol^{-1}$) and viscosity ($kg\cdot m^{-1}\cdot s^{-1}$) of the diluent, respectively.

To determine the effect of reaction on the pure mass transfer of acid from the aqueous to the organic phase, the enhancement factor for the reactive extraction of acid is calculated using Eq. 4.66.

$$\Phi = \frac{R_{HC,0}}{k_L C^*_{org}} \quad (4.66)$$

4.3 Differential Evolution Optimization Approach

In science and engineering, optimization is defined as the method of minimizing or maximizing an objective function comprised of different independent variables and finding the values of those variables for which the objective function takes on minimum or maximum value within the defined domains of variables. 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). Therefore, non-traditional optimization techniques based on natural phenomenon (survival of the fittest) 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. In this, differential evolution is used successfully to find the optimum values of various parameters (Babu and Sastry, 1999; Ownubolu and Babu, 2004; Angira and Babu, 2006; Babu and Munavar, 2007). Eqs. 4.19 and 29 are highly nonlinear and complex in nature. DE is used to solve these equations for the estimation of various model parameters of reactive extraction (K_E, K_{11}, K_{21}, K_{31}, K_{12}, *n, m* etc.).

The steps followed in DE are shown in Figure 4.2. At the beginning, a population of *NP* vectors is randomly generated within the range of the vectors and one of these vectors is selected as the *target vector* (Step 1). After that, two more vectors from the population are randomly selected (Step 2) and the difference between them (vector subtraction) is found out. This difference is multiplied by weighted constant, *F* and added to a third randomly selected vector to get a *noisy random vector* (Step 3). Now, crossover is performed between the target and noisy random vector to get a trial vector (Step 4). Then, a competition between the trial and target vector is performed and the winner is replaced into the population (Step 5). The same procedure is carried out *NP* times to

decide the next generation of vectors and till some convergence criterion is met. Certain guidelines and heuristics are available for the choice of DE parameters (Babu, 2004; Onwubolu and Babu, 2004; Price and Storn, 1997).

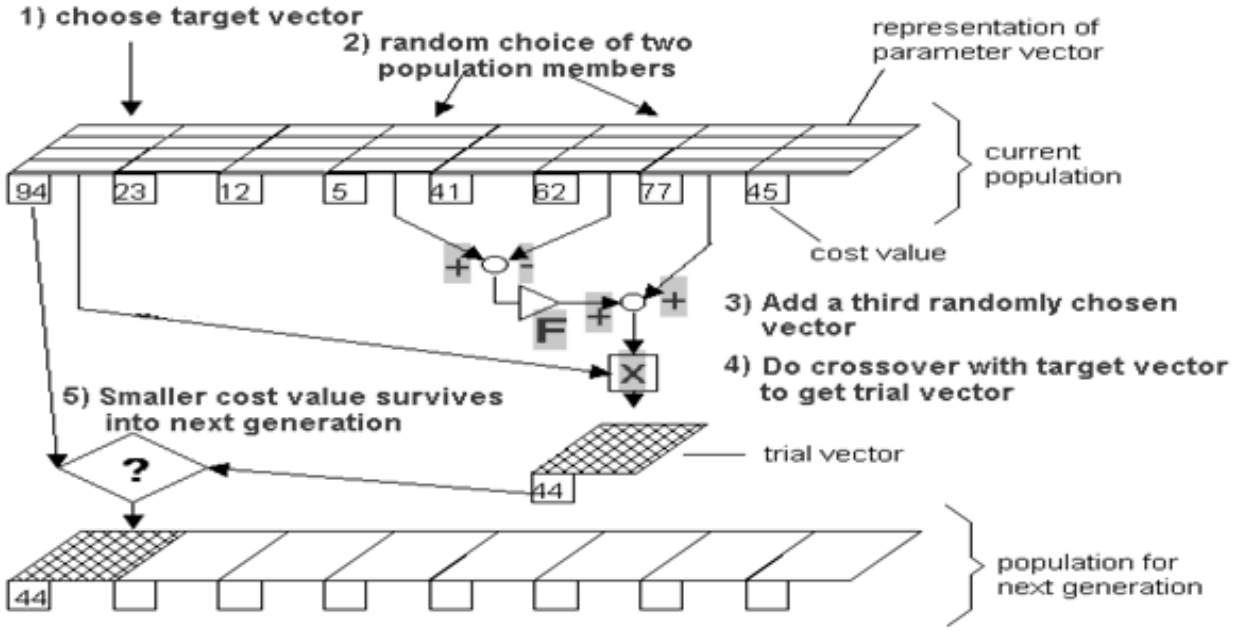


Figure 4.2 Schematic of differential evolution algorithm

CHAPTER – 5

RESULTS AND DISCUSSION

This chapter presents the experimental (equilibrium & kinetic) and theoretical (modeling, simulation & optimization) results obtained for the reactive extraction of carboxylic acids. The extraction of acids is carried out using (i) pure diluents (aliphatic, aromatic, chlorinated etc.), (ii) phosphorus based extractants [tri-*n*-butylphosphate (TBP), trioctylphosphine oxide (TOPO) and di-2-ethyl hexhyl phosphoric acid (D2EHPA)], and (iii) long chain aliphatic amine based extractants [tri-*n*-octylamine (TOA), tridodecylamine (TDDA) and trioctylmethylammonium chloride (Aliquat 336)]. Equilibrium studies are important to understand the reaction mechanism and to predict the stoichiometry and equilibrium constant of reactive extraction. These studies also help in understanding the effect of composition of phases, types of diluents and extractants, types of acids, temperature etc. on the extraction efficiency. Therefore, equilibrium studies are carried out extensively for the extraction of picolinic, nicotinic, isonicotinic, glycolic, itaconic, formic, and levulinic acids, and discussed in Section 5.1. It is also evident that kinetic studies are equally important as equilibrium studies to complete the design of a continuous reactive extraction unit. These kinetic data are useful to determine the rate constant and order of the reaction. Hence, intrinsic kinetics of nicotinic acid is described in Section 5.2. The extraction efficiency in terms of distribution coefficient (K_D), degree of extraction ($\%E$) and loading ratio (Z) is calculated using experimental data. Based on the mathematical models as described in Chapter 4, equilibrium (physical and chemical) and kinetic parameters are determined for the reactive extraction of different carboxylic acids.

5.1 Equilibrium Study

5.1.1 Reactive Extraction of Picolinic Acid

This section describes equilibrium studies on picolinic acid reactive extraction with various extractants (TBP, TOPO, D2EHPA, TOA, TDDA and Aliquat 336) dissolved in several diluents (dodecane, benzene, cyclohexane, chlorobenzene, 1-decanol, oleyl alcohol, DCM, MIBK and 1-octanol) at 298 K. The physical extraction results of picolinic acid using nine different diluents (dodecane, cyclohexane, chlorobenzene, benzene, DCM, MIBK, 1-octanol, 1-decanol and oleyl alcohol) are presented in Section 5.1.1.1. The chemical extraction studies are carried out with 3 phosphoric- (TBP, TOPO and D2EHPA) and 3 aminic (TOA, TDDA and Aliquat 336) extractants dissolved in two different diluents [benzene (inactive) and 1-decanol (active)] and explained in Section 5.1.1.2. To study the effect of diluent on the performance of reactive extraction, experiments are performed with TOA dissolved in five different diluents (cyclohexane, chlorobenzene, DCM, MIBK and 1-octanol) and results are described in Section 5.1.1.3. In Section 5.1.1.4, the recovery of picolinic acid with TBP and TDDA using dodecane and oleyl alcohol as nontoxic diluents is shown. The back-extraction study of picolinic acid reactive extraction is described in Section 5.1.1.5.

5.1.1.1 Using pure diluents

The physical extraction of picolinic acid (0.01 to 0.25 mol·L^{-1}) is carried out using dodecane, cyclohexane, chlorobenzene, benzene, DCM, MIBK, 1-octanol, 1-decanol and oleyl alcohol, and results are shown in Table 5.1. Low distribution of picolinic acid in all these diluents is observed with maximum values of $K_D^{diluent}$ of 0.081, 0.301, 0.27, 0.064, 0.534, 0.334, 0.867, 0.139 and 0.116 with dodecane, cyclohexane, chlorobenzene, benzene, DCM, MIBK, 1-octanol, 1-decanol, oleyl alcohol, respectively. The extent of

dissociation of the picolinic acid (pK_{a1} = 1.01, pK_{a2} = 5.29) and higher affinity of the acid for water (i.e. its hydrophilic nature, μ = 4.42 D; log P_a = -0.97) are the two main factors that affect the extractability. The values of the partition coefficient (P) and dimerization constants (D) are determined as physical extraction parameters using Eq. 4.10. From the linear fits of the experimental data of $K_D^{diluent}$ versus [HC], the values of P as intercept and D from the slope are estimated (Figure 5.1) and shown in Table 5.1.

Table 5.1 Physical extraction results of picolinic acid in different diluents

Diluent	C_{in} **mol·L^{-1}**	C_{HC} **mol·L^{-1}**	$\overline{C}_{HC}$ **mol·L^{-1}**	$K_D^{diluent}$	***P***	***D***	R^2	***SD***
Dodecane	0.010	0.0094	0.0006	0.068	0.069	5.77	0.95	0.001
	0.050	0.0466	0.0034	0.073				
	0.100	0.0930	0.0070	0.075				
	0.150	0.1392	0.0108	0.077				
	0.200	0.1852	0.0148	0.080				
	0.250	0.2312	0.0188	0.081				
Cyclohexane	0.010	0.0089	0.00109	0.122	0.115	24.19	0.99	0.002
	0.025	0.0222	0.0028	0.127				
	0.050	0.0438	0.0062	0.142				
	0.075	0.0648	0.0102	0.157				
	0.100	0.0769	0.0231	0.301				
Chlorobenzene	0.010	0.0092	0.0008	0.089	0.043	739.48	0.89	0.031
	0.025	0.0227	0.0023	0.101				
	0.050	0.0445	0.0055	0.122				
	0.075	0.0608	0.0142	0.233				
	0.100	0.0788	0.0213	0.270				
Benzene	0.010	0.0096	0.0004	0.042	0.042	70.10	0.94	0.002
	0.025	0.0238	0.0012	0.050				
	0.050	0.0474	0.0026	0.055				
	0.075	0.0707	0.0043	0.061				
	0.100	0.0940	0.0060	0.064				
DCM	0.010	0.0074	0.0026	0.351	0.313	32.75	0.94	0.023
	0.025	0.0182	0.0068	0.373				
	0.050	0.0359	0.0141	0.394				
	0.075	0.0506	0.0244	0.483				
	0.100	0.0652	0.0348	0.534				

Table 5.1 Physical extraction results of picolinic acid in different diluents (continued...)

Diluent	C_{in} mol·L^{-1}	C_{HC} mol·L^{-1}	$\overline{C}_{HC}$ mol·L^{-1}	$K_D^{diluent}$	*P*	*D*	R^2	*SD*
MIBK	0.010	0.0085	0.0015	0.172	0.150	48.49	0.92	0.020
	0.025	0.0208	0.0042	0.204				
	0.050	0.0408	0.0092	0.226				
	0.075	0.0596	0.0154	0.257				
	0.100	0.0750	0.0250	0.334				
1-Octanol	0.010	0.0079	0.0021	0.269	0.200	16.19	0.89	0.049
	0.025	0.0189	0.0061	0.320				
	0.050	0.0362	0.0138	0.379				
	0.075	0.0483	0.0267	0.552				
	0.100	0.0536	0.0465	0.867				
1-Decanol	0.010	0.0089	0.0011	0.124	0.125	5.57	0.89	0.003
	0.025	0.0221	0.0029	0.131				
	0.050	0.0446	0.0054	0.121				
	0.075	0.0660	0.0090	0.136				
	0.100	0.0878	0.0122	0.139				
Oleyl alcohol	0.010	0.0092	0.0008	0.087	0.085	9.28	0.97	0.002
	0.050	0.0458	0.0042	0.092				
	0.100	0.0912	0.0088	0.096				
	0.150	0.1364	0.0136	0.100				
	0.200	0.1802	0.0198	0.110				
	0.250	0.2240	0.0260	0.116				

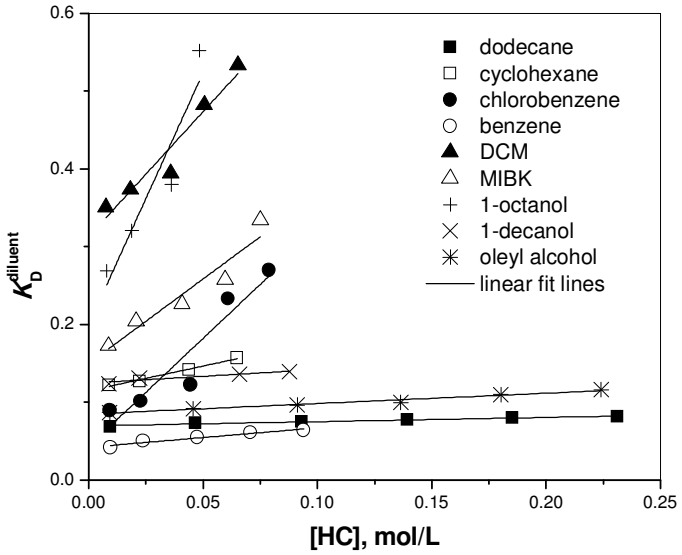


Figure 5.1 Determination of *P* and *D* for the physical extraction of picolinic acid in different diluents

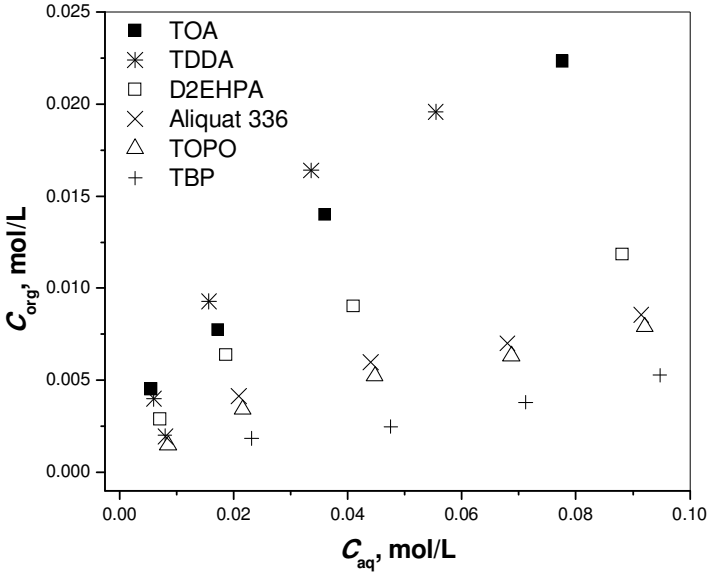
5.1.1.2 Using TBP, TOPO, D2EHPA, TOA, TDDA and Aliquat 336 in benzene and 1-decanol

Due to the insolubility of picolinic acid in conventional solvents, its separation by physical extraction with pure diluents is not efficient. Therefore, to achieve better extraction of acid, the reactive extraction studies are carried out with 3 phosphoric- (TBP, TOPO and D2EHPA) and 3 aminic (TOA, TDDA and Aliquat 336) extractants dissolved in two different diluents [benzene (inactive) and 1-decanol (active)]. The experimental data are presented in the form of isotherms at fixed extractant concentration (0.50 mol·L^{-1}), and shown in Figures 5.2a and 5.2b for benzene and 1-decanol, respectively. The maximum values of K_D are found to be 0.818 with TOA, 0.667 with TDDA, 0.405 with D2EHPA, 0.25 with TBP, 0.24 with Aliquat 336 and 0.171 with TOPO when benzene is used as a diluent, and 9 with TOA, 8.091 with TDDA, 0.506 with D2EHPA, 0.429 with TBP, 0.405 with Aliquat 336 and 0.318 with TOPO when 1-decanol is used as a diluent. The values of K_D are found to decrease with an increase in the initial acid concentration of aqueous phase by all the extractants in both diluents (benzene and 1-decanol). The solvent polarity is an important factor that controls the extraction efficiency and the reactive extraction has a direct correlation with the polarity of the two diluents (benzene and 1-decanol) used. The 1-decanol (protic or proton donor, μ = 2.62 D; dielectric constant, ε_r = 7.6) is an active diluent, which shows higher extractability compared to inactive and non-polar diluent (benzene, μ = 0 D; ε_r = 2.27). The experimental data on reactive extraction of picolinic acid show that the 1-decanol provides higher extraction efficiency with all the extractants (TBP, TOPO, D2EHPA, TDDA, TOA and Aliquat 336) used as compared to benzene.

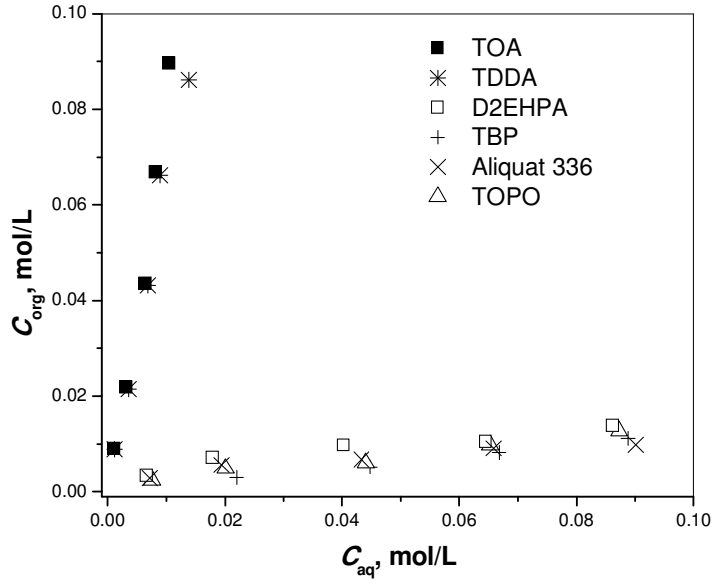
The p*H* value of the aqueous phase exhibits a significant influence on the degree of extraction. In the chemical extraction with all the extractants, the maximum pyridine

group ionization takes place at strong acidic pH domain (pK_{a1} = 1.01) and it limits the extraction efficiency. The increase of pH value induces the dissociation of –COOH group (pK_{a2} = 5.29) which also reduces the extraction efficiency. Thus, as the result of the two contrary effects, the optimum value of the aqueous phase pH should lie in between the pK_a's of the acid. In this study, the values of equilibrium pH are found to be in the range of 2.9 to 4.16 which is in between the pK_a's of the acid.

The values of Z (between 0.004 and 0.179) show mainly the formation of 1:1 acid-extractant complexes in the organic phase. This assumption is applied to predict the values of equilibrium constant of 1:1 complex formation (K_{11}) using model Eq. 4.32. The plots of $\frac{Z}{1-Z}$ versus [HC] yield a straight line (Figures 5.3a for benzene and 5.3b for 1-decanol) with a slope representing the corresponding K_{11} value of the reactive extraction. The values of K_{11} estimated by the Eq. 4.32 are listed in Table 5.2 with R^2 and SD. The values of R^2 > 0.95 and maximum value of SD = 0.017 show a good fit of the experimental data with the model predicted data.

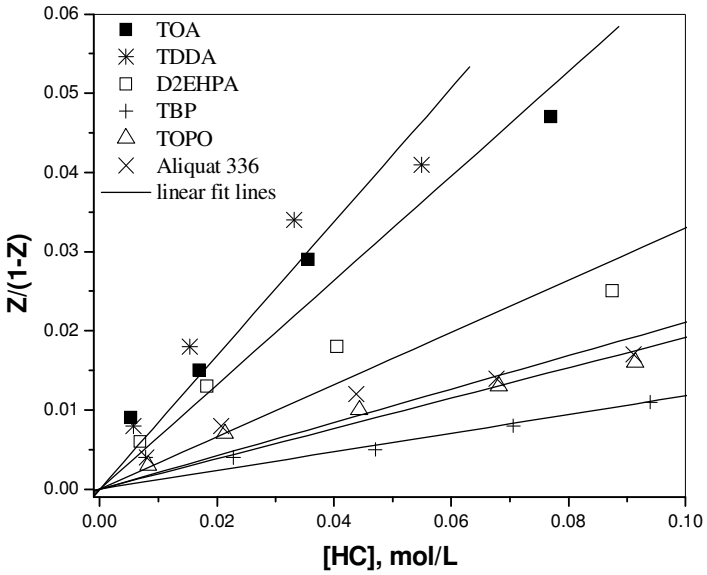


(a)

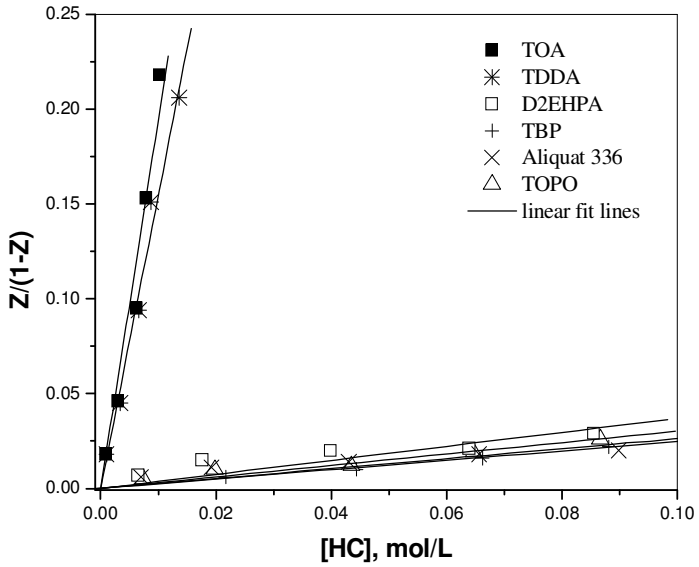


(b)

Figure 5.2 Equilibrium isotherms for the extraction of picolinic acid with six different extractants dissolved in (a) benzene and (b) 1-decanol



(a)



(b)

Figure 5.3 Determination of K_{11} for the extraction of picolinic acid with six different extractants in (a) benzene and (b) 1-decanol

Table 5.2 The values of equilibrium constant (K_{11}) for picolinic acid with six different extractants dissolved in benzene and 1-decanol

Diluents	Benzene			1-Decanol		
Extractants	K_{11}	R^2	*SD*	K_{11}	R^2	*SD*
TBP	0.118 ± 0.013	0.95	0.002	0.247 ± 0.019	0.97	0.002
TOPO	0.192 ± 0.016	0.99	0.002	0.302 ± 0.021	0.98	0.003
D2EHPA	0.330 ± 0.058	0.96	0.006	0.370 ± 0.050	0.95	0.006
TDDA	0.844 ± 0.087	0.97	0.006	15.49 ± 0.575	0.99	0.010
TOA	0.659 ± 0.063	0.99	0.005	19.448 ± 1.178	0.98	0.017
Aliquat 336	0.211 ± 0.023	0.98	0.003	0.262 ± 0.035	0.97	0.004

5.1.1.3 Using TOA in five different diluents

The reactive extraction of picolinic acid (0.01 to 0.10 mol·L^{-1}) with TOA (0.115 to 0.459 mol·L^{-1}) as extractant dissolved in five different diluents (cyclohexane, chlorobenzene, DCM, MIBK and 1-octanol) is also carried out, and results are presented in Tables 5.3 to 5.7. With an increase in the concentration of acid, the values of K_D are found to increase for cyclohexane, DCM and MIBK, and decease for chlorobenzene and 1-octanol. The extraction ability with TOA is obtained in the order of DCM ≥ MIBK > chlorobenzene > 1-octanol > cyclohexane. The maximum recovery of picolinic acid is found to 94.33% with TOA (0.456 mol·L^{-1}) in DCM at 0.1 mol·L^{-1} of acid concentration. In this study, the values of equilibrium pH (3.22 to 4.04) are found to be in between the pK_a's of the acid. The values of equilibrium constant (K_E) and number of extractant molecules (n) per acid molecule are estimated using Eq. 4.19, and minimizing the error between experimental and predicted values of K_D by applying DE and Eq. 4.20 (Table 5.8). The different values of K_E and n in different diluents indicate that the diluents solvate the acid molecule by making various types of complexes between acid and amine molecules. The values of K_D are also predicted by applying Eq. 4.19, and listed in Tables 5.3 to 5.7. These predicted values of K_D are found to be comparable with the experimental values.

Table 5.3 Equilibrium results of picolinic acid with TOA in cyclohexane

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	K_D^{model}	%E	Z	pH_{eq}
0.010	0.115	0.0067	0.0033	0.493	0.483	33.06	0.029	3.74
	0.229	0.0061	0.0039	0.639	0.642	38.80	0.017	3.76
	0.344	0.0057	0.0043	0.754	0.759	42.63	0.013	3.77
	0.459	0.0054	0.0046	0.852	0.853	46.45	0.010	3.79
0.025	0.115	0.0172	0.0078	0.453	0.453	31.15	0.068	3.53
	0.229	0.0164	0.0086	0.524	0.518	34.21	0.038	3.54
	0.344	0.0161	0.0089	0.553	0.560	35.74	0.026	3.55
	0.459	0.0157	0.0093	0.592	0.592	37.27	0.020	3.55
0.050	0.115	0.0404	0.0096	0.238	0.178	19.22	0.084	3.34
	0.229	0.0351	0.0149	0.425	0.442	29.79	0.065	3.37
	0.344	0.0294	0.0206	0.701	0.744	41.11	0.060	3.41
	0.459	0.0238	0.0262	1.101	1.073	52.44	0.057	3.46
0.075	0.115	0.0555	0.0195	0.351	0.352	26.05	0.170	3.27
	0.229	0.0478	0.0272	0.569	0.565	36.25	0.119	3.31
	0.344	0.0432	0.0318	0.736	0.743	42.37	0.092	3.33
	0.459	0.0394	0.0356	0.904	0.900	47.47	0.078	3.35
0.100	0.115	0.0539	0.0461	0.855	0.898	46.14	0.402	3.28
	0.229	0.0476	0.0524	1.101	1.031	52.44	0.229	3.31
	0.344	0.0471	0.0529	1.123	1.117	52.91	0.154	3.31
	0.459	0.0466	0.0534	1.146	1.182	53.38	0.116	3.31

Table 5.4 Equilibrium results of picolinic acid with TOA in chlorobenzene

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	K_D^{model}	%E	Z	pH_{eq}
0.010	0.115	0.0028	0.0072	2.571	2.527	72.46	0.063	3.93
	0.229	0.0023	0.0077	3.348	3.457	77.05	0.034	3.97
	0.344	0.0020	0.0080	4.000	4.137	80.11	0.023	4.01
	0.459	0.0017	0.0083	4.882	4.696	82.79	0.018	4.04
0.025	0.115	0.0073	0.0177	2.425	2.230	70.93	0.154	3.72
	0.229	0.0065	0.0185	2.846	3.112	73.99	0.081	3.74
	0.344	0.0054	0.0196	3.630	3.755	78.58	0.057	3.79
	0.459	0.0046	0.0204	4.435	4.287	81.64	0.044	3.82
0.050	0.115	0.0438	0.0062	0.142	0.145	12.42	0.054	3.33
	0.229	0.0385	0.0115	0.299	0.293	22.99	0.050	3.35
	0.344	0.0347	0.0153	0.441	0.443	30.54	0.044	3.38
	0.459	0.0313	0.0187	0.597	0.595	37.34	0.041	3.40
0.075	0.115	0.0634	0.0116	0.183	0.152	15.44	0.101	3.25
	0.229	0.0589	0.0161	0.273	0.294	21.48	0.070	3.26
	0.344	0.0532	0.0218	0.410	0.429	29.03	0.063	3.28
	0.459	0.0476	0.0274	0.576	0.559	36.58	0.060	3.31
0.100	0.115	0.0712	0.0288	0.404	0.391	28.81	0.251	3.22
	0.229	0.0662	0.0338	0.511	0.526	33.85	0.147	3.24
	0.344	0.0621	0.0379	0.610	0.623	37.95	0.110	3.25
	0.459	0.0583	0.0417	0.715	0.702	41.73	0.091	3.26

Table 5.5 Equilibrium results of picolinic acid with TOA in DCM

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	K_D^{model}	%E	Z	pH_{eq}
0.010	0.115	0.0055	0.0045	0.818	0.849	44.54	0.039	3.78
	0.229	0.0042	0.0058	1.381	1.294	57.93	0.025	3.84
	0.344	0.0038	0.0062	1.632	1.657	61.75	0.018	3.86
	0.459	0.0034	0.0066	1.941	1.970	66.34	0.014	3.89
0.025	0.115	0.0145	0.0105	0.724	0.797	41.86	0.092	3.57
	0.229	0.0111	0.0139	1.252	1.147	55.63	0.061	3.63
	0.344	0.0103	0.0147	1.427	1.421	58.69	0.043	3.64
	0.459	0.0096	0.0154	1.604	1.651	61.75	0.034	3.66
0.050	0.115	0.0302	0.0198	0.656	1.406	39.60	0.173	3.41
	0.229	0.0106	0.0394	3.717	3.035	78.86	0.172	3.64
	0.344	0.0083	0.0417	5.024	5.145	83.39	0.121	3.69
	0.459	0.006	0.0440	7.333	7.334	87.92	0.096	3.76
0.075	0.115	0.0472	0.0278	0.589	1.358	37.08	0.242	3.31
	0.229	0.0170	0.0580	3.412	2.768	77.35	0.253	3.53
	0.344	0.0132	0.0618	4.682	4.722	82.38	0.180	3.59
	0.459	0.0098	0.0652	6.653	6.720	86.91	0.142	3.65
0.100	0.115	0.0309	0.0691	2.236	3.023	69.13	0.603	3.40
	0.229	0.0106	0.0894	8.434	7.454	89.45	0.390	3.64
	0.344	0.0079	0.0921	11.658	12.167	92.13	0.268	3.70
	0.459	0.0057	0.0943	16.544	16.612	94.33	0.206	3.77

Table 5.6 Equilibrium results of picolinic acid with TOA in MIBK

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	K_D^{model}	%E	Z	pH_{eq}
0.010	0.115	0.0065	0.0035	0.538	0.581	34.98	0.031	3.74
	0.229	0.0051	0.0049	0.961	0.902	48.75	0.021	3.80
	0.344	0.0046	0.0054	1.174	1.167	54.10	0.016	3.82
	0.459	0.0042	0.0058	1.381	1.400	57.93	0.013	3.84
0.025	0.115	0.0168	0.0082	0.488	0.523	32.68	0.072	3.54
	0.229	0.0134	0.0116	0.866	0.813	46.45	0.051	3.59
	0.344	0.0122	0.0128	1.049	1.053	51.04	0.037	3.61
	0.459	0.0111	0.0139	1.252	1.264	55.63	0.030	3.63
0.050	0.115	0.0117	0.0383	3.274	3.328	76.60	0.334	3.62
	0.229	0.0102	0.0398	3.902	3.801	79.62	0.174	3.65
	0.344	0.0098	0.0402	4.102	4.107	80.37	0.117	3.65
	0.459	0.0094	0.0406	4.319	4.335	81.13	0.089	3.66
0.075	0.115	0.0181	0.0569	3.144	3.186	75.84	0.496	3.52
	0.229	0.0159	0.0591	3.717	3.622	78.86	0.258	3.55
	0.344	0.0155	0.0595	3.839	3.899	79.36	0.173	3.55
	0.459	0.0147	0.0603	4.102	4.103	80.37	0.131	3.57
0.100	0.115	0.0107	0.0893	8.346	7.887	89.29	0.779	3.64
	0.229	0.0095	0.0905	9.526	10.284	90.55	0.395	3.66
	0.344	0.0079	0.0921	11.658	11.831	92.13	0.268	3.70
	0.459	0.0069	0.0931	13.493	13.025	93.07	0.203	3.73

Table 5.7 Equilibrium results of picolinic acid with TOA in 1-octanol

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	K_D^{model}	%E	Z	pH_{eq}
0.010	0.115	0.0042	0.0058	1.381	1.325	57.93	0.051	3.84
	0.229	0.0030	0.0070	2.333	2.362	70.17	0.031	3.92
	0.344	0.0024	0.0076	3.167	3.304	76.29	0.022	3.96
	0.459	0.0019	0.0081	4.263	4.173	80.88	0.018	4.02
0.025	0.115	0.0111	0.0139	1.252	1.288	55.63	0.121	3.63
	0.229	0.0077	0.0173	2.247	2.173	69.40	0.075	3.71
	0.344	0.0065	0.0185	2.846	2.943	74.00	0.054	3.74
	0.459	0.0054	0.0196	3.630	3.634	78.58	0.043	3.79
0.050	0.115	0.0359	0.0141	0.393	0.430	28.28	0.123	3.37
	0.229	0.0310	0.0190	0.613	0.566	38.09	0.083	3.40
	0.344	0.0298	0.0202	0.678	0.666	40.36	0.059	3.41
	0.459	0.0291	0.0209	0.718	0.746	41.87	0.046	3.42
0.075	0.115	0.0544	0.0206	0.379	0.412	27.52	0.180	3.28
	0.229	0.0472	0.0278	0.589	0.546	37.08	0.121	3.31
	0.344	0.0453	0.0297	0.656	0.643	39.60	0.086	3.32
	0.459	0.0442	0.0308	0.697	0.722	41.11	0.067	3.32
0.100	0.115	0.0674	0.0326	0.484	0.487	32.60	0.284	3.23
	0.229	0.0655	0.0345	0.527	0.519	34.48	0.150	3.24
	0.344	0.0650	0.0350	0.538	0.538	34.95	0.102	3.24
	0.459	0.0646	0.0354	0.548	0.552	35.43	0.077	3.24

Table 5.8 Values of K_E and n for picolinic acid with TOA in different diluents

Diluents	$[\bar{S}]_{in}$ mol·L^{-1}	K_E	n	*rmsd*
Cyclohexane	0.010	1.17	0.41	0.015
	0.025	0.69	0.19	0.003
	0.050	3.15	1.26	0.047
	0.075	1.54	0.65	0.005
	0.100	1.38	0.19	0.052
Chlorobenzene	0.010	6.64	0.44	0.120
	0.025	6.17	0.45	0.219
	0.050	1.36	1.01	0.004
	0.075	1.20	0.91	0.026
	0.100	0.97	0.40	0.016
DCM	0.010	3.16	0.60	0.060
	0.025	2.49	0.52	0.079
	0.050	19.78	1.11	0.594
	0.075	18.13	1.05	0.580
	0.100	39.23	0.88	0.789
MIBK	0.010	2.30	0.63	0.041
	0.025	2.08	0.63	0.039
	0.050	5.02	0.19	0.071
	0.075	4.72	0.17	0.075
	0.100	16.98	0.31	0.532
1-Octanol	0.010	7.95	0.81	0.063
	0.025	6.50	0.72	0.083
	0.050	1.02	0.39	0.039
	0.075	1.00	0.39	0.035
	0.100	0.59	0.10	0.005

5.1.1.4 Using TBP and TDDA in dodecane and oleyl alcohol as nontoxic diluents

In the extractive fermentation process, use of nontoxic extractant-diluent system will offer less toxicity towards microorganisms. Thus, one of the best options is to use a nontoxic diluent or blend of a toxic diluent with a nontoxic diluent to yield a biocompatible mixture (Harington and Hossain, 2008; Wasewar *et al*., 2010). In a study reported by Waghmare *et al*. (2011), the reactive extraction studies of picolinic acid are presented with TBP dissolved in natural nontoxic diluents (sunflower oil and castor oil). The maximum recovery of acid with TBP in terms of K_D are found to be 0.65 (E = 42.9%) for sunflower oil and 0.9 (E = 74.6%) for castor oil.

In this study, the recovery of picolinic acid (0.01 to 0.25 mol·L^{-1}) with TBP (0.365 to 2.192 mol·L^{-1}) and TDDA (0.079 to 0.474 mol·L^{-1}) as extractants dissolved in dodecane (log P_a = 6.6) and oleyl alcohol (log P_a = 7.69) as nontoxic diluents is performed. The equilibrium isotherms are shown in Figures 5.4 and 5.5 for TBP and TDDA, respectively. The amount of acid recovered from the aqueous solution also strongly depends on the concentration of extractants and diluents. The value of K_D is found to increase from 0.16 to 0.302 with dodecane, and 0.19 to 0.309 with oleyl alcohol with an increase in the amount of TBP from 0.365 to 2.192 mol·L^{-1}. For an increase in the amount of TDDA from 0.079 to 0.474 mol·L^{-1}, the K_D value is increased from 0.232 to 0.453 with dodecane, and 0.984 to 9.87 with oleyl alcohol. The extraction efficiency is found to decrease with an increase in the acid concentration. The highest extraction efficiency in terms of K_D is found to be 9.87 (E = 90.8%) with TDDA (0.474 mol·L^{-1}) in oleyl alcohol at 0.01 mol·L^{-1} of acid concentration. The loading of acid on extractants (TBP and TDDA) is another important factor for the recovery of acid. It is observed that loading ratio (Z) decreases with an increase in the concentration of both extractants at a fixed concentration (0.01 mol·L^{-1}) of acid in both diluents which means free availability

of extractant molecules in the organic phase. The same trend is observed for other concentrations of acid. The extractants are more loaded with the acid at higher concentration of acid compared to lower concentration of acid. Also, the higher values of Z for oleyl alcohol than dodecane indicate that non-polar diluent by itself is relatively poor solvating medium for the polar complexes.

Now, based upon the values of Z, the equilibrium constants (K_{11}) of 1:1 complex formation are determined using Eq. 4.32. A plot of $\frac{Z}{1-Z}$ versus [HC] yields a straight line passing through origin with a slope of complexation constant (K_{11}). The plots are shown in Figures 5.6 for TBP and 5.7 for TDDA and the values of K_{11} are given in Table 5.9 with the values of R^2 and *SD*.

Three different extraction models (modified Langmuir, Freundlich and Temkin) described in Section 4.1.3 are also employed to describe the equilibrium behavior of the reactive extraction. The values of the model parameters are listed in Table 5.10. The equilibrium data obtained from the extraction of picolinic acid fit the Langmuir isotherm model (*rmsd* = 0.0025) more exactly than other two models (modified Freundlich and Temkin). This shows that the extraction of picolinic acid using TBP and TDDA is more of monolayer type having homogeneous energy distribution on the surface. The experimental and predicted extraction capacities by modified Langmuir isotherm model are also compared with those given by other models for TDDA (0.474 mol·L^{-1}) in oleyl alcohol (Figure 5.8).

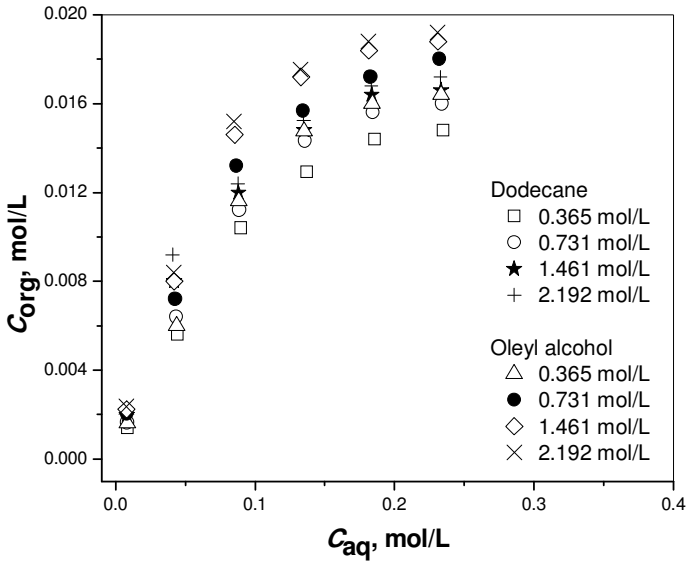


Figure 5.4 Equilibrium isotherms of picolinic acid with TBP in dodecane and oleyl alcohol

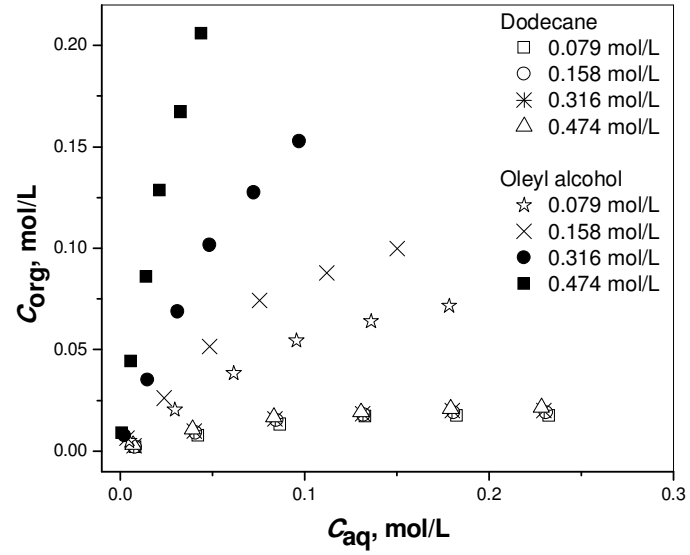


Figure 5.5 Equilibrium isotherms of picolinic acid with TDDA in dodecane and oleyl alcohol

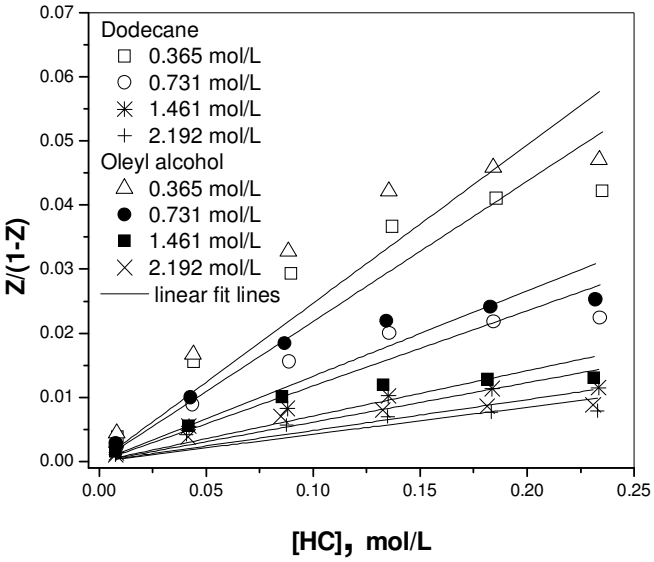


Figure 5.6 Determination of K_{11} of picolinic acid with TBP in dodecane and oleyl alcohol

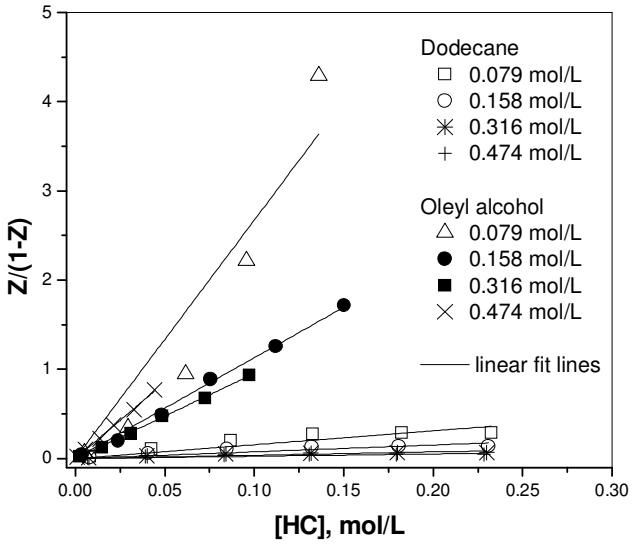


Figure 5.7 Determination of K_{11} of picolinic acid with TDDA in dodecane and oleyl alcohol

Table 5.9 The values of equilibrium constant (K_{11}) for picolinic acid extraction by TBP and TDDA in dodecane and oleyl alcohol

Extractant + diluent	$[\bar{S}]_{in}$ mol·L^{-1}	K_{11} L· mol^{-1}	R^2	*SD*
TBP + dodecane	0.365	0.218	0.956	0.0072
	0.731	0.116	0.951	0.0041
	1.461	0.061	0.937	0.0024
	2.192	0.042	0.928	0.0018
TBP + oleyl alcohol	0.365	0.247	0.953	0.0084
	0.731	0.133	0.946	0.0048
	1.461	0.071	0.928	0.0029
	2.192	0.048	0.932	0.0020
TDDA + dodecane	0.079	1.558	0.943	0.0579
	0.158	0.762	0.929	0.0315
	0.316	0.377	0.924	0.0161
	0.474	0.261	0.923	0.0112
TDDA + oleyl alcohol	0.079	26.728	0.950	0.5542
	0.158	11.309	0.998	0.0459
	0.316	9.533	0.999	0.0142
	0.474	17.120	0.999	0.0129

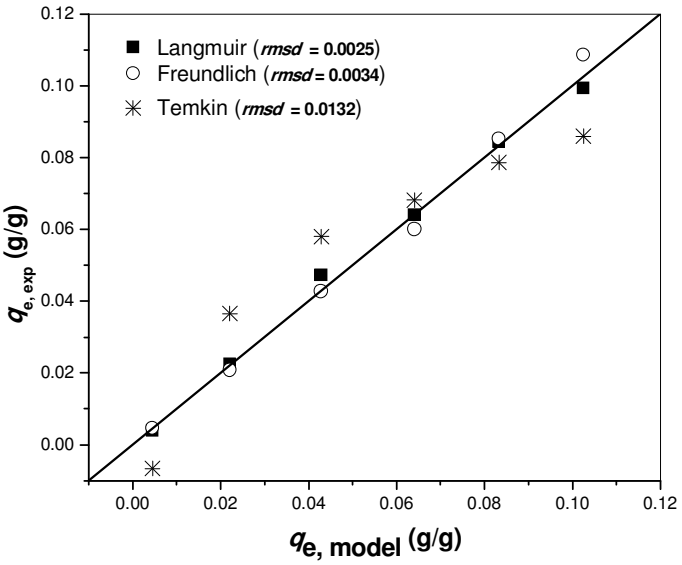


Figure 5.8 Adsorption model predicted versus experimental values of solute concentration in the organic phase (q_e, g·g^{-1}) of picolinic acid with TDDA (0.474 mol·L^{-1}) in oleyl alcohol

Table 5.10 Adsorption model parameters for picolinic acid extraction by TBP and TDDA in dodecane and oleyl alcohol

Extractant + diluent	$\bar{[S]}_{in}$ mol·L^{-1}	Modified Langmuir			Modified Freundlich			Modified Temkin		
		Q_0 (g·g^{-1})	K_L (L·g^{-1})	R^2	K_F [(g·g^{-1}) (L·g^{-1})$^{1/n}$]	n (-)	R^2	B_T (g·g^{-1})	K_T (L·g^{-1})	R^2
TBP + dodecane	0.365	0.0310	0.0591	0.974	0.0018	1.34	0.979	0.01258	1.05	0.963
	0.731	0.0157	0.0708	0.983	0.0011	1.41	0.979	0.0067	1.14	0.966
	1.461	0.0072	0.1021	0.995	0.0007	1.55	0.968	0.0033	1.40	0.987
	2.192	0.0047	0.1296	0.997	0.0006	1.69	0.960	0.0022	1.67	0.994
TBP + oleyl alcohol	0.365	0.0340	0.0618	0.961	0.0021	1.36	0.979	0.0140	1.08	0.953
	0.731	0.0165	0.0847	0.986	0.0014	1.50	0.978	0.0073	1.27	0.967
	1.461	0.0083	0.0994	0.982	0.0008	1.53	0.970	0.0038	1.38	0.9670
	2.192	0.0055	0.1078	0.985	0.0006	1.56	0.968	0.0026	1.45	0.969
TDDA + dodecane	0.079	0.0785	0.0854	0.966	0.0064	1.43	0.966	0.0353	1.25	0.961
	0.158	0.0411	0.0976	0.971	0.0036	1.45	0.949	0.0189	1.37	0.981
	0.316	0.0198	0.1280	0.994	0.0023	1.62	0.958	0.0094	1.63	0.986
	0.474	0.0134	0.1522	0.999	0.0019	1.77	0.968	0.0063	1.91	0.990
TDDA + oleyl alcohol	0.079	0.3835	0.0584	0.972	0.0223	1.30	0.994	0.1305	1.55	0.919
	0.158	0.2684	0.0689	0.946	0.0177	1.29	0.993	0.0883	1.83	0.907
	0.316	0.2361	0.0766	0.946	0.0163	1.23	0.997	0.0654	2.65	0.880
	0.474	0.2029	0.1763	0.943	0.0275	1.23	0.998	0.0559	6.35	0.868

5.1.1.5 Back-extraction study

Recovery of extractant and acid from the organic phase is an important step in reactive extraction. The extract phase can be regenerated by two methods: (i) temperature swing regeneration and (ii) diluent swing regeneration (Yunhai *et al*., 2011). The back-extraction of picolinic acid is carried out by pure water (temperature swing regeneration) at 353 K for TDDA (0.079 and 0.474 mol·L^{-1}) in oleyl alcohol and isothermal curve for the same is shown in Figure 5.9. The volume ratio of aqueous to organic phase is kept at 1:1 in the back-extraction experiment. It can be seen that the slope of the isotherm decreases with an increase in the concentration of TDDA i.e. distribution coefficient of back-extraction ($K_{D'} = C_{aq}/C_{org}$) of picolinic acid is reduced. The quantity of TDDA in the extractant may not only affect the distribution coefficient of acid in extraction step, but also plays an important role in the subsequent reverse extraction by pure water. Though, higher concentration of TDDA may provide better extraction of acid but would make the regeneration process difficult. The regeneration of the extractant loaded with high concentration of acid (C_{in} = 0.25 mol·L^{-1}) will be easier (Z = 0.907 at $[\overline{TDDA}]_{in}$ = 0.079 mol·L^{-1}), and higher distribution of acid ($K_{D'}$ = 9.52) can be achieved in back-extraction. Less loading of the extractant with the acid (Z = 0.435 at $[\overline{TDDA}]_{in}$ = 0.474 mol·L^{-1}) results in lower distribution of acid ($K_{D'}$ = 0.48) and incomplete regeneration of the extracting agent. Therefore, alternate methods such as neutralization with aqueous ammonia (diluent swing regeneration) can be adopted for the complete regeneration of the extractant loaded with very low concentration of picolinic acid.

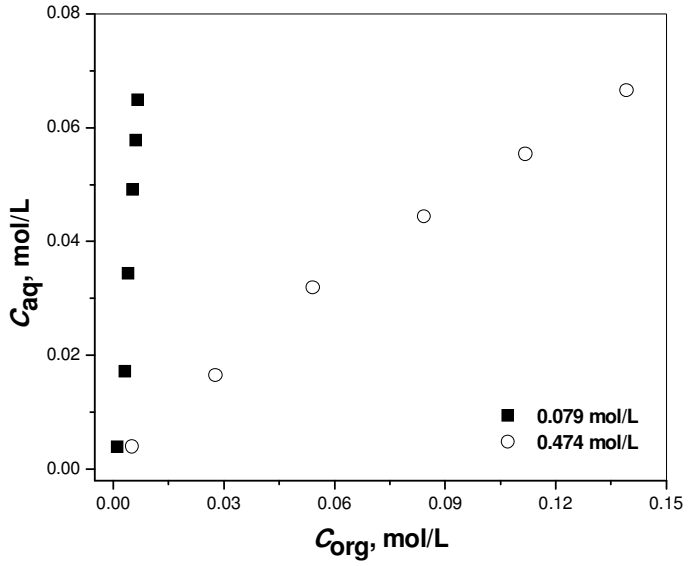


Figure 5.9 Back-extraction isotherm of picolinic acid using TDDA (0.079 and 0.474 mol·L^{-1}) in oleyl alcohol (V_{aq}/V_{org} = 1:1)

5.1.2 Reactive Extraction of Nicotinic Acid

In this section, the results on the reactive extraction of nicotinic acid (pK_a = 4.75, log P_a = -0.65; 0.02 to 0.12 mol·L^{-1}) with different extractants (TBP, TOPO, TOA and Aliquat 336) dissolved in several diluents are presented. Diluents chosen in the study are dodecane, toluene, cyclohexane and kerosene from inactive chemical class, 1-decanol, MIBK, chloroform, and 1-octanol from active chemical class, and sunflower oil (natural non toxic diluent) to examine the effect of diluent-complex interactions. The physical extraction of acid using mixture of diluents such as 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v) is presented in Section 5.1.2.1. The reactive extraction results with TBP (0.183 and 0.365 mol·L^{-1}), TOPO (0.10 to 0.50 mol·L^{-1}) and TOA (0.115 and 0.229 mol·L^{-1}) in 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v) are discussed in Section 5.1.2.2. To analyze the effect of diluent on extraction efficiency, reactive extraction studies are performed using TOA (0.229 mol·L^{-1}) in five different diluents (dodecane, toluene, 1-decanol, MIBK, and chloroform) and results are presented in Section 5.1.2.3. The equilibrium study on reactive extraction of nicotinic acid using TOA (0.44 mol·L^{-1}) and Aliquat 336 (0.44 mol·L^{-1}) in sunflower oil as non-toxic diluent is presented in Section 5.1.2.4. The effect of phase modifiers (dodecane and 1-octanol) on extraction efficiency is also explained in this section.

5.1.2.1 Using diluent mixtures

The physical extraction of nicotinic acid is carried out with diluent mixture of 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v), and results are given in Table 5.11. It can be seen that maximum values of $K_D^{diluent}$ are found to be 0.16 and 0.15 with 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v), respectively. The values of P and D are determined using Eq. 4.10 (Figure 5.10) and shown in Table 5.11. 1-

Decanol + cyclohexane (1:1 v/v) shows greater solvation ability of acid and less dimer formation tendency (P = 0.092, D = 39.69) than that of MIBK + kerosene (1:1 v/v) (P = 0.06, D = 114.58).

Table 5.11 Physical extraction equilibria results of nicotinic acid using 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v)

Diluents	C_{HC} **mol·L^{-1}**	$\overline{C}_{HC}$ **mol·L^{-1}**	$K_D^{diluent}$	**pH_{eq}**	***P***	***D*** **L·mol^{-1}**	R^2	***SD***
1-Decanol + cyclohexane (1:1 v/v)	0.01817	0.00183	0.101	3.37	0.092	39.69	0.98	0.004
	0.04452	0.00548	0.123	3.18				
	0.06995	0.01005	0.144	3.08				
	0.08722	0.01278	0.147	3.03				
	0.10357	0.01643	0.159	2.99				
MIBK + kerosene (1:1 v/v)	0.01862	0.00138	0.074	3.25	0.060	114.58	0.99	0.004
	0.04543	0.00457	0.101	3.05				
	0.07177	0.00823	0.115	2.95				
	0.08858	0.01142	0.129	2.90				
	0.10448	0.01552	0.149	2.87				

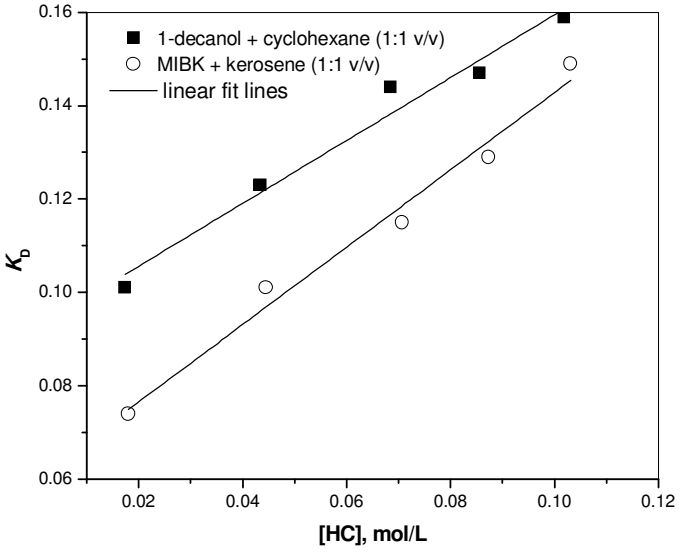


Figure 5.10 Determination of *P* and *D* for the physical extraction of nicotinic acid using 1-decanol + cyclohexane (1:1 v/v) and in MIBK + kerosene (1:1 v/v)

5.1.2.2 Using TBP, TOPO and TOA in diluent mixtures

Reactive extraction studies are performed using TBP (0.183 and 0.365 mol·L^{-1}) in 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v). The diluent mixtures with TBP in chemical extraction show higher distribution of nicotinic acid in the organic phase as compared to diluent mixture alone. The maximum values of K_D are found to be 0.641 and 0.389 at 0.02 mol·L^{-1} of acid with TBP in 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v), respectively. In general, the diluent alone also solvates some amount of acid from aqueous solution by physical extraction. Therefore, including the term for physical extraction and using Eq. 4.37 for $m = 1$ and $n = 1$, the equilibrium constants (K_{11}) are determined. The plots of $\frac{\overline{C}_{HC} - \nu \overline{C}_{HC}^{Diluent}}{\overline{[S]}_{in} - (\overline{C}_{HC} - \nu \overline{C}_{HC}^{Diluent})}$ on the y-axis versus [HC] on the x-axis yield are fitted linearly to get the values of K_{11} from the corresponding slope (Figure 5.11). The equilibrium constants (K_{11}) estimated are presented in Table 5.12 with the coefficient of determination (R^2) and standard deviation (SD). The values of K_{11} are showing good correlation with $R^2 > 0.97$ and maximum value of $SD = 0.008$. These values of K_{11} are also used to predict the values of K_D which are comparable with the experimental values.

Table 5.12 Chemical extraction data for nicotinic acid using TBP in 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v)

Diluents	$[\bar{S}]_{in}$ mol·L^{-1}	Experimental values						Model predicted values			
		C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	*%E*	*Z*	pH_{eq}	K_D	K_{11}	R^2	*SD*
1-Decanol + cyclohexane (1:1 v/v)	0.183	0.0150	0.0051	0.338	25.25	0.028	3.60	0.194	0.46 ± 0.05	0.97	0.007
		0.0404	0.0096	0.237	19.14	0.052	3.38	0.208			
		0.0654	0.0146	0.224	18.30	0.080	3.27	0.225			
		0.0820	0.0180	0.220	18.03	0.099	3.22	0.227			
		0.0969	0.0231	0.238	19.23	0.126	3.18	0.240			
	0.365	0.0122	0.0078	0.641	39.05	0.021	3.64	0.300	0.49 ± 0.06	0.99	0.008
		0.0360	0.0140	0.389	28.00	0.038	3.40	0.305			
		0.0598	0.0202	0.337	25.23	0.055	3.29	0.319			
		0.0764	0.0236	0.308	23.57	0.065	3.24	0.318			
		0.0914	0.0286	0.313	23.84	0.078	3.20	0.328			
MIBK + kerosene (1:1 v/v)	0.183	0.0155	0.0045	0.289	22.45	0.025	3.59	0.193	0.64 ± 0.04	0.99	0.005
		0.0404	0.0096	0.237	19.14	0.052	3.38	0.217			
		0.0648	0.0152	0.235	19.00	0.083	3.27	0.230			
		0.0809	0.0191	0.237	19.13	0.105	3.22	0.242			
		0.0953	0.0247	0.260	20.61	0.135	3.19	0.262			
	0.365	0.0144	0.0056	0.389	28.00	0.015	3.60	0.212	0.37 ± 0.03	0.98	0.004
		0.0399	0.0101	0.254	20.24	0.028	3.38	0.231			
		0.0643	0.0158	0.245	19.69	0.043	3.27	0.243			
		0.0806	0.0194	0.241	19.41	0.053	3.23	0.255			
		0.0942	0.0258	0.274	21.53	0.071	3.19	0.275			

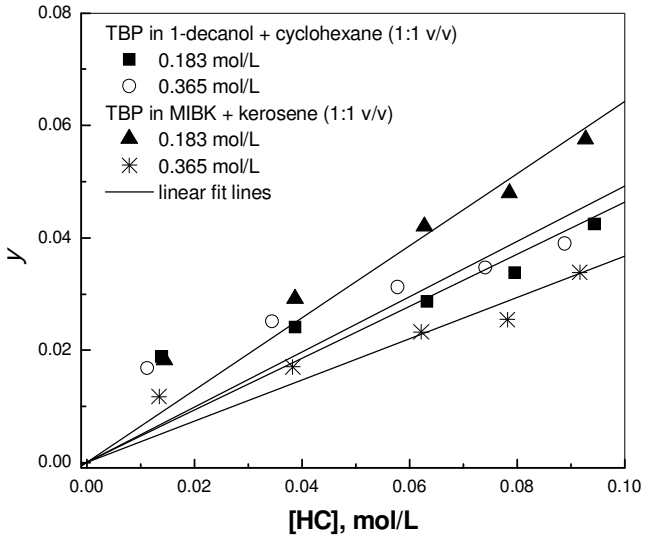


Figure 5.11 Determination of K_{11} for the extraction of nicotinic acid with TBP in 1-decanol + cyclohexane (1:1 v/v) and in MIBK + kerosene (1:1 v/v),

$$y = \frac{\overline{C}_{HC} - \nu \overline{C}_{HC}^{Diluent}}{[\overline{S}]_{in} - (\overline{C}_{HC} - \nu \overline{C}_{HC}^{Diluent})}$$

In the reactive extraction of nicotinic acid using TOPO (0.10 to 0.50 mol·L^{-1}) dissolved in MIBK + kerosene (1:1 v/v), the values of K_D and $\%E$ are found to decrease with an increase in the acid concentration at fixed TOPO concentration (Table 5.13). At low concentration of acid, there is more possibility of formation of solvates with TOPO. The values of K_D are found to increase with an increase in TOPO concentration from 0.10 to 0.50 mol·L^{-1}. TOPO with MIBK + kerosene (1:1 v/v) diluent mixture favors the formation of less-loaded (the values of Z restricted mainly between 0.032 and 0.684) complexes of acid-TOPO.

Now, for the estimation of equilibrium constant (K_E) and the number of extractant molecules per acid molecule (n), the theoretical study based on mass action law is carried out. Equation 4.19 for $m = 1$ with an assumption of $[\overline{S}]_{in} >> n[\overline{HC(S)_n}]$ is used to find the

values of K_E and n. This assumption is not valid at higher concentrations of acid due to an increased concentration of extractant in the complex. A plot of $\log K_D + \log\left(1+\frac{K_a}{[H^+]}\right)$ versus $\log[\bar{S}]_{in}$ 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 (Figure 5.12). The values of K_E and n are also estimated using model Eq. 4.19 and applying DE optimization approach. The values of K_E and n are presented in Table 5.14. In MIBK + kerosene (1:1 v/v) diluent mixture with TOPO, highest value of K_E (6.093) for acid-TOPO complexation is obtained at 0.02 mol·L^{-1} of initial acid concentration. A value of n = 0.67 is estimated which shows 1:1 and 2:1 stoichiometric association of acid-TOPO complex in the organic phase. The values of K_D are also predicted and listed in Table 5.13. It is observed that the experimental values of K_D show a good agreement with model predicted values with maximum error limit of ±15%.

Table 5.13 Chemical extraction results of nicotinic acid with TOPO dissolved in MIBK + kerosene (1:1 v/v)

C_{in} **mol·L^{-1}**	$[\bar{S}]_{in}$ **mol·L^{-1}**	C_{HC} **mol·L^{-1}**	$\bar{C}_{HC}$ **mol·L^{-1}**	K_D	K_D **(by graphical method)**	K_D **(by DE)**	*%E*	*Z*	pH_{eq}
0.02	0.10	0.0077	0.0123	1.58	1.46	1.23	61.29	0.123	3.44
	0.25	0.0065	0.0135	2.10	2.42	2.35	67.74	0.054	3.48
	0.40	0.0052	0.0148	2.88	3.14	3.24	74.20	0.037	3.53
	0.50	0.0039	0.0161	4.17	3.55	3.77	80.65	0.032	3.60
0.05	0.10	0.0206	0.0294	1.42	1.35	1.28	58.71	0.294	3.22
	0.25	0.0168	0.0332	1.98	2.16	2.17	66.45	0.133	3.27
	0.40	0.0135	0.0365	2.69	2.74	2.80	72.90	0.091	3.32
	0.50	0.0116	0.0384	3.30	3.07	3.16	76.78	0.077	3.35
0.08	0.10	0.0342	0.0458	1.34	1.28	1.16	57.26	0.458	3.11
	0.25	0.0284	0.0516	1.82	2.02	2.00	64.52	0.206	3.15
	0.40	0.0232	0.0568	2.45	2.55	2.59	70.97	0.142	3.20
	0.50	0.0194	0.0606	3.13	2.85	2.92	75.81	0.121	3.24
0.12	0.10	0.0516	0.0683	1.33	1.26	1.14	56.99	0.684	3.02
	0.25	0.0439	0.0761	1.74	1.96	1.96	63.44	0.305	3.06
	0.40	0.0361	0.0839	2.32	2.45	2.50	69.89	0.210	3.10
	0.50	0.0297	0.0903	3.04	2.73	2.80	75.27	0.181	3.14

Table 5.14 Values of K_E for nicotinic acid with TOPO in MIBK + kerosene (1:1 v/v)

	Using graphical method				**Using DE optimization**		
C_{in} **mol·L^{-1}**	K_E	*n*	R^2	*SD*	K_E	*n*	*rmsd*
0.02	5.196	0.55	0.880	0.075	6.093	0.67	0.398
0.05	4.376	0.51	0.962	0.038	4.631	0.52	0.171
0.08	4.032	0.50	0.941	0.047	4.301	0.51	0.210
0.12	3.808	0.48	0.918	0.055	4.044	0.47	0.243

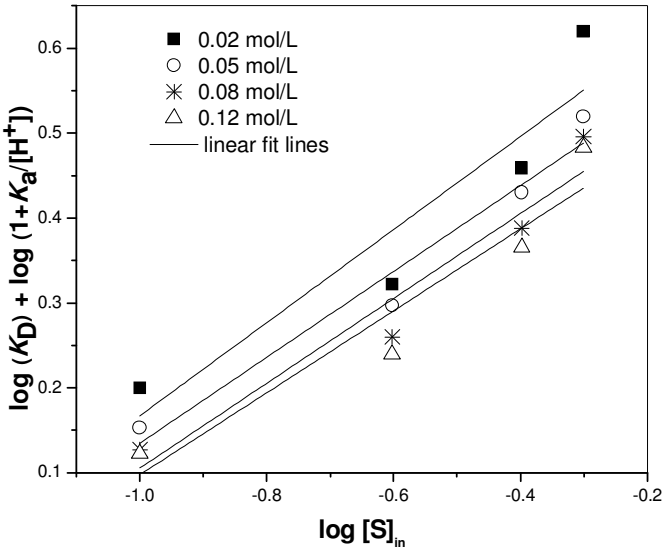


Figure 5.12 Determination of K_E and n using TOPO dissolved in MIBK + kerosene (1:1 v/v) with different initial nicotinic acid concentration

TBP and TOPO give lower distribution of nicotinic acid. Therefore, reactive extraction studies are also performed with TOA (0.115 and 0.229 mol·L^{-1}) dissolved in mixture of diluents [1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v)] and results are presented in Table 5.15. The maximum extraction ability of 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v) with TOA (0.229 mol·L^{-1}) in terms of K_D is found to be 7.368 and 0.805, respectively, at 0.02 mol·L^{-1} of acid concentration. Including the physical extraction term and using Eq. 4.37, the values of K_{11} are determined from the slope of the plots of $\frac{\overline{C}_{HC} - \nu \overline{C}_{HC}^{Diluent}}{[\overline{S}]_{in} - (\overline{C}_{HC} - \nu \overline{C}_{HC}^{Diluent})}$ versus [HC] (Figure 5.13). The estimated K_{11} values are presented in Table 5.30 with $R^2 > 0.94$ and maximum $SD = 0.122$. The values of K_D are also predicted and shown in Table 5.15, which are comparable with the experimental values. 1-Decanol + cyclohexane (1:1 v/v) with TOA gives highest extraction with E of 88.05% and K_{11} of 26.98 L·mol^{-1}.

Table 5.15 Chemical extraction results of nicotinic acid using TOA in 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v)

Diluents	$[\bar{S}]_{in}$ mol·L^{-1}	Experimental results						Model predicted results			
		C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	E	Z	pH_{eq}	K_D	K_{11}	R^2	SD
1-Decanol + cyclohexane (1:1 v/v)	0.115	0.0060	0.0140	2.356	70.20	0.122	3.80	1.852	15.56 ± 1.64	0.94	0.122
		0.0151	0.0349	2.309	69.78	0.303	3.59	1.773			
		0.0278	0.0522	1.875	65.21	0.454	3.46	1.595			
		0.0437	0.0563	1.287	56.27	0.489	3.36	1.352			
		0.0557	0.0644	1.156	53.63	0.560	3.31	1.248			
	0.229	0.0024	0.0176	7.368	88.05	0.077	4.00	5.557	26.98 ± 0.83	0.99	0.025
		0.0068	0.0432	6.396	86.48	0.189	3.77	5.420			
		0.0127	0.0673	5.289	84.10	0.294	3.63	4.969			
		0.0180	0.0820	4.556	82.00	0.358	3.55	4.555			
		0.0227	0.0973	4.296	81.12	0.425	3.50	4.295			
MIBK + kerosene (1:1 v/v)	0.115	0.0130	0.0070	0.536	34.90	0.061	3.63	0.380	2.64 ± 0.13	0.98	0.016
		0.0371	0.0129	0.347	25.78	0.112	3.40	0.390			
		0.0582	0.0218	0.376	27.30	0.190	3.30	0.395			
		0.0720	0.0280	0.389	28.00	0.243	3.25	0.404			
		0.0836	0.0364	0.435	30.30	0.316	3.22	0.425			
	0.229	0.0111	0.0089	0.805	44.60	0.039	3.66	0.496	1.82 ± 0.11	0.97	0.012
		0.0332	0.0168	0.505	33.54	0.073	3.42	0.510			
		0.0554	0.0246	0.444	30.76	0.107	3.31	0.509			
		0.0659	0.0341	0.517	34.09	0.149	3.27	0.525			
		0.0770	0.0430	0.559	35.84	0.188	3.24	0.544			

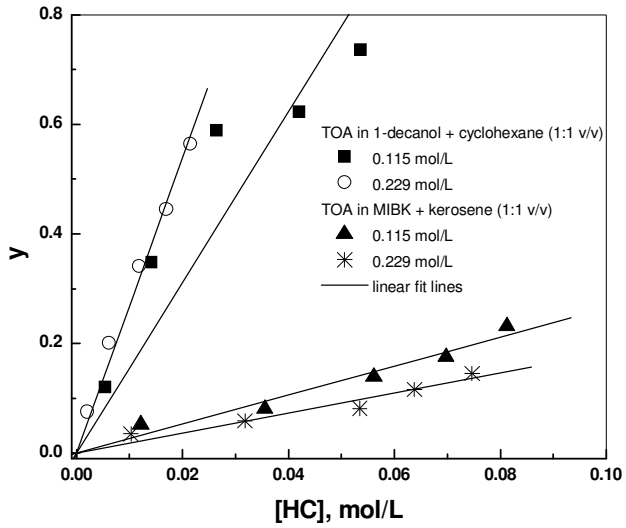


Figure 5.13 Determination of K_{11} for the extraction of nicotinic acid with TOA in 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v),

$$y = \frac{\overline{C}_{HC} - \nu \overline{C}_{HC}^{Diluent}}{[\overline{S}]_{in} - (\overline{C}_{HC} - \nu \overline{C}_{HC}^{Diluent})}$$

5.1.2.3 Using TOA in five different diluents

The reactive extraction of nicotinic acid with TOA (0.229 mol·L^{-1}) dissolved in dodecane, toluene, 1-decanol, MIBK and chloroform is carried out, and results are presented as isotherm at 298 K in Figure 5.14. The isotherms are mostly linear in nature showing the validity of Henry's law. Chloroform ($K_{D,max}$ = 45.154), 1-decanol ($K_{D,max}$ = 26.027) and MIBK ($K_{D,max}$ = 4.882) are found to be better diluents than toluene ($K_{D,max}$ = 1) and dodecane ($K_{D,max}$ = 0.111) with TOA. The values of Z (0.009 to 0.031 for dodecane, 0.044 to 0.154 for toluene, 0.082 to 0.499 for 1-decanol, 0.072 to 0.418 for MIBK, and 0.085 to 0.512 for chloroform) suggest no overloading of acid molecules on TOA, and formation of mainly 1:1 acid-TOA solvates in the organic phase.

The experimental values of equilibrium constant (K_{11}) are calculated using model Eq. 4.14 as 0.377 with dodecane, 2.774 with toluene, 172.67 with 1-decanol, 28.027 with

MIBK, and 318.408 with chloroform. Two models such LSER (Eq. 4.38) and relative basicity (Eq. 4.45) are also employed to estimate the equilibrium constants of 1:1 acid-TOA complexes (K_{11}). In the LSER model, the error between experimental values of $\log K_{11}$ and predicted values of $\log K_{11}$ is minimized to determine the model parameters. Using the least square minimization technique, the values of LSER model parameters are estimated and reported in Table 5.16. In the relative basicity model, the values of $\log K_{11}$ (experimental) versus $(pK_{a,B} - pK_a + \log P)$ are plotted (Figure 5.15) to determine the model parameters (C_1 and C_2). The estimated values of C_1 and C_2 are listed in Table 5.17. The model predicted values of K_{11} given by LSER and relative basicity models are plotted against experimentally determined values of K_{11} in Figures 5.16 and 5.17, respectively. The LSER and relative basicity models predict the values of K_{11} with in error limit of ±3% and ±20%, respectively. So, LSER model is found to fit the experimental values of K_{11} more exactly than the relative basicity model does.

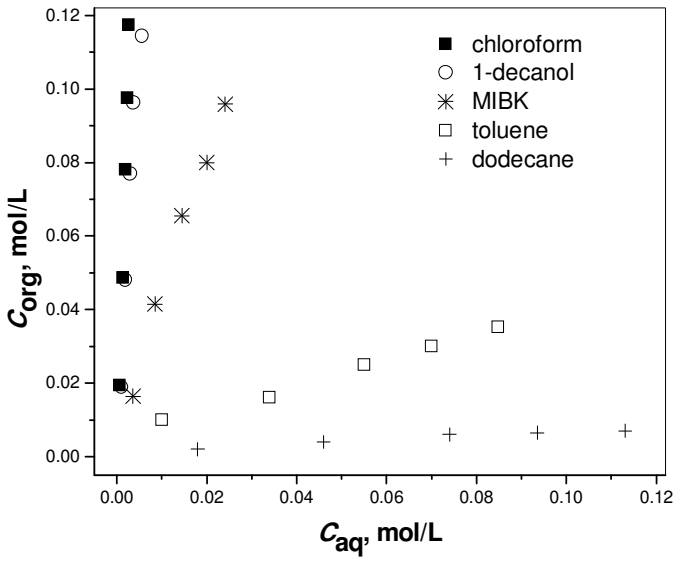


Figure 5.14 Equilibrium isotherms of nicotinic acid with TOA in different diluents

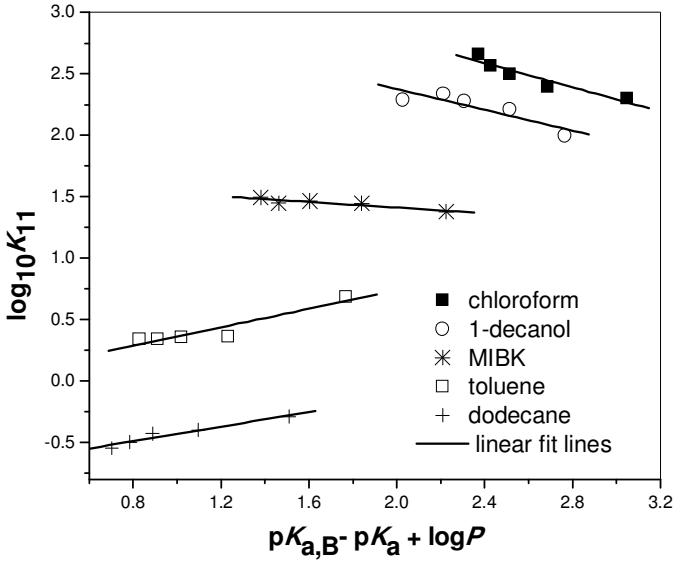


Figure 5.15 Determination of relative basicity model parameters for nicotinic acid with TOA in different diluents

Table 5.16 Estimated values of LSER model parameters for nicotinic acid with TOA in different diluents

C_{in} **mol·L^{-1}**	$\log_{10} K_{11}^0$	***a***	***b***	***s***	***d***
0.02	-0.1328	3.2916	0.5781	1.9573	-0.1533
0.05	-0.2289	3.8680	0.6820	2.1389	-0.2981
0.08	-0.2517	4.0749	0.6601	2.2210	-0.2975
0.10	-0.3174	4.3236	0.7428	2.2369	-0.2811
0.12	-0.3380	4.2598	0.3971	2.6041	-0.2959

Table 5.17 Estimated values of relative basicity model parameters for nicotinic acid with TOA in different diluents

Diluents	***C*$_1$**	***C*$_2$**	***R*^{2}**	***SD***
Dodecane	0.2967 ± 0.041	-0.7278 ± 0.042	0.973	0.026
Toluene	0.3751 ± 0.080	-0.0127 ± 0.096	0.939	0.060
1-Decanol	-0.4191 ± 0.126	3.2131 ± 0.300	0.887	0.072
MIBK	-0.1149 ± 0.028	1.6415 ± 0.049	0.920	0.019
Chloroform	-0.4927 ± 0.097	3.7702 ± 0.253	0.947	0.053

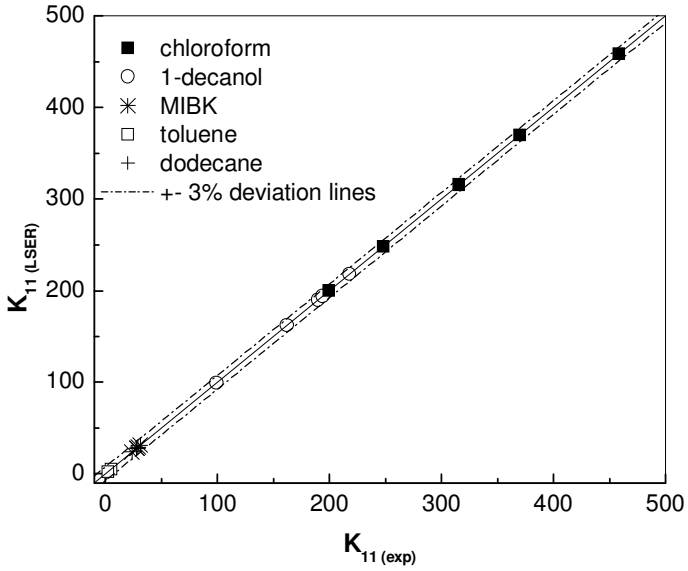


Figure 5.16 LSER model predicted versus experimental values of K_{11} for nicotinic acid extraction with TOA in different diluents

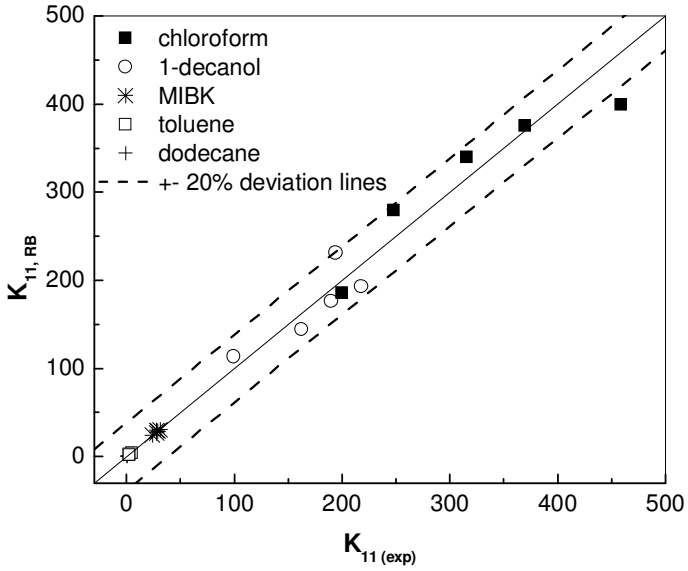


Figure 5.17 Relative basicity model predicted versus experimental values of K_{11} for nicotinic acid extraction with TOA in different diluents

5.1.2.4 Using TOA and Aliquat 336 in sunflower oil (a natural non toxic diluent)

Reactive extraction is a promising method to recover carboxylic acid from fermentation broth but suffers from toxicity problems of diluent and extractant used. This problem of toxicity in reactive extraction can be reduced by using a natural nontoxic diluent such as sunflower oil with an extractant. In this part of the work, reactive extraction of nicotinic acid (0.02 to 0.12 mol·L^{-1}) is presented using TOA (0.44 mol·L^{-1}) and Aliquat 336 (0.44 mol·L^{-1}) in sunflower oil (nontoxic diluent), and the equilibrium isotherms are presented in Figures 5.18 and 5.19, respectively. The value of K_D is found to decrease from 0.176 to 0.125 with TOA, and from 0.142 to 0.107 with Aliquat 336 with an increase in the concentration of acid from 0.02 to 0.12 mol·L^{-1}. The maximum extraction capacity of sunflower oil is observed to be 14.97% with TOA and 12.46% with Aliquat 336 at 0.02 mol·L^{-1} of initial acid concentration which is very low. Therefore, to increase the extraction capacity, phase modifiers (dodecane and 1-octanol) are added to sunflower oil in the ratio of 1:1 v/v. Due to the modifier's effect, the slope of isotherm is found to increase. The increase in the slope is more in case of active modifier, 1-octanol.

The values of m and K_E are estimated using Eq. 4.19, and applying DE optimization approach (Table 5.18). The values of m are found to be near about one with TOA implying mainly the formation of 1:1 acid-TOA complexes in the organic phase. In case of Aliquat 336, the values of m are found to be 0.90 for sunflower oil, 0.63 for sunflower oil + dodecane (1:1 v/v), and 0.52 for sunflower oil + 1-octanol (1:1 v/v). Extraction using sunflower oil + dodecane (1:1 v/v) (m = 0.63) and sunflower oil + 1-octanol (1:1 v/v) (m = 0.52) with Aliquat 336 indicates more than one solvation number of Aliquat 336 and possibility of 1:2 complex formation in the organic phase. The values of K_{11} and K_{12} for 1:1 and 1:2 complex formations, respectively, are also determined and listed in Table 5.18.

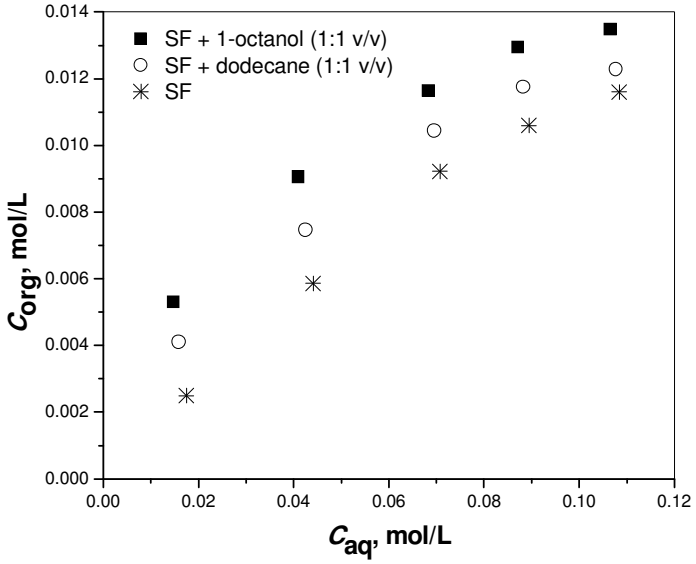


Figure 5.18 Equilibrium isotherms of nicotinic acid with TOA in sunflower oil

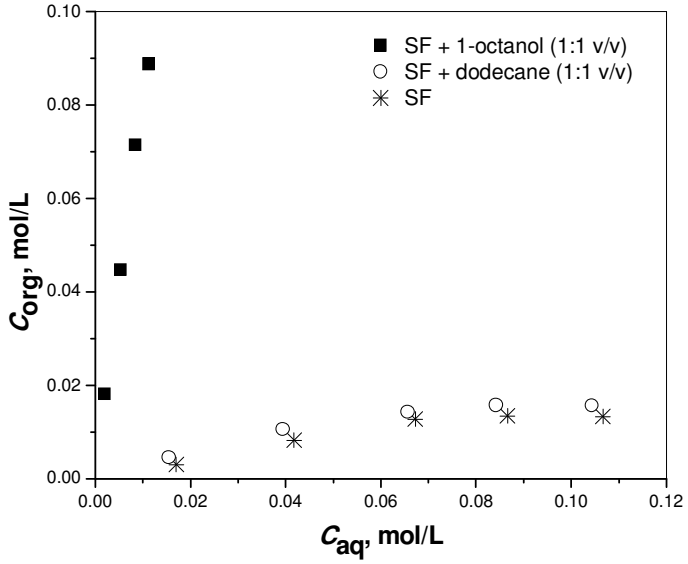


Figure 5.19 Equilibrium isotherms of nicotinic acid with Aliquat 336 in sunflower oil

Table 5.18 Values of m, n, K_E, K_{11} and K_{12} for nicotinic acid extraction with TOA and Aliquat 336 in sunflower oil, dodecane and 1-octanol

Extractants	**TOA (0.44 mol·L^{-1})**			**Aliquat 336 (0.44 mol·L^{-1})**					
Diluents	m	n	K_E	m	n	K_E	K_{11}	K_{12}	K_E
Sunflower oil (SF)	0.97	1	0.401	0.90	1	0.257	0.281	-	0.281
SF + dodecane (1:1 v/v)	0.87	1	0.433	0.63	1	0.208	0.237	0.811	0.192
SF + 1-octanol (1:1 v/v)	0.97	1	21.56	0.52	1	0.219	0.268	0.819	0.220

5.1.3 Reactive Extraction of Isonicotinic Acid

In this study, the experiments are conducted on the recovery of isonicotinic acid with TBP, TOA and TDDA as extractants using different types of diluents. The physical extraction of acid using hexane, toluene and DCM are shown in Section 5.1.3.1. Studies with TBP are also focused using three diluents (hexane, toluene and DCM) having different dielectric constants and presented in Section 5.1.3.2. The effect of phase modifiers (1-decanol and MIBK) on the extraction performance is also analyzed. Results obtained on extraction of isonicotinic acid with TOA in various diluents (dodecane, toluene, 1-decanol, MIBK and chloroform) are described in Section 5.1.3.3. The extractant, TDDA is used with nontoxic diluents (dodecane and oleyl alcohol) to recover the acid at four different temperatures (298, 313, 323 and 333 K) and explained in Section 5.1.3.4.

5.1.3.1 Using pure diluents

The equilibrium data on physical extraction of isonicotinic acid (0.0043 to 0.0349 mol·L^{-1}) using hexane, toluene, DCM, dodecane and oleyl alcohol are shown in Table 5.19. Lower values of distribution coefficient are found with hexane, toluene, DCM, dodecane, and oleyl alcohol with maximum values of $K_D^{diluent}$ of 0.084, 0.232, 0.419, 0.526 and 1.157, respectively. The values of the partition coefficient (P) and dimerization constants (D) are determined as physical extraction parameters using Eq. 4.10. From the linear fits of the experimental data of $K_D^{diluent}$ versus [HC], the values of P as intercept and D from the slope are estimated (Figure 5.20) and shown in Table 5.19.

Table 5.19 Physical equilibrium results of isonicotinic acid in different diluents

Diluents	C_{HC} mol·L^{-1}	$\overline{C}_{HC}$ mol·L^{-1}	$K_D^{diluent}$	*%E*	pH_{eq}	*P*	*D*	R^2	*SD*
Hexane	0.0040	0.0003	0.075	6.98	3.64	0.074	31.10	0.926	0.001
	0.0089	0.0007	0.076	7.08	3.46				
	0.0162	0.0013	0.080	7.43	3.33				
	0.0215	0.0018	0.083	7.64	3.27				
	0.0322	0.0027	0.084	7.74	3.18				
Toluene	0.0035	0.0008	0.222	18.14	3.67	0.220	4.52	0.926	0.001
	0.0079	0.0018	0.223	18.23	3.49				
	0.01426	0.0032	0.228	18.54	3.36				
	0.0189	0.0044	0.230	18.72	3.3				
	0.0283	0.0066	0.232	18.81	3.21				
DCM	0.0032	0.0011	0.344	25.58	3.69	0.346	11.81	0.993	0.002
	0.0070	0.0026	0.371	27.08	3.52				
	0.0127	0.0048	0.378	27.43	3.39				
	0.0167	0.0066	0.395	28.33	3.32				
	0.0246	0.0103	0.419	29.51	3.24				
Dodecane	0.0016	0.0004	0.221	18.10	4.38	0.217	188.88	0.95	0.031
	0.0038	0.0012	0.323	24.40	4.13				
	0.0095	0.0036	0.376	27.31	3.89				
	0.0139	0.0061	0.443	30.70	3.78				
	0.0164	0.0086	0.526	34.48	3.71				
Oleyl alcohol	0.0011	0.0009	0.764	43.30	4.31	0.718	35.10	0.97	0.031
	0.0028	0.0022	0.804	44.56	4.08				
	0.0066	0.0064	0.984	49.60	3.80				
	0.0098	0.0102	1.035	50.86	3.70				
	0.0116	0.0134	1.157	53.63	3.63				

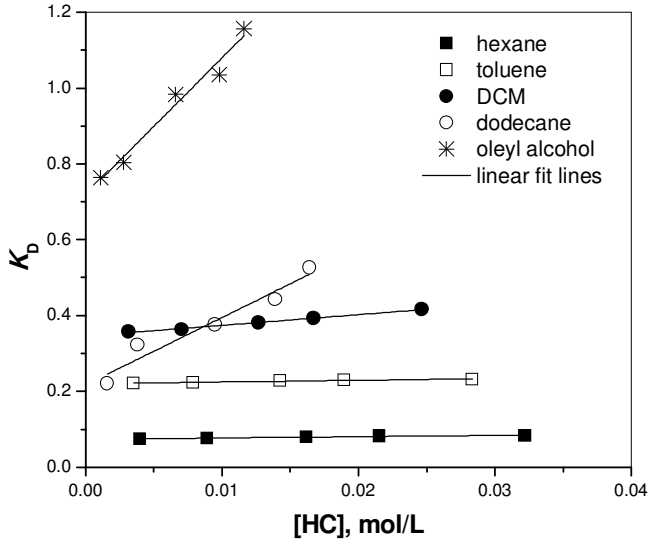


Figure 5.20 Determination of *P* and *D* for the physical extraction of isonicotinic acid in different diluents

5.1.3.2 Using TBP in different diluents and modifiers

The conventional solvents give lower distribution of acid and hence poor recovery of acid. Therefore, the reactive extraction of isonicotinic acid (0.0043 to 0.0349 mol·L^{-1}) using a phosphorous based extractant (TBP: 0.365 to 1.096 mol·L^{-1}) dissolved in three diluents [hexane (ε_r = 1.88), toluene (ε_r = 2.38) and DCM (ε_r = 9.08)] is investigated in this section. The study is also carried out to analyze the effect of phase modifiers (1-decanol and MIBK) on the extraction. The correlations between the solvent polarity and the number of phosphoric molecules participating in the inter-facial reaction with acid are studied. The chemical extraction results are presented in Tables 5.20 to 5.22. The highest extraction efficiency is achieved with DCM because of its superior ability to solubilize the complex molecules into the organic phase. In the absence of modifiers, the extraction yield of the acid with TBP is found to be 15.35% for hexane, 54.98% for toluene and 67.26% for DCM. The increase of extractant concentration in the solvent phase exhibits a favorable effect on the acid extraction due to the increase of the interfacial amount of one of the reactants.

The efficiency of reactive extraction can also be improved by the addition of a polar solvent in the organic phase. This solvent increases the organic phase polarity and, consequently, exhibits a favorable effect on the solubilization of polar molecules. Moreover, it possesses the ability to induce the breakage of the stable "third phase" emulsion which could appear at the interface of aqueous and organic phase and termed as "phase-modifier". Therefore, reactive extraction studies are also carried out using 1-decanol and MIBK as phase modifiers, and results are presented in Tables 5.23 to 5.25. The values of equilibrium constants (K_E) and number of acid molecules (m) per extractant molecule are estimated using Eq. 4.19 and minimizing the error between experimental and predicted values of K_D by applying DE. The structures of the interfacial complexes

are observed as 1:1 for hexane, and 1:1 & 1:2 for toluene and DCM without the use of phase modifiers. The addition of 1-decanol and MIBK does not make any change in the acid-TBP complex structure but exhibit a negative effect on the extraction constants and a positive effect on the extraction efficiency for all type of diluents used. Significant decrease in the extraction constant indicates that the increase of solvent polarity hinders the solute solvation at the interfacial equilibrium and increases the possibility of ion-pair formation which improves the extraction efficiency. These results confirm the important role of the solvent polarity on the extraction of ionizable solutes. The dielectric constant is considered as a characteristic of acid-TBP interactions due to the presence of ionizable groups in acid. The modification of dielectric constant has a smaller effect on the solubility and extraction of non-electrolytes or weak electrolytes, but it becomes an important factor for the extraction of dissociable solutes like isonicotinic acid (Prezho *et al*., 2002). Therefore, the mechanism of the interfacial reaction between acid and extractant is controlled by the organic phase polarity.

Table 5.20 Equilibrium results of isonicotinic acid with TBP in hexane

$[\bar{S}]_{in}$ **mol·L^{-1}**	C_{HC} **mol·L^{-1}**	$\bar{C}_{HC}$ **mol·L^{-1}**	K_D	*%E*	*Z*	pH_{eq}	*m*	K_E	*rmsd*
0.365	0.0038	0.0005	0.132	11.63	0.001	3.65	0.90	0.236	0.0039
	0.0085	0.0011	0.127	11.25	0.003	3.47			
	0.0156	0.0019	0.122	10.86	0.005	3.34			
	0.0210	0.0023	0.112	10.04	0.006	3.27			
	0.0316	0.0033	0.104	9.46	0.009	3.18			
0.731	0.0037	0.0006	0.156	13.49	0.001	3.66	0.85	0.109	0.0075
	0.0084	0.0012	0.143	12.5	0.002	3.48			
	0.0154	0.0021	0.139	12.23	0.003	3.34			
	0.0209	0.0024	0.114	10.21	0.003	3.28			
	0.0314	0.0035	0.111	10.03	0.005	3.19			
1.096	0.0036	0.0007	0.181	15.35	0.001	3.66	0.78	0.064	0.0094
	0.0082	0.0014	0.171	14.58	0.001	3.48			
	0.0153	0.0022	0.142	12.46	0.002	3.34			
	0.0208	0.0025	0.118	10.56	0.002	3.28			
	0.0313	0.0036	0.116	10.37	0.003	3.19			

Table 5.21 Equilibrium results of isonicotinic acid with TBP in toluene

$[\bar{S}]_{in}$ **mol·L^{-1}**	C_{HC} **mol·L^{-1}**	$\bar{C}_{HC}$ **mol·L^{-1}**	K_D	*%E*	*Z*	pH_{eq}	*m*	K_E	*rmsd*
0.365	0.0025	0.0018	0.745	42.70	0.005	3.75	0.66	0.415	0.0393
	0.0062	0.0034	0.558	35.83	0.009	3.55			
	0.0116	0.0058	0.507	33.62	0.016	3.4			
	0.0169	0.0064	0.379	27.48	0.018	3.32			
	0.0271	0.0078	0.288	22.34	0.021	3.22			
0.731	0.0023	0.0020	0.879	46.79	0.003	3.77	0.66	0.243	0.0526
	0.0056	0.0040	0.705	41.33	0.005	3.57			
	0.0109	0.0066	0.604	37.65	0.009	3.42			
	0.0162	0.0071	0.439	30.51	0.010	3.33			
	0.0260	0.0089	0.340	25.36	0.012	3.23			
1.096	0.0019	0.0024	1.221	54.98	0.002	3.8	0.58	0.144	0.0488
	0.0051	0.0045	0.881	46.83	0.004	3.59			
	0.0106	0.0069	0.657	39.66	0.006	3.43			
	0.0155	0.0078	0.504	33.53	0.007	3.34			
	0.0257	0.0092	0.358	26.37	0.008	3.23			

Table 5.22 Equilibrium results of isonicotinic acid with TBP in DCM

$[\bar{S}]_{in}$ **mol·L^{-1}**	C_{HC} **mol·L^{-1}**	$\bar{C}_{HC}$ **mol·L^{-1}**	K_D	*%E*	*Z*	pH_{eq}	*m*	K_E	*rmsd*
0.365	0.0023	0.0020	0.870	46.51	0.005	3.77	0.68	0.518	0.0501
	0.0056	0.0040	0.714	41.67	0.011	3.57			
	0.0109	0.0066	0.606	37.71	0.018	3.42			
	0.0158	0.0075	0.475	32.19	0.021	3.34			
	0.0260	0.0089	0.342	25.50	0.024	3.23			
0.731	0.0016	0.0027	1.688	62.79	0.004	3.85	0.53	0.221	0.0502
	0.0046	0.0050	1.087	52.08	0.007	3.61			
	0.0099	0.0076	0.768	43.43	0.010	3.44			
	0.0144	0.0089	0.618	38.20	0.012	3.36			
	0.0250	0.0099	0.396	28.37	0.014	3.24			
1.096	0.0014	0.0029	2.071	67.44	0.003	3.88	0.48	0.129	0.0533
	0.0048	0.0048	1.000	50.00	0.004	3.6			
	0.0097	0.0078	0.804	44.57	0.007	3.44			
	0.0141	0.0092	0.652	39.48	0.008	3.36			
	0.0246	0.0103	0.419	29.51	0.009	3.24			

Table 5.23 Equilibrium results of isonicotinic acid with TBP in hexane and effect of modifiers (1-decanol and MIBK)

$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	pH_{eq}	m	K_E	rmsd
Effect of modifier (1-decanol: 10%)									
0.365	0.0036	0.0007	0.194	16.28	0.0019	3.67	0.77	0.020	0.0124
	0.0081	0.0015	0.188	15.83	0.0042	3.49			
	0.0152	0.0023	0.151	13.14	0.0063	3.35			
	0.0207	0.0026	0.125	11.07	0.0071	3.28			
	0.0311	0.0038	0.121	10.83	0.0103	3.19			
0.731	0.0035	0.0008	0.222	18.14	0.0011	3.67	0.76	0.109	0.0138
	0.008	0.0016	0.200	16.67	0.0022	3.49			
	0.0148	0.0027	0.182	15.43	0.0037	3.35			
	0.0204	0.0029	0.142	12.45	0.0040	3.28			
	0.0310	0.0039	0.126	11.17	0.0053	3.19			
1.096	0.0034	0.0009	0.265	20.93	0.0008	3.68	0.84	0.116	0.0068
	0.0078	0.0018	0.231	18.75	0.0016	3.49			
	0.0146	0.0029	0.199	16.57	0.0026	3.35			
	0.0195	0.0038	0.196	16.39	0.0035	3.29			
	0.0292	0.0057	0.195	16.33	0.0052	3.20			
Effect of modifier (MIBK: 10%)									
0.365	0.0038	0.0005	0.144	12.56	0.002	3.66	0.87	0.227	0.0046
	0.0084	0.0012	0.137	12.08	0.003	3.48			
	0.0155	0.0020	0.128	11.31	0.005	3.34			
	0.0209	0.0024	0.116	10.39	0.007	3.28			
	0.0315	0.0034	0.107	9.68	0.009	3.19			
0.731	0.0036	0.0007	0.181	15.35	0.001	3.66	0.78	0.092	0.0032
	0.0083	0.0013	0.154	13.33	0.002	3.48			
	0.0154	0.0021	0.133	11.77	0.003	3.34			
	0.0208	0.0025	0.118	10.56	0.003	3.28			
	0.0313	0.0036	0.114	10.26	0.005	3.19			
1.096	0.0036	0.0007	0.208	17.21	0.001	3.67	0.73	0.059	0.0084
	0.0081	0.0015	0.182	15.42	0.001	3.48			
	0.0152	0.0023	0.148	12.91	0.002	3.35			
	0.0208	0.0025	0.122	10.90	0.002	3.28			
	0.0312	0.0037	0.119	10.60	0.003	3.19			

Table 5.24 Equilibrium results of isonicotinic acid with TBP in toluene and effect of modifiers (1-decanol and MIBK)

$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	*%E*	*Z*	pH_{eq}	*m*	K_E	*rmsd*
Effect of modifier (1-decanol: 10%)									
0.365	0.0016	0.0027	1.688	62.79	0.007	3.85	0.50	0.384	0.0355
	0.0048	0.0048	1.000	50.00	0.013	3.60			
	0.0102	0.0073	0.716	41.71	0.020	3.43			
	0.0151	0.0082	0.543	35.19	0.022	3.35			
	0.0253	0.0096	0.379	27.51	0.026	3.23			
0.731	0.0014	0.0029	2.071	67.44	0.004	3.88	0.46	0.177	0.0294
	0.0046	0.0050	1.087	52.08	0.007	3.61			
	0.0100	0.0075	0.750	42.86	0.010	3.44			
	0.0150	0.0083	0.553	35.62	0.011	3.35			
	0.0252	0.0097	0.385	27.79	0.013	3.23			
1.096	0.0013	0.0030	2.308	69.77	0.003	3.90	0.45	0.120	0.0336
	0.0044	0.0052	1.182	54.17	0.005	3.62			
	0.0099	0.0076	0.768	43.43	0.007	3.44			
	0.0148	0.0085	0.574	36.48	0.008	3.35			
	0.0250	0.0099	0.396	28.37	0.009	3.24			
Effect of modifier (MIBK: 10%)									
0.365	0.0018	0.0025	1.389	58.14	0.007	3.82	0.53	0.392	0.0428
	0.0049	0.0047	0.959	48.96	0.013	3.60			
	0.0106	0.0069	0.651	39.43	0.019	3.43			
	0.0155	0.0078	0.503	33.48	0.021	3.34			
	0.0257	0.0092	0.358	26.36	0.025	3.23			
0.731	0.0016	0.0027	1.688	62.79	0.004	3.85	0.50	0.188	0.0357
	0.0048	0.0048	1.000	50.00	0.007	3.60			
	0.0102	0.0073	0.716	41.71	0.010	3.43			
	0.0151	0.0082	0.543	35.19	0.011	3.35			
	0.0253	0.0096	0.379	27.51	0.013	3.23			
1.096	0.0015	0.0028	1.867	65.12	0.003	3.86	0.47	0.117	0.0295
	0.0046	0.0050	1.087	52.08	0.005	3.61			
	0.0102	0.0073	0.716	41.71	0.007	3.43			
	0.0151	0.0082	0.543	35.19	0.007	3.35			
	0.0253	0.0096	0.379	27.51	0.009	3.23			

Table 5.25 Equilibrium results of isonicotinic acid with TBP in DCM and effect of modifiers (1-decanol and MIBK)

$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	*%E*	*Z*	pH_{eq}	*m*	K_E	*rmsd*
Effect of modifier (1-decanol: 10%)									
0.365	0.0018	0.0025	1.389	58.14	0.007	3.82	0.55	0.413	0.0337
	0.0049	0.0047	0.959	48.96	0.013	3.60			
	0.0106	0.0069	0.651	39.43	0.019	3.43			
	0.0151	0.0082	0.543	35.19	0.022	3.35			
	0.0253	0.0096	0.379	27.51	0.026	3.23			
0.731	0.0014	0.0029	2.071	67.44	0.004	3.88	0.50	0.210	0.0396
	0.0044	0.0052	1.182	54.17	0.007	3.62			
	0.0097	0.0078	0.804	44.57	0.011	3.44			
	0.0141	0.0092	0.652	39.48	0.013	3.36			
	0.0246	0.0103	0.419	29.51	0.014	3.24			
1.096	0.0012	0.0031	2.583	72.09	0.003	3.91	0.44	0.122	0.0616
	0.0046	0.0050	1.087	52.08	0.005	3.61			
	0.0095	0.0080	0.842	45.71	0.007	3.45			
	0.0137	0.0096	0.701	41.20	0.009	3.37			
	0.0243	0.0106	0.436	30.37	0.010	3.24			
Effect of modifier (MIBK: 10%)									
0.365	0.0017	0.0026	1.529	60.47	0.007	3.83	0.51	0.373	0.0461
	0.0048	0.0048	1.000	50.00	0.013	3.60			
	0.0109	0.0066	0.606	37.71	0.018	3.42			
	0.0155	0.0078	0.503	33.48	0.021	3.34			
	0.0253	0.0096	0.379	27.51	0.026	3.23			
0.731	0.0016	0.0027	1.688	62.79	0.004	3.85	0.53	0.216	0.0550
	0.0046	0.0050	1.087	52.08	0.007	3.61			
	0.0098	0.0077	0.786	44.00	0.011	3.44			
	0.0146	0.0087	0.596	37.34	0.012	3.35			
	0.0252	0.0097	0.385	27.79	0.013	3.23			
1.096	0.0013	0.0030	2.308	69.77	0.003	3.90	0.46	0.123	0.0572
	0.0047	0.0049	1.043	51.04	0.004	3.61			
	0.0096	0.0079	0.823	45.14	0.007	3.45			
	0.0140	0.0093	0.664	39.91	0.008	3.36			
	0.0245	0.0104	0.424	29.80	0.009	3.24			

5.1.3.3 Using TOA in five different diluents

The extraction ability of TBP is found to be comparatively low. Therefore, recovery of isonicotinic acid is carried out with TOA dissolved in dodecane, toluene, 1-decanol, MIBK, and chloroform. Plots between aqueous and organic phase acid concentrations at equilibrium are drawn using different initial concentrations of acid (0.005 to 0.03 mol·L^{-1}) and a constant concentration of TOA (0.229 mol·L^{-1}) dissolved in various diluents (Figure 5.21). These isotherms are found to be almost linear with all diluents as dilute aqueous solution of acid is considered in the experiment, which obeys Henry's law. The slope of the isotherm is found to increase with the polarity of the diluent. The ability of diluent to solvate the acid-TOA complex follows the order of chloroform ($K_{D,max}$ = 25.79) > 1-decanol ($K_{D,max}$ = 19.13) > MIBK ($K_{D,max}$ = 2.5) > toluene ($K_{D,max}$ = 1.69) > dodecane ($K_{D,max}$ = 1.07).

The values of Z (0.011 to 0.02 for dodecane, 0.012 to 0.059 for toluene, 0.019 to 0.124 for 1-decanol, 0.012 to 0.094 for MIBK, and 0.019 to 0.126 for chloroform) suggest that the organic phase is not over loaded with acid and there are formations of 1:1 acid-TOA complexes in the organic phase. The experimental values of the equilibrium constants of 1:1 acid-TOA complex formation (K_{11}) are calculated using Eq. 4.14 based on mass action law. The equilibrium models such as relative basicity and LSER are employed to estimate the equilibrium constants of 1:1 acid-TOA complex formation (K_{11}). The parameters of relative basicity model are determined by fitting the curves linearly between $\log K_{11}$(experimental) versus $(pK_{a,B} - pK_a + \log P_a)$ [Figure 5.22]. The estimated values of C_1 and C_2 are listed in Table 5.26. To estimate the LSER model parameters, the error between experimental values of $\log K_{11}$ and predicted values of $\log K_{11}$ is minimized using the least square minimization technique and reported in Table 5.27 at different acid concentrations. The model predicted values of K_{11} given by relative

basicity and LSER models are plotted against experimentally determined values of K_{11} in Figures 5.23 and 5.24, respectively. The relative basicity and LSER models predict the values of K_{11} with an error limit of ±18% and ±3%, respectively. So, LSER model is showing a better fit to the experimental values of K_{11} than relative basicity model.

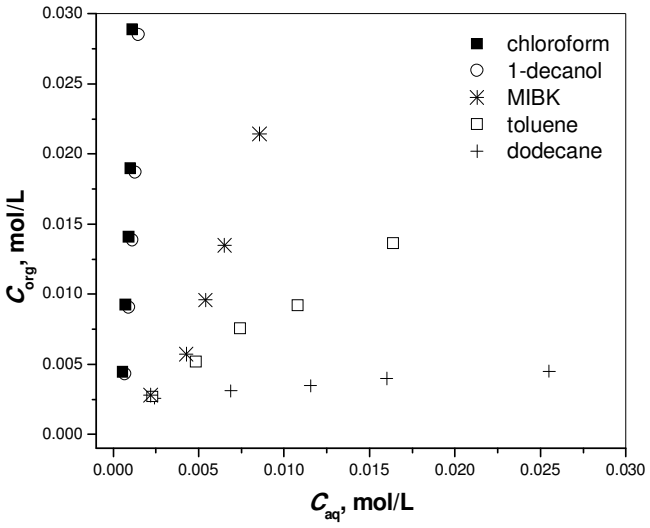


Figure 5.21 Equilibrium isotherms of isonicotinic acid with TOA in different diluents

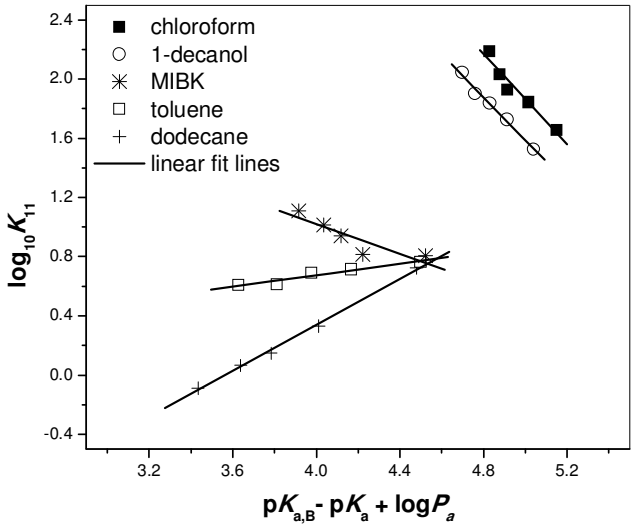


Figure 5.22 Determination of relative basicity model parameters for isonicotinic acid with TOA in different diluents

Table 5.26 Estimated values of relative basicity model parameters for isonicotinic acid with TOA in different diluents

Diluents	C_1	C_2	R^2	*SD*
Dodecane	0.7776 ± 0.024	-2.7728 ± 0.095	0.999	0.019
Toluene	0.1945 ± 0.029	-0.1035 ± 0.118	0.968	0.020
1-decanol	-1.4490 ± 0.090	8.8327 ± 0.439	0.994	0.024
MIBK	-0.5056 ± 0.145	3.0421 ± 0.603	0.896	0.067
Chloroform	-1.5197 ± 0.215	9.4637 ± 1.068	0.971	0.055

Table 5.27 Estimated values of LSER model parameters for isonicotinic acid with TOA in different diluents

C_{in} **mol·L^{-1}**	$\log_{10} K_{11}^0$	***a***	***b***	***s***	***d***
0.005	0.7001	2.3481	0.2977	-0.0777	-0.7607
0.010	0.3345	2.9134	0.7378	0.1796	1.0490
0.015	0.1794	3.0971	0.8972	0.5088	0.2484
0.020	0.1199	3.2776	0.8099	0.7846	-0.0367
0.030	-0.0104	3.6123	0.9324	1.0506	-0.0573

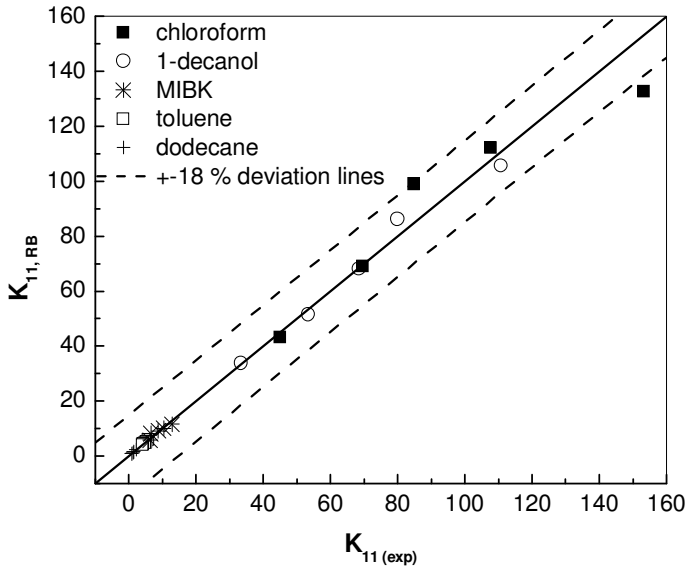


Figure 5.23 Comparison of K_{11} (relative basicity model versus experimental) for isonicotinic acid with TOA in different diluents

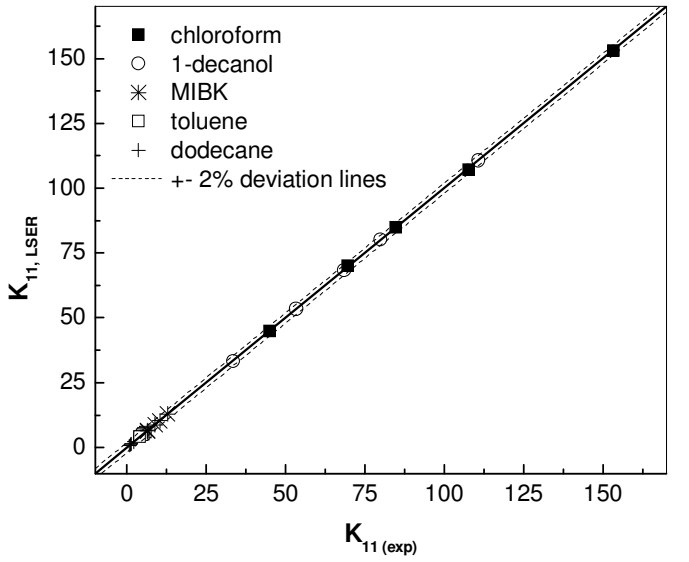


Figure 5.24 Comparison of K_{11} (LSER model versus experimental) for isonicotinic acid with TOA in different diluents

5.1.3.4 Using TDDA in dodecane and oleyl alcohol as nontoxic diluents

Distribution of isonicotinic acid between water and TDDA or Alamine 304, a tertiary aliphatic amine, dissolved in nontoxic diluents (dodecane and oleyl alcohol) is also studied. The concentration ranges of acid and TDDA are chosen as 0.002 to 0.025 mol·L^{-1} (Vejvoda *et al.*, 2006), and 5% to 20% (0.079 to 0.316 mol·L^{-1}), respectively. Experiments are also carried out to analyze the effect of temperature (298, 313, 323 and 333 K) on the K_D and E of reactive extraction.

Initially, the effect of extractant on the distribution coefficient is studied by adding 10%v/v (0.158 mol·L^{-1}) TDDA in both dodecane and oleyl alcohol (Figure 5.25). It is observed that there is a drastic increase in the values of K_D from 0.221 to 1.602 for dodecane, and 0.764 to 14.873 for oleyl alcohol at 0.002 mol·L^{-1} of acid concentration. Hence, TDDA could be used effectively to extract acid from the aqueous solution. Oleyl alcohol is relatively more viscous than dodecane and higher distribution of acid is found when 90% oleyl alcohol is used. Now to optimize the use of these two diluents and to reduce the viscosity of the organic phase, the composition of oleyl alcohol in the organic phase is varied from 0% to 90% at fixed acid (0.013 mol·L^{-1}) and TDDA (0.158 mol·L^{-1}) concentrations. With increase in the amount of oleyl alcohol, the degree of extraction is found to increase (Figure 5.26), but at the cost of increase in viscosity of the organic phase. Therefore, the volume ratio of dodecane and oleyl alcohol is fixed at 1:1 v/v. To optimize the use of TDDA, experiments are carried out considering four different concentrations (0.079 to 0.316 mol·L^{-1}) and results are shown as isotherms in Figure 5.27. It is observed that the extraction efficiency increases from 74.8% to 87.4% when TDDA concentration is changed from 0.079 to 0.316 mol·L^{-1} and becomes almost constant after 0.158 mol·L^{-1} of TDDA. The values of K_{11} are estimated for TDDA (0.079 to 0.316 mol·L^{-1}) in dodecane + oleyl alcohol (1:1 v/v) and plots are shown in Figure 5.28.

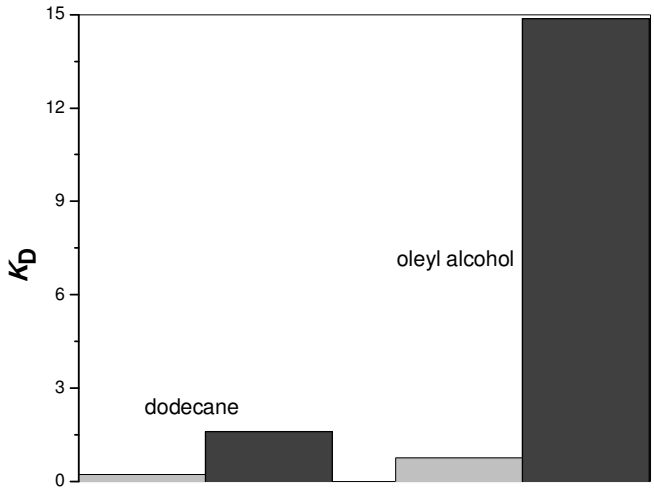


Figure 5.25 Effect of TDDA (10 %v/v, 0.158 mol·L^{-1}) on K_D for the extraction of isonicotinic acid (0.002 mol·L^{-1}) in dodecane and oleyl alcohol at 298 K

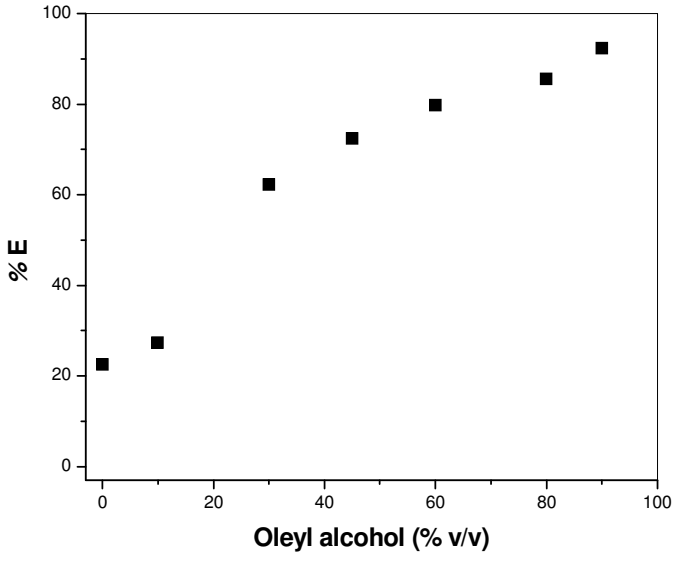


Figure 5.26 Effect of modifier (oleyl alcohol) on extraction efficiency of isonicotinic acid (0.013 mol·L^{-1}) using TDDA (10 %v/v, 0.158 mol·L^{-1}) at 298 K

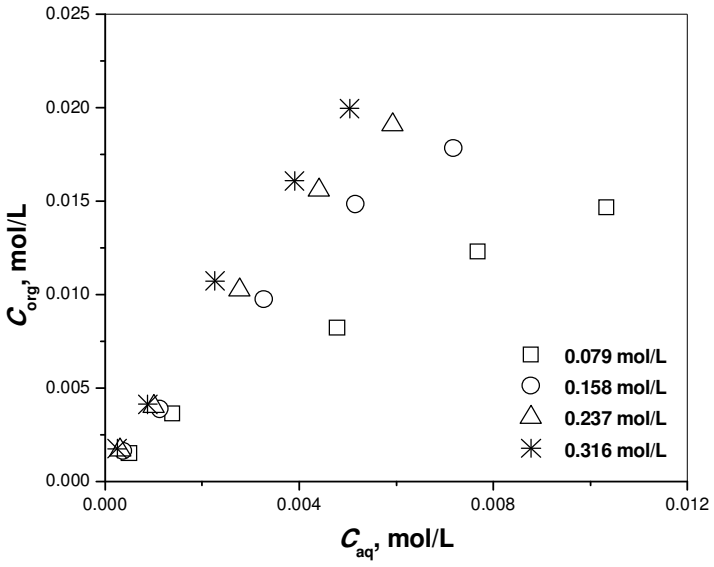


Figure 5.27 Effect of TDDA concentration on K_D for the extraction of isonicotinic acid in dodecane + oleyl alcohol (1:1 v/v) at 298 K

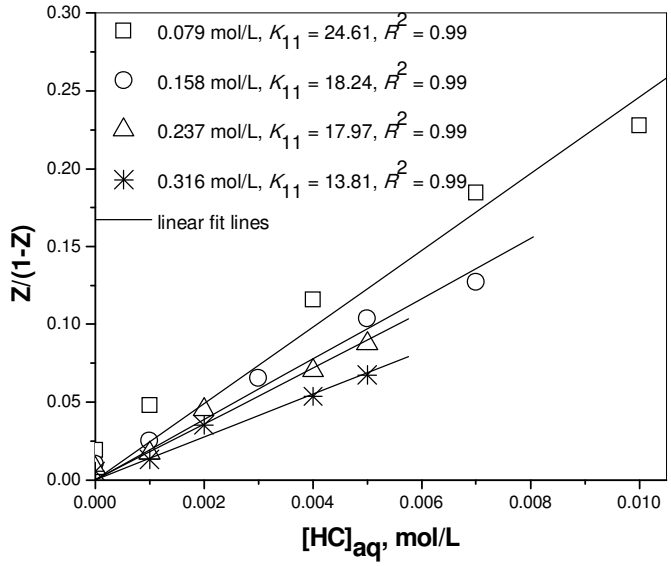


Figure 5.28 Estimation of K_{11} using TDDA in dodecane + oleyl alcohol (1:1 v/v) for isonicotinic acid

The effects of temperature (298, 313, 323 and 333 K) on the extraction of isonicotinic acid with TDDA (10 %v/v) in dodecane + oleyl alcohol (1:1 v/v) are presented in Table 5.28. As the temperature increases, the percentage amount of acid extracted decreases. In this concentration range of acid, the increase in the thermal energy disturbs the interaction between TDDA and acid in the organic phase, thus decreasing the extraction. 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. Estimation of K_{11} for isonicotinic acid at different temperatures is shown in Figure 5.29. The apparent enthalpy (ΔH) and entropy (ΔS) are estimated using calculated values of K_{11} at 298, 313, 323 and 333 K (Figure 5.30). The value of ΔH (-28.27 $kJ \cdot mol^{-1}$) indicates an exothermic reaction. Similarly, the entropy of the reaction is found to be -70.59 $Jmol^{-1}K^{-1}$. Based on the results obtained, it can be said that more the exothermicity of the reaction, the more is the equilibrium sensitivity to temperature.

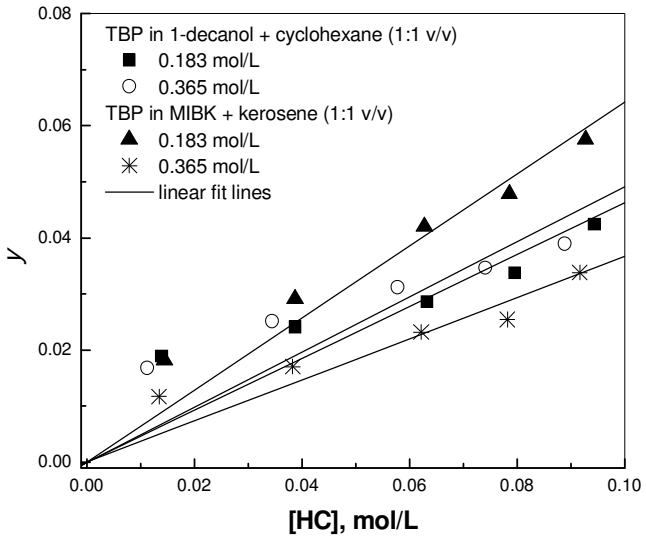


Figure 5.29 Determination of K_{11} for the extraction of nicotinic acid with TBP in 1-decanol + cyclohexane (1:1 v/v) and in MIBK + kerosene (1:1 v/v),

Table 5.28 Effect of temperature on the values of extraction efficiency using TDDA in dodecane + oleyl alcohol (1:1 v/v) for isonicotinic acid reactive extraction

T K	C_{HC} mol·L^{-1}	$\overline{C}_{HC}$ mol·L^{-1}	K_D	$\%E$	Z	pH_{eq}	K_{11}	R^2	SD
298	0.0004	0.0016	4.000	80.00	0.01	4.17	18.24	0.998	0.004
	0.0011	0.0039	3.545	78.00	0.025	3.93			
	0.0033	0.0097	2.939	74.62	0.061	3.68			
	0.0055	0.0145	2.636	72.50	0.092	3.57			
	0.0072	0.0178	2.472	71.20	0.113	3.51			
313	0.0005	0.0015	3.000	75.00	0.009	4.12	10.76	0.994	0.006
	0.0013	0.0037	2.846	74.00	0.023	3.9			
	0.0048	0.0082	1.708	63.08	0.052	3.6			
	0.0078	0.0122	1.564	61.00	0.077	3.49			
	0.0100	0.0150	1.500	60.00	0.095	3.44			
323	0.0008	0.0012	1.500	60.00	0.008	4.01	8.15	0.999	0.003
	0.0020	0.0030	1.500	60.00	0.019	3.8			
	0.0057	0.0073	1.281	56.15	0.046	3.56			
	0.0089	0.0111	1.247	55.50	0.070	3.46			
	0.0117	0.0133	1.137	53.20	0.084	3.4			
333	0.0009	0.0011	1.222	55.00	0.007	3.98	5.35	0.981	0.007
	0.0021	0.0029	1.381	58.00	0.018	3.79			
	0.0063	0.0067	1.063	51.54	0.042	3.54			
	0.0110	0.0090	0.818	45.00	0.057	3.42			
	0.0145	0.0105	0.724	42.00	0.066	3.36			

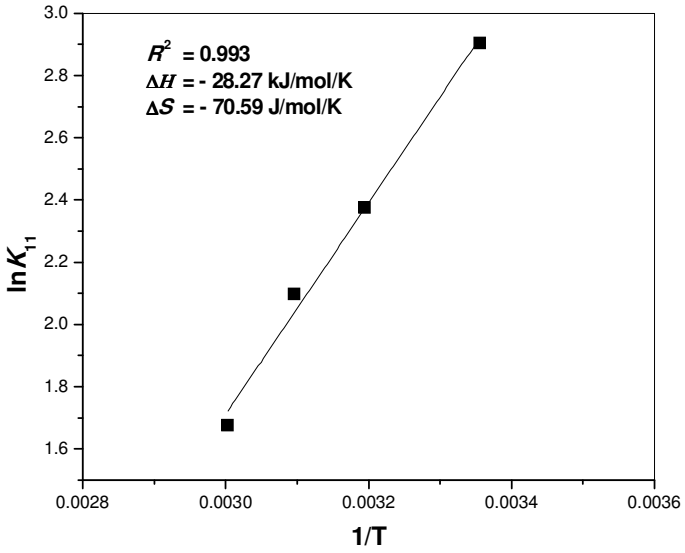


Figure 5.30 Estimation of ΔH and ΔS for isonicotinic acid with TDDA in dodecane + oleyl alcohol (1:1 v/v)

5.1.4 Reactive Extraction of Glycolic Acid

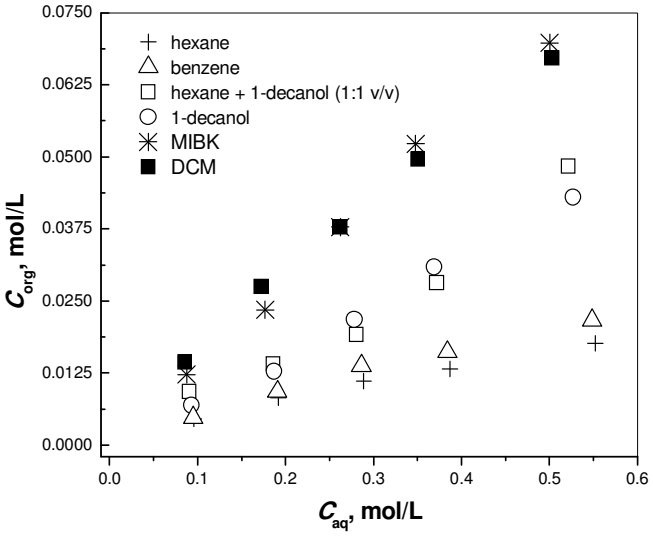
The equilibrium experiments on reactive extraction of glycolic acid are carried out with TBP and TOA dissolved in wide range of diluents such as alkanes (hexane), alcohol (1-decanol), ketone (MIBK), aromatic (benzene), and chloro-hydrocarbon (DCM) and the results are presented in Section 5.1.4.1. Using the equilibrium experimental data and a proposed mathematical model based on mass action law, the values of equilibrium constants (K_E), stoichiometry (m, n), and the individual equilibrium constants (K_{11} and K_{21}) are determined.

In Section 5.1.4.2, the experiments are designed based on central composite orthogonal design method (CCOD) for the reactive extraction of glycolic acid using TOA dissolved in mixture of inert diluent (cyclohexane) and modifier (1-decanol). These experimental data are modeled by employing response surface methodology (RSM) approach. The developed RSM model, then, is used to find the optimum values of operating variables by applying differential evolution (DE) optimization technique.

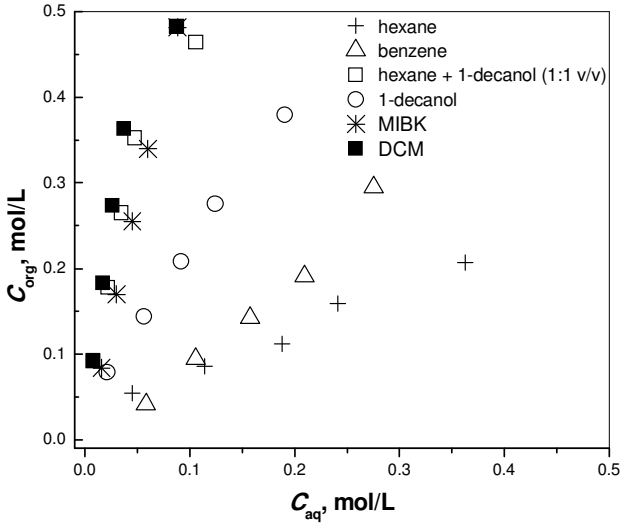
5.1.4.1 Using TBP and TOA in six different diluents

The glycolic acid (acid strength, pK_a = 3.83 and hydrophobicity, log P_a = -1.097) concentration in the aqueous solution (fermentation broth) is found to be less than 10% w/w (Inci, 2002). Therefore, the aqueous solutions of glycolic acid are prepared in the range of 0.10 to 0.57 mol·L^{-1} (0.81 to 4.6% w/w) using de-ionized water. The isotherms are drawn between experimental organic and aqueous phase concentrations of glycolic acid at 298 K (Figures 5.31a for TBP and 5.31b for TOA). It may be noted that there is mostly a linear relationship between aqueous and organic phase concentrations of acid with both extractants (TBP and TOA). This linear behaviour can be explained by Henry's law. The values of K_D are found to decrease with an increase in the concentration of acid.

That is because, at higher acid concentration the competition between acid and water molecule increases. In this study, 1-decanol, MIBK and DCM with higher dipole moment (μ) of 2.62 D, 2.79 D and 1.60 D, respectively, are used as active polar solvents, and hexane (μ = 0.00) and benzene (μ = 0.00) are used as inert diluents. The active diluents (DCM, 1-decanol and MIBK) are shown better efficiencies than those of inactive ones (hexane and benzene) with both the extractants (TBP and TOA) as shown in Figure 5.31. The comparison between the values of K_D for different diluents with TBP and TOA is shown in Figures 5.32a and 5.32b, respectively, at a constant concentration of glycolic acid (0.1 mol·L^{-1}). The extraction power of TBP/diluent and TOA/diluent system in terms K_D increases in the order of DCM ≥ MIBK > 1-decanol > hexane + 1-decanol (1:1 v/v) ≥ benzene ≥ hexane, and DCM ≥ 1-decanol > MIBK > hexane + 1-decanol (1:1 v/v) > benzene > hexane, respectively. The active diluents facilitate the extraction process by solvating the acid molecules with an effective competition with the water molecules that attract the acid molecules at the interface of aqueous and organic phase, and also by the specific interactions of the diluent with the complex by making H-bond (Kertes and King, 1986). The active diluents (DCM, 1-decanol and MIBK) are having active groups such as a chlorinated (both proton acceptor and donor) group, –OH (proton donor) group, and =CO (proton acceptor) group, which enhance the extracting capability of extractants. On the other hand, non-polar diluents do not affect the extraction process significantly. The degrees of extraction are found to be higher for DCM because it affects the diluent-complex aggregation more instantaneously through H-bonding and ion pair formation. This occurrence of DCM is confirmed by maximum value of loading ratios in case of TOA. Therefore, the maximum values of K_D and E are found with TOA in DCM (12.02 and 92.32%, respectively) for the extraction of glycolic acid.

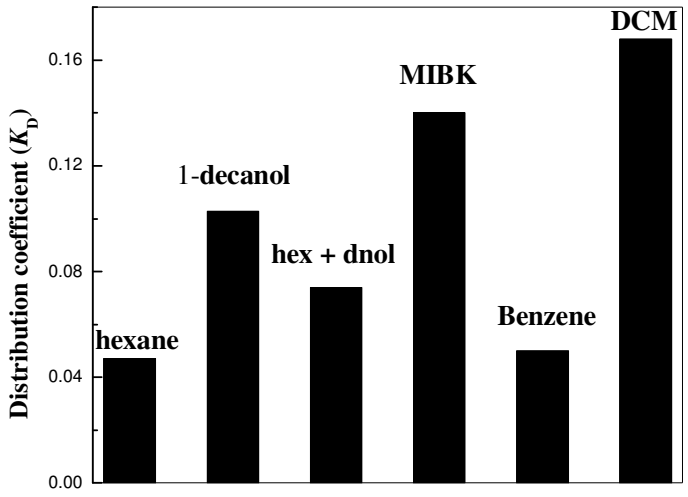


(a)

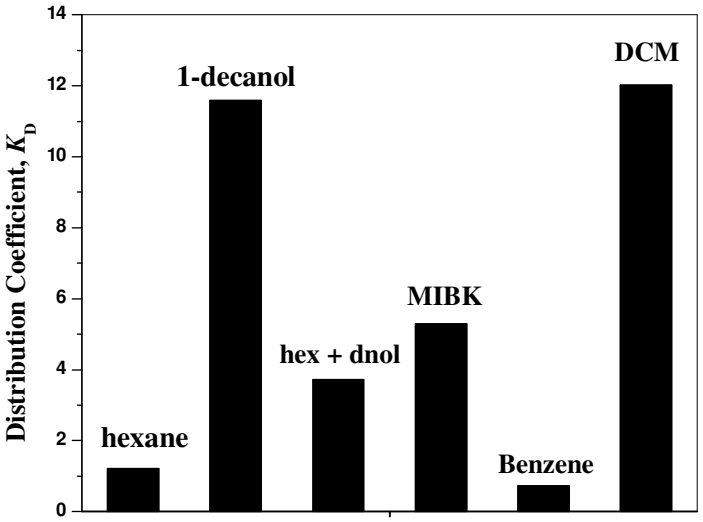


(b)

Figure 5.31 Equilibrium isotherms of glycolic acid with (a) TBP and (b) TOA in different diluents



(a)



(b)

Figure 5.32 Comparison of K_D at 0.1 mol·L^{-1} of glycolic acid with (a) TBP and (b) TOA in different diluents

In the reactive extraction of glycolic acid using TBP, the values of *Z* are found to be very less than 0.5 (0.008 to 0.031 for hexane, 0.016 to 0.084 for 1-decanol, 0.012 to 0.075 for hexane + 1-decanol (1:1 v/v), 0.021 to 0.122 for MIBK, 0.008 to 0.038 for benzene, and 0.025 to 0.117 for DCM) implying the formation of 1:1 acid-TBP solvates in the extract phase. The reactive extraction of glycolic acid occurs by solvating alkoxy groups in TBP. The studies also reported that the solvation number of the aliphatic carboxylic acids is same as the number (s) of carboxyl groups present on the acid for TBP. Since TBP extract the acid molecules mostly by solvation and hence the solvation number in the reactive extraction of glycolic acid using TBP can be considered to be one (Sekine, 1992; Kumar and Babu, 2009). This fact also confirms a stoichiometric 1:1 association between the individual phosphoryl group and individual acid group. The values of *Z* in the range of 0.096 to 0.361 for hexane suggest no overloading of acid on TOA. The values of *Z* greater than 0.5 for all other diluents (0.161 to 0.81 for 1-decanol, 0.137 to 0.662 for hexane + 1-decanol (1:1 v/v), 0.147 to 0.84 for MIBK, 0.073 to 0.514 for benzene, and 0.161 to 0.842 for DCM) suggest the overloading of acid on TOA and show possibility of simultaneous formation of 1:1 and 2:1 types of complexes between acid and TOA molecules. The stability of the complexes in the organic phase are decided by the ammonium salt formation of acid with the ion pair association of alkylammonium cation and the acid radical which is a acid-base-type reaction in case of extraction by TOA. The power of associating the proton is comparatively higher for TOA and depends on the characteristics of the diluent used. TOA extracted the acid molecules from the aqueous solution forming two types of complexes (1:1 and 2:1) where as there is formation of only 1:1 type of complexes with TBP. Therefore, the extraction of acid using TOA in different diluents is found to be much better than that of using TBP in different diluents.

Now, based on the values of Z, the values of number of reacting acid molecule (m) per extractant molecule and the equilibrium constants [(K_E (overall) and K_{11} and K_{21} (individual)] are estimated using Eqs. 4.19 and 4.29. The error between the experimental and predicted values of K_D is minimized for the determination of the values of m and K_E using Eq. 4.20. The estimated values are shown in Table 5.29. The estimated values of m are found to be close to one [0.80 for hexane, 0.92 for 1-decanol, 1.11 for hexane + 1-decanol (1:1 v/v), 1.06 for MIBK, 0.89 for benzene, 0.91 for DCM] with TBP and this shows that there is, mainly, formation of 1:1 acid-TBP complex in the organic phase. But the values of m for inactive diluents (0.80 for hexane and 0.89 for benzene) indicate more than one solvation number of TBP may also possible. The value of m (0.75) with TOA in hexane also suggest that there may be the possibility of a few 1:2 complex formation between acid and TOA. The estimated stoichiometric coefficients (1.19, 1.37 and 1.42 for DCM, MIBK and benzene, respectively) with TOA conclude that there are simultaneous formations of both types of 1:1 and 2:1 complexes in the extract phase.

The structures of acid-extractant complex in diluents were determined by Yerger and Barrow in 1955. They proposed that the proton (H^+) in the –COOH group of the first carboxylic acid molecule interacts directly with the extractant to form an ion pair ($OHCH_2COO^-$…H-S, Figure 5.33a) and hence the 1:1 complex. Then the -COOH group of another acid molecule combines with the conjugated =CO to form H-bond which results in 2:1 acid-extractant complex (=CO…. H-$OOCCH_2OH$, Figure 5.33b).

The highest value of K_E (56.01) in case of DCM with TOA shows it to be the best diluent-extractant system for the extraction of glycolic acid from aqueous solution. On the basis of estimated values of m, the individual equilibrium constants (K_{11} and K_{21}) for 1:1 and 2:1 complexes, respectively, are determined for TOA. The values of K_{11} and K_{21} are estimated by minimizing the error between the experimental and predicted values of

acid concentration in the organic phase (Eq. 4.31) and given in Table 5.29. The values of K_D using model Eq. 4.19 are predicted, and found to be comparable with the experimentally determined values of K_D (Figures 5.34a for TBP and 5.34b for TOA).

Table 5.29 Values of stoichiometry (*m, n*), equilibrium constants (K_E, K_{11}, K_{21}) with *rmsd* for the glycolic acid reactive extraction with TBP and TOA in different diluents

Diluents	TBP (0.573 mol·L^{-1})				TOA (0.573 mol·L^{-1})						
	m	*n*	K_E	*rmsd*	*m*	*n*	K_E	*rmsd*	K_{11}	K_{21}	*rmsd*
Hexane	0.80	1	0.07	0.001	0.75	1	1.49	0.073	1.47	-	0.224
Benzene	0.89	1	0.08	0.002	1.42	1	3.23	0.055	0.98	3.47	0.052
Hexane + 1-decanol (1:1 v/v)	1.11	1	0.15	0.004	0.94	1	6.79	0.236	7.75	-	0.263
1-Decanol	0.92	1	0.15	0.012	1.01	1	27.20	0.611	26.52	-	0.613
MIBK	1.06	1	0.28	0.005	1.37	1	38.84	0.255	9.67	8.44	0.047
DCM	0.91	1	0.28	0.002	1.19	1	56.01	0.272	33.15	1.75	1.178

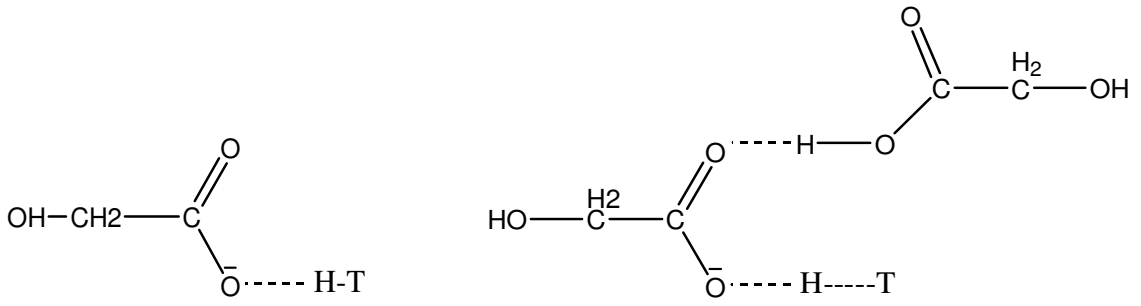
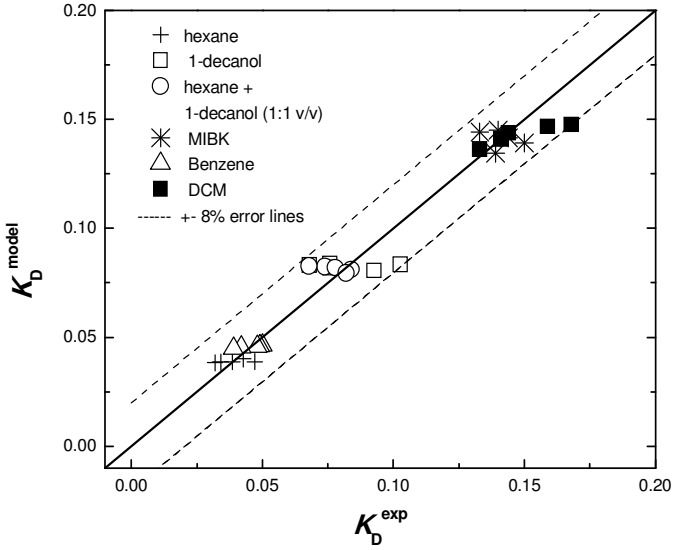
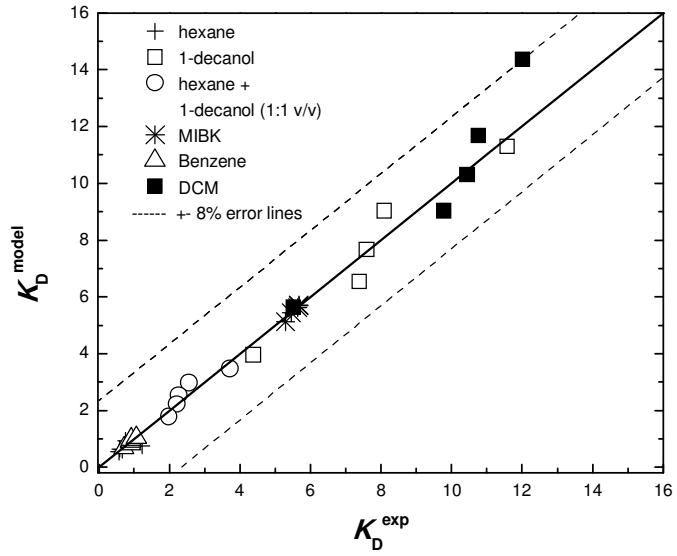


Figure 5.33 Representation of formation of (a) 1:1 and (b) 2:1 acid-extractant complexes in the organic phase of glycolic acid reactive extraction



(a)



(b)

Figure 5.34 The model predicted (Eq. 4.19) versus experimental values of K_D of glycolic acid with (a) TBP and (b) TOA in different diluents

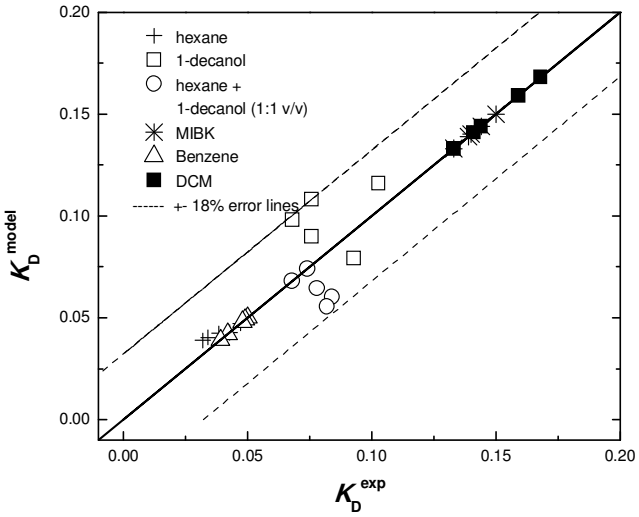
The LSER model is also applied to quantify the effect of diluent on K_D for the reactive extraction of glycolic acid. The values of the solvatochromic parameters (π^*, δ, β and α) of the diluents used in this study are given in Table 4.1. For the estimation of model parameters, least square regression is used to minimize the error between the experimental and model predicted values of $\log_{10} K_D$. The estimated values of LSER model parameters are presented in Table 5.30 with the values of coefficient of determination (R^2) and standard error (SE). The experimental values of K_D are showing good correlation to the LSER model predicted values of K_D with $R^2 > 0.9$ and maximum value of $SE = 0.21$ (Figures 5.35a and 5.35b).

The higher values of K_D in case of 1-decanol, MIBK and DCM can also be explained on the basis of the values of the solvatochromic parameters (Table 4.1). π* (measure of dipolarity or polarizability) value is lowest for hexane (-0.08) and highest for DCM (0.82), which shows that DCM has greater ability to stabilize a charge or a dipole by its own dielectric effect. α value is higher for 1-decanol ($\alpha = 0.33$) and DCM ($\alpha = 0.30$) than those of other diluents which means that the ability of 1-decanol and DCM to donate a proton in a solvent-to-solute hydrogen bond is higher. Therefore, 1-decanol and DCM can promote more 1:1 complex formation. β values for MIBK and 1-decanol are 0.52 and 0.45, respectively and this shows their ability to accept a proton or donate an electron pair in a solute-to-solvent interaction through H-bond.

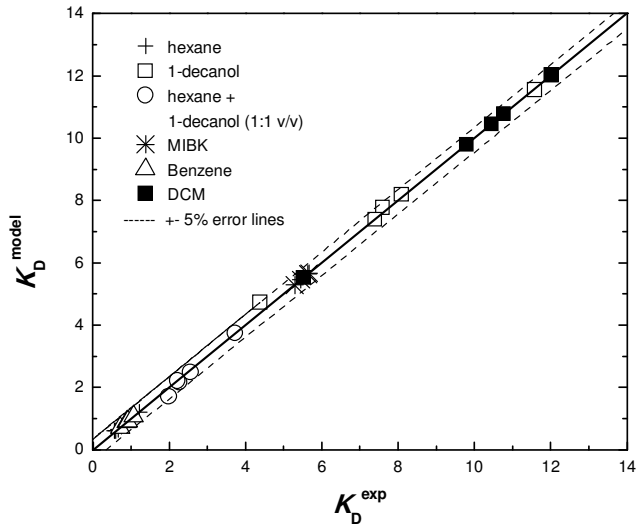
The power of associating the proton is comparatively higher for TOA than TBP. TOA extracts glycolic acid molecules from the aqueous solution forming two types of complexes such as 1:1 and 2:1 as there is formation of only 1:1 complexes with TBP. Therefore, the extraction of acid using TOA in different diluents is found to be better than that by using TBP in different diluents.

Table 5.30 Values of the LSER model parameters R^2 and *SE* for the glycolic acid reactive extraction with TBP and TOA in different diluents

C_{in} **mol·L^{-1}**	$\log_{10} K_D^0$	***a***	***b***	***s***	***d***	R^2	***SE***
TBP (0.573 mol·L^{-1})							
0.10	-1.26132	0.30022	-0.21965	0.81410	-0.61180	0.99	0.0002
0.20	-1.30291	0.28291	-0.19213	0.82379	-0.57504	0.99	0.0002
0.30	-1.30449	0.08071	-0.17162	0.86544	-0.58666	0.96	0.1022
0.40	-1.31633	-0.01670	-0.25834	0.97846	-0.62534	0.91	0.1775
0.57	-1.33032	-0.06824	-0.34145	1.01147	-0.63397	0.88	0.2087
TOA (0.573 mol·L^{-1})							
0.01	0.16987	1.74354	-0.23693	1.059619	-0.86487	0.99	0.0040
0.20	-0.01642	1.36080	-0.04652	1.25401	-0.61123	0.99	0.0130
0.30	-0.11140	1.33863	0.07349	1.31663	-0.54390	0.99	0.0232
0.40	-0.07768	1.24849	0.04938	1.28099	-0.56444	0.99	0.0007
0.57	-0.12084	0.61900	0.32124	1.11669	-0.48461	0.99	0.0813



(a)



(b)

Figure 5.35 The LSER model predicted (Eq. 4.41) versus experimental values of K_D of glycolic acid reactive extraction with (a) TBP and (b) TOA in different diluents

5.1.4.2 Using TOA in diluent mixtures (RSM modeling and optimization study)

The effective choice and optimum combinations of process parameters are essential to maximize the recovery of glycolic acid from the aqueous solution. In this study, the experiments are designed for reactive extraction of glycolic acid using central composite orthogonal design (CCOD) method, and modeled using response surface methodology (RSM) to relate a dependent variable (response) as a function of independent variables (design variables or factors). The critical and effective design variables are chosen as initial glycolic acid concentration (C_{in}), initial TOA composition ($[\bar{S}]_{in}$), modifier (1-decanol) composition (C_M) and equilibrium temperature (τ). The degree of extraction is considered as the dependent variable (response) of this design.

The actual values of design variables (C_{in}, $[\bar{S}]_{in}$, C_M and τ) are normalized as x_i (dimensionless) according to the following equations (Eqs. 5.1 to 5.4) and values are presented in Table 5.31.

$$x_1 = \frac{C_{in} - 0.1}{0.05} \tag{5.1}$$

$$x_2 = \frac{[\bar{S}]_{in} - 20}{5} \tag{5.2}$$

$$x_3 = \frac{C_M - 45}{20} \tag{5.3}$$

$$x_4 = \frac{\tau - 37}{10} \tag{5.4}$$

The experiments are designed considering (i) 2^k factorial CCOD points; (ii) n_c central points (coded as zero value); (iii) two axial points from the central design point at a distance of $\pm\alpha^*$; and (iv) $2k$ star points. Hence, the total number of experimental design points are become as, $n = 2^k + 2k + n_c$. With $k = 4$, $n_c = 6$ and $\alpha^* = \pm 1.414$ for CCOD, a

total of 30 batch experiments are carried out. Each experimental run represents a unique combination of factor's level. The degree of extraction is determined for each experimental run using Eq. 3.4 and presented in Table 5.32. These experimental data are regressed to obtain regression coefficients of the RSM model. The significance of each regression coefficient is determined by *t*-test and *F*-test values. Only the significant contribution of each design variable on the response function is considered. The empirical model in terms of actual variables is obtained as follows:

$$\begin{aligned} Y = & -11.342 - 294.875C_{in} + 4.5186[\bar{S}]_{in} + 1.8831C_M - 0.4749\tau \\ & - 0.0736([\bar{S}]_{in})^2 - 9.675\times10^{-3}C_M^2 + 4.652C_{in}[\bar{S}]_{in} \\ & + 2.807C_{in}C_M - 0.02119[\bar{S}]_{in}C_M \end{aligned} \tag{5.5}$$

$$\text{Subjected to: } \begin{aligned} & 0.0293 \le C_{in} \le 0.1707\,\text{mol/L} \\ & 12.93 \le [\bar{S}]_{in} \le 27.07(\%\text{v/v}) \\ & 16.72 \le C_M 73.28(\%\text{v/v}) \\ & 22.86 \le \tau \le 51.14^{o}\text{C} \end{aligned} \tag{5.6}$$

In Table 5.33, the ANOVA results are presented in terms of *DF*, *SS*, *MS*, *F*-value, *P*-value and R^2. An *F*-value (124.54) greater than unity, *P*-value (6.17×10^{-16}) near about zero, and the value of R^2 equal to 0.9794 indicate better fit of the RSM regression model (Figure 5.36).

The effect of design variables (C_{in}, $[\bar{S}]_{in}$, C_M and τ) on the degree of extraction are determined by obtaining projections of the response surface plots on the two dimensional planes for known factor values (Figures 5.37 to 5.42). In order to express the effect of initial glycolic acid concentration and TOA composition on the degree of extraction at fixed C_M (= 45 %v/v) and τ (= 37°C), Figure 5.37 is drawn. This figure also indicates the effect of interaction between both the variables (C_{in} and $[\bar{S}]_{in}$).

Table 5.31 Design variables and their coded & actual values for glycolic acid reactive extraction

Actual design variables	Coded variables	Coded levels				
		$-\alpha$	-1	0	+1	α*
C_{in} (mol·L^{-1})	x_1	0.0293	0.05	0.1	0.15	0.1707
$[\bar{S}]_{in}$ (%v/v)	x_2	12.93	15	20	25	27.07
C_M (%v/v)	x_3	16.72	25	45	65	73.28
τ (^{o}C)	x_4	22.86	27	37	47	51.14

* α = 1.414 (star point for CCOD); design variables, k = 4

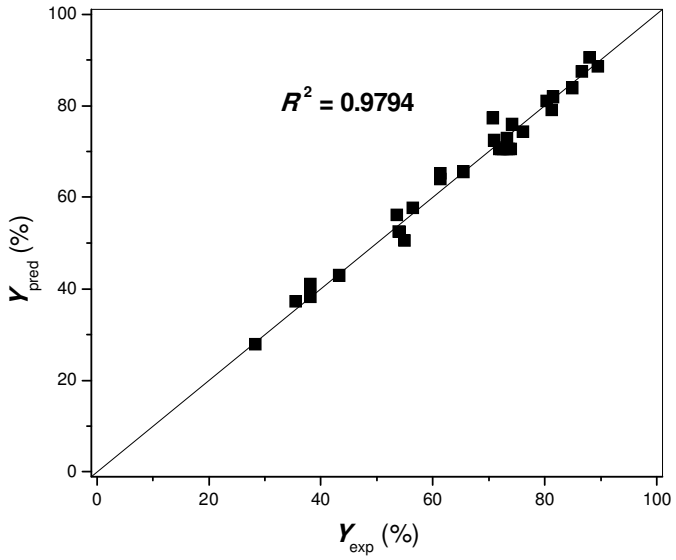


Figure 5.36 RSM model predicted versus experimental response of glycolic acid reactive extraction

Table 5.32 Experimental design points and response of glycolic acid reactive extraction

Run number and type		Design variables/factors								Response
		C_{in}	x_1	$[\bar{S}]_{in}$	x_2	C_M	x_3	τ	x_4	$\%Y$
1	O1	0.15	1	25	1	65	1	47	1	81.27
2	O2	0.05	-1	15	-1	65	1	47	1	76.12
3	O3	0.15	1	15	-1	25	-1	47	1	28.37
4	O4	0.05	-1	25	1	25	-1	47	1	53.65
5	O5	0.15	1	15	-1	65	1	27	-1	81.50
6	O6	0.05	-1	25	1	65	1	27	-1	88.00
7	O7	0.15	1	25	1	25	-1	27	-1	54.00
8	O8	0.05	-1	15	-1	25	-1	27	-1	55.00
9	O9	0.15	1	15	-1	65	1	47	1	70.97
10	O10	0.05	-1	25	1	65	1	47	1	80.34
11	O11	0.15	1	25	1	25	-1	47	1	43.35
12	O12	0.05	-1	15	-1	25	-1	47	1	38.20
13	O13	0.15	1	25	1	65	1	27	-1	89.50
14	O14	0.05	-1	15	-1	65	1	27	-1	85.00
15	O15	0.15	1	15	-1	25	-1	27	-1	35.50
16	O16	0.05	-1	25	1	25	-1	27	-1	65.50
17	S1	0.1707	α^*	20	0	45	0	37	0	61.33
18	S2	0.0293	$-\alpha^*$	20	0	45	0	37	0	73.64
19	S3	0.1	0	27.07	α^*	45	0	37	0	73.31
20	S4	0.1	0	12.93	$-\alpha^*$	45	0	37	0	56.46
21	S5	0.1	0	20	0	73.28	α^*	37	0	86.66
22	S6	0.1	0	20	0	16.72	$-\alpha^*$	37	0	38.20
23	S7	0.1	0	20	0	45	0	51.14	α^*	61.38
24	S8	0.1	0	20	0	45	0	22.86	$-\alpha^*$	70.75
25	C1	0.1	0	20	0	45	0	37	0	74.02
26	C2	0.1	0	20	0	45	0	37	0	71.91
27	C3	0.1	0	20	0	45	0	37	0	73.67
28	C4	0.1	0	20	0	45	0	37	0	73.31
29	C5	0.1	0	20	0	45	0	37	0	72.61
30	C6	0.1	0	20	0	45	0	37	0	72.26

O = orthogonal design points, C = center points, S = star points, −1 = low value, 0 = center value, +1 = high value, +/− α^* = star point value

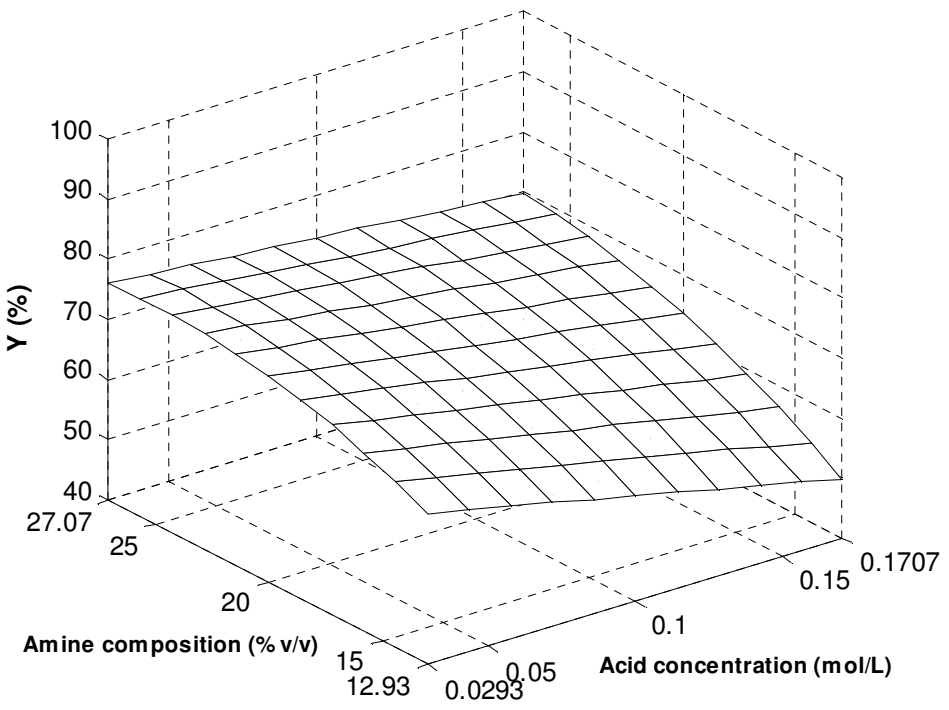
Table 5.33 ANOVA results of RSM model for glycolic acid reactive extraction

Source	*DF*	*SS*	*MS*	*F*-value	*P*-value	R^2
Model	8	7857.947	982.24	124.54	6.17×10^{-16}	0.9794
Error	21	165.633	7.887			
Total	29	8023.581	-			

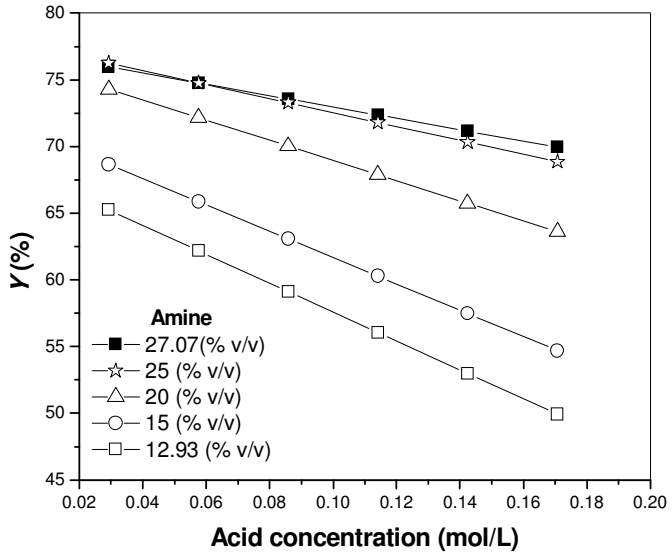
The degree of extraction decreases with an increase in the acid concentration at constant amine composition (Figure 5.37). At higher acid concentration, the competition between the acid molecules to get attached with the extractant molecules becomes more and hence less amount of acid molecule can be extracted by the amine molecule. The degree of extraction is increased to a maximum value of 76.25 % with the increase in the TOA composition from 12.93 %v/v to 27.07 %v/v at lower acid concentration (0.0293 mol·L^{-1}). It shows that sufficient numbers of amine molecules are available in the organic phase to form the complex with acid molecules at a particular acid concentration. Therefore, greater values of degrees of extraction are achieved at higher amine composition. It is also observed that the slope of the isothermal line becomes less with an increase in the amine composition. This statement depicts that an increase in the amine composition up to a certain limit will affect the degrees of extraction significantly.

Figure 5.38 elaborates the variation of degree of extraction as a function of acid concentration at different modifier composition keeping the other two factors at their constant values ($[\bar{S}]_{in}$ = 20 %v/v and τ = 37°C). The degrees of extraction of glycolic acid are found to increase with an increase in the concentration of 1-decanol (modifier) and reaches to a constant value at higher concentration of 1-decanol. This is because an increase in the modifier (1-decanol) composition facilitates the solubility of acid-amine complexes in the organic phase.

The effect of C_M on the degree of extraction with different values of $[\bar{S}]_{in}$, is shown in Figure 5.39 at C_{in} = 0.1 mol·L^{-1} and τ = 37°C. It is found that the modifier has a prominent effect on the response. This figure indicates that with increase in both values of $[\bar{S}]_{in}$ and C_M, the degree of extraction increases to a maximum.

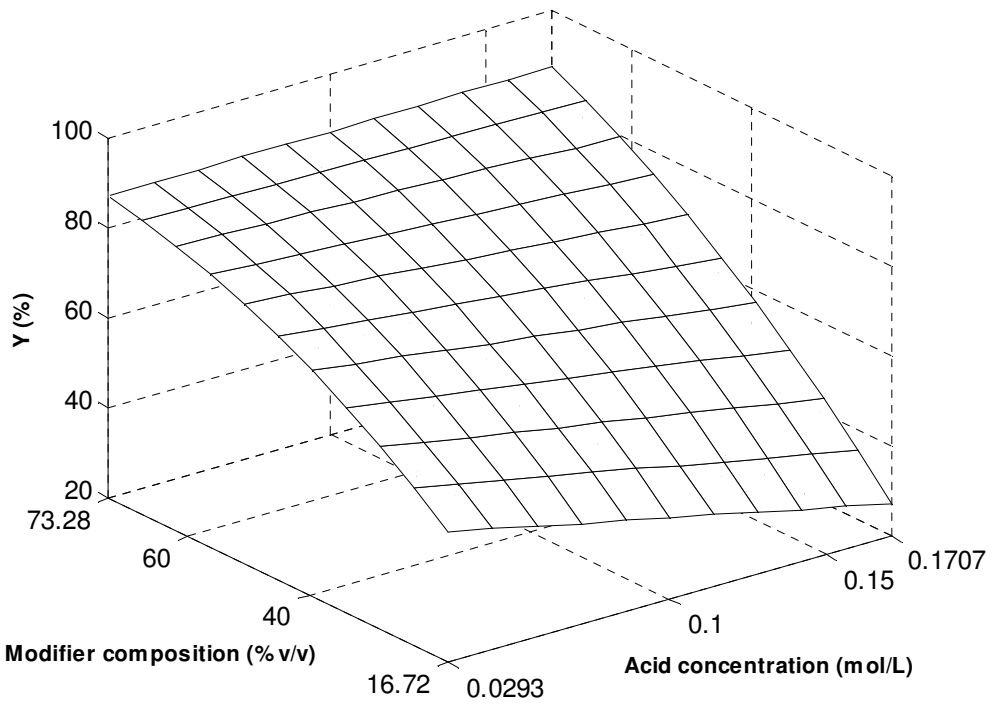


(a)

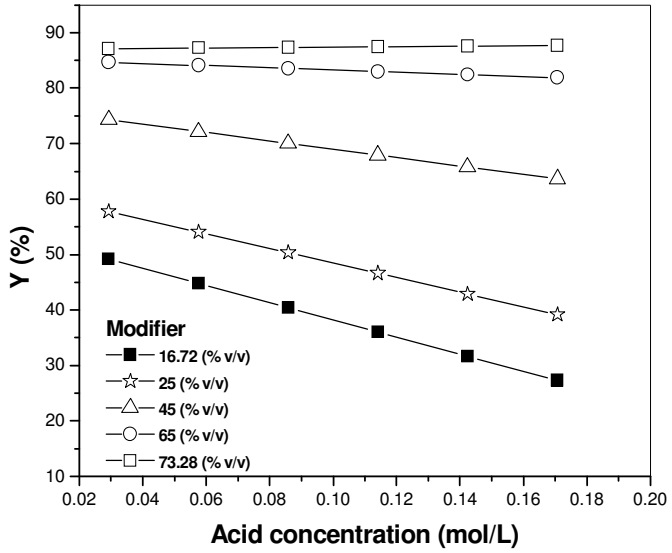


(b)

Figure 5.37 The effect of C_{in} and $[\bar{S}]_{in}$ on the Y (%) for the reactive extraction of glycolic acid (C_M = 45 %v/v, τ = 37°C)

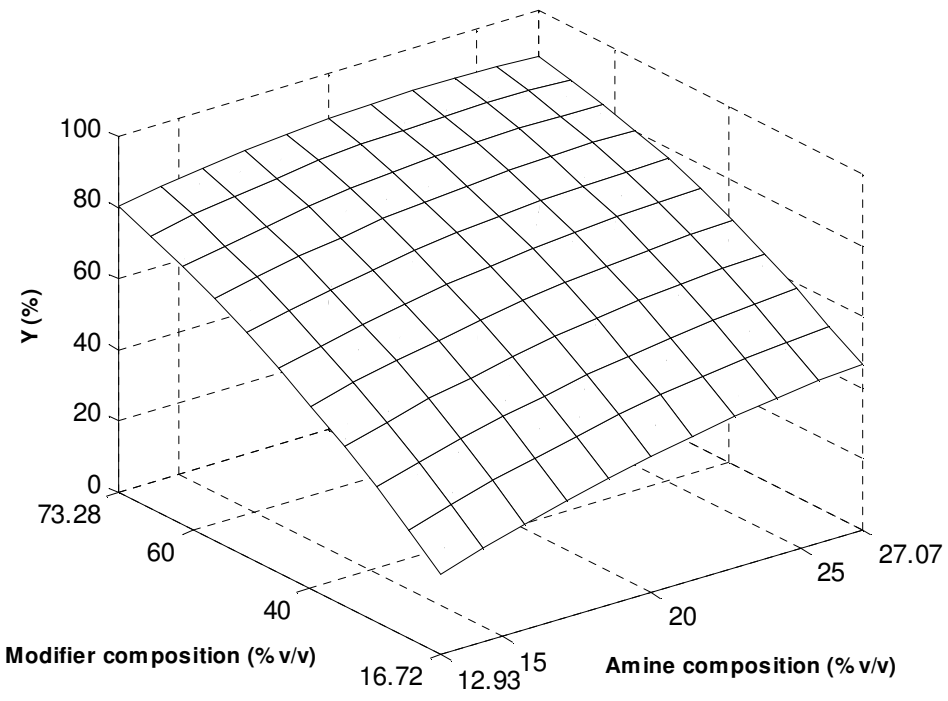


(a)

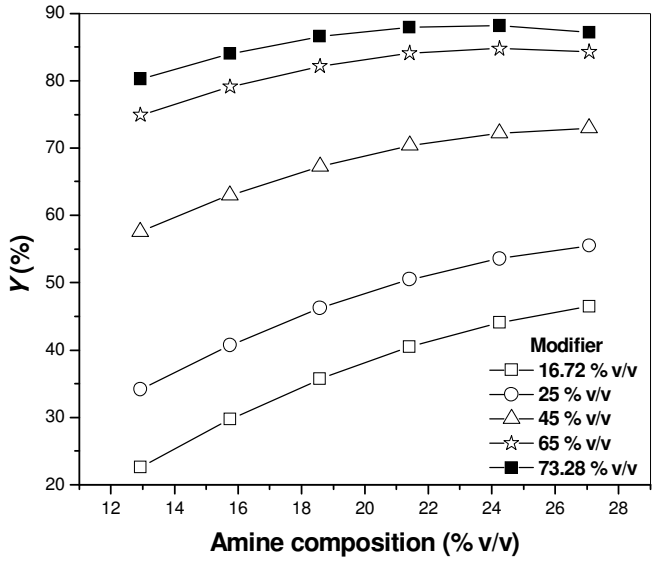


(b)

Figure 5.38 The effect of C_{in} and C_M on the Y (%) for the reactive extraction of glycolic acid ($[\bar{S}]_{in}$ = 20 %v/v, τ = 37°C)



(a)



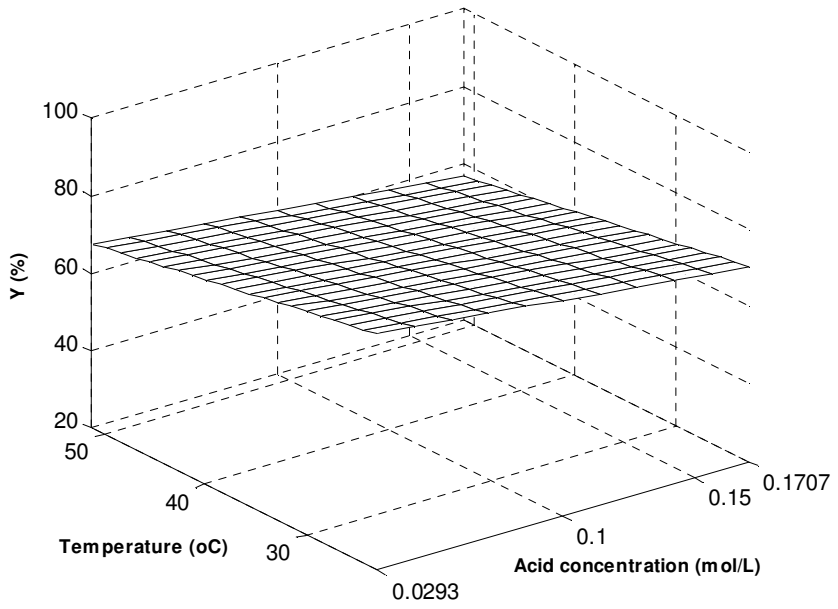
(b)

Figure 5.39 The effect of $[\bar{S}]_{in}$ and C_M on the *Y* (%) for the reactive extraction of glycolic acid (C_{in} = 0.1 mol·L^{-1}, τ = 37^{o}C)

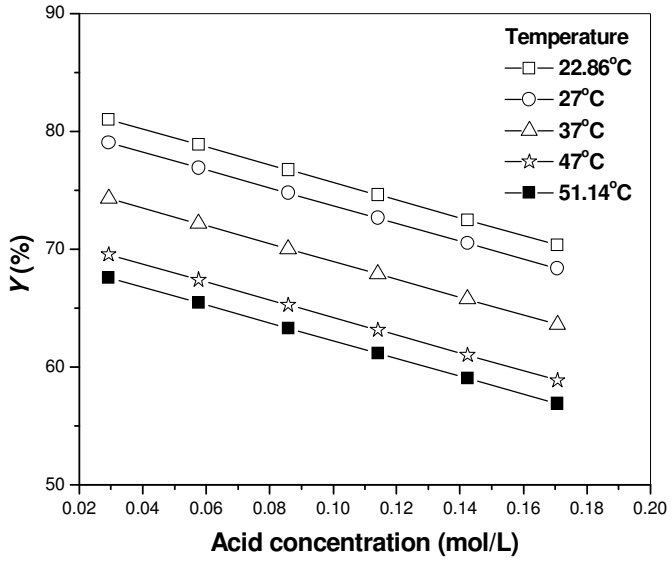
The variation in the values of degree of extraction at different temperatures are presented (i) as a function of acid concentration at constant $[\bar{S}]_{in}$ (20 %v/v) and C_M (45 %v/v), (ii) as a function of TOA composition at constant C_{in} (0.1 mol·L^{-1}) and C_M (45 %v/v), and (iii) as a function of C_M at constant C_{in} (0.1 mol·L^{-1}) and $[\bar{S}]_{in}$ (20 %v/v) in Figures 5.40, 5.41 and 5.42, respectively. These figures show that the distribution of acid in the organic phase decreases sharply with an increase in the equilibrium temperature facilitating more back-extraction of the acid molecule from the organic to aqueous phase. At lower temperatures, the formation of the acid-amine complex will make the system more ordered decreasing the entropy of the system and randomness. However, an improved separation of phases is observed at higher temperatures.

Figure 5.43 describes the effect of one of the parameters as coded variable keeping other constant on the degree of extraction. The values of objective function (Y) decrease with an increase in the values of x_1 and x_4, and increase with an increase in the values of x_2 and x_3. It means that there is a trade-off or balance between the values of x_i's which will optimize the response function. So, there is a need to optimize the process parameters of the reactive extraction process. Differential evolution (DE) technique of optimization is used to find the optimum values of design variables. For the present problem, the values of DE key parameters are taken as $D = 4$, $NP = 40$, $CR = 0.7$, and $F = 0.8$. In the Figures 5.44a to 5.44d, the evaluated fitness function values are plotted within the domain of the design parameters (x_1 to x_4). These figures show the convergence of the fitness function to its optimum value. Figure 5.45 depicts the values of the predicted Y after each generation. As it can be seen that the best value improves rapidly in the early generations, and almost after 6th generation, the value of Y becomes constant. Finally, DE has converged to the optimal value of Y after 15 generations only. At the optimum conditions (C_{in} = 0.1707 mol·L^{-1}, $[\bar{S}]_{in}$ = 22.31 %v/v, C_M =73.28 %v/v and $\tau = 23 \pm 0.5$

^{o}C), the predicted and experimental values of degrees of extraction are found to be 94.95% and 91.83%, respectively (Table 5.34).

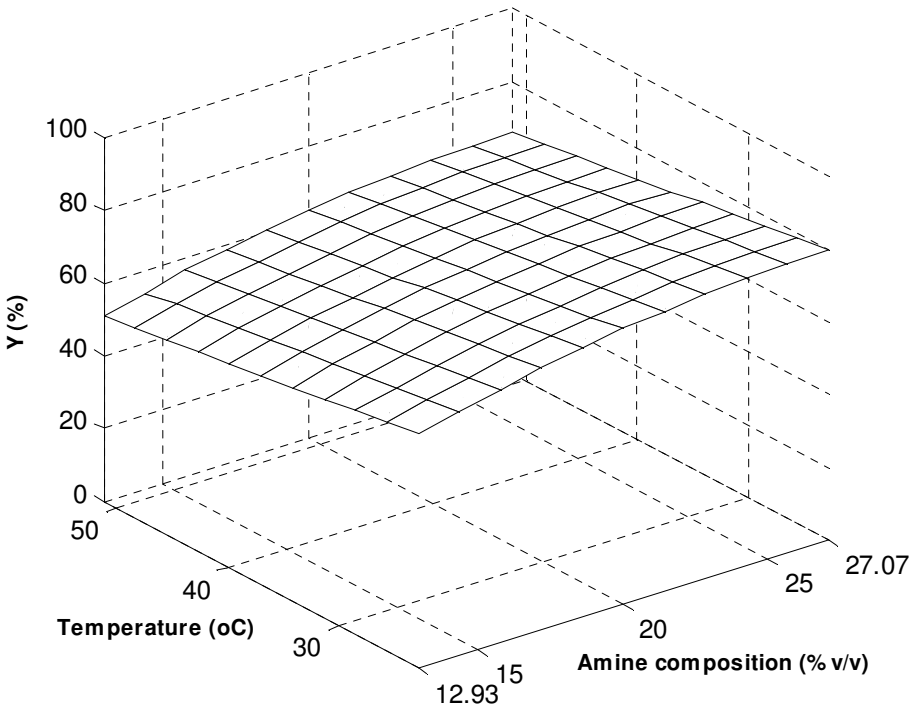


(a)

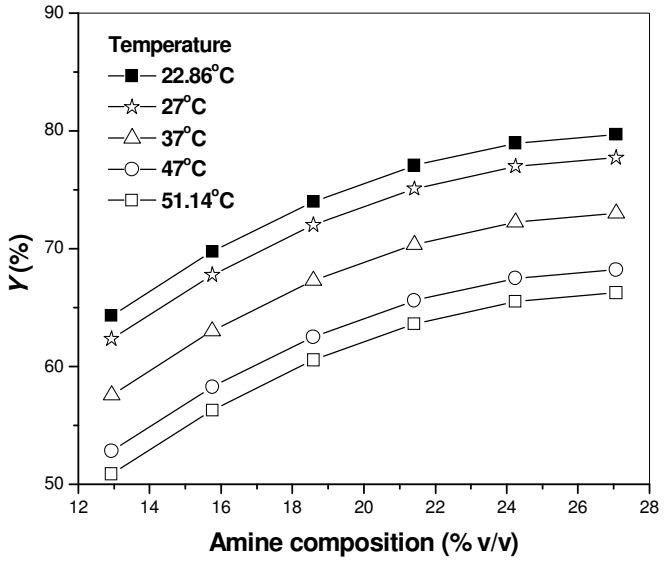


(b)

Figure 5.40 The effect of C_{in} and τ on the Y (%) for the reactive extraction of glycolic acid ($[\bar{S}]_{in}$ = 20 %v/v, C_M = 45 %v/v)

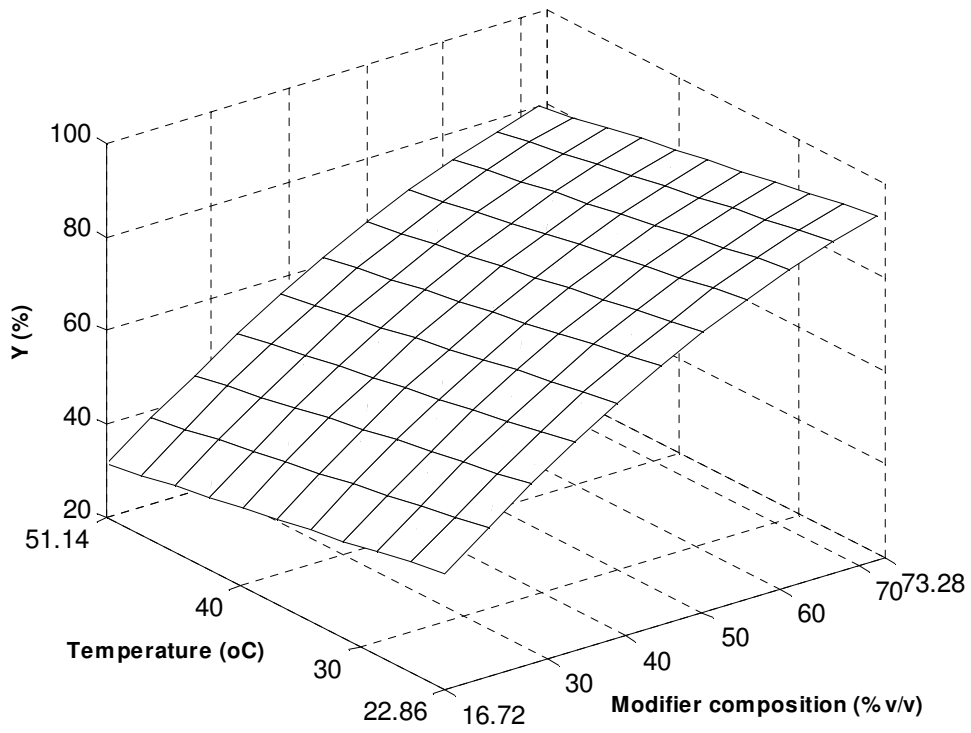


(a)

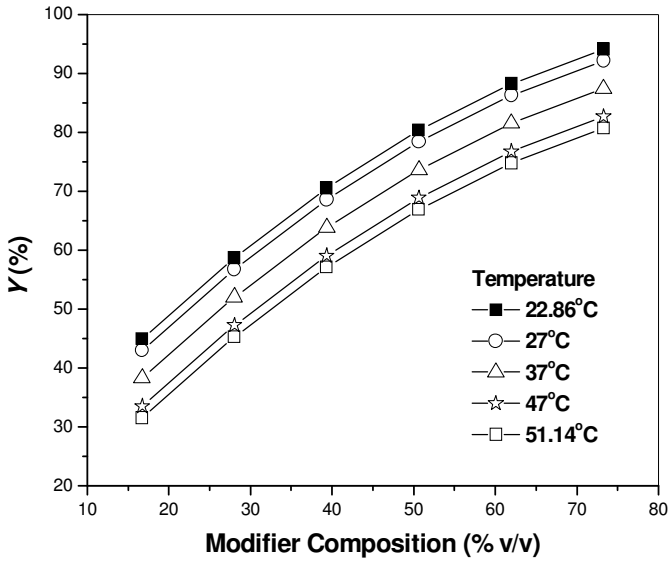


(b)

Figure 5.41 The effect of $[\bar{S}]_{in}$ and τ on the Y (%) for the reactive extraction of glycolic acid (C_{in} = 0.1 mol·L^{-1}, C_M = 45 %v/v)



(a)



(b)

Figure 5.42 The effect of C_M and τ on the Y (%) for the reactive extraction of glycolic acid (C_{in} = 0.1 mol·L^{-1}, $[\bar{S}]_{in}$ = 20 %v/v)

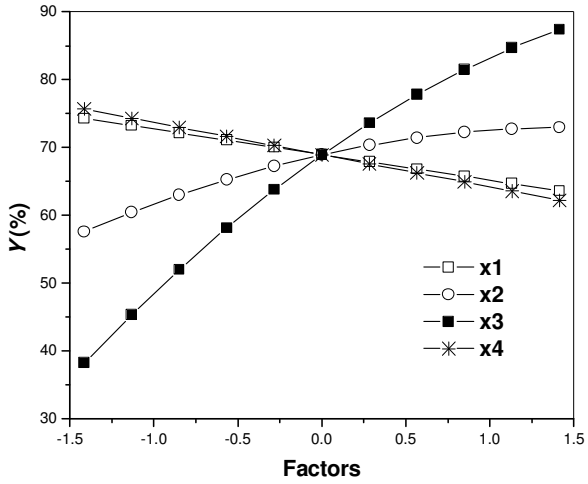
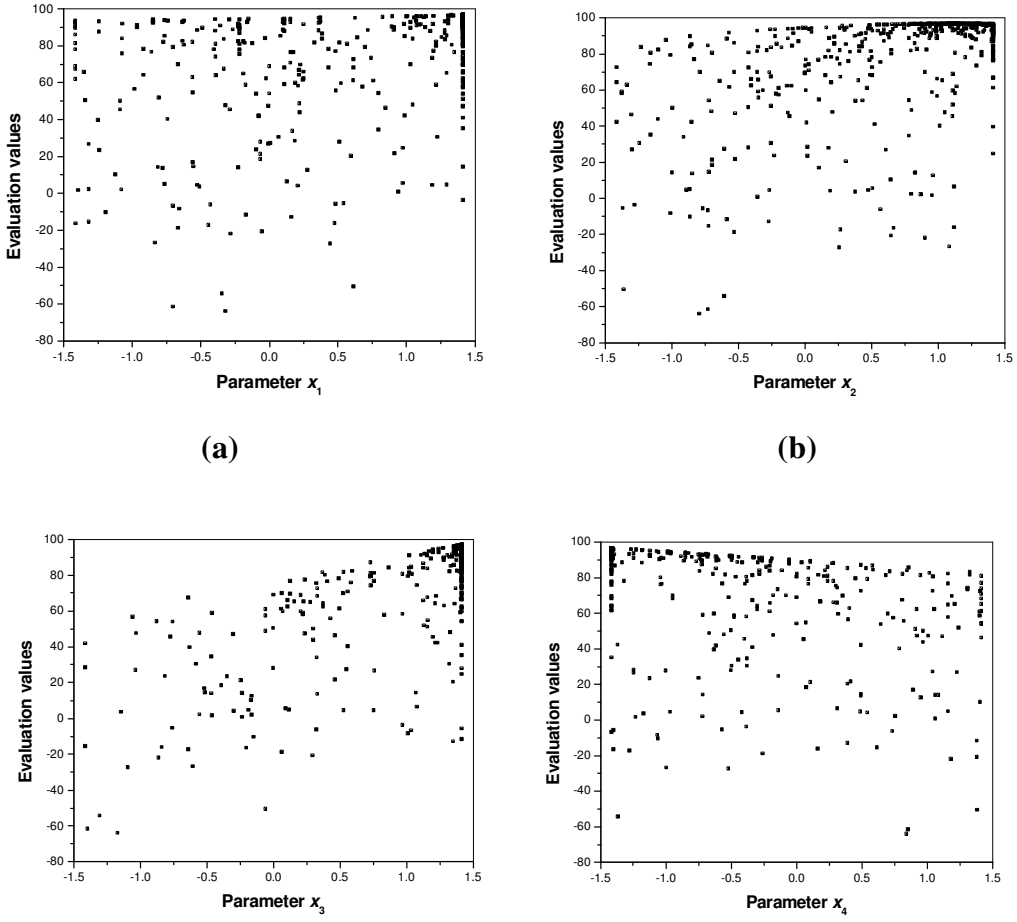


Figure 5.43 Effect of various factors on the degree of extraction of glycolic acid reactive extraction



(a) **(b)**

(c) **(d)**

Figure 5.44 Evaluation values of the fitness function in terms of coded variables obtained by DE for glycolic acid reactive extraction

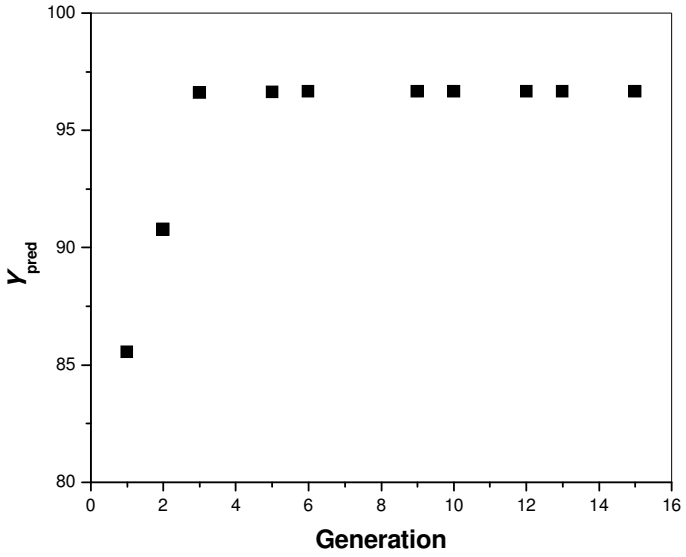


Figure 5.45 Fitness values against number of generations according to RSM-DE for glycolic acid reactive extraction

Table 5.34 Optimum values of design variables for glycolic acid reactive extraction

Factors (actual design variables)				**Response**	
C_{in}, mol·L^{-1}	$[\bar{S}]_{in}$, %v/v	C_M, %v/v	τ, ^oC	Y_{pred} (%)	Y_{exp} (%)
0.1707	22.31	73.28	23 ± 0.5	94.95	91.83

5.1.5 Reactive Extraction of Itaconic Acid

The equilibrium study on the reactive extraction of itaconic acid (pK_{a1} = 3.65 and pK_{a2} = 5.13 at 298 K, log P_a = -0.43) using TOA in six different diluents (heptane, kerosene, toluene, 1-decanol, MIBK and DCM) is carried out and results are presented in Section 5.1.5.1. The effect of the diluent on the extraction mechanism (stoichiometry and equilibrium constant) is also explained in this section. In the later part of this study (Section 5.1.5.2), RSM and artificial neural network (ANN) modeling for the reactive extraction of itaconic acid with TOA dissolved in the mixture of DCM (modifier) and cyclohexane (inert diluent) are also performed to predict the values of degrees of extraction.

5.1.5.1 Using TOA in six different diluents

The equilibrium results on the reactive extraction of itaconic acid (0.05 to 0.25 mol·L^{-1}) from aqueous solution by TOA (0.115 and 0.229 mol·L^{-1}) dissolved in six different diluents (heptane, kerosene, toluene, 1-decanol, MIBK and DCM) is shown in Table 5.35. The values of K_D are found to decrease with an increase in the initial acid concentration. That is because, at higher acid concentration the competition between acid and water molecule increases. The extraction ability (in terms of K_D) of TOA with six different diluents are found in the order of DCM > MIBK ≥ 1-decanol > toluene > kerosene > heptane. Solvation of the acid-TOA complex takes place by dipole-dipole interaction of solute-solvent molecule and plays a major role in the neutralization reaction between acid and extractant. Therefore, the solvation mechanism can be promoted by increasing the polarity of diluents. In case of slightly polar aromatic diluent (toluene), the K_D values are found comparatively higher than those of non-polar diluents (heptane and kerosene) due to the solvation of the acid-amine complex with the interaction of the aromatic π-electron.

The highest extraction efficiency (K_D = 32.478, E = 97.01 % and Z = 1.692) is found with TOA in DCM.

The values of Z in the range of 0.017 to 0.068 for heptane and 0.046 to 0.115 for kerosene suggest no overloading of acid on the TOA. The values of Z greater than 0.5 for all other diluents (0.124 to 0.845 for toluene, 0.206 to 1.562 for 1-decanol, 0.205 to 1.627 for MIBK, and 0.212 to 1.692 for DCM) indicate that the TOA molecules are overloaded with the acid. Loading ratio of all the diluents decreases with increasing TOA concentration at fixed acid concentration and increases with increasing acid concentration at fixed TOA concentration and this indicates presence of more than one acid molecule per complex. An increase in the concentration of TOA may lead to more formation of 1:1 complexes in case of active diluents (Table 5.35).

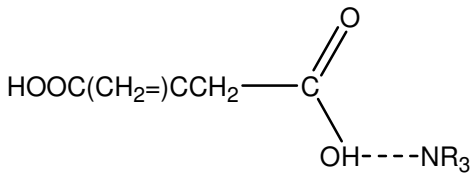
The values of m per extractant molecule and K_E are estimated using Eq. 4.19 and their values are presented in Table 5.36. The values of m less than one for heptane and kerosene indicate the association of two TOA molecules with one acid molecule promoting the formation of 1:1 and 1:2 acid-TOA complexes in the organic phase. m values greater than one for toluene, 1-decanol, MIBK and DCM with TOA suggest the simultaneous formation of both types of 1:1 and 2:1 complexes. The association of acid molecule with the extractant molecule is explained in Figure 5.46. From the values of individual equilibrium constants (Table 5.36), it can be observed that mostly (i) 1:2 type complexes are found with heptane and kerosene, and (ii) 1:1 and 2:1 complexes are found with toluene, 1-decanol, MIBK and DCM. The predicted values of K_D are also presented in Table 5.35 showing better agreement with the experimental values with maximum *rmsd* = 1.736. The estimated values of LSER model parameters are also presented in Table 5.37 at each initial itaconic acid concentration for 0.229 mol·L^{-1} of TOA.

Table 5.35 Equilibrium results of itaconic acid using TOA in different diluents

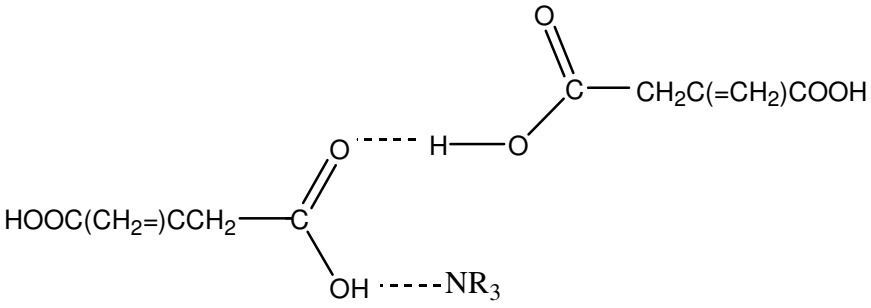
Diluents	$[\bar{S}]_{in}$ **mol·L^{-1}**	C_{HC} **mol·L^{-1}**	$\bar{C}_{HC}$ **mol·L^{-1}**	K_D	K_D^{model} **(Eq. 4.19)**	***% E***	Z	**pH$_{eq}$**
Heptane	0.115	0.047	0.003	0.057	0.062	5.43	0.024	2.86
		0.096	0.004	0.042	0.045	4.04	0.035	2.70
		0.145	0.005	0.036	0.038	3.45	0.045	2.61
		0.193	0.007	0.036	0.033	3.44	0.060	2.55
		0.242	0.008	0.032	0.030	3.13	0.068	2.50
	0.229	0.046	0.004	0.082	0.086	7.61	0.017	2.86
		0.094	0.006	0.062	0.064	5.80	0.025	2.71
		0.143	0.007	0.047	0.053	4.49	0.029	2.62
		0.191	0.009	0.046	0.047	4.38	0.038	2.55
		0.239	0.011	0.044	0.042	4.23	0.046	2.51
Kerosene	0.115	0.045	0.005	0.117	0.115	10.51	0.046	2.87
		0.091	0.009	0.103	0.088	9.33	0.081	2.72
		0.140	0.010	0.073	0.074	6.85	0.090	2.62
		0.188	0.012	0.062	0.065	5.80	0.101	2.56
		0.237	0.013	0.053	0.059	5.02	0.109	2.51
	0.229	0.038	0.012	0.313	0.332	23.86	0.052	2.90
		0.079	0.022	0.274	0.235	21.50	0.094	2.75
		0.124	0.026	0.213	0.188	17.55	0.115	2.65
		0.175	0.025	0.145	0.157	12.70	0.111	2.57
		0.226	0.024	0.109	0.137	9.79	0.107	2.52
Toluene	0.115	0.023	0.027	1.160	1.149	53.70	0.234	3.01
		0.051	0.049	0.969	1.032	49.22	0.429	2.84
		0.078	0.072	0.922	0.896	47.98	0.628	2.75
		0.112	0.088	0.786	0.755	43.99	0.767	2.67
		0.153	0.097	0.633	0.629	38.77	0.845	2.60
	0.229	0.022	0.028	1.309	1.537	56.69	0.124	3.03
		0.033	0.067	2.009	1.813	66.77	0.291	2.93
		0.047	0.103	2.188	1.999	68.64	0.449	2.86
		0.067	0.133	1.976	2.073	66.40	0.579	2.78
		0.086	0.164	1.899	2.033	65.50	0.714	2.73
1-Decanol	0.115	0.006	0.044	7.370	7.287	88.05	0.384	3.31
		0.013	0.087	6.652	6.728	86.93	0.758	3.14
		0.028	0.122	4.357	4.610	81.33	1.064	2.97
		0.045	0.155	3.464	3.242	77.60	1.354	2.87
		0.071	0.179	2.524	2.194	71.62	1.562	2.77
	0.229	0.003	0.047	16.855	15.357	94.40	0.206	3.47
		0.007	0.093	13.477	13.872	93.09	0.406	3.28
		0.012	0.138	11.174	11.604	91.79	0.600	3.15
		0.019	0.181	9.713	9.207	90.67	0.791	3.06
		0.030	0.220	7.266	6.844	87.90	0.958	2.95

Table 5.35 Equilibrium results of itaconic acid using TOA in different diluents (continued…)

Diluents	$[\bar{S}]_{in}$ **mol·L^{-1}**	C_{HC} **mol·L^{-1}**	$\bar{C}_{HC}$ **mol·L^{-1}**	K_D	K_D^{model} **(Eq. 4.19)**	***% E***	Z	**pH_{eq}**
MIBK	0.115	0.005	0.045	8.565	8.981	89.55	0.391	3.34
		0.011	0.089	7.928	8.066	88.80	0.775	3.17
		0.026	0.124	4.739	5.084	82.58	1.080	2.99
		0.047	0.153	3.251	3.177	76.48	1.334	2.86
		0.063	0.187	2.939	2.452	74.61	1.627	2.79
	0.229	0.003	0.047	15.739	15.267	94.03	0.205	3.46
		0.008	0.092	11.754	13.971	92.16	0.402	3.25
		0.012	0.138	11.959	11.753	92.28	0.604	3.16
		0.019	0.181	9.713	9.351	90.67	0.791	3.06
		0.026	0.224	8.565	7.684	89.55	0.976	2.99
DCM	0.115	0.004	0.046	12.391	11.450	92.53	0.404	3.41
		0.009	0.091	9.713	10.154	90.67	0.791	3.21
		0.022	0.128	5.696	6.154	85.07	1.113	3.02
		0.041	0.159	3.870	3.704	79.46	1.386	2.89
		0.056	0.194	3.464	2.797	77.60	1.692	2.82
	0.229	0.001	0.049	32.478	48.508	97.01	0.212	3.61
		0.004	0.096	25.783	26.666	96.27	0.420	3.41
		0.007	0.143	21.319	18.836	95.52	0.625	3.28
		0.015	0.185	12.391	10.706	92.53	0.807	3.11
		0.028	0.222	7.928	6.338	88.80	0.968	2.97



(a)



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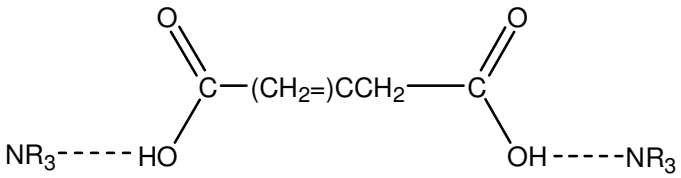


(c)

Figure 5.46 Representation of formation of (a) 1:1, (b) 2:1 and (c) 1:2 complexes in the organic phase for itaconic acid reactive extraction

Table 5.36 Values of stoichiometry and equilibrium constants for itaconic acid reactive extraction using TOA

Diluents	TOA (0.115 mol·L^{-1})								TOA (0.229 mol·L^{-1})							
	m	***n***	K_E	***rmsd***	K_{11}	K_{21}	K_{12}	***rmsd***	***m***	***n***	K_E	***rmsd***	K_{11}	K_{21}	K_{12}	***rmsd***
Heptane	0.60	1	0.28	0.003	0.002	-	1957.10	0.0004	0.60	1	0.19	0.003	0.002	-	703.00	0.001
Kerosene	0.67	1	0.58	0.006	0.003	-	2536.65	0.001	0.59	1	0.71	0.024	0.001	-	3766.56	0.005
Toluene	1.20	1	21.9	0.038	7.51	4.33	-	0.006	1.61	1	46.7	0.188	7.55	7.68	-	0.008
1-Decanol	1.46	1	615	0.207	49.68	32.62	-	0.004	1.18	1	198	0.398	52.15	22.69	-	0.011
MIBK	1.44	1	758	0.273	57.84	33.65	-	0.007	1.20	1	212	0.564	46.40	32.55	-	0.010
DCM	1.44	1	1092	0.344	71.80	43.70	-	0.009	0.90	1	155	1.736	121.80	-	-	0.037

Table 5.37 Values of LSER model parameters for itaconic acid reactive extraction at 0.229 mol·L^{-1} of TOA

C_{in} mol·L^{-1}	$\log_{10} K_D^0$	***a***	***b***	***s***	***d***
0.05	-0.89833	1.843436	1.283213	2.348199	-0.16775
0.10	-1.03810	1.803306	1.611195	2.118902	0.009268
0.15	-1.15601	1.574889	1.833396	2.148686	0.062406
0.20	-1.19117	1.467299	2.142185	1.825840	0.145340
0.25	-1.22266	1.158495	2.293840	1.673565	0.206230

5.1.5.2 Using TOA in diluent mixture (RSM and ANN modeling)

The study is aimed to predict the degree of extraction using RSM and ANN modeling approach for reactive extraction of itaconic acid with TOA in a mixture of DCM (modifier) and cyclohexane (inert diluent). The design parameters are chosen as initial acid (C_{in}), amine ($[\bar{S}]_{in}$) and modifier (C_M) compositions. The normalization of design variables is done according to the following equations (Eqs. 5.7 to 5.9) and values are presented in Table 5.38.

$$x_1 = \frac{C_{in} - 0.05}{0.025} \tag{5.7}$$

$$x_2 = \frac{[\bar{S}]_{in} - 10}{5} \tag{5.8}$$

$$x_3 = \frac{C_M - 50}{30} \tag{5.9}$$

With $k = 3$, $n_c = 2$ and $\alpha^* = \pm 1.215$ for CCOD, a total of 16 batch experiments are carried out (Table 5.39). Each experimental run represents a unique combination of factor's level. These experimental data are regressed to obtain regression coefficients of the RSM model. The approximate RSM model equation is represented as:

$$Y = 92.23 + 1.92x_1 + 5.82x_2 + 17.9x_3 - 4.76x_1^2 - 2.3x_2^2 - 16.02x_3^2 + 3.88x_1x_2 + 4.13x_1x_3 - 7x_2x_3$$

Subjected to: $-\alpha \le x_i \le +\alpha$ (i = 1, 2 and 3) (5.10)

The ANOVA results of RSM model are presented in Table 5.40. An F-value of 21.24, a P-value of 6.97×10^{-4} and a R^2 of 0.97 indicate a better fit of the RSM model (Figure 5.47).

Table 5.38 Design variables and their coded and actual values for itaconic acid reactive extraction with TOA

Actual design variables	Coded variables	Coded levels				
		$-\alpha^*$	-1	0	+1	α^*
C_{in}, mol·L^{-1}	x_1	0.02	0.025	0.05	0.075	0.08
$[\bar{S}]_{in}$, %v/v	x_2	3.925	5	10	15	16.075
C_M, %v/v	x_3	13.55	20	50	80	86.45

$\alpha^* = 1.215$ (star point for CCOD), $k = 3$ design variables

Table 5.39 Experimental design points and response of itaconic acid reactive extraction

Run number and type		Design variables and factors						Response
		C_{in} mol·L^{-1}	x_1	$[\bar{S}]_{in}$ (%v/v)	x_2	C_M (%v/v)	x_3	Y (%)
1	O1	0.075	1	15	1	80	1	93.50
2	O2	0.025	-1	15	1	80	1	79.00
3	O3	0.075	1	5	-1	80	1	88.00
4	O4	0.025	-1	5	-1	80	1	82.00
5	O5	0.075	1	15	1	20	-1	69.00
6	O6	0.025	-1	15	1	20	-1	64.00
7	O7	0.075	1	5	-1	20	-1	28.50
8	O8	0.025	-1	5	-1	20	-1	46.00
9	S1	0.080375	α^*	10	0	50	0	91.60
10	S2	0.019625	$-\alpha^*$	10	0	50	0	80.89
11	S3	0.05	0	16.075	α^*	50	0	91.00
12	S4	0.05	0	3.925	$-\alpha^*$	50	0	88.75
13	S5	0.05	0	10	0	86.45	α^*	94.75
14	S6	0.05	0	10	0	13.55	$-\alpha^*$	44.50
15	C1	0.05	0	10	0	50	0	91.00
16	C2	0.05	0	10	0	50	0	90.25

Table 5.40 ANOVA results for RSM model for itaconic acid reactive extraction

Source	*DF*	*SS*	*MS*	*F*-value	*P*-value	R^2
Model	9	6077.69	675.30	21.24	6.97×10^{-4}	0.97
Error	6	190.76	31.79			
Total	15	6268.44	-			

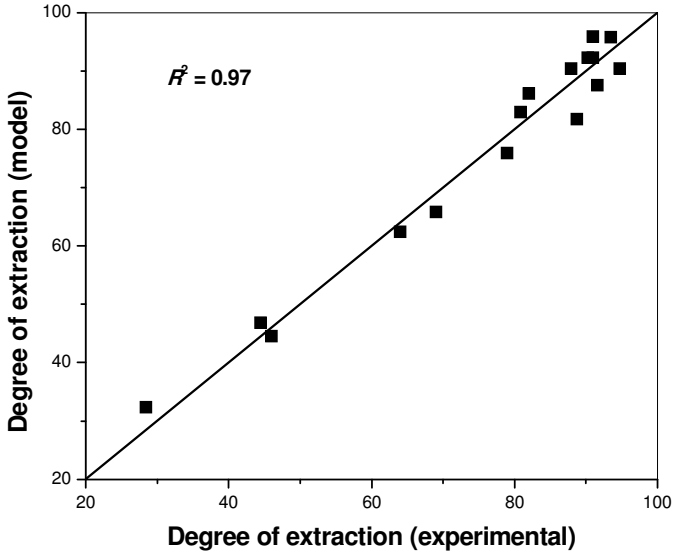


Figure 5.47 RSM model predicted versus experimental degree of extraction for itaconic acid reactive extraction

Table 5.41 Additional set of data used for construction and validation of ANN model for itaconic acid reactive extraction

Run No.	Design variables			Response
	C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ (%v/v)	C_M (%v/v)	Y (%)
17	0.030	5.00	95.00	85.96
18	0.030	5.00	47.50	78.93
19	0.025	3.13	62.50	80.34
20	0.025	15.00	35.00	77.53
21	0.010	18.75	25.00	1.69
22	0.010	10.00	75.00	33.29
23	0.100	18.75	81.25	94.73
24	0.090	10.00	58.75	95.71
25	0.075	15.00	0.00	8.71
26	0.075	6.25	46.88	83.15
27	0.060	12.50	0.00	16.90
28	0.060	5.00	18.75	36.21
29	0.090	3.13	81.25	83.22
30	0.015	5.00	50.00	88.30
31	0.015	12.50	43.75	74.25
32	0.100	5.00	76.25	92.63
33	0.040	6.25	56.25	86.83
34	0.040	3.13	15.63	17.49
35	0.050	6.25	37.50	73.32
36	0.050	12.5	87.50	92.98

A total of 36 experimental runs (Tables 5.39 and 5.41) are used to develop the ANN model. The inputs for the neural network are identical to the factors considered in RSM approach. Similar to RSM modeling, the degree of extraction is also considered as target in ANN modeling. These original data (36 samples) are divided as training subset (Run no. 1-20), validation subset (Run no. 21-28) and test subset (Run no. 29-36) to generalize the ANN model. In this study, the numbers of hidden layers and neurons are established by training different feed-forward networks and selecting the optimal one based on minimization of performance function, mean square error (*MSE*). The optimum architecture of ANN model is obtained as a 3:5:1, referring to the number of neurons in the input, hidden and output layers, respectively (Figure 5.48). Log-sigmoid transfer function (*logsig*) is used in the hidden layer while the output layer has linear transfer function (*purelin*). The optimum values of weights and biases are found out (Table 5.42) by training the network and using back-propagation method (BP) based on Levenberg-Marquardt Algorithm. The training is stopped after 10 iterations and at the point where the network error (*MSE*) becomes sufficiently small [$MSE = 9.59 \times 10^{-4} \leq E_0 = 10^{-3}$, where E_0 is the goal] (Figure 5.49). The ANN model for the prediction of degree of extraction can be described as:

$$\hat{Y}(x) = purelin(LW^{(2,1)} \log sig(LW^{(1,1)} + B^{(1)}) + B^{(2)}) \qquad (5.11)$$

The ANOVA (Table 5.43) gives a very high *F*-value (154.35) and a very low *P*-value (~ 0) with a value of correlation coefficient close to unity (R^2 = 0.993). The goodness-of-fit between the experimental and the predicted values of degrees of extraction given by ANN is shown in Figure 5.50. All points are located very near to the straight line indicating that ANN model prediction is excellent inside the valid region.

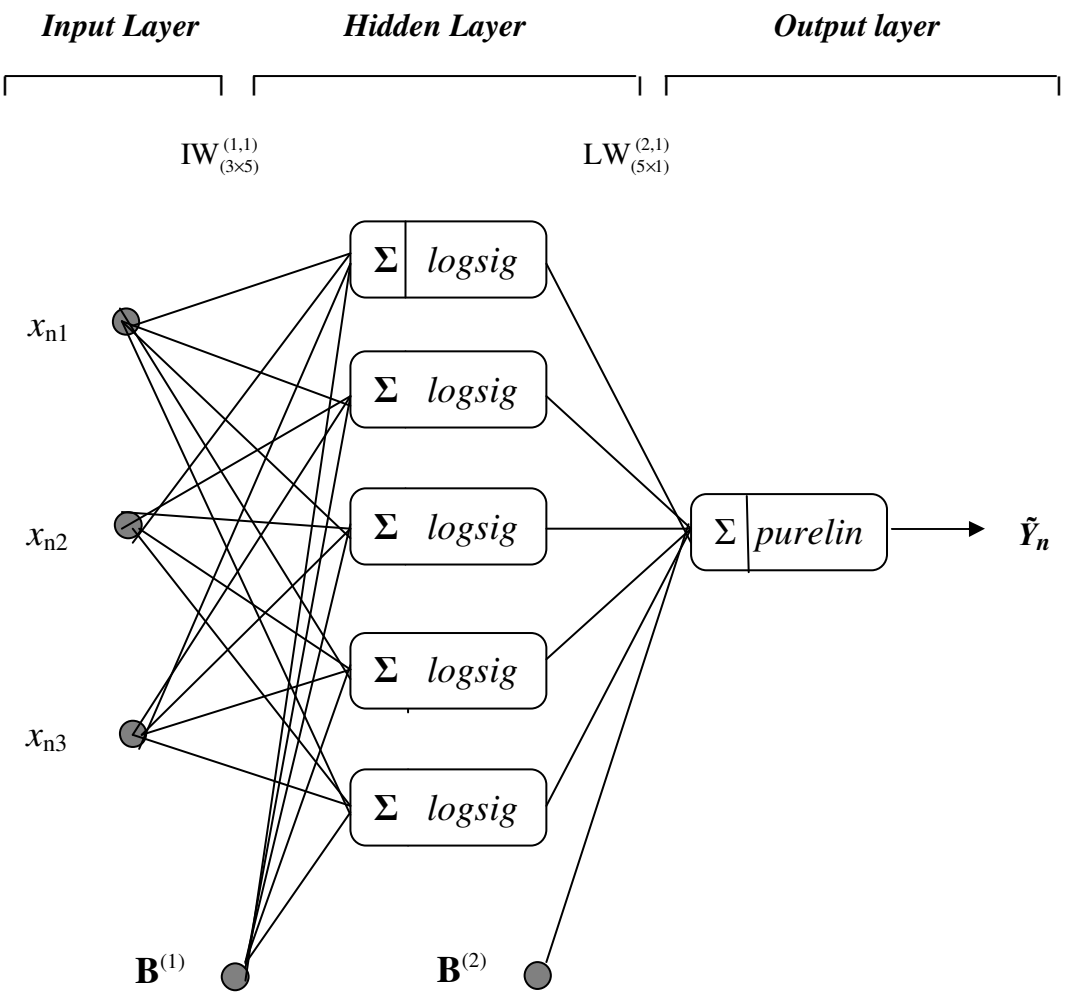


Figure 5.48 Architecture of ANN model used for prediction of extraction efficiency

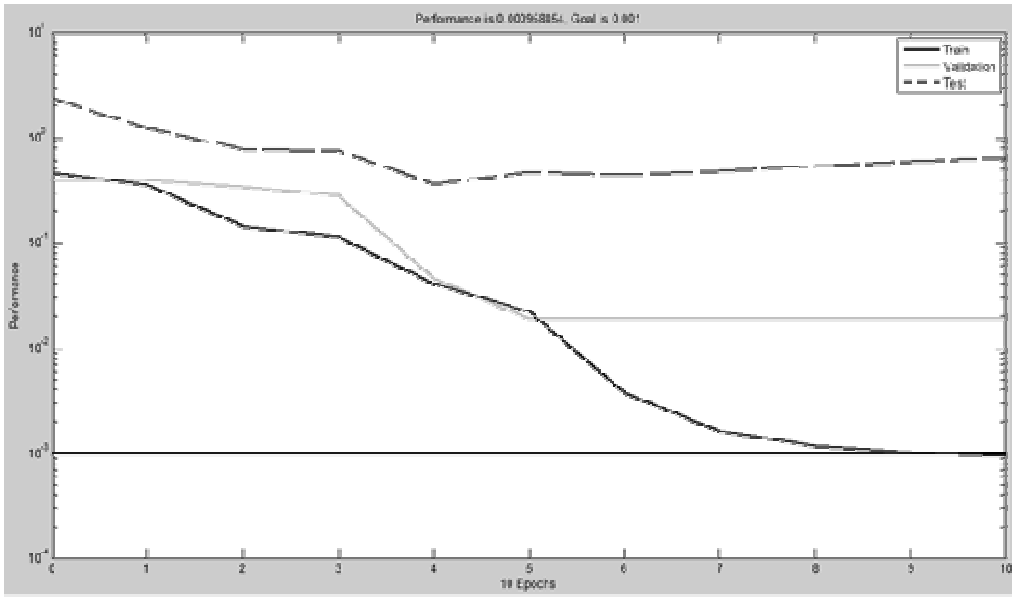


Figure 5.49 Evolution of MSE during ANN training phase, performance is 9.59×10^{-4} and goal is $E_0 = 1\times10^{-3}$

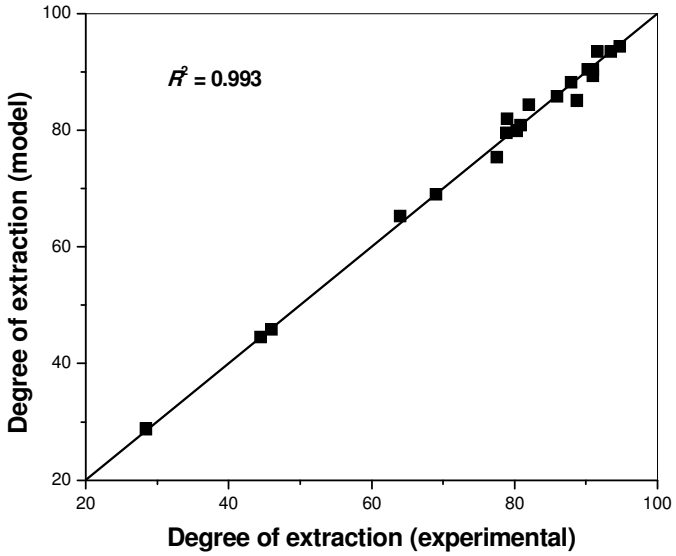


Figure 5.50 ANN model predicted versus experimental degree of extraction for itaconic acid reactive extraction

Table 5.42 Optimal values of weights and biases of ANN model for itaconic acid reactive extraction

Input weight matrix *destination*: HL source: inputs	$IW^{(1,1)} = \begin{vmatrix} 1.7458 & -1.5974 & -7.4646 \\ 3.0803 & -7.2771 & 2.2855 \\ 3.0494 & -0.0285 & 13.7218 \\ 0.33139 & -5.5905 & -2.2851 \\ -7.1348 & -7.6163 & -0.27631 \end{vmatrix}$
Layer weight matrix *destination*: OL source: HL	$LW^{(2,1)} = \lvert[-2.4346\ 0.16226\ 1.1277\ -0.1758\ -0.050307\rvert$
Bias vector *destination*: HL	$B^{(1)} = \lvert[-5.7425\ -0.19126\ 4.6086\ -1.1201\ -1.2751\rvert^{T}$
Bias vector *destination*: OL	$B^{(2)} = -0.31808$

Table 5.43 ANOVA results for ANN model for itaconic acid reactive extraction

Source	***DF***	***SS***	***MS***	***F*-value**	***P*-value**	R^2
Model	25	6289.69	251.588	154.35	5.87×10^{-10}	0.993
Error	10	42.379	1.63			
Total	35	6332.069	-			

5.1.6 Reactive Extraction of Formic Acid

In this equilibrium study, the reactive extraction of formic acid (pK_a = 3.75, log P_a = -0.538) from aqueous solution is carried out in six different diluents [decane, benzene, 1-decanol, decane + 1-decanol (3:1 v/v), MIBK, and chloroform] using TOA (as an extractant) at 4 different temperatures (298 to 343 K). The experimental data at 298 K are taken from the work done by Kumar in 2010, and are generated at 3 more different temperatures (313 K, 328 K and 343 K) to study the effect of temperature on the stoichiometry, equilibrium constants and efficiency of reactive extraction of formic acid.

The equilibrium isotherms are shown in Figures 5.51a at 298 K, 5.51b at 313 K, 5.51c at 328 K and 5.51d at 343 K. The distribution of formic acid into the organic phase decreases with an increase in temperature due to the back-extraction of the acid. The values of K_D is decreased by 77.85% for decane, 66.30% for benzene, 74.67% for 1-decanol, 95.48% for chloroform, 70.41% for MIBK and 64.17% for decane + 1-decanol (3:1 v/v) when the temperature is increased from 298 K to 343 K at 0.265 mol·L^{-1} concentration of acid. The overall effect of temperature is attributed to the effect of different parameters such as pK_a, the acid-amine interaction, the solubility of the acid in both phases, the extractant basicity, and water co-extraction (Canari and Eyal, 2004). pK_a values of common carboxylic acids decrease slightly with an increase in the temperature and leads to the dissociation of acid molecule in the aqueous phase which lowers extraction efficiency. Similarly, the solubilities of acid in both aqueous and organic phases are affected by temperature. It is observed that the solubility of carboxylic acids in water increases with an increase in the temperature (Apelblat and Manzurola, 1987).

The values of equilibrium constant (K_E), and stoichiometry (*m, n*) of reaction are determined at 298, 313, 328 and 343 K using model Eq. 4.19. The error between the experimental and predicted values of K_D is minimized (Eq. 4.20) employing differential

evaluation optimization approach. The estimated values of K_E and m are listed in Table 5.44 with standard errors (*SE*). The values of m are found to be more than two for decane, benzene and MIBK at 298 K implying simultaneous formation of 1:1, 2:1 and 3:1 acid-TOA complexes in the organic phase. The values of m less than two at 298 K for chloroform, 1-decanol and decane + 1-decanol (3:1 v/v) indicate simultaneous association of 1:1 and 2:1 acid-amine complexes. The equilibrium parameters (K_E and m) are found to be decreased with an increase in the temperature promoting back-extraction of acid and making the system more unstable (Table 5.44).

Based on the estimated values of m per TOA molecule, the formation of different types of complexes, i.e., 1:1, 2:1, 3:1 and 1:2 are considered and individual equilibrium constants (K_{11}, K_{21}, K_{31} and K_{12}) are determined at 4 different temperatures using Eq. 4.29. Their values are given in Table 5.44. An objective function is defined as Eq. 4.31 which minimizes the error between the experimental and predicted values of organic phase acid concentration at equilibrium ($\overline{C}_{HC}$). The values of individual equilibrium constants at 298 K for decane, benzene and MIBK show that these diluents with TOA extract the acid mainly by forming 3:1 complex whereas 1-decanol and chloroform primarily form 1:1 acid-TOA complexes in the organic phase. In case of decane + 1-decanol (3:1 v/v) 2:1 type of solvates are mainly observed (Table 5.44). The temperature also has an effect on the individual acid-TOA complex formation. At a temperature of 298 K, there is a formation of mainly 3:1 acid-TOA complex in case of decane, benzene and MIBK, but at a temperature of 343 K, there is no appearance of 3:1 acid-TOA complex. There is also formation of 1:2 complexes for decane at higher temperatures. This behavior also confirms that the reactive system becomes more unstable at higher temperatures. Generally, the equilibrium reaction is exothermic with the decrease in the randomness of the system by the formation of acid-extractant complex. If enthalpy and entropy of the

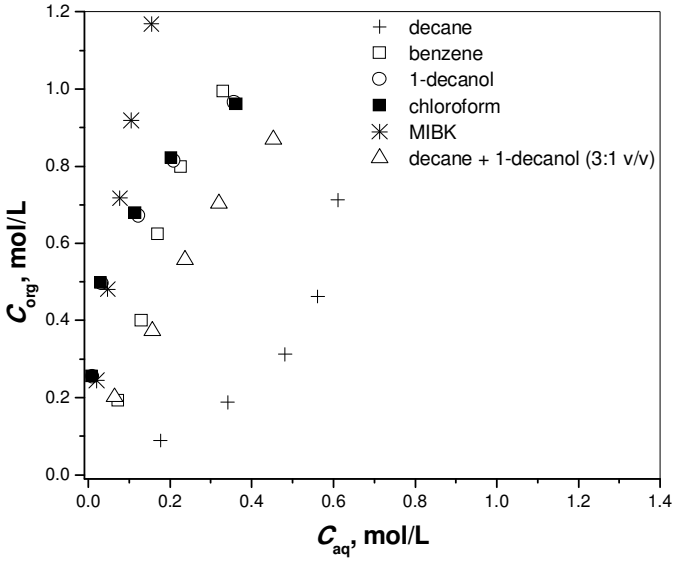
reaction are assumed to be constant over the temperature range (298 to 343 K), the equilibrium constant is related to the temperature by Eq. 5.12 (Tamada and King, 1990a; Smith *et al*., 2010).

$$\ln K_{\mathrm{E}} = \frac{-\Delta \mathrm{H}}{\mathrm{R}T} + \frac{\Delta \mathrm{S}}{\mathrm{R}} \qquad (5.12)$$

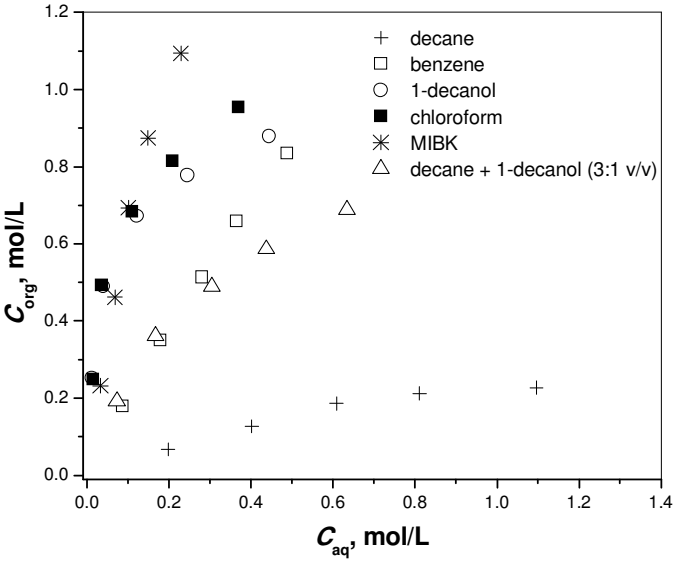
The plots of $\ln K_{\mathrm{E}}$ versus $1/T$ are shown in Figure 5.52 for the determination of the change in enthalpy (ΔH) and the change in entropy (ΔS). The negative values of ΔH and ΔS for all the diluents with TOA indicate that the equilibrium reaction is exothermic and more ordered (Table 5.45). It can be seen that highest ΔH (-96.64 $\mathrm{kJ \cdot mol^{-1}}$) and lowest ΔS (-263.583 $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$) values are found for chloroform with TOA (Table 5.45). Therefore, with chloroform, the acid-TOA complexation reaction is found to be more exothermic and lead to the increase in the orderliness (larger decrease in the entropy) of the system compared to other diluents.

Table 5.44 Effect of temperature on reaction stoichiometry and equilibrium constants of formic acid reactive extraction with TOA in different diluents

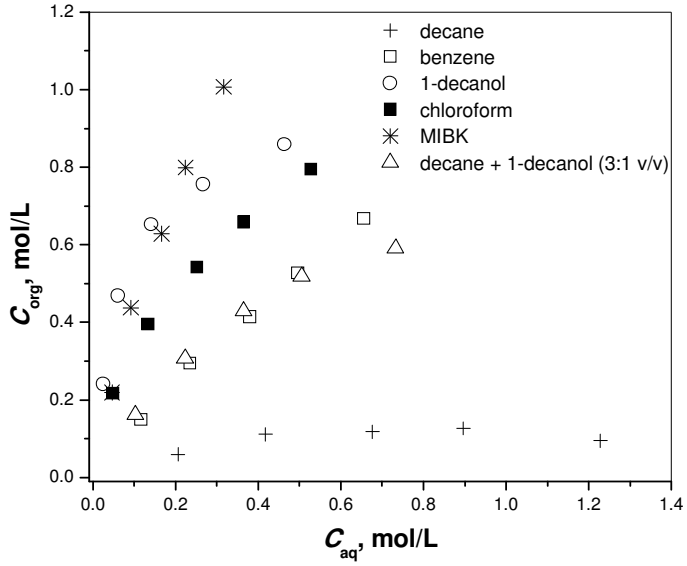
Diluents	Temperature K	*m*	*n*	K_E	*SE*	K_{11}	K_{21}	K_{31}	K_{12}	*SE*
Decane	298	2.69	1	2.721	0.123	0.890	0.023	159.95	-	0.153
	313	0.85	1	1.631	0.059	0.994	-	-	0.016	0.0095
	328	0.77	1	0.738	0.031	0.0004	-	-	7558.52	0.0197
	343	0.59	1	0.268	0.012	0.0003	-	-	993.03	0.0229
Benzene	298	2.38	1	96.311	0.276	4.143	2.529	14.67	-	0.0079
	313	1.81	1	19.794	0.115	1.386	15.623	-	-	0.0229
	328	1.56	1	7.342	0.084	1.970	3.302	-	-	0.0067
	343	1.30	1	3.442	0.062	1.950	0.921	-	-	0.0039
1-Decanol	298	1.71	1	602.483	2.395	13.755	7.562	-	-	0.0086
	313	1.67	1	505.107	2.444	65.281	11.926	-	-	0.0030
	328	1.68	1	209.878	1.483	24.407	11.130	-	-	0.0018
	343	1.69	1	106.005	0.786	13.680	9.501	-	-	0.0036
Chloroform	298	1.73	1	714.72	2.600	93.102	17.289	-	-	0.0196
	313	1.77	1	571.834	2.186	37.664	23.551	-	-	0.0143
	328	1.52	1	37.539	0.505	10.802	3.875	-	-	0.0118
	343	1.44	1	6.310	0.089	2.452	1.979	-	-	0.0077
MIBK	298	2.20	1	1012.819	0.953	44.957	0.069	1866.73	-	0.0037
	313	2.18	1	404.633	0.622	17.883	3.598	19.53	-	0.0015
	328	1.95	1	112.517	0.412	0.673	188.829	-	-	0.0450
	343	1.74	1	45.65	0.295	3.718	15.675	-	-	0.0387
Decane + 1-decanol (3:1 v/v)	298	1.80	1	32.907	0.192	3.320	11.474	-	-	0.0337
	313	1.47	1	18.249	0.284	6.692	2.345	-	-	0.0012
	328	1.45	1	8.634	0.148	3.860	1.529	-	-	0.0003
	343	1.38	1	4.879	0.081	2.605	1.047	-	-	0.0009


decane
benzene
1-decanol
chloroform
MIBK
decane + 1-decanol (3:1 v/v)
C_{org}, mol/L
C_{aq}, mol/L
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

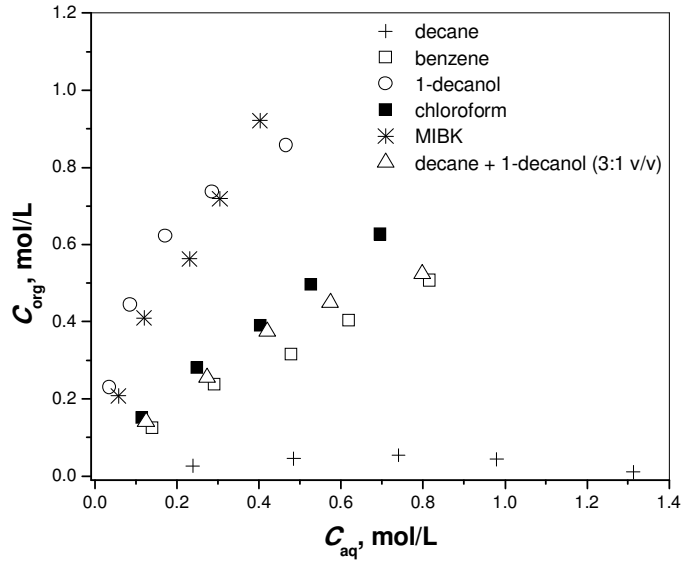
(a)


decane
benzene
1-decanol
chloroform
MIBK
decane + 1-decanol (3:1 v/v)
C_{org}, mol/L
C_{aq}, mol/L
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4

(b)



(c)



(d)

Figure 5.51 Equilibrium isotherm of formic acid with TOA in different diluents at (a) 298 K, (b) 313, (c) 328 and (d) 343 K

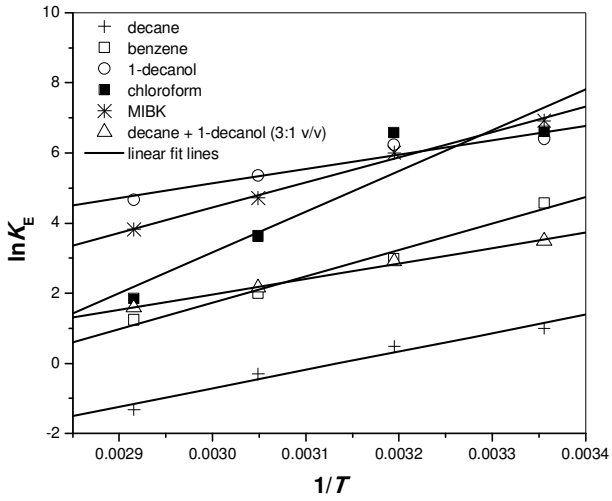


Figure 5.52 Determination of changes in enthalpy and entropy for formic acid reactive extraction

Table 5.45 The values of enthalpy and entropy for formic acid reactive extraction

Diluents	$-\Delta H$ kJ·mol^{-1}	$-\Delta S$ J·mol^{-1}·K^{-1}	R^2	*SD*
Decane	43.56	136.56	0.98	0.229
Benzene	62.60	173.44	0.99	0.225
1-Decanol	34.19	59.91	0.96	0.262
Chloroform	94.84	258.50	0.95	0.860
MIBK	59.85	142.65	0.99	0.136
Decane + 1-decanol (3:1 v/v)	36.64	93.56	0.99	0.065

5.1.7 Reactive Extraction of Levulinic Acid

The physical and chemical equilibrium results on the recovery of levulinic acid (0.111 to 0.541 mol·L^{-1}; pK_a = 4.6) using five different diluents (dodecane, benzene, 1-octanol, MIBK and DCM) and three different extractants (TBP, TOA and Aliquat 336) in diluents, respectively, are presented and discussed in this section.

Results of the physical extraction with pure diluents are presented in Table 5.46. The results for chemical extraction are obtained using four different concentrations of TBP (0.365 to 2.192 mol·L^{-1}), TOA (0.115 to 0.689 mol·L^{-1}), and Aliquat 336 (0.109 to 0.653 mol·L^{-1}) and reported in Tables 5.47 to 5.61. Among all the diluents studied, DCM yields a maximum value of K_D (1.656 with TBP, 12.151 with TOA, and 2.151 with Aliquat 336) due to polarity and hydrogen bonding ability with all the extractants. Aliphatic hydrocarbon (dodecane) exhibits low extraction ability. The values of Z are found to be in the range of 0.024 to 0.428 with TBP, 0.011 to 2.465 with TOA, and 0.044 to 1.522 with Aliquat 336 promoting probably 1:1 acid-TBP complex formation, and 1:n ($n \neq 1$) complex formation with both TOA and Aliquat 336.

A plot of $\log K_D + \log\left(1 + \frac{K_a}{[H^+]}\right)$ versus $\log[\bar{S}]_{in}$ based on mass action law 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 Figure 5.53 as a sample) and their values are presented in Tables 5.47 to 5.61. The graphical method is used with an assumption of $[\bar{S}]_{in} >> n[\overline{HC(T)_n}]$ in the extraction of levulinic acid which is applicable at a very dilute aqueous solution of acid compared to extractant concentration. The values of n ($\approx$ 1) are found mostly for inactive diluents (dodecane and benzene) at lower acid concentration and suggest the existence of a stoichiometric association between the individual acid and extractant molecules. The

values of *n* deviate in case of active diluents (1-octanol, MIBK and DCM) showing higher order of stoichiometric reactions such as 2:1, 3:1 etc. Higher values of dielectric constant for polar diluents are responsible for the values of *n* less than one. The strength of the complex solvation is found to be in the order of 1-octanol < dodecane < benzene < MIBK < DCM with both TBP and Aliquat 336, and dodecane < benzene < MIBK < 1-octanol < DCM with TOA. In all the tested diluents, DCM (chlorinated hydrocarbon) with TOA is found to be a good solvating agent for levulinic acid-amine complexation giving highest value of K_E (16.83). Extremely low values of equilibrium constant are found with dodecane.

Table 5.46 Physical equilibrium results of levulinic acid in different diluents

Diluents	C_{in} **mol·L^{-1}**	C_{HC} **mol·L^{-1}**	$\overline{C}_{HC}$ **mol·L^{-1}**	K_D	*%E*
Dodecane	0.111	0.1006	0.0104	0.103	9.34
	0.162	0.1490	0.0130	0.087	8.00
	0.288	0.2797	0.0083	0.030	2.91
	0.432	0.4252	0.0068	0.016	1.57
	0.541	0.5408	0.0002	~0	~0
Benzene	0.111	0.1064	0.0046	0.043	4.12
	0.162	0.1548	0.0072	0.047	4.49
	0.288	0.2724	0.0156	0.057	5.39
	0.432	0.4070	0.0250	0.061	5.75
	0.541	0.5083	0.0327	0.064	6.02
1-Octanol	0.111	0.0793	0.0317	0.400	28.57
	0.162	0.1182	0.0438	0.371	27.06
	0.288	0.209	0.0790	0.378	27.43
	0.432	0.3633	0.0687	0.189	15.90
	0.541	0.4719	0.0691	0.146	12.74
MIBK	0.111	0.0654	0.0456	0.697	41.07
	0.162	0.1006	0.0614	0.610	37.89
	0.288	0.1903	0.0977	0.513	33.91
	0.432	0.3243	0.1077	0.332	24.92
	0.541	0.4196	0.1214	0.289	22.42
DCM	0.111	0.0906	0.0204	0.225	18.37
	0.162	0.1374	0.0246	0.179	15.18
	0.288	0.2537	0.0343	0.135	11.89
	0.432	0.4036	0.0284	0.070	6.54
	0.541	0.5162	0.0248	0.048	4.58

Table 5.47 Equilibrium results of levulinic acid with TBP in dodecane

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.365	0.0937	0.0173	0.185	15.61	0.047	0.89	0.374	0.891	0.130
	0.731	0.0921	0.0189	0.205	17.01	0.026				
	1.461	0.0755	0.0355	0.470	31.97	0.024				
	2.192	0.0588	0.0522	0.888	47.03	0.024				
0.162	0.365	0.1490	0.0130	0.087	8.00	0.036	1.23	0.252	0.951	0.117
	0.731	0.1436	0.0184	0.128	11.35	0.025				
	1.461	0.1184	0.0436	0.368	26.90	0.030				
	2.192	0.0917	0.0703	0.767	43.41	0.032				
0.288	0.365	0.2869	0.0011	0.004	0.40	0.003	2.85	0.089	0.985	0.145
	0.731	0.2739	0.0141	0.051	4.85	0.019				
	1.461	0.2249	0.0631	0.281	21.94	0.043				
	2.192	0.1715	0.1165	0.679	40.44	0.053				
0.432	0.365	0.4281	0.0039	0.009	0.89	0.011	2.44	0.092	0.989	0.120
	0.731	0.4188	0.0132	0.032	3.10	0.018				
	1.461	0.3416	0.0904	0.265	20.95	0.062				
	2.192	0.2667	0.1653	0.620	38.27	0.075				
0.541	0.365	0.5384	0.0026	0.005	0.50	0.007	2.82	0.066	0.977	0.181
	0.731	0.5321	0.0089	0.017	1.67	0.012				
	1.461	0.4339	0.1071	0.247	19.81	0.073				
	2.192	0.3389	0.2021	0.596	37.34	0.092				

Table 5.48 Equilibrium results of levulinic acid using TBP in benzene

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.365	0.0824	0.0286	0.347	25.76	0.078	0.75	0.735	0.991	0.030
	0.731	0.0708	0.0402	0.568	36.22	0.055				
	1.461	0.0588	0.0522	0.888	47.03	0.036				
	2.192	0.0468	0.0642	1.372	57.84	0.029				
0.162	0.365	0.1254	0.0366	0.292	22.60	0.100	0.82	0.653	0.989	0.036
	0.731	0.1087	0.0533	0.490	32.89	0.073				
	1.461	0.0898	0.0722	0.804	44.57	0.049				
	2.192	0.0702	0.0918	1.308	56.67	0.042				
0.288	0.365	0.2278	0.0602	0.264	20.89	0.165	0.83	0.574	0.978	0.052
	0.731	0.2061	0.0819	0.397	28.42	0.112				
	1.461	0.1672	0.1208	0.722	41.93	0.083				
	2.192	0.1312	0.1568	1.195	54.44	0.072				
0.432	0.365	0.3791	0.0529	0.140	12.28	0.145	1.10	0.439	0.994	0.036
	0.731	0.3243	0.1077	0.332	24.92	0.147				
	1.461	0.2681	0.1639	0.611	37.93	0.112				
	2.192	0.2090	0.2230	1.067	51.62	0.102				
0.541	0.365	0.4941	0.0469	0.095	8.68	0.128	1.28	0.38	0.987	0.062
	0.731	0.4165	0.1245	0.299	23.02	0.170				
	1.461	0.3436	0.1974	0.575	36.51	0.135				
	2.192	0.2692	0.2718	1.010	50.25	0.124				

Table 5.49 Equilibrium results of levulinic acid using TBP in 1-octanol

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.365	0.0778	0.0332	0.427	29.92	0.091	0.38	0.592	0.912	0.050
	0.731	0.0759	0.0351	0.462	31.60	0.048				
	1.461	0.0677	0.0433	0.640	39.02	0.030				
	2.192	0.0600	0.0510	0.850	45.95	0.023				
0.162	0.365	0.1142	0.0478	0.419	29.53	0.131	0.38	0.557	0.826	0.073
	0.731	0.1146	0.0474	0.414	29.28	0.065				
	1.461	0.1018	0.0602	0.591	37.15	0.041				
	2.192	0.0886	0.0734	0.828	45.30	0.033				
0.288	0.365	0.2047	0.0833	0.407	28.93	0.228	0.38	0.536	0.817	0.075
	0.731	0.2061	0.0819	0.397	28.42	0.112				
	1.461	0.1831	0.1049	0.573	36.43	0.072				
	2.192	0.1600	0.1280	0.800	44.44	0.058				
0.432	0.365	0.3456	0.0864	0.250	20.00	0.236	0.55	0.400	0.935	0.061
	0.731	0.3344	0.0976	0.292	22.6	0.134				
	1.461	0.2957	0.1363	0.461	31.55	0.093				
	2.192	0.2581	0.1739	0.674	40.26	0.079				
0.541	0.365	0.4513	0.0897	0.199	16.60	0.246	0.62	0.346	0.965	0.049
	0.731	0.4307	0.1103	0.256	20.38	0.151				
	1.461	0.3840	0.1570	0.409	29.03	0.107				
	2.192	0.3373	0.2037	0.604	37.66	0.093				

Table 5.50 Equilibrium results of levulinic acid using TBP in MIBK

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.365	0.0673	0.0437	0.649	39.36	0.120	0.50	1.067	0.984	0.027
	0.731	0.0592	0.0518	0.875	46.67	0.071				
	1.461	0.0507	0.0603	1.189	54.32	0.041				
	2.192	0.0422	0.0688	1.630	61.98	0.031				
0.162	0.365	0.1037	0.0583	0.562	35.98	0.160	0.52	0.897	0.943	0.053
	0.731	0.0956	0.0664	0.695	41.00	0.091				
	1.461	0.0820	0.0800	0.976	49.39	0.055				
	2.192	0.0658	0.0962	1.462	59.38	0.044				
0.288	0.365	0.1898	0.0982	0.517	34.08	0.269	0.55	0.792	0.864	0.092
	0.731	0.1868	0.1012	0.542	35.15	0.138				
	1.461	0.1535	0.1345	0.876	46.70	0.092				
	2.192	0.1202	0.1678	1.396	58.26	0.077				
0.432	0.365	0.3010	0.1310	0.435	30.31	0.359	0.55	0.723	0.967	0.043
	0.731	0.2772	0.1548	0.558	35.82	0.212				
	1.461	0.2365	0.1955	0.827	45.27	0.134				
	2.192	0.1967	0.2353	1.196	54.46	0.107				
0.541	0.365	0.3848	0.1562	0.406	28.88	0.428	0.55	0.688	0.981	0.032
	0.731	0.3484	0.1926	0.553	35.61	0.264				
	1.461	0.3024	0.2386	0.789	44.10	0.163				
	2.192	0.2549	0.2861	1.122	52.87	0.131				

Table 5.51 Equilibrium results of levulinic acid using TBP in dichloromethane

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	K_E	R^2	SD
0.111	0.365	0.0921	0.0189	0.205	17.01	0.052	0.637	0.992	0.044
	0.731	0.0774	0.0336	0.434	30.26	0.046			
	1.461	0.0596	0.0514	0.862	46.29	0.035			
	2.192	0.0418	0.0692	1.656	62.35	0.032			
0.162	0.365	0.1370	0.0250	0.182	15.40	0.068	0.558	0.993	0.040
	0.731	0.1161	0.0459	0.395	28.32	0.063			
	1.461	0.0925	0.0695	0.751	42.89	0.048			
	2.192	0.0673	0.0947	1.407	58.45	0.043			
0.288	0.365	0.2465	0.0415	0.168	14.38	0.114	0.488	0.994	0.035
	0.731	0.2148	0.0732	0.341	25.43	0.100			
	1.461	0.1730	0.1150	0.665	39.94	0.079			
	2.192	0.1312	0.1568	1.195	54.44	0.072			
0.432	0.365	0.3791	0.0529	0.140	12.28	0.145	0.379	0.992	0.039
	0.731	0.3431	0.0889	0.259	20.57	0.122			
	1.461	0.2854	0.1466	0.514	33.95	0.100			
	2.192	0.2263	0.2057	0.909	47.62	0.094			
0.541	0.365	0.4830	0.0580	0.120	10.71	0.159	0.333	0.994	0.033
	0.731	0.4402	0.1008	0.229	18.63	0.138			
	1.461	0.3705	0.1705	0.460	31.51	0.117			
	2.192	0.3009	0.2401	0.798	44.38	0.110			

Table 5.52 Equilibrium results of levulinic acid with TOA in dodecane

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.115	0.1074	0.0040	0.034	3.29	0.031	0.45	0.090	0.996	0.012
	0.229	0.1062	0.0050	0.045	4.31	0.021				
	0.459	0.1046	0.0060	0.061	5.75	0.014				
	0.689	0.1031	0.0080	0.077	7.15	0.011				
0.162	0.115	0.1575	0.0050	0.029	2.82	0.039	0.57	0.091	0.941	0.060
	0.229	0.1564	0.0060	0.036	3.47	0.024				
	0.459	0.1540	0.0080	0.052	4.94	0.017				
	0.689	0.1498	0.0120	0.081	7.49	0.018				
0.288	0.115	0.2802	0.0080	0.028	2.72	0.068	0.18	0.042	0.994	0.006
	0.229	0.2792	0.0090	0.032	3.10	0.038				
	0.459	0.2782	0.0100	0.035	3.38	0.021				
	0.689	0.2772	0.0110	0.039	3.75	0.016				
0.432	0.115	0.4212	0.0110	0.026	2.53	0.094	0.25	0.044	0.996	0.007
	0.229	0.4193	0.0130	0.030	2.91	0.055				
	0.459	0.4173	0.0150	0.035	3.38	0.032				
	0.689	0.4153	0.0170	0.040	3.85	0.024				
0.541	0.115	0.5307	0.0100	0.019	1.86	0.090	0.36	0.046	0.908	0.047
	0.229	0.5250	0.0160	0.030	2.91	0.070				
	0.459	0.5231	0.0180	0.034	3.29	0.039				
	0.689	0.5212	0.0200	0.038	3.66	0.029				

Table 5.53 Equilibrium results of levulinic acid using TOA in benzene

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.115	0.0770	0.0340	0.442	30.65	0.296	0.51	1.291	0.976	0.034
	0.229	0.0708	0.0400	0.568	36.22	0.175				
	0.459	0.0615	0.0500	0.805	44.60	0.108				
	0.689	0.0525	0.0590	1.114	52.70	0.085				
0.162	0.115	0.1186	0.0430	0.366	26.79	0.378	0.55	1.242	0.993	0.020
	0.229	0.1035	0.0590	0.565	36.10	0.255				
	0.459	0.0920	0.0700	0.761	43.21	0.152				
	0.689	0.0805	0.0820	1.012	50.30	0.118				
0.288	0.115	0.2156	0.0720	0.336	25.15	0.631	0.55	1.167	0.982	0.031
	0.229	0.1848	0.1030	0.558	35.82	0.450				
	0.459	0.1669	0.1210	0.726	42.06	0.264				
	0.689	0.1490	0.1390	0.933	48.27	0.202				
0.432	0.115	0.3606	0.0710	0.198	16.53	0.622	0.86	1.413	0.973	0.060
	0.229	0.2951	0.1370	0.464	31.69	0.596				
	0.459	0.2553	0.1770	0.692	40.90	0.385				
	0.689	0.2186	0.2130	0.976	49.39	0.310				
0.541	0.115	0.4681	0.0730	0.156	13.49	0.635	1.00	1.53	0.970	0.074
	0.229	0.3791	0.1620	0.427	29.92	0.705				
	0.459	0.3241	0.2170	0.669	40.08	0.472				
	0.689	0.2710	0.2700	0.996	49.90	0.392				

Table 5.54 Equilibrium results of levulinic acid using TOA in 1-octanol

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.115	0.0311	0.0800	2.569	71.98	0.696	0.71	13.88	0.924	
	0.229	0.0159	0.0950	5.981	85.68	0.414				
	0.459	0.0132	0.0980	7.409	88.11	0.213				
	0.689	0.0105	0.1010	9.571	90.54	0.146				
0.162	0.115	0.0778	0.0840	1.082	51.97	0.733	0.56	4.04	0.936	0.085
	0.229	0.0529	0.1090	2.062	67.34	0.475				
	0.459	0.0463	0.1160	2.499	71.42	0.252				
	0.689	0.0399	0.1220	3.060	75.37	0.177				
0.288	0.115	0.1957	0.0920	0.472	32.07	0.804	0.60	2.02	0.898	0.061
	0.229	0.1421	0.1460	1.027	50.67	0.635				
	0.459	0.1282	0.160	1.246	55.48	0.348				
	0.689	0.1172	0.1710	1.457	59.30	0.248				
0.432	0.115	0.2981	0.1340	0.449	30.99	1.166	1.03	4.34	0.987	0.085
	0.229	0.2116	0.2200	1.042	51.03	0.960				
	0.459	0.1590	0.2730	1.717	63.19	0.595				
	0.689	0.1063	0.3260	3.064	75.39	0.473				
0.541	0.115	0.3791	0.1620	0.427	29.92	1.410	1.25	6.40	0.982	0.050
	0.229	0.2653	0.2760	1.039	50.96	1.201				
	0.459	0.1819	0.3590	1.974	66.38	0.782				
	0.689	0.0986	0.4420	4.487	81.78	0.642				

Table 5.55 Equilibrium results of levulinic acid using TOA in MIBK

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.115	0.0498	0.0610	1.229	55.14	0.533	0.13	1.746	0.761	0.030
	0.229	0.0440	0.0670	1.523	60.36	0.292				
	0.459	0.0436	0.0670	1.546	60.72	0.147				
	0.689	0.0432	0.0680	1.569	61.07	0.098				
0.162	0.115	0.0700	0.0920	1.314	56.78	0.801	0.18	1.975	0.990	0.007
	0.229	0.0642	0.0980	1.523	60.36	0.426				
	0.459	0.0607	0.1010	1.669	62.53	0.221				
	0.689	0.0576	0.1040	1.813	64.45	0.152				
0.288	0.115	0.1192	0.1690	1.416	58.61	1.470	0.21	2.206	0.941	0.022
	0.229	0.1143	0.1740	1.520	60.32	0.757				
	0.459	0.1033	0.1850	1.788	64.13	0.402				
	0.689	0.0934	0.1950	2.084	67.57	0.283				
0.432	0.115	0.1977	0.2340	1.185	54.23	2.041	0.34	2.392	0.972	0.024
	0.229	0.1838	0.2480	1.350	57.45	1.081				
	0.459	0.1515	0.2810	1.851	64.92	0.611				
	0.689	0.1391	0.2930	2.106	67.80	0.425				
0.541	0.115	0.2580	0.2830	1.097	52.31	2.465	0.39	2.491	0.971	0.028
	0.229	0.2369	0.3040	1.284	56.22	1.325				
	0.459	0.1876	0.3530	1.884	65.33	0.770				
	0.689	0.1730	0.3680	2.127	68.02	0.534				

Table 5.56 Equilibrium results of levulinic acid using TOA in dichloromethane

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.115	0.0311	0.0800	2.569	71.98	0.696	0.53	10.06	0.764	0.123
	0.229	0.0156	0.0950	6.115	85.95	0.416				
	0.459	0.0148	0.0960	6.500	86.67	0.210				
	0.689	0.0140	0.0970	6.929	87.39	0.141				
0.162	0.115	0.0467	0.1150	2.469	71.17	1.004	0.67	12.35	0.926	0.080
	0.229	0.0249	0.1370	5.506	84.63	0.597				
	0.459	0.0206	0.1410	6.864	87.28	0.308				
	0.689	0.0167	0.1450	8.701	89.69	0.211				
0.288	0.115	0.0844	0.2040	2.412	70.69	1.774	0.87	16.83	0.980	0.051
	0.229	0.0467	0.2410	5.167	83.78	1.051				
	0.459	0.0338	0.2540	7.521	88.26	0.554				
	0.689	0.0219	0.2660	12.151	92.40	0.386				
0.432	0.115	0.2047	0.2270	1.110	52.61	1.980	1.13	13.20	0.980	0.068
	0.229	0.1172	0.3150	2.686	72.87	1.371				
	0.459	0.0785	0.3540	4.503	81.83	0.770				
	0.689	0.0417	0.3900	9.360	90.35	0.567				
0.541	0.115	0.2938	0.2470	0.841	45.68	2.153	1.23	12.20	0.979	0.076
	0.229	0.1706	0.3700	2.171	68.46	1.613				
	0.459	0.1128	0.4280	3.796	79.15	0.933				
	0.689	0.0569	0.4840	8.508	89.48	0.703				

Table 5.57 Equilibrium results of levulinic acid using Aliquat 336 in dodecane

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.1089	0.1062	0.0050	0.045	4.31	0.044	1.25	1.021	0.874	0.200
	0.2177	0.0887	0.0220	0.251	20.06	0.102				
	0.4355	0.0819	0.0290	0.355	26.20	0.067				
	0.6532	0.0751	0.0360	0.478	32.34	0.055				
0.162	0.1089	0.1564	0.0060	0.036	3.47	0.051	1.35	0.942	0.921	0.165
	0.2177	0.1369	0.0250	0.183	15.47	0.115				
	0.4355	0.1237	0.0380	0.310	23.66	0.088				
	0.6532	0.1128	0.0490	0.436	30.36	0.075				
0.288	0.1089	0.2812	0.0070	0.024	2.34	0.062	1.54	0.964	0.946	0.155
	0.2177	0.2533	0.0350	0.137	12.05	0.159				
	0.4355	0.2275	0.0610	0.266	21.01	0.139				
	0.6532	0.2027	0.0850	0.421	29.63	0.131				
0.432	0.1089	0.3616	0.0700	0.195	16.32	0.647	0.63	0.923	0.886	0.094
	0.2177	0.2981	0.1340	0.449	30.99	0.615				
	0.4355	0.2802	0.1520	0.542	35.15	0.349				
	0.6532	0.2643	0.1680	0.635	38.84	0.257				
0.541	0.1089	0.4238	0.1170	0.277	21.69	1.077	0.52	1.070	0.772	0.119
	0.2177	0.3272	0.2140	0.653	39.50	0.982				
	0.4355	0.3186	0.2220	0.698	41.11	0.511				
	0.6532	0.3099	0.2310	0.746	42.73	0.354				

Table 5.58 Equilibrium results of levulinic acid using Aliquat 336 in benzene

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.1089	0.1008	0.0100	0.101	9.17	0.094	1.26	2.122	0.936	0.138
	0.2177	0.0770	0.0340	0.442	30.65	0.156				
	0.4355	0.0654	0.0460	0.697	41.07	0.105				
	0.6532	0.0533	0.0580	1.083	51.99	0.088				
0.162	0.1089	0.1451	0.0170	0.116	10.39	0.155	1.07	1.491	0.953	0.010
	0.2177	0.1179	0.0440	0.374	27.22	0.203				
	0.4355	0.1019	0.0600	0.590	37.11	0.138				
	0.6532	0.0875	0.0750	0.851	45.98	0.114				
0.288	0.1089	0.2543	0.0340	0.133	11.74	0.310	0.88	1.058	0.960	0.075
	0.2177	0.2156	0.0720	0.336	25.15	0.333				
	0.4355	0.1942	0.0940	0.483	32.57	0.215				
	0.6532	0.1709	0.1170	0.685	40.65	0.179				
0.432	0.1089	0.3239	0.1080	0.334	25.04	0.993	0.75	2.198	0.850	0.132
	0.2177	0.2176	0.2140	0.985	49.62	0.985				
	0.4355	0.2007	0.2310	1.152	53.53	0.531				
	0.6532	0.1808	0.2510	1.389	58.14	0.385				
0.541	0.1089	0.3777	0.1630	0.432	30.17	1.500	0.77	3.122	0.788	0.167
	0.2177	0.2177	0.3230	1.485	59.76	1.485				
	0.4355	0.204	0.3370	1.652	62.29	0.774				
	0.6532	0.1888	0.3520	1.865	65.10	0.539				

Table 5.59 Equilibrium results of levulinic acid using Aliquat 336 in 1-octanol

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.1089	0.0910	0.0200	0.220	18.03	0.184	0.25	0.391	0.995	0.007
	0.2177	0.0875	0.0240	0.269	21.20	0.108				
	0.4355	0.0848	0.0260	0.309	23.61	0.060				
	0.6532	0.0825	0.0290	0.345	25.65	0.044				
0.162	0.1089	0.1332	0.0290	0.216	17.76	0.265	0.27	0.390	0.982	0.016
	0.2177	0.1299	0.0320	0.247	19.81	0.147				
	0.4355	0.1245	0.0380	0.301	23.14	0.086				
	0.6532	0.1198	0.0420	0.352	26.04	0.065				
0.288	0.1089	0.2355	0.0530	0.223	18.23	0.482	0.27	0.395	0.967	0.021
	0.2177	0.2305	0.0580	0.249	19.94	0.264				
	0.4355	0.2206	0.0670	0.306	23.43	0.155				
	0.6532	0.2116	0.0760	0.361	26.52	0.117				
0.432	0.1089	0.3676	0.0640	0.175	14.89	0.592	0.28	0.313	0.951	0.026
	0.2177	0.3626	0.0690	0.191	16.04	0.319				
	0.4355	0.3477	0.0840	0.242	19.48	0.194				
	0.6532	0.3358	0.0960	0.286	22.24	0.147				
0.541	0.1089	0.4681	0.0730	0.156	13.49	0.670	0.28	0.284	0.971	0.020
	0.2177	0.4605	0.0810	0.175	14.89	0.370				
	0.4355	0.4435	0.0980	0.220	18.03	0.224				
	0.6532	0.4302	0.1110	0.258	20.51	0.170				

Table 5.60 Equilibrium results of levulinic acid using Aliquat 336 in MIBK

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.1089	0.0654	0.0460	0.697	41.07	0.419	0.34	1.350	0.797	0.072
	0.2177	0.0661	0.0450	0.679	40.44	0.206				
	0.4355	0.0576	0.0530	0.927	48.11	0.123				
	0.6532	0.0486	0.0620	1.284	56.22	0.096				
0.162	0.1089	0.0957	0.0660	0.693	40.93	0.609	0.30	1.312	0.959	0.026
	0.2177	0.0914	0.0710	0.772	43.57	0.324				
	0.4355	0.0817	0.0800	0.983	49.57	0.184				
	0.6532	0.0743	0.0880	1.180	54.13	0.134				
0.288	0.1089	0.1709	0.1170	0.685	40.65	1.076	0.29	1.328	0.992	0.011
	0.2177	0.1540	0.1340	0.870	46.52	0.615				
	0.4355	0.1431	0.1450	1.013	50.32	0.333				
	0.6532	0.1331	0.1550	1.164	53.79	0.237				
0.432	0.1089	0.2871	0.1450	0.505	33.55	1.331	0.30	1.037	0.947	0.030
	0.2177	0.2533	0.1790	0.705	41.35	0.821				
	0.4355	0.2424	0.1900	0.782	43.88	0.435				
	0.6532	0.2285	0.2040	0.891	47.12	0.312				
0.541	0.1089	0.3753	0.1660	0.442	30.65	1.522	0.32	0.959	0.937	0.035
	0.2177	0.3298	0.2110	0.640	39.02	0.970				
	0.4355	0.3146	0.2260	0.720	41.86	0.520				
	0.6532	0.2994	0.2420	0.807	44.66	0.370				

Table 5.61 Equilibrium results of levulinic acid using Aliquat 336 in DCM

C_{in} mol·L^{-1}	$[\bar{S}]_{in}$ mol·L^{-1}	C_{HC} mol·L^{-1}	$\bar{C}_{HC}$ mol·L^{-1}	K_D	%E	Z	n	K_E	R^2	SD
0.111	0.1089	0.0630	0.0480	0.762	43.25	0.441	0.53	2.364	0.961	0.045
	0.2177	0.0564	0.0550	0.968	49.19	0.251				
	0.4355	0.0467	0.0640	1.377	57.93	0.148				
	0.6532	0.0370	0.0740	2.000	66.67	0.113				
0.162	0.1089	0.0883	0.0740	0.835	45.50	0.677	0.50	2.505	0.979	0.031
	0.2177	0.0762	0.0860	1.126	52.96	0.394				
	0.4355	0.0646	0.0970	1.508	60.13	0.224				
	0.6532	0.0521	0.1100	2.109	67.84	0.168				
0.288	0.1089	0.1460	0.1420	0.973	49.32	1.304	0.43	2.526	0.988	0.020
	0.2177	0.1272	0.1610	1.264	55.83	0.739				
	0.4355	0.1083	0.1800	1.659	62.39	0.413				
	0.6532	0.0914	0.1970	2.151	68.26	0.301				
0.432	0.1089	0.3229	0.1090	0.338	25.26	1.002	0.92	2.538	0.991	0.036
	0.2177	0.2673	0.1650	0.616	38.12	0.756				
	0.4355	0.2086	0.2230	1.071	51.71	0.513				
	0.6532	0.1530	0.2790	1.824	64.59	0.427				
0.541	0.1089	0.4568	0.0840	0.184	15.54	0.773	1.20	2.685	0.994	0.038
	0.2177	0.3753	0.1660	0.442	30.65	0.761				
	0.4355	0.2871	0.2540	0.884	46.92	0.583				
	0.6532	0.2009	0.3400	1.693	62.87	0.521				

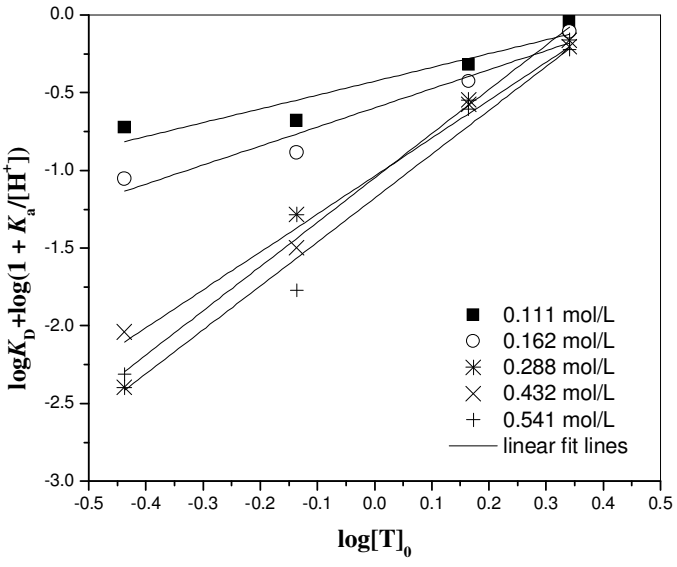


Figure 5.53 Determination of K_E and n using TBP dissolved in dodecane for levulinic acid reactive extraction

5.2 Kinetic Study of Nicotinic Acid using TOA

The design of an extraction process requires kinetic data for the acid-extractant system used. Therefore, the intrinsic kinetics of extraction of nicotinic acid by TOA dissolved in MIBK is also studied based on the theory of extraction accompanied by a chemical reaction. The values of rate constant and the order of the reaction are estimated using the experimental kinetic data and a model proposed by Doraiswamy and Sharma (1984).

5.2.1 Reaction Regime

The value of physical mass transfer coefficient (k_L) is required to confirm the regime of reaction in the reactive extraction. This is obtained by conducting physical extraction (with MIBK) of nicotinic acid. Using Eq. 4.57, the value of k_L is evaluated as 2.03×10^{-5} m/s (Figure 5.54).

The rate of a liquid-liquid reactive extraction in a stirred system can be controlled either by diffusion processes and/or the chemical reactions taking place in the system. In general, the rate of extraction increases with the increase in the stirring speed, while there is no effect of stirring speed on the rate of extraction governed by the chemical reaction (Hanna and Noble, 1985). With an increase in the stirring speed of the two phases, the rate of extraction increases in the diffusion controlled regime and reaches to a plateau where the rate of extraction remains constant with further increase in the stirring speed. In this region, the contribution of diffusion is minimized, and the rate of extraction becomes mainly controlled by chemical reaction. The film adjacent to the interface becomes the thinnest minimizing the individual film resistance to mass transfer. In this study, the speed of agitation (N) is varied between 30 rpm and 90 rpm to determine the hydrodynamic effects on initial rate of extraction (Figure 5.55). Further increase in the stirring speed disturbs the interfacial area between aqueous and organic phases. In this

range of N, it is observed that initial specific rate of reaction ($R_{HC,0}$) is almost constant and N has no effect on the rate of extraction. This shows that the kinetics fall either in Regime 1 or 3 (Table 4.2).

Now, to differentiate between Regimes 1 and 3, the effect of volume ratio of the phases (V_{org}/V_{aq}) on the initial specific rate of extraction is studied. Figure 5.56 shows that $R_{HC,0}$ varies linearly when V_{org}/V_{aq} is changed from 0.5 to 2. This is because the reaction between acid and TOA mainly takes place in the bulk which contributes to increase in the value of the initial specific rate of extraction. Thus, based on the results obtained and the guidelines provided by Doraiswamy and Sharma (1984), the reactive extraction of nicotinic acid with TOA in MIBK is determined taking place in Regime 1 (extraction accompanied by a slow chemical reaction).

5.2.2 Order of the Reaction

The reaction orders (α' and β') are determined keeping the concentration of one of the reactants constant and varying the concentration of others while maintaining a constant N and V_{org}/V_{aq}. The concentration profiles of organic phase are obtained experimentally at four initial concentrations (0.02, 0.05, 0.08 and 0.1 mol·L^{-1}) of nicotinic acid and 0.229 mol·L^{-1} of TOA (Figure 5.57), and at four initial concentrations (0.115, 0.229, 0.344 and 0.46 mol·L^{-1}) of TOA and 0.1 mol·L^{-1} of nicotinic acid (Figure 5.58). The corresponding plots of $R_{HC,0}$ are shown in Figures 5.59 and 5.60, respectively. Figures 5.59 and 5.60 show that $R_{HC,0}$ increases linearly with the equilibrium concentrations of nicotinic acid and initial TOA concentrations, respectively. The data are regressed using Eq. 4.60 to obtain orders of extraction as 0.7 with respect to acid and 0.5 with respect to TOA with a rate constant equal to 8.4×10^{-4} (mol·m^{-3})$^{-0.2}$s^{-1} .

For $\alpha' = 0.7$ and $\beta' = 0.5$, the rate expression (Eq. 5.13) and Hatta number (*Ha*) for slow reaction (Eq. 5.14) are expressed in the following form.

$$R_{HC,0} = k[\overline{HC}]^{0.7}[\overline{S}]^{0.5} \tag{5.13}$$

$$Ha = \frac{\sqrt{1.18k[\overline{HC}]^{-0.3}[\overline{S}]^{0.5} D_{HC}}}{k_L} \tag{5.14}$$

The value of D_{HC} is estimated using Wilke-Change (Eq. 4.61) and Reddy-Doraiswamy (Eq. 4.62) equations as 1.60×10^{-9} m^2/s and 1.54×10^{-9} m^2/s, respectively. Average of these two values i.e. 1.58×10^{-9} m^2/s is used as the coefficient of diffusivity in Eq. 5.14 to calculate *Hatta* number. The value of *Ha* is found to be 0.12 which is the condition for the validity of Regime 1. From the obtained forward rate constant and equilibrium constant, the rate constant of back-ward reaction (k_{-1}) is estimated to be 3.31×10^{-5} $(mol \cdot m^{-3})^{-0.2}s^{-1}$. The enhancement factor for the reactive extraction of nicotinic acid is also calculated using Eq. 4.63 to determine the effect of reaction on the pure mass transfer of nicotinic acid from the aqueous to the organic phase. The factor is calculated to be 5.34, which shows a significant facilitation of transfer of acid molecule by the chemical reaction.

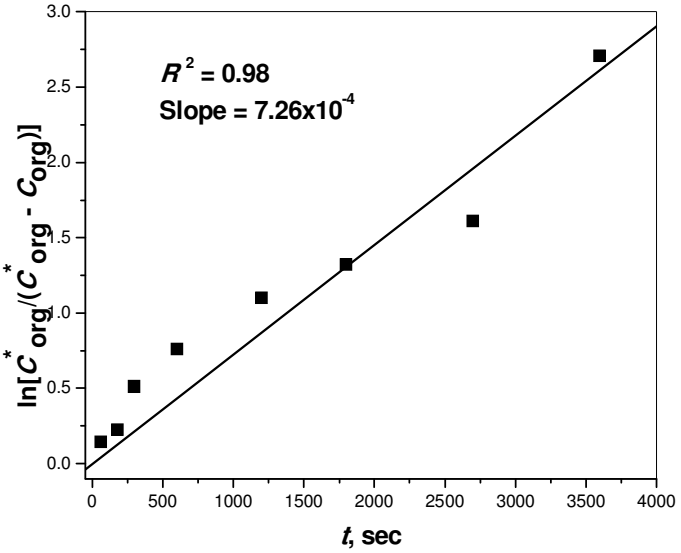


Figure 5.54 Plot of $\ln\left(\frac{C^*_{org}}{C^*_{org} - C_{org}}\right)$ **versus time (*t*) to determine k_L for nicotinic acid with TOA in MIBK**

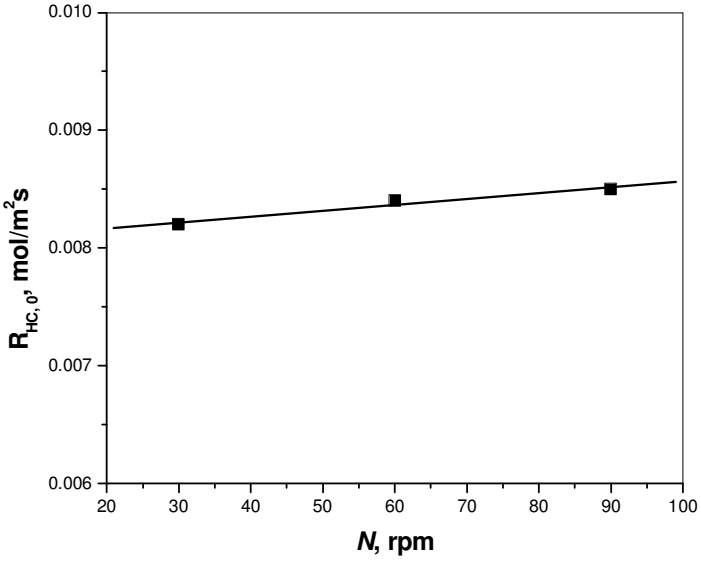


Figure 5.55 Variation of $R_{HC,0}$ with N for nicotinic acid with TOA in MIBK (T = 298 K, V_{org}/V_{aq} = 1, C_{in} = 0.1 mol·L^{-1}, $[\bar{S}]_{in}$ = 0.229 mol·L^{-1})

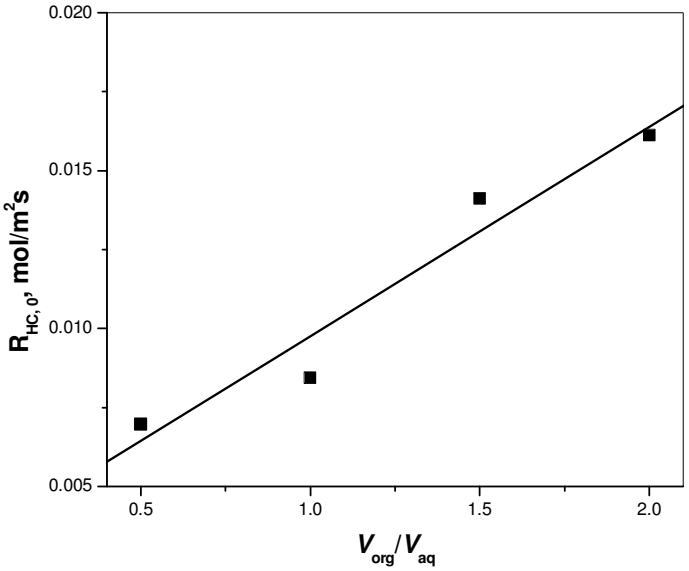


Figure 5.56 Variation of $R_{HC,0}$ with V_{org}/V_{aq} for nicotinic acid with TOA in MIBK (T = 298 K, N = 60 rpm, C_{in} = 0.1 mol·L^{-1}, $[\bar{S}]_{in}$ = 0.229 mol·L^{-1})

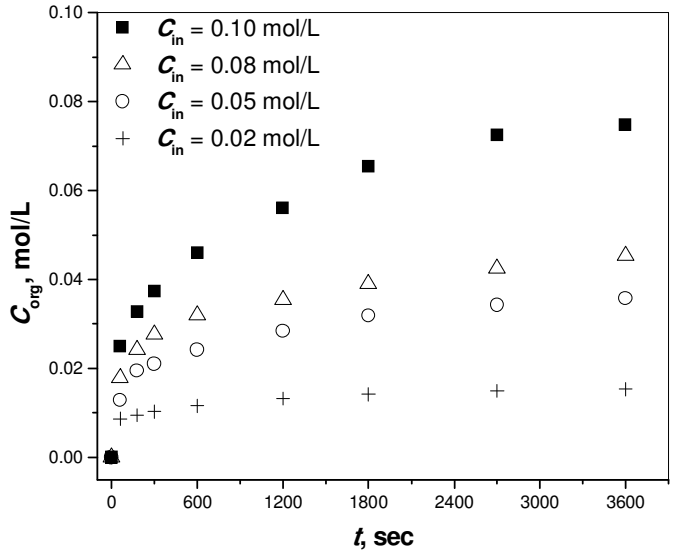


Figure 5.57 Concentration profiles of nicotinic acid in the organic phase with time with TOA in MIBK (T = 298 K, N = 60 rpm, V_{org}/V_{aq} = 1, $[\bar{S}]_{in}$ = 0.229 mol·L^{-1})

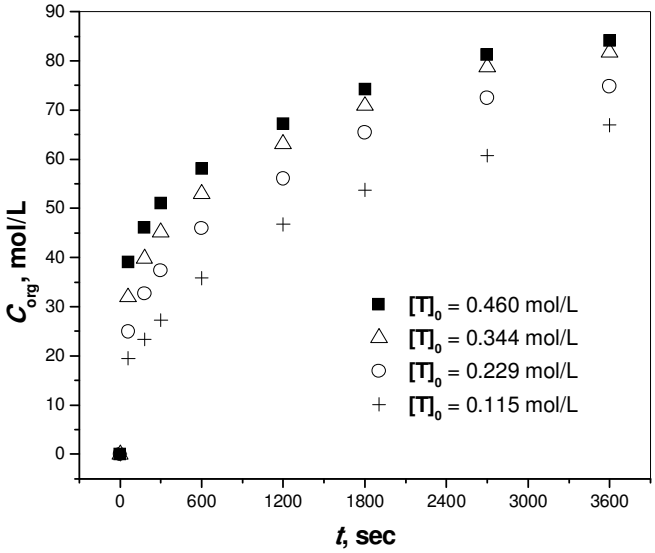


Figure 5.58 Concentration profiles of nicotinic acid in the organic phase with time with TOA in MIBK (T = 298 K, N = 60 rpm, V_{org}/V_{aq} = 1, C_{in} = 0.1 mol·L^{-1})

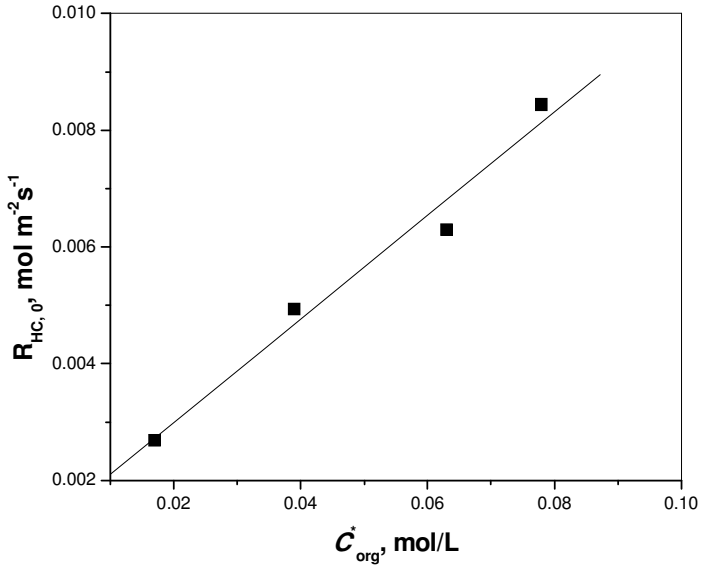


Figure 5.59 Variation of $R_{HC,0}$ with C^*_{org} for nicotinic acid with TOA in MIBK (T = 298 K, N = 60 rpm, V_{org}/V_{aq} = 1, $[\bar{S}]_{in}$ = 0.229 mol·L^{-1})

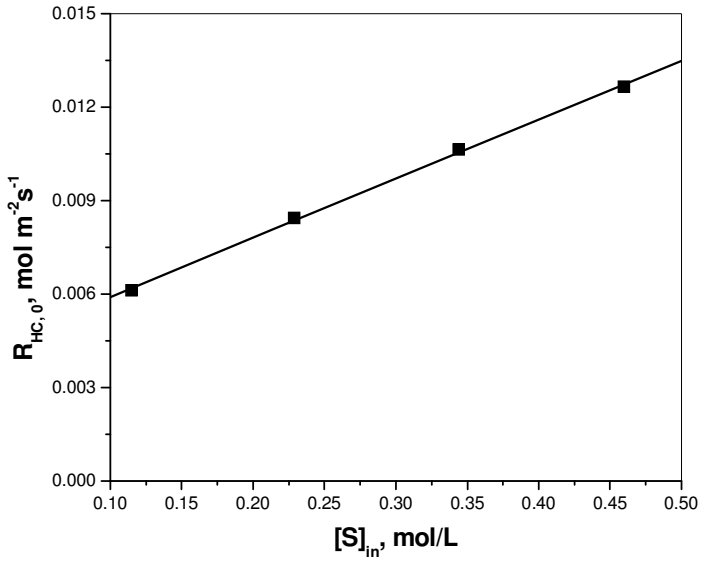


Figure 5.60 Variation of $R_{HC,0}$ with $[\bar{S}]_{in}$ of nicotinic acid with TOA in MIBK (T = 298 K, N = 60 rpm, V_{org}/V_{aq} = 1, C_{in} = 0.1 mol·L^{-1})

CHAPTER – 6

CONCLUDING REMARKS

Reactive extraction is a promising technique for the intensification of recovery process of carboxylic acids from the fermentation broths as well as aqueous waste streams. In the present study, equilibrium and kinetic experiments are carried out to recover different carboxylic acids from aqueous solutions. Various combinations of extractant and diluent with different compositions are used. A variety of modeling approaches are used to find the equilibrium and kinetic parameters. This chapter presents a brief summary of the work followed by conclusions, major contributions and future scope for research in this area.

6.1 Summary

6.1.1 Introduction

The production of carboxylic acids by fermentation technology using biomass as a renewable resource would provide necessary chemical for the sustainable development of industries. Now, to improve the biological production of acid and its derivatives, it is necessary to develop new efficient separation methods that will reduce the downstream processing cost of product recovery.

Among the several recovery methods (ion exchange, adsorption, electrodialysis, liquid extraction, membrane separation, precipitation etc.), reactive extraction is found to be a promising method for the recovery of carboxylic acids from a very dilute aqueous solution. In the reactive extraction, the classical extractants (aliphatics, aromatics, ketones, alcohols etc.) have almost no ability to extract acids from their aqueous solutions because of their low distribution coefficients (lower than 1). So, an extractant

(phosphorous- and amine based) is generally used with diluent to get better separation of acid and appropriate physical properties of the organic phase.

6.1.2 Gaps in Existing Literature

Pyridine carboxylic acids (picolinic, nicotinic and isonicotinic acids) and their derivatives are attracting considerable attention for their presence in many natural products. Therefore, experimental and theoretical studies are essential to find the best extractant-diluent system, operating conditions and biocompatible system for these acids. The use of modifier is also limited for the extraction of nicotinic and isonicotinic acid. There is no temperature study for the extraction of glycolic, formic, nicotinic and isonicotinic acids. There is limited study to optimize the process variables for reactive extraction using design of experiments and response surface methodology (RSM). These techniques may be useful to find out optimum operating conditions of the reactive extraction system. The differential evolution (DE) optimization technique for the determination of reactive extraction parameters is studied for propionic, acetic, and butyric acids, and still there is need to explore this technique for other acids. Hence, there is a wider scope for the experimental and theoretical investigations on the reactive extraction of carboxylic acids.

6.1.3. Scope of the Work

The production of carboxylic acids from renewable carbon sources using fermentation process is a promising approach but still restricted due to the limitations on product recovery. The reactive extraction with a specified extractant-diluent system is found to be an effective and efficient method for the recovery of bio-products from the aqueous solutions. In this thesis, an exhaustive experimental and theoretical studies on the reactive extraction of different carboxylic acids (picolinic, nicotinic, isonicotinic, glycolic, itaconic, formic, and levulinic acids) from their dilute aqueous solutions, is carried out.

The extractants are used from the phosphoric [tri-*n*-butyl phosphate (TBP), tri-octyl phosphine oxide (TOPO) and di-2-ethyl hexyl phosphoric acid (D2EHPA)] and aminic [tri-*n*-octyl amine (TOA), tri-dodecyl amine (TDDA) and Aliquat 336] category of extractants. These extractants are dissolved in various inert (hexane, cyclohexane, heptane, decane, dodecane, kerosene, toluene, and benzene), active (DCM, chloroform, MIBK, 1-octanol, 1-decanol, and oleyl alcohol) and non-toxic (sunflower oil, dodecane, and oleyl alcohol) diluents to prepare the organic solutions of different concentrations. The effect of initial concentration of acid in the aqueous phase, initial extractant concentration in the organic phase, type of extractant, polarity and toxicity of diluent, mixture of diluents and temperature is studied on the extraction efficiency.

The physical extraction of picolinic acid using nine different diluents, and chemical extraction with phosphoric and aminic extractants dissolved in inactive and active are carried out. Completely biocompatible system is also used to recover this acid. The back-extraction of picolinic acid is carried out by pure water. Nicotinic acid is separated from dilute aqueous solution using diluent mixture and using extractants in diluent mixtures. The effect of diluents on reactive extraction of nicotinic acid is studied with amine based extractant dissolved in five different diluents. A nontoxic diluent is also used to recover this acid. Physical and chemical extraction of isonicotinic acid is performed, and the effect of modifiers is also studied. Experiments are performed for this acid using nontoxic extractant-diluent system. Experiments are also carried out to analyze the effect of temperature (298, 313, 323 and 333 K) on the extraction efficiency.

The optimization of process variables to maximize the recovery of glycolic acid is done using experimental design and RSM model. The work is also done to predict the degree of extraction using RSM and ANN method for itaconic acid reactive extraction. The experiments are performed with aminic extractant dissolved in six different diluents for the recovery of formic acid at 4 different temperatures (298 to 343 K). Also, physical

and chemical extraction studies are carried out for levulinic acid using five different diluents and three different extractants. The intrinsic kinetics of extraction for nicotinic acid is described and the values of physical mass transfer coefficient, orders of extraction, and rate constants are determined.

6.1.4. Experimental Study

The stock solutions of the carboxylic acids are prepared to minimize experimental error and then diluted to the desired concentrations using deionized water to perform the equilibrium and kinetic experiments. The pH of initial aqueous solution is measured by a digital pH meter (ArmField Instruments, PCT 40, UK). The extraction of acids is carried out using (i) pure diluents (aliphatic, aromatic, chlorinated etc.), (ii) phosphorus based extractants [tri-*n*-butylphosphate (TBP), trioctylphosphine oxide (TOPO) and di-2-ethyl hexhyl phosphoric acid (D2EHPA)], and (iii) long chain aliphatic amine based extractants [tri-*n*-octylamine (TOA), tridodecylamine (TDDA) and trioctylmethylammonium chloride (Aliquat 336)]. Equal volumes (20 ml) of the aqueous and organic solutions are taken in conical flasks of 100 ml and shaken at 100 rpm for 8 hrs on a temperature controlled reciprocating shaker water bath (REMI Labs, HS 250, India) at constant temperature. In addition, the equilibrium experiments to study the effect of temperature are also carried out at different temperatures (313, 323, 328, 333 and 343 K). The back-extraction study is carried out using pure water (temperature swing regeneration) at 353 K. Kinetics experiments are carried out in a glass stirred cell (flat bottom with inside diameter 0.067 m and height 0.09 m) equipped with stainless steel dual flat blade stirrer. The analysis of the aqueous phase before and after extraction is performed using titration method and also by using UV-VIS spectrophotometer. The acid concentration in the organic phase is calculated by mass balance. The performance of the reactive extraction

process is analyzed by calculating the distribution coefficient, the degree of extraction and loading ratio.

6.1.5 Theoretical Study

A mathematical model based on mass action law is employed to determine the values of stoichiometry and equilibrium constants of reactive extraction. Using reaction stoichiometry, the simultaneous formation of various types of complexes is considered and individual equilibrium constants are estimated. The effect of diluent on the recovery of carboxylic acids is quantified by the LSER model using solvatochromic parameters of diluents. The modified Langmuir, Freundlich and Temkin models are also employed to describe the isothermal extraction process at equilibrium. To describe the influence of the nature, strength and hydrophobicity of the acid, the polarity and nature of the solvent and the basicity of extractant with respect to acid on the equilibrium constant of 1:1 complex formation, relative basicity model is employed. Design of experiments and response surface modeling approach are used to optimize the values of design variables of reactive extraction. An artificial neural network model is also used to solve non-linear and multivariate regression problem of reactive extraction. The kinetic model is used to predict the reaction regime, and estimate rate constants, and orders of chemical reaction.

6.1.6 Results and Discussion

In the following sections, experimental (equilibrium and kinetics), simulation and optimization results for the intensification of recovery of carboxylic acids by reactive extraction using pure diluents, phosphorus- and amine based extractants are presented and summarized.

6.1.6.1 Equilibrium Study

The equilibrium study on the recovery of various carboxylic acids [picolinic acid (0.01 - 0.25 mol·L^{-1}), nicotinic acid (0.02 - 0.12 mol·L^{-1}), isonicotinic acid (0.005 - 0.03 mol·L^{-1}), glycolic acid (0.01 - 0.57 mol·L^{-1}), itaconic acid (0.05 - 0.25 mol·L^{-1}), formic acid (0.265 - 1.323 mol·L^{-1}), and levulinic acid (0.111 - 0.541 mol·L^{-1})] from their dilute aqueous solutions using phosphorous [TBP (0.183 - 2.192 mol·L^{-1}), TOPO (0.10 - 0.50 mol·L^{-1}) and D2EHPA (0.50 mol.L^{-1})] as well as amine based extractants [TOA (0.115 - 0.648 mol·L^{-1}), TDDA (0.079 - 0.50 mol·L^{-1}) and Aliquat 336 (0.22 - 0.50 mol·L^{-1})] is carried out.

The physical extraction results of picolinic acid using nine different diluents (dodecane, cyclohexane, chlorobenzene, benzene, DCM, MIBK, 1-octanol, 1-decanol and oleyl alcohol) are presented. Low distribution of picolinic acid in all these diluents is observed with maximum value of $K_D^{diluent}$ of 0.867 with 1-octanol. The chemical extraction studies are carried out with 3 phosphoric- (TBP, TOPO and D2EHPA) and 3 aminic (TOA, TDDA and Aliquat 336) extractants dissolved in two different diluents [benzene (inactive) and 1-decanol (active)]. The order of extractant ability in terms of K_D is found to be TOA > TDDA > D2EHPA > TBP > Aliquat 336 > TOPO with both benzene and 1-decanol. The values of Z (between 0.004 and 0.179) show mainly the formation of 1:1 acid-extractant complexes in the organic phase.

To study the effect of diluent on the performance of reactive extraction of picolinic acid (0.01 to 0.10 mol·L^{-1}), experiments are performed with TOA (0.115 to 0.459 mol·L^{-1}) dissolved in five different diluents (cyclohexane, chlorobenzene, DCM, MIBK and 1-octanol). The extraction ability with TOA is obtained in the order of DCM ≥ MIBK > chlorobenzene > 1-octanol > cyclohexane. The maximum recovery of picolinic acid is found to 94.33% with TOA (0.456 mol·L^{-1}) in DCM at 0.1 mol·L^{-1} of acid concentration. The values of K_E and n per acid molecule are estimated by applying DE.

The recovery of picolinic acid (0.01 to 0.25 mol·L^{-1}) with TBP (0.365 to 2.192 mol·L^{-1}) and TDDA (0.079 to 0.474 mol·L^{-1}) dissolved in dodecane and oleyl alcohol as nontoxic diluents is performed. The values of K_D increase with an increase in extractant concentration, and decrease with an increase in the acid concentration. The highest extraction efficiency in terms of K_D is found to be 9.87 (E = 90.8%) with TDDA (0.474 mol·L^{-1}) in oleyl alcohol at 0.01 mol·L^{-1} of acid concentration. Now, based upon the values of Z, the equilibrium constants (K_{11}) of 1:1 complex formation are determined. Three different extraction models (modified Langmuir, Freundlich and Temkin) are also employed to describe the equilibrium behavior of the reactive extraction. The equilibrium data obtained from the extraction of picolinic acid fits the modified Langmuir isotherm model (*rmsd* = 0.0025) more exactly than that of the other two models (modified Freundlich and Temkin models).

The back-extraction of picolinic acid is carried out by pure water (temperature swing regeneration) at 353 K for TDDA (0.079 and 0.474 kmol·m^{-3}) in oleyl alcohol. It is found that the quantity of TDDA may not only affect the values of K_D in extraction step, but also plays an important role in the subsequent reverse extraction by pure water. Though, higher concentration of TDDA may provide better extraction of acid but would make the regeneration process difficult. The regeneration of the extractant loaded with high concentration of acid (C_{in} = 0.25 kmol·m^{-3}) will be easier (Z = 0.907 at $[\overline{TDDA}]_{in}$ = 0.079 kmol·m^{-3}) and higher distribution of acid ($K_{D'}$ = 9.524) can be achieved. Less loading of the extractant with the acid (Z = 0.435 at $[\overline{TDDA}]_{in}$ = 0.474 kmol·m^{-3}) results in lower distribution of acid ($K_{D'}$ = 9.524) and incomplete regeneration of the extracting agent. Therefore, alternate methods such as diluent swing regeneration can be adopted for the complete regeneration of the extractant loaded with very low concentration of picolinic acid.

The physical extraction of nicotinic acid is carried out with diluent mixture of 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v). The maximum values of $K_D^{diluent}$ are found to be 0.16 and 0.15 with 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v), respectively. Reactive extraction studies are also performed using TBP (0.183 and 0.365 mol·L^{-1}) dissolved in 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v). The maximum values of K_D are found to be 0.641 and 0.389 at 0.02 mol·L^{-1} of acid with TBP in 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v), respectively. In the reactive extraction of nicotinic acid using TOPO (0.10 to 0.50 mol·L^{-1}) dissolved in MIBK + kerosene (1:1 v/v), the maximum value of K_D is found to be 4.17 with highest value of K_E = 6.093. The values of K_E and n are estimated using graphical as well as optimization method (DE). The values of K_D are also predicted and it is observed that the experimental values of K_D show a good agreement with model predicted values with maximum error limit of ±15%. TBP and TOPO give lower distribution of acid. Therefore, reactive extraction studies are also performed with TOA (0.115 and 0.229 mol·L^{-1}) dissolved in mixture of diluents [1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v)]. The maximum extraction ability of 1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v) with TOA (0.229 mol·L^{-1}) in terms of K_D is found to be 7.368 and 0.805, respectively, at 0.02 mol·L^{-1} of acid concentration. 1-Decanol + cyclohexane (1:1 v/v) with TOA gives highest extraction with E of 88.05% and K_E of 26.98 L·mol^{-1}.

The effect of diluents on reactive extraction of nicotinic acid is studied with TOA (0.229 mol·L^{-1}) dissolved in dodecane, toluene, 1-decanol, MIBK and chloroform. Chloroform ($K_{D,max}$ = 45.154), 1-decanol ($K_{D,max}$ = 26.027) and MIBK ($K_{D,max}$ = 4.882) are found to be better diluents than dodecane ($K_{D,max}$ = 0.111) and toluene ($K_{D,max}$ = 1) with TOA. The values of Z suggest no overloading of acid molecules on TOA and formation of mainly 1:1 acid-TOA solvates in the organic phase. The experimental values

of equilibrium constant (K_{11}) are calculated and compared with the model (LSER and relative basicity) predicted values of K_{11}. The LSER and relative basicity models predict the values of K_{11} with an error limit of ±3% and ±20%, respectively.

The reactive extraction of nicotinic acid (0.02 to 0.12 mol·L^{-1}) is presented using TOA (0.44 mol·L^{-1}) and Aliquat 336 (0.44 mol·L^{-1}) in sunflower oil (a nontoxic diluent). The maximum extraction capacity of sunflower oil is observed to be 14.97% with TOA and 12.46% with Aliquat 336 at 0.02 mol·L^{-1} of initial acid concentration which is very low. Therefore, the effect of phase modifiers (dodecane and 1-octanol) is also studied. The values of m and K_E are estimated applying DE optimization approach. The values of m are found to be near about one with TOA implying mainly the formation of 1:1 acid-TOA complexes in the organic phase. In case of Aliquat 336, the values of m are found to be 0.90 for sunflower oil, 0.63 for sunflower oil + dodecane (1:1 v/v), and 0.52 for sunflower oil + 1-octanol (1:1 v/v). Extraction using sunflower oil + dodecane (1:1 v/v) (m = 0.63) and sunflower oil + 1-octanol (1:1 v/v) (m = 0.52) with Aliquat 336 indicates more than one solvation number of Aliquat 336, and possibility of 1:2 complex formation in the organic phase. The values of K_{11} and K_{12} for 1:1 and 1:2 complex formations, respectively, are also determined.

The equilibrium results on physical extraction of isonicotinic acid (0.0043 to 0.0349 mol·L^{-1}) using hexane, toluene, DCM, dodecane and oleyl alcohol are described in this study. Lower values of distribution coefficient are found with all the diluents. In the chemical extraction of this acid with TBP (0.365 to 1.096 mol·L^{-1}) dissolved in three diluents (hexane, toluene, and DCM), the extraction yield of the acid with TBP is found to be 15.35% for hexane, 54.98% for toluene and 67.26% for DCM. The reactive extraction studies are also carried out using 1-decanol and MIBK as modifiers. The structures of the interfacial complexes are observed as 1:1 for hexane, and 1:1 and 1:2 for toluene and DCM without the use of phase modifiers. The addition of 1-decanol and

MIBK does not make any change in the acid-TBP complex structure but exhibits a negative effect on the extraction constants and a positive effect on the extraction efficiency for all types of diluents used. Therefore, these findings indicate that the mechanism of the interfacial reaction between acid and extractant is controlled by the organic phase polarity.

The extraction ability of TBP is found to be comparatively low. Therefore, recovery of isonicotinic acid (0.005 to 0.03 mol·L^{-1}) is carried out with TOA (0.229 mol·L^{-1}) dissolved in dodecane, toluene, 1-decanol, MIBK, chloroform. The slope of the isotherms is found to increase with the polarity of the diluent. The ability of diluent to solvate the acid-TOA complex follows the order as chloroform ($K_{D,max}$ = 25.79) > 1-decanol ($K_{D,max}$ = 19.13) > MIBK ($K_{D,max}$ = 2.5) > toluene ($K_{D,max}$ = 1.69) > dodecane ($K_{D,max}$ = 1.07). The values of Z suggest that the organic phase is not over loaded with acid and there are formations of 1:1 acid-TOA complexes in the organic phase. The experimental values of the equilibrium constants of 1:1 acid-TOA complex formation (K_{11}) are determined using mass action law and compared with the model (relative basicity and LSER) predicted values of K_{11}. The relative basicity and LSER models predict the values of K_{11} with an error limit of ±18% and ±3%, respectively.

Distribution of isonicotinic acid (0.002 to 0.025 mol·L^{-1}) between water and TDDA (0.079 to 0.316 mol·L^{-1}) dissolved in nontoxic diluents (dodecane and oleyl alcohol) is studied. At first, optimum combination of diluents is chosen and then further experiments are carried out with a 1:1 v/v ratio of dodecane and oleyl alcohol. Experiments are also carried out to analyze the effect of temperature (298, 313, 323 and 333 K) on the K_D and E of reactive extraction of isonicotinic acid with TDDA (10 %v/v) in dodecane + oleyl alcohol (1:1 v/v). The increase in the temperature shows a negative effect on the extraction. The values of K_{11} are estimated at different temperatures and are used to find the values of change in enthalpy (ΔH) and entropy (ΔS) of reaction. The

negative value of ΔH (-28.27 kJ·mol^{-1}) is found which indicates that extraction reactions are exothermic in nature.

The equilibrium study on the reactive extraction of glycolic acid from aqueous solution by TBP and TOA at constant concentration of 0.573 mol·L^{-1} dissolved in a wide range of diluents [hexane, 1-decanol, hexane + 1-decanol (1:1 v/v), MIBK, benzene, and DCM] at 298 K is carried out. The effects of acid concentration (0.10 to 0.57 mol·L^{-1}) and diluent on the recovery of the acid from aqueous solution are derived. The values of equilibrium constants (K_E), number of reacting acid molecules (m) per extractant molecule, and also the equilibrium constants (K_{11} and K_{21}) for individual complex formation are estimated through a proposed mathematical model and using DE. Further, the experimental values of the distribution coefficients (K_D) are correlated using LSER model which is based on solute-solvent interaction parameters. The extraction power of TBP and TOA in terms of K_D increases in the order of DCM ≥ MIBK > 1-decanol > hexane + 1-decanol (1:1 v/v) ≥ benzene ≥ hexane, and DCM ≥ 1-decanol > MIBK > hexane + 1-decanol (1:1 v/v) > benzene > hexane, respectively.

To obtain optimum design variables and to maximize the recovery of glycolic acid, experimental design using CCOD is considered to carry out equilibrium experiments. RSM model, based on a statistical approach, is used to correlate the response (degree of extraction) as a function of design factors [initial acid concentration, TOA composition, modifier (1-decanol) composition and equilibrium temperature]. The F-value (124.54), P-value (6.169×10^{-16}) and R^2 (= 0.9794) obtained by ANOVA indicates better fit of the RSM regression model. The effect of design variables on the degree of extraction is also explained. The model equation given by RSM is optimized to find the global optimum conditions of variables using DE. The optimal solutions are obtained as: C_{in} = 0.1707 mol·L^{-1}, $[\bar{S}]_{in}$ = 22.31 %v/v, C_M =73.28 %v/v and τ = 23 ± 0.5

^{o}C. At these optimum conditions, the predicted and experimental values of degree of extraction are found to be 94.95% and 91.83%, respectively.

The equilibrium study on the reactive extraction of itaconic acid (five initial acid concentrations in the range of 0.05 to 0.25 mol·L^{-1}) from aqueous solution by TOA (0.115 and 0.229 mol·L^{-1}) as extractant dissolved in six different diluents (heptane, kerosene, toluene, 1-decanol, MIBK, and DCM) is performed. The highest value of the K_D is found to be 32.478 at 0.05 mol·L^{-1} of acid concentration with 0.229 mol·L^{-1} of TOA in DCM. A mathematical model is developed and used to estimate K_E, m, and n of the reactive extraction. Based on the stoichiometry, the corresponding values of K_{11}, K_{21} and K_{12} for the formation of 1:1, 2:1 and 1:2 acid-TOA complexes are also determined. Further, the experimental values of K_D are correlated using LSER model.

The work is also carried out to obtain predictive models using RSM and ANN techniques for the prediction of the degrees of extraction of reactive extraction of itaconic acid. The design parameters for the reactive extraction of itaconic acid are chosen as initial acid concentration, initial amine (TOA) and modifier composition (DCM). A value of R^2 equal to 0.97 along with values of F (21.24) and P (6.97×10^{-4}) indicate a better fit of the RSM regression model. An ANN model (3:5:1) is also proposed for itaconic acid reactive extraction. The optimum values of weights and biases are found using back-propagation method based on Levenberg-Marquardt Algorithm. During the training, the value of the performance function (9.59×10^{-4}) is found to be lower than the goal ($\leq 10^{-3}$). In addition, ANOVA gives a very high F-value (154.35) and a very low P-value (~ 0). All these statistical estimators indicate that RSM and ANN models can be used to predict degree of extraction of reactive extraction process.

The equilibrium experiments on the recovery of formic acid from aqueous solutions (industrial waste stream, bio-oil generated stream and fermentation broth) using reactive extraction with and without TOA in decane, benzene, 1-decanol, decane + 1-

decanol (3:1 v/v), MIBK, and chloroform are carried out. The maximum extraction efficiency, $K_{D,\,max}$ is found to be 29.11 with TOA in chloroform at 298 K. Differential evolution optimization technique is employed to estimate stoichiometry of reaction (*m* and *n*), overall (K_E) and individual (K_{11}, K_{21}, K_{31} and K_{12}) equilibrium constants through a proposed mathematical model. The effect of diluent on K_D is quantified by LSER model using solvatochromatic parameters of diluent. The effect of temperature (298 to 343 K) on K_D is also studied. The values of ΔH and ΔS of reactive extraction are also calculated.

The physical extraction of levulinic acid (0.111 to 0.541 mol·L^{-1}) using five different diluents (dodecane, benzene, 1-octanol, MIBK and DCM) is carried out, and chemical extraction results are obtained using four different concentrations of TBP (0.365 to 2.192 mol·L^{-1}), TOA (0.115 to 0.689 mol·L^{-1}), and Aliquat 336 (0.109 to 0.653 mol·L^{-1}). Among all the diluents studied, DCM yields a maximum value of K_D (1.656 with TBP, 12.151 with TOA, and 2.151 with Aliquat 336) due to polarity and hydrogen bonding ability with all the extractants. Aliphatic hydrocarbon (dodecane) exhibits low extraction ability. The values of Z are found to be in the range of 0.024 to 0.428 with TBP, 0.011 to 2.465 with TOA, and 0.044 to 1.522 with Aliquat 336 promoting probably 1:1 acid-TBP complex formation, and 1:*n* ($n \neq 1$) complex formation with both TOA and Aliquat 336.

6.1.6.2 Kinetic Study of Nicotinic acid using TOA

The intrinsic kinetics of extraction of nicotinic acid by TOA in MIBK is also studied based on the theory of extraction accompanied by a chemical reaction. The value of physical mass transfer coefficient (k_L) is evaluated as 2.03×10^{-5} m·s^{-1}. The effect of speed of agitation (30 rpm to 90 rpm) and volume ratio of the phases (0.5 to 2) on the initial specific rate of extraction is studied. The reactive extraction of nicotinic acid with TOA in MIBK is determined to be taking place in Regime 1 (extraction accompanied by a slow chemical reaction) with *Hatta number* equal to 0.12. The data are regressed to

obtain orders of extraction as 0.7 with respect to acid and 0.5 with respect to TOA. The rate constant of forward reaction (k_1) and back-ward reaction (k_{-1}) are found to be 8.4×10^{-4} $(\text{mol}\cdot\text{m}^{-3})^{-0.2}\text{s}^{-1}$ and 3.31×10^{-5} $(\text{mol}\cdot\text{m}^{-3})^{-0.2}\text{s}^{-1}$, respectively.

6.2 Conclusions

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

1. Reactive extraction with a specified extractant and diluent system is found to be a promising technique (efficient, economical, and environmental friendly) for the separation of carboxylic acids from fermentation broths and wastewater streams.
2. In the physical extraction of carboxylic acids, lower values of distribution coefficient (< 1) are obtained.
3. Polar diluents solvate acid molecule with less dimer formation in the organic phase and greater amount of acid molecule is distributed between the phases, but existence of acid dimer is observed for non-polar diluents.
4. Extraction results on carboxylic acids show that active solvents (1-decanol, MIBK, DCM etc.) are found to be better solvating agents compared to inactive ones (hexane, decane, dodecane etc.). The presence of active groups enhances the extracting capability of extractant.
5. Mixed diluents [1-decanol + cyclohexane (1:1 v/v) and MIBK + kerosene (1:1 v/v)] as used in the extraction studies avoid the formation of a stable emulsion and dimer in the organic phase and assure a higher solubility of the formed acid-extractant complex in the organic phase. 1-Decanol + cyclohexane (1:1 v/v) shows better solvation of acid compared to MIBK + kerosene (1:1 v/v).
6. Organophosphorus compounds (TBP, TOPO and D2EHPA) show stronger Lewis basicity than those of pure diluents which is responsible for better extraction of carboxylic acids from dilute aqueous solution.

7. The specific affinity of long chain aliphatic amines (TOA, TDDA and Aliquat 336) for carboxylic acid gives high selectivity for acid and eventually non-acidic species in the mixture.
8. For the extraction of pyridine carboxylic acids, ionization of the pyridine group takes place at strong acidic pH domain (~ pK_{a1}) and an increase in the value of pH induces dissociation of -COOH group (~ pK_{a2}). Both phenomena reduce extraction efficiency. So, the optimum value of the aqueous phase pH should lie in between pK_a's of the acids.
9. With increase in concentration of picolinic acid, the values of K_D are found to increase for cyclohexane, DCM and MIBK, and decease for chlorobenzene and 1-octanol. The maximum removal of picolinic acid is obtained as 94.33% with TOA (0.456 mol·L^{-1}) in DCM at 0.1 mol·L^{-1} of picolinic acid initial concentration.
10. Picolinic acid is extracted by phosphoric (TBP, TOPO and D2EHPA) and aminic (TOA, TDDA and Aliquat 336) extractants in benzene and 1-decanol. The order in which the extractants recover the acid from the aqueous solution is found to be TOA > TDDA > D2EHPA > TBP > Aliquat 336 > TOPO.
11. In the intensification of the recovery of picolinic acid using TBP and TDDA in dodecane and oleyl alcohol as nontoxic diluents, the higher synergistic effect of extraction in terms of K_D is found to be 9.87 with TDDA (0.474 mol·L^{-1}) in oleyl alcohol at lower acid concentration.
12. Modified Langmuir, Freundlich and Temkin models are employed to describe the equilibrium behavior of the reactive extraction of picolinic acid using TBP and TDDA. The equilibrium data obtained from the extraction of picolinic acid fits the modified Langmuir isotherm model (*rmsd* = 0.0025) more exactly than other two models, which shows that the extraction of picolinic acid using TBP and TDDA is more of monolayer extraction.

13. In the back-extraction of picolinic acid by pure water at 353 K for TDDA (0.079 and 0.474 kmol·m^{-3}) in oleyl alcohol, an increase in the concentration of TDDA reduces distribution coefficient of back-extraction. Though, higher concentration of TDDA may provide better extraction of acid but would make the regeneration process difficult.
14. The regeneration of the extractant loaded with high concentration of acid will be easier, but low loading results in incomplete regeneration of the extracting agent. In this case, diluent swing regeneration can be adopted for complete regeneration of the organic phase.
15. Results obtained on reactive extraction of nicotinic acid with TOA (0.229 mol·L^{-1}) dissolved in dodecane, toluene, 1-decanol, MIBK and chloroform show that equilibrium isotherms are almost linear and can be explained by Henry's law.
16. In the reactive extraction of nicotinic acid with TOA and Aliquat 336, sunflower oil is used as a natural nontoxic diluent. The maximum removal capacity of sunflower oil is found to be 14.97% with TOA and 12.46% with Aliquat 336. The increase in the extraction capacity is found when dodecane (non-polar) and 1-octanol (polar) are used as phase modifiers. The increase is more in case of 1-octanol.
17. The ability of diluent to solvate the isonicotinic acid-TOA complex follows the order as chloroform ($K_{D,max}$ = 25.79) > 1-decanol ($K_{D,max}$ = 19.13) > MIBK ($K_{D,max}$ = 2.5) > toluene ($K_{D,max}$ = 1.69) > dodecane ($K_{D,max}$ = 1.07).
18. Studies on the recovery of isonicotinic acid with TBP show that in absence of modifiers the extraction yield of acid is found to be 15.35% for hexane, 54.98% for toluene and 67.26% for DCM. The addition of 1-decanol and MIBK as modifiers does not make any change in the acid-TBP complex structure but

exhibits a negative effect on the extraction constants and a positive effect on the extraction efficiency for all type of solvents.

19. The extraction power of TBP/diluent and TOA/diluent system for glycolic acid extraction in terms of K_D is found to be in the order of DCM ≥ MIBK > 1-decanol > hexane + 1-decanol (1:1 v/v) ≥ benzene ≥ hexane, and DCM ≥ 1-decanol > MIBK > hexane + 1-decanol (1:1 v/v) > benzene > hexane, respectively.
20. In the reactive of extraction of glycolic acid, the values of Z less than 0.5 for hexane suggest no overloading of acid on the TOA and greater than 0.5 for all other diluents [1-decanol, hexane + 1-decanol (1:1 v/v), MIBK, benzene and DCM] indicate TOA is overloaded with acid. This shows possible formation of 1:1 and 2:1 complexes between the glycolic acid and TOA. Using TBP, the values of Z are found to be less than 0.5 with all the diluents and this implies the formation of 1:1 acid-TBP solvates in the organic phase.
21. Design variables for reactive of extraction of glycolic acid are modeled using RSM which is then optimized using differential evolution. ANOVA analysis shows that a larger F-value (124.54) and P-value near about zero (6.17×10^{-16}) with R^2 of 0.9794 are obtained for RSM. At optimum conditions (C_{in} = 0.1707 mol·L^{-1}, $[\bar{S}]_{in}$ = 22.31 %v/v, C_M =73.28 %v/v and T = 23 ± 0.5 ^{o}C), the predicted and experimental values of degree of extraction are found to be 94.95% and 91.83%, respectively.
22. The diluents ability to recover itaconic acid with TOA in terms of K_D is found in the order of DCM > MIBK ≥ 1-decanol > toluene > kerosene > heptane and the highest extraction efficiency (K_D = 32.478, E = 97.01 % and Z = 1.692) is found with TOA in DCM.
23. RSM and ANN techniques are used to obtain predictive models for the estimation of the degrees of extraction of reactive extraction of itaconic acid using TOA in

DCM (modifier) and cyclohexane (inert diluent). The ANOVA results for RSM model (F-value = 21.24, P-value = 6.97×10^{-4} and R^2 =0.97) and ANN model (F-value = 154.35, P-value = 5.87×10^{-10} and R^2 = 0.993) dictate better fit of model predicted and experimental values of degree of extraction.

24. Physical and chemical equilibria results on the recovery of levulinic acid show that among all the diluents studied, DCM yields a maximum value of K_D (1.656 with TBP, 12.151 with TOA and 2.151 with Aliquat 336) due to polarity and hydrogen bonding ability with all the extractants. Aliphatic hydrocarbon (dodecane) exhibits low extraction ability.
25. In levulinic acid extraction, the values of n ($\approx$ 1) are found mostly for inactive diluents (dodecane and benzene) at lower acid concentration and suggest the existence of a stoichiometric association between the individual acid and extractant molecule. The values of n deviate in case of active solvents (1-octanol, MIBK and DCM) showing higher order of stoichiometric reactions, 2:1, 3:1 etc.
26. The effect of temperature on the degree of extraction shows that distribution of acid (formic acid and isonicotinic acid) into the organic solvent phase decreases sharply with an increase in temperature due to the back-extraction of the acid from the solvent to a fresh aqueous phase without overall dilution of the acid**.**
27. The LSER model is applied in the extraction of glycolic-, itaconic-, formic-, nicotinic-, and isonicotinic acids to predict the values of K_D for extractant-diluent systems. The estimated values of K_D are found to show good correlation with the experimental values.
28. In the reactive extraction kinetics of nicotinic acid with MIBK, the speed of agitation has no effect on the initial specific rate of extraction but varies linearly with volume ratio of phases. In this region, the diffusion contribution is minimized and the rate of extraction becomes mainly controlled by chemical reactions.

29. The kinetics of nicotinic acid with TOA in MIBK is determined to be taking place in regime 1 (extraction accompanied by a slow chemical reaction). The orders of extraction are found to be 0.7 with respect to acid and 0.5 with respect to TOA with rate constant of forward and back-ward reaction of 8.4×10^{-4} $(mol \cdot m^{-3})^{-0.2}s^{-1}$ and 3.31×10^{-5} $(mol \cdot m^{-3})^{-0.2}s^{-1}$, respectively.

6.3 Major Contributions

1. Physical and chemical equilibria data on the recovery of picolinic, nicotinic, isonicotinic, glycolic, itaconic, formic and levulinic acids are generated using different diluent systems comprised of inert-, active- and non-toxic diluents with/without phosphoric and aminic extractants.
2. The effect of initial concentration of acid in the aqueous phase, initial extractant concentration in the organic phase, type of extractant, polarity and toxicity of diluent, mixture of diluents and temperature is studied on the extraction efficiency.
3. Reactive extraction studies are performed with natural and conventional non-toxic diluent and non-toxic extractant systems to propose biocompatible extractant system.
4. Regeneration of organic phase (back-extraction study) is done for picolinic acid reactive extraction.
5. Kinetic studies are carried out for the extraction of nicotinic acid using TOA in MIBK.
6. Design of experiments method is used to conduct the experiments and optimum of design variables is found for reactive extraction of glycolic acid using DE.

7. Mass action law, linear solvation energy relationship, response surface methodology, artificial neural network, modified Langmuir, modified Freundlich, modified Temkin, and relative basicity models are used in the equilibrium study.
8. Differential evolution (DE) optimization approach is employed to determine the values of equilibrium constants (K_E) and the stoichiometries (m, n) of reactive extraction.

6.4 Future Scope of Research

The future scope of this work is enumerated below:

1. Equilibrium and kinetic study on the extraction of picolinic, nicotinic, isonicotinic and glycolic acids can be carried out using a porous membrane supported with amine or ionic liquid based extractants.
2. Designing a continuous system (fermentor + extractor + regenerator) for the intensification of microbial production of organic acids.

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APPENDIX - I

Code in MATLAB to Estimate 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 = [];
CHLbar = [];
R3Nin = [];

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

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

objFctHandle = @rosenbrocksaddle;

paramDefCell = {
   'parameter1', [ ], 0.01
   'parameter2', [ ], 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' to Estimate the Values of 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 20
#define D 2
#define genmax 200

#define F 0.7
#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\\dipaloy_DE code\\code\\test.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 'C' to Estimate the Values of K_{11}, K_{21} and K_{31}

```
#include <stdio.h>
#include <stdlib.h>
#include <math.h>
#include <time.h>

#define D 3.0
#define NP 30.0
#define F 0.9
#define CR 0.5
#define GEN 1000
#define La 0.0
#define Ha 200.0
#define Lb 0.0
#define Hb 1000.0
#define Lc 0.0
#define Hc 2000.0
#define RAND(X,Y) (X+(rand()/(double)RAND_MAX)*(Y-X))

int main()
{
        srand(time(NULL));
        double X[(int)D], Pop[(int)D][(int)NP], Fit[(int)NP], f;
        int Best = 0;
        int i,j,g;
        int Rnd, r[3];
        double exp[6] = {0.052325,0.102175,0.149554901,0.19785,0.2475,0.295};
        double Chla[6] = {0.0144,0.0315,0.0513,0.0702,0.0883,0.1076};
        double Chlo[6], c11[6], c21[6], c31[6], Cr3n[6];
        double s;

        for (j=0; j<NP; j++)
        {
                Pop[0][j] = X[0] = RAND(La,Ha);       // X[0] = k11, X[1] = k21, X[2] =
k31 //
                Pop[1][j] = X[1] = RAND(Lb,Hb);
                Pop[2][j] = X[2] = RAND(Lc,Hc);

                for (i=0; i<6; i++)
                {
                        Cr3n[i]                                                    =
0.46/(1+(X[0]*Chla[i])+(X[0]*X[1]*Chla[i]*Chla[i])+(X[0]*X[1]*X[2]*Chla[i]*Chla[i]
*Chla[i]));
                        c11[i] = Chla[i]*Cr3n[i]*X[0];
                        c21[i] = Chla[i]*c11[i]*X[1];
                        c31[i] = Chla[i]*c21[i]*X[2];
```

```
                Chlo[i] = c11[i] + (2*c21[i]) + (3*c31[i]);
        }
        s = 0;
        for (i=0; i<6; i++)
                s = s + ((Chlo[i] - exp[i])*(Chlo[i] - exp[i]))/Chlo[i];

        Fit[j] = s;
    }
    for (g=0; g<GEN; g++)
    {
        for (j=0; j<NP; j++)
        {
                r[0] = (int) (RAND(0,NP));

                while (r[0]==j)
                        r[0] = (int) (RAND(0,NP));

                r[1] = (int) (RAND(0,NP));

                while ((r[1]==r[0]) || (r[1]==j))
                        r[1] =  (int) (RAND(0,NP));

                r[2] = (int) (RAND(0,NP));

                while ((r[2]==r[0]) || (r[2]==r[1]) || (r[2]==j))
                        r[2] = (int) (RAND(0,NP));

                Rnd = (int) (RAND(0,D));
    for (i=0; i<D; i++)
                {
                        if (RAND(0,1)<CR)
                                X[i] = Pop[i][r[2]] + F * (Pop[i][r[0]] -
Pop[i][r[1]]);
                        else
                                X[i] = Pop[i][j];
                }

                //Verifying boundary conditions//
                if (X[0]<La || X[0]>Ha)
                        X[0] = RAND(La,Ha);
                if (X[1]<Lb || X[1]>Hb)
                        X[1] = RAND(Lb,Hb);
                if (X[2]<Lc || X[2]>Hc)
                        X[2] = RAND(Lc,Hc);

                for (i=0; i<6; i++)
                {
                        Cr3n[i]                                                 =
0.46/(1+(X[0]*Chla[i])+(X[0]*X[1]*Chla[i]*Chla[i])+(X[0]*X[1]*X[2]*Chla[i]*Chla[i]
*Chla[i]));
                        c11[i] = Chla[i]*Cr3n[i]*X[0];
```

```
                        c21[i] = Chla[i]*c11[i]*X[1];
                        c31[i] = Chla[i]*c21[i]*X[2];
                        Chlo[i] = c11[i] + (2*c21[i]) + (3*c31[i]);
                }

                s = 0;
                for (i=0; i<6; i++)
                        s = s + ((Chlo[i] - exp[i])*(Chlo[i] - exp[i]))/Chlo[i];
                f = s;

                if (f <= Fit[j])
                {
                        for (i=0; i<D; i++)
                                Pop[i][j] = X[i];
                        Fit[j] = f;

                        if (f <= Fit[Best])
                                Best = j;
                }
        }
    }

    // RESULTS //
    printf("OPTIMUM : \n");
    printf("K11 = %lf\n",Pop[0][Best]);
    printf("K21 = %lf\n",Pop[1][Best]);
    printf("K31 = %lf\n",Pop[2][Best]);
    printf("Error Sum = %lf\n",Fit[Best]);
    printf("\n\nExperimental Values - ");
    for(i=0; i<6;i++)
        printf("  %lf",exp[i]);
    printf("\n\nCalculated Values - ");
    for (i=0; i<6; i++)
    {
        Cr3n[i]                                                                    =
0.46/(1+(Pop[0][Best]*Chla[i])+(Pop[0][Best]*Pop[1][Best]*Chla[i]*Chla[i])+(Pop[0][B
est]*Pop[1][Best]*Pop[2][Best]*Chla[i]*Chla[i]*Chla[i]));
        c11[i] = Chla[i]*Cr3n[i]*Pop[0][Best];
        c21[i] = Chla[i]*c11[i]*Pop[1][Best];
        c31[i] = Chla[i]*c21[i]*Pop[2][Best];
        Chlo[i] = c11[i] + (2*c21[i]) + (3*c31[i]);
        printf("  %lf",Chlo[i]);
    }
    printf("\n\n");
    return 0;
}
```

APPENDIX - IV

Code in 'MATLAB' for the Response Surface Model Optimization

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

x1 = params.parameter1(1);
x2 = params.parameter2(1);
x3 = params.parameter3(1);
x4 = params.parameter4(1);
y = params.parameter5(1);

z = (y - (70.556 - 3.776*x1 + 5.439*x2 + 17.384*x3 - 4.749*x4 - 2.642*x2.^2 -
3.87*x3.^2 + 2.807*x1.*x3 - 2.119*x2.*x3));

val = scale*(z);
pause(0.001);

function demo1

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

% specify objective function
objFctHandle = @rosenbrocksaddle;

% define parameter names, ranges and quantization:
paramDefCell = {
   'parameter1', [-1.414 1.414], 0.001
   'parameter2', [-1.414 1.414], 0.001
   'parameter3', [-1.414 1.414], 0.001
   'parameter4', [-1.414 1.414], 0.001
   'parameter5', [0 100], 0.5
};

% set initial parameter values in struct objFctParams
objFctParams.parameter1 = 1.414;
objFctParams.parameter2 = 1.111;
objFctParams.parameter3 = 1.414;
objFctParams.parameter4 = -1.414;
objFctParams.parameter5 = 100;

% set single additional function parameter
objFctSettings = 100;

% get default DE parameters
DEParams = getdefaultparams;

% set number of population members (often 10*D is suggested)
```

```
DEParams.NP = 50;

% do not use slave process here
DEParams.feedSlaveProc = 0;

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

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

% do not send E-mails
emailParams = [];

% set random state in order to always use the same population members here
rand('state', 1);

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

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

LIST OF PUBLICATIONS

International Journals (Referred)

1. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Glycolic Acid using Tri-*n*-Butylphosphate and Tri-*n*-Octylamine in Six Different Diluents: Experimental Data and Theoretical Predictions, *Industrial Engineering and Chemistry Research,* 2011, 50 (5), 3041 - 3048.
2. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of 2-Methylidenebutanedioic Acid with *N*, *N*-Dioctyloctan-1-amine Dissolved in Six Different Diluents: Experimental and Theoretical Equilibrium Studies at (298 ± 1) K. *Journal of Chemical and Engineering Data,* 2011, 56 (5), 2574 - 2582.
3. **Dipaloy Datta**, Sushil Kumar and Kailash L. Wasewar, Reactive Extraction of Benzoic Acid and Pyridine-3-Carboxylic Acid using Organophosphoric- and Aminic Extractant Dissolved in Binary Diluent Mixtures, *Journal of Chemical and Engineering Data***,** 2011, 56 (8), 3367 - 3375.
4. **Dipaloy Datta**, Sushil Kumar, Kailash L. Wasewar and B. V. Babu, Comparative Study on Reactive Extraction of Picolinic Acid with Six Different Extractants (Phosphoric and Aminic) in Two Different Diluents (Benzene and Decan-1-ol), *Separation Science and Technology*, 2012, 47, 997- 1005.
5. **Dipaloy Datta** and Sushil Kumar, Modeling and Optimization of Recovery Process of Glycolic Acid using Reactive Extraction, *International Journal of Chemical Engineering and Applications*, 2012, 3 (2), 141-146.
6. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Pyridine Carboxylic Acids with N, N-Dioctyloctan-1-amine: Experimental and Theoretical Studies, *Separation Science and Technology* (In press).
7. **Dipaloy Datta** and Sushil Kumar, Intensification of Recovery of Formic Acid from Aqueous Stream using Reactive Extraction with N, N-dioctyloctan-1-amine: Effect of Diluent and Temperature, *Chemical Engineering Communications* (In press).
8. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Picolinic Acid with Tri-*n*-Octylamine Dissolved in Petroleum Ether, MIBK and Iso-amyl Alcohol, *Journal of Environmental Research and Development* (In press).
9. **Dipaloy Datta** and Sushil Kumar, Modeling Using Response Surface Methodology and Optimization Using Differential Evolution of Reactive Extraction of Glycolic Acid, *Chemical Engineering Communications* (Accepted).
10. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Picolinic Acid Using Nontoxic Extractant and Diluent Systems, *Journal of Chemical and Engineering Data* (Communicated).
11. **Dipaloy Datta** and Sushil Kumar, Equilibrium and Kinetic Studies on Reactive Extraction of Nicotinic Acid with Tri-*n*-octylamine Dissolved in MIBK (Communicated).
12. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Isonicotinic Acid from Aqueous Solution by Nontoxic Reactive System (To be communicated).
13. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Isonicotinic Acid with Tri-*n*-Butylphosphate Dissolved in Different Diluents: Effect of Modifier (To be communicated).

14. **Dipaloy Datta** and Sushil Kumar, Artificial Neural Network Modeling and Differential Evolution Optimization of Reactive Extraction of Itaconic Acid (To be communicated).
15. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Picolinic Acid with Tri-*n*-Octylamine Dissolved in Different Diluents (To be communicated).
16. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Levulinic Acid with Tri-*n*-Butyl Phosphate, Tri-*n*-Octylamine and Aliquat 336 Dissolved in Different Diluents (To be communicated).

International Conference Proceedings (in India)

1. **Dipaloy Datta** and Sushil Kumar, Reactive Extraction of Itaconic Acid using Tri-*n*-Octylamine (TOA) Dissolved in Different Diluents, International Symposium and 63rd Annual Session of IIChE (CHEMCON-2010), Annamalai University, Annamalainagar, December 27-29, 2010.
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BIOGRAPHIES

Biography of the Candidate

Mr Dipaloy Datta is working as Lecturer in the Department of Chemical Engineering at Birla Institute of Technology and Science (BITS) - Pilani, and currently pursuing his PhD under the supervision of Dr Sushil Kumar. He has completed his B E (Hons.) and M E in Chemical Engineering from BITS-Pilani. He also worked with Tripura Institute of Technology, Agartala, Tripura as Lecturer from November, 2004 to June, 2007. He joined BITS-Pilani as a Teaching Assistant in August 2007 and as a Lecturer in January 2010.

He has 8 years of teaching experience and has guided 1 BE Dissertation student, 2 Research Practice students, 1 ME dissertation student and around 10 project students. He taught courses such as Chemical Engineering Thermodynamics, Thermodynamics, Fluid Flow Operations, Extractive Metallurgy, Cement Technology, Structure and Properties of Materials, Chemical Process Calculations, and involved in the tutorials of Process Design Decisions and Chemical Process Technology. His research areas include *Process Intensification using Reactive Extraction, Separation Processes, Modeling, Simulation and Optimization*.

He is a Member of Organizing Committee for "Conference on Technological Advancements in Chemical and Environmental Engineering (TACEE – 2012)" held at BITS-Pilani during March 23-24, 2012, and for SCHEMCON 2012, September 27-28, 2012, BITS Pilani. He is a Life Associate Member of Indian Institute of Chemical Engineers (IIChE), Member of Asia-Pacific Chemical, Biological and Environmental Engineering Society (APCBEES), and American Institute of Chemical Engineers (AIChE - 2012).

Biography of the Supervisor

Dr Sushil Kumar, Assistant Professor, Department of Chemical Engineering at Birla Institute of Technology and Science (BITS) - Pilani, has over 10 years of industrial, teaching, and research experience. He did his B Tech from Harcourt Butler Technological Institute (HBTI) - Kanpur, M Tech from Indian Institute of Technology (IIT) - Kanpur and PhD from BITS - Pilani.

His current research interests include *Separation Processes, Process Intensification, Biochemical Engineering, Polymer Technology, Modeling and Simulation Liquid-Liquid Equilibria,* and *Renewable Energy Sources*. He has around 70 research publications (23 refereed journals, 45 conferences and 2 book chapters) to his credit which have been published over the years in various International and National Journals and Conference Proceedings. Dr Kumar is supervising 3 scholars for their doctoral research. Besides this, he has guided 7 ME Dissertations and around 20 BE Project students under his supervision.

He is the referee and expert reviewer of 14 International Journals (Journal of Chemical and Engineering Data, Industrial and Engineering Chemistry Research, Biotechnology and Bioprocess Engineering, Desalination etc.). He also reviewed three books of Tata McGraw Hill publisher. He is awarded Research Project by Department of Science and Technology, New Delhi, India under Fast Track Scheme for Young Scientists, 2012-2014.

Dr Kumar is the Life member of Indian Institute of Chemical Engineers (IIChE), a Member of AIChE for the year - 2010 and 2012, and Executive Committee Member, Pilani Regional Centre of IIChE chapter. He is the Organizing Secretary for "Conference on Technological Advancements in Chemical and Environmental Engineering (TACEE - 2012)" held at BITS-Pilani during March 23-24, 2012, and Treasurer for SCHEMCON 2012 held during September 27-28, 2012 at BITS-Pilani.