RECOVERY OF GLYCOLIC AND GLYOXALIC ACIDS BY REACTIVE EXTRACTION

A DISSERTATION

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

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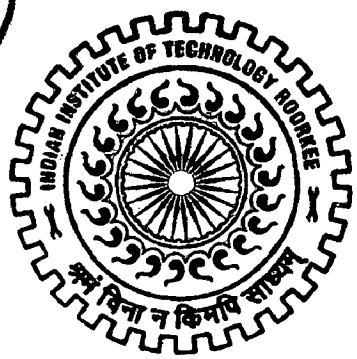
in

CHEMICAL ENGINEERING

(With Specialization in Industrial Pollution Abatement)

By

MANU AGARWAL



DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE - 247 667 (INDIA)

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ABSTRACT

RECOVERY OF GLYCOLIC AND GLYOXALIC ACIDS BY REACTIVE EXTRACTION

Manu Agarwal

M. Tech., Department of Chemical Engineering

Guide: Assistant Prof. Dr. Kailas L. Wasewar

June 2008,

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

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

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

resulted higher degree of extraction. Higher equilibrium coefficient was obtained for aliquat 336 in 1-decanol for both the carboxylic acids.

Among the different extratants highest degree of extraction was with 10% Aliquat 336 in 1-Decanol for both the acids for the extraction of 0.05 N acid solution.

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

Keywords: Reactive extraction, Glycolic acid, Glyoxalic acid, Equilibrium studies, Aliquat 336, TBP, Temperature studies, Kinetics.

CANDIDATE'S DECLARATION

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

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

Date: 30-6-2008

Place: Roorkee

(MANU AGARWAL)

CERTIFICATE

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

30/6/8

Dr. Kailas L. Wasewar
Assistant Professor
Department of Chemical Engineering,
Indian Institute of Technology
Roorkee – 247 667, INDIA.

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Manu

(MANU AGARWAL)

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LIST OF SYMBOLS AND ABBREVATIONS

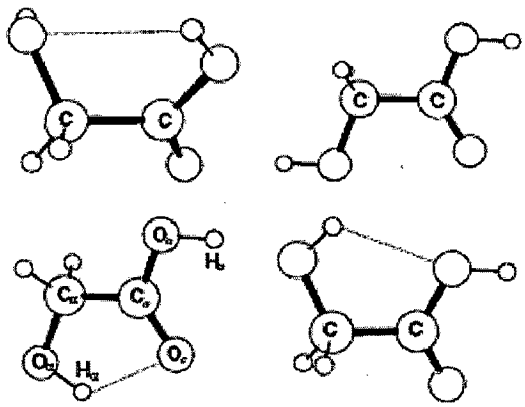
$[B]_{i, org}$	Initial concentration of extractant in the diuent ($kmol/m^3$)
$[B]_{org}$	Concentration of unreacted extractant in the organic phase ($kmol/m^3$)
$[BHA]_{org}$	Equilibrium concentration of the complex in the organic phase ($kmol/m^3$)
$C_{i\ aq}$	Initial concentration of acid in the aqueous phase ($kmol/m^3$)
C_{aq}	Equilibrium concentration of acid in the aqueous phase in all forms ($kmol/m^3$)
C_{org}	Equilibrium concentration of acid in the organic phase in all forms ($kmol/m^3$)
D	Degree of extraction
$[HA]_{aq}$	Equilibrium concentration of undissociated acid in the aqueous phase ($kmol/m^3$)
k_1	Forward reaction rate constant
k_2	Backward reaction rate constant
K_{11}	Equilibrium complexation constant of (1, 1) acid – extractant complex
K_{12}	Equilibrium complexation constant of (1, 2) acid – extractant complex
K_D	Distribution constant of acid
$(-)r_A$	Rate of reaction with respect to equilibrium acid concentration in the aqueous phase ($kmol\ m^{-3}\ sec^{-1}$)
Z	Loading factor

CHAPTER 1

INTRODUCTION

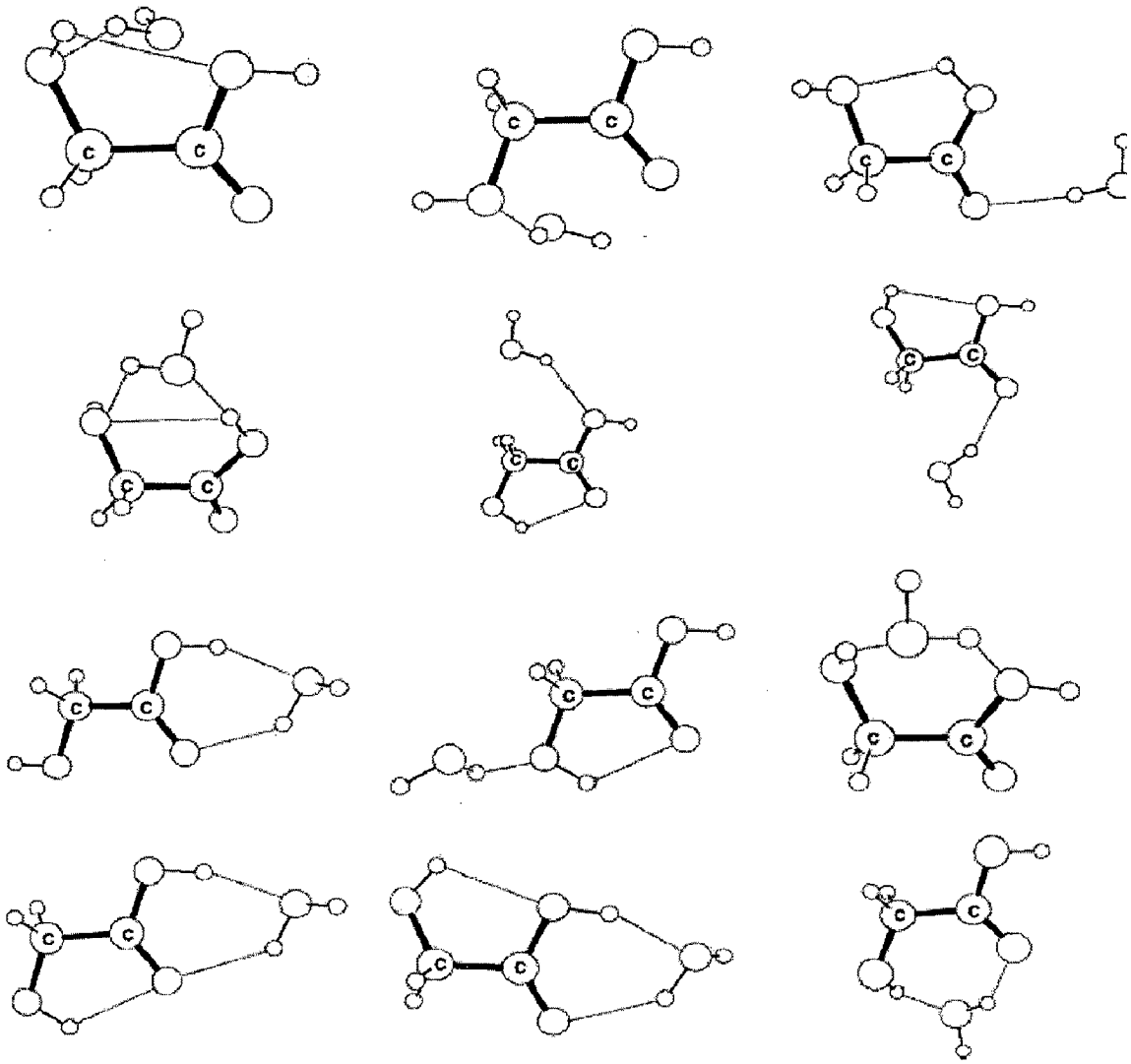
1.1. Glycolic Acid

Glycolic acid ($HOCH_2COOH$) is the simplest member of the α-hydroxy carboxylic acid family of carboxylic acids. Pure glycolic acid is white crystalline solid and 70% aqueous solution is colorless. It is odorless and water soluble. It is readily biodegradable and nonvolatile in nature. Glycolic Acid uses both the hydroxyl and carboxylic acid groups to form five-member ring complexes called chelates with polyvalent metals. It has rich functionality that allows it to simultaneously form intra- and intermolecular hydrogen bonds, and also allows for weaker C–H-----O interactions. Glycolic acid has some biological significance because it is involved in several life processes (Zelitch, I., 1992), and because it has a structure very similar to that of glycine, the simplest a-amino acid. There have been several studies, both experimental and theoretical, on the various rotamers of glycolic acid. Eight local minima on the potential energy surface have been found.



F 1.1 Most stable rotamers of glycolic acid

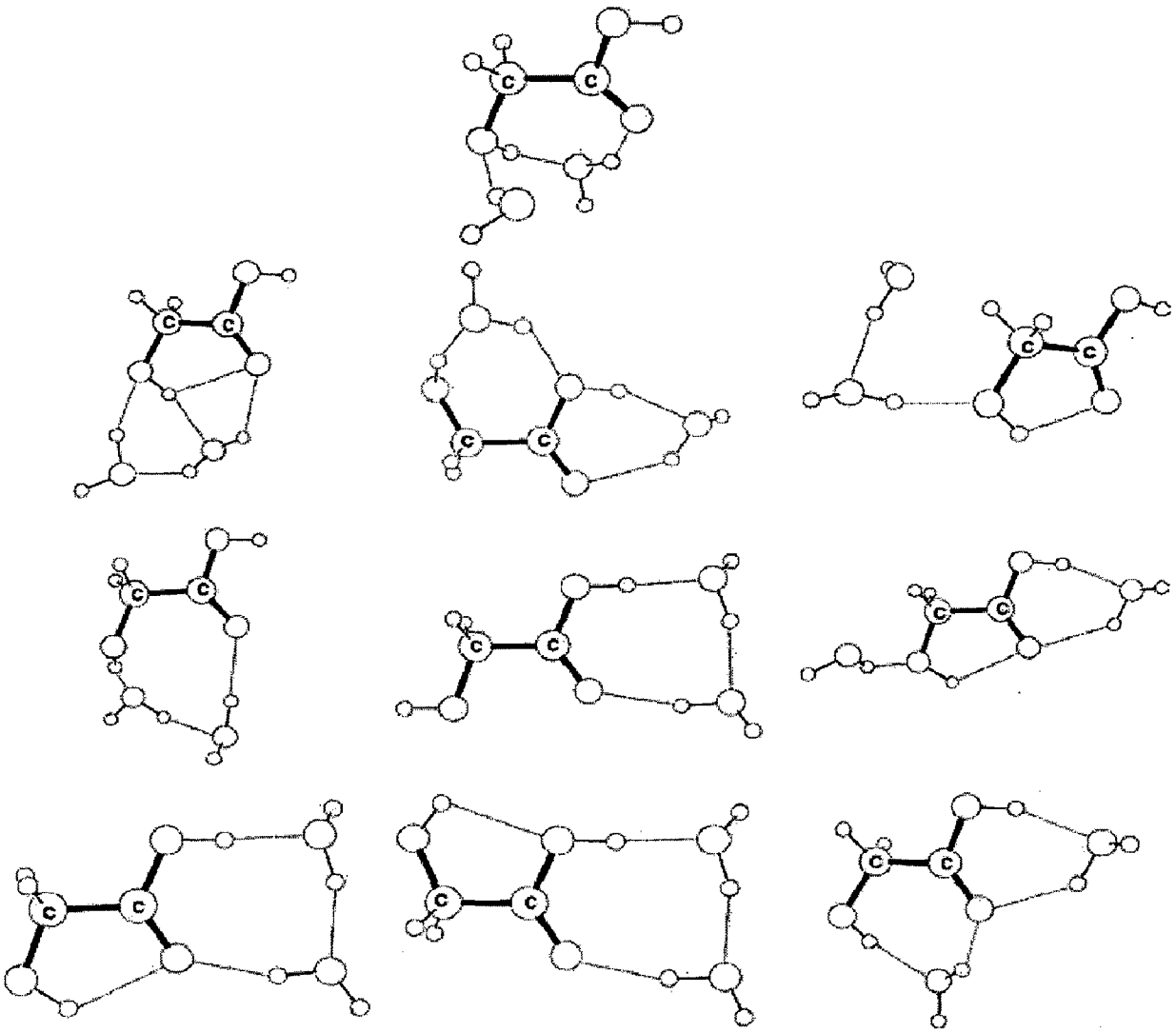
Glycolic acid forms dimer and cluster (Thakkar et al., 2004) with water. Each of the eight rotamers of glycolic acid can form several intermolecular H-bonds by accepting protons at the O_a and O_α atoms, and by donating protons H_a and H_α. Water can act as both a proton donor and acceptor. Thus there are probably 25–35 local minima on the glycolic acid–water dimer potential energy surface. Other properties of glycolic acid are given in table T 1.



F 1.2 Most stable structures of glycolic acid – water dimers

Properties	Glycolic acid	Glyoxalic acid
Common name	Glycolic acid	Glyoxylic acid
IUPAC name	2-Hydroxy Ethanoic acid	2-Keto Ethanoic acid
Formula	$CH_2(OH)COOH$	CHO-COOH
Molecular weight	76.05	74.06
Boiling point (^{0}C)	100	111
Freezing point (^{0}C)	80	-93
pKa	3.83	3.34
log (P^a)	-1.097	-0.413

Table T 1: Properties of Glycolic and Glyoxalic acid



F 1.3 Most stable structures of clusters of glycolic acid and two water molecules

Glycolic Acid undergoes typical oxidation reactions to give glyoxalic acid and oxalic acid, and reduction reactions with active metals to form acetic acid. Glycolic acid undergoes reactions with organic alcohols and acids to form esters. Computer simulations and laboratory studies of solvency suggest that the low molecular weight alkyl glycolic esters have unusual solvency properties and may be used as a substitute for n- and iso-propanol, ethylenediamine, phenol, m-cresol, 2-ethoxyethyl acetate (EE acetate), and ethyl and methyl lactate.

$$CH_2(OH)COOH + 2O_2 \rightarrow CHO - COOH + COOH - COOH$$

$$CH_2(OH) - COOH + C_2H_5OH \rightarrow C_2(OH)COOC_2H_5 + H_2O$$

$$CH_2(OH)COOH + C_2H_5COOH \rightarrow C_2H_5COOCH_2COOH$$

Glycolic acid reacts with itself to form dimeric glycolide, head-to-tail polyester oligomers and long-chain polymers. Copolymers can be made with other alpha hydroxy

acids like lactic acid. Polyester polymers gradually hydrolyze in aqueous environments at controllable rates, making them useful in biomedical applications such as dissolvable sutures and wherever controlled acid release is needed to reduce pH.

$$2nCH_2(OH)COOH \rightarrow [-CH_2COOCH_2COO-]_n$$

Glycolic acid (70% solution) is slightly toxic via the oral route, having an LD_{50} in rats of 193 8 mg/kg. It is moderately toxic via the inhalation route in male rats with a 4-hour LD_{50} of 3.6 mg/L. Glycolic acid is a skin and eye corrosive, but it is not a skin sensitizer in animals. However, numerous studies in humans with cosmetic products containing lower percentages of glycolic acid have shown some skin irritation potential, but no corrosivity. Repeated exposures to glycolic acid via inhalation produced liver, spleen, thymus changes, and gastrointestinal tract alterations. Repeated administration of glycolic acid to rats by oral intubation caused decreases in body weight, body weight gain, food consumption, and food efficiency. In addition, toxicologically significant changes in hematologic measurements, clinical chemistry, and urinalysis parameters, as well as kidney lesions were observed. Maternal and developmental toxicity of crystalline, 99.6% pure, glycolic acid in the rat was seen at 300 and 600 mg/kg/day. The maternal and developmental NOEL was 150 mg/kg/day, thus glycolic acid is not considered a unique developmental hazard to the conceptus. Glycolic acid did not affect reproductive performance in rats during a one-generation reproduction study following a 90-day feeding study.

Its properties make it ideal for a broad spectrum of consumer and industrial applications, including use in water well rehabilitation, the leather industry, the oil and gas industry, the laundry and textile industry, as a monomer in the preparation of polyglycolic acid (PGA), and as a component in personal care products. Glycolic acid also is a principle ingredient for cleaners in a variety of industries (dairy and food processing equipment cleaners, household and institutional cleaners, industrial cleaners [for transportation equipment, masonry, printed circuit boards, stainless steel boiler and process equipment, cooling tower/heat exchangers], and metals processing [for metal pickling, copper brightening, etching, electroplating, electropolishing]).

Acne is a common disease, representing the most frequent dermatitis among teenagers (Cunliffe, W., 1994; Stern, RS., 1992). Although diagnosis is simple, the choice of treatment is very critical due to the multifactorial aetiology and the chronic nature of the disease. An important objective is that of inducing rapid initial improvement, so that the patient may become confident in the therapy, for this purpose, treatment with glycolic acid, an alpha hydroxy acid that is at present among the most commonly used high concentration (70%) chemical peeling agents (Van Scott and Yu, 1989). This technique produces a partial, controlled cutaneous wound that induces first removal and then regeneration of part of the epidermis and/or dermis depending on the concentration of the acid and exposure time (Ghersetich et al., 1997; Cotellesa et al., 1995). The advantages of glycolic acid over

some of the other available peeling agents are its stability, the close correlation between application times and depth of peeling, and the fact that it is easily neutralized. Its therapeutic value in acne is mild epidermolysis, with dislodgement of comedones and unroofing of pustules that affect the follicular epithelium at the sebaceous gland level, while excess keratinization of the pilosebaceous duct is avoided

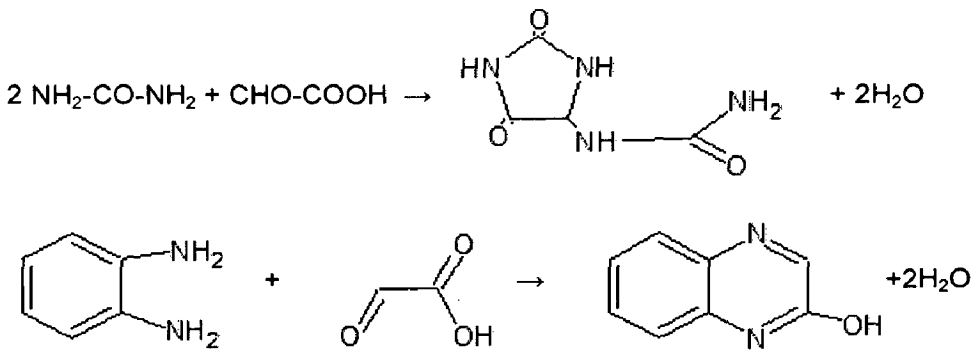
Recently, it has been found that polyglycolic acid is useful as a gas barrier material (i.e., exhibits high oxygen barrier characteristics) for packing foods and carbonated drinks. However, traditional chemical synthesis of glycolic acid produces a significant amount of impurities that must be removed prior to use in preparing polyglycolic acid for gas barrier materials. New technology to commercially produce glycolic acid, especially one that produces glycolic acid in high purity and at low cost, would be eagerly received by industry.

1.2. *Glyoxalic acid*

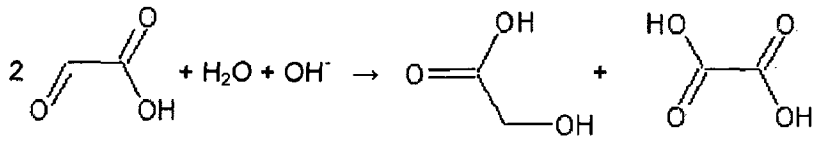
Glyoxalic acid (CHOCOOH) is the smallest α-keto carboxylic acid in its family. It is also known by the names formyl-formic acid, oxo-ethanoic acid and glyoxalic acid. Pure glyoxalic acid is light yellow liquid. It has obnoxious odor and soluble in water. The acid has a ketone group and an acid group, thus shows a dual functional nature of both aldehyde and carboxylic acid. One more example of small molecular weight alpha-keto acid is pyruvic acid which has methyl branch. Other properties of Glyoxalic acid are given in table T 1.

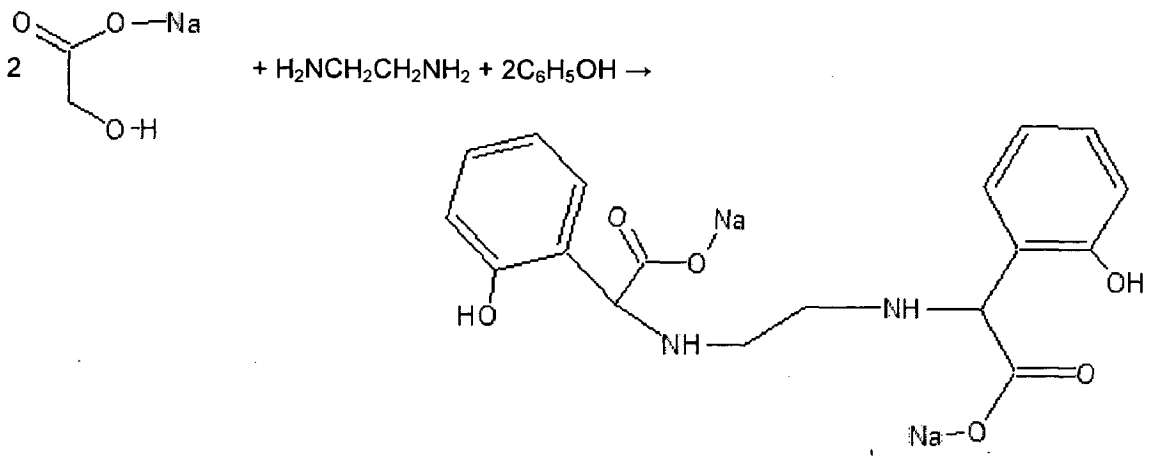
Glyoxalic acid has LD_{50} of 2500mg/kg in rats. It is corrosive to eye in rabbits, does not irritate the skin. It is has allergic sensitization in guinea pigs. No mutagenic effect was found in the Ames mutagenicity test. The acid is completely inactive in the so called micronucleus mutagenicity test in mice. Glyoxalic acid is a metabolite in mammalian biochemical pathways.

Glyoxalic acid is strongly hydrophilic in nature. It is soluble n alcohols and water miscible solvents. It has very low solubility in ether and other organic solvents. It forms complexes with ions of alkali and alkaline-earth metals and has a chelating power 30 mg of calcium carbonate per gram of 50% aqueous solution. The aldehyde group of the acid reacts readily with nuecleophilic reagents, hydrated aldehyde and the hemiacetal. The carboxylic group of the acid reacts with ambident nucleophiles, leading to intramolecular ring formation. The acid combines with polyneucleophiles to produce heterocyclic compounds.

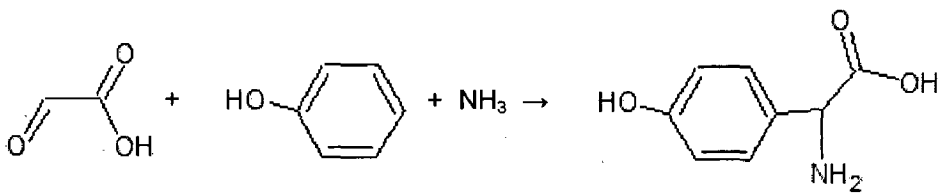


On heating, glyoxalic acid disproportionates to a mixture of glycolic acid oxalic acid. Glyoxalic acid oxidized to oxalic acid by nitric acid. Reactions that have been used industrially include the Mannich reaction and amidoalkylation. Thus, with phenol and ethylenediamine in alkaline medium, glyoxalic acid leads to the sodium salt of *N,N'*-ethylenebis[2-(2-hydroxy-phenyl)glycine], which forms complexes with iron (III).

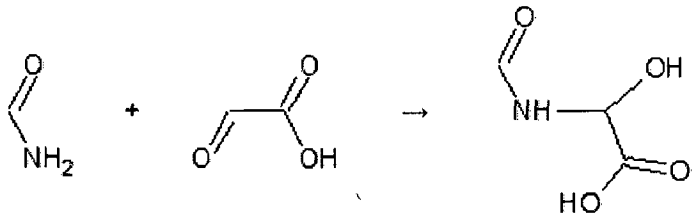




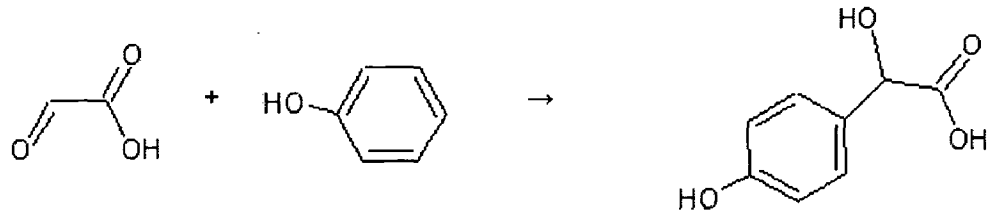
Glyoxalic acid, phenol and ammonia react to give 4-hydroxyphenylglycine, an intermediate for the semisynthetic penicillin amoxicillin.



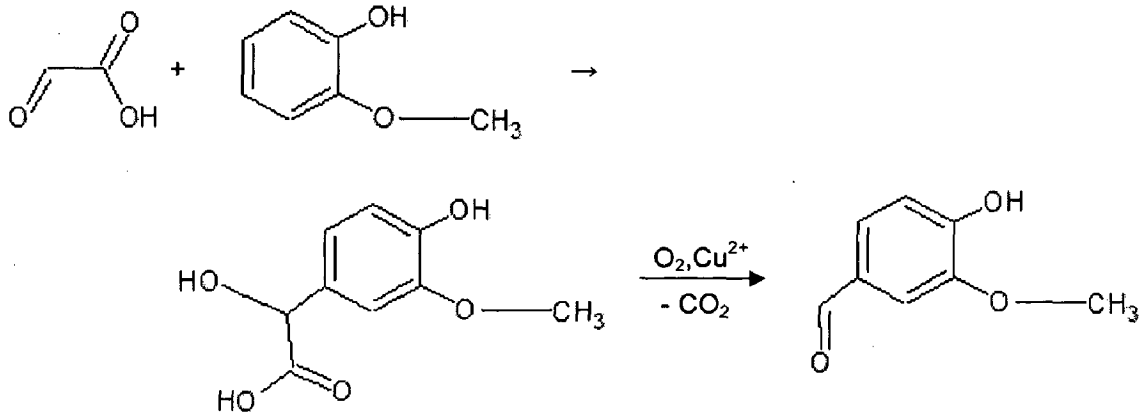
At slightly alkaline pH, glyoxalic acid reacts with amides such as acrylamide to form acrylamidoglycolic acid, which is used as a copolymerizable cross-linking agent. Several derivatives of acrylamidoglycolic acid have industrial applications e.g., in coatings and paint for automobiles.



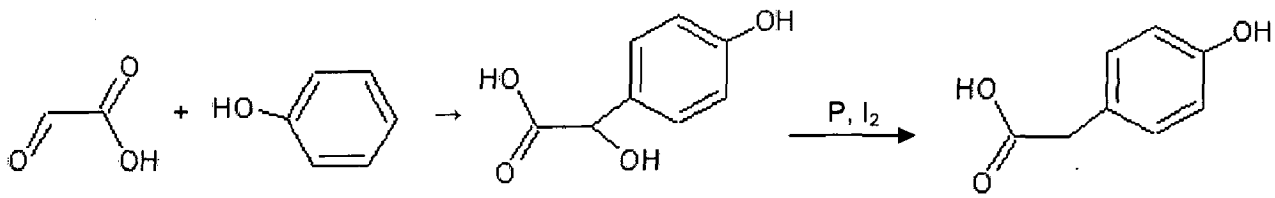
Glyoxalic acid combines with phenol in alkaline medium to give 4-hydroxymandelic acid with good selectivity.



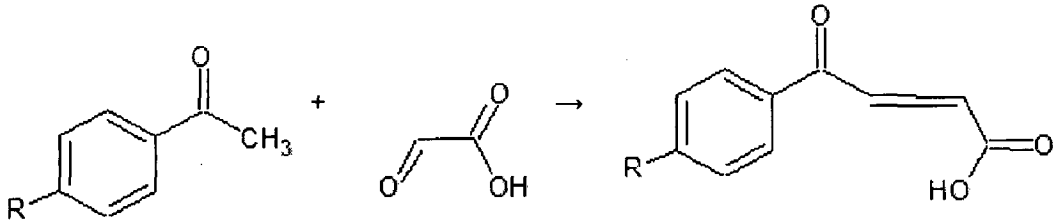
The reaction with phenols is used in several industrial syntheses of benzaldehydes, e.g. guaiacol is converted to vanillin by oxidative decarboxylation of the corresponding mandelic acid.



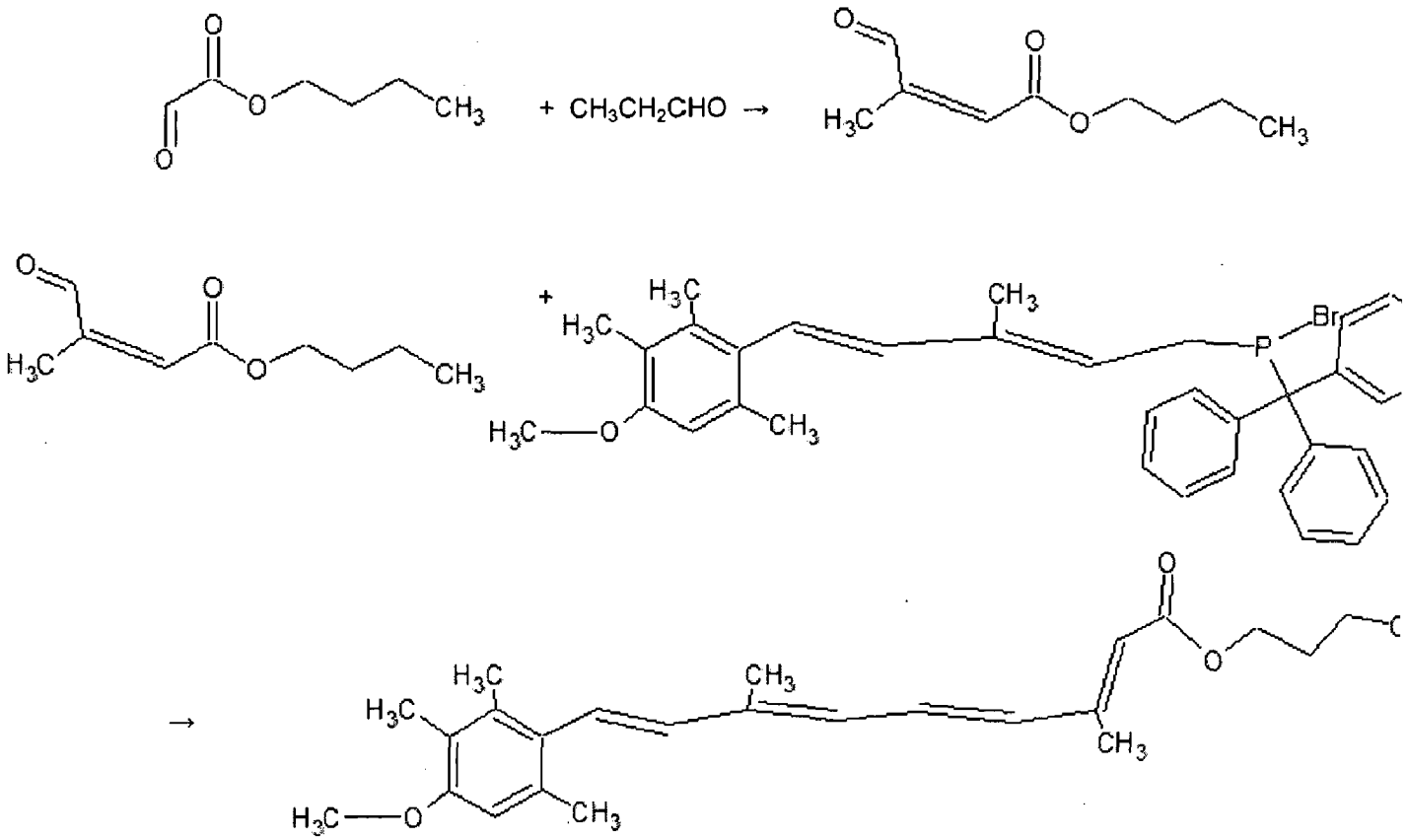
The mandelic acid intermediate may be modified further: reaction of phenol and glyoxalic acid in the presence of a reducing agent such as phosphorus – iodine leads directly to hydroxyl phenyl acetic acid, a building block for pharmaceuticals such as *Atenolol*.



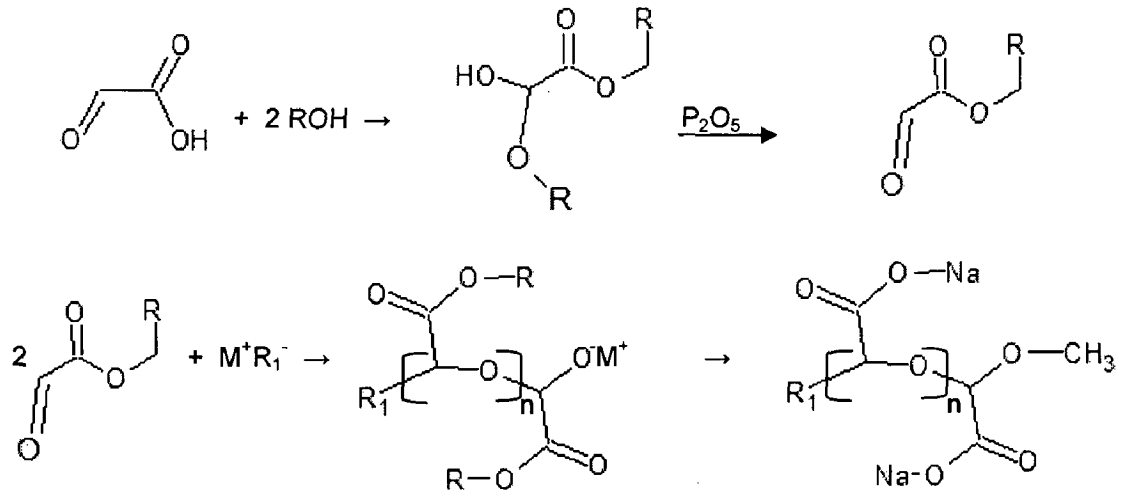
The above reaction with thiophene yields 2-thienyl acetic acid, which is used to prepare the semisynthetic cephalosporins cephalothin and cefoxitin. Glyoxalic acid undergoes aldol reaction with acetophenones and yields benzoyl acrylic acids



Glyoxalic acid when treated with Wittig ylides forms carbonyl functional polyenes of the vitamin A type.



Esters of glyoxalic acid, obtained by dehydrative distillation of the hemiacetal esters in the presence of phosphorus pentoxide, can be polymerized under the action of a base. After saponification, the resulting polymers show useful chelating properties with the advantage of good biodegradability. Low molecular mass polyglyoxalates have been proposed as substitutes for sodium tripolyphosphates in detergents to control water hardness.



1.3. Production Methods

1.1.1 Electrochemical Reduction of Oxalic acid

In the first step of electrochemical reduction of oxalic acid (Pickett and Yap, 1974), the acid is reduced to glyoxalic acid by a two-electron process

$$COOH - COOH + 2H^+ + 2e^- \rightarrow CHO - COOH + H_2O$$

The production of glycolic acid then takes place by the further two-electron process:

$$CHO - COOH + 2H^+ + 2e^- \rightarrow CH(OH)COOH + H_2O$$

The free energy change in both the reactions is less than 20 KJmol-1, so at a given electrode potential both the reactions occur simultaneously. To model the system, other possible side reactions together with hydrogen evolution are ignored and for simplicity the two reactions will be denoted by the scheme where A, B, and C denote oxalic, glyoxalic and glycolic acids respectively.

$$A \rightarrow B \rightarrow C$$

In an electrolyte cell having a cathode compartment of volume V and assumed to be operating at a constant cathode potential and current, the rate of production of B is given by

$$V\frac{dC_B}{dt} = \frac{I\gamma}{2F} - \frac{I}{2F}(1-\gamma) \qquad (1.3.1.1)$$

The above equation assumes that mass transfer effects are absent and sufficient hydrogen ions are available from the indifferent electrolyte. γ is the current efficiency of the reaction A →B, and 1- γ of the reaction B→C.

If both reactions have the same exchange current densities, over potential relationships and are solely charge transfer dependent, then the current efficiency γ will be proportional to the concentration of A and B at the electrode

$$\frac{\gamma}{1-\gamma} = f\frac{C_A}{C_B} \qquad (1.3.1.2)$$

f incorporates the exchange currents and over potentials. At a fixed total current the sum of the combined concentrations of C_A and C_a at the electrode surface must be equal to C_{Ao}, the initial concentration of A so that

$$\frac{\gamma}{1-\gamma} = f\frac{C_{A0} - C_B}{C_B} \qquad (1.3.1.3)$$

Incorporating equation (3) in (1) and integrating it enables the concentration of B, i.e., glyoxalic acid to the quantity of electricity passed

$$\frac{Q}{2VF} = \frac{2fC_{A0}}{(1=f)^2}\ln\left[\frac{fC_{Ao}}{fC_{A0} - C_B(1=f)}\right] - \frac{1-f}{1+f}C_B \qquad (1.3.1.4)$$

However, the above equation will only be an approximation for the bulk electrolyte where the total concentrations of each species are related by

$$C_{Ao} = C_A + C_B + C_C \qquad (1.3.1.5)$$

The cell is made from two pyrex glass tubes separated by a sintered glass disc fused in between them to act as a diaphragm. The larger (cathode) compartment has a drainage tap and two side tubes are attached to give provision for a Luggin capillary and stirrer. The anode compartment also has a drainage tap and a side tube for a thermometer.

1.3.2. Synthesis from Glyoxal

The First Step of synthesis from glyoxal (Yadav and Gupta, 2000) involves conversion of gloxal to glycolic acid in presence of a base.

$$CHO - CHO + H_2O \rightarrow CH_2(OH)COOH$$

This reaction is called CANNIZZARO REACTION. The reaction with the addition of hydroxyl ion (base) to the carbonyl carbon (aldehyde) resulting in an alkoxide. Since the reaction is base catalysed, the concentrations of both catalyst (OH^-) and glyoxal (G) are significant and the typical rate of reaction of glyoxal is given by:

$$\frac{dC_G}{dt} = k_2 C_{OH^-} C_G = k_0 C_G \qquad (1.3.2.1)$$

Where CG is the concentration of glyoxal and C_{OH^-} is the concentration of the base. The equation can be rearranged and integrated for a fixed concentration of the base

$$k_o t = \ln\left[\frac{1}{1-X_G}\right] \qquad (1.3.2.2)$$

XG is the fractional conversion of glyoxal and $k0 = k_2 C_{OH^-}$

The second step involves oxidation of glycolic acid to gloxylic acid with spinach glycolate oxidase by sparging air at atmospheric pressure with continuous stirring. The pH of the mixture is maintained 8 to maximize the product. The conversion increases with time but, at the cost of selectivity. This decrease in selectivity accounts to decomposition of glyoxalic acid to formic and oxalic acid in the presence of hydrogen peroxide.

1.3.3 Synthesis from Ethylene Glycol

In the process of synthesis from Ethylene glycol (Kuznetsov et al., 1964), Ethylene glycol is oxidized in presence of platinum oxide and palladized charcoal as catalyst to produce glycolic acid. The reaction is very slow. The another route is through glyoxal. Ethylene glycol is first dehydrogenated in presence of silver as a catalyst to glyoxal.

$$CH_2OH - CH_2OH \rightarrow CHO - CHO + 2H_2O$$

Now, sodium bisulfite is added to the reaction mixture to produce glyoxal bisulfite.

$$CHO - CHO + 2NaHSO_3 \rightarrow NaSO_3 - CH(OH) - CH(OH) - NaSO_3$$

The reaction product is separated, washed and dried in air. This solid is then treated with hydrochloric acid followed by cation exchange process. This ensures removal of mineral salts which are formed along with glycolic acid. The product is vacuum-evaporated to dryness.

1.3.4. Production of Glyoxalic acid using Alcaligene sp. GOX373

Microorganisms capable of producing glyoxalic acid (Isobe, K. and Nishise, H., 1999) from glycolic acid, as determined by the cell reaction, are cultured in the basal medium containing 5% 2-propanediol at 30°C for 3 days.

Cells harvested from culture broth are incubated with 1.0 M glycolic acid sodium salt in 0.2 M N-tris(hydroxymethyl)-methyl-2-aminoethanesulfonic acid-Sodium hydroxide buffer, pH 7.0 at 20°C for 16 h with shaking. The reaction is terminated by centrifuging the cells (10000 rpm, 10 min).

The initial rate of glyoxalic acid production is high at 60 mg of cell amount but high concentration of glyoxalic acid is not obtained. The glyoxalic acid formation gradually stops at acid pH and so the reaction pH is maintained neutral.

Metals and nitrogen sources effect the cell growth of strain GOX373 and enzyme activity for gloxylic acid production. Ferrous ion effectively enhances the cell growth and enzyme activity. Manganese ion is effective for cell growth, but not for enzyme activity. Cobalt and Zinc ion effect neither the cell growth nor the enzyme activity. Malt extract, Yeast extract and corn steep liquor also effectively enhance cell growth and enzyme activity.

1.3.5 Production of Glycolic acid from Glycolonitrile

Glycolic acid is produced from glycolonitrile (Yunhai et al., 2006) by contacting it in a suitable aqueous reaction mixture with an enzyme catalyst comprising a polypeptide having an amino acid sequence (of the Acidovorax facilis 72W nitrilase encoded by the nucleotide sequence of the Acidovorax facilis 72W nitrilase coding sequence comprising a change in the start codon from TTG to ATG to facilitate recombinant expression in E. coli.) with at least one amino acid substitution selected from the group consisting of:

a)A substitution at amino acid residue 168 with lysine, methionine, threonine or valine

b)A substitution at amino acid residue 201 with glutamine, glycine, histidine, lysine, asparagine, serine, alanine, cysteine, or threonine

Recovery of the glycolic acid produced is in the form of a salt or acid; wherein said enzyme catalyst provides at least a 1.5-fold increase in nitrilase activity relative to the nitrilase activity of the Acidovorax facilis 72W nitrilase when converting glycolonitrile to glycolic acid under identical reaction conditions.

1.3.6. Production of Glyoxalic acid using Microbial Transformant Catalyst

Glyoxalic acid is produced (Gavagan et al., 1996) by oxidizing glycolic acid with oxygen in aqueous solution and in the presence of a di-alkyl-amino-methyl phosphonate (AMPA) and two enzyme catalysts, glycolate oxidase ((S)-2-hydroxy-acid oxidase), catalase

The catalyst is a genetically-engineered microbial transformant, which expresses both the enzyme glycolate oxidase from spinach and an endogenous catalase. AMPA reversibly inhibited the endogenous catalase produced by

Hansenula polymorpha or Pichiapastons transformants from decomposing hydrogen peroxide to water and oxygen, which resulted in the production of significant quantities of formate (a product of the oxidation of glyoxylate by hydrogen peroxide). The addition of a second source of catalase (e.g., soluble catalase from Aspergillus Niger) to the reaction mixture gives high yield of glyoxalic acid when using either H. polymorpha or P. pastoris transformant catalysts.

1.4. Recovery Methods

1.4.1. Acidification of fermentation Liquor

The first requirement for acid recovery is to design a process where the pH of fermentation liquor is reduced to pH 4.8 or less from the optimum fermentation pH which can frequently be near pH 7. This requirement can be met by several ways. The bacteria used can be selected for good growth at low pH, or immobilized bacteria can be used in which growth is not as important as maintenance of metabolic rate. A two stage fermentation system can be designed where the first stage is maintained at pH 6-7 to allow for optimum conversion of cellulose substrate, and second stage is not allowed to neutralize by alkali but to self acidify. Acidogenic fermentations acidify quite rapidly to pH 4.8-5.2 if alkali is not added. Traditionally, sulfuric acid was used but precipitates of calcium sulfate created disposal problems. Later, the use of Carbon-di-oxide under pressure was advocated to acidify the fermentation solution. This idea has recently been revived. Certainly, carbon-di-oxide is an attractive choice since the gas is readily available from nearly all fermentation processes and does not cause disposal and environmental problems. Alternatively, acidification could be achieved by addition of cation exchange resins. Regeneration of the resin could be performed externally with the acids and the resin recycled.

Acidification may be avoided if an anion exchange system could be developed for direct removal of carboxylate anions. Unfortunately, the capacity of anion-exchange resins is reduced rapidly by colloidal particles present in fermentation liquor. This would lead to depletion of essential nutrients for microbial growth, and competition with acid anions for exchange sites.

1.4.2. Solvent Extraction and Distillation

Early methods for recovery of acids included evaporation of the acid salts in the fermentation liquor and their subsequent decomposition to free acids, distillation with an entrainer (butanol, ketones, ethyl acetate etc), or solvent extraction followed by entrainment distillation. An entrainer is included in distillation methods to avoid refluxing large volumes of water and to alter the composition of the azeotropic mixture.

Solvent extraction and distillation is only advantages over distillation with an entrainer if the ratio of acid to water in solvent is higher than in aqueous feed. Solvent extraction can act as a purification step if the solvent chosen does not absorb impurities. The solvent can also act as an entrainer in subsequent distillation step.

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

The choice of solvent system is very critical and has to be tailored to the acid being extracted. It is a compromise between a high partition coefficient for the acid and solubility of water in the solvent. On these grounds dichloromethane has been claimed to be good solvent for acid extraction. Conventional solvent extraction followed by distillation has not proved to be an economic system for acid extraction from solutions less than 50 g/l concentration.

1.4.3. Esterification of Acids

Esterification of acids with ethanol or butanol has been proposed to separate product acids. This process takes advantage over lower water solubility of esters compared with that of their respective acids and their lower boiling points. There are three approaches proposed to ester formation:

1. Adsorption of organic acids with simultaneous catalytic conversion to esters by alcohol vapors.
2. Extraction of acids into an organic solvent phase, followed by chemical esterification in that phase with added alcohol.
3. Enzymic esterification in dilute solutions by suitable microorganisms.

1.4.4. Calcium Hydroxide Precipitation

Propionic acid has been recovered from the fermentation broth by precipitation of calcium propionate with calcium hydroxide. In this recovery scheme, calcium propionate is precipitated, recovered by filtration, and converted to Propionic acid by the addition of sulfuric acid. The dilute Propionic acid product is

then sequentially purified using activated carbon, evaporation, and crystallization. This is very simple and reliable but, has few drawbacks:

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

1.4.5 Membrane Technique

Emulsification problems during solvent extraction of acids from fermentation solutions have led to an interest in the use of membranes. Membranes selective to short chain fatty acids are being developed. These function either as water splitting, electrodialysis membranes or as carrier mediated hydrophobic membranes. The advantage of electrodialysis membrane is that sodium hydroxide is generated and can be recycled into the fermenter to control the pH. Secondly, since these are essentially ion exchange membranes the feed can consist of sodium salts of the acid. The disadvantages are that nutrient cations and anions are to be separated and recycled into the fermenter and electrical current densities 20-50 mAcm-1 has to be applied across the membrane system.

Carrier mediated transport membrane are analogous to solvent extraction in their principles of operation. Microporous membranes are not durable so, have been worked with homogeneous membrane which has a semi solid structure. This structure results in lower permeability coefficients than micro porous membrane. This problem can be solved by fabricating thin membranes and providing porous support to them. The best result so far achieved is in PVC membrane with TOPO as carrier.

1.4.6 Electrodialysis

Electrodialysis is a process where ion exchange membranes are used for removing ions from an aqueous solution under the driving force of electrical field. Electrodialysis is applied to remove salts from solutions or to concentrate ionic substances. A special type of electrodialysis is water-splitting electrodialysis. Instead of anion exchange membranes in desalting, bipolar membranes are used in watersplitting electrodialysis. Water-splitting electrodialysis is applied to electroconversion of salts to the corresponding acids. There are two different methods for recovery of lactic acid (Wasewar, 2005). It is a two stage electrodialysis method in the first case and electrodialysis with double exchange reaction in the second case. In the first step of desalting, sodium lactate is recovered, purified and concentrated, in the water-splitting or acidification step, lactic acid is regenerated from sodium lactate, and sodium hydroxide is recovered and purified.

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

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

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

At the start of the process the product stream volume is low. The feed and the electrolyte stream are high. Now voltage is supplied and conductivity of the product stream is measured. The process terminates once the conductivity stops rising.

The ratio of final to initial total acid concentration at pH 7 ranges from 9.2 to 4.1 for the one pass runs and 4.1 to 2.4 for recycle runs, representing an important degree of concentration. In absolute terms, the final concentration is limited by the electroosmotic water flux.

1.4.7 Emulsion Liquid Membrane Extraction

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

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

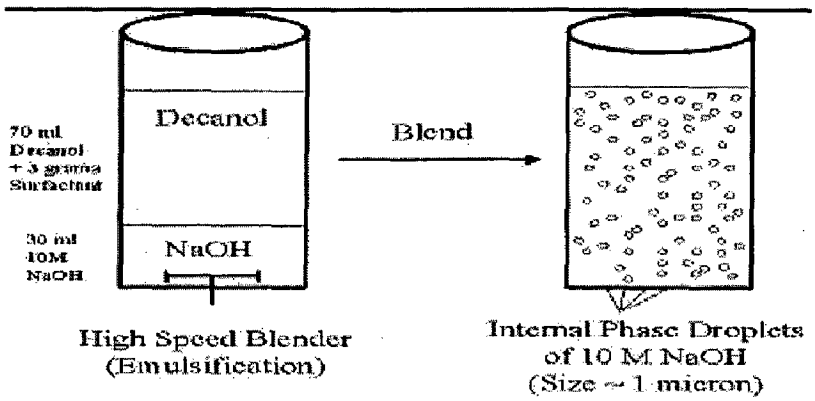
(1) A settling stage is usually required after the extraction, making continuous operation more difficult.

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

More recently, dispersion-free solvent extraction using microporous hollow-fiber contactors (HFCs) has been shown to be an effective alternative to normal dispersed (stirred tank) extraction. HFCs consist of microporous hollow fibers arranged in a shell-and-tube configuration. The fiber material can be either hydrophilic or hydrophobic. When a hydrophobic fiber is used, higher pressure is applied on the aqueous phase. The aqueous phase will not penetrate or wet the hydrophobic membrane. The organic phase is present in the pores but cannot penetrate into the aqueous side because the aqueous phase is at a higher pressure. Thus, a stable aqueous-organic interface is established at the pore openings. The advantage of HFCs lies in their ability to offer a very high surface area/volume ratio without dispersion or mixing of the two phases. The use of hollow-fiber contactors eliminates the need for a settling stage and allows for direct scale-up due to modular design. In addition, the high energy needed in the mechanical dispersion method is eliminated. Naturally, the extent of extraction is still limited by the equilibrium. To circumvent equilibrium constraints, emulsion liquid membranes (ELMs) combine extraction and stripping into a single operation. ELMs have been successfully used to treat a variety of aqueous streams contaminated with heavy metal ions, like copper, zinc, cadmium, nickel, mercury, lead and chromium. ELMs, first invented by Li, are made by forming an emulsion between two immiscible phases, usually stabilized by surfactants. In this case, an emulsion liquid membrane (ELM) (Wiensek, J. M. and Su, S. Y., 2000) is first prepared by mixing under high shear (a milkshake blender is typically used in the laboratory) a physical mixture of 10 M NaOH and an immiscible organic phase (e.g. decanol). The mixture is a physical mixture + the water and oil do not dissolve into one another; rather the smaller volume phase is dispersed into the larger volume phase (see Fig. F 1.4.7 A).

Typically, 30%v/v of the dispersion is the internal phase, which in this case is the aqueous NaOH solution. The mechanical action of the blender will form the dispersion or emulsion but the two phases will quickly separate into bulk coalesced phases if there is no stabilizing surfactant present. The ELM cocktail is a mixture of an oil membrane phase, an aqueous stripping phase which is encapsulated in the interior of the oil membrane, and finally a surfactant is added to stabilize the emulsion. Each application requires its own special mixture to obtain optimal results, and other additives may be present which increase the solubility of the solute in the oil membrane phase by some form of chemical complexation. Once the ELM is prepared, it can then be further dispersed into the feed phase containing the organic acids to be separated (see Fig. F 1.4.7 B). The emulsion globules are dispersed into this aqueous feed phase by gentle mixing at 400±500 rpm. Thus, the ELM contains very small droplets of 10MNaOH and this emulsion is further dispersed into the feed phase as 0.1±1 millimeter size globules. The net effect is

that an organic phase (or membrane phase) physically separates two aqueous phases. The aqueous feed phase contains the solute to be separated which has a modest partition coefficient into the oil membrane phase. Once in the membrane phase, the organic acid diffuses towards the center of the globule due to a concentration gradient (there is no solute in the center of the globule). Eventually, the organic acid will encounter an internal droplet containing the NaOH and partition into that droplet where a fast, irreversible acid base reaction will ionize the organic acid. Ionized organic acids have essentially zero solubility in the oil membrane phase so that once this reaction occurs; the organic acid is trapped within the aqueous internal phase and will not be able to diffuse back out of the emulsion.

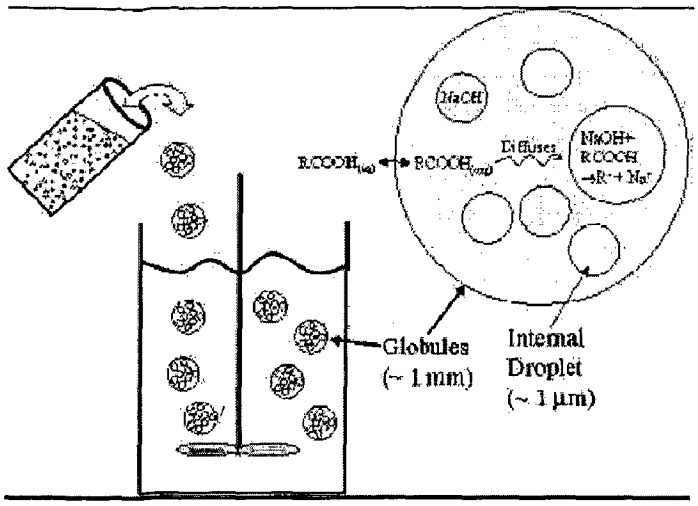


F 1.4.7 A Method for preparation of emulsion liquid membrane (ELM) phase

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

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

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

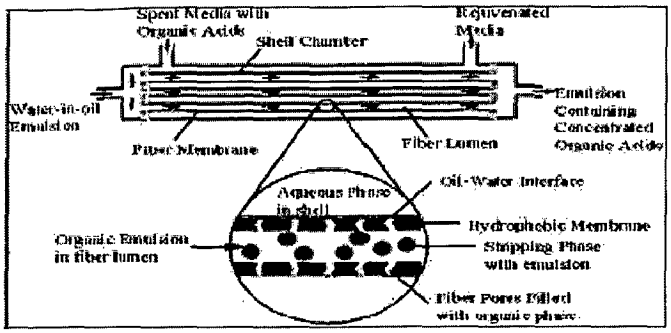


F 1.4.7 B Mechanism of organic acid removal from water

1.4.8. Supported Emulsion Liquid Membrane

Supported emulsion liquid membranes (SELMs) (Wiensek, J. M. and Su, S. Y., 2000) combine the advantages of emulsion liquid membrane separation and dispersion-free solvent extraction. In this design, an ELM carries out simultaneous extraction and stripping from the feed stream by a liquid-liquid, dispersion-free contacting in an HFC (see Fig. F 1.4.8 A). The membrane pores are not wetted by the internal aqueous droplets, so the stripping phase is never in the proximity of the external aqueous feed phase. This wettability effect as well as the absence of high shear rates, which are encountered in agitated dispersion, eliminates leakage of the internal stripping phase. In addition, since the internal aqueous droplets cannot directly contact the feed aqueous phase due to the intervening hydrophobic membrane, the amount of surfactant required in the system is minimal (in fact, no surfactant should be needed). Swell is primarily caused by the surfactant which is readily hydrated in the low ionic strength environment of the feed phase. This hydrated surfactant then diffuses in toward the center of the emulsion globule until it encounters an internal phase droplet at high ionic strength where it is quickly stripped of its waters of hydration. Thus, minimizing the surfactant in the system also limits the swell.

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



F 1.4.8 A Emulsion liquid membrane extraction in a hollow-fiber contactor.

1.4.9. Ion Exchange

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

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

1.4.10. Adsorption

Lactic acid may be recovered by the adsorption of lactic acid on solid adsorbent or by the adsorption of lactate on ion exchange resins (Vickroy, 1985). Sugimoto (Sugimoto et al., 1976) patented a process for the production of lactic acid in which strongly acidic and alkaline ion exchange resins were used to separate the acid from the broth. Kawabata (Kawabata et al., 1982) separated carboxylic acid by using a polymer adsorbent of pyridine skeletal structure and a cross-linked structure. The polymer adsorbent showed good selectivity and high adsorption capacity for carboxylic acids even in the presence of inorganic salts. The selected elutants were aliphatic alcohol, aliphatic ketone, and carboxylic ester.

Kulprathipanja and Oroshar (Kulprathipanja and Oroshar, 1991) recovered lactic acid from fermentation broth by using anion polymeric adsorbents, which were strong, moderate, or weak basic anion exchange resins, adsorbing lactic acid below its p*Ka*. For tertiary amine and pyridine function-containing ion exchange resin, the lone electron pair of the nitrogen atom enables nitrogen atom to form

hydrogen bond by sulfate ion. IRA-400, strongly basic quaternary ammonium ion exchange resin has positive charge and can form ionic bond with sulfate ion. The sulfate form of quaternary ammonium of anion exchange resin has a weakly basic property and can adsorb lactic acid through acid-base interaction. Consequently, the adsorption of lactic acid is not affected by inorganic salt in fermentation broth. Srivastava et al (Srivastava et al., 1992) separated lactic acid using IRA-400 column coupled with fermenter. This study was focused on improving fermentation yield. The Amberlite IRA-400 resin has proper size and high adsorption property for recovery of lactic acid and it can adsorb lactic acid in wide pH range.

Zihao and Kefeng (Zihao and Kefeng, 1995) examined an anion exchange method for lactic acid recovered from lactic acid – glucose solution in an ion-exchange membrane – based extractive fermentation system. They found that the separation method with anion exchange resins may be used in the production of lactic acid by fermentation. Dai and King (Dai and King, 1996) studied the selectivity between lactic acid and glucose during recovery of lactic acid with basic extractants and polymeric sorbents. They found that extraction with Alamine 336 provides a much higher selectivity, but a lower efficacy, than the polymeric sorbents.

Evangelista and Nikolov (Evangelista and Nikolov, 1996) recovered lactic acid from fermentation broth by weak base polymer adsorbents MWA-1, IRA-35, and VI-15. The pH for the adsorption of lactic acid was below its *pKa*, and fermentation broth was acidified by using cation exchange resin instead of using inorganic acid to eliminate possible competition between inorganic acid and lactate in the subsequent adsorption steps. Methanol and 5 % NH_4OH were used as elutants. Though 1.5 times of bed volume of 5 % NH_4OH could recover all the adsorbed lactic acid from MWA-1 column, product purity was not high. However, 6.8 times of bed volume of methanol could completely desorb lactic acid from VI-15 anion exchange resin with higher purity.

Monteagudo and Aldavero (Monteagudo and Aldavero, 1999) investigated the lactic acid production in a continuous fermenter-ion exchange resin system and compared with conventional fermentation. The principle of this method is to remove the lactate during the course of fermentation as it is formed by adsorption to an anion exchange resin (Amberlite IRA-420) in the carbonate form and to overcome its inhibitory effects on lactic acid bacteria by maintaining low lactate concentrations in the medium. Ammonium lactate was formed by percolating ammonium carbonate solution through this resin and it was converted to lactic acid by treatment with a cation exchange resin (Amberlite IR-120) in hydrogen form. Compared with a conventional fermentation, this fermentation- ion exchange resin system enhanced the fermentation, controlled the pH, and showed the remarkable effect of increasing the yields of lactic acid from sucrose and biomass from

sucrose, due to complete utilization of sucrose. Many adsorbents have been examined for lactic acid removal from fermentation.(Aradhana et al., 1992; Davidson and James, 1992; Moldes et al., 2001; Ye et al., 1996) Compared with extraction, adsorption offers the advantage of low or no negative effects to cells.(Srivastava et al., 1992; Davidson and James, 1992) Adsorption is also potentially simpler and cheaper than electrodialysis. However, ion-exchange resins also remove essential anions other than lactate from the broth. Non-ion-exchange adsorbents deserve more attention.

Chen and Ju (Chen and Ju, 1998) reported the adsorption characteristics of lactic acid and lactate on polyvinylpyridine (PVP) and activated carbon. They evaluated polyvinylpyridine (PVP) and activated carbon for coupled lactic acid fermentation and adsorption, to prevent the product concentration from reaching inhibitory levels. The lactic acid production doubled as a result of periodical circulation of the fermentation broth through a PVP adsorption column. Each adsorption-regeneration cycle caused about 14% loss of the adsorption capacity, thus limiting the practical use of this rather expensive adsorbent. Activated carbon was found much more effective than PVP in lactic acid and lactate adsorption.

Raya-Tonetti et al. (Raya-Tonetti et al., 1999) used a strong anionic exchange resin (Amberlite IRA) to recover lactic acid directly from fermentation in an upflow fluidized bed column. They found that the resin did not alter its binding capacity after 23 cycles.

Sosa et al. (Sosa et al., 2000) measured the static adsorption isotherm over a strong anionic exchange resin, Amberlite TM IRA-400, and quantified the static binding capacity parameters for lactic acid recovery. Early recovery of lactic acid was performed in a liquid solid fluidized bed, with the resin as the solid adsorbent, and the dynamic adsorption capacity was calculated. Good agreement was found between static and dynamic binding capacity values. The fluidized bed height was twice the settled bed height and the overall process was controlled by the liquid solid mass transfer. This operation was also simulated by continuously well stirred tanks arranged in series and superficial solid deactivation as in a gas solid catalytic reactor. The deactivation process takes into account liquid channeling and agglomerations of solid induced by the viscosity of the broth and also by the cells during the adsorption.

Chen and Ju (Chen and Ju, 2002) studied the coupled fermentation and adsorption to prevent the product concentration from reaching inhibitory levels for lactic acid production. They used polyvinylpyridine (PVP) and activated carbon as an adsorbent. Lactic acid production doubled as a result of periodical circulation of the fermentation broth through a PVP adsorption column. The adsorbent was then regenerated and the adsorbed lactate harvested by passing 0.1 mol dm^{-3} NaOH through the column. However, each adsorption–regeneration cycle caused about

14% loss of the adsorption capacity, thus limiting the practical use of this rather expensive adsorbent. Activated carbon was found much more effective than PVP in lactic acid and lactate adsorption. The cells of *Lactobacillus delbrueckii* subsp. *Delbrueckii* (LDD) also had strong tendency to adsorb on the carbon. Therefore, they studied using an activated carbon column for simultaneous cell immobilization and lactate adsorption, in a semi-batch process with periodical medium replacement.

Cao et al. (Cao et al., 2002) studied the adsorption of lactic acid on IRA-400, strongly basic quaternary ammonium anionic exchange resin, at the pH above and below the pK_a of lactic acid. The adsorption isotherm, breakthrough curve, washing condition, elution condition, and column separation process for lactic acid were described. Recovery experiment coupled with fermentation was carried out successfully by using a column without autoclaving.

Ye et al. (*Ye* et al., 1996) developed and studied a novel integrated fermentation system in which cross-flow filtration was coupled to an anion exchange resin column to achieve biomass recycle and broth reuse for lactic acid fermentation. They reused spent broth for three consecutive biomass recycle fermentation with no significant decrease in fermentation performance.

1.4.11. Reverse Osmosis

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

1.4.12. Reactive Extraction

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

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

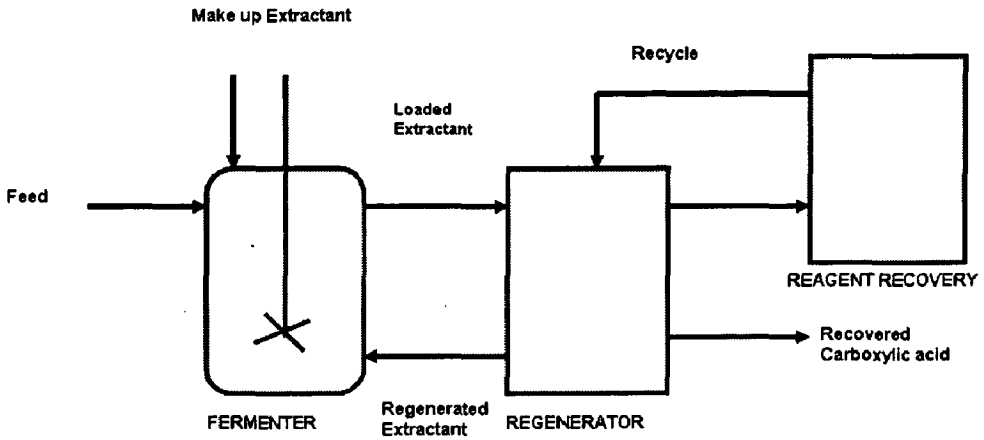
The method is described by a simple complexation reaction with equilibrium of the form:

$$\text{Solute} + n\ \text{Extractant} \leftrightarrow \text{Complex}$$

The equilibrium is described by an equilibrium constant K_E

$$K_E = \frac{[Complex]}{[Solute][Extrac\tan t]^n} \qquad (1.4.12.1)$$

Since in the mixture from the electrochemical process the concentration of the glycolic and glyoxalic acid is low, the separations by reactive extraction tend to be more attractive. The method can be described by a simple flow diagram (see Fig. F 1.4.10).



F 1.4.10 Flow Diagram of Reactive Extraction

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

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

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

1. Active diluent containing chlorine atoms (methylene chloride, 1-chlorobutane, chlorobenzene, chloroform).
2. Carbon bonded oxygen donor active diluents (MIBK, 1-octanol, 1-decanol).
3. Phosphorous- bonded oxygen donor active diluents (tri-butyl phosphate).

In some cases, the solute –extractant adduct separates from the diluent to form third phase. The solution for this kind of problem is either control solvent loading or add a modifier (third component) to solvent mixture. The reactive equilibrium description of the system can be written as a set of equilibliria involving the dissociation of acid in water and formation of complex with acid and extractant by ion pair association or hydrogen-bonding. It assumes that the reactive extraction between acid and extractant takes place at the organic-aqueous interface and two types of complexes, HAS and HAS2 form in stepwise manner.

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

$$K_D = \frac{C_{org}}{C_{aq}} = \frac{[HA]_{org} + [BHA]_{org} + [B_2HA]_{org}}{[HA]^*_{aq}} = \frac{\phi m + K_{11}[B]_{org} + K_{11}K_{12}[B]^2_{org}}{1 + 10^{pH-pKa}} \qquad (1.4.12.2)$$

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

$$Z = \frac{[BHA]_{org}}{[B]_{i,org}} \qquad (1.4.12.3)$$

$$\frac{Z}{(1-Z)} = K_{11}[HA]_{aq} \qquad (1.4.12.4)$$

$$\frac{Z}{(2-Z)} = K_{12}[HA]^2_{aq} \qquad (1.4.12.5)$$

CHAPTER 2

REACTIVE EXTRACTION

2.1. Reactive Extraction of Carboxylic acids

Fermentation route is one of the oldest known routes for the production of organic acids. With the development of petrochemical industry and increase in demand of organic acids fermentation was replaced by organic synthesis. Recently with the rise in petroleum costs and development of new biotechnology, the fermentation route is of interest again.

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

2.1.1. Reactive Extraction of glycolic and glyoxalic acid

Research done on reactive extraction of glycolic and glyoxalic acid is very less compared to that with simple aliphatic monoacids. The presence of a functional group on a α-carbon of acid molecule deviates the two acids from their corresponding aliphatic carboxylic acid. They show low degree of extraction and low equilibrium compared to their corresponding aliphatic carboxylic acids. The degree of extraction of the acids depend on the acidity and hydrophobicity of the acids.

2.1.2. Effect of Extractants and Diluents

In case of Tri-alkyl Phosphine oxide in MIBK (Qin et al, 2003) the degree of extraction for glycolic and glyoxalic acids is directly proportional to the extractant concentration for a fixed equilibrium acid concentration in the aqueous phase. Glycolic acid forms (1, 1) and (1, 2) type acid – amine complex with Tri-alkyl Phosphine Oxide were as glyoxalic acid forms only (1, 1) acid – amine complex. This phenomenon is in contrast to the extraction rules that more the hydrophobic and acidic in nature the greater degree of extraction is obtained. This may be due to extra association with extractant and glycolic acid or less steric hindrance for phosphorus bonded oxygen containing extractants. Glycolic acid shows higher degree of extraction compared to glyoxalic acid with Tri-alkyl Phosphine oxide in MIBK.

In case of Tri-octyl Amine in 1-Octanol the degree of extraction for both the acids increases with increase in the extractant concentration but is not directly proportional to the extractant concentration for a fixed equilibrium acid concentration in the aqueous phase. This fact ascertains that the polar diluents provide additional solvating power that allows higher levels of polar acid – amine complexes to stay in the organic phase. Both the acids form (1, 1) and (1, 2) type of complex with Tri-octyl Amine. Glyoxalic acid shows higher degree of extraction compared to glycolic acid with Tri-octyl Amine in 1-octanol.

2.1.3. Effect of Temperature

Water immiscible amines are observed to be selective and powerful extractants for separation of carboxylic acids from their dilute solutions. The distribution coefficient in the extraction of citric acid by amine based extractants is higher, by 1 or 2 magnitude, compared to those by extraction with other solvents, such as ketones, alkanols, esters, amides, and organic alkyl phosphates (Yu-Ming et al, 1983). This enables high separation yield, using less stages and low phase ratio. However, this conflicts with the recovery of the acid from the extractant.

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

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

Tamada and others (Tamada et al, 1989; Tamada and King, 1990) showed that on increasing the temperature there is a decrease in extraction of succinic and lactic acid by Alamine 304 in MIBK or in chloroform. Based on van't Hoff's equation, they calculated enthalpy and entropy for the association in these extraction systems. Tamada research concluded that molar complexation of 1:1 acid – amine ratio is much more exothermic and involves much greater loss of entropy than the formation of 2:1 and 3:1 complexes.

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

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

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

On differentiating above equation

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

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

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

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

Sadaka and Garcia (Sadaka and Garcia, 1998) tested the extraction of shikimic and guinic acid by Alamine 304 in Heptanol at various temperature. Ratios of 2-3 were observed between the distribution coefficients at 5°C and those at 60°C. they proposed extracting the acids at low temperatures and recovering them at high temperatures. In addition they suggested adding a "displacer" (oleic acid) to the organic phase in the back extraction stage.

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

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

i. Ion pair formation
ii. Hydrogen bonding and Solvation

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

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

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

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

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

2.1.4. Kinetics

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

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

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

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

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

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

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

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

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

The condition to be satisfied for this mechanism is given by

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

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

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

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

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

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

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

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

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

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

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

The boundary conditions are

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

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

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

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

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

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

Applying boundary conditions

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

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

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

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

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

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

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

For the study of kinetics for reactive extraction of carboxylic acids the interface is not disturbed if is carried out in stirred cell. The stirred cell has low rotation speeds and so the interfacial area is undisturbed. The study can broadly be classified into following:

i. Effect of speed of agitation
ii. Effect of phase volume
iii. Order with respect to carboxylic acid
iv. Order with respect to extractant

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

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

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

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

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

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

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

and first order rate constant, k_1 was calculated as 0.013 $mol^3\ kmol^{-1}s^{-1}$.

2.1.5 Toxicity of Extractants

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

i. Molecular toxicity: Dissolution in the aqueous broth

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

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

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

1. Replace of the toxic solvent component with a non toxic one.
2. Add of an immiscible, biocompatible component (oils) to the medium to entrap any toxic solvent dissolving into the aqueous medium phase.

2.1.6. Back Extraction

Once the acid is extracted from the aqueous phase it is regenerated from the organic phase and the organic phase is recycled for further acid extraction. The various methods (King et al, 1990; Poole and King, 1991) used for regeneration are:

1. Acid-Base treatment
2. Distillation
3. Temperature swing
4. Diluent swing

5. Gas Anti-solvent induced regeneration

6. Aqueous solution of volatile amine

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

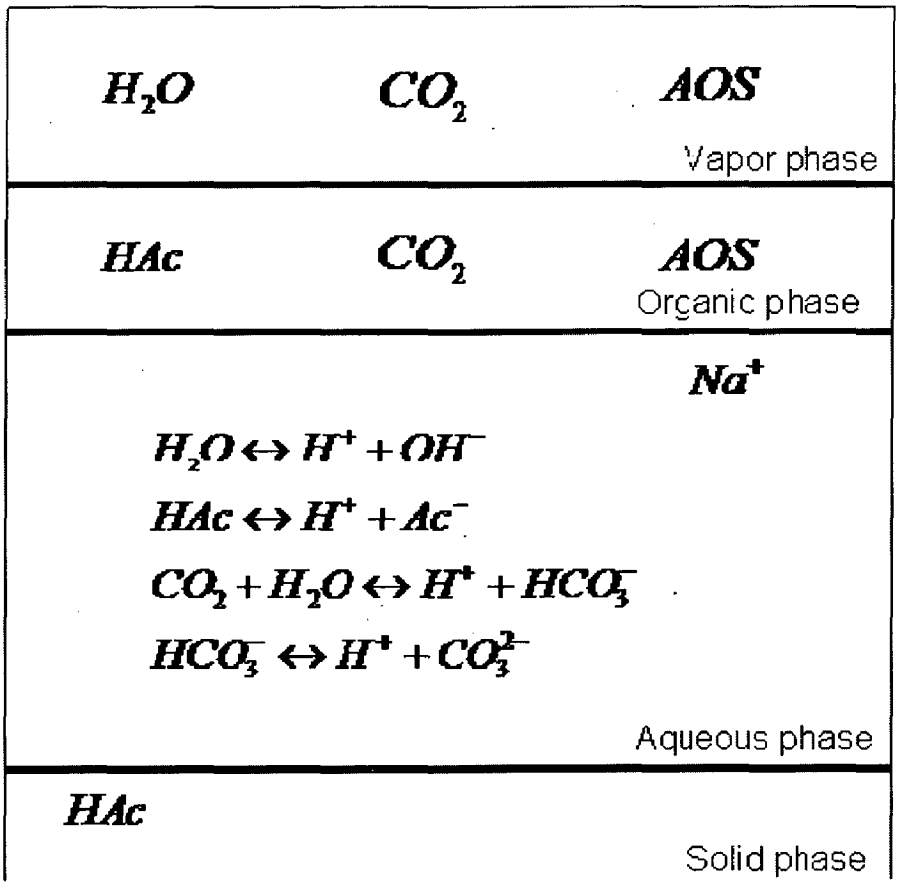
In distillation the acid is recovered from the organic phase removing the diluent in form of top product and the extractant - acid complex is the bottom product. The organic phase free from acid is recycled.

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

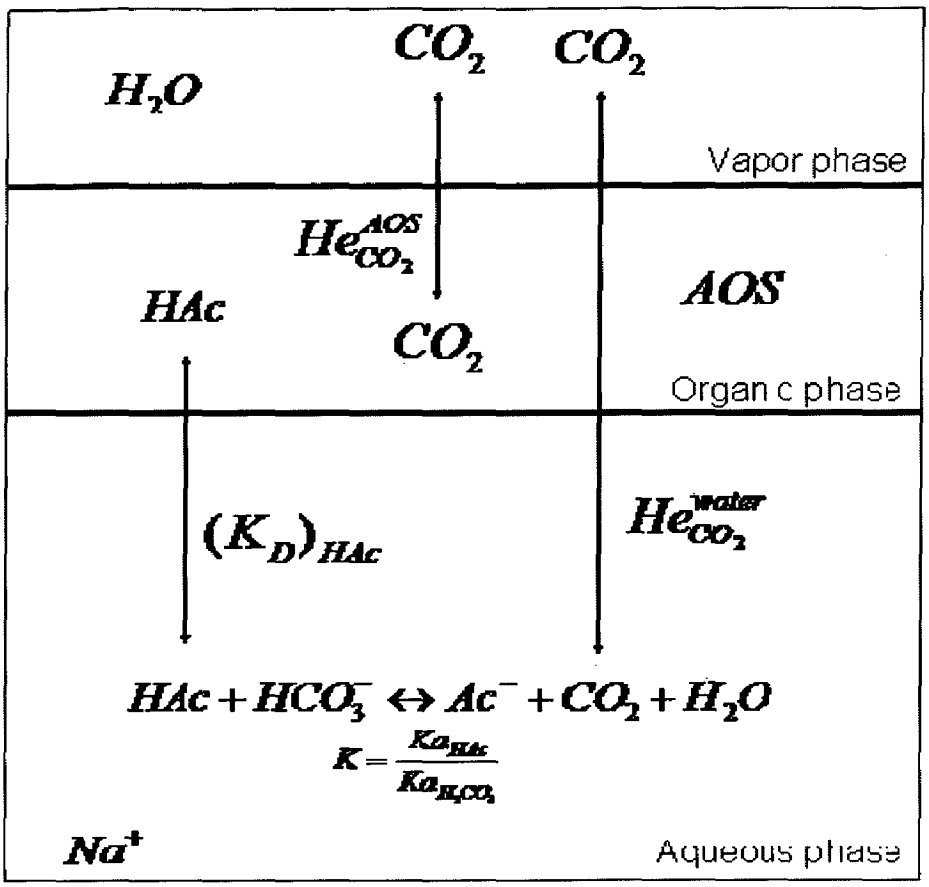
Diluent swing regeneration method is based on change in diluent composition. In this process the extraction is carried out in a solvent composed of the extractant and diluent that promotes distribution of acid in the organic phase. The composition of acid – laden organic phase leaving the extractor is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

After extraction of the carboxylic acids from the organic phase, the carboxylate is required to be converted back into the acid. Commonly, this is done by introducing a strong mineral acid and performing back – extraction into an apolar organic solvent from which the acid is subsequently distilled. As a large scale example of such recovery, the fermentative production of lactic and citric acids can be mentioned. Although feasible, a major disadvantage of this recovery process is generation of salt which is to be removed to allow recycle of the aqueous solution in the extraction section. In the Gas Anti - solvent induced mechanism , an aqueous solution of bicarbonate is used for the extraction of carboxylic acids, followed by back recovery of extracted acid using carbon di-oxide under pressure (Kuzmanovic, B. et al, 2005). In the extraction step, the bicarbonate salt causes dissociation of the acid where carbon di-oxide and water are formed (Fig. F 2.1.6 A), whereas in the back recovery, carbon di-oxide under shifts the carboxylic acid equilibrium towards the undissociated form generating only bicarbonate ion (Fig. F 2.1.6 B). in this way no new salts are formed, but only carbon di-oxide in the extraction and bicarbonate in the back recovery step, which can be recycled to the next recovery or extraction cycle, respectively.

The carboxylic acid is back extracted from amine – carboxylic acid extracts into aqueous base. In order to avoid consumption os chemicals and creation of salt byproduct, the aqueous base is volatile, thereby enabling thermal decomposition of the acid – base complex in the aqueous back – extract. The decomposition forms the carboxylic acid as product and the free base as a vapor is reabsorbed in water and recycled for reuse.



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



F 2.1.6 B Considered equilibria in the extraction of carboxylic acids

CHAPTER 3

MATERIALS AND METHODS

3.1. Materials

Glycolic acid (HIMEDIA, India) was chemically pure aqueous solution with minimum assay 70.0%. Glyoxalic acid (HIMEDIA, India) was laboratory grade chemical in monohydrate form with minimum assay 97.0%. Aliquat 336 (HIMEDIA, India) was chemically pure solution with minimum assay 80.0%. Tri-butyl Phosphate (HIMEDIA, India) is chemically pure solution with 99.0%. 1-Decanol (HIMEDIA, India) is reagent grade chemical with purity 99.0%. Oleyl Alcohol (S. d. fine Chemicals, India) was reagent grade chemical with 35.0% minimum assay. Butyl Acetate (SISCO, India) is a reagent grade chemical with 99.0% minimum assay.

3.2. Experiment

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

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

3.3. Experimental Procedure

3.3.1. Preparation of Glycolic and Glyoxalic acids Stock Solutions

Glycolic acid obtained was aqueous solution with 70% concentration. The concentration was calculated in kmol/m^3 and then it was diluted to prepare various concentration of acid from 0.05 kmol/m^3 to 0.40 kmol/m^3 and verified using sodium hydroxide solution. The solutions were stored in standard flasks as stock solution.

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

3.3.2. Preparation of Aqueous phase for Extraction

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

3.3.3. Preparation of Organic phase for Extraction

Organic phase of desired concentration was prepared by well mixing the extractant with the diluent. In the physical extraction experiments pure diluent were used alone as the organic phase.

3.3.4. Extraction Experiment

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

CHAPTER 4

RESULTS AND DISCUSSION

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

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

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

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

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

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

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

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

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

In the case of glycolic and glyoxalic acid extraction from their aqueous solutions by Aliquat 336 and TBP, the loading of the extractant can be calculated as the ratio of the concentration of the acids that was calculated to be present in the organic phase to the total concentration of extractant (Aliquat 336, TBP) in the organic phase. Loading value for all

the extractions with extractants are calculated and listed in the tables together with degree of extraction and K_D values.

4.1. Physical Extraction with pure diluents

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

4.1.1. Diluents with alcohol as functional group

The extraction experiments were carried out by contacting organic phases composed of pure 1-decanol and pure oleyl alcohol, with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of these experiments are given in the table T 4.1.1 A, B, C and D, which show the variation in the concentration of aqueous phase for the different initial concentrations of glycolic and glyoxalic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction (D) and distribution coefficient (K_D) are calculated from equation 4.1, 4.2.

These results are plotted in figure F 4.1.1 A and B for different concentrations in aqueous phases, to observe the variation of the degree of extraction. From the plot it can be seen that degree of extraction with 1-decanol was higher as compared to that with oleyl alcohol for glycolic acid (10 times) and glyoxalic acid (3 times). This is in consistent with the previous literature which explains it based on the electronegetivity of the diluent. Decanol having a smaller alkyl group compared to oleyl alcohol is less electronegative.

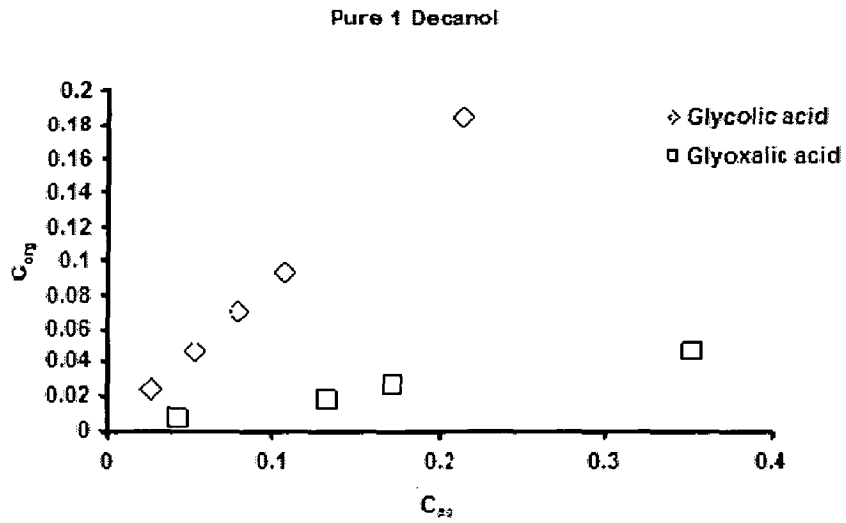


Fig. F 4.1.1 A: Equilibrium isotherm of carboxylic acids in pure 1-Decanol

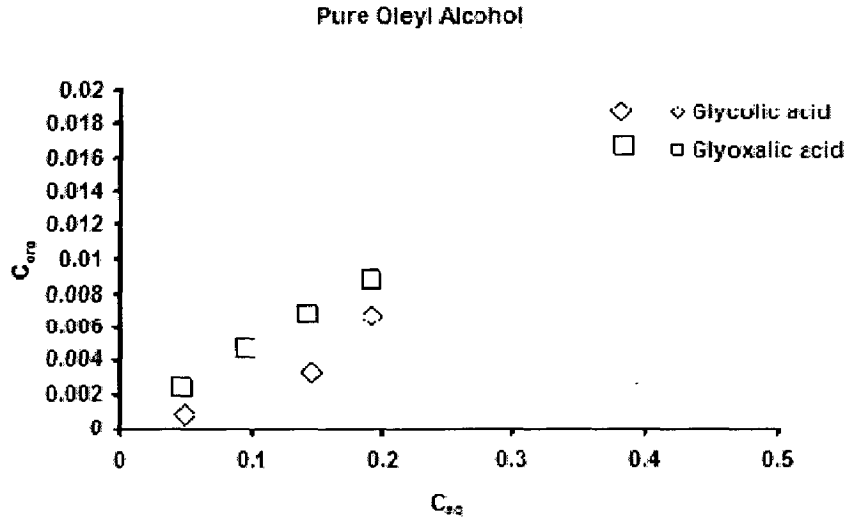


Fig. F 4.1.1 B: Equilibrium isotherm of carboxylic acids in pure Oleyl Alcohol

4.1.2. Diluents with ester as functional group

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

These results are plotted in figure F 4.1.2 A for different concentrations in aqueous phases, to observe the variation of the degree of extraction. From the plot it can be seen that degree of extraction with butyl acetate is far lower than that with 1-decanol for glycolic acid (3 times) and glyoxalic acid (3 times). This is in consistent with the previous literature which explains it based on the number of alkoxy groups the diluent. Decanol has no alkoxy group compared to one alkoxy group in butyl acetate.

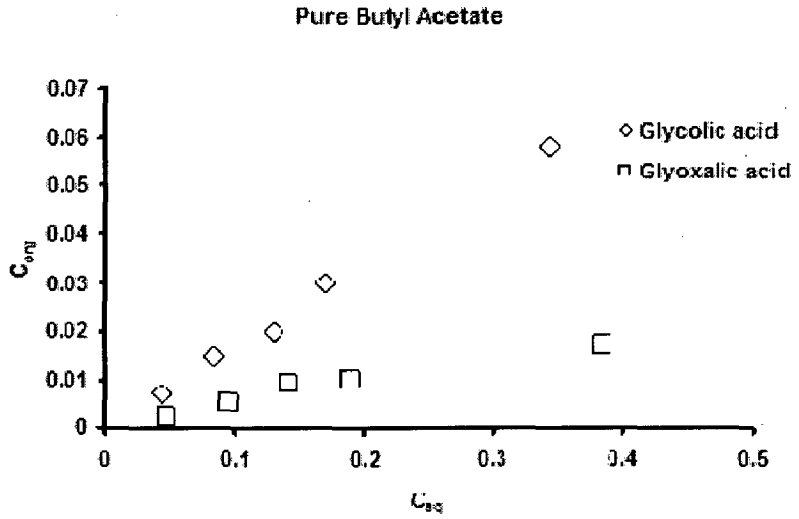


Fig. F 4.1.2 A: Equilibrium isotherm of carboxylic acids in pure Butyl Acetate

4.1.3 Inert diluents

The extraction experiments were carried out by contacting organic phases composed of pure kerosene and pure sunflower oil, with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of these experiments are given in the table T 4.1.3 A, B, C and D, which show the variation in the concentration of aqueous phase for the different initial concentrations of glycolic and glyoxalic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction (D) and distribution coefficient (K_D) are calculated from equation 4.1, 4.2.

These results are plotted in figure F 4.1.3 A and B for different concentrations in aqueous phases, to observe the variation of the degree of extraction. From the plot it can be seen that degree of extraction with kerosene is higher than that with sunflower oil for glycolic acid (3 times) and glyoxalic acid (1.2 times). Sunflower oil is mixture of fatty acids (lenoleic, oleic, palmitic, stearic, alpha lenoleic acids) and fatty acids have alkoxy group so, has higher electronegetivity compared to kerosene, which is mixture of alkanes. This is in consistent with the

previous literature which explains it based on the number of alkoxy groups the diluent.

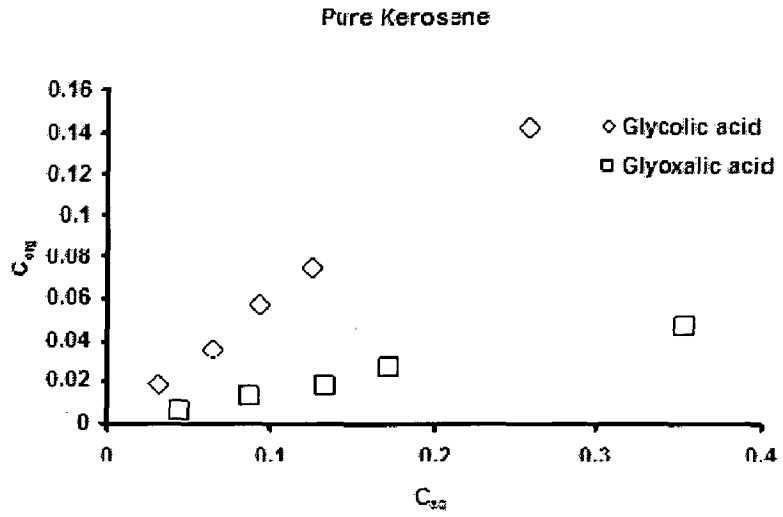


Fig. F 4.1.3 A: Equilibrium isotherm of carboxylic acids in pure Kerosene

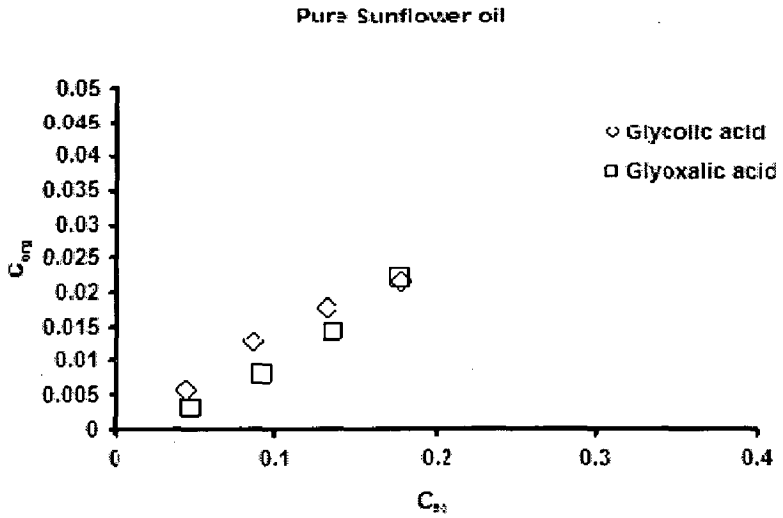


Fig. F 4.1.3 A: Equilibrium isotherm of carboxylic acids in pure Sunflower oil

4.2. Chemical Extraction with Aliquat 336 dissolved in diluents

Extraction of proton baring organic and inorganic compounds from aqueous media by long chain aliphatic amines dissolved in water immiscible organic solvents is one of the new developments in separation technology. The extractability of acids, in contrast to that of anionic acidic metal complexes, depends more on the cokposition of the organic phase, amine, and the diluent than on th aqueous phase conditions. The requirements for

practical extraction applications are rather general for both weak and strong acids and are fairly well described in the chemical literature.

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

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

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

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

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

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

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

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

The extent to which the organic phase can be loaded with acid is expressed as the loading factor Z. When the diluent used has an acid interaction functional group or a solvent that dissolves the acid to a considerable extent, $C_{HA(w)}$ should be corrected for the

acid extracted into the diluent alone. The value of Z depends on extractability of the acid (strength of acid-base interaction) and its aqueous phase concentration and is independent of amine content in an inert diluent. If the organic phase is not highly concentrated (Z<0.5), the constant Ks can be expressed via the experimental accessible loading ratio

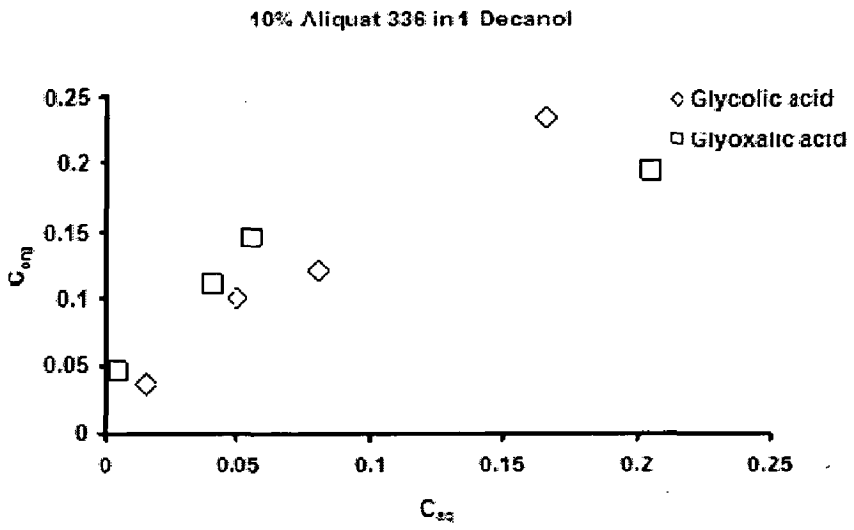
$$\frac{Z}{(1-Z)} = K_E[HA]_{(w)} \qquad (4.2.4)$$

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

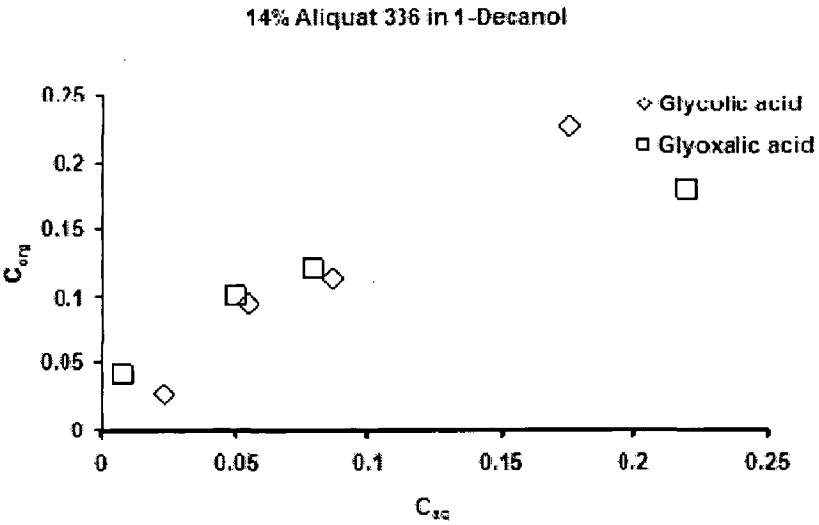
4.2.1 Extraction with Aliquat 336 dissolved in 1-decanol

The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in 1-decanol at various concentrations; with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of these experiments are given in the table T 4.2.1 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of glycolic and glyoxalic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 1.4.12.3.

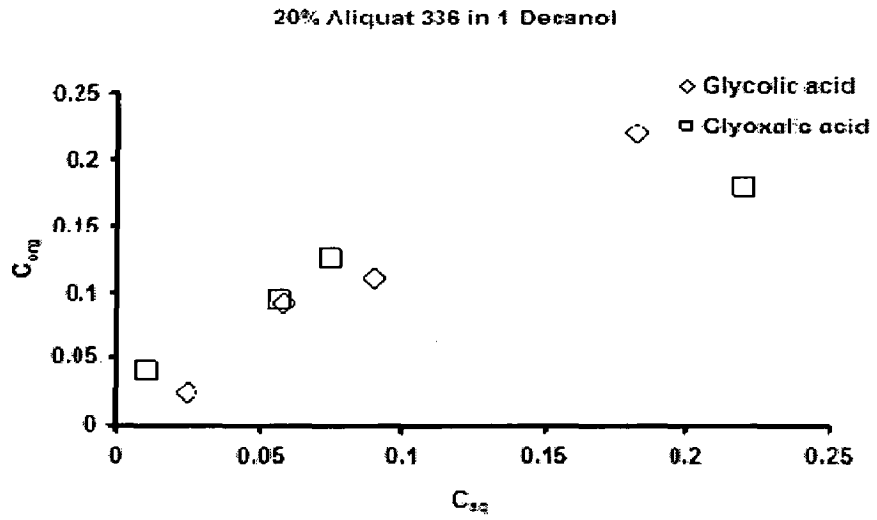
These results are plotted in figure F 4.2.1 A, B, C and D different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that on increase in extractant concentration there is a decrease in degree of extraction for both the acids. In the extraction of glycolic and glyoxalic acids it can be observed that the loading factor reduces with increase in extractant concentration for a particular acid concentration. Systems that include diluent specifically in the complex stoichiometry show this kind of behavior (Tamada et al. 1990a). In case of both the acids, when the acid concentration is increased there is decrease in degree of extraction. The values of equilibrium constant (K_{11}) for both the acids, from the plot of Z/(1-Z) Vs. C_{aq} was obtained by fitting a straight line through origin according to the equation 1.4.12.4. The K_{11} for glycolic and glyoxalic acid are 6.6512 and 4.8101 respectively.



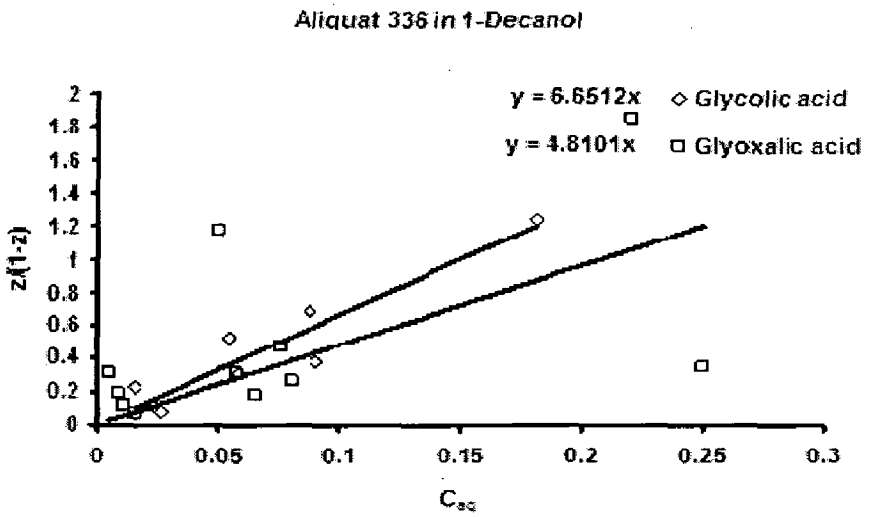
F 4.2.1 A Equilibrium isotherm of carboxylic acids with 10% Aliquat 336 in 1-Decanol



F 4.2.1 B Equilibrium isotherm of carboxylic acids with 14% Aliquat 336 in 1-Decanol



F 4.2.1 C Equilibrium isotherm of carboxylic acids with 20% Aliquat 336 in 1-Decanol



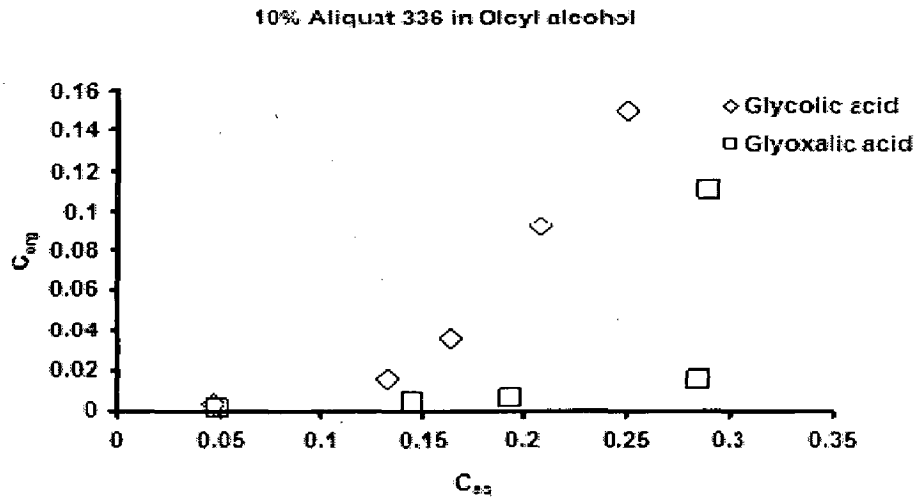
F 4.2.1 D Plot of Z/(1-Z) versus C_{aq} for estimation of (1,1) acid – Aliquat 336 equilibrium constants with 1-decanol as the diluent

4.2.2 Extraction with Aliquat 336 dissolved in oleyl alcohol

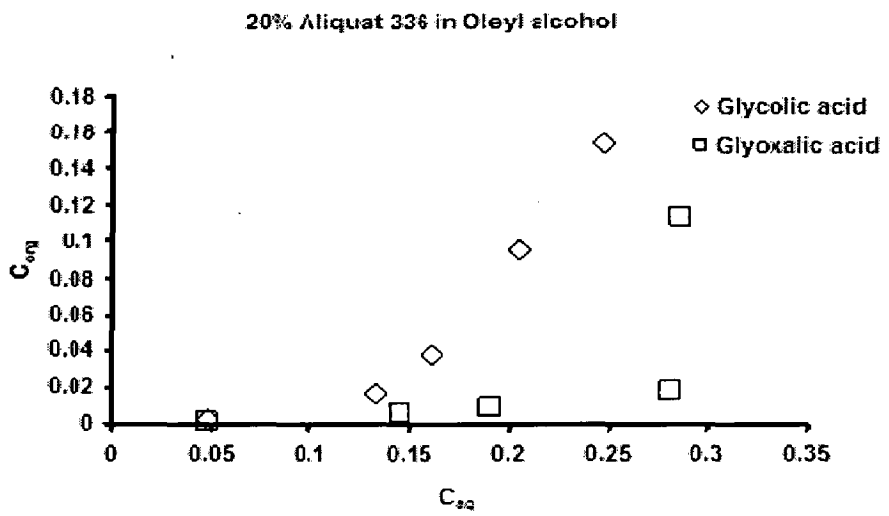
The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in oleyl alcohol at various concentrations; with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of these experiments are given in the table T 4.2.2 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of glycolic and glyoxalic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The

degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 1.4.12.3.

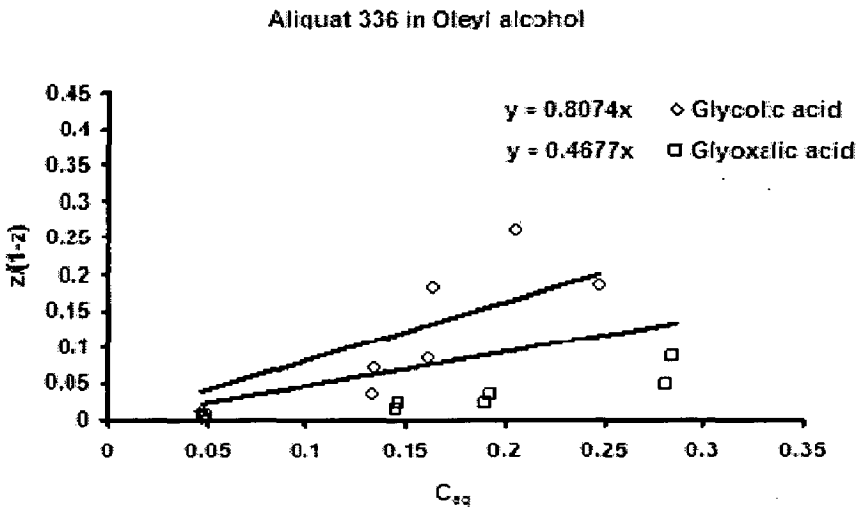
These results are plotted in figure F 4.2.2 A, B and C different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for glycolic acid on increase in extractant concentration there is a decrease in degree of extraction but is converse for glyoxalic acid. In the extraction of glycolic and glyoxalic acids it can be observed that the loading factor reduces with increase in extractant concentration for a particular acid concentration. Systems that include diluent specifically in the complex stoichiometry show this kind of behavior (Tamada et al. 1990a). In case of both the acids, when the acid concentration is increased there is an increase in degree of extraction. The values of equilibrium constant (K_{11}) for both the acids, from the plot of Z/(1-Z) Vs. C_{aq} was obtained by fitting a straight line through origin according to the equation 1.4.12.4. The K_{11} for glycolic and glyoxalic acid are 0.8074 and 0.4677 respectively.



F 4.2.2 A Equilibrium isotherm of carboxylic acids with 10% Aliquat 336 in oleyl alcohol



F 4.2.2 B Equilibrium isotherm of carboxylic acids with 14% Aliquat 336 in oleyl alcohol



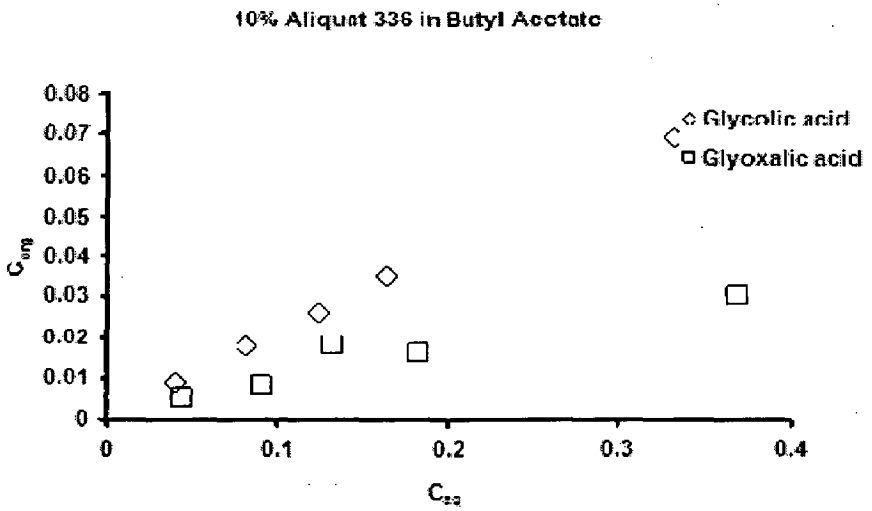
F 4.2.2 C Plot of Z/(1-Z) versus C_{aq} for estimation of (1,1) acid – Aliquat 336 equilibrium constants with oleyl alcohol as the diluent

4.2.3 Extraction with Aliquat 336 dissolved in butyl acetate

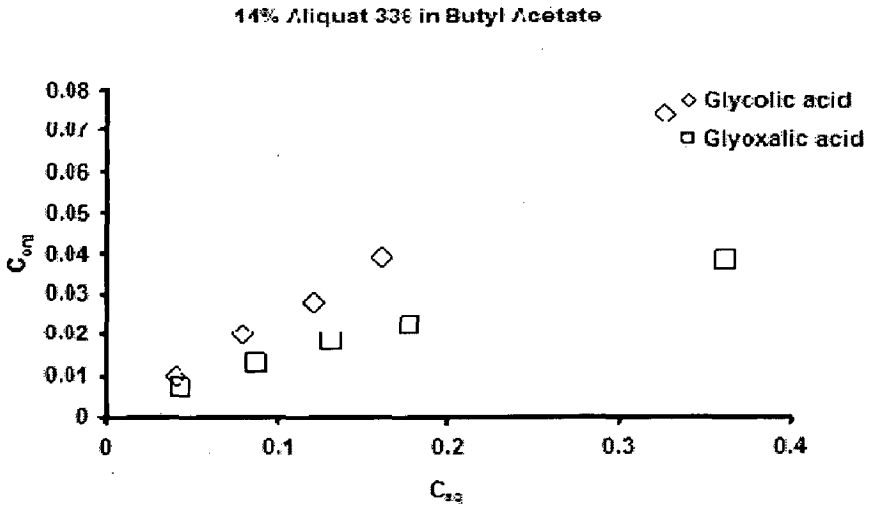
The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in butyl acetate at various concentrations; with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of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

degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 1.4.12.3.

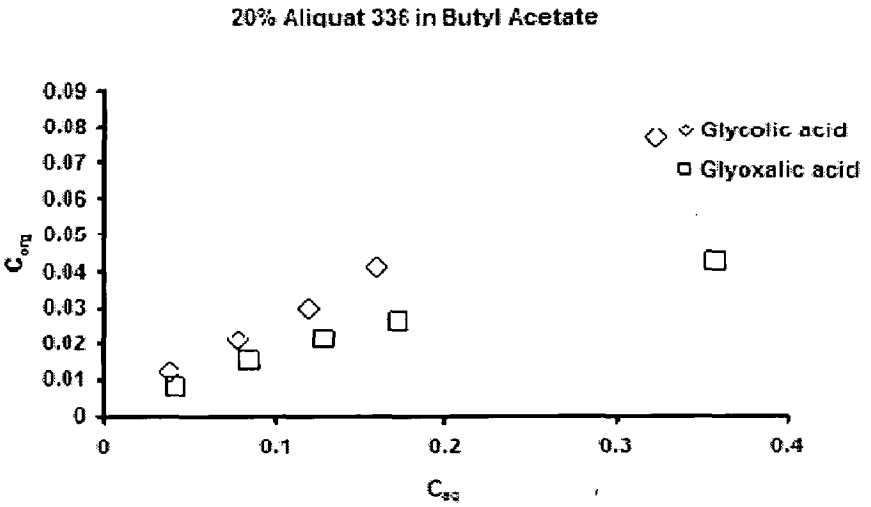
These results are plotted in figure F 4.2.3 A, B, C and D different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for glycolic and glyoxalic acid on increase in extractant concentration there is an increase in degree of extraction. In the extraction of glycolic and glyoxalic acids it can be observed that the loading factor reduces with increase in extractant concentration for a particular acid concentration. Systems that include diluent specifically in the complex stoichiometry show this kind of behavior (Tamada et al. 1990a). In case of both the acids, when the acid concentration is increased there is a decrease in degree of extraction. The values of equilibrium constant (K_{11}) for both the acids, from the plot of $Z/(1-Z)$ Vs. C_{aq} was obtained by fitting a straight line through origin according to the equation 1.4.12.4. The K_{11} for glycolic and glyoxalic acid are 0.1809 and 0.208 respectively.



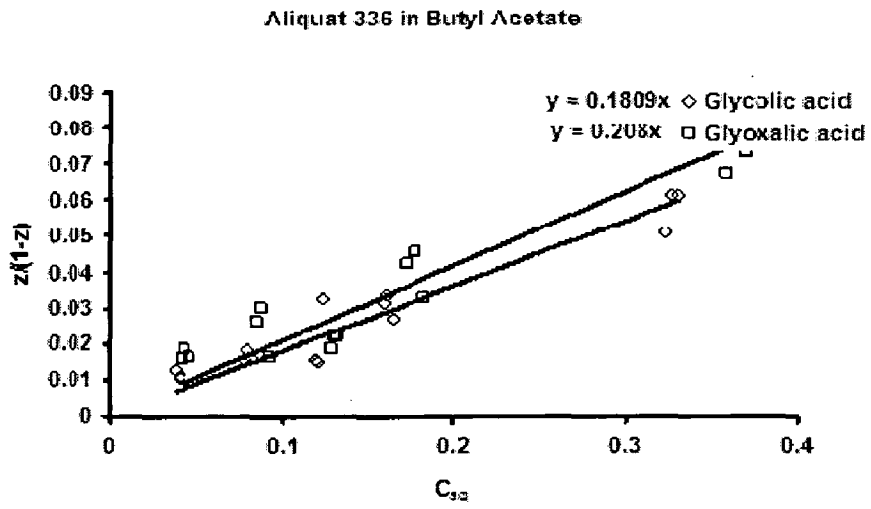
F 4.2.3 A Equilibrium isotherm of carboxylic acids with 10% Aliquat 336 in butyl acetate



F 4.2.3 B Equilibrium isotherm of carboxylic acids with 14% Aliquat 336 in butyl acetate



F 4.2.3 C Equilibrium isotherm of carboxylic acids with 20% Aliquat 336 in butyl acetate

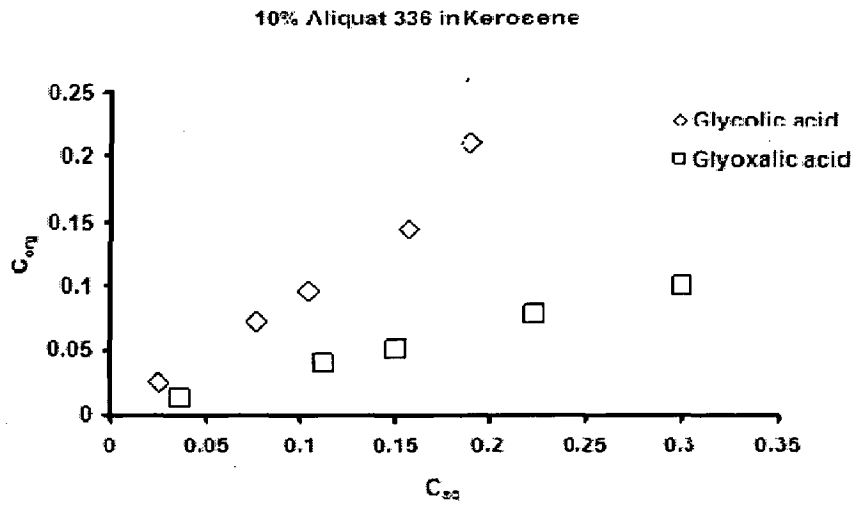


F 4.2.3 D Plot of Z/(1-Z) versus C_{aq} for estimation of (1,1) acid – Aliquat 336 equilibrium constants with butyl acetate as the diluent

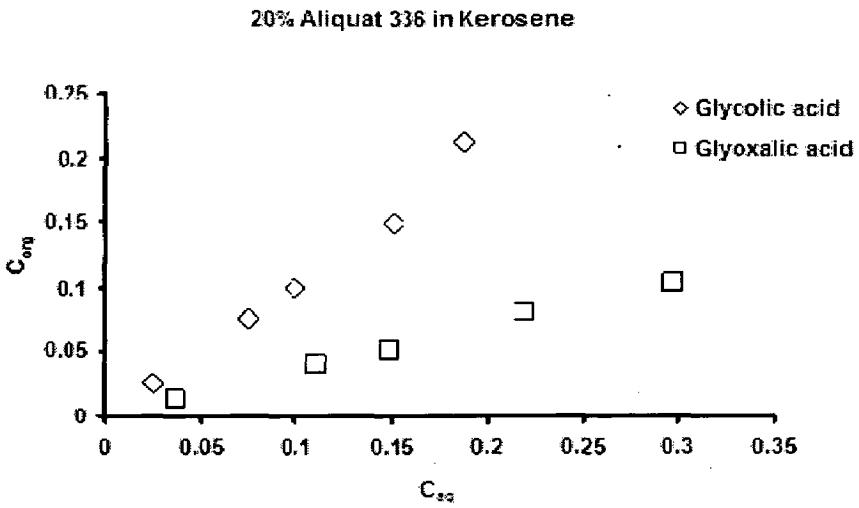
4.2.4 Extraction with Aliquat 336 dissolved in kerosene

The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in kerosene at various concentrations; with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of these experiments are given in the table T 4.2.4 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of glycolic and glyoxalic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 1.4.12.3.

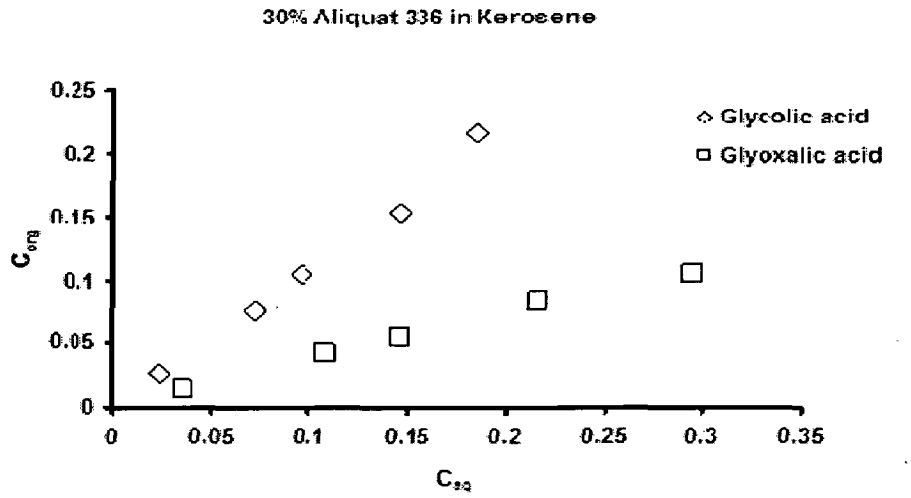
These results are plotted in figure F 4.2.4 A, B, C and D different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for glycolic and glyoxalic acid on increase in extractant concentration there is an increase in degree of extraction. In the extraction of glycolic and glyoxalic acids it can be observed that the loading factor reduces with increase in extractant concentration for a particular acid concentration. Systems that include diluent specifically in the complex stoichiometry show this kind of behavior (Tamada et al. 1990a). In case of both the acids, when the acid concentration is increased there is no regular pattern in degree of extraction. The values of equilibrium constant (K_{11}) for both the acids, from the plot of Z/(1-Z) Vs. C_{aq} was obtained by fitting a straight line through origin according to the equation 1.4.12.4. The K_{11} for glycolic and glyoxalic acid are 5.6643 and 0.7969 respectively.



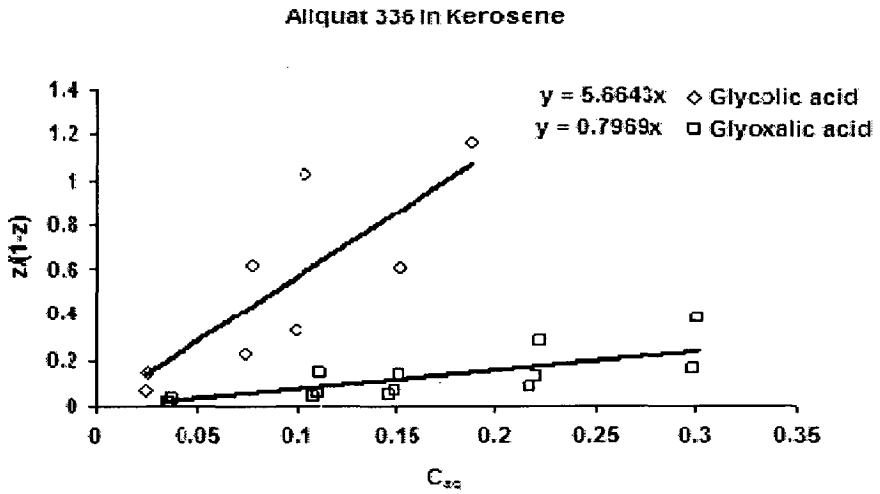
F 4.2.4 A Equilibrium isotherm of carboxylic acids with 10% Aliquat 336 in kerosene



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



F 4.2.4 C *Equilibrium isotherm of carboxylic acids with 30% Aliquat 336 in kerosene*



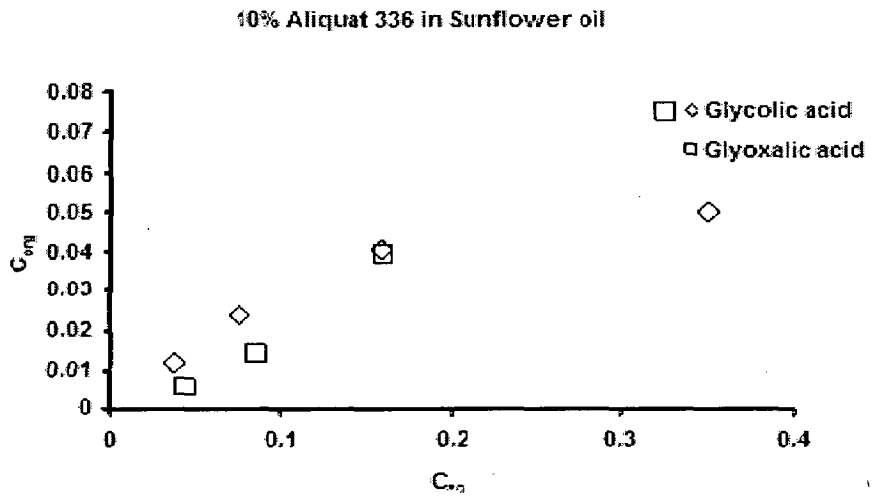
F 4.2.4 D Plot of Z/(1-Z) versus C_{aq} for estimation of (1,1) acid – Aliquat 336 equilibrium constants with kerosene as the diluent

4.2.5 Extraction with Aliquat 336 dissolved in sunflower oil

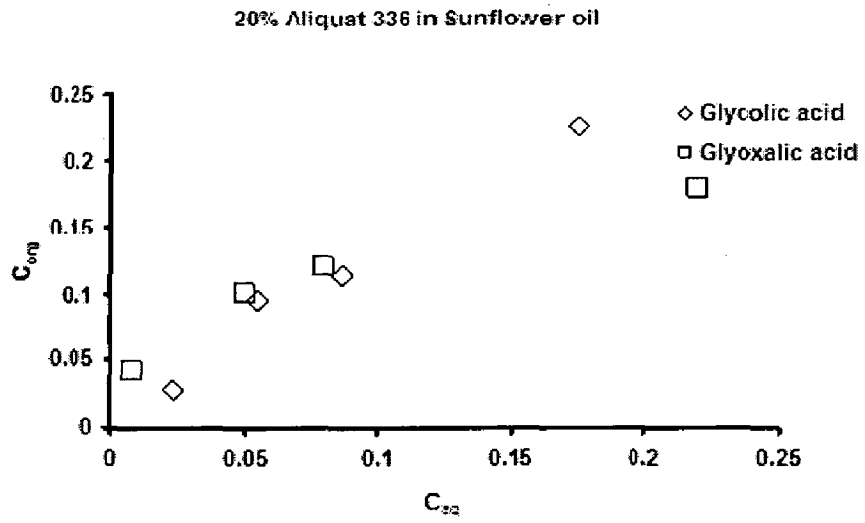
The extraction experiments were carried out by contacting organic phase composed of aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in sunflower oil at various concentrations; with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of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

degree of extraction, distribution coefficient and the loading factor are calculated from equation 4.1, 4.2 and 1.4.12.3.

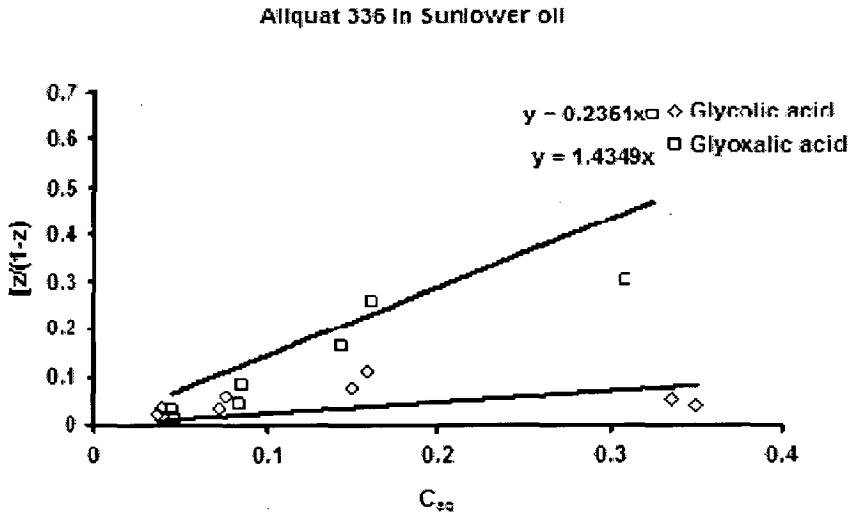
These results are plotted in figure F 4.2.5 A, B and C different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for glycolic acid on increase in extractant concentration there is an increase in degree of extraction and decrease in loading factor but in case gloxalic acid both, degree of extraction and loading factor, decrease from this it can be concluded that for extracting glycolic acid from glycolic acid and glyoxalic acid mixture use of high aliquat 336 concentration is favorable. Systems that include diluent specifically in the complex stoichiometry show decrease in loading factor with amine extractant concentration (Tamada et al. 1990a). In case glycolic acid, when the acid concentration is increased there is a decrease in degree of extraction but, for glyoxalic acid its increases initially and then decreases. The values of equilibrium constant (K_{11}) for both the acids, from the plot of Z/(1-Z) Vs. C_{aq} was obtained by fitting a straight line through origin according to the equation 1.4.12.4. The K_{11} for glycolic and glyoxalic acid are 0.2351 and 1.4349 respectively.



F 4.2.5 A Equilibrium isotherm of carboxylic acids with 10% Aliquat 336 in sunflower oil



F 4.2.5 B Equilibrium isotherm of carboxylic acids with 20% Aliquat 336 in sunflower oil



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

4.3. Chemical Extraction with TBP dissolved in diluents

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

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

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

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

and the formation of the acid solvates in the organic phase,

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

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

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

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

(4.3.3)

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

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

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

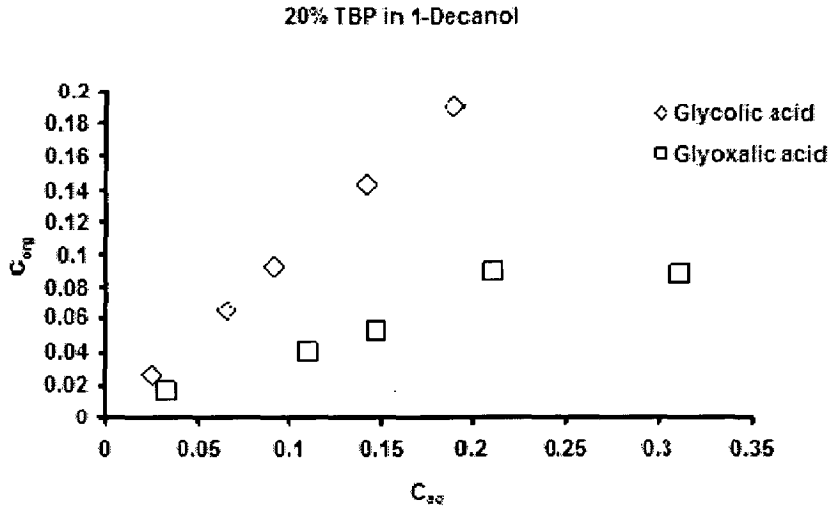
Yielding slope p and intercept K_E. Both o these quantities are dependent on the solute and extractant concentration however, remain constant over some range. At high solute concentration, as an appreciable fraction of extractant molecule becomes bound to acid, lower values of p will predominate, and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

4.3.1 Extraction with TBP dissolved in 1-decanol

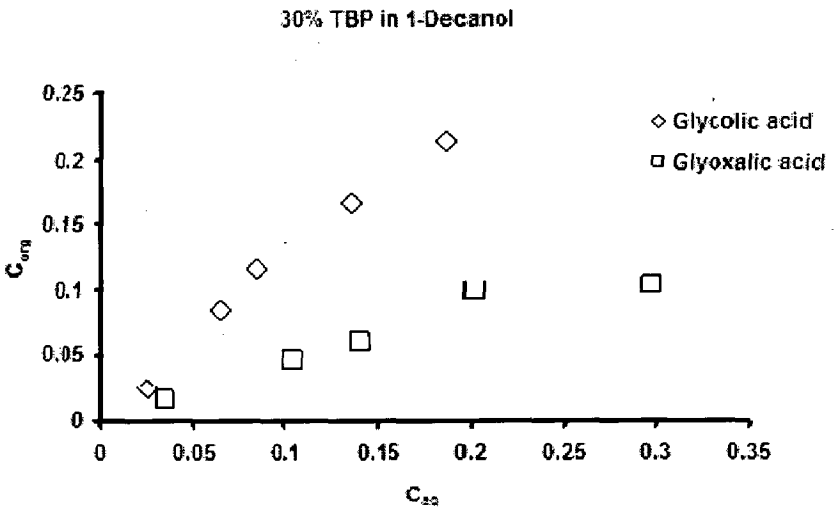
The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in 1-decanol at various concentrations; with aqueous phases containing glycolic and glyoxalic acids at concentrations 0.05 – 0.4 kmol/m^3. The results of these experiments are given in the table T 4.3.1 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of glycolic and glyoxalic acids before and after extraction. The difference between the two is calculated to be the organic

phase acid concentration, from the mass balance. The degree of extraction is calculated from equation 4.1.

These results are plotted in figure F 4.3.1 A, B different concentrations in aqueous phases, to observe the variation of the degree of extraction. From the plots it can be analyzed that for glycolic acid on increase in extractant concentration there is an increase in degree of extraction but, for gloxalic acid degree of extraction decreases. In case glycolic acid, when the acid concentration is increased there is an increase and then decrease in degree of extraction but, for glyoxalic acid, no regular pattern in degree of extraction. The values of equilibrium constant (K_{11}) for both the acids, from the plot of log (K_D) Vs $\log([B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The K_{11} and p values for glycolic and glyoxalic acid are tabulated in table T 4.3.R.



F 4.3.1 A Equilibrium isotherm of carboxylic acids with 20% TBP in 1-decanol

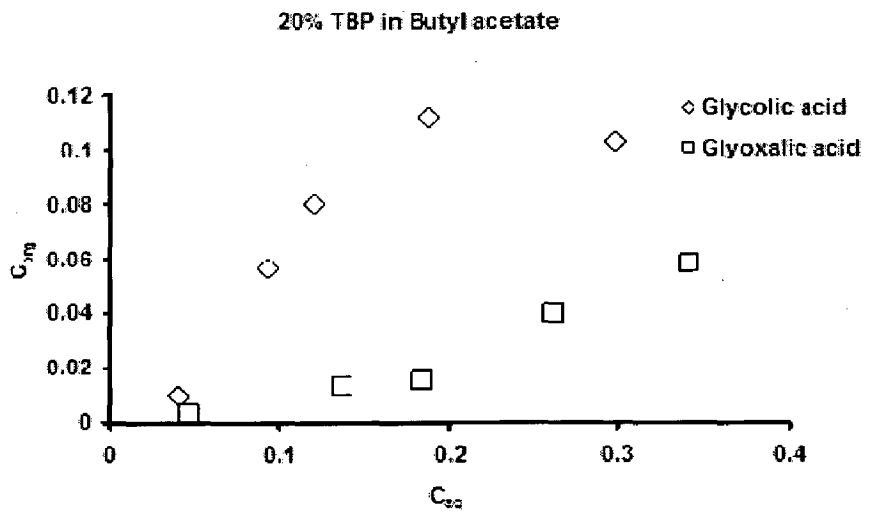


F 4.3.1 B Equilibrium isotherm of carboxylic acids with 30% TBP in 1-decanol

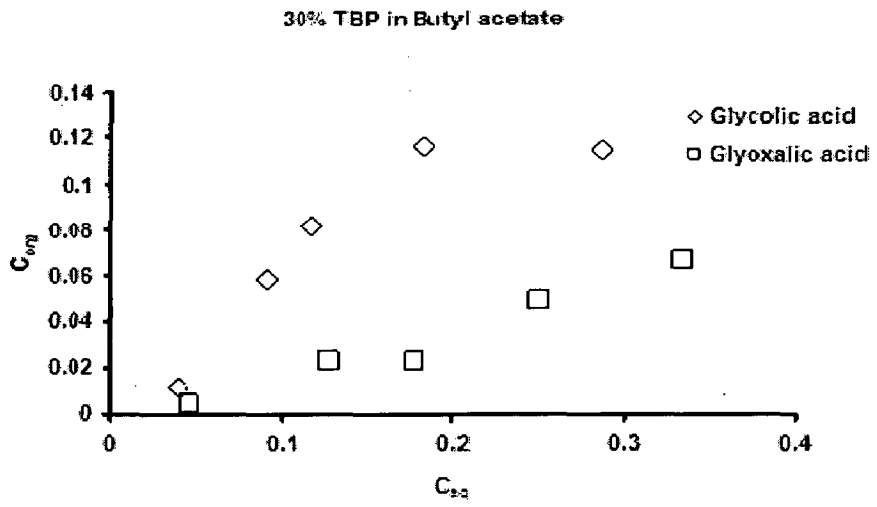
4.3.2 Extraction with TBP dissolved in butyl acetate

The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in butyl acetate at various concentrations; with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of these experiments are given in the table T 4.3.2 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of glycolic and glyoxalic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction is calculated from equation 4.1.

These results are plotted in figure F 4.3.2 A, B different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for glycolic acid on increase in extractant concentration there is an increase in degree of extraction but, in case gloxalic acid degree of extraction decreases. In case glycolic acid, when the acid concentration is increased there is an increase and then decrease in degree of extraction but, for glyoxalic acid, there is an increase in degree of extraction. The values of equilibrium constant (K_{11}) for both the acids, from the plot of log (K_D) Vs $\log([B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The K_{11} and p values for glycolic and glyoxalic acid are tabulated in table T 4.3.R.



F 4.3.2 A Equilibrium isotherm of carboxylic acids with 20% TBP in butyl acetate

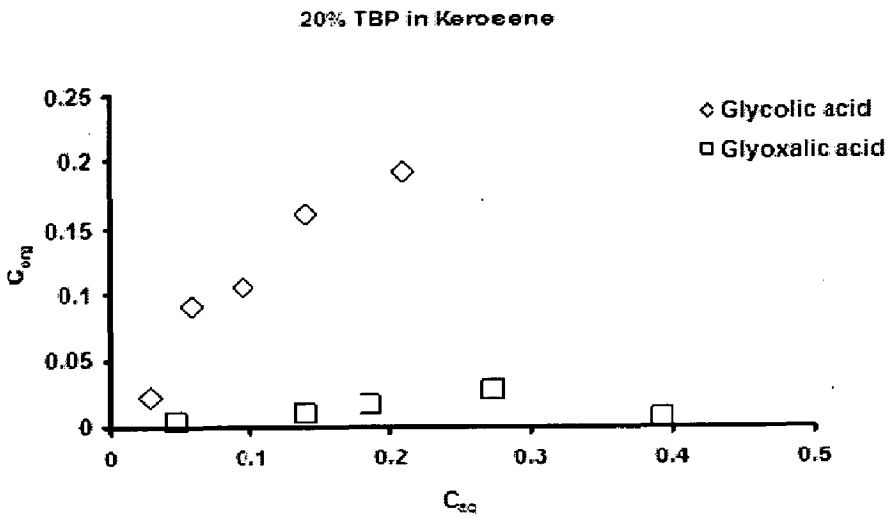


F 4.3.2 B Equilibrium isotherm of carboxylic acids with 30% TBP in Butyl Acetate

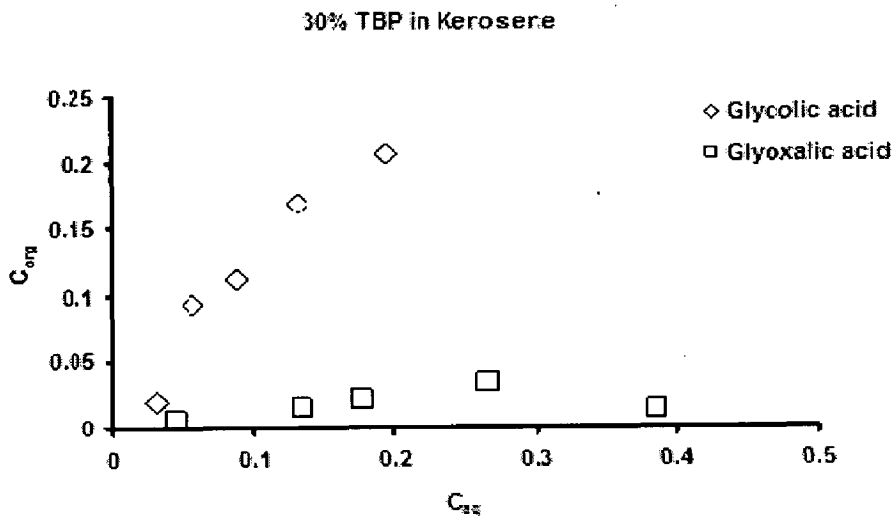
4.3.3 Extraction with TBP dissolved in kerosene

The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in kerosene at various concentrations; with aqueous phases containing glycolic and glyoxalic acids at concentration 0.05 – 0.4 kmol/m^3. The results of these experiments are given in the table T 4.3.3 A and B, which show the variation in the concentration of aqueous phase for the different initial concentrations of glycolic and glyoxalic acids before and after extraction. The difference between the two is calculated to be the organic phase acid concentration, from the mass balance. The degree of extraction is calculated from equation 4.1.

These results are plotted in figure F 4.3.3 A, B different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for glycolic acid on increase in extractant concentration there is an increase in degree of extraction but, in case gloxalic acid degree of extraction decreases. In case glycolic acid, when the acid concentration is increased there is a decrease in degree of extraction but, for glyoxalic acid, there is no considerable change in degree of extraction. The values of equilibrium constant (K_{11}) for both the acids, from the plot of log (K_D) Vs $\log([B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The K_{11} and p values for glycolic and glyoxalic acid are tabulated in table T 4.3.R.



F 4.3.3.A Equilibrium isotherm of carboxylic acids with 20% TBP in Kerosene

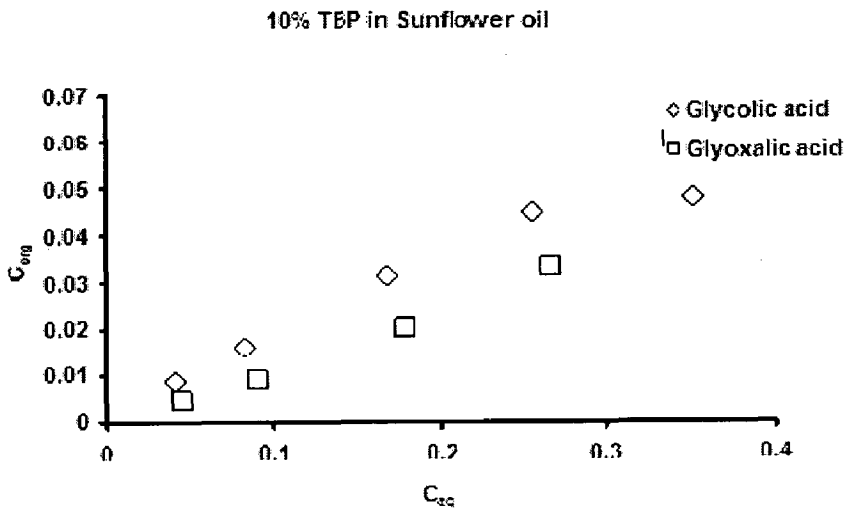


F 4.3.3 B Equilibrium isotherm of carboxylic acids with 30% TBP in Kerosene

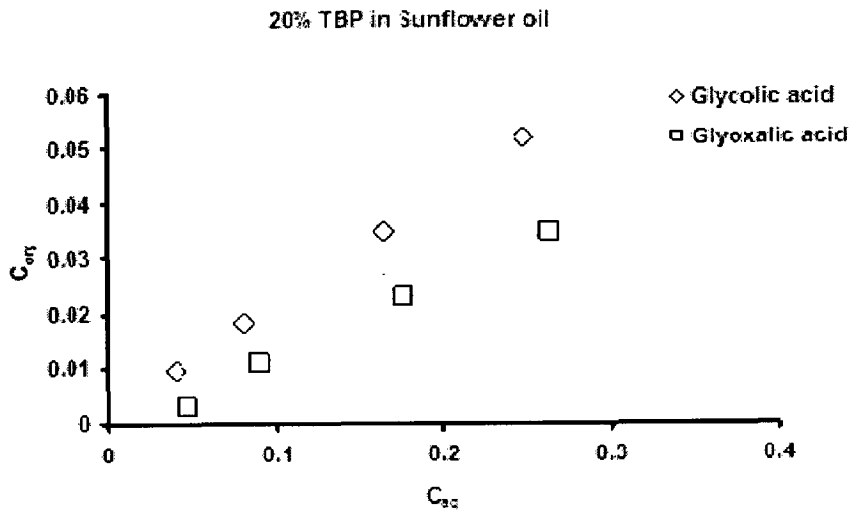
4.3.4 Extraction with TBP dissolved in sunflower oil

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

These results are plotted in figure F 4.3.4 A, B different concentrations in aqueous phases, to observe the variation of the degree of extraction and calculate equilibrium constant. From the plots it can be analyzed that for glycolic acid on increase in extractant concentration there is an increase in degree of extraction but, in case gloxalic acid degree of extraction decreases. In case glycolic acid, when the acid concentration is increased there is an increase in degree of extraction but, for glyoxalic acid, there is a decrease in degree of extraction. The values of equilibrium constant (K_{11}) for both the acids, from the plot of log (K_D) Vs $\log([B]_{org}/(1+10^{(pH-pKa)})$ was obtained according to the equation 4.3.3. The K_{11} and p values for glycolic and glyoxalic acid are tabulated in table T 4.3.R.



F 4.3.4 A Equilibrium isotherm of carboxylic acids with 10% TBP in Sunflower oil

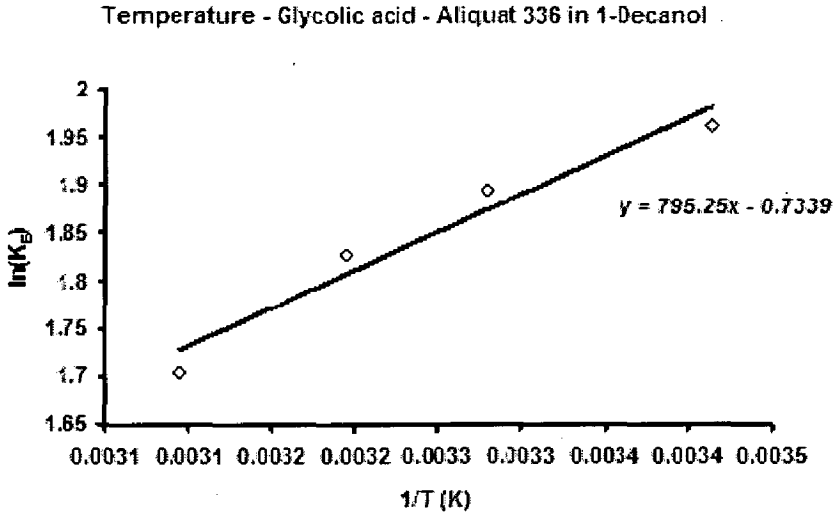


F 4.3.4 B Equilibrium isotherm of carboxylic acids with 20% TBP in Sunflower oil

4.4. Effect of Temperature

4.4.1 Extraction of Glycolic acid with Aliquat 336 in 1-decanol

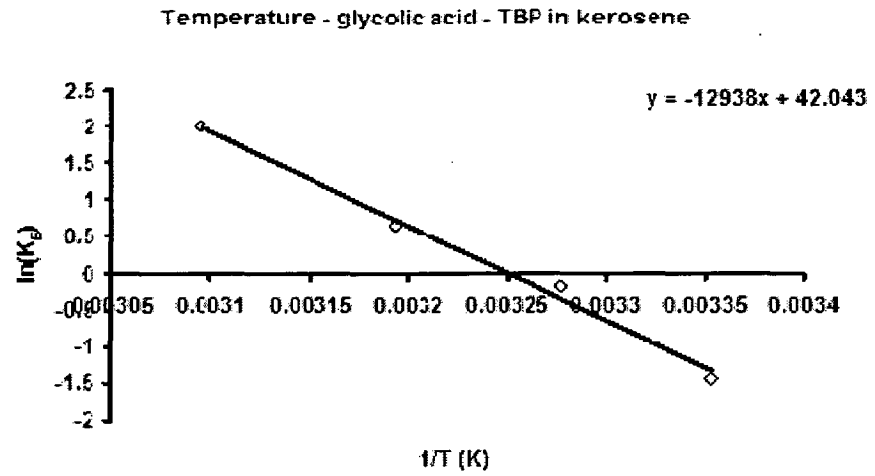
The extraction experiments were carried out by contacting organic phase composed of Aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in 1-decanol at various concentrations; with aqueous phases containing glycolic acid at concentration varring from 0.05 to 0.4 kmol/m^3. The results of these experiments are given in the table T 4.4.1 A, B, C and D, which show the equilibrium data of extraction at temperatures 298.15 K, 305.15 K, 313.15 K and 323.15 K respectively. The enthalpy and entropy are calculated from equation 2.1.3.2 and plotting a graph 1/T (K) Vs. ln(K_E) (F 4.4.1). The enthalpy and entropy are -6.61171 KJ/mol and -6.10164 J/mol K.



F 4.4.1 Plot of K_{11} versus 1/T for estimation of enthalpy and entropy of glycolic acid – Aliquat 336 with 1-Decanol

4.4.2 Extraction of Glycolic acid with TBP in kerosene

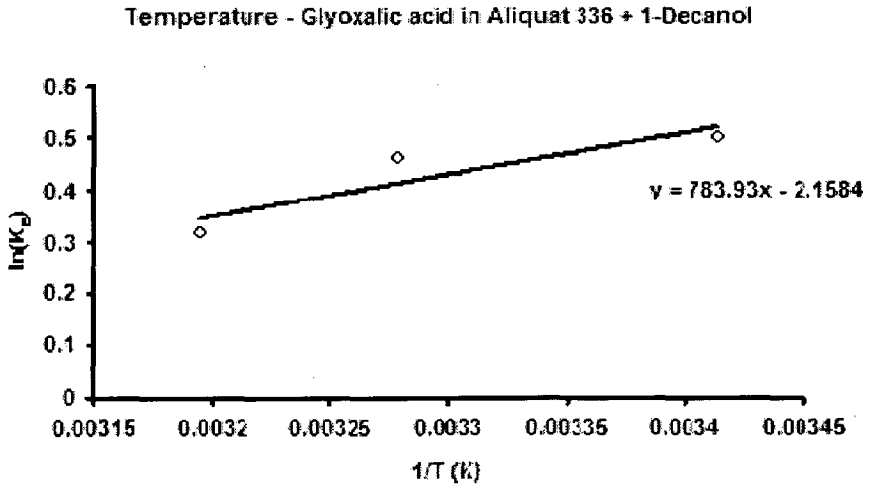
The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in kerosene at various concentrations; with aqueous phases containing glycolic acid at concentration varring from 0.05 to 0.4 kmol/m^3. The results of these experiments are given in the table T 4.4.2 A, B, C and D, which show the equilibrium data of extraction at temperatures 298.15 K, 305.15 K, 313.15 K and 323.15 K respectively. The enthalpy and entropy are calculated from equation 2.1.3.2. The enthalpy and entropy are 107.56 KJ/mol and 349.545 J/mol K.



F 4.4.2 Plot of K_{11} versus 1/T for estimation of enthalpy and entropy of glycolic acid – TBP with kerosene

4.4.3 Extraction of Glyoxalic acid with Aliquat 336 in 1-decanol

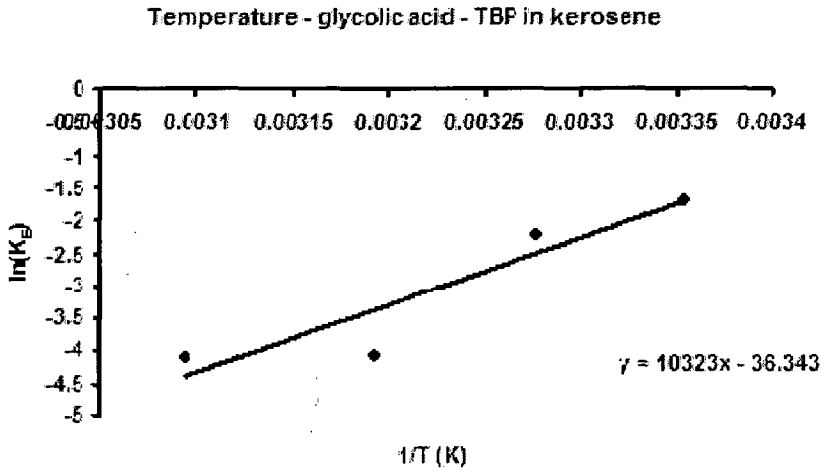
The extraction experiments were carried out by contacting organic phase composed of Aliquat 336 (tri-capryl methyl ammonium chloride) dissolved in 1-decanol at various concentrations; with aqueous phases containing glyoxalic acid at concentration varying from 0.05 to 0.4 kmol/m^3. The results of these experiments are given in the table T 4.4.3 A, B, C and D, which show the equilibrium data of extraction at temperatures 298.15 K, 305.15 K, 313.15 K and 323.15 K respectively. The enthalpy and entropy are calculated from equation 2.1.3.2. The enthalpy and entropy are -6.51759 KJ/mol and -17.9449 J/mol K.



F 4.4.3 Plot of K_{11} versus 1/T for estimation of enthalpy and entropy of glyoxalic acid – Aliquat 336 with 1-Decanol

4.4.4 Extraction Glyoxalic acid with TBP in Kerosene

The extraction experiments were carried out by contacting organic phase composed of TBP (tri-butyl phosphate) dissolved in 1-decanol at various concentrations; with aqueous phases containing glyoxalic acid at concentration varying from 0.05 to 0.4 kmol/m^3. The results of these experiments are given in the table T 4.4.3 A, B, C and D, which show the equilibrium data of extraction at temperatures 298.15 K, 305.15 K, 313.15 K and 323.15 K respectively. The enthalpy and entropy are calculated from equation 2.1.3.2. The enthalpy and entropy are -85.825 KJ/mol and -302.155 J/mol K.



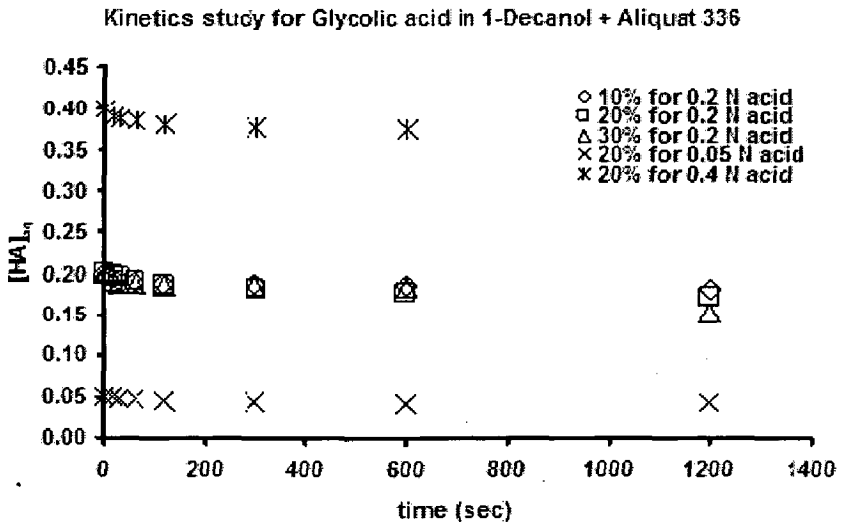
F 4.4.4 Plot of K_{11} versus 1/T for estimation of enthalpy and entropy of glyoxalic acid – TBP with Kerosene

4.5 Kinetics Study

4.5.1 Extraction of Glycolic acid with Aliquat 336 in 1-Decanol

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

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

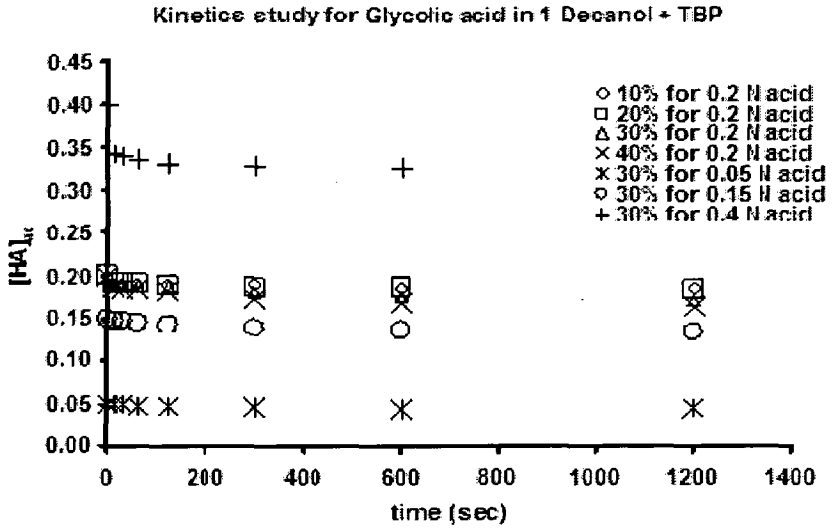


F 4.5.1 Kinetics curves of glycolic acid with Aliquat 336 in 1-decanol

4.5.2 Extraction Glycolic acid with TBP in 1-decanol

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

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

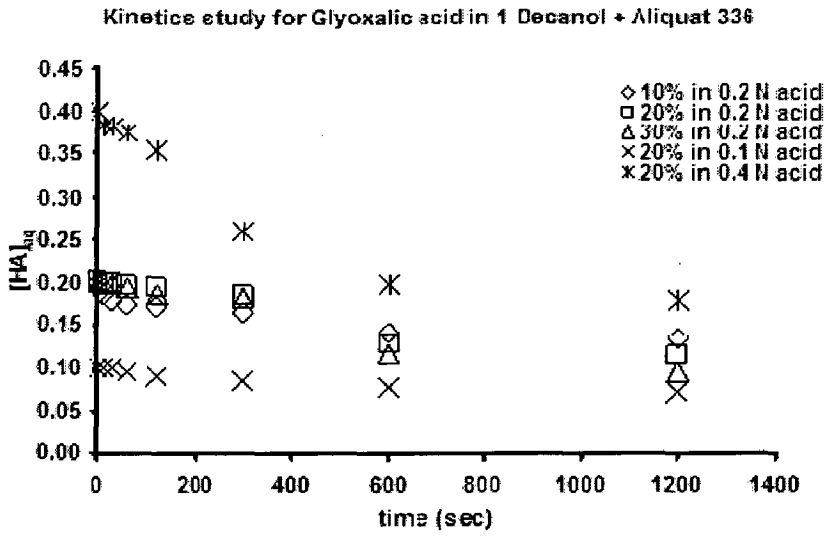


F 4.5.2 Kinetics curves of glycolic acid with TBP in 1-decanol

4.5.3 Extraction of Glyoxalic acid with Aliquat 336 in 1-decanol

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

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

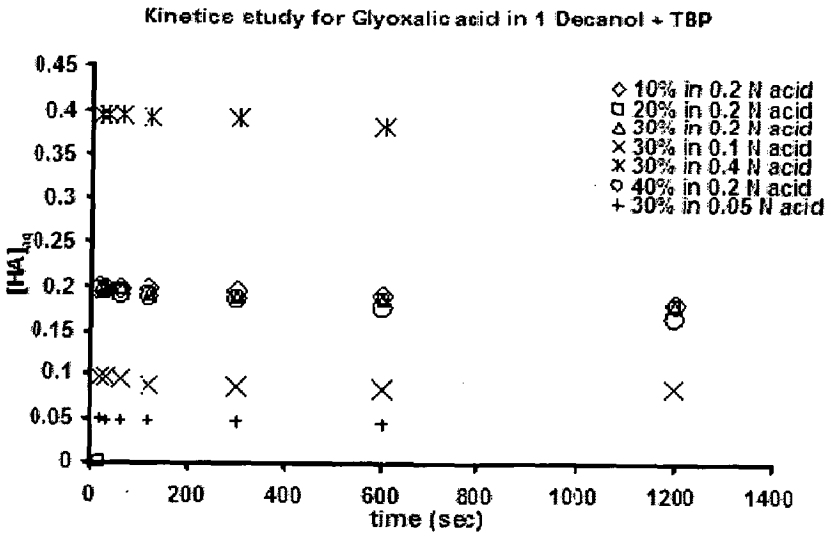


F 4.5.3 Kinetics curves of glyoxalic acid with Aliquat 336 in 1-decanol

4.5.4 Extraction Glyoxalic acid with TBP in 1-decanol

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

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



F 4.5.4 Kinetics curves of glyoxalic acid with TBP in 1-decanol

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Equilibrium investigations on the reactive extraction of glycolic and glyoxalic acids from their aqueous phases at different concentrations and temperatures were conducted by contacting and equilibrating the aqueous phases with organic phases which contain tri-butyl phosphate (TBP) or Aliquat 336 (tri-capryl methyl ammonium chloride) as extractants in various diluents.

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

1. 1-Decanol as diluent has the higher solvating power than other functional group diluents. Better extraction was obtained for TBP dissolved in 1-decanol than other functional group diluents. It also has better solvating power towards the acid-amine complex.
2. Degree of extraction is higher for quaternary amines than phosphorus bonded oxygen extractants when dissolved in any type of diluent.
3. Degree of extraction is high for aliquat 336 dissolved in functional group baring diluents and it decreases on concentrating the organic phase in contrast to inert diluents except for butyl acetate.
4. Degree of extraction decreases with increase in acid concentration for all organic phase of aliquat 336 except for aliquat 336 dissolved in oleyl alcohol.
5. Degree of extraction is high for pure tri-butyl phosphate and it decreases on dilution of the organic phase with any of the diluent.
6. Degree of extraction increases upto an acid concentration of 0.15 – 0.20 kmol/m^3 and then decreases for all organic phases of tri-butyl phosphate except for sunflower oil as diluent, where a constant decrease is seen.
7. Enthalpy for the reactive extraction with aliquat 336 in 1-decanol is negetive, this shows that the formation of acid - amine complex is exothermic in nature.
8. Enthalpy for the reactive extraction with tri-butyl phosphate in kerosene is positive, this shows that the formation of acid - TBP complex is endothermic in nature.
9. The acid - extractant complexation reaction is a mass tansfered accompanied fast pseudo mth order reaction falling in regime 3.

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

1. 1-Decanol as diluent has the higher solvating power than other functional group diluents. Better extraction was obtained for TBP dissolved in 1-decanol than

other functional group diluents. It also has better solvating power towards the acid-amine complex.

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

Effect of dissolved salts, pH and back extraction technique showed be carried as next step, in the design of industrial reactive extraction process that is going to attempt forward and backward extraction of glycolic and glyoxalic acid simultaneously to achieve continuous product recovery.

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ANNEXURE

A. PHYSICAL EXTRACTION WITH PURE DILUENTS

T 4.1.1 A Equilibrium data of glycolic acid in pure 1-decanol

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.026	0.024	0.923077	48
0.10	0.053	0.047	0.886792	47
0.15	0.08	0.07	0.875	46.66667
0.20	0.107	0.093	0.869159	46.5
0.40	0.215	0.185	0.860465	46.25

T 4.1.1 B Equilibrium data of glycolic acid in pure oleyl alcohol

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.04922	0.00078	0.015847	1.56
0.15	0.146667	0.003333	0.022727	2.222222
0.20	0.193333	0.006667	0.034483	3.333333
0.40	0.381333	0.018667	0.048951	4.666667

T 4.1.1 C Equilibrium data of glyoxalic acid in pure 1-decanol

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.043333	0.006667	0.153846	13.33333
0.15	0.132	0.018	0.136364	12
0.20	0.173333	0.026667	0.153846	13.33333
0.40	0.353333	0.046667	0.132075	11.66667

T 4.1.1 D Equilibrium data of glyoxalic acid in pure oleyl alcohol

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.04761	0.00239	0.0502	4.78
0.10	0.095333333	0.004667	0.048951	4.666667
0.15	0.143333333	0.006667	0.046512	4.444444
0.20	0.191333333	0.008667	0.045296	4.333333
0.40	0.383333333	0.016667	0.043478	4.166667

T 4.1.2 A Equilibrium data of glycolic acid in pure butyl acetate

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.0	0.007	0.162791	14
0.10	0.1	0.015	0.176471	15
0.15	0.1	0.02	0.153846	13.33333
0.20	0.2	0.03	0.176471	15
0.40	0.3	0.058	0.169591	14.5

T 4.1.2 B Equilibrium data of glyoxalic acid in pure butyl acetate

$C_{i\,aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.0	0.002	0.041667	4
0.10	0.1	0.005	0.052632	5
0.15	0.1	0.009	0.06383	6
0.20	0.2	0.01	0.052632	5
0.40	0.4	0.017	0.044386	4.25

T 4.1.3 A Equilibrium data of glycolic acid in pure kerosene

$C_{i\,aq}$	C_{aq} final	C_{org}	K_D	D
0.05	0.031733	0.018267	0.57563	36.53333
0.10	0.06426	0.03574	0.556178	35.74
0.15	0.093613	0.056387	0.602336	37.59111
0.20	0.125347	0.074653	0.595575	37.32667
0.40	0.257833	0.142167	0.55139	35.54167

T 4.1.3 B Equilibrium data of glycolic acid in pure sunflower oil

$C_{i\,aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.044427	0.005573	0.12545	11.14667
0.10	0.087267	0.012733	0.145913	12.73333
0.15	0.132487	0.017513	0.132189	11.67556
0.20	0.1785	0.0215	0.120448	10.75
0.40	0.357	0.043	0.120448	10.75

T 4.1.3 C Equilibrium data of glyoxalic acid in pure kerosene

$C_{i\,aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.044	0.006	0.136364	12
0.10	0.087	0.013	0.149425	13
0.15	0.133	0.017	0.12782	11.33333
0.20	0.174	0.026	0.149425	13
0.40	0.354	0.046	0.129944	11.5

T 4.1.3 D Equilibrium data of glyoxalic acid in pure sunflower oil

$C_{i\,aq}$	C_{aq}	C_{org}	K_D	D
0.05	0.047	0.003	0.06383	6
0.10	0.092	0.008	0.086957	8
0.15	0.136	0.014	0.102941	9.333333
0.20	0.178	0.022	0.123596	11
0.40	0.36	0.04	0.111111	10

B. CHEMICAL EXTRACTION WITH ALIQUAT 336 IN DILUENTS

T 4.2.1 A Equilibrium data of glycolic acid with Aliquat 336 in 1-decanol

10% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.015	0.035	2.333333	0.19	0.011	0.179	0.057895	0.061452514	-0.747147	0.367977	70
0.15	0.05	0.1	2	0.19	0.045	0.145	0.236842	0.310344828	-0.838632	0.30103	66.66667
0.20	0.08	0.12	1.5	0.19	0.027	0.163	0.142105	0.165644172	-0.787812	0.176091	60
0.40	0.165	0.235	1.424242	0.19	0.050	0.14	0.263158	0.357142857	-0.853872	0.153584	58.75
14% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.023	0.027	1.173913	0.277	0.003	0.274	0.01083	0.010948905	-0.562249	0.069636	54
0.15	0.055	0.095	1.727273	0.277	0.04	0.237	0.144404	0.168776371	-0.625252	0.237361	63.33333
0.20	0.087	0.113	1.298851	0.277	0.02	0.257	0.072202	0.077821012	-0.590067	0.113559	56.5
0.40	0.175	0.225	1.285714	0.277	0.049	0.228	0.176895	0.214912281	-0.642065	0.109144	56.25
20% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.025	0.025	1	0.395	0.001	0.394	0.002532	0.002538071	-0.404504	0	50
0.15	0.058	0.092	1.586207	0.395	0.037	0.358	0.093671	0.103351955	-0.446117	0.20036	61.33333
0.20	0.09	0.11	1.222222	0.395	0.017	0.378	0.043038	0.044973545	-0.422508	0.08715	55
0.40	0.181	0.219	1.209945	0.395	0.043	0.352	0.108861	0.122159091	-0.453457	0.082766	54.75

T 4.2.1 B Equilibrium data of glyoxalic acid with Aliquat 336 in 1-decanol

10% Aliquat

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.00506	0.04494	8.881423	0.19	0.038	0.151667	0.201753	0.252744499	-0.819109	0.948483	89.88
0.15	0.04	0.11	2.75	0.19	0.092	0.098	0.484211	0.93877551	-1.008774	0.439333	73.33333
0.20	0.055	0.145	2.636364	0.19	0.118	0.071667	0.622805	1.65115046	-1.144681	0.421005	72.5
0.40	0.205	0.195	0.95122	0.19	0.148	0.041667	0.7807	3.55996352	-1.380208	-0.021719	48.75

14% Aliquat

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.00805	0.04195	5.21118	0.277	0.035283	0.241717	0.127375	0.145968219	-0.616693	0.716936	83.9
0.15	0.05	0.1	2	0.277	0.082	0.195	0.296029	0.420512821	-0.709965	0.30103	66.66667
0.20	0.08	0.12	1.5	0.277	0.09333	0.18367	0.336931	0.508139598	-0.735962	0.176091	60
0.40	0.22	0.18	0.818182	0.277	0.133333	0.143667	0.481347	0.928069772	-0.842643	-0.08715	45

20% Aliquat

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0	0.03988	3.940711	0.395	0.033213	0.361787	0.084084	0.091802635	-0.441547	0.595575	79.76
0.15	0.1	0.093	1.631579	0.395	0.075	0.32	0.189873	0.234375	-0.49485	0.212608	62
0.20	0.1	0.125	1.666667	0.395	0.098333	0.296667	0.248944	0.331459178	-0.527731	0.221849	62.5
0.40	0.2	0.166	0.709402	0.395	0.119333	0.275667	0.302109	0.432888231	-0.559615	-0.149108	41.5

T 4.2.2 A Equilibrium data of glycolic acid with Aliquat 336 in oleyl alcohol

10% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.047	0.003	0.06383	0.19	0.002	0.18778	0.011684	0.011822345	-0.726351	-1.194977	6
0.15	0.134	0.016	0.119403	0.19	0.013	0.177333	0.066668	0.071430585	-0.75121	-0.922985	10.66667
0.20	0.164	0.036	0.219512	0.19	0.029	0.160667	0.154384	0.182570161	-0.794073	-0.658541	18
0.30	0.208	0.092	0.442308	0.19	0.079	0.11063	0.417737	0.7174365	-0.956127	-0.354276	30.66667
0.40	0.25	0.15	0.6	0.19	0.131	0.058667	0.691226	2.238617962	-1.231606	-0.221849	37.5
20% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.048	0.002	0.041667	0.395	0.00022	0.39478	0.000557	0.000557272	-0.403645	-1.380211	4
0.15	0.133	0.017	0.12782	0.395	0.013667	0.381333	0.0346	0.035840066	-0.418696	-0.893403	11.33333
0.20	0.162	0.038	0.234568	0.395	0.031333	0.363667	0.079324	0.086158491	-0.439296	-0.629731	19
0.30	0.205	0.095	0.463415	0.395	0.08237	0.31263	0.208532	0.263474395	-0.504969	-0.33403	31.66667
0.40	0.247	0.153	0.619433	0.395	0.061667	0.333333	0.156119	0.185001185	-0.477122	-0.208006	38.25

T 4.2.2 B Equilibrium data of glyoxalic acid with Aliquat 336 in oleyl alcohol

10% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.049	0.001	0.020408	0.19	0.001	0.189	0.005263	0.005291005	-0.723538	-1.690196	2
0.15	0.146	0.004	0.027397	0.19	0.004	0.186	0.021053	0.021505376	-0.730487	-1.562293	2.666667
0.20	0.194	0.006	0.030928	0.19	0.006	0.184	0.031579	0.032608696	-0.735182	-1.50965	3
0.30	0.285	0.015	0.052632	0.19	0.015	0.175	0.078947	0.085714286	-0.756962	-1.278754	5
0.40	0.289	0.111	0.384083	0.19	0.111	0.079	0.584211	1.405063291	-1.102373	-0.415575	27.75
20% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0485	0.0015	0.030928	0.395	0.0015	0.3935	0.003797	0.003811944	-0.405055	-1.50965	3
0.15	0.145	0.005	0.034483	0.395	0.005	0.39	0.012658	0.012820513	-0.408935	-1.462398	3.333333
0.20	0.191	0.009	0.04712	0.395	0.009	0.386	0.022785	0.023316062	-0.413413	-1.326791	4.5
0.30	0.282	0.018	0.06383	0.395	0.018	0.377	0.04557	0.047745358	-0.423659	-1.194977	6
0.40	0.286	0.114	0.398601	0.395	0.114	0.281	0.288608	0.40569395	-0.551294	-0.399461	28.5

T 4.2.3 A Equilibrium data of glycolic acid with Aliquat 336 in butyl acetate

10% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.041	0.009	0.219512	0.19	0.002	0.188	0.010526	0.010638298	-0.725842	-0.658541	18
0.10	0.082	0.018	0.219512	0.19	0.003	0.187	0.015789	0.016042781	-0.728158	-0.658541	18
0.15	0.124	0.026	0.209677	0.19	0.006	0.184	0.031579	0.032608696	-0.735182	-0.678448	17.33333
0.20	0.165	0.035	0.212121	0.19	0.005	0.185	0.026316	0.027027027	-0.732828	-0.673416	17.5
0.40	0.331	0.069	0.208459	0.19	0.011	0.179	0.057895	0.061452514	-0.747147	-0.680979	17.25
14% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.04	0.01	0.25	0.277	0.003	0.274	0.01083	0.010948905	-0.562249	-0.60206	20
0.10	0.08	0.02	0.25	0.277	0.005	0.272	0.018051	0.018382353	-0.565431	-0.60206	20
0.15	0.122	0.028	0.229508	0.277	0.004	0.273	0.01444	0.014652015	-0.563837	-0.639202	18.66667
0.20	0.161	0.039	0.242236	0.277	0.009	0.268	0.032491	0.03358209	-0.571865	-0.615761	19.5
0.40	0.326	0.074	0.226994	0.277	0.016	0.261	0.057762	0.061302682	-0.583359	-0.643986	18.5
20% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.038	0.012	0.315789	0.395	0.005	0.39	0.012658	0.012820513	-0.408935	-0.500602	24
0.10	0.079	0.021	0.265823	0.395	0.006	0.389	0.01519	0.015424165	-0.41005	-0.575408	21
0.15	0.12	0.03	0.25	0.395	0.006	0.389	0.01519	0.015424165	-0.41005	-0.60206	20
0.20	0.159	0.041	0.257862	0.395	0.012	0.383	0.03038	0.031331593	-0.416801	-0.588613	20.5
0.40	0.323	0.077	0.23839	0.395	0.019	0.376	0.048101	0.050531915	-0.424812	-0.622712	19.25

T 4.2.3 B Equilibrium data of glyoxalic acid with Aliquat 336 in butyl acetate

10% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.045	0.005	0.111111	0.19	0.003	0.187	0.015789	0.016042781	-0.728158	-0.954243	10
0.10	0.092	0.008	0.086957	0.19	0.003	0.187	0.015789	0.016042781	-0.728158	-1.060698	8
0.15	0.132	0.018	0.136364	0.19	0.004	0.186	0.021053	0.021505376	-0.730487	-0.865301	12
0.20	0.184	0.016	0.086957	0.19	0.006	0.184	0.031579	0.032608696	-0.735182	-1.060698	8
0.40	0.37	0.03	0.081081	0.19	0.013	0.177	0.068421	0.073446328	-0.752027	-1.09108	7.5
14% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.043	0.007	0.162791	0.277	0.005	0.272	0.018051	0.018382353	-0.565431	-0.78837	14
0.10	0.087	0.013	0.149425	0.277	0.008	0.269	0.028881	0.029739777	-0.570248	-0.825576	13
0.15	0.13	0.02	0.153846	0.277	0.006	0.271	0.021661	0.022140221	-0.567031	-0.812913	13.33333
0.20	0.178	0.022	0.123596	0.277	0.012	0.265	0.043321	0.045283019	-0.576754	-0.907997	11
0.40	0.362	0.038	0.104972	0.277	0.021	0.256	0.075812	0.08203125	-0.59176	-0.978925	9.5
20% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.042	0.008	0.190476	0.395	0.006	0.389	0.01519	0.015424165	-0.41005	-0.720159	16
0.10	0.085	0.015	0.176471	0.395	0.010	0.385	0.025316	0.025974026	-0.414539	-0.753328	15
0.15	0.129	0.021	0.162791	0.395	0.007	0.388	0.017722	0.018041237	-0.411168	-0.78837	14
0.20	0.174	0.026	0.149425	0.395	0.016	0.379	0.040506	0.042216359	-0.421361	-0.825576	13
0.40	0.358	0.042	0.117318	0.395	0.025	0.37	0.063291	0.067567568	-0.431798	-0.930634	10.5

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

10% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0255	0.0245	0.960784	0.19	0.025	0.1655	0.128947	0.148036254	-0.781202	-0.017374	49
0.15	0.0775	0.0725	0.935484	0.19	0.073	0.1175	0.381579	0.617021277	-0.929962	-0.028964	48.33333
0.20	0.104	0.096	0.923077	0.19	0.096	0.094	0.505263	1.021276596	-1.026872	-0.034762	48
0.30	0.157	0.143	0.910828	0.19	0.143	0.047	0.752632	3.042553191	-1.327902	-0.040564	47.66667
0.40	0.19	0.21	1.105263	0.19	0.210	-0.02	1.105263	-10.5	#NUM!	0.043466	52.5
20% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0245	0.0255	1.040816	0.395	0.0255	0.3695	0.064557	0.069012179	-0.432386	0.017374	51
0.15	0.075	0.075	1	0.395	0.075	0.32	0.189873	0.234375	-0.49485	0	50
0.20	0.1	0.1	1	0.395	0.1	0.295	0.253165	0.338983051	-0.530178	0	50
0.30	0.151	0.149	0.986755	0.395	0.149	0.246	0.377215	0.605691057	-0.609065	-0.005791	49.66667
0.40	0.188	0.212	1.12766	0.395	0.212	0.183	0.536709	1.158469945	-0.737549	0.052178	53
30% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0235	0.0265	1.12766	0.59	0.027	0.5635	0.044915	0.047027507	-0.249106	0.052178	53
0.15	0.073	0.077	1.054795	0.59	0.077	0.513	0.130508	0.150097466	-0.289883	0.023168	51.33333
0.2	0.096	0.104	1.083333	0.59	0.104	0.486	0.176271	0.21399177	-0.313364	0.034762	52
0.3	0.146	0.154	1.054795	0.59	0.154	0.436	0.261017	0.353211009	-0.360514	0.023168	51.33333
0.4	0.186	0.214	1.150538	0.59	0.214	0.376	0.362712	0.569148936	-0.424812	0.060901	53.5

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

10% Aliquat

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0375	0.0125	0.333333	0.19	0.007	0.1835	0.034211	0.035422343	-0.736364	-0.477121	25
0.15	0.112	0.038	0.339286	0.19	0.024	0.166	0.126316	0.144578313	-0.779892	-0.469434	25.33333
0.20	0.151	0.049	0.324503	0.19	0.023	0.167	0.121053	0.137724551	-0.777284	-0.488781	24.5
0.30	0.223	0.077	0.345291	0.19	0.042	0.14824	0.219789	0.281705343	-0.829035	-0.461814	25.66667
0.40	0.301	0.099	0.328904	0.19	0.053	0.137	0.278947	0.386861314	-0.863279	-0.482931	24.75

20% Aliquat

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0365	0.0135	0.369863	0.395	0.0075	0.3875	0.018987	0.019354839	-0.411728	-0.431959	27
0.15	0.1105	0.0395	0.357466	0.395	0.0225	0.3725	0.056962	0.060402685	-0.428874	-0.446765	26.33333
0.20	0.149	0.051	0.342282	0.395	0.025	0.37	0.063291	0.067567568	-0.431798	-0.465616	25.5
0.30	0.22	0.08	0.363636	0.395	0.04476	0.35024	0.113316	0.127798081	-0.455634	-0.439333	26.66667
0.40	0.298	0.102	0.342282	0.395	0.056	0.339	0.141772	0.16519174	-0.4698	-0.465616	25.5

30% Aliquat

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0355	0.0145	0.408451	0.59	0.009	0.5815	0.014407	0.014617369	-0.23545	-0.38886	29
0.15	0.109	0.041	0.376147	0.59	0.024	0.566	0.040678	0.042402827	-0.247184	-0.424643	27.33333
0.2	0.146	0.054	0.369863	0.59	0.028	0.562	0.047458	0.049822064	-0.250264	-0.431959	27
0.3	0.217	0.083	0.382488	0.59	0.048	0.54224	0.080949	0.088079079	-0.265808	-0.417382	27.66667
0.4	0.295	0.105	0.355932	0.59	0.059	0.531	0.1	0.111111111	-0.274905	-0.448633	26.25

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

10% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0375	0.0125	0.333333	0.19	0.007	0.1835	0.034211	0.035422343	-0.736364	-0.477121	25
0.15	0.112	0.038	0.339286	0.19	0.024	0.166	0.126316	0.144578313	-0.779892	-0.469434	25.33333
0.20	0.151	0.049	0.324503	0.19	0.023	0.167	0.121053	0.137724551	-0.777284	-0.488781	24.5
0.30	0.223	0.077	0.345291	0.19	0.042	0.14824	0.219789	0.281705343	-0.829035	-0.461814	25.66667
0.40	0.301	0.099	0.328904	0.19	0.053	0.137	0.278947	0.386861314	-0.863279	-0.482931	24.75
20% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0365	0.0135	0.369863	0.395	0.0075	0.3875	0.018987	0.019354839	-0.411728	-0.431959	27
0.15	0.1105	0.0395	0.357466	0.395	0.0225	0.3725	0.056962	0.060402685	-0.428874	-0.446765	26.33333
0.20	0.149	0.051	0.342282	0.395	0.025	0.37	0.063291	0.067567568	-0.431798	-0.465616	25.5
0.30	0.22	0.08	0.363636	0.395	0.04476	0.35024	0.113316	0.127798081	-0.455634	-0.439333	26.66667
0.40	0.298	0.102	0.342282	0.395	0.056	0.339	0.141772	0.16519174	-0.4698	-0.465616	25.5
30% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0355	0.0145	0.408451	0.59	0.009	0.5815	0.014407	0.014617369	-0.23545	-0.38886	29
0.15	0.109	0.041	0.376147	0.59	0.024	0.566	0.040678	0.042402827	-0.247184	-0.424643	27.33333
0.2	0.146	0.054	0.369863	0.59	0.028	0.562	0.047458	0.049822064	-0.250264	-0.431959	27
0.3	0.217	0.083	0.382488	0.59	0.048	0.54224	0.080949	0.088079079	-0.265808	-0.417382	27.66667
0.4	0.295	0.105	0.355932	0.59	0.059	0.531	0.1	0.111111111	-0.274905	-0.448633	26.25

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

10% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0445	0.0055	0.123596	0.19	0.006	0.1845	0.028947	0.029810298	-0.734004	-0.907997	11
0.10	0.086	0.014	0.162791	0.19	0.014	0.176	0.073684	0.079545455	-0.754487	-0.78837	14
0.20	0.161	0.039	0.242236	0.19	0.039	0.151	0.205263	0.258278146	-0.821023	-0.615761	19.5
0.40	0.325	0.075	0.230769	0.19	0.075	0.115	0.394737	0.652173913	-0.939302	-0.636822	18.75
20% Aliquat											
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	z	z/(1-z)	$Log([B]_{org})$	$Log(K_D)$	D
0.05	0.0455	0.0045	0.098901	0.395	0.0045	0.3905	0.011392	0.011523688	-0.408379	-1.004799	9
0.10	0.084	0.016	0.190476	0.395	0.016	0.379	0.040506	0.042216359	-0.421361	-0.720159	16
0.20	0.144	0.056	0.388889	0.395	0.056	0.339	0.141772	0.16519174	-0.4698	-0.410174	28
0.40	0.309	0.091	0.294498	0.395	0.091	0.304	0.23038	0.299342105	-0.517126	-0.530917	22.75

C. CHEMICAL EXTRACTION WITH TBP IN DILUENTS

T 4.3.1 A Equilibrium data of glycolic acid with TBP in 1-decanol

20% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.026	0.024	0.923077	0.74	0	3.83	48	3.664653	-0.034762
0.15	0.066	0.084	1.272727	0.74	0.014	3.83	56	3.602864	0.104735
0.20	0.092	0.108	1.173913	0.74	0.015	3.83	54	3.565287	0.069636
0.30	0.143	0.157	1.097902	0.74	0.018	3.83	52.33333	3.497492	0.040564
0.40	0.19	0.21	1.105263	0.74	0.025	3.83	52.5	3.441954	0.043466
30% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.025	0.025	1	1.1	0.001	3.83	50	3.666259	0
0.15	0.065	0.085	1.307692	1.1	0.015	3.83	56.66667	3.60435	0.116506
0.20	0.084	0.116	1.380952	1.1	0.023	3.83	58	3.576632	0.140179
0.30	0.135	0.165	1.222222	1.1	0.026	3.83	55	3.507609	0.08715
0.40	0.187	0.213	1.139037	1.1	0.028	3.83	53.25	3.4453	0.056538

T 4.3.1 B Equilibrium data of glyoxalic acid with TBP in 1-decanol

20% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.034	0.016	0.470588	0.74	0.009333	3.34	32	3.522717	-0.327359
0.15	0.11	0.04	0.363636	0.74	0.022	3.34	26.66667	3.419667	-0.439333
0.20	0.148	0.052	0.351351	0.74	0.025333	3.34	26	3.377271	-0.454258
0.30	0.211	0.089	0.421801	0.74	0.05308	3.34	29.66667	3.320395	-0.374892
0.40	0.312	0.088	0.282051	0.74	0.041333	3.34	22	3.26412	-0.549672
30% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.035	0.015	0.428571	1.1	0.01	3.34	30	3.521203	-0.367977
0.15	0.104	0.046	0.442308	1.1	0.03	3.34	30.66667	3.426917	-0.354276
0.20	0.14	0.06	0.428571	1.1	0.03	3.34	30	3.385691	-0.367977
0.30	0.202	0.098	0.485149	1.1	0.06	3.34	32.66667	3.327496	-0.314125
0.40	0.298	0.102	0.342282	1.1	0.55	3.34	25.5	3.269353	-0.465616

T 4.3.2 A Equilibrium data of glycolic acid with TBP in butyl acetate

20% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.0405	0.0095	0.234568	0.74	0.0025	3.83	19	3.641697	-0.629731
0.15	0.0935	0.0565	0.604278	0.74	0.0365	3.83	37.66667	3.563181	-0.218763
0.20	0.12	0.08	0.666667	0.74	0.05	3.83	40	3.527096	-0.176091
0.30	0.188	0.112	0.595745	0.74	0.06853	3.83	37.33333	3.444182	-0.22494
0.40	0.297	0.103	0.346801	0.74	0.045	3.83	25.75	3.340338	-0.459919
30% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.039	0.011	0.282051	1.1	0.00	3.83	22	3.644043	-0.549672
0.15	0.0915	0.0585	0.639344	1.1	0.04	3.83	39	3.56599	-0.194265
0.20	0.118	0.082	0.694915	1.1	0.05	3.83	41	3.529746	-0.158068
0.30	0.184	0.116	0.630435	1.1	0.07	3.83	38.66667	3.448673	-0.20036
0.40	0.286	0.114	0.398601	1.1	0.06	3.83	28.5	3.349194	-0.399461

T 4.3.2 B Equilibrium data of glyoxalic acid with TBP in butyl acetate

20% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.047	0.003	0.06383	0.74	0.001	3.34	6	3.503364	-1.194977
0.15	0.1375	0.0125	0.090909	0.74	0.0035	3.34	8.333333	3.388377	-1.041393
0.20	0.185	0.015	0.081081	0.74	0.005	3.34	7.5	3.34184	-1.09108
0.30	0.261	0.039	0.149425	0.74	0.02544	3.34	13	3.287162	-0.825576
0.40	0.342	0.058	0.169591	0.74	0.041	3.34	14.5	3.255687	-0.770598
30% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.0455	0.0045	0.098901	1.1	0.0025	3.34	9	3.50556	-1.004799
0.15	0.128	0.022	0.171875	1.1	0.013	3.34	14.66667	3.398826	-0.764787
0.20	0.178	0.022	0.123596	1.1	0.012	3.34	11	3.348101	-0.907997
0.30	0.251	0.049	0.195219	1.1	0.03544	3.34	16.33333	3.292965	-0.709478
0.40	0.334	0.066	0.197605	1.1	0.049	3.34	16.5	3.257565	-0.704203

T 4.3.3 A Equilibrium data of glycolic acid with TBP in kerosene

20% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.029	0.021	0.724138	0.74	0.002733	3.83	42	3.659851	-0.140179
0.15	0.059	0.091	1.542373	0.74	0.034613	3.83	60.66667	3.613329	0.188189
0.20	0.095	0.105	1.105263	0.74	0.030347	3.83	52.5	3.561082	0.043466
0.30	0.139	0.161	1.158273	0.74	0.0531	3.83	53.66667	3.502526	0.063811
0.40	0.209	0.191	0.913876	0.74	0.048833	3.83	47.75	3.421391	-0.039113
30% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.03	0.02	0.666667	1.1	0.00	3.83	40	3.658257	-0.176091
0.15	0.057	0.093	1.631579	1.1	0.04	3.83	62	3.616346	0.212608
0.20	0.088	0.112	1.272727	1.1	0.04	3.83	56	3.570935	0.104735
0.30	0.132	0.168	1.272727	1.1	0.06	3.83	56	3.511452	0.104735
0.40	0.195	0.205	1.051282	1.1	0.06	3.83	51.25	3.436437	0.021719

T 4.3.3 B Equilibrium data of glyoxalic acid with TBP in kerosene

30% TBP										
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	D	pH	pK_a	$Log(K_D)$
0.05	0.0445	0.0055	0.123596	1.1	0	1.1	11	3.50703	3.34	-0.907997
0.15	0.135	0.015	0.111111	1.1	0.002	1.098	10	3.39109	3.34	-0.954243
0.20	0.178	0.022	0.123596	1.1	0.022	1.078	11	3.348101	3.34	-0.907997
0.30	0.267	0.033	0.123596	1.1	0.033	1.067	11	3.283882	3.34	-0.907997
0.40	0.386	0.014	0.036269	1.1	0.014	1.086	3.5	3.250181	3.34	-1.440459
20% TBP										
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	$[B]_{org}$	D	pH	pK_a	$Log(K_D)$
0.05	0.0475	0.0025	0.052632	0.74	0.0025	0.7375	5	3.502634	3.34	-1.278754
0.15	0.14	0.01	0.071429	0.74	0.01	0.73	6.666667	3.385691	3.34	-1.146128
0.20	0.185	0.015	0.081081	0.74	0.015	0.725	7.5	3.34184	3.34	-1.09108
0.30	0.274	0.026	0.094891	0.74	0.026	0.714	8.666667	3.280247	3.34	-1.022777
0.40	0.394	0.006	0.015228	0.74	0.006	0.734	1.5	3.250056	3.34	-1.817345

T 4.3.4 A Equilibrium data of glycolic acid with TBP in sunflower oil

10% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.0415	0.0085	0.204819	0.37	0.002927	3.83	17	3.640137	-0.688629
0.10	0.084	0.016	0.190476	0.37	0.003267	3.83	16	3.576632	-0.720159
0.20	0.169	0.031	0.183432	0.37	0.0095	3.83	15.5	3.465947	-0.736525
0.30	0.255	0.045	0.176471	0.37	0.01238	3.83	15	3.376112	-0.753328
0.40	0.352	0.048	0.136364	0.37	0.005	3.83	12	3.301527	-0.865301
20% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.0405	0.0095	0.234568	0.74	0.003927	3.83	19	3.641697	-0.629731
0.10	0.0815	0.0185	0.226994	0.74	0.005767	3.83	18.5	3.580217	-0.643986
0.20	0.165	0.035	0.212121	0.74	0.0135	3.83	17.5	3.470667	-0.673416
0.30	0.248	0.052	0.209677	0.74	0.01938	3.83	17.33333	3.382591	-0.678448
0.40	0.346	0.054	0.156069	0.74	0.011	3.83	13.5	3.305318	-0.806682

T 4.3.4 B Equilibrium data of glyoxalic acid with TBP in sunflower oil

10% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.0455	0.0045	0.098901	0.37	0.0015	3.34	9	3.50556	-1.004799
0.10	0.0915	0.0085	0.092896	0.37	0.0005	3.34	8.5	3.442509	-1.032002
0.20	0.18	0.02	0.111111	0.37	0.002	3.34	10	3.346291	-0.954243
0.30	0.267	0.033	0.123596	0.37	0.00269	3.34	11	3.283882	-0.907997
0.40	0.34	0.06	0.176471	0.37	0.02	3.34	15	3.256131	-0.753328
20% TBP									
$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[BHA]_{org}$	pK_a	D	pH	$Log(K_D)$
0.05	0.047	0.003	0.06383	0.74	0.00	3.34	6	3.503364	-1.194977
0.10	0.0895	0.0105	0.117318	0.74	0.00	3.34	10.5	3.445065	-0.930634
0.20	0.177	0.023	0.129944	0.74	0.00	3.34	11.5	3.349012	-0.886245
0.30	0.265	0.035	0.132075	0.74	0.00	3.34	11.66667	3.284958	-0.879178
0.40	0.346	0.054	0.156069	0.74	0.01	3.34	13.5	3.254849	-0.806682

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

	Glycolic acid		Glyoxalic acid	
	K_{11}	p	K_{11}	p
1-decanol	2.7061	0.7365	0.8567	1.0128
butyl acetate	0.2689	0.915	0.613	1.24
sunflower oil	0.068	0.88	0.6216	1.78
kerosene	0.8278	0.7885	0.11	0.84

D. EFFECT OF TEMPERATURE ON REACTIVE EXTACTION

T 4.6.1 A Equilibrium data of glycolic acid with Aliquat 336 in 1-decanol at 293 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	z	z/(1-z)	D
0.05	0.014	0.036	2.571429	0.19	0.184211	0.225806	72
0.15	0.048	0.102	2.125	0.19	0.605263	1.533333	68
0.20	0.076	0.124	1.631579	0.19	0.631579	1.714286	62
0.40	0.16	0.24	1.5	0.19	1.236842	-5.222222	60
0.05	0.022	0.028	1.272727	0.277	0.101083	0.11245	56
0.15	0.053	0.097	1.830189	0.277	0.350181	0.538889	64.66667
0.20	0.086	0.114	1.325581	0.277	0.411552	0.699387	57
0.40	0.17	0.23	1.352941	0.277	0.830325	4.893617	57.5
0.05	0.024	0.026	1.083333	0.395	0.065823	0.070461	52
0.20	0.086	0.114	1.325581	0.395	0.288608	0.405694	57
0.40	0.178	0.222	1.247191	0.395	0.562025	1.283237	55.5

T 4.6.1 B Equilibrium data of glycolic acid with Aliquat 336 in 1-decanol at 305 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	z	z/(1-z)	D
0.05	0.015	0.035	2.333333	0.19	0.184211	0.225806	70
0.15	0.05	0.1	2	0.19	0.605263		66.66667
0.20	0.08	0.12	1.5	0.19	0.631579		60
0.40	0.165	0.235	1.424242	0.19	1.236842		58.75
0.05	0.023	0.027	1.173913	0.277	0.097473	0.108	54
0.15	0.055	0.095	1.727273	0.277	0.34296	0.521978	63.33333
0.20	0.087	0.113	1.298851	0.277	0.407942	0.689024	56.5
0.40	0.175	0.225	1.285714	0.277	0.812274		56.25
0.05	0.025	0.025	1	0.395	0.063291	0.067568	50
0.15	0.058	0.092	1.586207	0.395	0.232911	0.30363	61.33333
0.20	0.09	0.11	1.222222	0.395	0.278481	0.385965	55
0.40	0.181	0.219	1.209945	0.395	0.55443	1.244318	54.75

T 4.6.1 C Equilibrium data of glycolic acid with Aliquat 336 in 1-decanol at 313 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	z	z/(1-z)	D
0.05	0.0155	0.0345	2.225806	0.19	0.184211	0.225806	69
0.15	0.051	0.099	1.941176	0.19	0.605263		66
0.20	0.083	0.117	1.409639	0.19	0.631579		58.5
0.40	0.167	0.233	1.39521	0.19	1.236842		58.25
0.05	0.024	0.026	1.083333	0.277	0.093863	0.103586	52
0.15	0.057	0.093	1.631579	0.277	0.33574	0.505435	62
0.20	0.09	0.11	1.222222	0.277	0.397112	0.658683	55
0.40	0.181	0.219	1.209945	0.277	0.790614		54.75
0.05	0.026	0.024	0.923077	0.395	0.060759	0.06469	48
0.15	0.06	0.09	1.5	0.395	0.227848	0.295082	60
0.20	0.093	0.107	1.150538	0.395	0.270886	0.371528	53.5
0.40	0.185	0.215	1.162162	0.395	0.544304	1.194444	53.75

T 4.6.1 D Equilibrium data of glycolic acid with Aliquat 336 in 1-decanol at 323 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	z	z/(1-z)	D
0.05	0.0185	0.0315	1.702703	0.19	0.184211	0.225806	63
0.15	0.06	0.09	1.5	0.19	0.605263	1.533333	60
0.20	0.089	0.111	1.247191	0.19	0.631579	1.714286	55.5
0.40	0.174	0.226	1.298851	0.19	1.236842	-5.222222	56.5
0.05	0.027	0.023	0.851852	0.277	0.083032	0.090551	46
0.15	0.062	0.088	1.419355	0.277	0.31769	0.465608	58.66667
0.20	0.094	0.106	1.12766	0.277	0.382671	0.619883	53
0.40	0.186	0.214	1.150538	0.277	0.772563	3.396825	53.5
0.05	0.027	0.023	0.851852	0.395	0.058228	0.061828	46
0.15	0.064	0.086	1.34375	0.395	0.217722	0.278317	57.33333
0.20	0.098	0.102	1.040816	0.395	0.258228	0.348123	51
0.40	0.193	0.207	1.072539	0.395	0.524051	1.101064	51.75

T 4.6.2 A Equilibrium data of glycolic acid with TBP in kerosene at 293 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	pK_a	D	pH
0.05	0.0395	0.0105	0.265823	0.74	3.83	21	3.64326
0.15	0.1025	0.0475	0.463415	0.74	3.83	31.66667	3.550688
0.20	0.141	0.059	0.41844	0.74	3.83	29.5	3.500003
0.20	0.132	0.068	0.515152	1.1	3.83	34	3.511452
0.30	0.196	0.104	0.530612	1.1	3.83	34.66667	3.435343
0.40	0.303	0.097	0.320132	1.1	3.83	24.25	3.335661

T 4.6.2 B Equilibrium data of glycolic acid with TBP in kerosene at 305 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	pK_a	D	pH
0.05	0.04	0.01	0.25	0.74	3.83	20	3.642478
0.15	0.105	0.045	0.428571	0.74	3.83	30	3.547262
0.20	0.144	0.056	0.388889	0.74	3.83	28	3.496242
0.20	0.138	0.062	0.449275	1.1	3.83	31	3.503792
0.30	0.2	0.1	0.5	1.1	3.83	33.33333	3.430996
0.40	0.305	0.095	0.311475	1.1	3.83	23.75	3.334126

T 4.6.2 C Equilibrium data of glycolic acid with TBP in kerosene at 313 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	pK_a	D	pH
0.05	0.045	0.005	0.111111	0.74	3.83	10	3.634702
0.15	0.131	0.019	0.145038	0.74	3.83	12.66667	3.512739
0.20	0.181	0.019	0.104972	0.74	3.83	9.5	3.452074
0.30	0.268	0.032	0.119403	0.74	3.83	10.66667	3.364471
0.40	0.362	0.038	0.104972	0.74	3.83	9.5	3.29545
0.05	0.048	0.002	0.041667	1.1	3.83	4	3.630072
0.15	0.137	0.013	0.094891	1.1	3.83	8.666667	3.505062
0.20	0.178	0.022	0.123596	1.1	3.83	11	3.455501
0.30	0.265	0.035	0.132075	1.1	3.83	11.66667	3.367112
0.40	0.377	0.023	0.061008	1.1	3.83	5.75	3.286899
0.15	0.132	0.018	0.136364	0.92	3.83	12	3.511452
0.20	0.182	0.018	0.098901	0.92	3.83	9	3.450937

T 4.6.2 D Equilibrium data of glycolic acid with TBP in kerosene at 323 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	pK_a	D	pH
0.05	0.0	0.0035	0.075269	0.74	3.83	7	3.632384
0.15	0.1	0.014	0.102941	0.74	3.83	9.333333	3.506334
0.20	0.2	0.015	0.081081	0.74	3.83	7.5	3.447546
0.30	0.3	0.017	0.060071	0.74	3.83	5.666667	3.351672
0.40	0.4	0.012	0.030928	0.74	3.83	3	3.281059
0.05	0.0	0.001	0.020408	1.1	3.83	2	3.628535
0.15	0.1	0.01	0.071429	1.1	3.83	6.666667	3.501263
0.20	0.2	0.014	0.075269	1.1	3.83	7	3.446422
0.30	0.3	0.031	0.115242	1.1	3.83	10.33333	3.363597
0.40	0.4	0.004	0.010101	1.1	3.83	1	3.277041
0.20	0.2	0.008	0.041667	0.92	3.83	4	3.439738
0.30	0.3	0.029	0.107011	0.92	3.83	9.666667	3.361857

T 4.6.3 A Equilibrium data of glyoxalic acid with Aliquat 336 in 1-decanol at 293 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	z	z/(1-z)	D
0.05	0.0325	0.0175	0.538462	0.19	0.092105	0.101449	35
0.15	0.1085	0.0415	0.382488	0.19	0.218421	0.279461	27.66667
0.20	0.1465	0.0535	0.365188	0.19	0.281579	0.391941	26.75
0.30	0.2095	0.0905	0.431981	0.19	0.476316		30.16667
0.40	0.31	0.09	0.290323	0.277	0.32491	0.481283	22.5
0.05	0.0345	0.0155	0.449275	0.277	0.055957	0.059273	31
0.15	0.103	0.047	0.456311	0.277	0.169675	0.204348	31.33333
0.20	0.1385	0.0615	0.444043	0.277	0.222022	0.285383	30.75
0.30	0.2005	0.0995	0.496259	0.395	0.251899	0.336717	33.16667
0.40	0.296	0.104	0.351351	0.395	0.263291	0.357388	26

T 4.6.3 B Equilibrium data of glyoxalic acid with Aliquat 336 in 1-decanol at 305 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	z	z/(1-z)	D
0.05	0.034	0.016	0.470588	0.19	0.084211	0.091954	32
0.15	0.11	0.04	0.363636	0.19	0.210526	0.266667	26.66667
0.20	0.148	0.052	0.351351	0.19	0.273684	0.376812	26
0.30	0.211	0.089	0.421801	0.19	0.468421		29.66667
0.40	0.312	0.088	0.282051	0.277	0.31769	0.465608	22
0.05	0.035	0.015	0.428571	0.277	0.054152	0.057252	30
0.15	0.104	0.046	0.442308	0.277	0.166065	0.199134	30.66667
0.20	0.14	0.06	0.428571	0.277	0.216606	0.276498	30
0.30	0.202	0.098	0.485149	0.395	0.248101	0.329966	32.66667
0.40	0.298	0.102	0.342282	0.395	0.258228	0.348123	25.5

T 4.6.3 C Equilibrium data of glyoxalic acid with Aliquat 336 in 1-decanol at 313 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	z	z/(1-z)	D
0.05	0.036	0.014	0.388889	0.19	0.073684	0.079545	28
0.15	0.1115	0.0385	0.345291	0.19	0.202632	0.254125	25.66667
0.20	0.1495	0.0505	0.337793	0.19	0.265789	0.362007	25.25
0.30	0.2125	0.0875	0.411765	0.19	0.460526		29.16667
0.40	0.3135	0.0865	0.275917	0.19	0.455263	0.835749	21.625
0.05	0.0365	0.0135	0.369863	1.1	0.012273	0.012425	27
0.15	0.106	0.044	0.415094	1.1	0.04	0.041667	29.33333
0.20	0.142	0.058	0.408451	1.1	0.052727	0.055662	29
0.30	0.2035	0.0965	0.474201	1.1	0.087727	0.096163	32.16667
0.40	0.3	0.1	0.333333	1.1	0.090909	0.1	25

T 4.6.3 D Equilibrium data of glyoxalic acid with Aliquat 336 in 1-decanol at 323 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	z	z/(1-z)	D
0.05	0.038	0.012	0.315789	0.19	0.063158	0.067416	24
0.15	0.1145	0.0355	0.310044	0.19	0.186842	0.229773	23.66667
0.20	0.153	0.047	0.30719	0.19	0.247368	0.328671	23.5
0.30	0.2165	0.0835	0.385681	0.19	0.439474		27.83333
0.40	0.3155	0.0845	0.267829	0.19	0.444737	0.800948	21.125
0.05	0.0375	0.0125	0.333333	0.395	0.031646	0.03268	25
0.15	0.1085	0.0415	0.382488	0.395	0.105063	0.117397	27.66667
0.20	0.1445	0.0555	0.384083	0.395	0.140506	0.163476	27.75
0.30	0.208	0.092	0.442308	0.395	0.232911	0.30363	30.66667
0.40	0.3065	0.0935	0.305057	0.395	0.236709	0.310116	23.375

T 4.6.4 A Equilibrium data of glyoxalic acid with TBP in kerosene at 293 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	pK_a	D	pH
0.05	0.0425	0.0075	0.176471	0.74	3.34	15	3.509982
0.15	0.125	0.025	0.2	0.74	3.34	16.66667	3.402205
0.2	0.169	0.031	0.183432	0.74	3.34	15.5	3.356454
0.3	0.255	0.045	0.176471	0.74	3.34	15	3.290593
0.4	0.38	0.02	0.052632	0.74	3.34	5	3.250451
0.05	0.0455	0.0045	0.098901	1.1	3.34	9	3.50556
0.15	0.1375	0.0125	0.090909	1.1	3.34	8.333333	3.388377
0.2	0.18	0.02	0.111111	1.1	3.34	10	3.346291
0.3	0.2675	0.0325	0.121495	1.1	3.34	10.83333	3.283615
0.4	0.3865	0.0135	0.034929	1.1	3.34	3.375	3.250165

T 4.6.4 B Equilibrium data of glyoxalic acid with TBP in kerosene at 305 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	pK_a	D	pH
0.05	0.0445	0.0055	0.123596	0.74	3.34	11	3.50703
0.15	0.135	0.015	0.111111	0.74	3.34	10	3.39109
0.2	0.178	0.022	0.123596	0.74	3.34	11	3.348101
0.3	0.267	0.033	0.123596	0.74	3.34	11	3.283882
0.4	0.386	0.014	0.036269	0.74	3.34	3.5	3.250181
0.05	0.0475	0.0025	0.052632	1.1	3.34	5	3.502634
0.15	0.14	0.01	0.071429	1.1	3.34	6.666667	3.385691
0.2	0.185	0.015	0.081081	1.1	3.34	7.5	3.34184
0.3	0.274	0.026	0.094891	1.1	3.34	8.666667	3.280247
0.4	0.394	0.006	0.015228	1.1	3.34	1.5	3.250056

T 4.6.4 C Equilibrium data of glyoxalic acid with TBP in kerosene at 313 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	pKa	D	pH
0.05	0.0465	0.0035	0.075269	0.74	3.34	7	3.504095
0.15	0.138	0.012	0.086957	0.74	3.34	8	3.387838
0.2	0.1805	0.0195	0.108033	0.74	3.34	9.75	3.345841
0.3	0.2785	0.0215	0.077199	0.74	3.34	7.166667	3.27802
0.4	0.3925	0.0075	0.019108	0.74	3.34	1.875	3.250059
0.05	0.0485	0.0015	0.030928	1.1	3.34	3	3.501176
0.15	0.1435	0.0065	0.045296	1.1	3.34	4.333333	3.381974
0.2	0.189	0.011	0.058201	1.1	3.34	5.5	3.338355
0.3	0.276	0.024	0.086957	1.1	3.34	8	3.279247
0.4	0.395	0.005	0.012658	1.1	3.34	1.25	3.25006

T 4.6.4 D Equilibrium data of glyoxalic acid with TBP in kerosene at 323 K

$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	pK_a	D	pH
0.05	0.048	0.002	0.041667	0.74	3.34	4	3.501904
0.15	0.141	0.009	0.06383	0.74	3.34	6	3.384624
0.2	0.1835	0.0165	0.089918	0.74	3.34	8.25	3.343164
0.3	0.2815	0.0185	0.065719	0.74	3.34	6.166667	3.276582
0.4	0.395	0.005	0.012658	0.74	3.34	1.25	3.25006
0.05	0.0495	0.0005	0.010101	1.1	3.34	1	3.499724
0.15	0.1455	0.0045	0.030928	1.1	3.34	3	3.379874
0.2	0.1905	0.0095	0.049869	1.1	3.34	4.75	3.337066
0.3	0.2785	0.0215	0.077199	1.1	3.34	7.166667	3.27802
0.4	0.3965	0.0035	0.008827	1.1	3.34	0.875	3.250073

E. KINETCS OF REACTIVE EXTRACTION

T 4.7.1 A *Kinetics data of 0.20 N glycolic acid with 10% Aliquat 336 in 1-decanol*

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0.00		0.19	0.19	
15	0.20	0.2	0.005	0.025641	0.19	0.185	-0.000245266
30	0.20	0.2	0.0075	0.038961	0.19	0.1825	-0.00020054
60	0.20	0.2	0.00875	0.045752	0.19	0.18125	-0.000138084
120	0.20	0.2	0.01125	0.059603	0.19	0.17875	-0.000101664
300	0.20	0.2	0.013125	0.070234	0.19	0.176875	-0.0003825
600	0.20	0.2	0.015	0.081081	0.19	0.175	-0.00114
1200	0.20	0.2	0.02	0.111111	0.19	0.17	-0.01278

T 4.7.1 B Kinetics data of 0.20 N glycolic acid with 20% Aliquat 336 in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0.00		0.395	0.395	
15	0.20	0.196355	0.003645	0.018563	0.395	0.391355	-0.000171972
30	0.20	0.19458	0.00542	0.027855	0.395	0.38958	-0.000147676
60	0.20	0.190256	0.009744	0.051215	0.395	0.385256	-0.000109074
120	0.20	0.185932	0.014068	0.075662	0.395	0.380932	-6.40256E-05
300	0.20	0.181608	0.018392	0.101273	0.395	0.376608	-5.9E-05
600	0.20	0.175843	0.024157	0.13738	0.395	0.370843	-8E-05
1200	0.20	0.171519	0.028481	0.166054	0.395	0.366519	-0.003848

T 4.7.1 C Kinetics data of 0.20 N glycolic acid with 30% Aliquat 336 in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0		0.59	0.59	
15	0.20	0.19	0.01	0.052632	0.59	0.58	-0.000176668
30	0.20	0.18875	0.01125	0.059603	0.59	0.57875	-0.000154646
60	0.20	0.1875	0.0125	0.066667	0.59	0.5775	-0.000114368
120	0.20	0.18625	0.01375	0.073826	0.59	0.57625	-0.000047744
300	0.20	0.185	0.015	0.081081	0.59	0.575	0.000064
600	0.20	0.1825	0.0175	0.09589	0.59	0.5725	0.000112
1200	0.20	0.15125	0.04875	0.322314	0.59	0.54125	0.000856

T 4.7.1 D Kinetics data of 0.05 N glycolic acid with 20% Aliquat 336 in 1-decanol

time (s)	$C_{i\,aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\,org}$	$[B]_{org}$	$(-)r_A$
0	0.05	0.05	0.00		0.395	0.395	
15	0.05	0.049726	0.000274	0.00551	0.395	0.394726	-4.41336E-05
30	0.05	0.048645	0.001355	0.027855	0.395	0.393645	-3.85292E-05
60	0.05	0.047564	0.002436	0.051215	0.395	0.392564	-2.80733E-05
120	0.05	0.046123	0.003877	0.084066	0.395	0.391123	-9.94465E-06
300	0.05	0.044681	0.005319	0.119036	0.395	0.389681	0.000026962
600	0.05	0.04324	0.00676	0.156337	0.395	0.38824	0.000062992
1200	0.05	0.04324	0.00676	0.156337	0.395	0.38824	0.000298672

T 4.7.1 E Kinetics data of 0.40 N glycolic acid with 20% Aliquat 336 in 1-decanol

time (s)	$C_{i\,aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\,org}$	$[B]_{org}$	$(-)r_A$
0	0.40	0.4	0.00		0.395	0.395	
15	0.40	0.39	0.01	0.025641	0.395	0.385	-0.000386482
30	0.40	0.388	0.012	0.030928	0.395	0.383	-0.000284876
60	0.40	0.384	0.016	0.041667	0.395	0.379	-0.000111303
120	0.40	0.38	0.02	0.052632	0.395	0.375	0.000156909
300	0.40	0.376	0.024	0.06383	0.395	0.371	0.0009955
600	0.40	0.372	0.028	0.075269	0.395	0.367	0.004948
1200	0.40	0.37	0.03	0.081081	0.395	0.365	0.010828

T 4.7.2 A Kinetics data of 0.20 N glycolic acid with 10% TBP in 1-decanol

time (s)	$C_{i\,aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\,org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0.00		0.37	0.37	
15	0.20	0.191	0.009	0.04712	0.37	0.361	-0.000462251
30	0.20	0.191	0.009	0.04712	0.37	0.361	-0.000329186
60	0.20	0.19	0.01	0.052632	0.37	0.36	-0.00027188
120	0.20	0.19	0.01	0.052632	0.37	0.36	-0.00043249
300	0.20	0.189	0.011	0.058201	0.37	0.359	0.001574
600	0.20	0.186	0.014	0.075269	0.37	0.356	6.8E-05
1200	0.20	0.186	0.014	0.075269	0.37	0.356	0.614276

T 4.7.2 B Kinetics data of 0.20 N glycolic acid with 20% TBP in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0.00		0.74	0.74	
15	0.20	0.191	0.009	0.04712	0.74	0.731	-0.000228426
30	0.20	0.19	0.01	0.052632	0.74	0.73	1.12087E-05
60	0.20	0.19	0.01	0.052632	0.74	0.73	-7.19603E-05
120	0.20	0.188	0.012	0.06383	0.74	0.728	-0.00176497
300	0.20	0.186	0.014	0.075269	0.74	0.726	-0.012676
600	0.20	0.184	0.016	0.086957	0.74	0.724	-0.074332
1200	0.20	0.183	0.017	0.092896	0.74	0.723	-0.139324

T 4.7.2 C Kinetics data of 0.20 N glycolic acid with 30% TBP in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_{HA}$
0	0.20	0.2	0.00		1.1	1.1	
15	0.20	0.191	0.009	0.04712	1.1	1.091	-0.000462
30	0.20	0.19	0.01	0.052632	1.1	1.09	-0.000329
60	0.20	0.188	0.012	0.06383	1.1	1.088	-0.000266
120	0.20	0.187	0.013	0.069519	1.1	1.087	-0.000344
300	0.20	0.18	0.02	0.111111	1.1	1.08	0.004166
600	0.20	0.176	0.024	0.136364	1.1	1.076	0.018212
1200	0.20	0.17	0.03	0.176471	1.1	1.07	0.158084

T 4.7.2 D Kinetics data of 0.20 N glycolic acid with 40% TBP in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0.00		1.48	1.48	
15	0.20	0.187	0.013	0.069519	1.48	1.467	-0.000625776
30	0.20	0.185	0.015	0.081081	1.48	1.465	-0.000367987
60	0.20	0.184	0.016	0.086957	1.48	1.464	-0.000311654
120	0.20	0.183	0.017	0.092896	1.48	1.463	-0.000975
300	0.20	0.173	0.027	0.156069	1.48	1.453	0.001882
600	0.20	0.168	0.032	0.190476	1.48	1.448	0.015124
1200	0.20	0.165	0.035	0.212121	1.48	1.445	0.662068

T 4.7.2 E Kinetics data of 0.05 N glycolic acid with 30% TBP in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.05	0.05	0		1.1	1.1	
15	0.05	0.049	0.001	0.020408	1.1	1.099	-3.457E-05
30	0.05	0.049	0.001	0.020408	1.1	1.099	-2.37997E-05
60	0.05	0.048	0.002	0.041667	1.1	1.098	-1.3814E-05
120	0.05	0.047	0.003	0.06383	1.1	1.097	-2.90723E-05
300	0.05	0.046	0.004	0.086957	1.1	1.096	-0.00036878
600	0.05	0.045	0.005	0.111111	1.1	1.095	-0.00377096
1200	0.05	0.044	0.006	0.136364	1.1	1.094	-0.01976072

T 4.7.2 F Kinetics data of 0.15 N glycolic acid with 30% TBP in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.15	0.15	0		1.1	1.1	
15	0.15	0.148	0.002	0.013514	1.1	1.098	-7.79715E-05
30	0.15	0.147	0.003	0.020408	1.1	1.097	-5.96761E-05
60	0.15	0.146	0.004	0.027397	1.1	1.096	-3.30736E-05
120	0.15	0.144	0.006	0.041667	1.1	1.094	-1.20256E-05
300	0.15	0.139	0.011	0.079137	1.1	1.089	-0.000079
600	0.15	0.137	0.013	0.094891	1.1	1.087	-0.00022
1200	0.15	0.134	0.016	0.119403	1.1	1.084	-0.004228

T 4.7.2 G Kinetics data of 0.40 N glycolic acid with 30% TBP in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.40	0.4	0.00		1.1	1.1	
15	0.40	0.342	0.058	0.169591	1.1	1.042	-0.012387548
30	0.40	0.34	0.06	0.176471	1.1	1.04	-0.001760042
60	0.40	0.335	0.065	0.19403	1.1	1.035	0.004982656
120	0.40	0.33	0.07	0.212121	1.1	1.03	-0.012171008
300	0.40	0.328	0.072	0.219512	1.1	1.028	-0.1388
600	0.40	0.326	0.074	0.226994	1.1	1.026	-3.164
1200	0.40	0.325	0.075	0.230769	1.1	1.025	-47.7704

T 4.7.3 A Kinetics data of 0.20 N glyoxalic acid with 10% Aliquat 336 in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0.00		0.19	0.19	
15	0.20	0.1872	0.0128	0.068376	0.19	0.1772	-0.000342012
30	0.20	0.18	0.02	0.111111	0.19	0.17	-0.000287992
60	0.20	0.1755	0.0245	0.139601	0.19	0.1655	-0.000191536
120	0.20	0.171	0.029	0.169591	0.19	0.161	-4.2688E-05
300	0.20	0.1638	0.0362	0.221001	0.19	0.1538	9.8E-05
600	0.20	0.1422	0.0578	0.40647	0.19	0.1322	-0.000376
1200	0.20	0.135	0.065	0.481481	0.19	0.125	-0.001648

T 4.7.3 B Kinetics data of 0.20 N glyoxalic acid with 20% Aliquat 336 in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0.00		0.395	0.395	
15	0.20	0.198	0.002	0.010101	0.395	0.393	-6.16656E-05
30	0.20	0.197	0.003	0.015228	0.395	0.392	-5.46244E-05
60	0.20	0.196	0.004	0.020408	0.395	0.391	-4.41952E-05
120	0.20	0.194	0.006	0.030928	0.395	0.389	-3.63616E-05
300	0.20	0.183	0.017	0.092896	0.395	0.378	-0.0000844
600	0.20	0.127	0.073	0.574803	0.395	0.322	-0.0001852
1200	0.20	0.114	0.086	0.754386	0.395	0.309	0.0011684

T 4.7.3 C Kinetics data of 0.20 N glyoxalic acid with 30% Aliquat 336 in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.20	0.2	0.00		0.59	0.59	
15	0.20	0.199	0.001	0.005025	0.59	0.589	-0.000172012
30	0.20	0.197	0.003	0.015228	0.59	0.587	-0.000147992
60	0.20	0.193	0.007	0.036269	0.59	0.583	-0.000111536
120	0.20	0.185	0.015	0.081081	0.59	0.575	-0.000082688
300	0.20	0.182	0.018	0.098901	0.59	0.572	-0.000302
600	0.20	0.116	0.084	0.724138	0.59	0.506	-0.001376
1200	0.20	0.094	0.106	1.12766	0.59	0.484	-0.003848

T 4.7.3 D Kinetics data of 0.10 N glyoxalic acid with 20% Aliquat 336 in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.10	0.1	0.00		0.395	0.395	
15	0.10	0.099	0.001	0.010101	0.395	0.394	-5.25776E-05
30	0.10	0.098	0.002	0.020408	0.395	0.393	-2.67987E-05
60	0.10	0.094	0.006	0.06383	0.395	0.389	-2.11654E-05
120	0.10	0.09	0.01	0.111111	0.395	0.385	-8.75E-05
300	0.10	0.085	0.015	0.176471	0.395	0.38	0.0001982
600	0.10	0.078	0.022	0.282051	0.395	0.373	0.0015224
1200	0.10	0.071	0.029	0.408451	0.395	0.366	0.0662168

T 4.7.3 E Kinetics data of 0.40 N glyoxalic acid with 20% Aliquat 336 in 1-decanol

time (s)	$C_{i\ aq}$	C_{aq}	C_{org}	K_D	$[B]_{i\ org}$	$[B]_{org}$	$(-)r_A$
0	0.40	0.4	0.00		0.395	0.395	
15	0.40	0.3852	0.0148	0.038422	0.395	0.3802	-5.26E-05
30	0.40	0.3816	0.0184	0.048218	0.395	0.3766	-2.68E-05
60	0.40	0.3744	0.0256	0.068376	0.395	0.3694	-2.12E-05
120	0.40	0.3528	0.0472	0.133787	0.395	0.3478	-8.75E-05
300	0.40	0.2592	0.1408	0.54321	0.395	0.2542	0.000198
600	0.40	0.198	0.202	1.020202	0.395	0.193	0.001522
1200	0.40	0.18	0.22	1.222222	0.395	0.175	0.066217

T 4.7.4 A Kinetics data of 0.20 N glyoxalic acid with 10% TBP in 1-decanol

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

T 4.7.4 B Kinetics data of 0.20 N glyoxalic acid with 20% TBP in 1-decanol

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

T 4.7.4 C Kinetics data of 0.20 N glyoxalic acid with 30% TBP in 1-decanol

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

T 4.7.4 D Kinetics data of 0.20 N glyoxalic acid with 40% TBP in 1-decanol

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

T 4.7.4 E Kinetics data of 0.05 N glyoxalic acid with 30% TBP in 1-decanol

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

T 4.7.4 F Kinetics data of 0.10 N glyoxalic acid with 30% TBP in 1-decanol

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

T 4.7.4 G Kinetics data of 0.40 N glyoxalic acid with 30% TBP in 1-decanol

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

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

		Aliquat 336 in 1-decanol	TBP in 1-decanol
Glycolic acid	k_1	0.0181	0.0738
	k_2	0.00273	0.0273
	α	1.3	1
	β	0.5	0.68
	γ	1	1
Glyoxalic acid	k_1	0.1024	0.022
	k_2	0.02129	0.0256
	α	1	0.9
	β	0.5	0.7
	γ	1	1