

EQUILIBRIUM STUDIES ON THE BACK EXTRACTION OF LACTIC ACID  
FROM ORGANIC PHASES

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Approval of the Graduate School of Natural and Applied Sciences

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Füsun Karaburun

## **ABSTRACT**

# **EQUILIBRIUM STUDIES ON THE BACK EXTRACTION OF LACTIC ACID FROM ORGANIC PHASES**

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Lactic acid is a fermentation-derived organic acid used in a wide range of industries, such as food processing and pharmaceuticals. Its market is expected to expand due to the worldwide concern for the environment, as it is an essential feedstock for biodegradable polymers. However, fermentation product is a very dilute, multicomponent aqueous solution. Subsequent separation, purification and concentration of organic acids is difficult because of high affinity of the acids for water. Reactive extraction is a viable alternative to classical separation techniques. Amine extractants dissolved in organic diluents are suitable agents with reasonable ranges of viscosity and density of the solvent phase. The product is obtained in an organic phase after reactive extraction.

The aim of this study is to obtain equilibrium data of back extraction of lactic acid into appropriate aqueous solutions from the organic phase. Aqueous solutions of NaCl, NaOH, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were examined as back extractant in various initial concentrations (0.005 – 3 M). The organic phase consists of tri-n-octylmethylammonium lactate (TOMA(La)) dissolved in either oleyl alcohol or octanol with initial concentrations between 0.1 and 0.3 M.

According to results of the experiments, the level of back extraction generally increased with increasing initial salt concentration in aqueous phase and decreased with increasing initial TOMA(La) concentration in organic phase. For all salts investigated, considerable levels of back extraction were obtained. NaOH was considered as the most suitable back extractant among the salts investigated since it exhibits higher distribution coefficients, regenerates tri-n-octylmethylammonium hydroxide (TOMAOH) in the organic phase and has no adverse effect on fermentation medium when forward and backward extraction steps are coupled with the fermentation. The effect of diluent type of TOMA(La) was also investigated during the experiments and it was concluded that octanol is a better diluent since it gives higher equilibrium distribution coefficients in addition to its higher solvating power and lower viscosity.

The present work is a part of a comprehensive research program aiming to collect data and develop knowledge for the design of an industrial reactive extraction process coupling forward and backward extraction of lactic acid in a single unit and integrating fermentation and product separation. The kinetic parameters should be obtained as the next step for the design of such a process.

Keywords: Back extraction, reactive extraction, lactic acid, phase equilibrium studies

## **ÖZ**

# **LAKTİK ASİDİN ORGANİK ORTAMDAN GERİ ÖZÜTLENMESİ İLE İLGİLİ DENGE ÇALIŞMALARI**

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Laktik asit, fermantasyon yoluyla üretilen bir organik asit olup gıda ve ilaç sanayilerde geniş bir kullanım alanına sahiptir. Biyoindirgenabilir polimerler için temel bir girdi olması sebebiyle pazar payının, tüm dünyanın çevreye olan hassasiyetinin artmasıyla genişlemesi beklenmektedir. Ancak, fermantasyon ürünleri oldukça seyreltik, çok bileşenli sulu çözeltilerdir. Organik asitlerin üretimden sonra ayrılmaları, saflaştırılmaları ve derişik hale getirilmeleri suya olan yüksek ilgilerinden ötürü zordur. Tepkimeli özütleme klasik ayırım tekniklerine nazaran daha uygulanabilir bir alternatiftir. Uygun organik seyrelticiler içinde çözündüklerinde amin özütleyiciler, kabul edilebilir viskozite ve özkütleleriyle başarılı birer özütleyici olarak kullanılabilir. Tepkimeli özütleme sonucunda ürün organik bir faza aktarılmaktadır.

Bu çalışmanın amacı, laktik asidin organik fazdan, sulu çözeltilere geri özütlenmesi ile ilgili denge verilerinin elde edilmesidir. NaCl, NaOH, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub> ve Na<sub>2</sub>CO<sub>3</sub> tuzlarının sulu çözeltileri çeşitli başlangıç derişimleriyle (0,005 – 3 M) geri özütleyici olarak incelenmiştir. Organik faz oleyil alkol veya oktanol içerisinde çözünmüş tri-n-oktilmetilamonyum laktat' ın (TOMA(La)) 0,1 ve 0,3 M arasındaki derişimlerini içerir.

Gerçekleştirilen deneylerin sonuçlarına göre, geri özütleme seviyeleri genellikle, sulu fazdaki tuzun başlangıç derişiminin artmasıyla artmakta ve organik fazdaki TOMA(La)' ın başlangıç derişiminin artmasıyla azalmaktadır. İncelenen tüm tuzlar için laktik asidin önemli oranlarda geri özütlenmesi sağlanmıştır. Denge dağılım katsayısının yüksek oluşu, tri-n-oktilmetilamonyum hidroksit'in (TOMA(OH)) organik fazda rejenerasyonunu sağlaması, özütleme süreçlerinin, laktik asit fermantasyonu ile birleştirildiğinde ortam üzerinde olumsuz etkileri olmaması nedeniyle NaOH' in incelenen tuzlar arasında en uygun geri özütleyici olduğu sonucuna varılmıştır. Çalışmada TOMA(La) için kullanılan seyreltici türü de incelenmiş ve oktanol' un daha iyi çözme gücü ve daha düşük vizkositesine ek olarak yüksek dağılım katsayıları sağlaması nedeniyle daha iyi bir seyreltici olduğu sonucuna varılmıştır.

Bu çalışma, ileri ve geri özütlemeleri tek bir üniteye birleştirecek ve laktik asit fermantasyonuyla bütünleştirecek tepkimeli özütleme prosesinin tasarımı için gerekli verileri toplamayı ve bilgi sağlamayı amaçlayan kapsamlı bir projenin bir parçasıdır. Prosesin tasarımı için ikinci adım kinetik parametrelerin elde edilmesi olmalıdır.

Anahtar kelimeler: Geri özütleme, tepkimeli özütleme, laktik asit, faz dengesi çalışmaları

*to my family,*



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## LIST OF SYMBOLS AND ABBREVIATIONS

HA	Lactic acid
K	Equilibrium distribution coefficient
L <sup>-</sup>	Lactate ion
pK <sub>a</sub>	Equilibrium dissociation constant
Q <sup>+</sup>	Quaternary amine
R	Alkyl amine
X <sup>-</sup>	Anion
Z	Loading ratio of the extractant
[ ]	Concentration of the species specified in moles per liter
DOA	Dioctylamine
D2EHPA	di(2-ethylhexyl) phosphoric acid
IC	Ion chromatograph
MIBK	Methylisobutyl ketone
TAA	Trialkylamine
TBP	Tri-n-butylphosphate
TMA	Trimethylamine
TOA	Tri-n-octylamine
TOPO	Tri-n-octylphosphineoxide
TOMAC	Tri-n-octylmethylammonium chloride
TOMA(La)	Tri-n-octylmethylammonium lactate
TOMAHSO <sub>4</sub>	Tri-n-octylmethylammonium hydrogensulphate
TOMAOH	Tri-n-octylmethylammonium hydroxide

TOMASO<sub>4</sub> Tri-n-octylmethylammonium sulphate

*Subscripts*

aq. Aqueous phase

org. Organic phase

*Superscripts*

\* Equilibrium

<sup>0</sup> Initial

## **CHAPTER 1**

### **INTRODUCTION**

Lactic acid, 2-hydroxypropionic acid, is the simplest hydroxy acid and is predominantly produced by fermentation in the industry. It is utilized in many fields especially in food and pharmaceutical industries. Lactic acid can be converted to ethanol, propylene glycol, acrylic polymers and polyesters. Lactic acid undergoes self-esterification resulting in the formation of lactoyllactic acid in its aqueous solutions. Usage of lactic acid copolymers for packaging purposes receives considerable attention due to advantage of being biodegradable (Holten, 1971; San-Martin et. al., 1992).

The demand for lactic acid is increasing due to the expansion of its application areas. Fermentation processes for the production of organic acids produce multicomponent, aqueous solutions with product acid concentrations below 10% w/w. Consequently separation methods for recovery of lactic acid from aqueous solutions are receiving increasing attention. Recovery of these acids by purification and concentration is challenging since the organic acids have a high affinity for water. The classical product recovery method for lactic acid from fermentation broth is based on the precipitation of calcium lactate with the addition of calcium hydroxide to the aqueous fermentation broth. The solid is

filtered off and treated with sulphuric acid leading to the precipitation of calcium sulphate. The lactic acid product in the filtrate is then purified using activated carbon, evaporation and crystallization to yield crystals of the lactic acid. These separation and final purification stages account for approximately fifty per cent of the production costs. Consequently they are undesirable and also environmentally unfriendly due to the consumption of lime and sulphuric acid and the production of large quantities of calcium sulphate sludge as a solid waste (Kertes and King, 1986; Tamada et. al., 1990; Wasewar<sup>1</sup> et. al, 2002; Wasewar<sup>2</sup> et. al., 2002).

Reactive extraction is a promising alternative to conventional methods for the recovery of lactic acid from fermentation medium. It has been reported that organophosphorus and aliphatic amines are capable of extracting organic acids from aqueous solutions (Kertes and King, 1986). The strong interaction between the acid and the amine creates acid-amine complexes and provides higher equilibrium distribution ratios than the conventional solvents such as ketones and alcohols. The high affinity of the amine for the organic acid also gives higher selectivity for the acid over other non-acidic components in the fermentation medium. Reactions between the acid and the amine extractant are reversible and allow recovery of the acid and regeneration of the extractant.

High concentrations of product in medium may be inhibitory to microbial growth. Product inhibition, a problem which is widespread in biotechnology, occurs during the lactic acid fermentation. Recovery of lactic acid by reactive extraction simultaneously during the production of lactic acid is very beneficial from the viewpoint of suppression of the end-product inhibition and enhanced reactor efficiency (Matsumoto et. al., 2001).

There are two stages in extractive separation. The first is the extraction of the acid to produce an acid-amine complex and a relatively acid free aqueous raffinate. The second step is necessary for stripping the lactic acid from the organic complex to obtain amine free aqueous lactic acid as a product and also for simultaneously regenerating the extractant recycled back to the extraction unit. The integration of the fermentation and separation steps is represented in Figure 1.1.

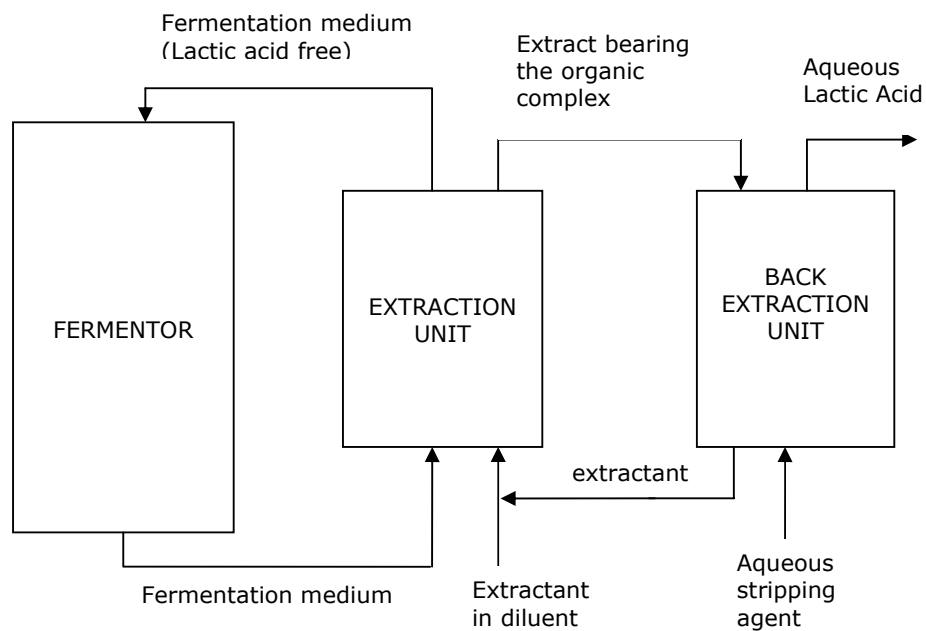


Figure 1.1 Schematic Representation of Coupled Fermentation and Recovery in Lactic Acid Production

An appropriate extraction system is expected to have some properties such as: it should have no adverse effect on fermentation; the optimum pH of extraction should be consistent with that of fermentation; stable emulsions should not form. The last demand can be met by utilizing a non-dispersive membrane functioning as a phase barrier between the organic and the aqueous phase. Forward and backward extraction steps can be achieved in a single unit



by means of microporous hollow fiber membrane extractor (Figure 1.2) eliminating many problems associated with the conventional extraction systems (Juang and Huang, 1995; Juang and Huang, 1997; Juang et. al.,1997; Tong<sup>2</sup> et. al., 1998; Tong et. al., 1999).

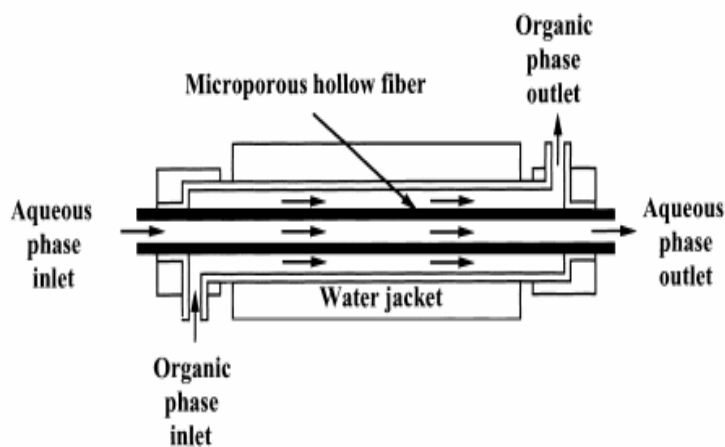


Figure 1.2 Hollow Fiber Membrane Extractor (Tong et. al., 1999)

The present study is focused on the back extraction step. The aim is to obtain data related to equilibrium behavior for the back extraction of lactic acid from the organic phase consisting of a diluent and a quaternary amine salt-lactate complex to aqueous salt solutions. It has been reported that the forward extraction of lactic acid from its aqueous solutions by quaternary ammonium salts (chloride, sulphate and hydroxide salts of tri-n-octylmethylammonium or Aliquat 336) dissolved in oleyl alcohol or octanol can be achieved to form tri-n-octylmethylammonium lactate complex in the organic phase (Tong<sup>1,2</sup> et. al., 1998; Acan, 2003). The present study aims to obtain equilibrium data for the back extraction of lactic acid from tri-n-octylmethylammonium lactate dissolved in either oleyl alcohol or octanol. Since the reactions taking place during the forward extractions are anion-exchange reactions, lactic acid is expected to be effectively stripped by exchanging with the anions of the inorganic salts. Sodium

salts of chloride, hydroxide, sulphate, nitrate and carbonate have been utilized as the back extractants in the study. The anion exchange reactions between the sodium salts and the quaternary amine lactate complex provide for the regeneration of the extractant in the organic phase as well as to obtain the amine free lactic acid in the aqueous phase (Figure 1.3).

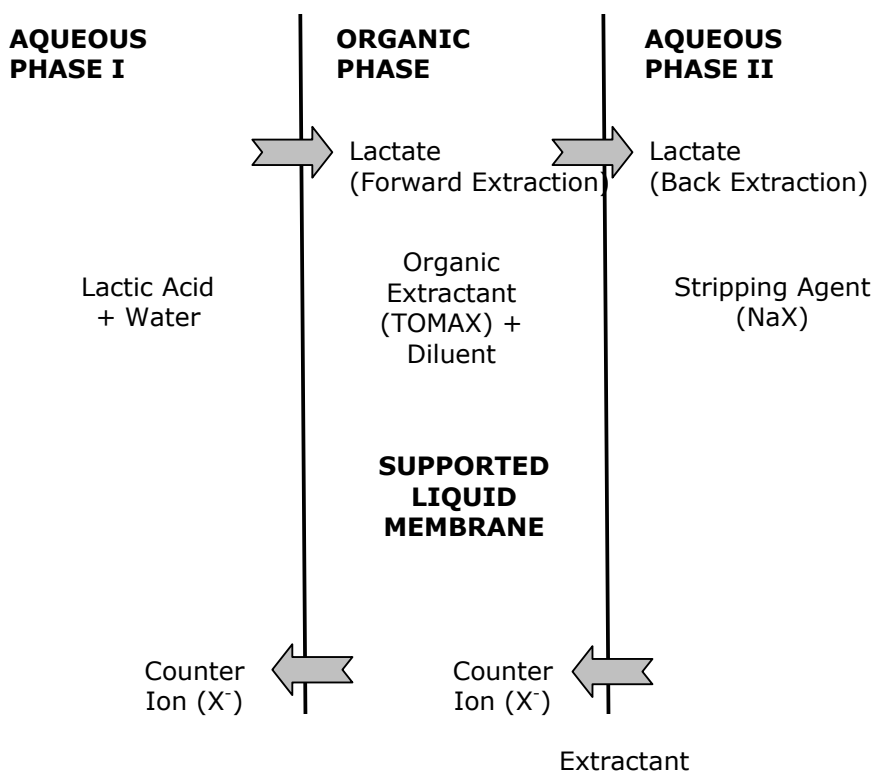


Figure 1.3 Schematic Representation of the Transfer of Ions between Phases through Supported Liquid Membrane with Forward and Backward Extraction Steps

Back extraction equilibrium experiments are carried out by contacting the aqueous and the organic phases in flasks which are placed in a constant temperature shaking bath. The effect of the initial concentrations of lactate in

the organic phase and that of the anion in the aqueous phase are investigated for selected types of salts and the diluents -oleyl alcohol and octanol- to determine the best stripping agent and the optimum conditions for back extraction of lactic acid from tri-n-octylmethylammounium lactate dissolved in the organic diluent.

Process design for reactive forward extraction and back extraction require knowledge on four major topics (Bart<sup>1</sup>, 2001):

- reactive phase equilibria
- microkinetics
- macrokinetics
- apparatus selection and design

The present study aims to furnish data and information on the first step. Microkinetic parameters can be obtained experimentally in a Lewis-type stirred cell where the true kinetic parameters of the reaction without any diffusional contribution can be determined. The effective mass transfer parameters can be obtained by the superposition of the kinetic, diffusional and turbulent contributions and may be verified experimentally either utilizing a rising droplet apparatus or a Venturi-tube. The final process design stage is apparatus selection and sizing. The data obtained in this study together with those of Açı̇n (Açı̇n, 2003) may be considered as the first step required for the design of an extractive fermentation unit coupling fermentation with separation.

## CHAPTER 2

### LITERATURE SURVEY

#### 2.1 Reactive Extraction

The history of extraction has originated in 3500 BC in "life-science" applications. Solid feed materials from vegetables or animals were extracted under reflux with hot water or oil to produce perfumes, pharmaceutical oils and waxes in 2100 BC by Sumerians. The first liquid-liquid extraction column was patented containing all features of modern columns in the late 19<sup>th</sup> century. Many improvements to extraction processes were introduced in mining practice. Nowadays, liquid ion exchangers are used for the extraction of organic and inorganic acids, organic intermediates and pharmaceuticals as well as all metals in mining (Bart<sup>1</sup>, 2001).

Extraction is the unit operation that partitions at least one solute between two partially miscible liquid phases that differ in bulk density. In order to improve the efficiency of separation, it is often coupled with reversible or irreversible chemical reactions. In practice, reactive extraction is utilized when (Brunt and Karel, 2002):

- The reactants are relatively immiscible

- The product(s) undergoes subsequent undesired reactions in reaction phase
- The reaction products to be separated are immiscible with the reaction phase
- The phase equilibrium can be positively influenced
- The heat transfer is to be improved during the reaction
- The product-catalyst separation can be affected by a liquid-liquid separation

Reactive extraction has many applications in chemical and pharmaceutical industries (intermediates, organic acids, vitamins ...) or in hydrometallurgical and environmental science (heavy metals, inorganic acids ...). The liquid ion exchangers are used to promote a certain reaction to accomplish very selective separations (Bart<sup>2</sup>, 2001). There are many liquid ion exchangers commercially available. They work basically with three different types of mechanisms: anion exchange, cation exchange, solvation. It is practical to use ion-exchangers in a diluent which is immiscible with water since they are highly viscous or solid materials. The diluent makes the organic phase easier to handle (Bart<sup>1</sup>, 2001).

## **2.2 Reactive Extraction of Organic Acids**

There are a significant number of studies on reactive extraction of organic acids in the literature. These studies investigate various aspects of reactive extraction of organic acids: chemical interactions between acids and extractants, reaction mechanisms, type of extractants and diluents, effect of temperature and pH, effect of aqueous and organic phase compositions on extraction, effect of modifiers, extractive fermentation processes, kinetics of extraction, stripping the acid from the organic phase etc.

The starting point of reactive extraction studies on carboxylic acids was the identification of novel powerful extractants. Kertes and King (1986) have investigated and reviewed three categories of extractants for recovery of organic acids:

- carbon-bonded oxygen donor extractants: hydrocarbon and substituted hydrocarbon solvents
- phosphorous-bonded oxygen donor extractants
- aliphatic amine extractants

They studied extraction of propionic, pyruvic, lactic, succinic, fumaric, maleic, itaconic, tartaric, citric and isocitric acids. They have reported that carbon-bonded and phosphorus bonded oxygen donor extractants extract with no exception the undissociated monomeric acids. Long-chain tertiary amines also give high distribution coefficients and form bulky salts in the organic phase.

Since it has been found that long-chain, aliphatic amines have a capacity to extract carboxylic acids from their aqueous solutions, focus has been on these type of extractants. King and his co-workers studied Alamine 336, an aliphatic tertiary amine with a mixture of C<sub>8</sub> and C<sub>10</sub> side chains, as the extractant dissolved in various diluents to examine equilibria, stoichiometry of acid-amine complexes, effect of diluent-complex interactions, effect of temperature on extraction and co-extraction of water during the extraction (Tamada<sup>1,2,3</sup> et. al., 1990). They studied acetic, lactic, succinic, malonic, fumaric, and maleic acids which differed in equilibrium dissociation constants (pK<sub>a</sub>) with the presence or absence of functional groups other than the primary carboxyl group. The diluents were chloroform, methylene chloride, methyl isobutyl ketone (MIBK), nitrobenzene, and 1-octanol as the active diluent and n-heptane as an inert diluent. Active diluent is a solvent with functional groups which interacts with the

acid-amine complex. These interactions were classified into different groups: electron donor, electron acceptor, polar, non-polar. It is reported that these interactions affect both the stoichiometry of the reaction and the value of the equilibrium distribution constant (Tamada<sup>1</sup> et. al., 1990). These agree with the results from spectroscopic studies defining chemical interactions during the complex formation between carboxylic acids and Alamine 336 in various diluents (Tamada<sup>2</sup> et. al., 1990). The third part of that study is about the temperature effect on extraction, coextraction of water with acid-amine complex and regeneration of the acid from the acid-amine complex by back extraction (Tamada<sup>3</sup> et. al., 1990). They have reported that the selectivity of the acid compared to water during reactive extraction by amine extractants is high and has little effect on process viability as compared to conventional solvent extraction processes. They have also reported enthalpy and entropy data which indicate an exothermic behavior for the reactions during complex formation of Alamine 336 dissolved in various diluents with lactic and succinic acids.

Tung and King (1994) studied Alamine 336 and Amberlite LA-2, an asymmetric alkylamine with a straight C<sub>12</sub> chain and a highly branched chain of 12-15 carbon atoms, dissolved in methyl isobutyl ketone (MIBK), chloroform or 1-octanol to extract lactic and succinic acids. They investigated pH effect on extraction and have reported that the loading values obtained with Amberlite LA-2 are significantly lower than loading values obtained with Alamine 336 for all pH values studied. They have also reported that the performance of the diluents are different from each other and this indicates the ability of the diluents to stabilize the acid-amine complex.

The quaternary amines are first studied by Yang et al. (Yang et. al., 1991). They have investigated Alamine 336 and Aliquat 336, quaternary amine

produced by the methylation of Alamine 336 and composed of a large organic cation with a chloride ion, dissolved in kerosene or 2-octanol to extract lactic, acetic, propionic and butyric acids. It has been reported that while Alamine 336 can extract only the undissociated acid, Aliquat 336 can extract both dissociated and undissociated acids and always gives higher distribution coefficients than Alamine 336 at all pH values. It is also reported in this study that the extraction power of Alamine 336 is increased by the polar diluent, 2-octanol. On the other hand a diluent effect could not be detected on the extraction power of Aliquat 336.

Prochazka et al. (1994) have studied trialkylamine, a mixture of straight chain tertiary amine with 7-9 carbon atoms, dissolved in the mixture of 1-octanol and n-heptane to extract lactic, malic and citric acids. It is reported that all systems used in this study are sensitive to temperature and solvent composition.

Another tertiary amine extractant tri-n-octylamine (TOA) dissolved in xylene was studied by Juang and Huang to extract succinic and tartaric acids (Juang and Huang, 1996). They obtained thermodynamic data on extraction and compared extraction equilibria of succinic and tartaric acids with TOA dissolved in xylene. They have reported that the equilibrium distribution coefficient of the acids extracted with TOA increases with initial concentration of amine in the organic phase and of the acid in the aqueous phase. TOA has also been investigated by Poposka et al. as an extractant dissolved in an isodecanol/n-heptane mixture for extraction equilibria of citric acid (Poposka et. al., 1997). The data were obtained as a function of acid, amine and isodecanol concentrations at 298 K and an appropriate mathematical model was proposed.



Most of the studies on reactive extraction in the literature are focused on a single acid in the aqueous phase. However, Juang et. al. (1997) have reported that extraction characteristics are affected by the presence of more than one acid in the aqueous phase. Separation mechanisms of lactic and citric acids in the aqueous phase with TOA dissolved in xylene have been investigated via the supported liquid membrane technique. They have reported large synergistic effects compared to single acid systems for low initial concentration ratio of citric to lactic acid ( $\alpha$ ) and an antagonistic effect at  $\alpha=2$ . The presence of the second acid has a positive effect on the transport of citric acid but a negative effect on that of the lactic acid. Transport rate of the acids also increases with TOA concentration and temperature.

New synergistic extraction system for organic acids was developed by Matsumoto et. al. (2001). The extraction equilibria were investigated for acetic, glycolic, propionic, lactic, succinic, fumaric, malic and itaconic acids by tri-n-octyl amine (TOA) and/or tri-n-butylphosphate (TBP) dissolved in hexane. It is reported that when a mixture of extractants are used a synergy is developed and a more effective extraction of all organic acids is achieved.

### **2.3 Regeneration of Organic Acid Extracts**

The organic acid must be regenerated from the organic phase after the reactive extraction step. This is necessary to recover the organic acid and to regenerate the extractant for reuse. Distillation cannot be utilized for regeneration when the acid is not sufficiently volatile (e.g. dicarboxylic and hydroxycarboxylic acids).

There are a significant number of investigations in the literature on the back extraction of organic acids from the organic phase obtained by the reactive extraction of the acid with amine extractants. Tamada and King have considered two approaches for regeneration of fumaric, malonic, maleic, succinic, lactic and acetic acids from Alamine 336 extract to aqueous phase through back extraction (Tamada<sup>3</sup> et. al., 1990). Equilibrium characteristics could be modified by a swing of temperature and a swing of diluent composition. In the temperature swing approach, the forward extraction is performed at a lower temperature to obtain the acid-amine complex in the organic phase. The extract is then contacted with a fresh aqueous stream at a higher temperature to strip the acid into the aqueous phase and to obtain acid-free organic phase. In the diluent swing process, the diluent content of the organic phase is changed either by the removal of the diluent or the addition of another diluent after the forward extraction step. This altered organic phase is contacted with a fresh aqueous system to obtain the acid in the aqueous phase and to regenerate the acid-free extractant in the organic phase. The authors have reported that removal of the active diluent has a strong effect on the equilibrium distribution of succinic acid. Removal of the diluent may be achieved by distillation. This approach has the additional advantage of concentration of the acid in the organic extract before the regeneration step at the expense of high cost. They have suggested a combination of the two approaches to decrease the cost of the process and to obtain more favorable equilibria.

Poole and King (1991) have suggested back extraction of lactic, succinic and fumaric acids from tertiary amine-acid complex in organic phase into a solution of aqueous base, with a water-soluble, volatile tertiary amine. The acid-base complex in the aqueous extract is decomposed thermally to obtain carboxylic acid as a product and the free base as a vapor that can be reabsorbed

into water to be regenerated for back extraction. For this purpose a volatile, water soluble, tertiary amine is chosen as back extractant in aqueous phase. Ammonia or primary and secondary amines cannot be used for this purpose, since they form stable amides when heated with carboxylic acids. Poole and King have investigated trimethylamine (TMA) which is a very volatile tertiary amine as back extractant in their study. Pure TMA boils at 3 °C and thermally decomposes above 350 °C. They have investigated equilibria for back extraction of the acids from the Alamine 336/MIBK extract into aqueous solutions of TMA. They have reported for all acids investigated that complete recovery of the acid from organic phase is achieved at conditions in which there is at least 1 mole of TMA for every equivalent weight of acid. The equilibrium concentration of TMA in organic phase is less than 0.0005 wt% at this condition. If the stoichiometric ratio of TMA to acid is greater than 1, equilibrium concentration of TMA in organic phase is much greater (e.g., 2.5 wt% for 2.1 mol TMA/mol of lactic acid, 1.4 wt% for 3.1 mol TMA/mol of succinic acid). Thermal decomposition experiments have also been performed by Poole and King. It has been reported that, fumaric and succinic acids are obtained in crystalline form by thermal decomposition of the back extract. However for the case lactic acid, only 63% of the water and 62% of the TMA present in the initial aqueous back extract can be removed, because of great water solubility and tendency for self-association of lactic acid.

pH swing is another possibility for regeneration of carboxylic acids. If the pH of the aqueous solution is increased above the  $pK_a$  of the acid, back extraction of lactic acid is promoted. However, the carboxylate salt is formed by adding a base. It is required to add another acid to obtain carboxylic acid as a product from carboxylate salt. This process therefore has drawbacks as

consumption of extra chemicals and formation of a waste salt (King et. al., 1992).

Juang and Huang (1995) have studied the kinetics of the reactive extraction of citric acid from aqueous solutions with tri-n-octyl amine (TOA). They used a membrane-based cell to investigate both forward and backward extractions simultaneously. For the forward extraction process, the organic phase includes TOA dissolved in xylene and for back extraction, the aqueous phase is comprised of either 0.1 M  $\text{Na}_2\text{CO}_3$  or deionized water. They have reported that both forward extraction and back extraction processes are mainly controlled by the chemical reactions occurring at the interface on the organic side. The activation energy for back extraction is significantly greater than that for forward extraction.  $\text{Na}_2\text{CO}_3$  is a better stripping agent than deionized water for stripping citric acid from the organic phase by temperature swing technique due to a larger activation energy.  $\text{Na}_2\text{CO}_3$  solution also provided higher rates of back extraction than deionized water during the transfer of the citric acid into the strip phase.

Another membrane process is utilized for separation of citric and lactic acids simultaneously from aqueous solutions with TOA (Juang et. al., 1997). A supported liquid membrane is used to separate feed and strip phases and provides the means for simultaneous forward and back extraction. The effect of the composition of the stripping phase and temperature has been examined in supported liquid membrane separation. The stripping phase is either deionized water or aqueous  $\text{Na}_2\text{CO}_3$ . It is reported that  $\text{Na}_2\text{CO}_3$  is a better stripping phase than deionized water since it enhances the transport and the dissociation reaction rates of the acid-amine complex. The acid is released from the complex according to following reaction:



The transport rate of the acid is enhanced at higher concentrations of  $\text{Na}_2\text{CO}_3$ , since the concentration of the undissociated acid is lowered. The maximum transport rate is obtained at  $50 \text{ mol/m}^3$  concentration of  $\text{Na}_2\text{CO}_3$  aqueous solution.

## 2.4 Reactive Extraction of Lactic Acid

### 2.4.1 Properties of Lactic Acid

Lactic acid is first isolated from sour milk by the Swedish chemist Scheele in 1780. Lactic acid is first produced by the fermentation of carbohydrates such as sucrose, lactose, mannitol, starch and dextrin by Fremy in 1839. Industrial manufacture of lactic acid was established in 1881 (Elvers et. al., 1990).

Lactic acid which has both a hydroxyl group and a carboxyl group is the simplest hydroxycarboxylic acid and one of the smallest molecules that is optically active (Lipinsky and Sinclair, 1986). Structural formula of lactic acid is represented in Figure 2.4.1.

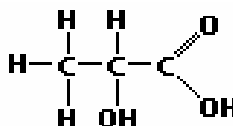


Figure 2.4.1 Structural Formula of Lactic Acid

Lactic acid is an odorless and colorless substance and is normally obtained as a concentrated solution up to 90 wt%. It is completely soluble in water, ethanol, diethyl ether and other organic solvents that are miscible with water

(Elvers et. al., 1990). The equilibrium distribution data of lactic acid in some solvents is given in Appendix A.

Pure and anhydrous lactic acid is a white crystalline solid which has a low melting point varying between 18 °C and 33 °C. Pure and anhydrous lactic acid is rarely available due to its physical properties and difficulty of its preparation. Lactic acid goes intermolecular esterification to form lactolylactic acid and chain polyesters spontaneously. Depending on the concentration and age of the solution, commercial aqueous lactic acid solutions contain varying amounts of lactolylactic and polylactic acids (Elvers et. al., 1990; Holten, 1971).

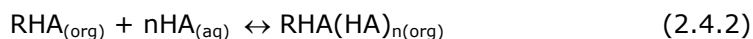
#### 2.4.2 Reactive Extraction Studies on Lactic Acid

Increasing demand of lactic acid makes it one of the most studied organic acids in order to improve production processes. Reactive extraction of lactic acid from fermentation broth has been receiving increasing attention in the last two decades. The most studied extractants for reactive extraction of lactic acid are aliphatic amines dissolved in organic solvents. There are many studies in literature, which examines primary, secondary, tertiary and quaternary amines as extractant for lactic acid recovery.

The extraction process for recovery of lactic acid from its aqueous solutions is based on an acid-base complexation reaction between the alkylamine (R) and the acid (HA) (Kertes and King, 1986).



The organic phase is, in some cases, capable of taking up an excess amount of acid according to the following stoichiometry:



The capacity of the extractant for taking up the acid can be quantified by loading ratio. The loading ratio is the ratio of the total concentration of acid (all forms) in the organic phase to the total concentration of extractant (all forms) in the organic phase (Kertes and King, 1986).

$$Z = [HA]_{org} / [R]_{org} \quad (2.4.3)$$

#### 2.4.2.1 Reactive Extraction of Lactic Acid with Tertiary Amines

The most studied amine types in literature are tertiary amines. There are many investigations about reactive extraction of lactic acid from its aqueous solutions by Alamine 336 and tri-n-octyl amine (TOA); both are tertiary amines, dissolved in various water-immiscible organic diluents. The systems studied for reactive extraction of lactic acid by tertiary amines are summarized in Table 2.4.1.

Table 2.4.1 Equilibrium Studies on Reactive Extraction of Lactic Acid by Tertiary Amines

Extractant(s)	Diluent(s)	Parameters	Results	Ref.
Alamine 336	<ul style="list-style-type: none"> <li>• active diluents: chloroform, methylene chloride, MIBK, 1-octanol</li> <li>• inert diluent: n-heptane</li> </ul>	<ul style="list-style-type: none"> <li>• diluent type</li> <li>• amine concentration</li> </ul>	<ul style="list-style-type: none"> <li>• loading ratio is independent of amine concentration but dependent on whether active or inert diluent used</li> </ul>	Tamada <sup>1</sup> et. al., 1990

Table 2.4.1 (cont.)

Alamine 336	chloroform, MIBK, nitrobenzene	<ul style="list-style-type: none"> <li>• temperature</li> <li>• coextraction of water</li> </ul>	<ul style="list-style-type: none"> <li>• water coextraction has little effect on process</li> <li>• extraction decreases with increasing temperature</li> </ul>	Tamada <sup>3</sup> et. al., 1990
Alamine 336, Aliquat 336*	<ul style="list-style-type: none"> <li>• polar diluent: kerosene</li> <li>• nonpolar diluent: 2-octanol</li> </ul>	<ul style="list-style-type: none"> <li>• extractant type</li> <li>• diluent type</li> <li>• pH</li> </ul>	<ul style="list-style-type: none"> <li>• Aliquat 336 gives higher <math>K_D</math> values than Alamine 336</li> <li>• <math>K_D</math> decreases with equilibrium pH of aqueous phase</li> </ul>	Yang et. al., 1991
Alamine 336	toluene	<ul style="list-style-type: none"> <li>• temperature</li> <li>• amine concentration in organic phase</li> <li>• presence of NaCl, HCl and lactose in aqueous phase</li> </ul>	<ul style="list-style-type: none"> <li>• more lactic acid is transferred to the organic phase than stoichiometry of the reaction requires (overloading)</li> <li>• <math>K_D</math> values decrease with temperature</li> <li>• lactose has no effect on extraction</li> <li>• extraction decreases with presence of NaCl</li> </ul>	San-Martin et. al., 1992



Table 2.4.1 (cont.)

trialkylamine (TAA)	1-octanol, n-heptane	<ul style="list-style-type: none"> <li>• temperature</li> <li>• solvent composition</li> </ul>	<ul style="list-style-type: none"> <li>• the exponential relations have derived for the prediction of effects of temperature and solvent composition</li> </ul>	Prochazka et. al., 1994
Alamine 336, Amberlite LA-2**	1-octanol, MIBK, chloroform	<ul style="list-style-type: none"> <li>• extractant type</li> <li>• pH</li> </ul>	<ul style="list-style-type: none"> <li>• 100% loading of the amines are achieved for all diluent at low pH values</li> </ul>	Tung and King, 1994
<ul style="list-style-type: none"> <li>• secondary amines: di-n-hexyl amine, di-n-octyl amine, di-n-decyl amine</li> <li>• tertiary amines: tri-n-pentyl amine, tri-n-hexyl amine, tri-n-octyl amine, tri-n-decyl amine, Alamine 336</li> </ul>	oleyl alcohol	<ul style="list-style-type: none"> <li>• extractant type</li> <li>• organic phase concentration</li> <li>• toxicity of the extractant toward cell growth of lactic acid bacteria -<i>L. delbrueckii</i>-</li> </ul>	<ul style="list-style-type: none"> <li>• 40% Alamine 336 dissolved in oleyl alcohol can be used continuous extractive fermentation.</li> <li>• lactic acid accumulation in the broth significantly suppressed, while the cell growth does not reduce</li> </ul>	Honda et. al., 1995
TOA	<ul style="list-style-type: none"> <li>• active diluents: 1-octanol, n-decanol methylene chloride,</li> </ul>	<ul style="list-style-type: none"> <li>• temperature</li> <li>• diluent type</li> </ul>	<ul style="list-style-type: none"> <li>• a modified mass action model proposed for equilibrium data</li> </ul>	Han and Hong, 1996

Table 2.4.1 (cont.)

TOA	xylene	<ul style="list-style-type: none"> <li>• temperature</li> <li>• amine concentration in organic phase</li> <li>• effect of a water-insoluble organic acid, di(2-ethylhexyl) phosphoric acid (D2HEPA)</li> </ul>	<ul style="list-style-type: none"> <li>• distribution of acid in organic phase increases with TOA concentration</li> <li>• loading of the acid depends on the concentration of the amine in organic phase</li> <li>• the amount of lactic acid extracted decreases with temperature</li> <li>• synergistic effect of D2HEPA is observed for the concentration ratio of D2HEPA to TOA is between 0.05 and 3</li> </ul>	Juang <sup>2</sup> et. al., 1997
TOA, Aliquat 336*	MIBK, octanol, paraffin liquid	<ul style="list-style-type: none"> <li>• amine concentration in organic phase</li> <li>• pH of aqueous phase</li> <li>• extractant type</li> <li>• diluent type</li> </ul>	<ul style="list-style-type: none"> <li>• TOA is a better extractant than Aliquat 336</li> <li>• no diluent effect on extraction with Aliquat 336</li> <li>• the extraction of lactic acid is promoted at low pH values</li> </ul>	Choudhury et. al., 1998

Table 2.4.1 (cont.)

<p>TOMAC*, TOA, dioctylamine (DOA), tri-n-octylphosphine oxide (TOPO), tri-n-butylphosphat (TBP)</p>	<p>oleyl alcohol, hexane, butyl acetate</p>	<ul style="list-style-type: none"> <li>• extractant type</li> <li>• diluent type</li> <li>• bio-compatibility of the extractants with lactic acid bacteria</li> </ul>	<ul style="list-style-type: none"> <li>• TOMAC dissolved in oleyl alcohol is the most suitable system because of high extraction capacity and simplicity of operation</li> <li>• the optimum pH for this system is 5-6</li> <li>• among the diluents only oleyl alcohol exhibits no toxicity to lactic acid bacteria</li> </ul>	<p>Tong<sup>1</sup> et. al., 1998</p>
<p>Alamine 336</p>	<p>oleyl alcohol</p>	<ul style="list-style-type: none"> <li>• initial lactic acid concentration</li> <li>• pH</li> <li>• temperature</li> <li>• stirring rate</li> <li>• amine concentration in organic phase</li> <li>• the ratio of organic phase volume to aqueous phase volume</li> </ul>	<p>the optimum conditions are (by Linear Box-Wilson experimental design method):</p> <ul style="list-style-type: none"> <li>• initial lactic acid conc: 21 g/L; pH: 2.0; temp: 32 °C; stirring rate: 120 rpm; Alamine 336 concentration: 41%; volume ratio: 1/1</li> </ul>	<p>Kahya et. al., 2001</p>

Table 2.4.1 (cont.)

Alamine 336	oleyl alcohol	<ul style="list-style-type: none"> <li>• amine concentration in organic phase</li> <li>• sun flower oil effect on immobilization</li> </ul>	<ul style="list-style-type: none"> <li>• addition of sun flower oil into fermentation medium increases lactic acid production</li> <li>• oleyl alcohol has no toxic effect on lactic acid bacteria but Alamine 336 does</li> <li>• a maximum lactic acid concentration is obtained with 15% Alamine 336 in oleyl alcohol together with immobilized cells with 15% sun flower oil</li> </ul>	Tik et. al., 2001
Alamine 336	MIBK, decanol	<ul style="list-style-type: none"> <li>• amine concentration in organic phase</li> <li>• lactic acid concentration in aqueous phase</li> </ul>	organic phase extracts more acid than stoichiometry of the reaction requires (overloading)	Wasewar <sup>1, 2</sup> et. al., 2002

\*: Aliquat 336, TOMAC, tri-n-octylmethylammonium chloride, a quaternary amine salt

\*\* : Amberlite LA-2, an asymmetric alkyl amine with a straight C<sub>12</sub> chain and a highly branched chain of 12-15 carbon atoms

#### 2.4.2.2 Reactive Extraction of Lactic Acid with Quaternary Amines

Aliquat 336 which has the commercial name of tri-n-octylmethylammonium chloride (TOMAC), is a quaternary amine salt used in the reactive extraction of lactic acid from its aqueous solutions. It is produced by methylation of Alamine 336 and composed of a large organic cation associated with a chloride ion (Figure 2.4.2). It has a specific gravity of 0.884, viscosity of 1450 cp at 30 °C, average molecular weight of 442 g/mol and solubility in water of about 0.12% w/w (Yang et. al., 1991).

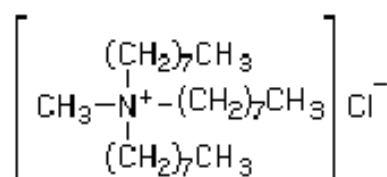
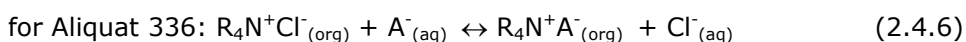
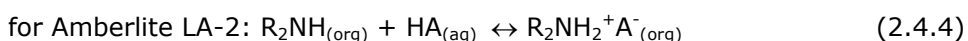


Figure 2.4.2 Structural Formula of TOMAC

Aliquat 336 (TOMAC) has been first suggested as an extractant for carboxylic acids by Yang in 1991 as described earlier in Section 2.2 (Yang et. al., 1991). According to this study, it is impossible to utilize Alamine 336 at pH values above 6 at which fermentation of lactic acid occurs. Aliquat 336 provides for high values of the distribution coefficients for lactic acid at this pH range and this makes possible the realization of an extractive fermentation process. Equilibrium distribution coefficient values of lactic acid are dependent on the initial concentration of Aliquat 336 in the organic phase and always the highest with undiluted solutions. However, Aliquat 336 requires use of a diluent due to its physical properties. Diluents lower the viscosity of Aliquat 336 and make it much easier to handle than the pure amine.

Hartl and Marr (1993) have investigated Amberlite LA-2 (didodecyl/tridecylamine), Hostarex A327 (tri-n-octyl/n-decylamine) and Aliquat 336 -which are secondary, tertiary and quaternary amines, respectively- dissolved in Shellsol T (aliphatic hydrocarbons) to extract lactic acid, gluconic acid and L-leucine from their aqueous solutions. They have proposed extraction mechanism for lactic acid with secondary, tertiary and quaternary amines as follows:



It is reported that Aliquat 336 dissolved in Shellsol T gives low distribution coefficients for lactic acid. The maximum extraction level is achieved at pH about 14. The reason for poor extraction in low pH values may be explained by dissociation constant of lactic acid compared to that of hydrochloric acid. Hydrochloric acid forms in aqueous phase as a result of ion exchange during reactive extraction process as shown in Equation 2.4.6.

Tong et al. (1998) have investigated a number of extractants dissolved in various diluents over a wide range of pH values. Among the extractants TOMAC, TOA, dioctylamine (DOA), tri-n-octylphosphineoxide (TOPO), tri-n-butylphosphate (TBP) and diluents oleyl alcohol, hexane and butyl acetate, the most suitable system has been reported as TOMAC dissolved in oleyl alcohol, butyl acetate, and a mixture of hexane and oleyl alcohol in terms of high extraction power and simplicity of operation. They have also examined biocompatibility between the extraction reagents and lactic acid bacteria. It has been reported that TOMAC is

a highly toxic material whereas oleyl alcohol is not. Butyl acetate and hexane have also some detrimental effects to lactic acid bacteria. Therefore, oleyl alcohol has been suggested as the most suitable diluent for TOMAC to be used in reactive extraction of lactic acid. However, both TOMAC and oleyl alcohol tend to form stable emulsions in conventional mixer-settle extraction system. Therefore, membrane extraction has been suggested by Tong et al. (1998). A microporous hollow fiber membrane was utilized to carry out the continuous extraction of lactic acid (Figure 1.2).

Choudhury has compared the extractants TOA and Aliquat 336 in three different diluents (MIBK, octanol and paraffin liquid) and reported that TOA is a better extractant than Aliquat 336 in all diluents (Choudhury et. al., 1998). It is also reported that while MIBK improves extraction ability of TOA compared to other two diluents, there is no diluent effect on extraction ability of Aliquat 336. This result agrees with the results of Yang and co-workers (Yang et. al., 1991). The toxicity of the extractants and diluents towards lactic acid bacteria has been also examined. It is reported that TOA is a highly toxic material even at low concentrations. The toxicity of Aliquat 336 has not been investigated in this study due to its poor extraction ability, but it had been reported as toxic towards lactic acid bacteria by Tong<sup>1</sup> et al. (1998). The diluents MIBK and octanol have been reported as highly toxic whereas paraffin liquid is not by Choudhury. Since both the molecular level and the phase level toxicities of MIBK are very high, it is not recommended to use in extractive fermentation process. On the other hand, while the phase level toxicity of octanol is high, the molecular level toxicity is low. Therefore, it could be used by utilizing a membrane-based non-dispersive extraction or by an immobilized cell system to eliminate phase level toxicity effect.

Another study for the determination of the toxicity effect of Aliquat 336 (TOMAC) dissolved in 1-octanol towards lactic acid bacteria has been done by Jaquet et. al. (1999). They have studied fermentation with the bacteria *Pseudomonas putida* and reported that there is no inhibition on the growth of the bacteria in the presence of Aliquat 336 and octanol. The counter ion of Aliquat 336, which is chloride, was exchanged with hydrogensulphate ( $\text{HSO}_4^-$ ) by adding sulphuric acid to observe the effect of the counter ion on the growth of the bacteria. It has been reported that the only difference observed is the shift in the lag phase of the bacteria due to the change in pH profile. Both ions have not shown a negative effect on the growth rate or productivity of the bacteria.

The exchange of counter ion of Aliquat 336 from chloride to either hydroxide or hydrogensulphate has also been attempted by Aan (2003). Chloride ion is exchanged to hydroxide by adding sodium hydroxide and to hydrogensulphate by adding sulphuric acid. Since the complete exchange can not be achieved, TOMAOH or TOMAHSO<sub>4</sub> are used as an admixture with TOMAC for reactive extraction of lactic acid. It has been reported that TOMAOH exhibits the highest levels of extraction among the extractants investigated. TOMAHSO<sub>4</sub> also gives higher levels of extraction than TOMAC, but lower than that of TOMAOH.

## **2.5 Back Extraction of Lactic Acid from Organic Phase**

While there have been many investigations on the reactive extraction of lactic acid, few of these are on the recovery of the acid from the organic phase. Studies on the regeneration of organic acids from the organic phase are generally focused on swing processes. During the swing process, a certain factor



-temperature, diluent composition or pH- is altered following the extraction to promote back extraction of the acids into the aqueous phase.

Tamada<sup>3</sup> et. al. (1990) have investigated the temperature and diluent swing processes for lactic and succinic acid as mentioned earlier in Section 2.3. It is reported that temperature swing regeneration for lactic acid is less effective than succinic acid since the extraction of lactic acid by Alamine 336 in MIBK and chloroform does not show a large temperature effect. Prochazka et. al. (1994) have also suggested diluent and temperature swing for recovery and purification of lactic acid from trialkylamine mixtures of 1-octanol/n-heptane since the system is sensitive to both temperature and solvent composition.

A two-stage extractive fermentation process has been developed for the purification and concentration of lactic acid as well as elimination of product inhibition by the removal of the lactic acid (Honda et. al., 1995). Alamine 336 dissolved in oleyl alcohol and oleyl alcohol have been suggested as the extractant and the back extractant, respectively, for extractive fermentation of lactic acid. Since the amine extractants have a toxic effect towards lactic acid bacteria, it should be removed from the fermentation medium after the extraction step. This is achieved by the addition of oleyl alcohol in the second extraction step. Lactic acid is separated from the extractant by the addition of aqueous sodium hydroxide.

Regeneration of lactic acid from Alamine 336/MIBK extract has been achieved by Poole utilizing aqueous trimethylamine (TMA) as a stripping agent (Poole and King, 1991). After the back extraction step, trimethylammonium lactate is formed in aqueous phase. The aqueous solution is heated to remove all

the TMA, leaving behind a concentrated aqueous lactic acid solution. Schematic representation of the process can be seen in Figure 2.5.1.

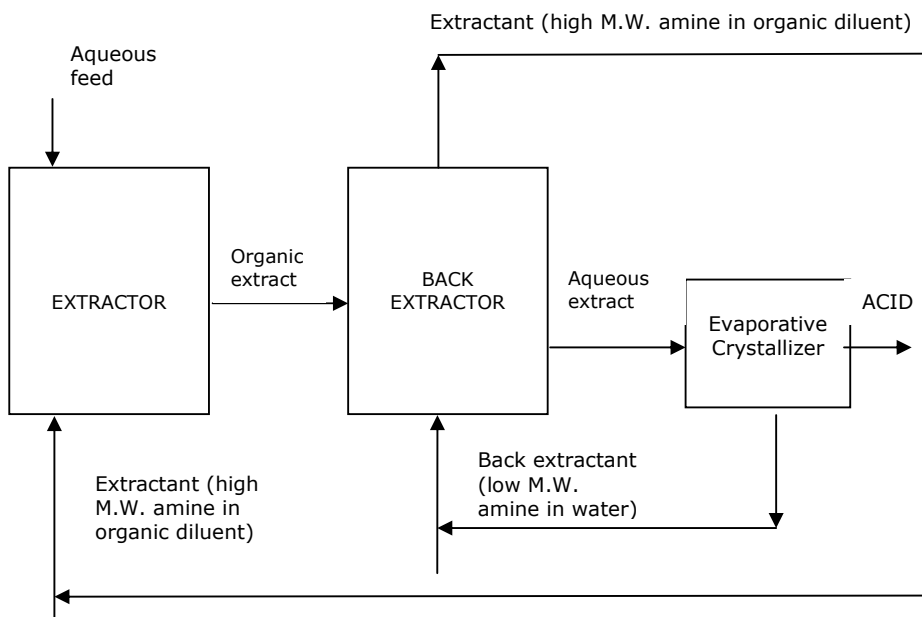
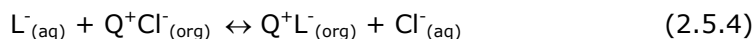


Figure 2.5.1 Recovery of Lactic Acid by Regenerative Extraction Utilizing an Aqueous Solution (Poole and King, 1991)

A microporous hollow fiber unit (Figure 1.2) has been utilized to achieve the integration of back extraction with extractive fermentation for lactic acid production (Tong et. al., 1999). The reactive extraction had been achieved by utilizing TOMAC dissolved in oleyl alcohol (Tong<sup>1</sup> et. al., 1998). Since TOMAC and oleyl alcohol tend to form a stable emulsion, microporous hollow fiber unit had been successfully developed for extractive fermentation of lactic acid (Tong<sup>2</sup> et. al., 1998). In order to integrate back extraction with extractive fermentation, back extraction reagents –inorganic salts- have been investigated from the viewpoint of high stripping power, low cost and capability of simultaneously

regenerating the extractant. Since TOMAC is an anion exchange type extractant, the forward extraction is expected to occur according to reaction:



The counter cation should be removed from TOMA-lactate complex, in order to recover of lactic acid. Therefore, sodium salts of  $Cl^{-}$ ,  $OH^{-}$ ,  $NO_3^{-}$ ,  $SO_4^{2-}$ ,  $CO_3^{2-}$  are examined for their stripping power. The stripping power of the anions has been reported in the following order:  $Cl^{-} > NO_3^{-} > OH^{-} > SO_4^{2-} > CO_3^{2-}$ . Use of chloride ion has the additional advantage of regenerating the extractant TOMAC simultaneously during back extraction. For all these reasons chloride salt of sodium has been selected as the best stripping agent among others. Chloride salt of potassium, ammonium and calcium has been also investigated to observe cation effect on the stripping step. An effect of the cation type has not been detected.

The present study is also focused on the recovery of lactic acid from TOMA-lactate by inorganic sodium salt solutions. The main aim of the study is to determine optimum conditions for the back extraction step for the removal of lactic acid from fermentation medium. Hence wide ranges of concentration of both aqueous and organic phases were examined. Additionally, regeneration of the organic phase with chloride, hydroxide, sulphate, nitrate and carbonate anions was investigated. Octanol was also utilized since it has been reported a better solvent than oleyl alcohol for TOMAC from the viewpoint of good solvating power, a higher distribution coefficient for lactic acid and a lower tendency to form emulsions (Açan, 2003).

## **CHAPTER 3**

### **EXPERIMENTAL**

Extraction equilibrium data were obtained for the parametric values of the following: salt type as the stripping agent, diluent type of the organic phase and the initial concentrations of aqueous and organic phases. Aqueous solutions of inorganic salts were used in back extraction in order to provide the ions required for the ion exchange reaction. Since the back extraction reaction only involves anion exchange, the anions of the salts were considered as a parameter. As the cation, sodium was chosen due to its abundance. The diluent type -oleyl alcohol or octanol- in the organic phase was another parameter. The diluents are used in the organic phase to modify the physical properties of the extractant and to moderate its toxic effect.

Initial concentration of the lactate in either oleyl alcohol or octanol and initial concentration of salts in aqueous phase were other parameters considered. The initial concentration of TOMA(La) in the organic phase was set according to the concentration of TOMA(La) in the organic phase obtained in the forward extraction step (Açan, 2003). The concentration of the aqueous phase was investigated in a large range in order to determine the best conditions. The ranges of parameters studied in this work are reported in Table 3.1.

Table 3.1 Ranges of Parameters Used in the Back Extraction Experiments

Parameter	Range
Organic phase concentration	0.10 – 0.30 M TOMA(La) in diluent
Aqueous phase concentration	0.005 - 3 M sodium salt in water
Type of the salt	Cl <sup>-</sup> , OH <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , NO <sub>3</sub> <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> salts of sodium
Type of diluent	Oleyl alcohol or octanol

Some of the experiments were randomly selected and duplicated in order to check reproducibility. Duplicate measurements differed 1-5 % which was considered to be within reasonable limits.

### 3.1 Equipment

Back extraction experiments were carried out in 100 mL Erlenmeyer flasks which were placed in a temperature-controlled shaking water bath (GFL 1083) for 24 hours at 303 K.

After equilibrium was attained, the phases were separated by filtering via filter paper (Schleicher and Schuell Blue Ribbon filter paper). In some cases, centrifugation was needed because of emulsion formation. These batches were centrifuged at 11000 rpm (17324 rcf) for 30 minutes by Sigma High Speed Laboratory Centrifuge.

An Ion Chromatograph (Dionex DX-100), equipped with a Dionex IonPac AS15 4 mm Column, a conductivity detector and a suppressor, the mobile phase

being 30 mM NaOH solution with a pH of 11.95, flowing at 1.5 mL/min was used for the analysis of the lactate ion in the aqueous phases.

### **3.2 Materials**

The materials used in this study were lactic acid (Merck Co.) which has an analytical purity of 88-92%, Aliquat 336 (TOMAC) (Aldrich) which has a quaternary ammonium chloride content of 88.3%, oleyl alcohol, 1-octanol, NaCl, NaOH, Na<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> (Merck Co.) and deionized water produced by Millipore Milli-Q Water System. All chemicals used in this study were of reagent grade and were used without pretreatment except lactic acid.

### **3.3 Experimental Procedure**

#### 3.3.1 Preparation of the Lactic Acid Solution

Since lactic acid usually self-esterifies or dimerizes in aqueous solutions for concentrations over 20% (w/w) (Holten, 1971), the purchased lactic acid was diluted to approximately 15% (w/w) with deionized water and boiled under reflux for 24 hours. The monomerized lactic acid solution was then analyzed for the lactic acid content by volumetric titration with 0.1 N NaOH solution and was used for forward reactive extraction to obtain TOMA(La) in the organic phase.

#### 3.3.2 Preparation of the Organic Phase for Back Extraction

The organic phase used in back extraction was obtained by reactive extraction of lactic acid from its aqueous solution by tri-n-octylmethyl ammonium chloride (TOMAC) and was composed of tri-n-octylmethyl ammonium lactate (TOMA(La)) dissolved in oleyl alcohol or octanol. To obtain the desired

organic phase, aqueous lactic acid with a known concentration (app. 15% w/w) was stirred with an equal volume of the organic phase containing 1.93 M TOMAC for 24 hours at the ambient temperature. This time is sufficient to achieve equilibrium between phases (Tong, 1999; Aan, 2003). After equilibrium was reached, the solutions were poured into a separatory funnel and allowed to settle for 3 weeks. This time is sufficient to achieve complete separation of the phases. The aqueous phase was diluted and analyzed for the residual lactic acid content. The lactate content of the organic phase was calculated by a mass balance. The organic phase containing tri-n-octylmethyl ammonium lactate was dissolved in oleyl alcohol or octanol to the desired concentration level and was used as the organic phase during back extraction experiments.

### 3.3.3 Preparation of the Aqueous Phase for Back Extraction

The sodium salts were dissolved in deionized water and diluted to desired concentration levels. These solutions were used as the aqueous phase for back extraction experiments.

### 3.3.4 Back Extraction Experiments

Back extraction experiments were carried out by contacting equal volumes (10 mL) of the organic and the aqueous phase in Erlenmeyer flasks, placed in a temperature-controlled shaking water bath for 24 h at 303 K. After equilibration, the phases were separated by filtering via a filter paper. It was measured that the volumes of the phases remains equal after back extraction experiment. For concentration of salts lower than 0.1 M, emulsion formation was observed between the aqueous and the organic phases. These samples were centrifuged at 11000 rpm for 30 minutes. The aqueous phase is diluted and analyzed for

lactic acid content which is transferred from the organic phase and also for the residual anion content.

### 3.3.5 Analytical Method

An ion chromatograph (IC) as described in Section 3.1 is used for the analyses of the aqueous phases for the lactic acid and the anion of the salts.

Analysis were performed in very dilute concentration ranges since the calibration curve becomes non-linear above a certain concentration and the reliability of the measurements decrease.

Calibration curves obtained in this study for lactate, chloride, sulphate and nitrate are given in Figures C.1-2-3-4, respectively, in Appendix C.



## CHAPTER 4

### RESULTS AND DISCUSSION

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

The organic phase, obtained by the reactive extraction of lactic acid from aqueous solution, contains TOMA(La) complex, unreacted TOMAC and the diluent. The aqueous phase is the stripping agent and contains sodium salts.

Known concentrations of organic and aqueous phases were contacted in a constant temperature shaking water bath until equilibrium was achieved. The aqueous phase was filtered, diluted to the desired concentration range and was analyzed for concentration of lactic acid formed and also for the residual anion concentration. One of the methods to quantify the success of extraction is the level of extraction which is defined as:

$$\text{Level of extraction (\%)} = \frac{[LA]_{aq}^*}{[LA]_{org}^0} \times 100 \quad (4.1)$$

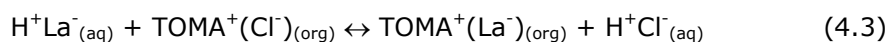
Since the volumes of the organic and the aqueous phases are equal and remain constant during extraction, concentration terms can be used instead of

the number of moles in the mass balance. It is desired to obtain higher values of the level of extraction meaning that more lactate is transferred from the organic phase to the aqueous phase.

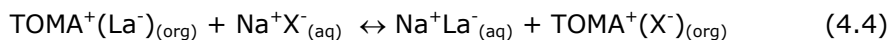
The distribution coefficient,  $K$ , which is defined as the ratio of the equilibrium concentration of lactic acid in the aqueous phase to that in the organic phase for back extraction, is another method to quantify success of extraction. Distribution coefficients for back extraction experiments performed are calculated and tabulated. A higher distribution coefficient indicates a potentially higher level of back extraction.

$$K = \frac{[LA]_{aq}^*}{[LA]_{org}^*} \quad (4.2)$$

The forward extraction of lactic acid from the aqueous phase to the organic phase occurs according to the following reaction:



It is desired to obtain an aqueous solution of the lactate ion which in the organic phase exists as  $TOMA^+(La^-)$  complex. To achieve this, back extraction by a suitable stripping agent is necessary. Inorganic sodium salts ( $NaX$ ) were used as stripping agents. The reaction for back extraction can be written as follows:



#### **4.1 Kinetic Studies on Back Extraction of Lactic Acid from TOMA(La) dissolved in Oleyl Alcohol**

Preliminary experiments were performed to determine the time required to attain equilibrium for back extraction of lactic acid from TOMA(La) dissolved in

oleyl alcohol. For this purpose, 0.2 M TOMA(La) dissolved in oleyl alcohol was shaken with equal volumes of either 0.8 M NaCl or 0.8 M NaOH in flasks for varying amounts of time at 303 K. The data are reported in Tables B.6.1 and B.6.2 in Appendix B. As can be seen from Figure 4.1.1, equilibrium is attained in 3 hours when NaCl is used as the back extractant and in 6 hours when NaOH is used as the back extractant. Further back extraction experiments were carried out for 24 hours to make sure that equilibration is achieved. Since ionic reactions occur very fast, the extraction process should be mass transfer controlled. Mass transfer rate was calculated as 0.050 mol/h when the back extractant is NaCl and 0.024 mol/h when the back extractant is NaOH to attain equilibrium.

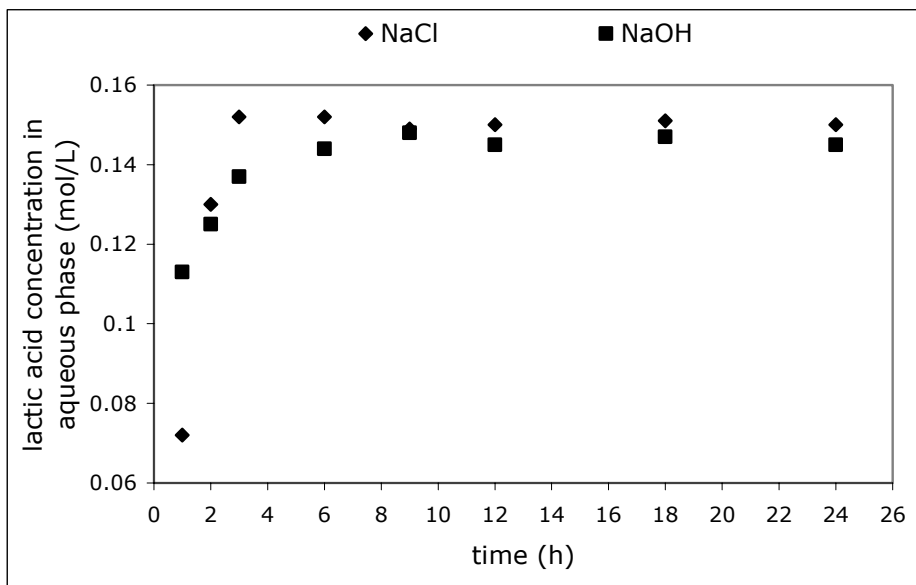


Figure 4.1.1 Variation of the Concentration of Lactic Acid in Aqueous Phase with Time for the Back Extraction of Lactic Acid from TOMA(La) Dissolved in Oleyl Alcohol

## 4.2 Determination of the Initial Concentration of Back Extractants

TOMA(La) solutions were prepared at 0.10 M, 0.15 M, 0.20 M, and 0.30 M concentrations in either oleyl alcohol or octanol. The range of concentrations for the complex in the organic phase was determined based on forward extraction results of Aan (Aan, 2003). The initial NaX concentrations were kept in the range 0.005 M and 3 M. The concentration ranges used for each salt are presented in Table 4.1. Experiments were performed at 303 K without pH control.

Table 4.1 Concentration Ranges of Each Salt Used in Back Extraction Experiments

TOMA(La) concentration in organic phase (M)	Initial concentration of salt in aqueous phase (M)				
	NaCl	NaOH	Na <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>
<i>Diluent: oleyl alcohol</i>					
0.10	0.05 – 3	0.05 – 3	0.2 – 1.5	-	-
0.20	0.2 – 3	0.2 – 3	0.2 – 1.5	-	-
0.30	0.2 – 3	0.2 – 3	0.2 – 1.5	-	-
<i>Diluent: octanol</i>					
0.10	0.2 – 3	0.2 – 3	0.2 – 1.5	-	-
0.15	0.2 – 3	0.2 – 3	0.2 – 1.5	0.2 – 3	0.2 – 3
0.20	0.005 – 3	0.005 – 3	0.2 – 1.5	-	-
0.30	0.2 – 3	0.2 – 3	0.2 – 1.5	0.2 – 3	0.2 – 3

In the earlier phases of the study, both low and high concentrations (0.005, 0.01, 0.05, 0.01, 0.1 and 0.2 M) of NaCl and NaOH as well as pure deionized water were attempted to be utilized as the stripping agent for back extraction of lactic acid. It has been observed that there is a tendency of emulsion formation that can not be eliminated without centrifugation when

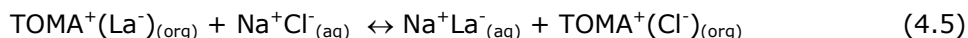
deionized water and concentrations of salts lower than 0.1 M were used as the stripping agent. Additionally, a general trend of increasing level of back extraction with an increase in the concentration of the stripping agent was observed (see Tables B.1.1-2, B.2.1-2 in Appendix B). Hence, the lower limit of concentration of the salt in aqueous phase was set for most cases at 0.2 M.

Back extraction of lactic acid from the organic phase by aqueous NaX solutions was investigated for two different diluents: oleyl alcohol and octanol. Since octanol was observed to be a better diluent than oleyl alcohol due to its higher solvating power, lower viscosity and easier phase separation after extraction, investigations with octanol have been done more extensively. This is in accordance with the strategy of Aan (Aan, 2003).

Experimental data were utilized to calculate the level of extraction and the equilibrium distribution coefficients with Equation 4.1 and 4.2, respectively. These are reported in Appendix B.

#### **4.3 Back Extraction Results with Sodium Chloride Solutions**

Back extraction of lactic acid by aqueous NaCl solutions is expected to take place according to:



This reaction regenerates the forward extractant TOMAC in the organic phase and transfers lactate to the aqueous phase.

It can be seen from the Figure 4.3.1 that level of back extraction of lactate from TOMA(La) dissolved in oleyl alcohol increases with NaCl concentration in

the aqueous phase and decreases with lactate concentration in the organic phase. The same trend is also observed for TOMA(La) dissolved in octanol (Figure 4.3.2). Tong has also observed such a trend for recovery of lactic acid with sodium salts such as chloride, hydroxide, nitrate, sulphate and carbonate at 0.18 M TOMA(La) dissolved in oleyl alcohol (Tong et. al.,1999). In the present study, the level of back extraction with octanol is higher than with oleyl alcohol. It is possible to obtain complete recovery of lactate at 0.1 and 0.15 M TOMA(La) dissolved in octanol for aqueous NaCl concentrations higher than 0.8 M while the maximum level of back extraction obtained for lactate dissolved in oleyl alcohol is 90%. Tong et. al. (1999) have reported that the maximum level of back extraction is about 95% for 0.18 M TOMA(La) in oleyl alcohol at 298 K. It can be said that utilizing octanol as a diluent instead of oleyl alcohol promotes the stripping of lactate from the organic phase to the aqueous NaCl solution. It has also been reported that a higher level of extraction is obtained for TOMAC dissolved in octanol rather than in oleyl alcohol (Açan, 2003). Octanol is also reported as a better solvent for acid-amine complex than oleyl alcohol and no emulsion formation is observed during forward extraction in contrast to oleyl alcohol. These properties make the extractant with octanol a better performer than with oleyl alcohol. The decreasing values of the level of back extraction with higher TOMA(La) concentration should be due to an insufficient amount of the chloride anion in the aqueous phase to exchange with the lactate ion.

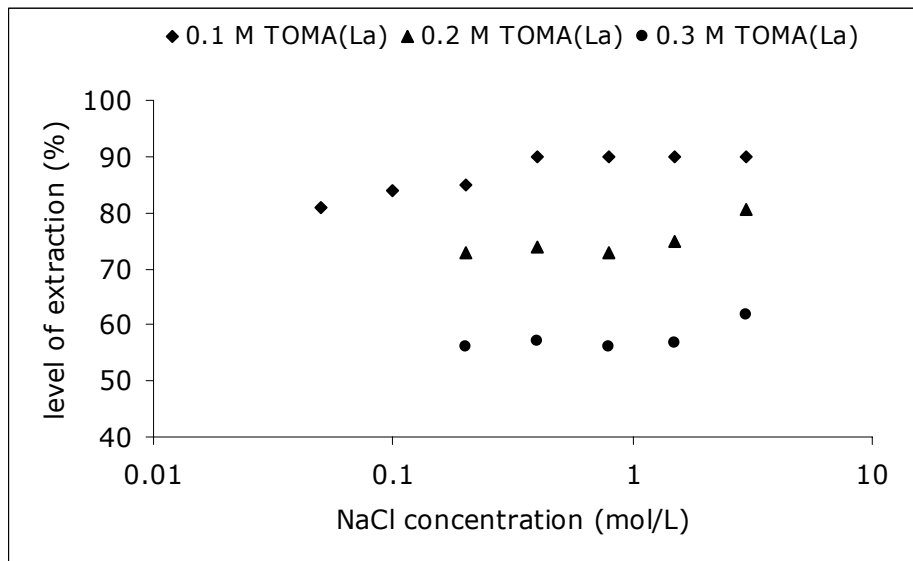


Figure 4.3.1 Variation of Level of Back Extraction with Initial Concentration of Aqueous NaCl for TOMA(La) Dissolved in Oleyl Alcohol

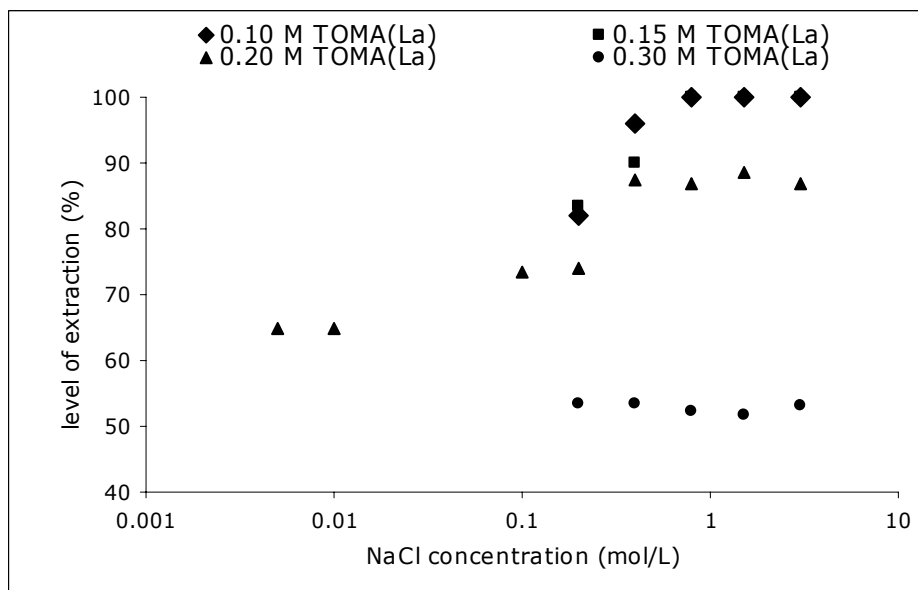


Figure 4.3.2 Variation of Level of Back Extraction with Initial Concentration of Aqueous NaCl for TOMA(LA) Dissolved in Octanol

Equilibrium isotherms for back extraction of lactate for TOMA(La) dissolved in oleyl alcohol and octanol for various concentrations of aqueous NaCl are plotted in Figures 4.3.3 and 4.3.4, respectively. It is observed that there is a leveling of the lactic acid concentration in the aqueous phase for higher values of the lactic acid concentration in the organic phase. Due to solubility limitations, NaCl concentration in the aqueous phase higher than 3 M can not be utilized as a stripping agent. Aqueous equilibrium concentrations of lactic acid also increases with NaCl concentration when octanol is utilized as the diluent. However, the leveling of the equilibrium concentrations is much sooner with NaCl concentration in this case. Isotherms for 0.8 M, 1.5 M and 3 M NaCl are nearly the same. Thus, there is no real advantage in using NaCl concentrations larger than 0.8 M.

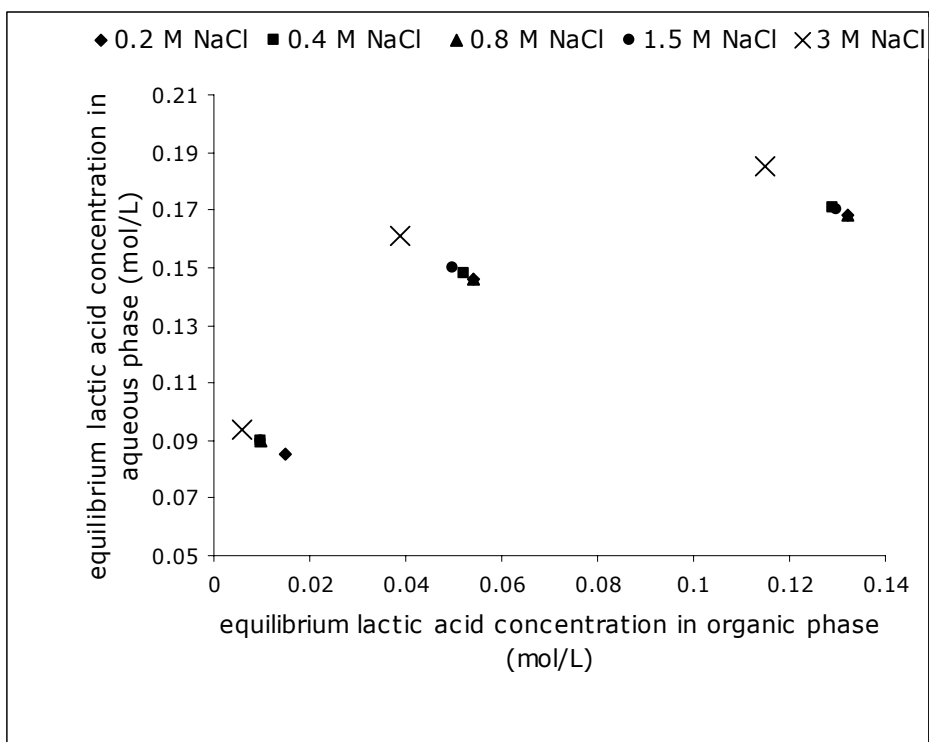


Figure 4.3.3 Equilibrium Isotherms for Back Extraction of Lactate at 303 K (TOMA(La) Dissolved in Oleyl Alcohol; Aqueous NaCl Solution )



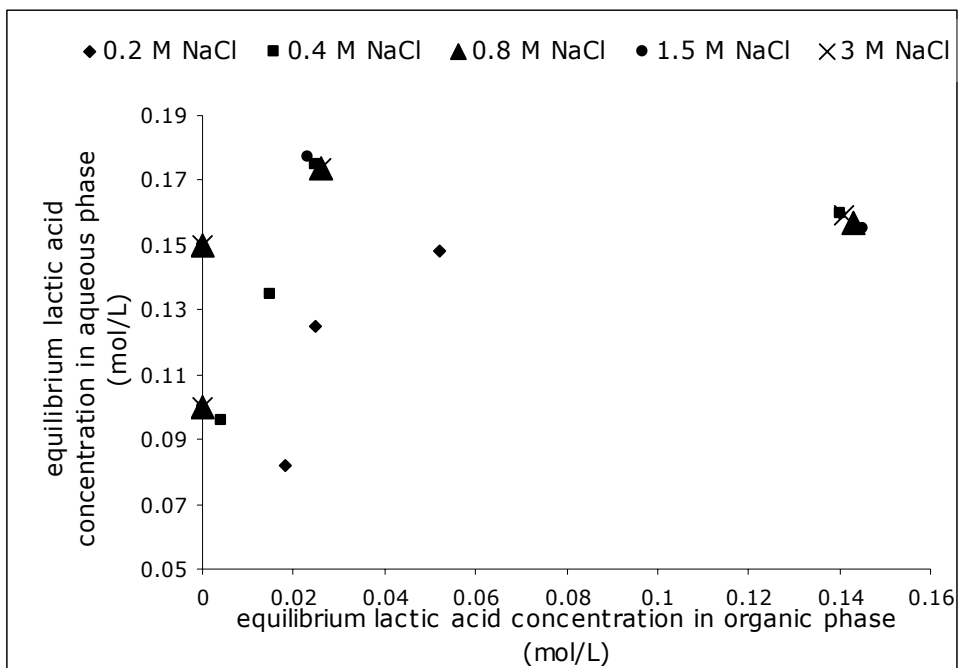
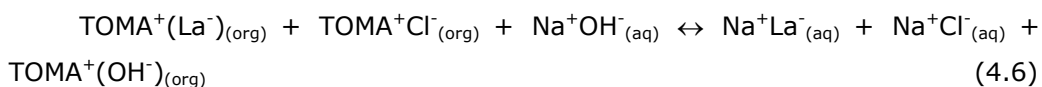


Figure 4.3.4 Equilibrium Isotherms for Back Extraction of Lactate at 303 K (TOMA(La) Dissolved in Octanol; Aqueous NaCl Solution )

#### 4.4 Back Extraction Results with Sodium Hydroxide Solutions

Back extraction of lactic acid by aqueous NaOH solution is expected to take place according to:



This reaction regenerates TOMA<sup>+</sup>OH<sup>-</sup> and may convert some TOMAC to TOMA<sup>+</sup>OH<sup>-</sup> in the organic phase and transfers lactate to the aqueous phase.

As can be seen from the Figures 4.4.1 and 4.4.2, the increase with increasing NaOH concentration in the aqueous phase and the decrease with increasing lactate concentration in the organic phase were again observed for the level of back extraction. On the other hand, values of the level of back

extraction for NaOH are quite different compared to those obtained for NaCl. The recovery of lactate achieved is generally higher with NaCl compared to NaOH at lower concentrations (0.10 and 0.15 M) of TOMA(La) and lower at higher concentrations (0.20 and 0.30 M) of TOMA(La) in the organic phase. Tong et. al. (1999) has reported that stripping capacity of chloride is greater than that of hydroxide at 0.18 M TOMA(La) dissolved in oleyl alcohol. It is observed that with NaOH, octanol as a diluent yields higher levels of back extraction than oleyl alcohol as a diluent does except at 0.1 M TOMA(La). Results with octanol deserve much more attention, since it has been reported as a better diluent than oleyl alcohol as has been already indicated earlier in section 4.2 (Açan, 2003). Additionally, TOMAOH has been reported as a better extractant for lactate from the aqueous phases. It yields higher levels of extraction than TOMAC and TOMAHSO<sub>4</sub>. Also, it has no adverse effect on the fermentation broth since the transfer of counter ion OH<sup>-</sup> into aqueous phase results in the formation of water. Hence, NaOH should be preferred to NaCl as a back extractant, even though it is more expensive, to regenerate TOMAOH in the organic phase.

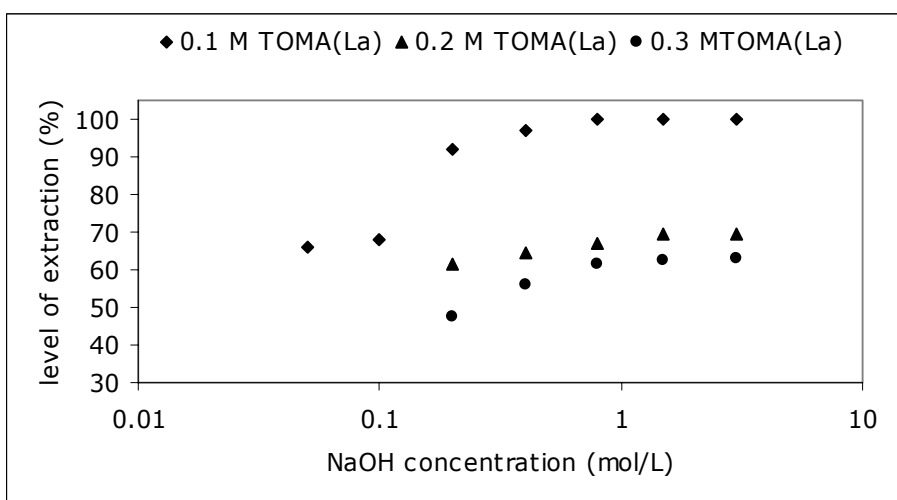


Figure 4.4.1 Variation of Level of Back Extraction with Initial Concentration of Aqueous NaOH for TOMA(La) Complex Dissolved in Oleyl Alcohol

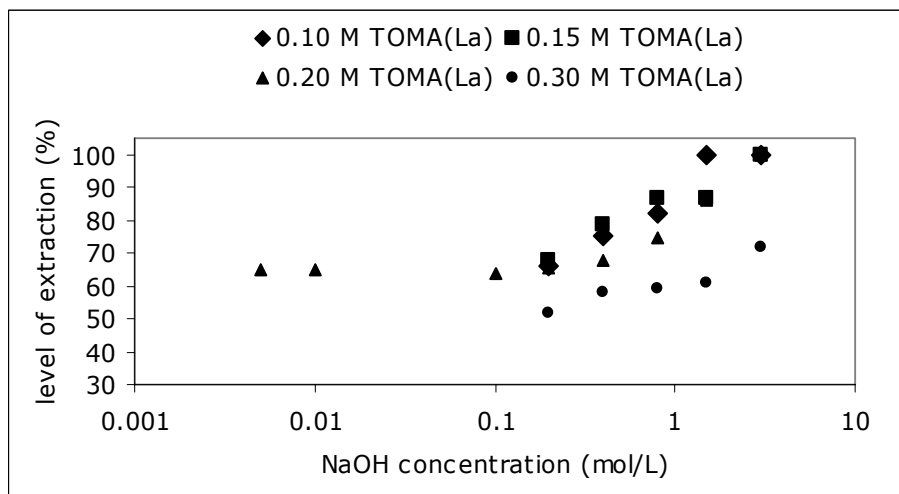
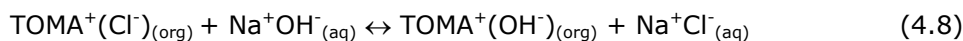
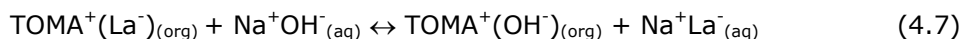


Figure 4.4.2 Variation of Level of Back Extraction with Initial Concentration of Aqueous NaOH for TOMA(La) Complex Dissolved in Octanol

During the analysis of the aqueous phase following back extraction, chloride ion was detected in addition to lactate when NaOH was used as the back extractant. Chloride concentrations in the aqueous phase after back extraction are tabulated in Tables B.2.1-2 in Appendix B. The existence of chloride ion is due to the presence of unconverted TOMAC during the forward extraction step. Unconverted TOMAC in the organic phase goes into reaction with stripping agent, resulting in an extra consumption of NaOH, during back extraction as explained also by Tong et. al. (1999). On the other hand, due to reaction 4.6, NaCl accompanies NaOH during back extraction as a stripping agent. The phenomenon may be better explained by considering reaction 4.6 in two steps:



Equilibrium isotherms at 303 K for back extraction of lactate for TOMA(La) dissolved in oleyl alcohol and octanol for various concentrations of aqueous NaOH are plotted in Figures 4.4.3 and 4.4.4. When oleyl alcohol is the diluent, the isotherms for 1.5 M and 3 M NaOH are nearly the same, therefore there is no advantage in utilizing NaOH solutions more concentrated than 1.5 M. Complete extraction of lactate is achieved for TOMA(La) dissolved in oleyl alcohol only at 0.1 M TOMA(LA) with 1.5 M and 3 M NaOH, while it is achieved for TOMA(La) dissolved in octanol at all organic phase concentrations investigated with 3 M NaOH in addition to that for 0.1 M TOMA(La) with 1.5 M NaOH (Figures 4.4.1 – 2). Tong et. al. (1999) has reported a maximum recovery of 90% with NaOH at 0.18 M TOMA(La) in oleyl alcohol. It can be concluded again that the use of octanol as a diluent instead of oleyl alcohol promotes the back extraction of lactate from TOMA(La) complex.

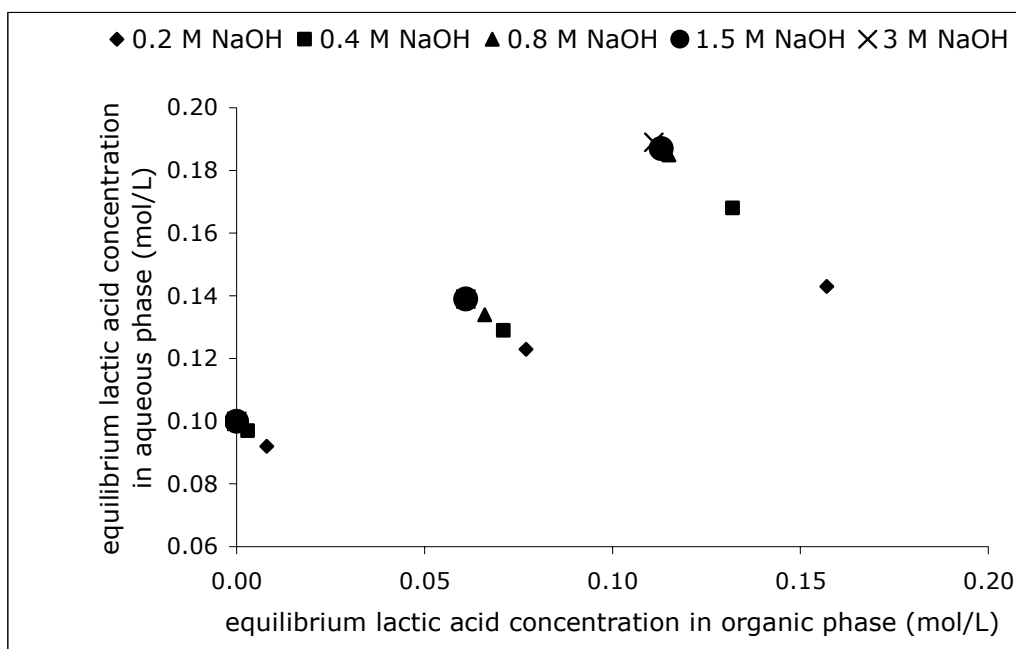


Figure 4.4.3 Equilibrium Isotherms for Back Extraction of Lactate at 303 K (TOMA(La) Dissolved in Oleyl Alcohol; NaOH Aqueous Solution)

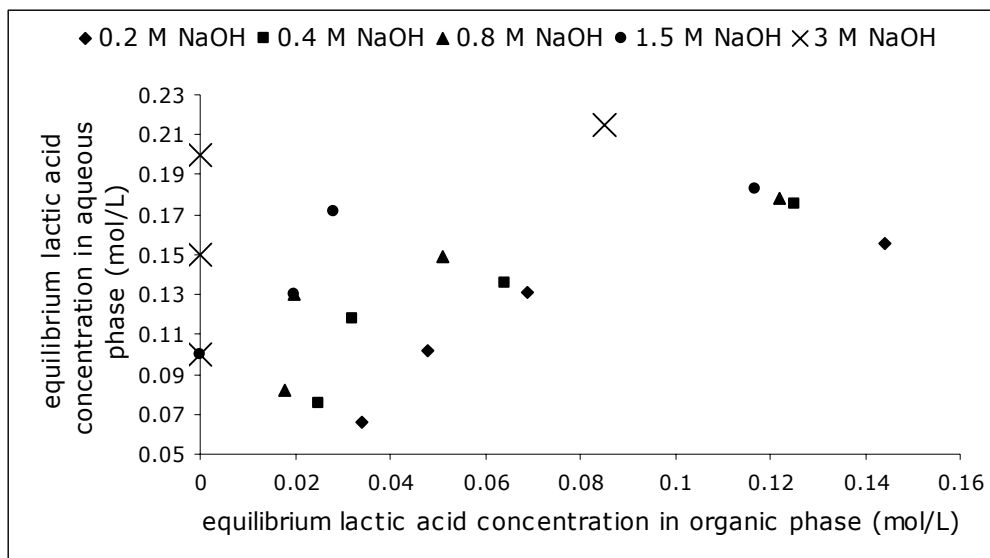


Figure 4.4.4 Equilibrium Isotherms for Back Extraction of Lactate at 303 K (TOMA(La) Dissolved in Octanol; NaOH Aqueous Solution)

#### 4.5 Back Extraction Results with Sodium Sulphate Solutions

In this part of the study, aqueous  $\text{Na}_2\text{SO}_4$  was utilized as the back extractant for recovery of lactic acid from organic solutions of TOMA(La) complex.

As can be seen from the Figures 4.5.1 and 4.5.2, there is no consistent trend for levels of back extraction with initial concentration of aqueous  $\text{Na}_2\text{SO}_4$  in contrast to the case with NaCl and NaOH. When oleyl alcohol is the diluent, level of back extraction with initial salt concentration increases at 0.1 M initial TOMA(La) concentration whereas it surprisingly decreases at 0.2 M initial TOMA(La) concentration and remains nearly constant at 0.3 M initial TOMA(La) concentration. Tong et. al. (1999) have observed increasing trend for level of back extraction with initial salt concentration and obtained 70% level of back extraction as similar to present study. When octanol is the diluent, an obvious

trend for a change in the level of back extraction with a change in the initial aqueous phase concentration is not observable. Level of extraction values obtained with  $\text{Na}_2\text{SO}_4$  lie in a narrower range than those with  $\text{NaCl}$  and  $\text{NaOH}$ . The results of the  $\text{Na}_2\text{SO}_4$  experiments are reported in Tables B.3.1 and B.3.2 in Appendix B.

The recovery of lactic acid achieved with  $\text{Na}_2\text{SO}_4$ , like the case with  $\text{NaCl}$  and  $\text{NaOH}$ , tends to decrease with decreasing initial concentration of lactate in the organic phase. Similar to the earlier cases, decreasing values of the level of back extraction obtained with higher TOMA(La) concentration should be due to an insufficient amount of sulphate anion in the aqueous phase.

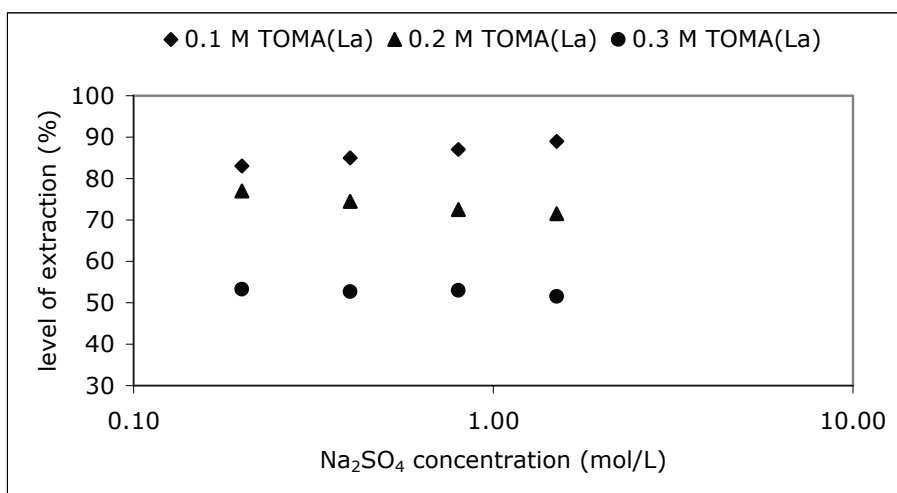


Figure 4.5.1 Variation of Level of Back Extraction with Initial Concentration of Aqueous  $\text{Na}_2\text{SO}_4$  for TOMA(La) Complex Dissolved in Oleyl Alcohol

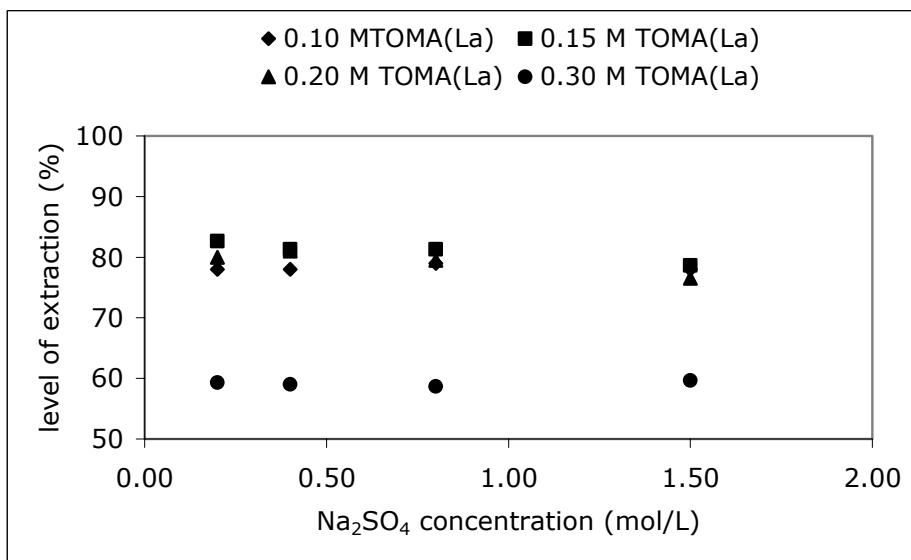
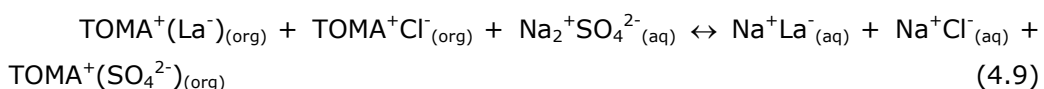


Figure 4.5.2 Variation of Level of Back Extraction with Initial Concentration of Aqueous Na<sub>2</sub>SO<sub>4</sub> for TOMA(La) Complex Dissolved in Octanol

Equilibrium isotherms at 303 K for back extraction of lactate for TOMA(La) dissolved in oleyl alcohol and octanol for various concentrations of aqueous Na<sub>2</sub>SO<sub>4</sub> are plotted in Figures 4.5.3 and 4.5.4, respectively. Data could not be obtained for Na<sub>2</sub>SO<sub>4</sub> larger than 1.5 M, due to solubility limitations. Obviously the isotherm is not sensitive to the initial concentration of the salt in the aqueous phase.

The reaction for the back extraction of lactic acid by Na<sub>2</sub>SO<sub>4</sub> solution is expected to take place according to:



This reaction allows us to regenerate the forward extractant TOMA(SO<sub>4</sub>) in the organic phase as well as to obtain lactic acid in the aqueous phase. An earlier study on TOMASO<sub>4</sub> as an extractant could not be found in the literature. Also TOMASO<sub>4</sub> solution is not commercially available. Ağan has attempted to obtain

TOMASO<sub>4</sub> by contacting H<sub>2</sub>SO<sub>4</sub> with pure TOMAC (Açan, 2003). However, HSO<sub>4</sub><sup>-</sup> has been detected during the analysis. Hence, TOMAHSO<sub>4</sub> was obtained instead of TOMASO<sub>4</sub>. On the other hand, chloride ion was detected in the present study during the analysis of the aqueous phase after back extraction of lactic acid with Na<sub>2</sub>SO<sub>4</sub>. The concentration of chloride determined are reported in Tables B.3.1-2 in Appendix B. This is the evidence of the following reaction:



It is seen from the reaction 4.10 that it is possible to obtain TOMASO<sub>4</sub> complex in the organic phase.

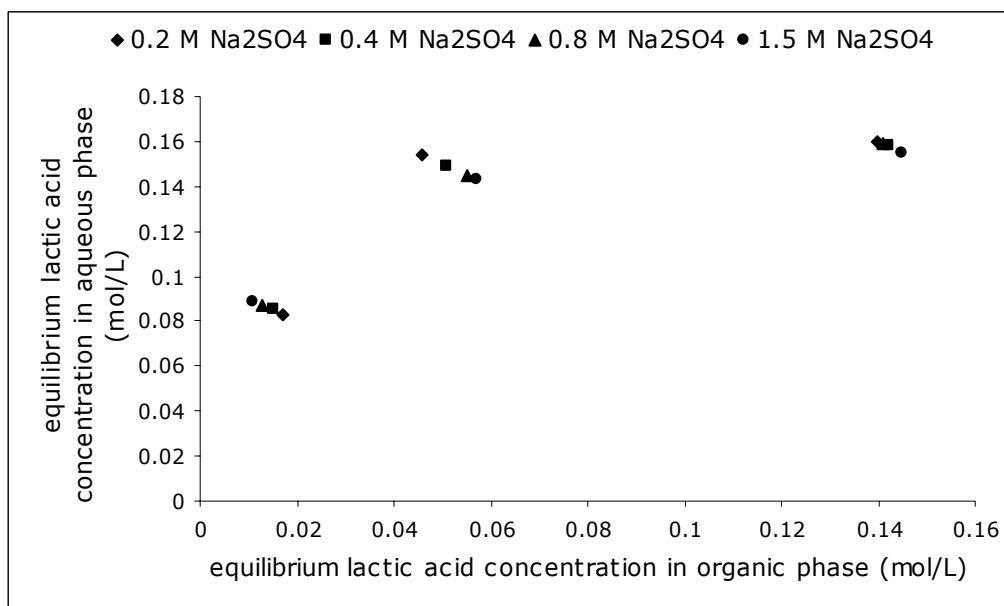


Figure 4.5.3 Equilibrium Isotherms for Back Extraction of Lactate at 303 K (TOMA(La) Dissolved in Oleyl Alcohol; Aqueous Na<sub>2</sub>SO<sub>4</sub> Solution )



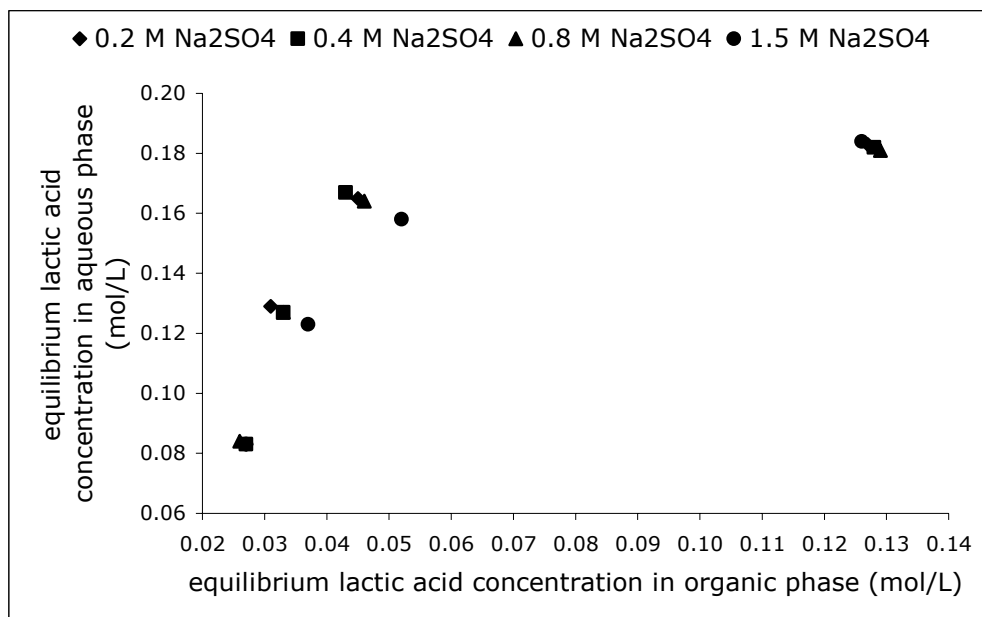


Figure 4.5.4 Equilibrium Isotherms for Back Extraction of Lactate at 303 K (TOMA(La) Dissolved in Octanol; Aqueous Na<sub>2</sub>SO<sub>4</sub> Solution )

It deserves reporting that emulsion formation between the phases was not observed when aqueous Na<sub>2</sub>SO<sub>4</sub> was utilized as a back extractant. However, this does not make Na<sub>2</sub>SO<sub>4</sub> a serious competitor to NaOH as a back extractant of lactate from TOMA(La) dissolved in octanol, since the levels of back extraction obtained with Na<sub>2</sub>SO<sub>4</sub> are significantly lower than that with NaOH.

#### 4.6 Back Extraction Results with Sodium Nitrate and Sodium Carbonate Solutions

Aqueous solutions of NaNO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> were also utilized to recover lactate from TOMA(La) dissolved in octanol. Results of the experiments are reported in Table B.2.4 for NaNO<sub>3</sub> and Table B.2.5 for Na<sub>2</sub>CO<sub>3</sub>. As can be seen from Figures 4.6.1 and 4.6.2 significant levels of extraction were obtained for these salts. However, the levels are much lower than these obtained for other

salts. As expected the levels of extraction for both salts decrease with the initial concentration of TOMA(La) in the organic phase.

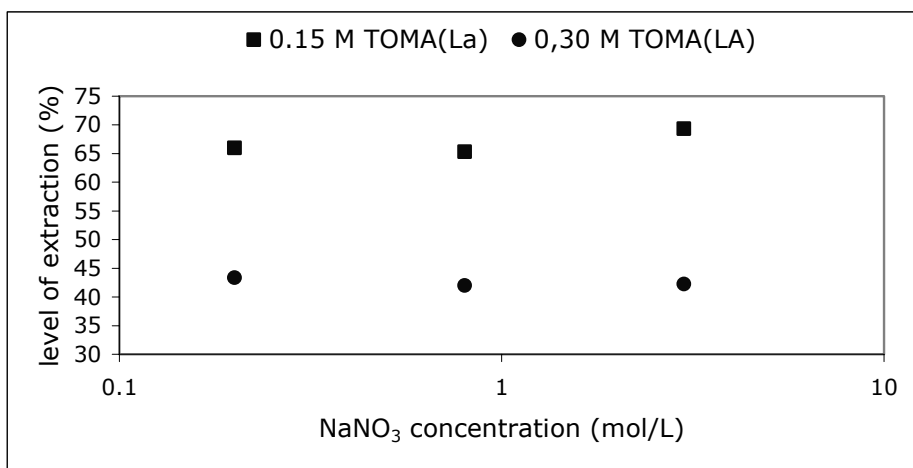


Figure 4.6.1 Variation of the Level of Back Extraction with Initial Concentration of Aqueous NaNO<sub>3</sub> for TOMA(La) Dissolved in Octanol

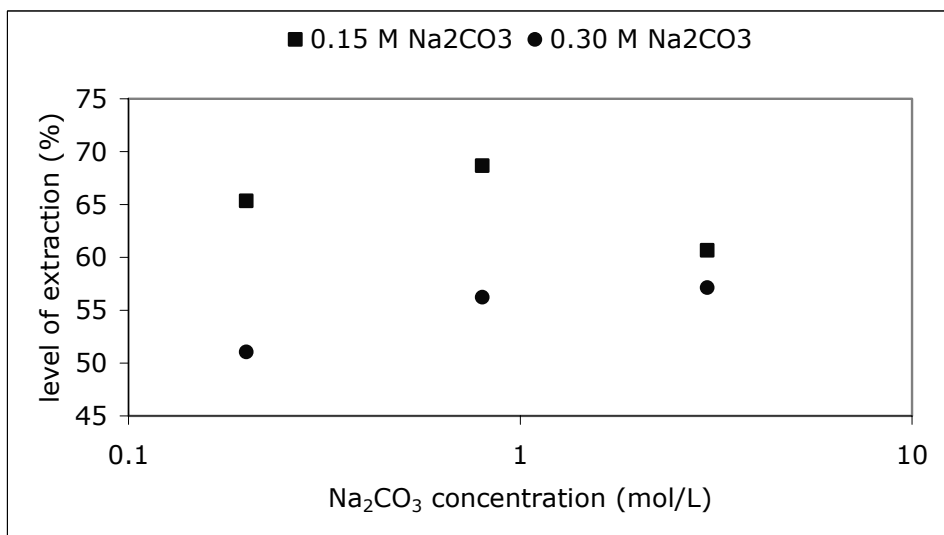


Figure 4.6.2 Variation of the Level of Back Extraction with Initial Concentration of Aqueous Na<sub>2</sub>CO<sub>3</sub> for TOMA(La) Dissolved in Octanol

#### 4.7 Equilibrium Distribution Coefficients with Respect to Salt Type

Variation of the equilibrium distribution coefficient of lactate with the equilibrium lactic acid concentration in the aqueous phase for all experiments are tabulated in Appendix B Tables B.1.1-2 when NaCl is used as the back extractant, Tables B.2.1-2 when NaOH is used as the back extractant, Tables B.3.1-2 when Na<sub>2</sub>SO<sub>4</sub> is used as the back extractant, Table B.4.1 when NaNO<sub>3</sub> is used as the back extractant and Table B.5.1 when Na<sub>2</sub>CO<sub>3</sub> is used as the back extractant. The data are plotted in the following figures.

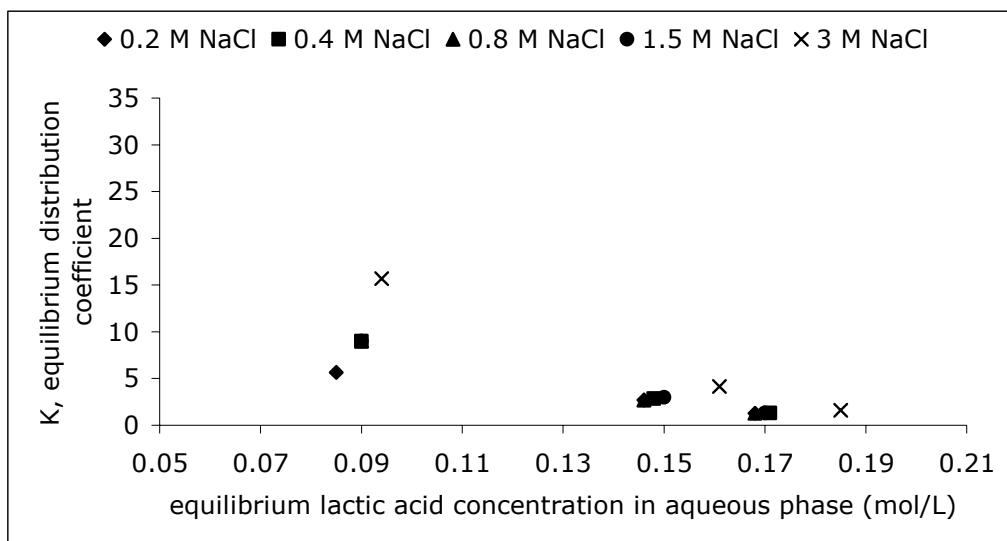


Figure 4.7.1 Variation of the Equilibrium Distribution Coefficient of Lactate with Equilibrium Lactic Acid Concentration in the Aqueous Phase for Equilibria between Oleyl Alcohol and Aqueous NaCl at 303 K

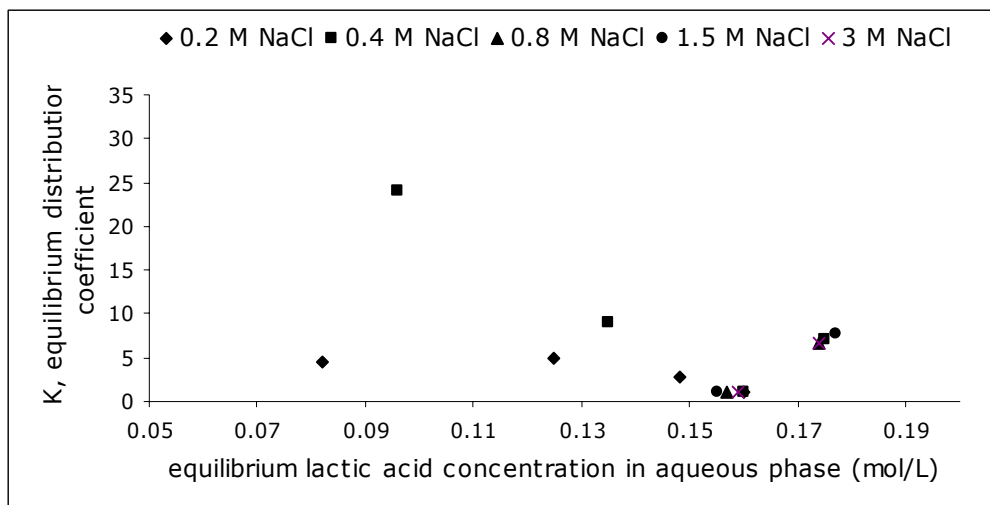


Figure 4.7.2 Variation of the Equilibrium Distribution Coefficient of Lactate with Equilibrium Lactic Acid Concentration in the Aqueous Phase for Equilibria between Octanol and Aqueous NaCl at 303 K

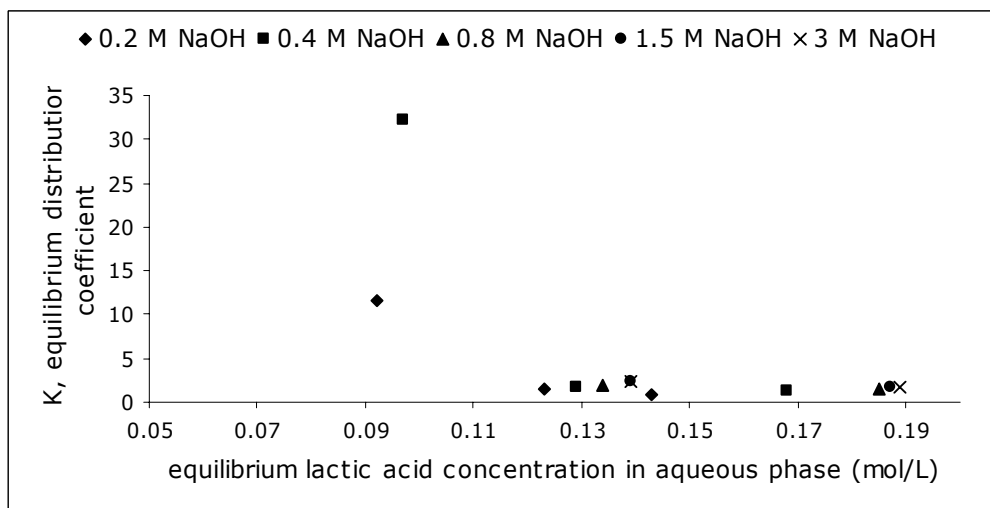


Figure 4.7.3 Variation of the Equilibrium Distribution Coefficient of Lactate with Equilibrium Lactic Acid Concentration in the Aqueous Phase for Equilibria between Oleyl Alcohol and Aqueous NaOH at 303 K

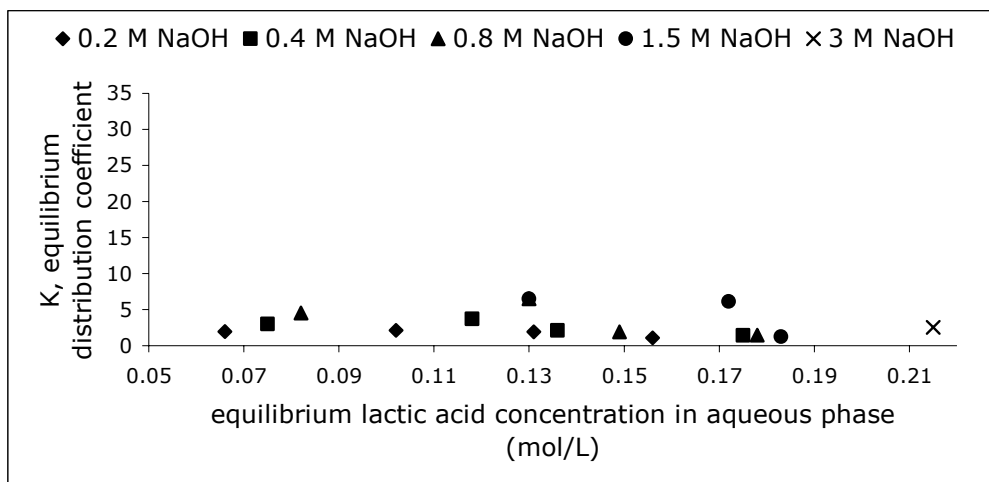


Figure 4.7.4 Variation of the Equilibrium Distribution Coefficient of Lactate with Equilibrium Lactic Acid Concentration in the Aqueous Phase for Equilibria between Octanol and Aqueous NaOH at 303 K

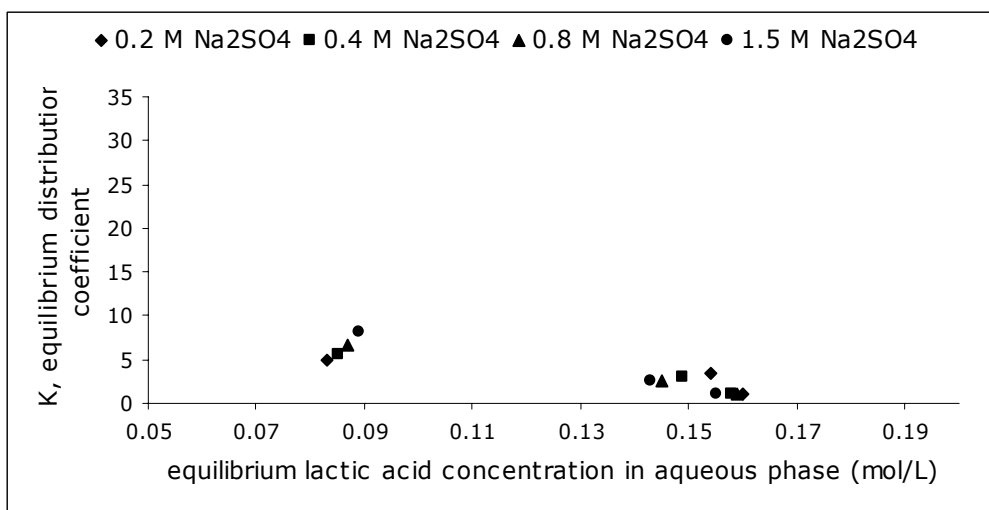


Figure 4.7.5 Variation of the Equilibrium Distribution Coefficient of Lactate with Equilibrium Lactic Acid Concentration in the Aqueous Phase for Equilibria between Oleyl Alcohol and Aqueous  $\text{Na}_2\text{SO}_4$  at 303 K

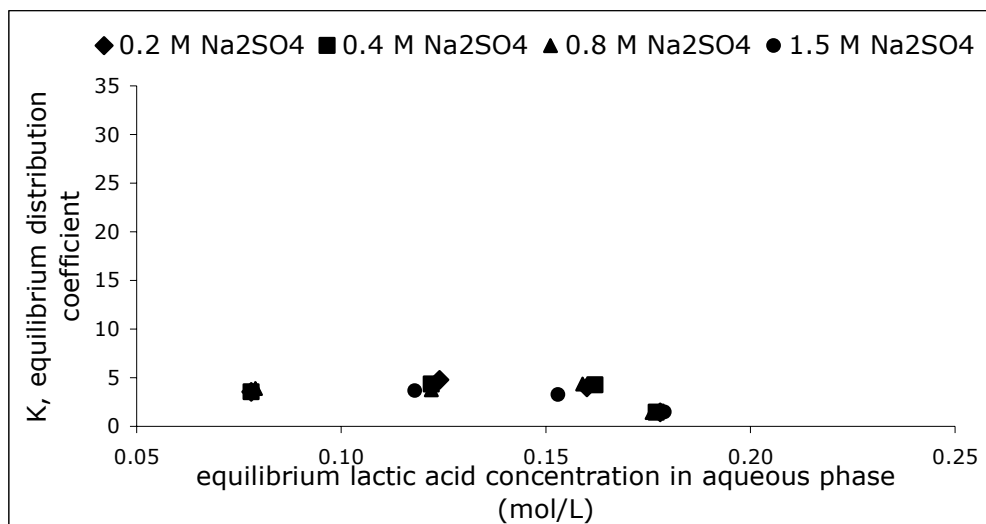


Figure 4.7.6 Variation of the Equilibrium Distribution Coefficient of Lactate with Equilibrium Lactic Acid Concentration in the Aqueous Phase for Equilibria between Octanol and Aqueous Na<sub>2</sub>SO<sub>4</sub> at 303 K

The maximum value of the equilibrium distribution coefficient that could be reported on the figures was 32.4 for back extraction of lactic acid from 0.1 M TOMA(La) in oleyl alcohol with 0.4 M NaOH. On the other hand, the value of the equilibrium distribution coefficient for 0.10 M and 0.15 M TOMA(La) in octanol with aqueous NaCl concentrations higher than 0.8 M (Figure 4.7.2); for 0.1 M TOMA(La) dissolved in oleyl alcohol with aqueous NaOH concentration higher than 0.8 M (Figure 4.7.3); for 0.1 M and 0.15 M TOMA(La) in octanol with aqueous concentration of NaOH 3 M (Figure 4.7.4) go to infinity, since complete recovery is achieved. These can not be shown on the figures.

In order to compare the back extraction performance of the salts investigated, equilibrium distribution coefficient for back extraction of lactic acid from 0.2 M and 0.3 M TOMA(La) in either oleyl alcohol or octanol are plotted in Figures 4.7.7-8-9 and 10. As can be seen from the Figures for 0.2 M TOMA(La)

in octanol, NaCl gives the best equilibrium distribution coefficients for all initial salt concentrations except the case of complete recovery with 3 M. NaOH gives better equilibrium distribution coefficients for back extraction from 0.3 M TOMA(La) in octanol. NaOH has an additional advantage of regenerating TOMAOH in the organic phase as described in Section 4.4. TOMAOH has been reported as a better extractant for lactic acid from organic phases than TOMAC (Açan, 2003). Recovery of lactic acid was also achieved with aqueous  $\text{NaNO}_3$  and  $\text{Na}_2\text{CO}_3$ , however, equilibrium distribution coefficients obtained were much lower (i.e. max. 2.26 for  $\text{NaNO}_3$  and 2.19 for  $\text{Na}_2\text{CO}_3$ ) compared to other salts investigated.

Higher equilibrium distribution coefficients are observed for back extraction of lactic acid from TOMA(La) in octanol rather than oleyl alcohol. Other advantages on using octanol as the diluent have been already discussed in Section 4.3.

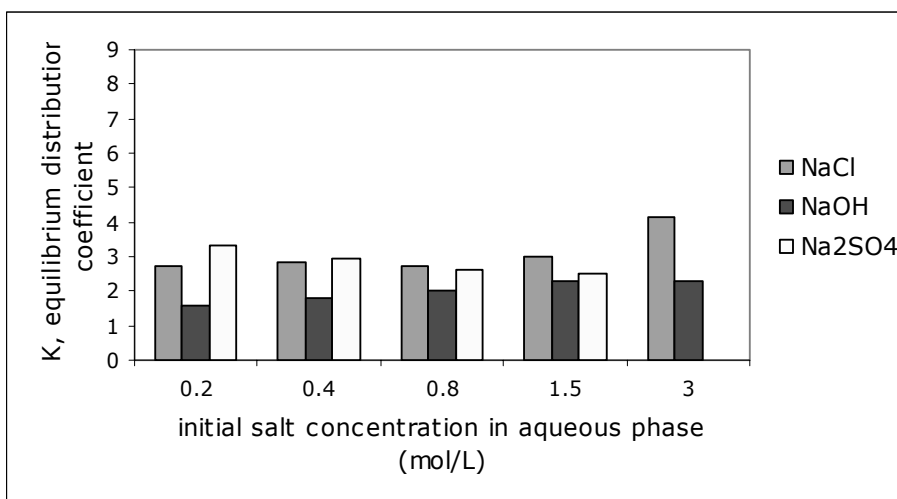


Figure 4.7.7 Variation of Equilibrium Distribution Coefficients of Lactate at 303 K for Back Extraction of Lactic Acid from 0.2 M TOMA(La) Dissolved in Oleyl Alcohol

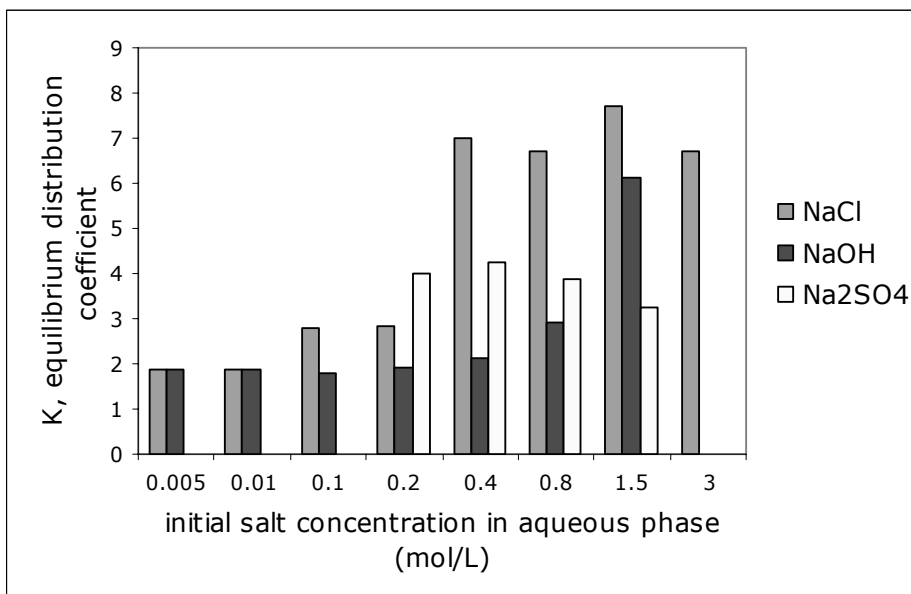


Figure 4.7.8 Variation of Equilibrium Distribution Coefficients of Lactate at 303 K for Back Extraction of Lactic Acid from 0.2 M TOMA(La) Dissolved in Octanol

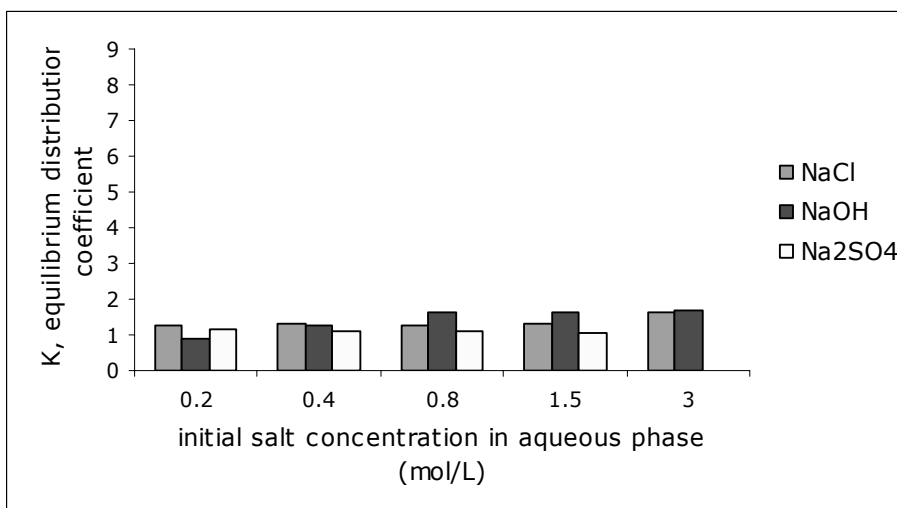


Figure 4.7.9 Variation of Equilibrium Distribution Coefficients of Lactate at 303 K for Back Extraction of Lactic Acid from 0.3 M TOMA(La) Dissolved in Oleyl Alcohol



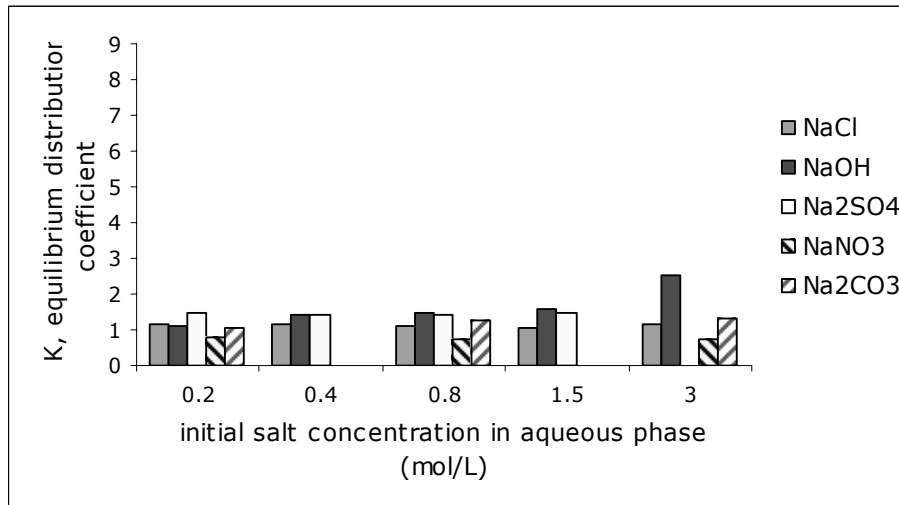


Figure 4.7.10 Variation of Equilibrium Distribution Coefficients of Lactate at 30°C  
 K for Back Extraction of Lactic Acid from 0.3 M TOMA(La) Dissolved in Octanol

## CHAPTER 5

### CONCLUSIONS AND RECOMMENDATIONS

Equilibrium investigations on back extraction of lactic acid from organic phases have been carried out by contacting an organic phase containing TOMA(La) dissolved in either oleyl alcohol or octanol and an aqueous phase containing sodium salts of chloride, hydroxide, sulphate, nitrate or carbonate.

The results of the experiments have been discussed in Chapter 4. According to these results and discussion the following conclusions have done:

- Complete recovery of lactic acid from the organic phase, which means irreversible transfer of lactate from quaternary amine lactate complex to sodium lactate salt, is achieved for initial concentrations specified in Table 5.1.

Table 5.1 Initial Concentrations of Species for which Complete Recovery is Achieved by Back Extraction

<b>Organic Phase</b>	<b>Aqueous Phase</b>
0.10 M TOMA(La) in oleyl alcohol	0.8, 1.5, 3 M NaOH
0.10 M TOMA(La) in octanol	0.8, 1.5, 3 M NaCl 1.5, 3 M NaOH

Table 5.1 (cont.)

0.15 M TOMA(La) in octanol	0.8, 1.5, 3 M NaCl 3 M NaOH
----------------------------	--------------------------------

- The maximum concentration of lactic acid in the aqueous phase after back extraction is 0.215 M for an initial concentration of 0.30 M TOMA(La) in octanol and 3 M NaOH in aqueous phase. Volume ratio of the phases may be altered to obtain a higher concentration of lactic acid in the aqueous phase.
- The maximum equilibrium distribution coefficient obtained is 32.3, except for cases of complete recovery, at an initial concentrations of 0.1 M TOMA(La) in oleyl alcohol and 0.4 M NaOH. Equilibrium distribution coefficients tend to increase with the initial concentration of the salts in the aqueous phase and to decrease with the initial concentration of TOMA(La) in the organic phase for all salts investigated. The maximum concentration of the salts in the aqueous phase is limited with their solubility in water.
- Octanol is a better solvent for TOMA(La) due to its higher solvating power and lower viscosity compared to oleyl alcohol and usually gives higher distribution coefficients for lactic acid for back extraction. Octanol also exhibits higher distribution coefficients during forward extraction of lactic acid by TOMAC (Açan, 2003). Its another advantage is that emulsion formation tendency is reduced when octanol is utilized instead of oleyl alcohol (Açan, 2003).
- Among the salts investigated, NaOH is the best candidate as a stripping agent for back extraction of lactic acid from TOMA(La) in

organic phase from the viewpoint of a higher equilibrium distribution coefficient and the regeneration of TOMAOH as an extractant in the organic phase. TOMAOH has been reported as the best extractant among TOMAC, TOMAOH and TOMAHSO<sub>4</sub> due to its higher equilibrium distribution coefficients and having no adverse effect on fermentation medium (Açan, 2003).

- The optimum conditions which may be recommended to recover lactic acid to have 0.1 M TOMA(La) in octanol treated with 1.5 M NaOH resulting in complete recovery.
- The data obtained in this study together with those of Açan (Açan, 2003) constitute the initial steps for the design of an extractive fermentation unit integrating fermentation and separation units. In the next steps, the microkinetic and macrokinetic parameters should be obtained.

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## APPENDIX A

### DISTRIBUTION COEFFICIENTS OF LACTIC ACID in VARIOUS SOLVENTS

Table A.3.1 Distribution of Lactic Acid in Hydrocarbons, Halogen Compounds and Nitro Compounds

Solvent	Temperature (K)	[LA] <sub>aq</sub> (M)	K
Hexane	298	5.16	<0.01
Cyclohexane	298	5.16	<0.01
Benzene	298	5.94	<0.01
Toluene	298	5.16	<0.01
Toluene	293	8.95	0.003
p-Cymene	301	1.86	0.0017
Pinene	301	1.87	0.013
Limonene	301	1.83	0.0036
Turpentine (sulfite)	301	1.87	0.01
Chloroform	301	1.87	0.01
Chloroform	293	8.84	0.011
Tetrachloromethane	298	5.97	<0.01
o-Dichlorobenzene	298	5.18	<0.01
Nitromethane	298	5.22	0.112
Nitroethane	298	5.69	0.043
Nitroethane	301	1.81	0.09
1-Nitropropane	298	5.86	0.031
2-Nitropropane	298	5.87	0.028
Nitrobenzene	298	5.98	0.005

Table A.3.2 Distribution of Lactic Acid in Alcohols

<b>Solvent</b>	<b>Temperature (K)</b>	<b>[LA]<sub>aq</sub> (M)</b>	<b>K</b>
1-Butanol	298	3.12	0.721
2-Methyl-1-propanol	298	3.28	0.630
2-Butanol	298	3.19	0.929
1-Pentanol	293	4.59	0.438
1-Pentanol	293	4.50	0.571
3-Methyl-1-butanol	298	4.28	0.447
3-Methyl-1-butanol	293	6.95 (%w)	0.691
3-Pentanol	299	3.18	0.493
2-Methyl-1-butanol	301	1.68	0.406
2-Methyl-2-butanol	298	3.42	0.813
Pentanol (mixed)	299	3.07	0.435
1-Hexanol	298	4.79	0.313
2-Ethyl-1-butanol	299	3.18	0.493
4-Methyl-2-pentanol	298	0.5	0.37
4-Methyl-2-pentanol	298	1.0	0.43
Cyclohexanol	298	3.95	0.578
Cyclohexanol	293	6.26	0.389
Benzyl alcohol	298	4.27	0.446
1-Octanol	298	5.21	0.198
2-Octanol	298	5.15	0.195
2-Ethyl-1-hexanol	301	1.98	0.147
Octylene glycol	298	4.20	0.489
Phenethyl alcohol	301	1.73	0.423
2-Phenoxyethanol	301	1.68	0.415
Pentylcyclohexanol	299	2.71	0.143
Phenol	299	2.56	0.740
Phenol	298	3.60	0.722
Eugenol	301	1.80	0.067

Table A.3.3 Distribution of Lactic Acid in Ethers

<b>Solvent</b>	<b>Temperature (K)</b>	<b>[LA]<sub>aq</sub> (M)</b>	<b>K</b>
Ethyl ether	293	4.91	0.087
Ethyl ether	293	5.11	0.136
Isopropyl ether	298	16.21	0.029
Isopropyl ether	293	16.82 (%w)	0.0951
Ethyl butyl ether	298	5.85	0.026
Butyl ether	301	2.23	0.014
Butyl ether	298	5.97	0.009
Petyl ether	301	2.20	0.01
Ethylene glycol dibutyl ether	298	5.82	0.039
Phenyl ether	298	6.02	0.002
Furan	299	3.04	0.012

Table A.3.4 Distribution of Lactic Acid in Ketones

<b>Solvent</b>	<b>Temperature (K)</b>	<b>[LA]<sub>aq</sub> (M)</b>	<b>K</b>
2-Butanone	298	4.8 (%w)	0.81
3-Pentanone	298	5.04	0.164
3-Methyl-2-butanone	298	4.69	0.253
4-Methyl-2-pentanone	298	5.40	0.116
2-Heptanone	298	5.59	0.095
2-Heptanone	299	3.18	0.103
3-Heptanone	298	5.73	0.055
4-Heptanone	298	5.74	0.048
Mesityl oxide	301	1.84	0.266
Phorone	301	4.80	0.064
Cyclohexanone	298	3.85	0.524
Isophorone	298	4.27	0.419

Table A.3.4 (cont.)

2,6 Dimethyl-3-heptanone	301	2.22	0.028
2,6 Dimethyl-3-heptanone	298	5.87	0.023
Acetophenone	301	2.04	0.114
Acetophenone	298	5.46	0.109
Furfural	300	1.84	0.301

Table A.3.5 Distribution of Lactic Acid in Esters

<b>Solvent</b>	<b>Temperature (K)</b>	<b>[LA]<sub>aq</sub> (M)</b>	<b>K</b>
Ethyl acetate	298	5.03	0.259
Ethyl acetate	293	6.64 (%w)	0.484
Propyl acetate	298	5.43	0.114
Butyl acetate	298	5.45	0.107
Butyl acetate	293	7.00 (%w)	0.436
Pentyl acetate	299	2.80	0.114
Amyl (fusel) acetate	299	2.15	0.091
4-Methylpentyl acetate	298	5.83	0.039
Cyclohexyl acetate	301	2.08	0.077
2-Ethoxyethyl acetate	298	4.03	0.530
2-Butoxyethyl acetate	301	2.78	0.107
Ethyl propionate	298	5.55	0.103
Butyl lactate	298	4.26	0.569
Isobutyl lactate	301	1.61	0.537
Pentyl lactate	300	1.87	0.347
Ethyl acetoacetate	298	4.47	0.265
Diethyl carbonate	301	2.12	0.048
Tributyl phosphate	298	3.19	0.907

Table A.3.6 Distribution of Lactic Acid in Amines

<b>Solvent</b>	<b>Temperature (K)</b>	<b>[LA]<sub>aq</sub> (M)</b>	<b>K</b>
Tributylamine	298	4.68	0.090
Aniline	298	5.33	0.108
o-Toluidine	303	6.95 (%w)	0.19

## APPENDIX B

### RESULTS OF BACK EXTRACTION EXPERIMENTS

#### B.1 Results with Aqueous NaCl as Back Extractant

Table B.1.1 Back Extraction of Lactic Acid with Aqueous NaCl from TOMA(La) in Oleyl Alcohol

$[LA]_{org}^0$ (M)	$[Cl]_{aq}^0$ (M)	Ratio of $[Cl]_{aq}^0$ to $[LA]_{org}^0$	$[LA]_{aq}^*$ (M)	$[LA]_{org}^*$ (M)	$[Cl]_{aq}^*$ (M)	Level of extraction (%)	K
0.10	0.05	0.532	0.081	0.019	0.049	81.0	4.26
	0.10	1.072	0.084	0.016	0.081	84.0	5.25
	0.21	2.119	0.085	0.015	0.165	85.0	5.67
	0.42	4.213	0.090	0.010	0.362	90.0	9.00
	0.88	8.880	0.090	0.010	0.811	90.0	9.00
	1.56	15.65	0.090	0.010	1.499	90.0	9.00
	3.10	31.03	0.094	0.006	3.002	94.0	15.7
0.20	0.21	1.059	0.146	0.054	0.124	73.0	2.70
	0.42	2.106	0.148	0.052	0.380	74.0	2.85
	0.88	4.440	0.146	0.054	0.785	73.0	2.70
	1.56	7.824	0.150	0.050	1.462	75.0	3.00
	3.10	15.52	0.161	0.039	2.002	80.5	4.13
0.30	0.21	0.706	0.168	0.132	0.083	56.0	1.27
	0.42	1.404	0.171	0.129	0.215	57.0	1.33
	0.88	2.960	0.168	0.132	0.713	56.0	1.27
	1.56	5.216	0.170	0.130	1.482	56.7	1.31
	3.10	10.34	0.185	0.115	2.365	61.7	1.61

Table B.1.2 Back Extraction of Lactic Acid with Aqueous NaCl from TOMA(La) in Octanol

<b>[LA]<sup>0</sup><sub>org</sub> (M)</b>	<b>[Cl]<sup>0</sup><sub>aq</sub> (M)</b>	<b>Ratio of [Cl]<sup>0</sup><sub>aq</sub> to [LA]<sup>0</sup><sub>org</sub></b>	<b>[LA]<sup>*</sup><sub>aq</sub> (M)</b>	<b>[LA]<sup>*</sup><sub>org</sub> (M)</b>	<b>[Cl]<sup>*</sup><sub>aq</sub> (M)</b>	<b>Level of extraction (%)</b>	<b>K</b>
0.10	0.21	0.026	0.082	0.018	0.186	82.0	4.56
	0.42	0.052	0.096	0.004	0.389	96.0	24.0
	0.88	0.536	0.100	0	0.831	100	∞
	1.56	1.059	0.100	0	1.531	100	∞
	3.10	1.413	0.100	0	3.098	100	∞
0.15	0.21	2.106	0.125	0.025	0.191	83.3	5.00
	0.42	2.119	0.135	0.015	0.386	90.0	9.00
	0.88	2.809	0.150	0	0.808	100	∞
	1.56	4.213	0.150	0	1.392	100	∞
	3.10	4.440	0.150	0	3.094	100	∞
0.20	0.005	5.920	0.130	0.070	0.005	65.0	1.86
	0.01	7.824	0.130	0.070	0.010	65.0	1.86
	0.11	8.880	0.147	0.053	0.089	73.5	2.77
	0.21	10.43	0.148	0.052	0.178	74.0	2.85
	0.42	15.52	0.175	0.025	0.375	87.5	7.00
	0.88	15.65	0.174	0.026	0.764	87.0	6.69
	1.56	20.69	0.177	0.023	1.476	88.5	7.70
	3.10	31.03	0.174	0.026	2.142	87.0	6.69
0.30	0.21	0.706	0.160	0.140	0.119	53.4	1.15
	0.42	1.404	0.160	0.140	0.270	53.4	1.15
	0.88	2.960	0.157	0.143	0.744	52.3	1.09
	1.56	5.216	0.155	0.145	1.525	51.6	1.07
	3.10	10.34	0.159	0.141	2.405	53.1	1.13



## B.2 Results with Aqueous NaOH as Back Extractant

Table B.2.1 Back Extraction of Lactic Acid with Aqueous NaOH from TOMA(La) in Oleyl Alcohol

$[LA]^{0}_{org}$ (M)	$[OH]^{0}_{aq}$ (M)	Ratio of $[OH]^{0}_{aq}$ to $[LA]^{0}_{org}$	$[LA]^{*}_{aq}$ (M)	$[LA]^{*}_{org}$ (M)	$[Cl]^{*}_{aq}$ (M)	Level of extraction (%)	K
0.10	0.05	0.5	0.066	0.034	0.016	66.0	1.94
	0.1	1	0.064	0.036	0.025	62.0	1.78
	0.2	2	0.092	0.008	0.037	92.0	11.5
	0.4	4	0.097	0.003	0.054	97.0	32.3
	0.8	8	0.100	0	0.068	100	$\infty$
	1.5	15	0.100	0	0.073	100	$\infty$
	3	30	0.100	0	0.092	100	$\infty$
0.20	0.2	1	0.123	0.077	0.050	61.5	1.60
	0.4	2	0.129	0.071	0.066	64.5	1.82
	0.8	4	0.134	0.066	0.082	67.0	2.03
	1.5	7.5	0.139	0.061	0.085	69.5	2.28
	3	15	0.139	0.061	0.103	69.5	2.28
0.30	0.2	0.7	0.143	0.157	0.069	47.7	0.91
	0.4	1.3	0.168	0.132	0.074	56.0	1.27
	0.8	2.7	0.185	0.115	0.085	61.7	1.61
	1.5	5	0.187	0.113	0.091	62.3	1.65
	3	10	0.189	0.111	0.129	63.0	1.70

Table B.2.2 Back Extraction of Lactic Acid with Aqueous NaOH from TOMA(La) in Octanol

$[LA]^{0}_{org}$ (M)	$[OH]^{0}_{aq}$ (M)	Ratio of $[OH]^{0}_{aq}$ to $[LA]^{0}_{org}$	$[LA]^{*}_{aq}$ (M)	$[LA]^{*}_{org}$ (M)	$[Cl]^{*}_{aq}$ (M)	Level of extraction (%)	K
0.10	0.2	2	0.066	0.034	0.049	66.0	1.94
	0.4	4	0.075	0.025	0.071	75.0	3.00
	0.8	8	0.082	0.018	0.094	82.0	4.56
	1.5	15	0.100	0	0.116	100	$\infty$
	3	30	0.100	0	0.130	100	$\infty$
0.15	0.2	1.3	0.102	0.048	0.068	68.0	2.13
	0.4	2.7	0.118	0.032	0.093	78.7	3.69
	0.8	5.3	0.130	0.020	0.126	86.7	6.50
	1.5	10	0.130	0.020	0.145	86.7	6.50
	3	20	0.150	0	0.191	100	$\infty$
0.20	0.005	0.025	0.130	0.070	0.009	65.0	1.86
	0.01	0.05	0.130	0.070	0.010	65.0	1.86
	0.1	0.5	0.128	0.072	0.087	64.0	1.78
	0.2	1	0.131	0.069	0.069	65.5	1.90
	0.4	2	0.136	0.064	0.089	68.0	2.13
	0.8	4	0.149	0.051	0.124	74.5	2.93
	1.5	7.5	0.172	0.028	0.175	86.0	6.14
	3	15	0.200	0	0.228	100	$\infty$
0.30	0.2	0.7	0.156	0.144	0.073	52.0	1.08
	0.4	1.3	0.175	0.125	0.093	58.3	1.40
	0.8	2.7	0.178	0.122	0.139	59.3	1.46
	1.5	5	0.183	0.117	0.176	61.0	1.56
	3	10	0.215	0.085	0.389	71.7	2.53

### B.3 Results with Aqueous Na<sub>2</sub>SO<sub>4</sub> as Back Extractant

Table B.3.1 Back Extraction of Lactic Acid with Aqueous Na<sub>2</sub>SO<sub>4</sub> from TOMA(La) in Oleyl Alcohol

[LA] <sup>0</sup> <sub>org</sub> (M)	[SO <sub>4</sub> ] <sup>0</sup> <sub>aq</sub> (M)	[LA] <sup>*</sup> <sub>aq</sub> (M)	[LA] <sup>*</sup> <sub>org</sub> (M)	[Cl] <sup>*</sup> <sub>aq</sub> (M)	[SO <sub>4</sub> ] <sup>*</sup> <sub>aq</sub> (M)	Level of extraction (%)	K
0.10	0.22	0.083	0.017	0.049	0.126	83.0	4.88
	0.44	0.085	0.015	0.059	0.283	85.0	5.67
	0.88	0.087	0.013	0.064	0.604	87.0	6.69
	1.69	0.089	0.011	0.071	0.951	89.0	8.09
0.20	0.22	0.154	0.046	0.076	0.118	77.0	3.35
	0.44	0.149	0.051	0.086	0.272	74.5	2.92
	0.88	0.145	0.055	0.091	0.552	72.5	2.64
	1.69	0.143	0.057	0.105	0.918	71.5	2.51
0.30	0.22	0.160	0.140	0.097	0.104	53.3	1.14
	0.44	0.158	0.142	0.107	0.260	52.7	1.11
	0.88	0.159	0.141	0.140	0.506	53.0	1.13
	1.69	0.155	0.145	0.154	1.885	51.6	1.07

Table B.3.2 Back Extraction of Lactic Acid with Aqueous Na<sub>2</sub>SO<sub>4</sub> from TOMA(La) in Octanol

[LA] <sup>0</sup> <sub>org</sub> (M)	[SO <sub>4</sub> ] <sup>0</sup> <sub>aq</sub> (M)	[LA] <sup>*</sup> <sub>aq</sub> (M)	[LA] <sup>*</sup> <sub>org</sub> (M)	[Cl] <sup>*</sup> <sub>aq</sub> (M)	[SO <sub>4</sub> ] <sup>*</sup> <sub>aq</sub> (M)	Level of extraction (%)	K
0.10	0.22	0.078	0.022	0.049	0.175	78.0	3.55
	0.44	0.078	0.022	0.055	0.378	78.0	3.55
	0.88	0.079	0.021	0.057	0.821	79.0	3.76
	1.69	0.078	0.022	0.054	1.583	78.0	3.55
0.15	0.22	0.124	0.026	0.076	0.174	82.7	1.46
	0.44	0.122	0.028	0.079	0.389	81.3	1.44
	0.88	0.122	0.028	0.076	0.814	81.3	1.42
	1.69	0.118	0.032	0.080	1.607	78.7	1.48

Table B.3.2 (cont.)

0.20	0.22	0.160	0.040	0.080	0.188	80.0	4.00
	0.44	0.162	0.038	0.092	0.371	81.0	4.26
	0.88	0.159	0.041	0.097	0.812	79.5	3.88
	1.69	0.153	0.047	0.093	1.564	76.5	3.26
0.30	0.22	0.178	0.122	0.081	0.186	59.3	1.46
	0.44	0.177	0.123	0.118	0.248	59.0	1.44
	0.88	0.176	0.124	0.122	0.624	58.7	1.42
	1.69	0.179	0.121	0.119	1.319	59.7	1.48

#### B.4 Results with Aqueous NaNO<sub>3</sub> as Back Extractant

Table B.4.1 Back Extraction of Lactic Acid with Aqueous NaNO<sub>3</sub> from TOMA(La) in Octanol

[LA] <sup>0</sup> <sub>org</sub> (M)	[NO <sub>3</sub> ] <sup>0</sup> <sub>aq</sub> (M)	[LA] <sup>*</sup> <sub>aq</sub> (M)	[LA] <sup>*</sup> <sub>org</sub> (M)	[Cl] <sup>*</sup> <sub>aq</sub> (M)	[NO <sub>3</sub> ] <sup>*</sup> <sub>aq</sub> (M)	Level of ext. (%)	K
0.15	0.20	0.099	0.051	0.144	0.033	66.0	1.94
	0.80	0.098	0.052	0.231	0.473	65.3	1.88
	3.73	0.104	0.046	0.258	1.922	69.3	2.26
0.30	0.20	0.130	0.170	0.081	0.013	43.4	0.77
	0.80	0.126	0.174	0.252	0.115	42.0	0.72
	3.73	0.127	0.173	0.322	1.876	42.2	0.73

### B.5 Results with Aqueous Na<sub>2</sub>CO<sub>3</sub> as Back Extractant

Table B.5.1 Back Extraction of Lactic Acid with Aqueous Na<sub>2</sub>CO<sub>3</sub> from TOMA(La) in Octanol

[LA] <sup>0</sup> <sub>org</sub> (M)	[CO <sub>3</sub> ] <sup>0</sup> <sub>aq</sub> (M)	[LA] <sup>*</sup> <sub>aq</sub> (M)	[LA] <sup>*</sup> <sub>org</sub> (M)	[Cl] <sup>*</sup> <sub>aq</sub> (M)	Level of extraction (%)	K
0.15	0.2	0.098	0.052	0.092	65.3	1.88
	0.8	0.103	0.047	0.099	68.7	2.19
	3	0.091	0.059	0.083	60.7	1.54
0.30	0.2	0.153	0.147	0.120	51.0	1.04
	0.8	0.169	0.131	0.128	56.2	1.28
	3	0.171	0.129	0.129	57.1	1.33

### B.6 Preliminary Kinetic Studies on Back Extractions of Lactic Acid from TOMA(La) dissolved in Oleyl Alcohol

Table B.6.1 Kinetic Studies on Back Extraction of Lactic Acid from 0.2 M TOMA(La) in Oleyl Alcohol with 0.8 M NaCl

Time (h)	[LA] <sup>*</sup> <sub>aq</sub> (M)
1	0.072
2	0.130
3	0.152
6	0.152
9	0.149
12	0.150
18	0.151
24	0.150

Table B.6.2 Kinetic Studies on Back Extraction of Lactic Acid from 0.2 M TOMA(La) in Oleyl Alcohol with 0.8 M NaOH

<b>Time (h)</b>	<b>[LA]<sup>*</sup><sub>aq</sub> (M)</b>
1	0.113
2	0.125
3	0.137
6	0.144
9	0.148
12	0.145
18	0.147
24	0.145

## **APPENDIX C**

### **ANALYSIS WITH ION CHROMATOGRAPHY AND SAMPLE CALIBRATION CURVES**

The analyses were conducted with an ion chromatograph equipped with a conductivity detector which measures the conductivities of ions present in the samples in microsiemens ( $\mu\text{S}$ ) units. The maximum measurement range of the chromatograph determines the sensitivity of the measurements and could be varied between 10 and 1000  $\mu\text{S}$ . The calibration curves were obtained for lactic acid and chloride at 100  $\mu\text{S}$ ; for sulphate and nitrate at 30  $\mu\text{S}$  depending on amplitude of the output signal. The curves are presented in Figures C.1-4 below. The samples were injected to the chromatograph at the specified range according to its content. The areas under the chromatogram peaks were automatically integrated and converted into concentration units via the calibration curves. The mobile phase was 30 mM NaOH having pH of 11.95, therefore lactic acid and other substances present in the samples were essentially in the ionized form.

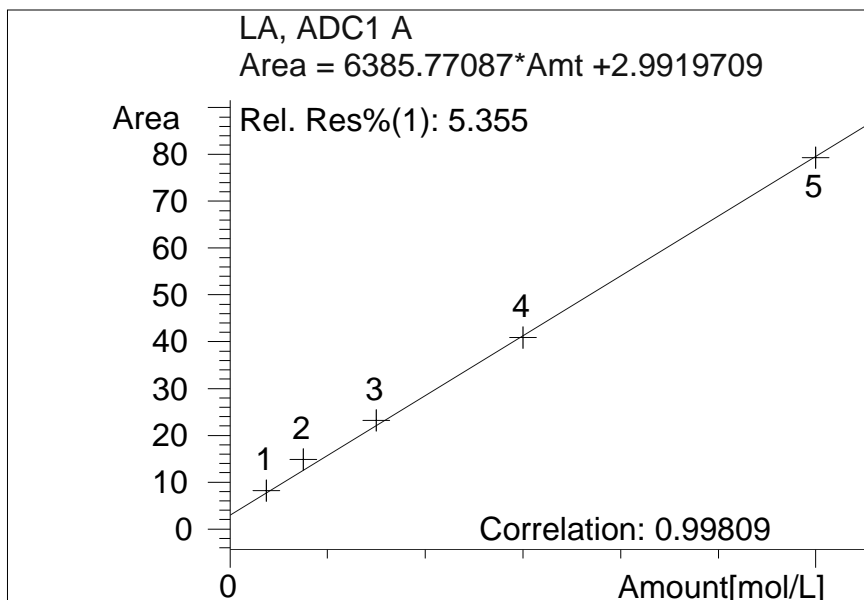


Figure C.1 Lactic acid calibration curve drawn at 100  $\mu\text{S}$  range

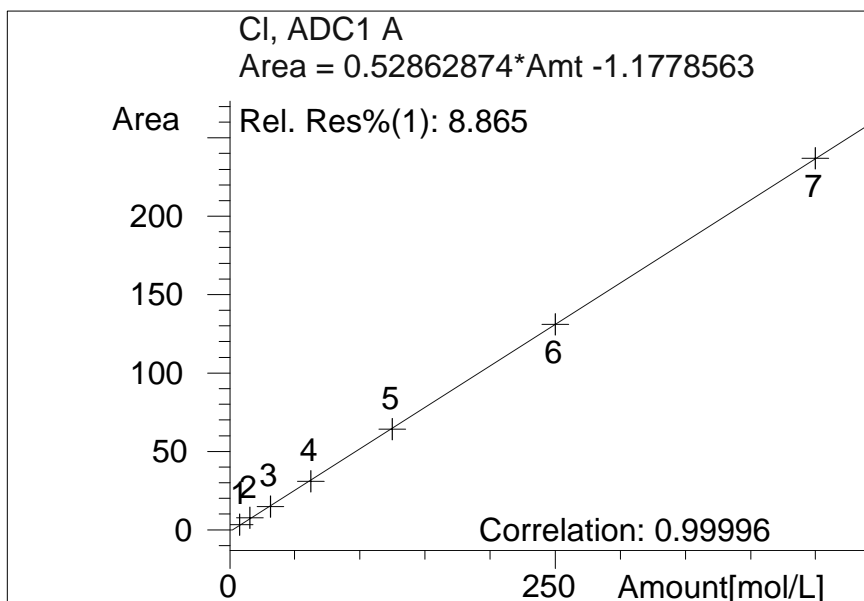


Figure C.2 Chloride calibration curve drawn at 100  $\mu\text{S}$  range



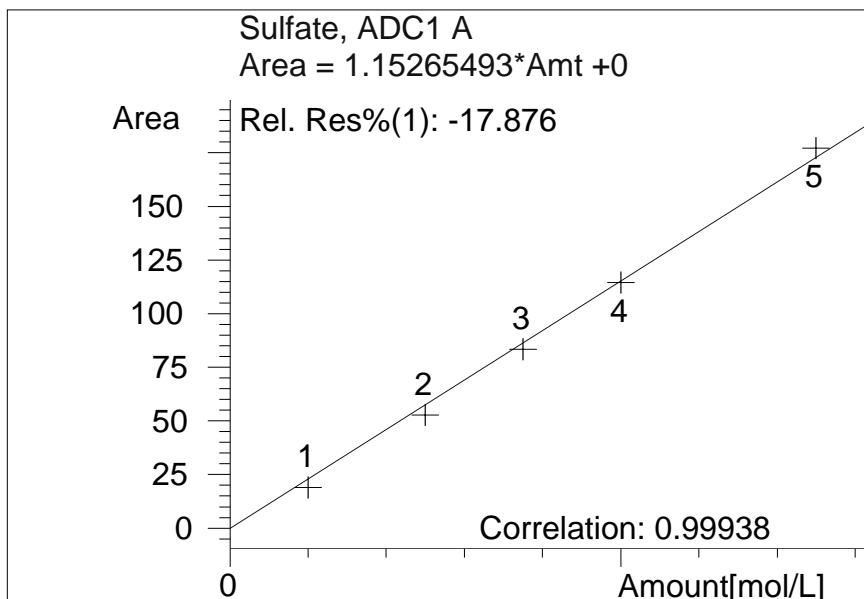


Figure C.3 Sulphate calibration curve drawn at 30  $\mu$ S range

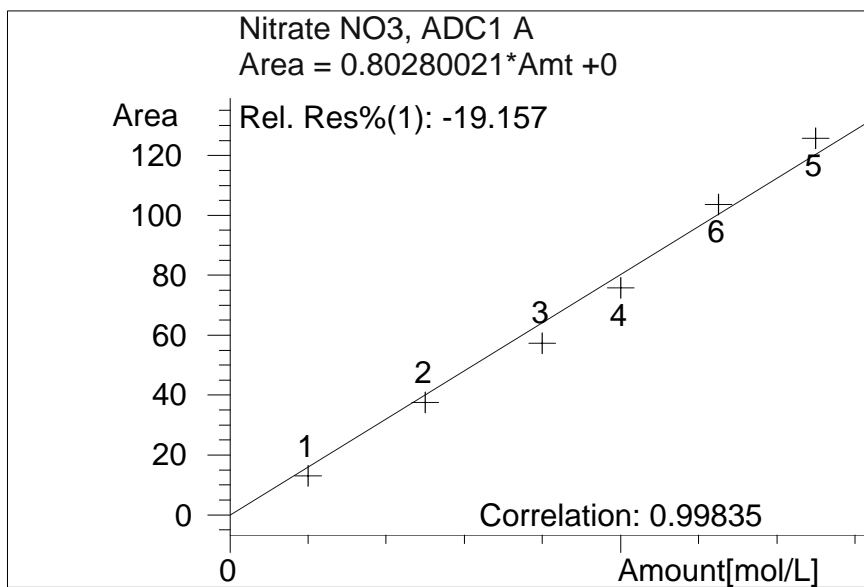


Figure C.4 Nitrate calibration curve drawn at 30  $\mu$ S range

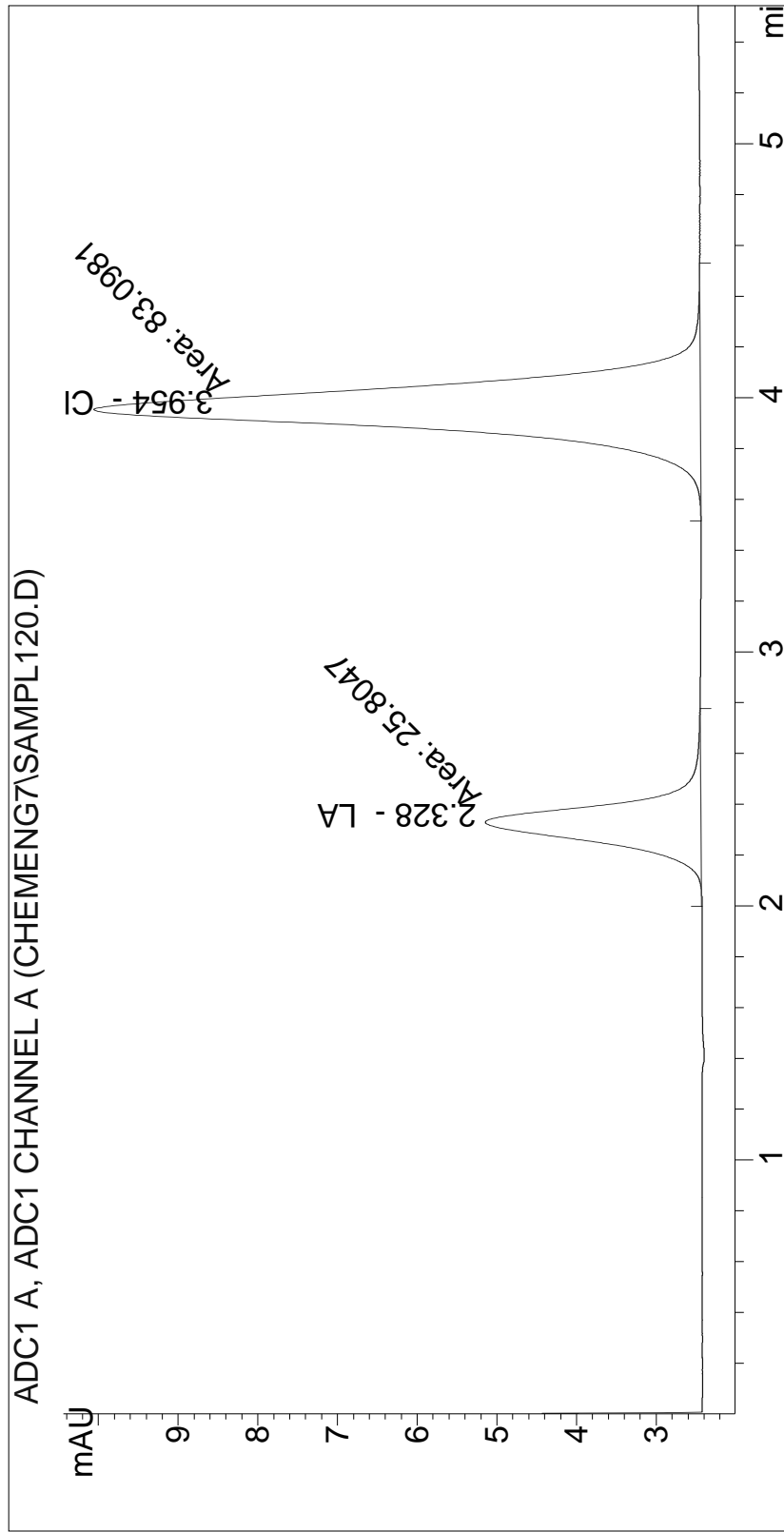


Figure C.5 A Sample Chromatogram (Aqueous Phase after Back Extraction of Lactic Acid with 0.2 M NaCl from 0.2 M TOMA(La) dissolved in Oleyl Alcohol)