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Reactive extraction of lactic acid from acidic and alkaline aqueous solution with supported liquid membrane permeation

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Abstract

The substitution of chemicals derived from petroleum with chemicals derived from biomass is receiving an increasing amount of attention. Lactic acid is one of these latter types of chemicals, as it can be converted into a large variety of materials that can be used as building blocks for other compounds. Crud formation prevented in-situ extraction of lactic acid, by using liquid membrane permeation this problem can be overcome.

The present study is divided into two parts. The first part targets the acid isolation from a modelled fermentation broth using tri-*n*-octylamine (TOA) in 1-octanol and *n*-undecane as solvent. Lactic acid isolation was compared with the isolation of formic and acetic acid, which are by products in the fermentation process. Partition and dimerization coefficients were determined from equilibrium measurements by physical and reactive extraction. Modelling of the phase equilibrium data is performed with the law of mass action. Physical extraction provides very low acid distribution coefficients compared to reactive extraction. Data for the single acids show the improvement of equilibrium constant and stoichiometry using TOA in combination with the modifier, 1-octanol in comparison with TOA diluted in *n*-undecane. The back-extraction was performed with $NaHCO_3$ solution and the transfer to supported liquid membrane permeation was successfully performed. Mass transfer of lactic acid in liquid membrane permeation is inversely proportional to the viscosity of the solvent.

The second part of the study targets the isolation of lactic acid from highly alkaline aqueous solution. The results for reactive extraction of lactic acid from alkaline aqueous solution using an ammonium-based ionic liquid (Aliquat 336) and its carbonated form are reported. The data gained from experiments show that the use of the carbonated form of Aliquat 336 increases the extraction efficiency. The use of the polar-aprotic solvent MIBK was significantly more effective in terms of lactic acid extraction than 1-octanol and *n*-hexane. A successful attempt to improve the extraction efficiency was made by using solvent mixtures of carbonated form of Aliquat 336 with the modifier MIBK diluted in *n*-hexane. Back-extraction was performed with $NaHCO_3$, water and HCl. Water was found to be more effective as stripping solution than $NaHCO_3$, which is a result of osmotic water flux in the direction of the feed phase.

Kurzfassung

Beim Umstieg von einem erdölbasierten auf ein biobasiertes Wirtschaftssystem kommt der Erzeugung von Chemikalien aus nachwachsenden Rohstoffen eine wichtige Rolle zu. Milchsäure als Monomer für die Polymilchsäureherstellung ist dabei ein prominenter Vertreter. Großtechnisch wird Milchsäure mittels Fermentation hergestellt, die Produktisolierung und Reinigung ist dabei aufwendig und kostspielig. Prozessintensivierung und/oder neue Technologien sind notwendig um die Produktionskosten zu senken. Die in-situ Extraktion der Milchsäure aus der Fermentationsbrühe ist derzeit aufgrund der Crud- und Emulsionsbildung nicht möglich. Durch die Verwendung der Flüssigmembranpermeation mit gestützten Membranen kann die Emulsionsbildung unterbunden werden.

Die vorliegende Arbeit hat zum Ziel die Grundlagen für die Anwendung der Flüssigmembranpermeation mit gestützten Membranen zur Milchsäureabtrennung aus sauren und basischen Prozessströmen zu erarbeiten. Die Arbeit gliedert sich in zwei Teile, der erste Teil der Arbeit beschäftig sich mit der Abtrennung von Milchsäure aus modellierten Fermentationsbrühen und der zweite Teil erarbeitet die Grundlagen für die Abtrennung aus Prozessströmen der Zellstoffkochung. Beide Teile der Arbeit beinhalten Phasengleichgewichtsmessungen in Abhängigkeit der Zusammensetzung der Flüssigmembran und die Überführung in den Dreiphasenkontakt bei der Flüssigmembran in einem U-Rohr - Versuchsaufbau.

Die Phasengleichgewichte wurden mit dem Massenwirkungsgesetz modelliert und der Verteilungs- sowie der Dimerisationskoeffizient berechnet. Für die Extraktion von Milchsäure aus Fermentationsbrühen wurde eine optimale Flüssigmembranzusammensetzung von 60%TOA in n-Undecan gefunden, welche zu einem Stoffaustauschkoeffizienten von 7.2×10^{-6} m/s im Dreiphasenkontakt führt. Als Strippphase wurde $NaHCO_3$ verwendet.

Für die Extraktion aus alkalischen Lösungen wurde Aliquat 336 in die carbonisierte Form überführt und im Dreiphasenkontakt ein Stoffaustauschkoeffizient von 5.8×10^{-5} m/s mit einer Mischung aus 37.5 w% Aliquat/ 37.5 w% MIBK/ 25 w% *n*-Hexan. Die Variation der Strippphase zeigte, dass Wasser im Vergleich mit HCl und $NaHCO_3$ am besten geeignet ist, das ist durch den osmotischen Wasserfluss zu begründen.

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ขอกราบขอบพระคุณ คุณพ่อ คุณแม่ ป้าปุ๊ แม่ใหญ่ แม่ณัฐ ครอบครัวฉิมบรรเทิง และมั่งมา ที่เลี้ยงดูข้าพเจ้ามาอย่างดีด้วยความรัก สนับสนุน และเป็นแรงใจให้ผ่านพ้นทุกอุปสรรค จนสำเร็จลุล่วงไปด้วยดี

Contents

1 Introduction

Application of lactic acid ranges from food, pharmaceutical, cosmetic, and chemical industry but it is of upmost interest as monomer for the production of poly-lactic acid (PLA), a biodegradable and bioactive thermoplastic. The growing interest in the production of PLA for bio-plastics has fueled an increase in demand for lactic acid. Global warming is the driving force for the transition of the present fossil based economy into a bio-based economy. PLA is compostable and environmentally friendly and therefore it provides an ideal alternative to fossil fuel-based plastics. Lactic acid is commonly produced through fermentation followed by isolation and several purification steps. The downstream processing is based on the precipitation of poorly soluble calcium lactate, followed by filtration. The precipitated calcium lactate cake is acidified with strong mineral acids to free lactic acid. This procedure leads to the formation of calcium sulfate at the rate of 1 metric ton per metric ton of lactic acid as by product (Pal et al., 2009). Due to the low volatility and strong water affinity the isolation process of lactic acid is complex and costly. Abdel et al. (2013) reported that the separation and purification of lactic acid from fermentation broth accounts for approximately 50% of the total production costs. To minimize the costs of downstream processing, much research focuses on process intensification of the isolation of lactic acid. Liquid-liquid extraction of carboxylic acids is a well-established, and in terms of selective separation as well as process intensification, it is a promising approach (Painer et al., 2017). Reactive extraction offers the connection between chemical and physical phenomena and has been proposed to be an effective primary separation step for the recovery of bio-products from a dilute fermentation process (López-Garzón and Straathof, 2014).

In-situ liquid-liquid extraction is expected to be an efficient technology for the recovery of carboxylic acids from fermentation broth (Woodley et al., 2008) since it can simultaneously isolate the acid as well as prevent product inhibition. Main difficulty when using liquid-liquid extraction in complex matrixes like fermentation broth is crud formation. Liquid membrane permeation combines extraction and back-extraction in one step and has shown to be able to prevent emulsion formation due to the rigid surface and cross flow operation, emulsion formation as well as membrane fouling and scaling can be avoided in liquid membrane permeation (Kienberger et al., 2018).

Therefore, this work focuses on the lactic acid isolation by using liquid membrane permeation.

Besides lactic acid from fermentation, it is present to in industrial effluents, for example in black liquor from Kraft pulping. The black liquor serves as fuel in the chemical recovery cycle and is at the same time used for energy production. Due to the low heating value of lactic acid, downcycle raw material utilization added-value can be created by isolation of lactic acid as an intermediate substance. Different to lactic acid from fermentation broth, black liquor is a highly alkaline process stream, hence here anion extraction needs to be investigated.

The present worked is divided into two parts. The first part deals with the reactive extraction of lactic acid from acidic solution which targets the acid isolation from fermentation broth. The aim of this part is to optimize the composition of the solvent phase for the recovery of lactic acid from a diluted aqueous process stream. Besides the reaction itself, the solvent polarity and the viscosity mainly influence the extraction efficiency in reactive extraction. The optimum solvent composition provide the highest mass transfer. Thus, the extraction equilibrium constant is required to optimize this separation process. Therefore, the phase equilibrium is measured in dependence on the solvent composition. The solvent consist of a reactive extractant, a modifier and a diluent, in the present work, tri-*n*-octylamine was selected as reactive extractant due to its potential utilization for the extraction of monocarboxylic acids (Datta et al., 2014),(Cascaval et al., 2011),(Thakre et al., 2016). 1-octanol was chosen as the modifier because its high capability of the acid-amine salt solubility, whereas *n*-undecane was selected as the diluent. While, the distribution coefficient and extraction efficiency were obtained from the equilibrium studies, the extraction equilibrium constant and the degree of association are modeled using the law of mass action. Further, the mass transfer coefficient in supported liquid membrane permeation is evaluated.

The second part deals with the separation of lactic acid from alkaline aqueous solutions, which targets the recovery of lactic acid from pulping effluent. The basic knowledge from the first part was applied to highly alkaline process streams. However, extraction at high pH-value leads to the necessity of anion separation which is a challenging task. Ionic liquid, Aliquat 336 and the carbonated form thereof, which have shown the potential to be used as reactive extractant (Kyuchoukov et al., 2004), were selected as the reactive extractant whereas MIBK and *n*-hexane were used as the modifier and diluent, respectively. Subsequently, mass transfer in liquid membrane permeation is discussed.

2 Task

The main task of this work is to study the isolation of lactic acid form aqueous process streams. Two different process streams are targeted, on the one side a model fermentation broth and on the other side a modeled black liquor from Kraft pulping was investigated. Both process streams suffer from low concentration of lactic acid, the concentration thereof is in the fermentation broth 1 mol/L and in the black liquor even lower with 0.2 mol/L. Commercial available extraction cannot be applied the process streams as this results in crud formation and separation of aqueous and organic phase gets impossible.

First part of the work investigates the physical and chemical mechanism of reactive extraction of lactic acid by measuring the phase equilibrium in dependence on temperature and the solvent composition. As target parameter the extraction efficiency of lactic acid was defined. The modeling of the data based on the law of mass action determines the extraction equilibrium constant and the degree of association. After having investigated the basics the transfer to liquid membrane permeation to perform extraction and back-extraction at the same time was done. The mass transfer characteristic shall be evaluated based on the first order kinetic.

Second part of the work investigates chemical mechanism of reactive extraction of lactic acid from highly alkaline solution by measuring the phase equilibrium in dependence on solvent composition. The extraction efficiency was defined for determine the optimum solvent composition. Subsequently, the transferring of results obtained from the phase equilibrium to liquid membrane permeation was done

3 State of the art

The US FDA (Food and drug administration) classifies lactic acid as GRAS (generally recognized as safe) for use as food additive. Only L(+)-lactic (Fig. 3-1) acid is assimilated in human body which makes preferential focus to the food and drug industries. Currently, lactic acid is used for different purposes, but the demand increases mainly due to the utilization as feedstock for polylactic acid (PLA) production. PLA is an environmental friendly bio-polymer and is used in biodegradable plastics, which can be a substitute for petroleum derived plastics. The different lactic acid isomer compositions influence the physical properties of synthesized polylactic acid, e.g. the melting point. The purity of optical isomer L(+)-lactic acid or D(-)-lactic acid can be polymerized to a high crystalline polylactic acid. Therefore, the pure lactic acid isomer form is more valuable for different specific applications (Yong Wang et al., 2015).

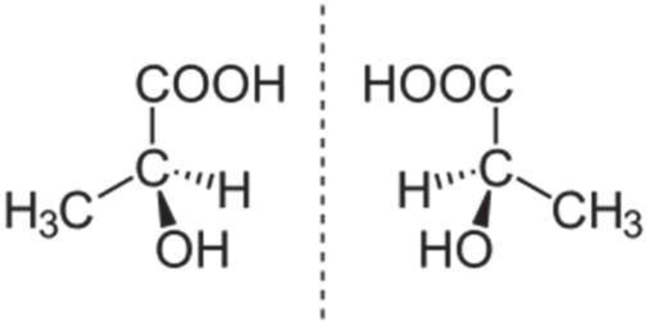

Fig. 3-1 Structure of L(+) lactic acid (left) and D(-)lactic acid (right)

3.1 Demand and supply

Lactic acid demand is forecasted to increase by 5-8% annually. The global demand of lactic acid in 2016 was 1,220.0 kilo tons. Apart from growing consumer awareness in environmental friendly material usage and sustainability, the regulation establishment is also projected to drive the lactic acid market. For example, Japan has set the objective to reach 20% bioplastics in the plastics market by 2020. EU commission proposes to reduce the use of plastic bags of below 50 micron by 50% in 2017 and 80% in 2019. (Research Grand View, 2017)

The rising demand of lactic acid in various applications drives the market growth in various market segments including packaging, personal care and textile, see Fig. 3-2.

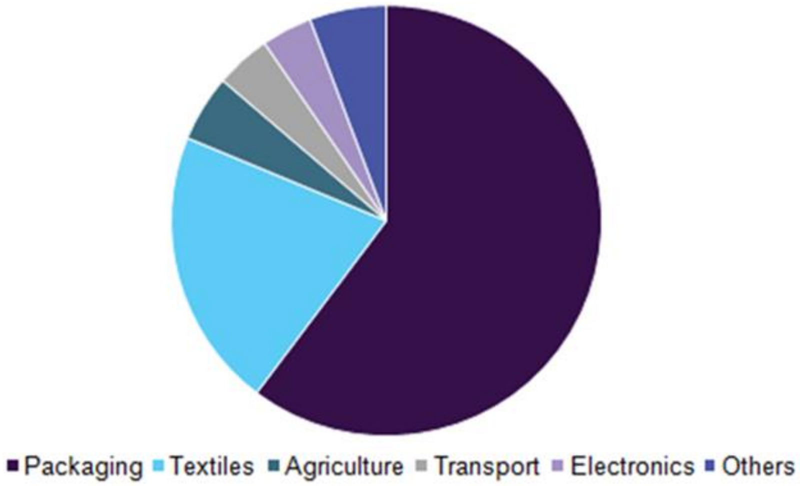

Fig. 3-2 Global polylactic acid market segment in 2016. (Research Grand View, 2017)

The highest market share was found for packaging at 59.1% that is in line with the higher substitution of petroleum-derived plastics by biodegradable plastic bags. Moreover, biodegradable plastics show the superior properties of high resistance to moisture and grease, odor and flavor barrier characteristics. With this benefit, biodegradable plastics are expected to drive the industry competition.

There are many competitors investing in this market. The major manufacturers of lactic acid include Archer Daniels Midland Company (USA), NatureWorks LLC (USA), Purac (Thailand), Galactic S.A. (Belgium), among them NatureWorks is the major manufacturers of fermentation based lactic acid which holds over 95% of the current PLA worldwide production capacity. (Abdel Rahman et al., 2013)

Lactic acid can be produced by microbial fermentation and chemical synthesis. By far the most important production rout is produced by microbial fermentation with a share of 90% (Ying Wang et al., 2015). The overview of the lactic acid manufacturing by chemical synthesis and microbial fermentation can be seen in Fig. 3-3.

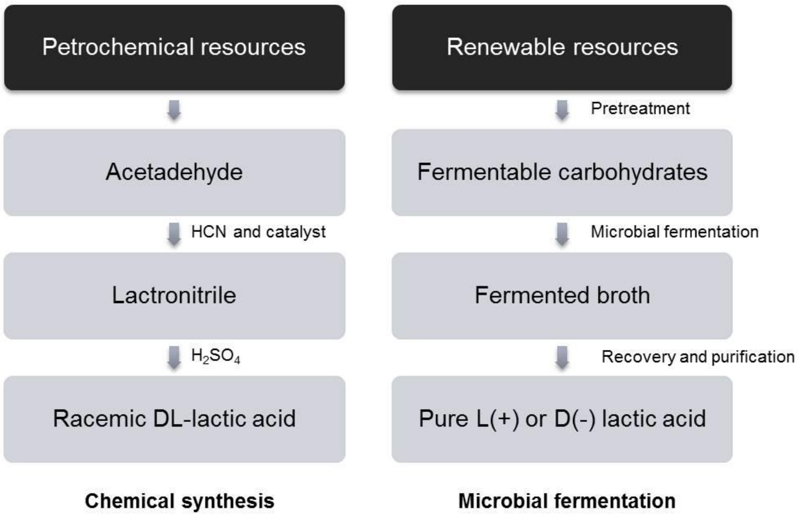

Fig. 3-3 Overview of the two manufacturing methods of lactic acid. Modified from (Wee et al., 2006)

3.2 Chemical synthesis

Lactic acid can be synthesized from petrochemical resource under high atmospheric pressure and basic catalyst. The reaction between acetaldehyde and hydrogen cyanide with optimum conditions produces lactonitrile as main product. After its recovery by distillation, lactonitrile is subsequently hydrolyzed by strong acid like sulphuric acid. Purification of hydrolyzed lactic acid is then followed by esterification with methanol to form methyl lactate. Then, multiple processes for final purification require distillation and hydrolysis to obtain highly pure lactic acid and methanol. Chemically produced lactic acid is a racemic mixture of DL-lactic acid. Racemic mixtures of PLA affect the physical properties of the polymer.

3.3 Fermentation

The chemical synthesis of lactic acid requires additional chemicals that substantially affect to the production cost. Therefore, much attention has been focused on the microbial fermentation of renewable resources. The benefits of this process are environmental concerns, low production temperature, low energy requirement and high product purity (Ying Wang et al., 2015).

Lactic acid production bases on the fermentation of carbohydrate resources. The two main resources are monosaccharide and disaccharide. Refined sugar is an effective source in fermentation processes and its cost affect the production costs. It has been reported that the commercial production of lactic acid by fermentation depends on the cost of raw materials which accounts for 34% (Ghaffar et al., 2014). Alternative raw materials like lignocellulosic biomass are of interest, but, they require additional pretreatment, like size reducing process steps or acid pretreatment, and the main difficulty is the biological de-lignification.

For the production of lactic acid four groups of microorganism are used, namely , bacteria, yeast, fungi and algae. Because of its ability to produce lactic acid with high yield and high productivity lactic acid bacteria (LAB) dominate the current attention in literature. However, each kind of microorganism provides different production yield and requires different handling as well as process conditions such as temperature, pH, nutrients. Yeast for example tolerates pH-values in the fermentation broth as low as 1.5, which facilitates further recovery of lactic acid. This low pH-value operation leads to a reduction of the neutralizing agent and the minimization in lactate precipitate recovery (Praphailong and Fleet, 1997). However, most wild-type yeasts naturally produce lactic acid at low concentration. Thus, yeast engineering is required to increase the production rate (Abdel Rahman et al., 2013). Fungi such as Rhizopus species can convert starchy materials directly to lactic acid from their amylolytic characteristics without any additional saccharification process however, it has low production rate caused by mass transfer limitation (Jin et al., 2003).

Nowadays, much attention focuses on the global warming concern. Photosynthetic microorganisms, such as algae that can grow with captured CO_2 is possibly a candidate for the use in lactic acid production. It can convert starchy materials to lactic acid under light and aerobic conditions. Apart from lactic acid, acetic acid, ethanol and formic acid are formed as byproducts.

In general, the temperature and pH-value are the main process parameters to ensure respectively adjust the optimum process conditions. The acidification from the produced lactic acid results in the inhibition of cell growth and its production during fermentation. For example, lactic acid production by bacteria, the operation pH-value varies between 5 and 7, and depends on the microorganism used. The cell metabolism can be harmed by the non-dissociated form of lactic acid diffusing into the bacteria cell membrane (Jantasee et al., 2017).Thus, neutralizing agent such as sodium hydroxide, calcium hydroxide or calcium carbonate is needed to control the pH-value during fermentation. Alternatively, selective removal of lactic acid during fermentation can be implemented in order to overcome inhibition.

3.4 Lactic acid from the pulp and paper industry

The production of paper is one of the most intensive industrial process converting predominantly woody plant material into a wide variety of pulps, papers and paperboards and is an energy intensive industry, with 1 ton of paper requiring 5–17 GJ of process heat (Szabó et al., 2009). Austria is packed with wood by 47.6% of the country area, reflecting the high competition in the paper market section. The production of paper and card board accounts to 4,964,516 metric tons in 2015 (Association of the Austrian Wood Industry, n.d.). The main paper and paperboard consumption was more than 90% of the total consumption in the region of North America, Europe and Asia in 2004.

Approximately 80% of world paper production uses the Kraft process, because this process leads to high pulp strength properties and it is applicability to various kinds of wood. In the Kraft process, wood fibers are liberated from the wood matrix by cooking at high temperature about 170°C with sodium hydroxide and sodium sulphide. The solid pulp is separated from the black liquor and treated in the fiber line. The substances leached from wood and the cooking chemicals is called black liquor which is generated in an amount of 170 mio tons per year globally. The black liquor contains 15-17% solids, which is made up of dissolved organic material from the wood and leftover pulping chemicals (Bioenergy, 2007). The pH-value of black liquor from Kraft process is approximately 13. The main components of black liquor are water, organic residue and the inorganic chemicals. The organic compounds in black liquor are mostly a mixture of lignin, polysaccharides, polyphenols, non-volatile hydroxy acids and mono or dicarboxylic acids. Non-volatile hydroxy acids and mono or dicarboxylic acids originate from degradation of carbohydrates that are dissolved during the Kraft pulping process while polyphenols and other cyclic components are created by the degradation of the lignin (Bajpai, 2016),(Magnin et al., 2017). The main inorganic substances in black liquor are sodium hydroxide and sodium sulphide (Sjoestroem, 1977).

The composition of black liquor varies with the feed and the cooking conditions. High kappa numbers are related to high lignin content and vice versa. Regarding the acid content in black liquor, low kappa number corresponds with extended degradation of the hemicellulose and hence results in higher concentration of carboxylic and hydroxyl carboxylic acids (Colodette et al., 2002). The approximate amount of carboxylic acids and hydroxyl carboxylic acid in black liquor is about 15%, with an approximate amount of lactic acid of 2%. In the chemical recovery cycle, the black liquor is incinerated in the recovery boiler after evaporation of the major amount of water in order to recover NaOH and Na2S. Besides the chemical recovery, steam and electricity are produced in the chemical recovery cycle.

Lignin is the main fuel constituent. It has a heating value of 23.4 MJ/kg. The heating value of lactic acid is with 14.72 MJ/kg much lower. Due to the low heating value and the low concentration of lactic acid in the black liquor compared to lignin, alternatives to incineration of lactic acid offer a fascinating and challenging research topic. Tab. 3-1 summarizes the black liquor composition from Kraft process using pine tree.

Tab. 3-1 The organic composition of black liquor after dehydration (Sjoestroem, 1977).

Chemical	Mass fraction (%)
Lignin	83
Formic acid	2.72
Acetic acid	1.87
Lactic acid	1.87
Glycolic acid	0.68
2- Hydroxybutanoic acid	0.68
2,5- Dihydroxypentanoic acid	0.51
Xyloisosaccharinic acid	0.68
Glucoisosaccharinic acid	6.63
Other	1.53

3.5 Lactic acid recovery

Lactic acid isolation and purification is an important step in lactic acid production process since the fermentation broth contains several impurities such as cell debris, residual sugars, nutrients and other organic acids. These impurities need purification in order to obtain pure lactic acid. Different purification processes have been commercialized on industrial scale, in all cases the microorganisms of cells must be removed from the broth. Fig. 3-4 shows the process for lactic acid isolation from the fermentation broth.

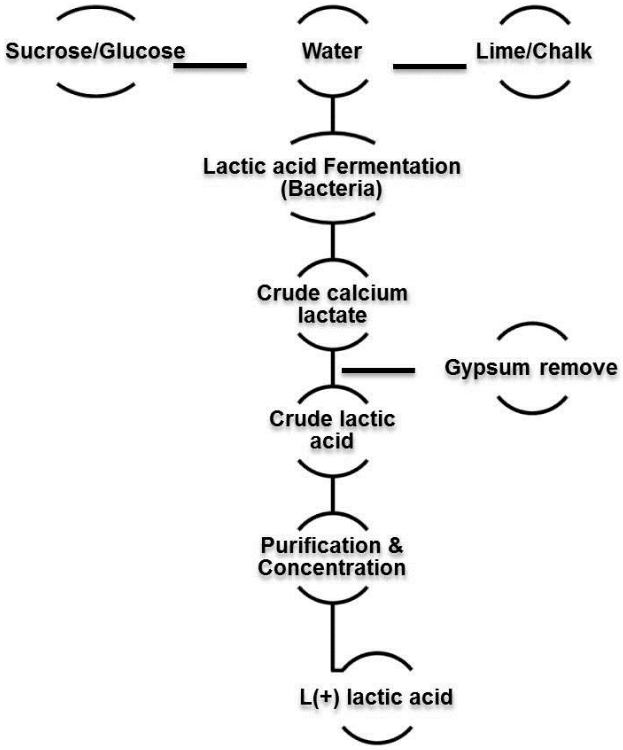

Fig. 3-4 Lactic acid recovery process from the fermentation broth.

Various recovery and purification technologies for lactic acid used in the industry were discussed by (Wasewar, 2005),(Clara et al., 2012). A process for the purification of lactic acid by calcium lactate precipitation prevents product inhibition, as the pH-value is adjusted around 6. This process can be described according to the following three steps:

1) fermentation and neutralization

2) hydrolysis crude calcium lactate with H_2SO_4

3) gypsum removal

4) purification and concentration

Alkali, such as lime, sodium carbonate or ammonium hydroxide is added to the clarified fermentation broth to adjust the pH-value. At low pH-value lactate exists in dissociated form; most industrial processes add sulfuric acid to the broth to crystallize calcium sulfate (gypsum). To be able to obtain pure lactic acid, esterification and subsequently distillation of crude lactic acid are operated. Finally, hydrolysis of the distilled lactate ester to observe the alcohol and lactic acid is carried out.

Since, the downstream processing of lactic acid production is accounted to be 50 % of the total production cost (Abdel Rahman et al., 2013). It also produces a large quantity of calcium sulphate sludge as solid waste. Thus, the development of cost-effective and efficient downstream process should be further studied.

3.6 Process development strategies for lactic acid isolation

This part of the work summarizes the evaluation of potential separation technologies for the separation of lactic acid using the systematic approach of a decision matrix. The method builds upon physical properties of the targeted substance such as heat capacity, dissociation constant, solubility, boiling point et cetera. These specific properties are matched with unit operations. A grading if the respective unit operation can be used is made. In terms of costs the approach follows a strict sequence: mechanical unit operations were hierarchically evaluated before investigation of mass transfer unit operations and reactive separation.

3.6.1 Methodology

In order to assess the suitability of a lactic acid recovery process, a decision matrix was set up. For the development of the decision matrix, it is assumed that a binary mixture of water and lactic acid has to be separated. The evaluation legends are “+” which indicates the possibility to apply the mentioned processes in lactic acid recovery while “-“ indicates the impossibility of using the respective technology, as well as irrelevant parameters which will not concern the separation process. At the bottom of the table the summation of “+” is given. With the unit operations with the highest score deduced from this analysis, the separation task may be accomplished. The total score does not guarantee that the unit operation leads to a positive accomplishment of the separation task, however this methodology ensures an objective view on the separation task. The tables of the decision matrix are shown in Appendix.

3.6.2 Result and Discussion

The evaluation results show that the only mechanical separation technique, which may be applied for the separation of water /lactic acid, is electrophoresis. Due to the limitation in technical transfer to industrial scale, this operation is not addressed. The evaluation of mass transfer unit operations shows, that most of the unit operations may be used for the separation task. It recommends the processes permeation, pervaporation, electrodialysis and molecular sieving. It is important to note that the decision matrix does not rate the substance properties; it may be that even with a high total score a specific unit operation may not be useful for this separation task because of the main substance property. For instance, even the significantly different boiling point between lactic acid and water is not useful, because the fermentation broth is a dilute solution and hence all the water would need to be removed from the fermentation broth instead of lactic acid. Hence, huge energy consumption would be required. Moreover, direct distillation is difficult as the tendency to homopolymerization of lactic acid increases with increasing temperature (Khunnonkwao et al., 2012).

Extraction has been found to be a promising alternative and it has outstanding advantages, such as a short operation cycle, and fast mass transfer for the recovery of lactic acid from fermentation broth with high purity and high yield (Li et al., 2016). Liquid-liquid extraction of carboxylic acids is well established and in terms of selective separation as well as process intensification, reactive extraction is a promising approach. Several authors have reported the reactive extraction of carboxylic acids from aqueous solution. Cascaval et al.(2011) studied the reactive extraction of acetic acid with tri-*n*-octylamine. Their experimental results showed that the interfacial reaction between acid and reactive extractant is controlled by the polarity of the solvent. Several reactive extractants and diluents have also been investigated in order to achieve highest extraction efficiency. Han et al. (2000) compared the extraction abilities between amine extractant and phosphorous extractant i.e., tributylphosphate (TBP), Dibutylphosphate(DBP), trioctylphosphine oxide (TOPO) and trioctylamine (TOA). Among them, TOA was found to be the most effective reactive extractant for lactic acid extraction. Lux et al.(2013) found that Cyanex 923 diluted in Shellsol T is a suitable extractant for lactic acid extraction referring to the highest distribution coefficient.

Permeation is one of the technologies, which shows promising results in lactic acid isolation. Ultrafiltration was used to investigate and effectively separate lactic acid from a modeled fermentation (Wojtyniak and Szaniawska, 2015). Li et al.(2008) obtained high productivity and purity from the study of a combination of nanofiltration and reverse osmosis. Furthermore, process intensification of lactic acid production by in-situ removal of lactic acid using a combination of extraction and membrane process, called liquid membrane permeation, may help to obtain high purity and high yield of lactic acid.

Liquid membrane permeation combines extraction and back-extraction in one step. By optimization of the liquid membrane a high degree of separation can be reached. Further, no limitation in the aqueous/organic phase ratio, no emulsification, little solvent amount needed and little solvent loss characterizes liquid membrane permeation (Parhi, 2013). Due to the non-equilibrium mass-transfer characteristics, liquid membrane permeation leads to higher recovery rates than common extraction processes. Morales et al.(2015) used liquid membrane permeation for the recovery of succinic acid, they proofed the shift of extraction equilibrium when coupling extraction and back extraction. The acid recovery from the feed stream was five times higher than by extraction with subsequent back-extraction.

4 Theoretical background

4.1 Liquid-liquid extraction

In this chapter, the basics needed to interpret the data, are explained. Modeling of the equilibria data is performed using the law of mass action. Equilibrium measurements with pure solvents are designated as physical extraction, and the extraction equilibrium with reactive extractants are designated as chemical extraction. Different mass action law approaches are used to represent the physical and chemical extraction discussed in section 4.1.1 and 4.1.2 , respectively.

4.1.1 Physical extraction

Physical extraction refers to the extraction of a solute with a non-reactive solvent such as hydrocarbons, alcohols, ketone, ethers and alike. Basically, there are three mechanisms involved in physical extraction 1) dissociation of the acid in the aqueous phase 2) partition of non-dissociated acid between aqueous and organic phase and 3) dimerization of non-dissociated acid in the organic phase (Datta et al., 2014). The exact partition number of the acid molecules in the organic phase is usually undetermined, but it is known that a large number of solvent molecules are needed for an efficient competition with the water molecules that form hydrates with the acid at the interface. Fig. 4-1 illustrates the mechanisms of physical lactic acid extraction.

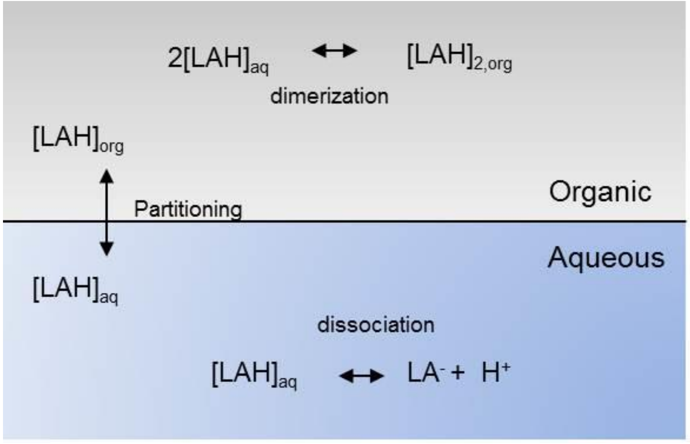

Fig. 4-1 Physical extraction mechanism of lactic acid (Wasewar, 2012)

4.1.1.1 Law of mass action

The dissociation of carboxylic acid depends on the acid strength, which can be described by Equation 4-1:

$$[HA]_{aq} \leftrightarrow H^{+} + A^{-} \qquad \text{Equation 4-1}$$

The dissociation constant (K_a) can be calculated from Equation 4-2;

$$K_a = \frac{[H^{+}][A^{-}]}{[HA]} \qquad \text{Equation 4-2}$$

The overall concentration of acid in the aqueous phase (c_{HA}) takes into account the non-dissociated acid [HA] and dissociated acid [A$^-$] concentration, see Equation 4-3:

$$c_{HA} = [HA] + [A^{-}] \qquad \text{Equation 4-3}$$

The combination of equation (4-2) and (4-3), reads:

$$HA = \frac{c_{HA}}{(1+(\frac{K_a}{H^{+}}))} \qquad \text{Equation 4-4}$$

and the non-dissociated acid can be calculated following. The partition of non-dissociated acid between two phases is given by;

$$[HA]_{aq} \leftrightarrow [HA]_{org} \qquad \text{Equation 4-5}$$

$$P = \frac{[HA]_{org}}{[HA]_{aq}} \qquad \text{Equation 4-6}$$

Acid molecules in the organic phase can interact through hydrogen bonding because the solute-solute interaction is stronger than solute-solvent interaction. The dimerization (D) of the non-dissociated acid in the organic phase $[HA]_{org}$ is represented by;

$$2[HA]_{aq} \leftrightarrow [HA]_{2,org} \qquad \text{Equation 4-7}$$

$$D = \frac{[HA]_{2,org}}{[HA]^{2}_{aq}} \qquad \text{Equation 4-8}$$

The distribution coefficient (K_d) can be determined from the ratio of total concentration of acid in the organic phase and total concentration of acid in the aqueous phase as following;

$$K_d = \frac{[HA]_{org}}{[HA]_{aq}} \qquad \text{Equation 4-9}$$

The distribution coefficient from physical extraction can be defined including the partition coefficient (*P*) and the dimerization constant (*D*) following Equation 4-10

$$K_d = \frac{P+2P^2\ D[\mathrm{HA}]_{aq}}{(1+(\frac{K_a}{\mathrm{H}^+}))} \qquad \text{Equation 4-10}$$

At low acid concentration as well as low operation pH (lower than pK_a), the denominator can be neglected hence the simplified equation reads:

$$K_d = P+2P^2\ D[\mathrm{HA}]_{aq} \qquad \text{Equation 4-11}$$

4.1.2 Chemical extraction

Reactive extraction is a promising approach towards the process intensification of lactic acid recovery. The combination of reaction and separation is simple and effective. When the reaction substantially improves separation, for example through enhanced mass transfer rates caused by chemical conversion of the constituent in the solvent phase, the separation drives the reaction to higher conversions. The combined operations are useful in capital and operating cost savings and the successful scale up of industrial operations (Wasewar, 2012). For the extraction of acid from a fermentation broth, reactive liquid-liquid extraction allows the acid to be removed easily, preventing a pH drop in the broth with the additional advantage that the acid can be re-extracted from the organic phase and the reactive extractant recycled into the process. Fig. 4-2 illustrates the mechanisms of chemical lactic acid extraction. Other advantages of this recovery method include:

- pH control without the need for base addition
- High purity of recovered acid, eliminating the need for further purification steps

The efficiency of reactive extraction depends on various parameters such as the distribution coefficient, loading ratio, equilibrium constant, selectivity of individual acids over others, and properties of the solvents (reactive extractants and diluents). The reactive extractant can be categorized as follows:

- extraction by solvation with carbon-bonded oxygen-bearing extractants

- extraction by solvation with phosphorous-bonded oxygen-bearing extractants and
- extraction by proton transfer or by ion pair formation.

Among the reactive extractants tri-*n*-octylamine, a ternary aliphatic amine, is the most effective extractant for carboxylic acids and was also investigated among others in the present work.

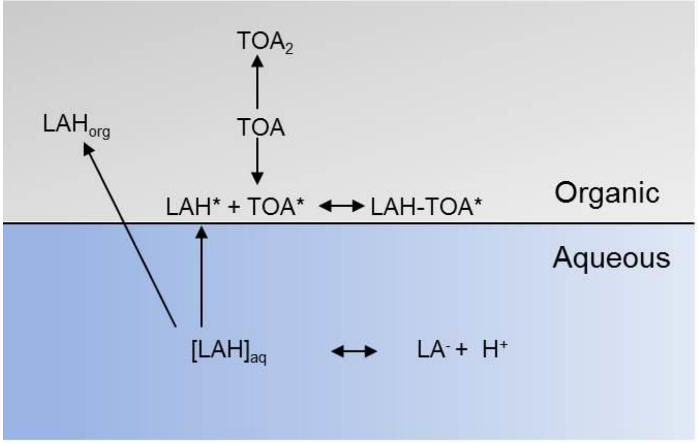

Fig. 4-2 Chemical extraction mechanism of lactic acid extraction

4.1.2.1 Law of Mass Action

The extraction process is based on an acid–base reaction between the alkylamine and the acid. The extraction equilibrium of lactic acid can be expressed by:

$$nLA_{aq} + TOA_{org} \leftrightarrow (TOA(LA)_n)_{org} \qquad \text{Equation 4-12}$$

Where *n* represents the association factor, which is the number of lactic acid molecule per molecule of TOA.

The extraction process is commonly analyzed by the degree of extraction and the distribution (or partition) coefficient. The distribution coefficient, K_d, describes the ratio of concentrations of a compound in two immiscible phases at equilibrium and therefore is a measure for the difference in solubility of the compound in the two phases. The distribution coefficient differs from the partition coefficient as the partition coefficient is defined as the ratio of the non-dissociated compound in the two phases and

K_d describes the ratio of the dissociated and non-dissociated acid. Since the partition coefficient refers only to the equilibrium of non-dissociated compound between the phases, it is independent of pH-value. The distribution coefficient is pH dependent since the degree of dissociation in the aqueous phase is affected by the pH and the pK_a of the compound (Kwon, 2002).

The distribution coefficient can be calculated from:

$$K_d = \frac{c_{LA,org}}{c_{LA,aq}} \qquad \text{Equation 4-13}$$

Where $c_{LA,org}$ is the total concentration of acid in the organic phase and $c_{LA,aq}$ is the total concentration of acid in the aqueous phase (dissociated and non-dissociated) at equilibrium.

The degree of extraction, or extraction efficiency, is defined as the ratio between acid concentration in the solvent phase to the initial acid concentration in the aqueous feed:

$$E = \frac{K_d}{(1+K_d)} \times 100 \qquad \text{Equation 4-14}$$

From equation 4-12, the equilibrium constant can be expressed as:

$$K_{st} = \frac{c_{TOA(LA)_{n},org}}{c^{n}_{HA,aq} \cdot c_{TOA,org}} \qquad \text{Equation 4-15}$$

It also has to be taken into account that non-dissociated lactic acid is extracted into the organic phase due to additional adduct formation with the extractant. By substitution of $c_{TOA(LA)_{n,\,org}} = \frac{c_{HA,org}}{n}$ and $c_{TOA,org} = c_{TOA,0,org} - \frac{c_{HA,org}}{n}$, Equation 4-15 becomes:

$$K_{st} = \frac{c_{LA,org}}{n \cdot c^{n}_{LA,aq,nondiss} \cdot (c_{TOA,0,org} - c_{LA,org}/n)} \qquad \text{Equation 4-16}$$

The dissociation of lactic acid is:

$$LAH \leftrightarrow LA^{-} + H^{+} \qquad \text{Equation 4-17}$$

The dissociation of the acid is expressed by the dissociation constant, K_{diss}

$$K_{diss} = \frac{c_{H^{+}} \cdot c_{LA}}{c_{LAH}} = \frac{c^{2}_{LAH,0} \cdot \alpha^{2}}{c_{LAH,0} \cdot (1-\alpha)} \qquad \text{Equation 4-18}$$

Whereas the non-dissociated fraction of the acid phase is expressed by:

$$c_{\mathrm{HA,aq,nondiss}} = c_{\mathrm{HA,aq}}\left(1-\alpha\right) \qquad \text{Equation 4-19}$$

Where α is the degree of dissociation defined as:

$$\alpha = \frac{-K_{diss} \pm \sqrt{K_{diss}^{2}+4\cdot c_{\mathrm{HA,0}}\cdot K_{diss}}}{2\cdot c_{\mathrm{LA,0}}} \qquad \text{Equation 4-20}$$

Subsequently, Equation 4-21 represents the analytical expression of liquid-liquid phase equilibrium for the reactive extraction. The equilibrium concentration of the species extracted into the organic phase $c_{\mathrm{LA,org}}$ is given as a function of feed concentration of reactive extractant $c_{\mathrm{TOA,0,org}}$ and the corresponding concentration of non-dissociated acid in the aqueous phase ($c_{\mathrm{LA,aq,nondiss}}$).

$$c_{\mathrm{LA,org}} = \frac{n\cdot K_{st}\cdot c_{\mathrm{LA,aq,nondiss}}^{n}\cdot c_{\mathrm{TOA,0,org}}}{1+K_{st}\cdot c_{\mathrm{LA,aq,nondiss}}^{n}} \qquad \text{Equation 4-21}$$

With the specified initial concentration of TOA and varying the degree of association, a linear fitted curve can be plot using a professional graphics software to estimate the equilibrium constants and the degree of association according to equation 4-22.

$$\frac{1}{c_{\mathrm{LA,\,org}}} = \frac{1}{n\cdot K_{st}\cdot c_{\mathrm{LA,aq,nondiss}}^{n}\cdot c_{\mathrm{TOA,0,org}}} + \frac{1}{c_{\mathrm{TOA,0,org}}}\,n \qquad \text{Equation 4-22}$$

4.2 Liquid membrane permeation

A membrane is defined as a semipermeable barrier between two phases. Conventionally, the semipermeable barrier is provided by an inorganic or polymer material for allowing or reject component transport. The concept of liquid membrane permeation incorporates liquid-liquid extraction and membrane separation in one-step. In liquid-liquid separation applications, the liquid membrane phase is usually a solvent while the feed and stripping phase are aqueous. Liquid membranes can be categorized into three groups: bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM). Each has different advantages and disadvantages. For example, in BLM, the feed and stripping phase are separated by a water-immiscible liquid membrane phase. Due to the relatively small surface area to volume ratio, industrial application is not attractive (Kocherginsky et al., 2007). Emulsion liquid membranes offer large surface area to volume ratio but poor stability and require multiple steps for membrane recovery and phase separation. Supported liquid membranes offer a simpler configuration and processing. SLM provides larger surface area to volume ratio the BLM, but lower than ELM, allowing rapid mass transfer (Pancharoen et al., 2011). SLM has received the interest in a broad range of separation applications, especially in hydrometallurgical processing for selective removal of various metals (i.e., copper, zinc) (Siebenhofer et al., 2015), (Jean et al., 2018).

4.2.1 Supported liquid membrane

The supported liquid membrane is a nondispersive type of liquid membrane. The liquid membrane, further called solvent phase, is impregnated in the pores of a polymeric porous layer. The support layer itself does not play an active role in the separation as the liquid membrane does, however, it provides a structure support for the liquid membrane. Since the organic liquid remains in the porous support, only a small amount of solvent is necessary. Apart from the support layer and the reactive extraxctant, diluents are generally used for the preparation of liquid membranes. The primary diluent requirement is to adjust the liquid membrane viscosity; hence, the diffusivity of the solute through the membrane is influenced.

4.2.1.1 Mass transfer in supported liquid membrane

Supported liquid membrane uses the same principle of liquid-liquid equilibrium, in which, mass transfer is driven by the difference in chemical potential between two phases. Unlike the equilibrium limitation in conventional extraction, where two phases are in contact, mass transfer governs the transport through the membrane. Fig. 4-3 depicts a schematic of lactic acid transport in SLM with the reactive extractant TOA, which can be described as follow:

(1) Diffusive lactic acid transport through the interfacial layer the feed-membrane interphase

(2) Reaction between lactic acid and TOA takes place at the interphase

(3) Diffusion of Lactic-TOA salt through the pores of the membrane

(4) The reaction of the Lactic-TOA salt with the stripping agent at the membrane-strip interface

(5) Diffusion of lactic acid through the interfacial layer into stripping solution

(6) Back-diffusion of lactic-free TOA

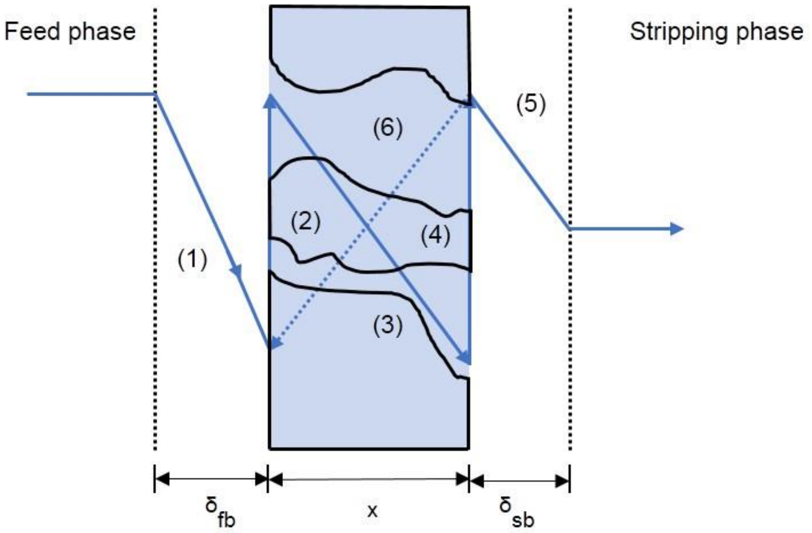

Fig. 4-3 Transport process of lactic acid in SLM

The molar flux (*J*) of lactic acid through the membrane from the feed to the stripping phase is obtained by:

$$J = -\frac{V}{A}\frac{dc_f}{dt} \qquad \text{Equation 4-23}$$

With the integration of equation 4-23 , the overall mass transfer coefficient can be determined (Yang et al., 2003).

$$\ln\frac{c_t}{c_0} = -\frac{kA}{V}t \qquad \text{Equation 4-24}$$

The overall mass transfer coefficient ($k_{overall}$) in the aqueous and the organic phase is also related to the individual mass transfer coefficient by the following equation (Madhumala et al., 2014):

$$\frac{1}{k_{overall}} = \frac{1}{k_f} + \frac{1}{K_d k_{mf}} + \frac{1}{k_o} \qquad \text{Equation 4-25}$$

Where k_f, k_{mf} and k_o refer to the mass transfer coefficient in the feed side, at membrane and in stripping phase, respectively.

There are many correlations to calculate the individual mass transfer coefficients, based on the experimental conditions and equipment set up. Yang (Yang et al., 2003) summarized the method to calculate k_f and k_{mf} as follow:

$$k_f = \frac{D_a}{\delta_{fb}} \qquad \text{Equation 4-26}$$

$$k_{mf} = \frac{D_m}{\delta_m}\,\frac{\epsilon}{\tau} \qquad \text{Equation 4-27}$$

The diffusion coefficient (D_{eff}) can be calculated from the correlation of flux with the assumption of steady state as following:

$$J = \frac{V}{A}\frac{dc_f}{dt} = -D\frac{dc}{dx} \qquad \text{Equation 4-28}$$

Since the membrane thickness is constant for all experiment, hence, dx = Δx. Integration of both sides, therefore, gives the access to calculate the diffusion coefficient from the following equation:

$$D_{eff} = \frac{V \cdot \Delta x \cdot (\ln[c_0] - \ln[c_t])}{A \cdot t} \qquad \text{Equation 4-29}$$

where c_0 and c_t refers to the initial acid concentration and acid concentration at feed phase by time.

5 Experimental

In this chapter the chemical preparation, experimental set up and experimental approach and analytical method are summarized in the chapter 5.1,5.2,5.3 and 5.4, respectively.

5.1 Chemicals preparation

For the preparation of the aqueous feed phase in the study of lactic acid isolation from acidic solution, de-ionized water and a single acid were mixed at room temperature. Acetic acid (CAS 64-19-7) and formic acid (CAS 64-18-16) with a purity of >99%. were purchased from Chem-Lab. Lactic acid (CAS 79-33-4) with a purity of 80%, purchased from Carl Roth, was used. The single acid solution contained the respective acid with a concentration between 0.2-1.0 mol/L which is related to the concentration of lactic acid in fermentation broth. The solvent phase contained tri-*n*-octylamine (CAS 1116-76-3) with a purity 97%, purchased from Acros organics, n-undecane (CAS 1120-21-4) with a purity >95% and 1-octanol (CAS 111-87-5) with a purity of >99%, both purchased from Sigma Aldrich. The solvent phase was prepared by mixing the components at room temperature. The stripping solution contained de-ionized water and sodium hydrogen carbonate with a purity of 99.5% (CAS 144-55-8), purchased from Carl Roth. All chemicals were used as received.

For the preparation of the aqueous feed phase in the study of lactic acid isolation from alkaline solution, sodium hydroxide (CAS 1310-73-2), purchased from JT Baker. solutions were utilized to adjust the pH-value of the aqueous phase. The lactic acid concentration in the aqueous solution was 0.2 mol/L, similar to that in the black liquor (Sjoestroem, 1977). The reactive extractants used in this study were tri-octylmethylammonium chloride (Aliquat 336), tri-hexyltetradecylphosphonium chloride (Cyphos101) and tri-hexyltetradecylphosphonium bis 2,4,4-trimethylpentyl phosphinate (Cyphos 104) all purchased from Sigma Aldrich. To decrease the viscosity, the reactive extractant was diluted with solvents. The solvents used were isobutyl methylketone (MIBK, CAS 108-10-1, Merck), toluene (CAS 108-88-3, Sigma Aldrich), 1-heptanol (CAS 111-70-6, Fluka AG), 1-octanol (CAS111-87-5, Sigma Aldrich) and methoxybenzene (anisole, CAS 100-66-3,Fluka AG). The solvent phase was prepared by mixing the components at room temperature. As stripping solution, either deionized water, sodium hydrogen carbonate, or hydrochloric acid was used.

Carbonated form of Aliquat 336 was prepared by mixing 100 mL of 1 mol/L sodium carbonate with 50 mL of Aliquat 336 in a shaking flask (Janke&Kunkel HS-500) for 60 minutes at 200 rpm. The temperature was controlled at 56.2 °C. After the shaking, the solution was left overnight to achieve phase separation. Then the phases were simply separated by letting out on the bottom of the flask. The conversion was determined by measuring the chloride concentration in the aqueous phase by ion chromatography (IC, Dionex IonPac AS 11 column). The substitution of the chloride ion by the carbonate ion was calculated by determining the mass balance according to the following reaction:

$$2[R_4NCl]_{sol} + [CO_3^{2-}]_{aq} \leftrightarrow [(R_4N)_2CO_3]_{sol} + 2[Cl^-]_{aq} \qquad \text{Equation 5-1}$$

The degree of conversion (*x*) was calculated to assess the concentration of chloride ions removed following Equation 5-2 where $c_{Cl,o}$ and $c_{Cl,eq}$ represent the initial chloride concentration and the chloride concentration at equilibrium, respectively and was determined to be 43%.

$$x = \frac{c_{cl,0} - c_{cl,eq}}{c_{cl,0}} \qquad \text{Equation 5-2}$$

5.2 Experimental set up

5.2.1 Phase equilibrium measurement

Phase equilibrium measurements for acid isolation from acidic solution were performed in an automatic shaking separation funnel 100 mL (Janke&Kunkel HS-500) (see Fig. 5-1) which are connected to a circulated temperature-controlled water bath. Temperature was maintained constant the by a water thermostat. The shaking speed was set up at 200 rpm for ensuring the intensive mixing for all the experiments.

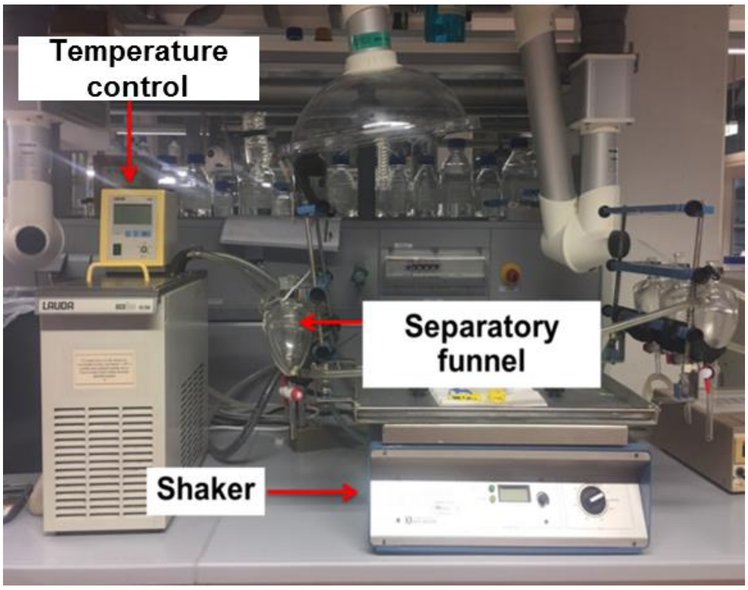

Fig. 5-1 Phase equlibrium measurement set up for acidic solution.

Phase equilibrium measurement for highly alkaline solution was measured in 5 mL glass vials due to a high price of the reactive extractants used, and was mixed using a magnetic stirrer plate (Janke & Kunkel, ES5) (see Fig. 5-2) at 1200 rpm for 2 hours at room temperature. After mixing, the solution was transferred to the separatory funnel for phase separation overnight.

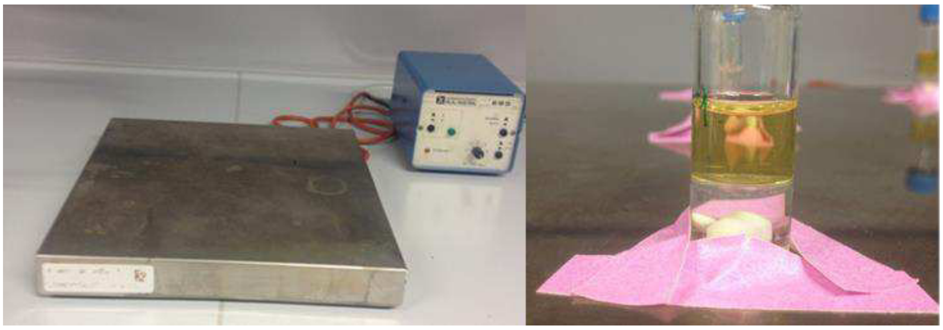

Fig. 5-2 Phase equilibrium measurement set up for alkaline solution.

5.2.2 Supported membrane material

Polyethylene (PE) sheet was used as a porous supported layer. Tab. 5-1 summarizes the specifications of the used supported layer.

Tab. 5-1 summarizes the specifications of the supported layer

Specifications	
Support layer material	Polyethylene (PE)
Porosity [%]	35
Pore size range [µm]	7-12
Support layer thickness [mm]	1

5.2.3 Supported liquid membrane reactor

Two different membrane reactors were used. First, the membrane reactor made with PVC-U (see Fig. 5-3) was set up for acid isolation from acidic solution. The membrane reactor consists of two main parts, the chambers for the feed - and stripping phase, and the membrane module. The membrane module consists of a PVC-U frame where the polyethylene sheet is glued inside. Tab. 5-2 summarizes the specifications of the membrane reactor set up.

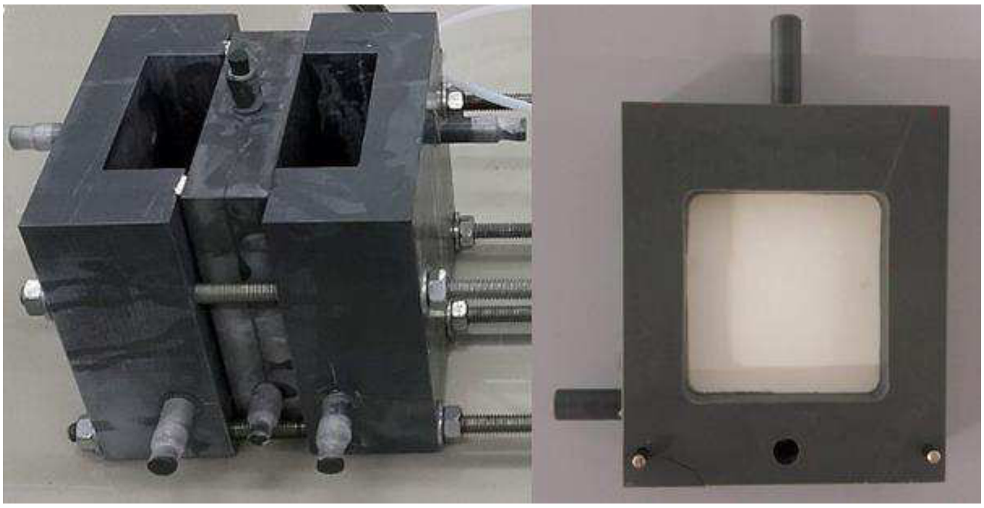

Fig. 5-3 Supported liquid membrane reactor configurations

Tab. 5-2 summarizes the specifications of the membrane reactor

Specifications	
Chamber material	PVC-U
Volume of chamber [ml]	95
Membrane area (exchange area) [cm^2]	25

Another membrane reactor, U-tube membrane reactor (see Fig. 5-4), was set up for the study of acid isolation isolation from alkaline solution. The tubes were made of DIN 15 glass with and the PE support layer was placed between the tubes. The equipment consists of two halves that could be separated, and joined, using three screws. Tab. 5-3 summarizes the specifications of the U-tube membrane reactor set up.

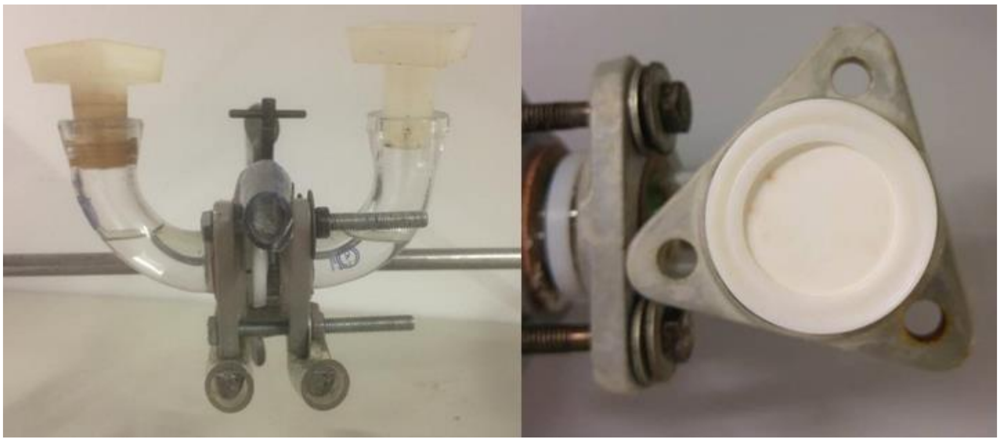

Fig. 5-4 U-tube membrane reactor configuration.

Tab. 5-3 Summary of the specifications of the used U-tube membrane reactor

Specifications	
Chamber material	Glass
Volume of chamber [ml]	10
Membrane area (exchange area) [mm^2]	62

5.3 Experimental approach

5.3.1 Phase equilibrium measurement

A flow chart of phase equilibrium measurement experiment is shown in Fig. 5-5. First, the aqueous phase was prepared by dissolving acids in de-ionized water. The pH of the solution was adjusted by using NaOH solution. The solvent phase for reactive extraction experiments was prepared by dissolving the reactive extractants into the diluents depending on the type of the experiment. An aqueous to solvent weight ratio of 1:1 was mixed and equilibrated for at least 3 hours, the minimum time sufficient for complete phase separation using a constant temperature. This was followed by measure of the residual of acid in the aqueous phase using High Performance Liquid Chromatography (HPLC), which will be explained in chapter 5.4.1. Equilibrium concentration of lactic acid in the solvent phase was calculated via mass balance. Following extraction, the laden solvent phase comprised then transferred to back-extraction with a stripping phase. This back-extraction occurred under the same conditions and timescales as the extraction, with and equivalent mass of stripping solution and laden solvent phase being equilibrated in the mixing flasks after their washing with acetone.

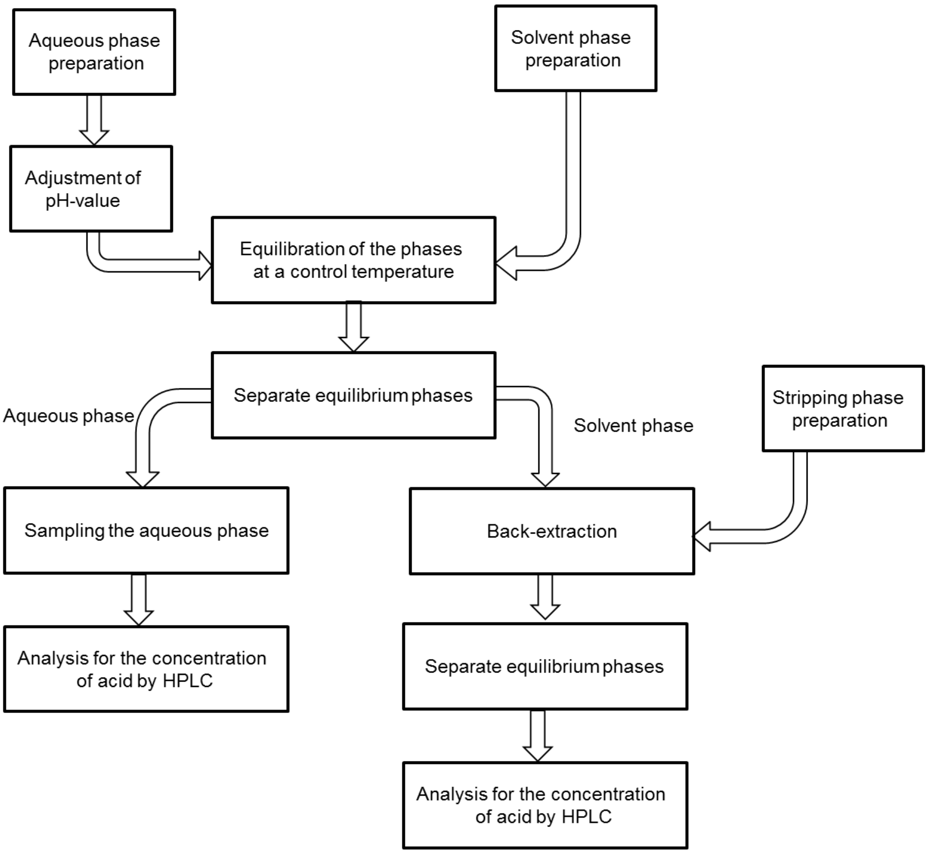

Fig. 5-5 Flow chart of phase equilibrium study

5.3.2 Liquid membrane permeation

Before starting an experiment, the PE support layer is impregnated with the liquid membrane via ultrasonication for 30 minutes to prevent air inclusion in the support layer respectively to ensure fully wetting of the porous support layer. Then the support layer was taken out and dried from droplets on the surface. The impregnated support layer was sealed and placed between the two phases chamber. The assembled reactor is filled with the equal volume of feed- and stripping phase at the same time, which is the starting point of the experiments. Samples from both phases were then collected at the defined time intervals. After finishing the experiment, PE support layer was cleaned by acetone several times for removing the impregnated liquid membrane and left overnight before using for other experiment.

5.4 Analytical

5.4.1 High Performance Liquid Chromatography (HPLC)

Acid concentration in the aqueous phase were determined by high-performance liquid chromatography (Dionex) (see Fig. 5-6). The HPLC systems consists of a REZEX-ROA column and an UV/VIS detector, using a wavelength of 210 nm. As mobile phase 0.005 M H_2SO_4 in ultrapure water with a flow rate of 0.5 mL/min was used. All samples were analyzed at room temperature. The concentration of extracted acid in the solvent phase was calculated by mass balance. The peak area that is obtained from HPLC measurement was recalculated to the concentration of lactic acid (c_{LA}) using the calibration curves. The calibration curves for lactic acid, formic acid and acetic acid are summarized in Appendix.

Fig. 5-6 High performance liquid chromatography (HPLC)

5.4.2 Viscosity and density measurement

Dynamic viscosity and density are simultaneously measured with the Stabinger Viscometer SVM 3000, made by Anton Paar (see Fig. 5-7). The measurement of dynamic viscosity with Stabinger Viscometer SVM 3000 relies on the Couette principle, therefore the outer cylinder is a tube rotating at constant speed and the conical-shape internal cylinder is centered within the sample liquid by hydrodynamic lubrication effects and centrifugal forces. In this way all bearing friction, an inevitable factor in most rotational devices, is fully avoided. The density is measured by an electronic measurement of the vibration time. The measured sample was introduced into the U-tube shaped bent glass oscillator. The vibrator is electronically excited to an undamped oscillation. The density is then calculated with two references substance, air and deionized water.

Fig. 5-7 Viscosity and density measurement equipment.

6 Results and discussion

The results of experimental studies are presented and discussed in this chapter. First, physical extraction of lactic acid using two different solvents will be discussed. The second part summarizes the results for equilibrium studies on reactive extraction of lactic acid from the acidic solution in dependence on the solvent phase. Further, the transfer to liquid membrane permeation is discussed. The third part discusses the studies performed for the reactive extraction of lactic acid from alkaline solution. At the end the transfer from liquid-liquid extraction to liquid membrane permeation is discussed.

6.1 Physical Extraction

Physical extraction principle as well as the mechanism of lactic acid extraction is explained in section 4.1.1. In this chapter, the physical extraction of lactic acid is investigated in dependence on the solvent polarity. Therefore, *n*-undecane was selected as non-polar solvent and as polar solvent 1-octanol was used. The evaluation of the experiments use the distribution coefficient ($K_{d,\text{solvent}}$) as a function of the partition coefficient (P) and the dimerization constant (D) which is explained by Equation 4-11. Phase equilibria data of both solvents were measured by varying the initial acid concentration in the range of 0.2-1 mol/L.

Tab. 6-1 shows the correlation of the distribution coefficient for *n*-undecane and 1-octanol for different initial acid concentration. These results indicate poor acid extraction by physical extraction, and distribution coefficients less than 1 were found for both solvents. The K_d values were in the range of 0.01-0.05 and 0.24-0.27 for *n*-undecane and 1-octanol, respectively. Since, acid removal by physical extraction is basically occurred by the solvation of acid molecules to the solvent by donor bonds, the equilibrium solubility is the criterion for determining the maximum loading of solvent (Keshav et al., 2009). Due to its donor and acceptor characteristic, 1-octanol interacts by hydrogen bonding, and hence provides higher partition coefficients, compared to *n*-undecane, for which only nonspecific directional, induction and dispersion forces are employed (Wasewar et al., 2010).

Tab. 6-1 Summary of the calculated distribution coefficient, partitioning coefficient and dimerization factor for lactic acid using *n*-undecane and 1-octanol; $c_{\mathrm{acid,\ initial}}$= 0.2-1.0 mol/L; T= 25°C

Solvent	$c_{\mathrm{LA,ini}}$ (mol/L)	K_d	P	D
n-undecane	0.22	0.055	0.06	6.62
	0.47	0.029		
	0.74	0.057		
	1.00	0.016		
1-octanol	0.22	0.242	0.24	0.46
	0.47	0.212		
	0.74	0.273		
	1.00	0.271		

The dimerization constant (*D*) of lactic acid noticeably decreases by a factor of ~14 when changing the solvent from *n*-undecane to 1-octanol. The dimerization constant was 6.62 and 0.46 for *n*-undecane and 1-octanol, respectively. It can be concluded that in *n*-undecane, the acid-acid bond is preferred especially, while acid-solvent hydrogen bonds are observed when 1-octanol was used. These results fit well to the data from literature. Maurer.(2006) described the dimerization by intermolecular hydrogen bonding of acetic acid in low polar solvents.

Fig. 6-1 depicts the phase equilibrium isotherm performed at 25°C for *n*-undecane and 1-octanol. Results indicate the stronger solute-solvent interaction by high polar solvent 1-octanol compared to *n*-undecane. However, these two solvents provide poor performance to extract lactic acid from aqueous solution, as low distribution coefficient were observed. Thus, reactive extraction is needed and will be discussed in the following sections.

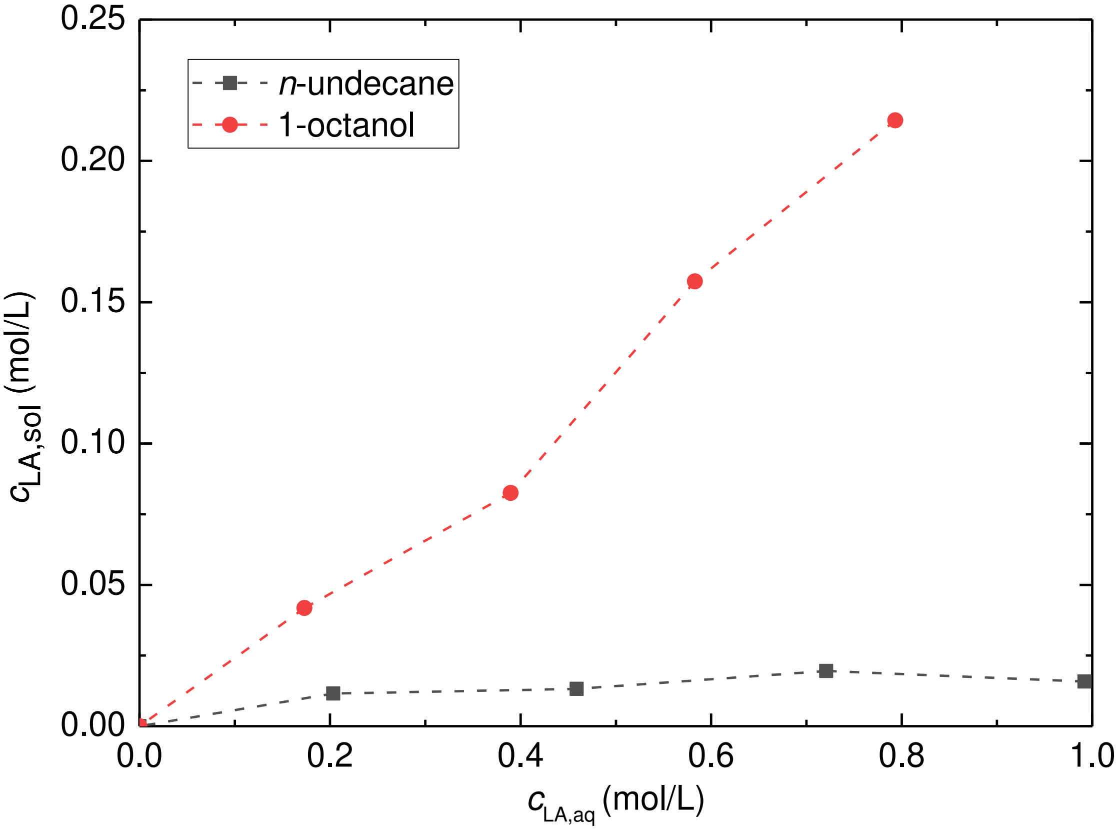

Fig. 6-1 Phase equilibria data for physical extraction of lactic acid by *n*-undecane and 1-octanol; $c_{LA,\ initial}$= 0.2-1.0 mol/L; T= 25°C; ambient pressure.

6.2 Reactive extraction of lactic acid from acidic solution

In this section, phase equilibrium of lactic acid extraction using TOA is investigated. Therefore, the temperature, solvent composition was varied. Effect of parameters, equilibrium constant determination and back-extraction are discussed in the following sections.

6.2.1 Effect of temperature on lactic acid extraction

In general phase equilibrium depends on the temperature, therefore the influence of temperature on lactic acid extraction was investigated in a range between 25-45°C at constant initial acid concentration of 0.2 mol/L. The solvent contains 20 wt% TOA in 1-octanol or *n*-undecane.

Fig. 6-2 shows that temperature has a negligible effect on the extraction efficiency of lactic acid in both diluents. The reaction between lactic acid and TOA is anticipated to be an exothermic reaction. Within the observation range there is no influence on temperature found. Since, the fermentation of lactic acid in the industry operates in the temperature range of 25-60°C (Jantasee et al., 2017) , this temperature span is considered efficient for applying to in-situ lactic acid extraction. As the temperature influence is negligible, all experiments in this work were performed 25°C.

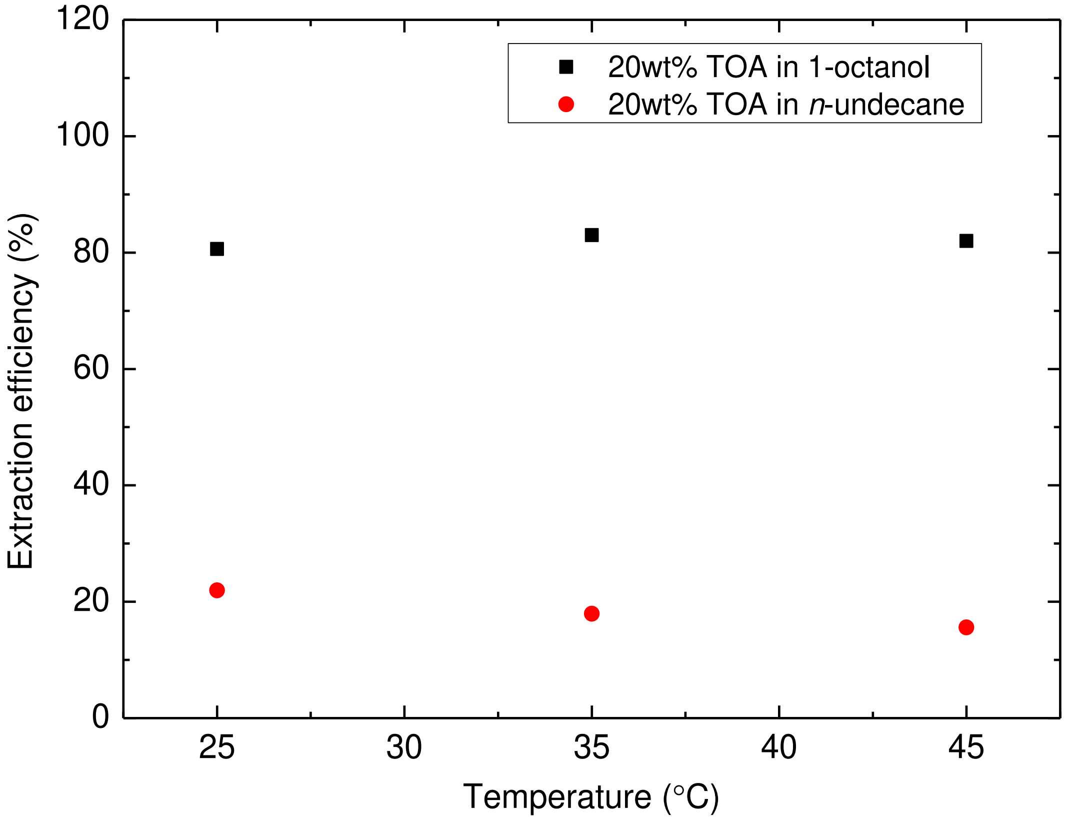

Fig. 6-2 Phase equilibria data for lactic acid extraction in dependence on the temperature. ; $c_{\mathrm{LA,\ initial}}$= 0.2mol/L; ambient pressure.

6.2.2 Effect of solvent composition on lactic acid extraction

The results presented in section 6.1 , emphasize to use reactive extraction for lactic acid recovery. Due to its high Brønsted basicity tri-*n*-octylamine (TOA), a tertiary long-chain aliphatic amine, has been reported to provide high distribution coefficients for carboxylic acids and low aqueous solubility at the same time (Painer et al., 2017). Besides the reactive extractants, the solvent phase in reactive extraction also consists of the modifier and the diluent. Purpose of the diluent is to decreases the density and the viscosity, the modifier increases the solubility of the formed complex or salt in the solvent phase. In the following chapter, the equilibrium study for lactic acid extraction using TOA dissolved in non-polar diluent and polar solvent as a modifier are presented. Experiments performed in chapter 6.1 indicate already, that *n*-undecane can be used as diluent, and 1-octanol may be used as modifier.

Fig. 6-3 shows the influence of the reactive extractant concentration on the extraction efficiency of lactic acid with an initial concentration 1 mol/L. The results signify the role of chemical extraction involving TOA in 1-octanol and/or *n*-undecane on lactic acid extraction over physical extraction. The synergistic extraction ability of TOA diluted in 1-octanol is significantly higher than *n*-undecane. Reason is the simultaneous effect of solvation and chemical interaction. The substantially increase of extraction efficiency from 31% to 80% when the TOA concentration is increased from 0 wt% TOA (physical extraction) to 20 wt% demonstrates the effective combination of reactive extraction with solvation when 1-octanol is applied.

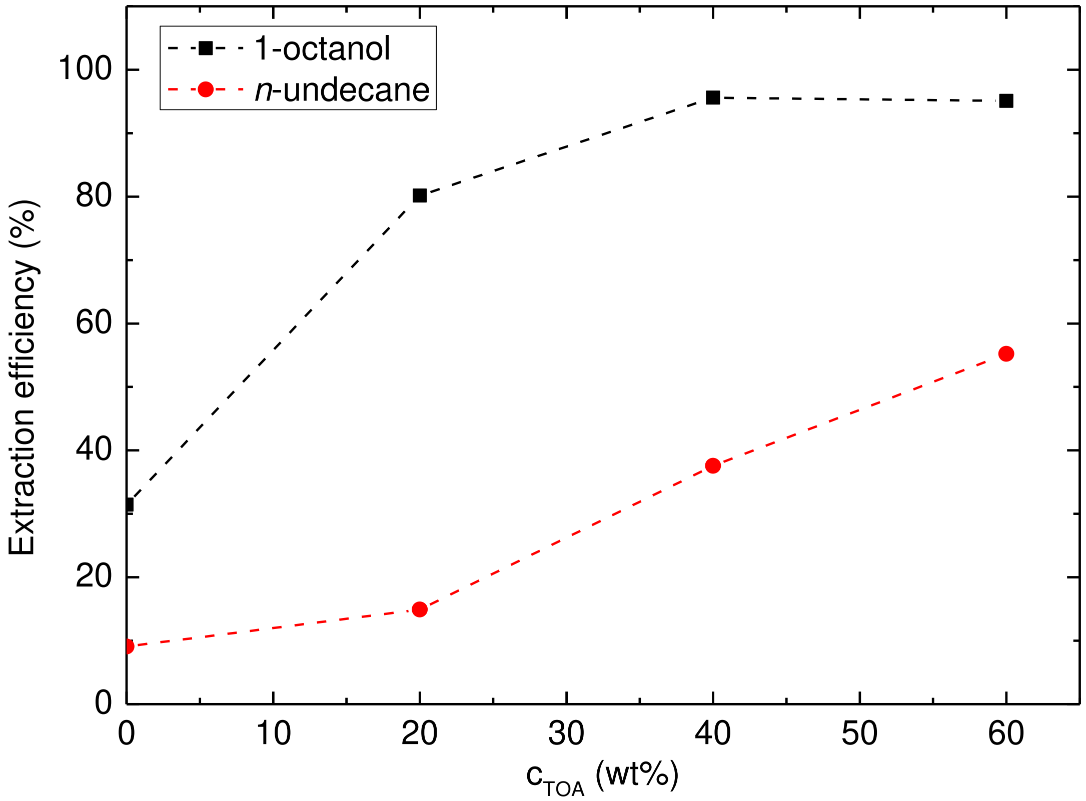

Fig. 6-3 Effect of TOA concentration diluted in *n*-undecane and 1-octanol on the extraction efficiency of lactic acid; $c_{LA,initial}$= 1 mol/L; T= 25°C; ambient pressure

The extraction efficiency increases when TOA concentration increases and undergoes a maximum of 95% for the binary mixture of 40 wt% TOA. In comparison to mixtures of TOA/*n*-undecane, the extraction efficiency gradually increases with increasing TOA concentration. Similar observations have been obtained by Cascaval et al. (2011). They stated that with increasing interfacial amount of amine by increasing its concentration in the solvent phase, the acid concentration in the solvent phase increases too. It is obvious that the polarity of 1-octanol boosts the solubility of the acid-amine salt in the solvent. 1-octanol contributes to the solubility of the acid-amine salt by forming H-bonds, and thus raises the extraction efficiency. The degree of acid association (*n*) from both solvents will be discussed in chapter 6.2.3

When comparing the two binary mixtures, TOA/*n*-undecane and TOA/1-octanol, the binary mixture of TOA/1-octanol leads to higher extraction efficiency and hence is preferred compared to the binary mixture TOA/*n*-undecane.

To increase the extraction efficiency by combine the synergistic extraction ability of TOA/1-octanol and decrease the viscosity, the ternary mixture solvent (TOA/1-octanol/*n*-undecane) was investigated. The influence of the mixture of diluent (*n*-undecane) and modifier (1-octanol) with TOA was first investigated (see Tab. 6-2). The ratio between the modifier, 1-octanol and TOA was kept constant at one by weight for all experiments since at the maximum content of amine and modifier has been shown to be an optimized solvent composition (Siebenhofer and R, 1983) and the equilibrium data of lactic acid were elaborated.

Tab. 6-2 The influence of the mixture of diluent (*n*-undecane) and modifier (1-octanol) with TOA; $c_{LA,initial}$= 1.0 mol/L; T= 25°C; ambient pressure

TOA (wt%)	1-octanol (wt%)	*n*-undecane (wt%)	Solvent viscosity (m·Pas, 20°C)	$c_{LA,aq}$ (mol/L)
40	60	-	9.9	0.96
40	40	20	4.8	0.86

The results show that by decreasing the 1-octanol concentration from 60 to 40 wt%, the equilibrium lactic acid concentration slightly decreases from 0.96 mol/L for the binary mixture to 0.86 mol/L for the ternary mixture whereas the viscosity is decreased by about two time. The data show that the diluent in the ternary solvent systems is needed in terms of viscosity control.

In a follow up series of experiments the extractant concentration (TOA) was varied from 15-40 wt% in the presence of 1-octanol diluted in *n*-undecane. The initial concentration of lactic acid in the aqueous phases was between 0.2 and 1.0 mol/L. An experimental matrix and the summary of the distribution coefficient and extraction efficiency is shown in Tab. 6-3. The concentration of TOA was limited at a maximum concentration of 40 wt% according to the outcome shown in Fig. 6-3 and due to its high viscosity and prevention from third phase formation. For all experiments with a concentration of ≥ 40 wt% TOA third phase formation was observed. Undesired third phase formation during extraction leads to a loss of extracted acid. Third phase formation was also observed in experiments using 25 wt% TOA above an acid concentration of 0.8 mol/L. By increasing the acid concentration the formation of ring structures and hence emulsions due to substitution of solvent molecules with water is most likely (Kislik, 2012).

Tab. 6-3 Summary of the distribution coefficient and extraction efficiency for lactic acid extraction with different solvent compositions and different initial lactic acid concentrations.; T= 25°C; ambient pressure

TOA:-1-octanol:*n*-undecane (wt%)	$c_{\mathrm{LA,initial}}$ (mol/L)	$c_{\mathrm{LA,aq}}$ (mol/L)	$c_{\mathrm{LA,sol}}$ (mol/L)	K_d	E (%)
15:15:70	0.215	0.092	0.123	1.35	57.5
	0.472	0.236	0.236	1.01	50.2
	0.740	0.414	0.326	0.83	45.4
	1.007	0.599	0.408	0.69	40.7
25:25:50	0.215	0.037	0.178	4.89	83.0
	0.471	0.099	0.372	3.75	78.9
	0.740	0.189	0.551	2.91	74.4
	1.007	0.324	0.683	2.11	67.8
40:40:20	0.215	0.006	0.209	34.79	97.2
	0.472	0.020	0.452	22.18	95.7
	0.740	0.045	0.695	15.76	94.0
	1.002	0.079	0.923	11.71	92.1

Fig. 6-4 shows the third phase in the solvent phase occurring at TOA concentrations ≥ 40 wt% TOA and acid concentrations ≤ 1 mol/L or ≥ 25 wt% TOA and an acid concentration ≥ 0.8 mol/L. Third phase formation was described by Schulz (Schulz et al., 2016), they developed a model related to the hydrophilic and lipophilic structure between formic acid and terpenyl amine in the emulsion. However, it is difficult to know anything about the chemical or physical properties of the third phase observed at this stage because separating it from the other two phases is not possible with the volumes used. In order to determine physical and chemical properties of the third phase, the same extraction should be performed with larger volumes so that the third phase can be sampled and analyzed.

Fig. 6-4 Third phase in the solvent phase after the removal of the aqueous phase for formic acid with 25:25 TOA:1-octanol by weight, diluted in *n*-undecane; $c_{\mathrm{FA,\ initial}}$ = 0.8 mol/L; T= 25°C; ambient pressure

Fig. 6-5 depicts phase equilibrium data of lactic acid with different solvent compositions. The results show that the equilibrium concentration of lactic acid in the solvent phase increases with increasing TOA as well as 1-octanol concentration.

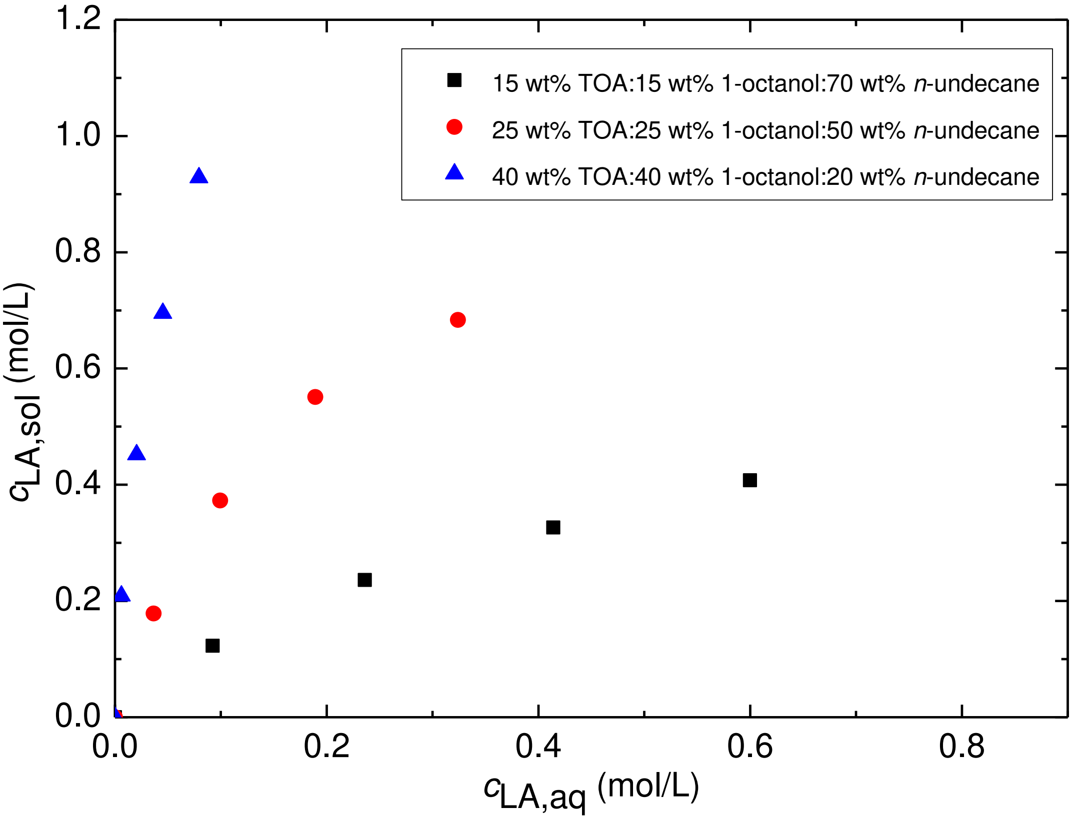

Fig. 6-5 Phase equilibrium data for lactic acid for three different solvent compositions; $c_{LA, initial}$= 0.2-1.0 mol/L; T= 25°C; ambient pressure.

For all solvent compositions, the distribution coefficients were found decrease with increasing initial acid concentration. The distribution coefficients were found increasing in the range of 0.69-1.35, 2.11-4.89 for the solvent composed of 15:15 TOA:1-octanol and 25:25 TOA:1-octanol by weight, respectively. The increasing was highest for the solvent composed of highest amount of 1-octanol at 40 wt% in the range of 11.71-34.79. This result is beneficial for the application of reactive extraction from fermentation broth since the lactic acid concentration acid is in general less than 10 wt%.

6.2.3 Determination of equilibrium constant and the degree of association

Law of mass action is applied for the determination of the stoichiometric equilibrium constant (K_{st}) and the degree of association (n) from the equations summarized in section 4.1.2. The equation is solved based on the equilibrium data obtained from the experiments of lactic acid extraction with different solvent concentrations. The results were fitted according to Equation 4-22 with a linear cure fit function. By altering the degree of association, the slope of the best fit determines the equilibrium constant.

The graphical representation is proceeded to determine the values of K_{st} and n for different solvent system as depicted in Fig. 6-6,Fig. 6-7 and Fig. 6-8. This could be confirmed that the data is well descripted by the equation since all graphical plot have the R^2 value of 0.99. The estimated values for the stoichiometric equilibrium constant and the degree of association for the different solvent compositions are summarizes in Tab. 6-4.The modeled data point out a significantly difference in the degree of association for reactive solvent composed of 1-octanol or *n*-undecane. The value of $n \approx 1$ estimated from TOA with 1-octanol suggests the 1:1 adduction of lactic acid to TOA whereas $n > 1$ was found for the TOA composed of *n*-undecane.

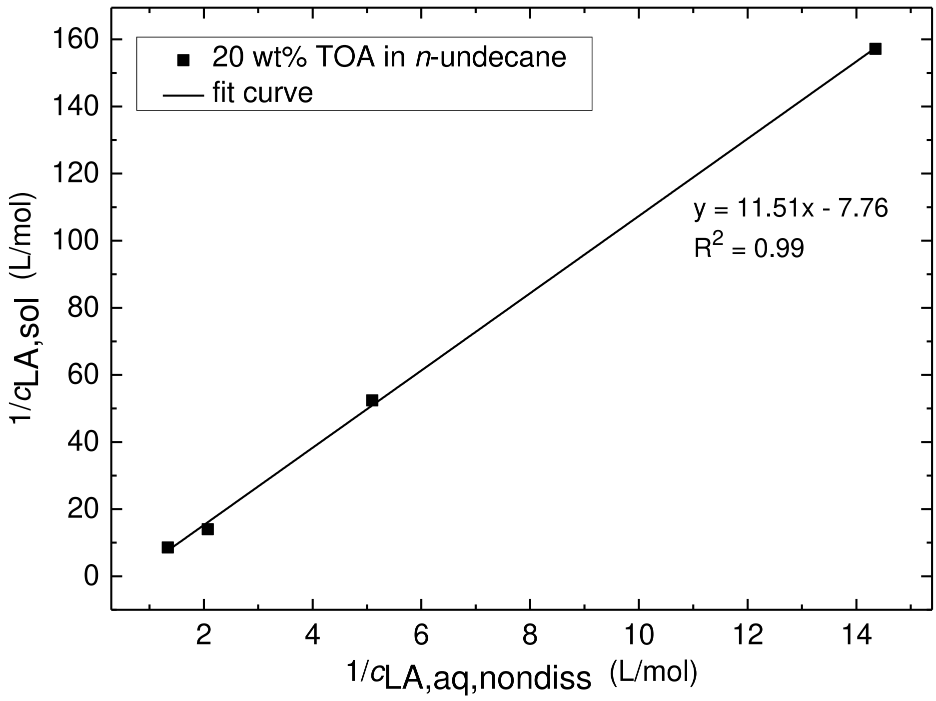

Fig. 6-6 Determination of the equilibrium constant and the degree of acid association of lactic acid; solvent composition: 20 wt% TOA in *n*-undecane; T= 25°C; ambient pressure

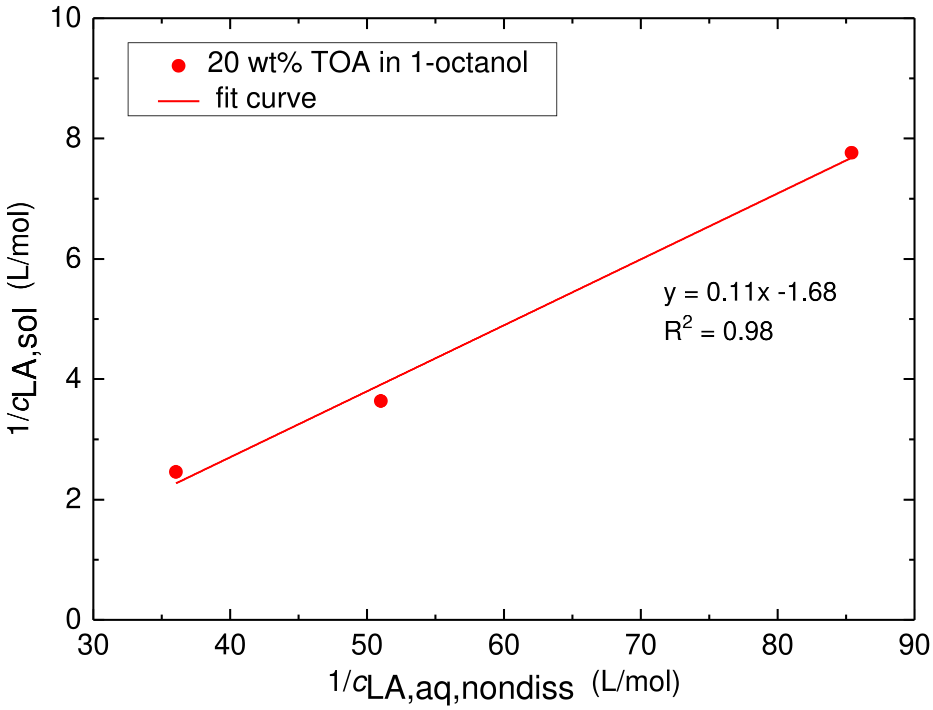

Fig. 6-7 Determination of the extraction equilibrium constant and the degree of acid association of lactic acid. solvent composition: 20 wt% TOA in 1-octanol; T= 25°C; ambient pressure

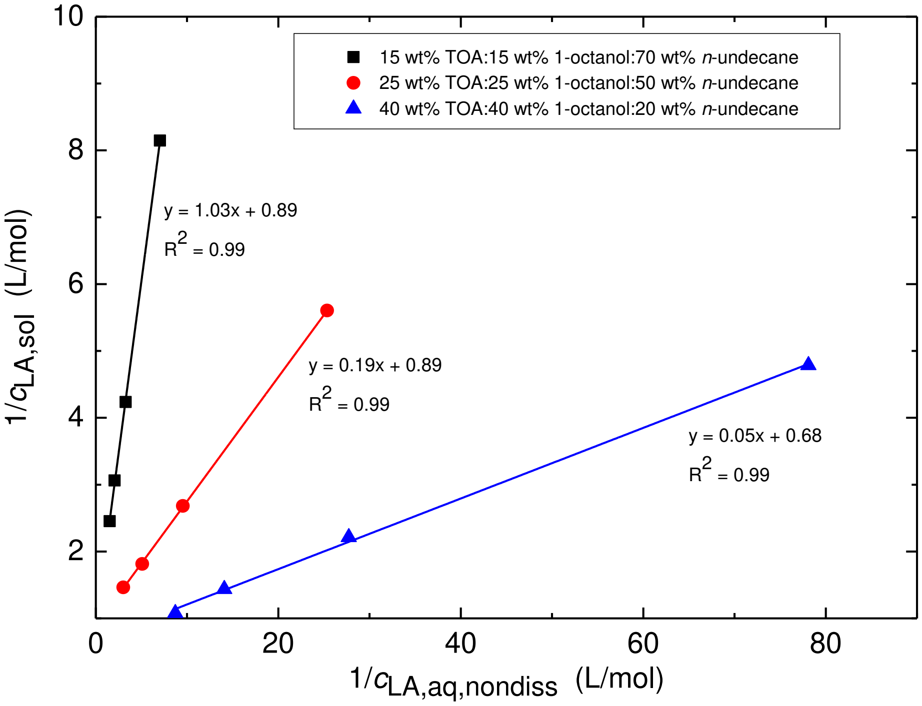

Fig. 6-8 Determination of the extraction equilibrium constant and the degree of acid association of lactic acid with different solvent compositions; T= 25°C; ambient pressure

The stoichiometric equilibrium constant of lactic acid increases with increasing 1-octanol concentration. The maximum K_{st} with 24 is related the solvent composition of 40 wt%TOA:40 wt% 1-octanol in *n*-undecane, reason is the high solvation ability. It is noticeable that the polarity of 1-octanol improves the solubility of the acid-amine salt in both binary and ternary solvent mixture.

Tab. 6-4 Summary of calculated K_{st} and n for physical and reactive extraction of lactic acid for different solvent compositions; $c_{LA,initial}$= 0.2-1.0 mol/L; T= 25°C; ambient pressure

TOA (wt%)	1-octanol (wt%)	*n*-undecane (wt%)	Solvent viscosity (m·Pas, 20°C)	n	K_{st}
20	-	80	1.65	1.42	0.13
20	80	-	9.56	0.99	20.03
15	15	70	2.34	0.81	3.53
25	25	50	2.92	0.97	9.73
40	40	20	4.85	0.85	24.48

Depending on the microorganism used, during the fermentation of lactic acid other carboxylic acids, such as formic acid and acetic acid, are produced as by-product (Lee et al., 2004). Therefore, phase equilibrium data of formic acid and acetic acid were elaborated as the same method with lactic acid in order to determine the equilibrium constant and degree of extraction as shown in Fig. 6-9 and Fig. 6-10. The summary of the calculated K_{st} and n are given in Tab. 6-5

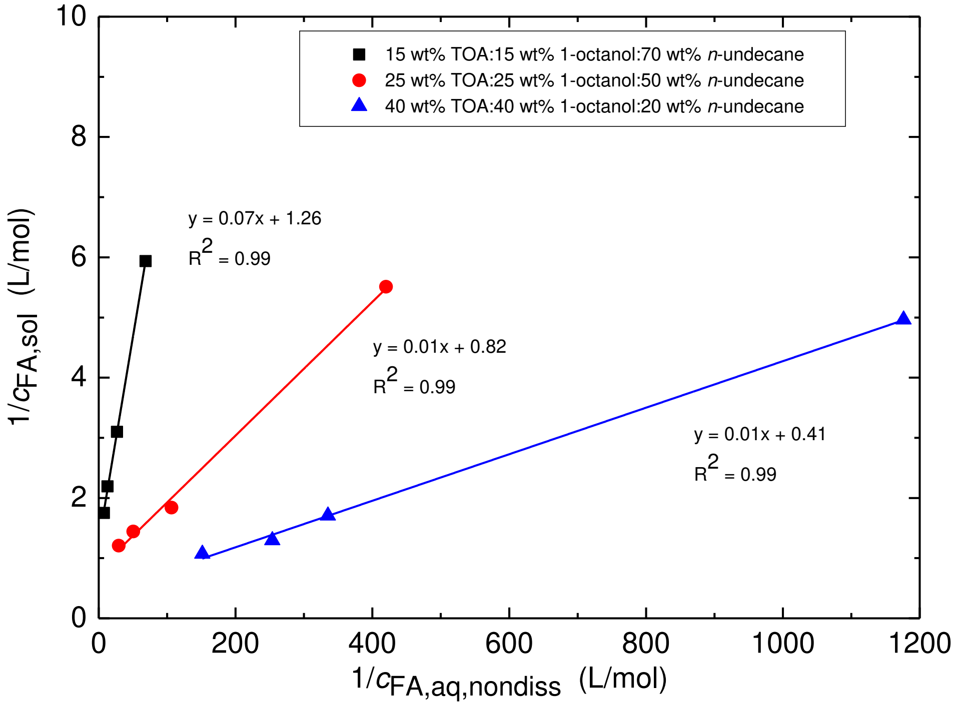

Fig. 6-9 Determination of the extraction equilibrium constant and the degree of acid association of formic acid with different solvent compositions; T= 25°C; ambient pressure

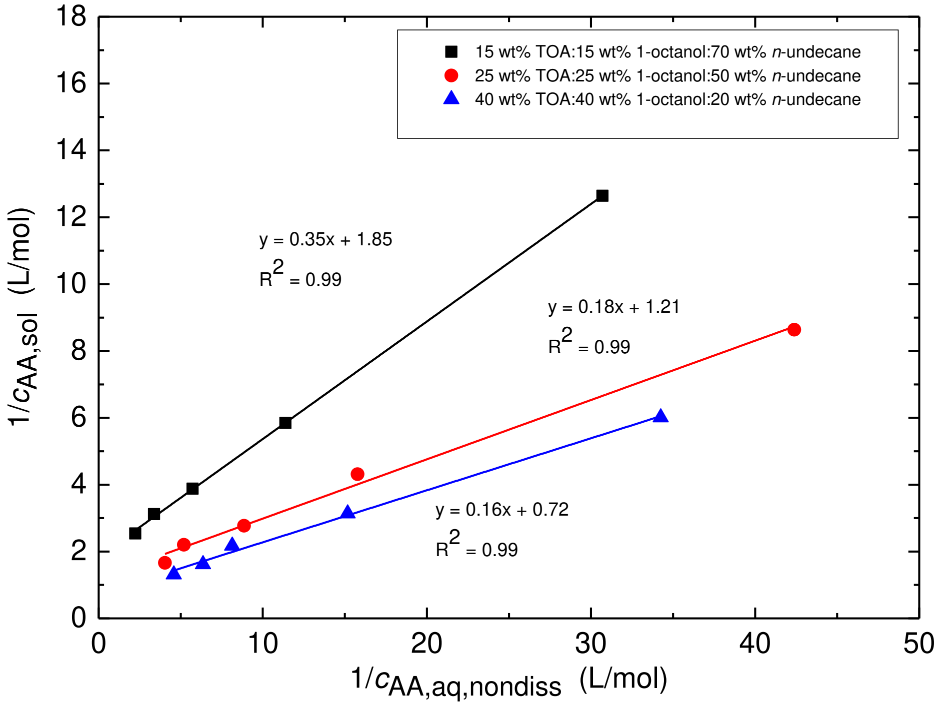

Fig. 6-10 Determination of the extraction equilibrium constant and the degree of acid association of acetic acid with different solvent compositions; T= 25°C; ambient pressure

Tab. 6-5 Summary of calculated K_{st} and n for reactive extraction of formic acid and acetic acid with solvent composition of TOA:1-octanol diluted in *n*-undecane; $c_{acid,initial}$= 0.2-1.0 mol/L; T= 25°C; ambient pressure

TOA (wt%)	1-octanol (wt%)	*n*-undecane (wt%)	Solvent viscosity (m·Pas, 20°C)	Acid	n	K_{st}
15	15	70	2.34	Formic	1.55	27.79
				Acetic	1.65	5.07
25	25	50	2.92	Formic	1.99	79.35
				Acetic	1.55	5.25
40	40	20	4.85	Formic	1.99	142.79
				Acetic	1.09	6.48

The results show that, the K_{st} is for formic acid the highest and for acetic acid the smallest, values for lactic acid are between the two other acids. The K_{st} values follow the pK_a of the respective acids. The pK_a value of formic acid is 3.75, for lactic acid it is 3.86 and acetic acid has a pK_a value of 4.75. Generally, the hydrophobicity and acidity of the acids are the most important factors affecting the degree of extraction, extraction has been shown to increase with increasing acidity of the acid (Eyal and Canari, 1995). The lower the pK_a value of the acid, the higher the degree of dissociation and the more easily it is extracted because the ion exchange mechanism can occur more easily due to a higher abundance of H^+. The results fit well to published data (Qin et al., 2003). Moreover, the determined values of n for the extraction of formic acid and acetic acid by the solvent system of TOA/1-octanol/n-undecane indicate the possibility of higher complex formation acid molecule on TOA could be formed.

6.2.4 Back extraction of lactic acid by $NaHCO_3$

Liquid-liquid extraction of carboxylic acids requires a second separation step for recovery of the acid from the solvent phase. Back-extraction of lactic acid is done by reversible complexation from the laden solvent phase to an aqueous stripping phase. Since the reactions taking place during the forward extractions are anion-exchange reactions, the reverse reaction with pure water, hence, provides poor distribution of acid from solvent to aqueous phase. Therefore, a strong chemical bond is needed to enhance the back-extraction reaction. Stripping solutions containing sodium hydrogen carbonate ($NaHCO_3$), have been reported to be effectively used as stripping agent for lactic acid from laden tri-*n*-octylamine (Kyuchoukov and Yankov, 2010).

In this chapter, back-extraction of laden solvent phase with lactic acid was carried out using $NaHCO_3$. The concentration of $NaHCO_3$ was fixed at 1 mol/L for the experiments, since the back-extraction efficiency was reported to have a maximum when the concentration of $NaHCO_3$ is higher than the concentration of lactic acid in the solvent phase (Kyuchoukov and Yankov, 2010).

The back-extraction phase equilibrium data of lactic acid is depicted in Fig. 6-11. As can be seen, the equilibrium concentration of lactic acid in the stripping phase increased with the equilibrium concentration of lactic acid in the solvent phase. The slope of the linearity indicates the stripping distribution coefficient of lactic acid. The results indicate that lactic acid is more easily recovered from the solvent composed of 1-octanol than *n*-undecane.

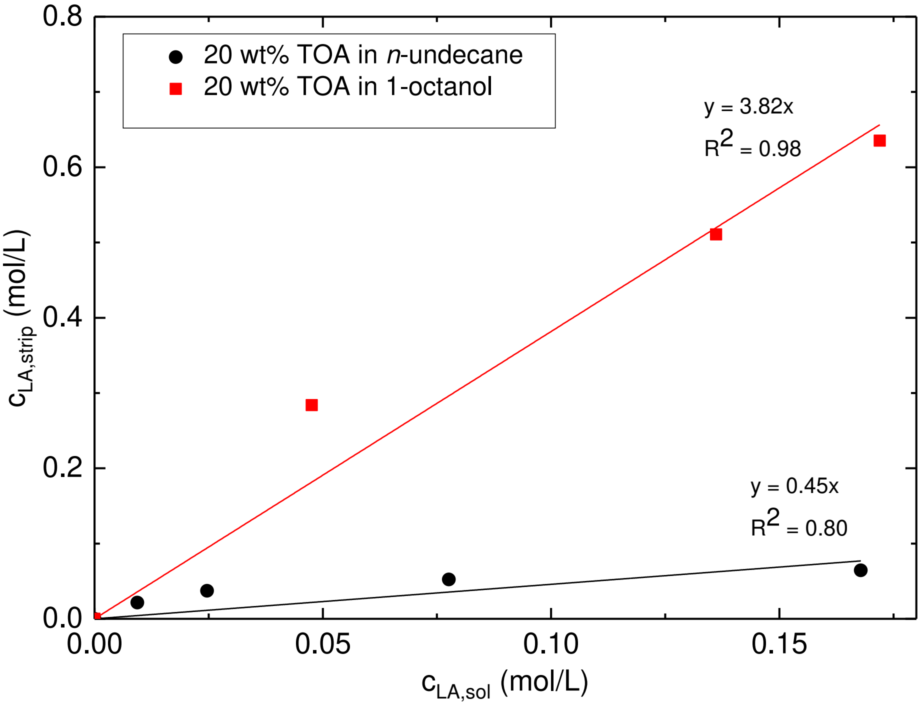

Fig. 6-11 Phase equilibrium for lactic acid back-extraction.; solvent composition: 20 wt% TOA in 1-octanol and 20 wt% TOA in *n*-undecane ; T= 25°C; ambient pressure

Fig. 6-12 shows the extraction and back-extraction efficiency of lactic acid dependence on initial lactic acid concentration. The back-extraction of lactic acid depends, same as the extraction on the lactic acid concentration in the solvent phase. The trend of back-extraction efficiency was found to slightly decrease for increase of acid concentration of the TOA composed of 1-octanol, whereas a decrease was found with *n*-undecane. This result signifies that 1-octanol is a better solvent for acid-amine salt compare to *n*-undecane due to it exhibits higher distribution coefficients during forward extraction and back-extraction.

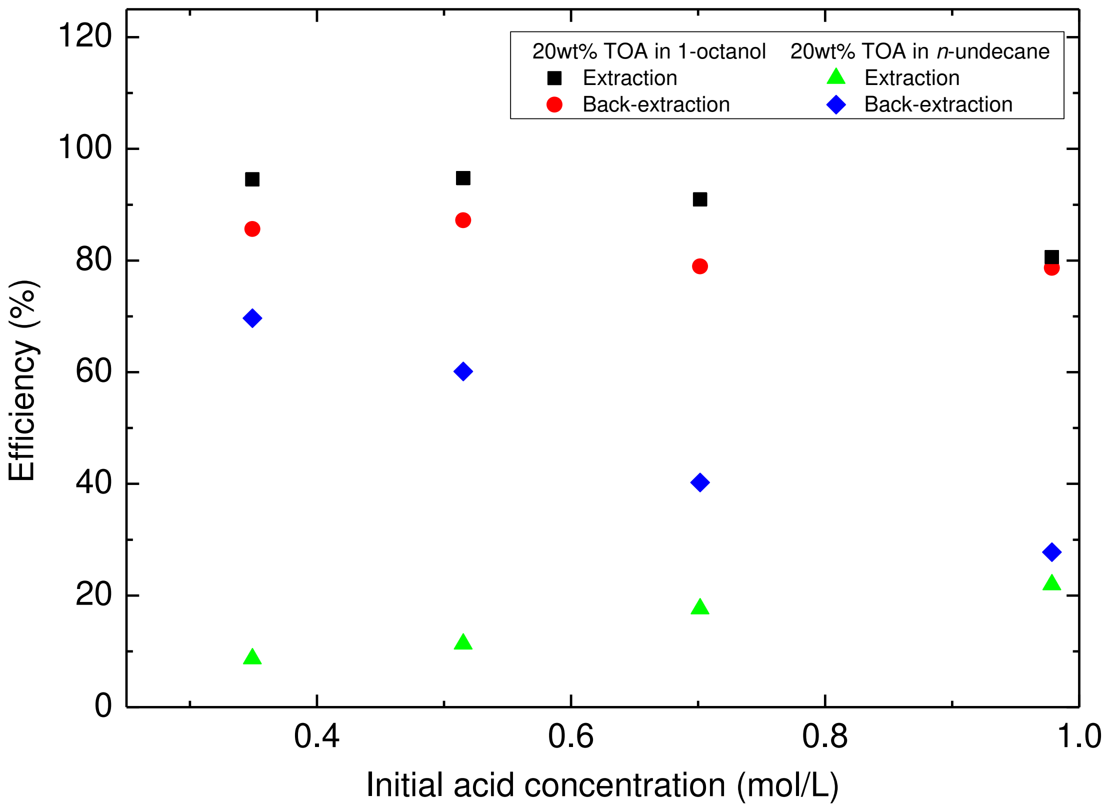

Fig. 6-12 Extraction and back-extraction efficiency with 1 mol/L $NaHCO_3$ of lactic acid. ; solvent composition: 20 wt% TOA in 1-octanol and 20 wt% TOA in *n*-undecane ; T= 25°C; ambient pressure

Moreover, CO_2 liberation from the aqueous phase was observed during shaking according to Equation 6-1 this is expected.

$$2HL+CO_3^{-2} \leftrightarrow 2L^{-}+H_2CO_3 \leftrightarrow 2L^{-}+H_2O+CO_2 \qquad \text{Equation 6-1}$$

This leads to the necessity of stopping the shaker after at least 10 min and opening it, and the gas was removed from the system to decrease the pressure and avoid leaking during the experiment from the flask.

Further, back extraction efficiency was compared for lactic acid, acetic acid and formic acid at the same initial acid concentration of 0.4 mol/L.

Fig. 6-13 shows the comparison of back-extraction efficiency of lactic acid, formic acid and acetic acid. Similar to the extraction step, the back-extraction relates to the pK_a value and follows: formic acid>lactic acid >acetic acid.

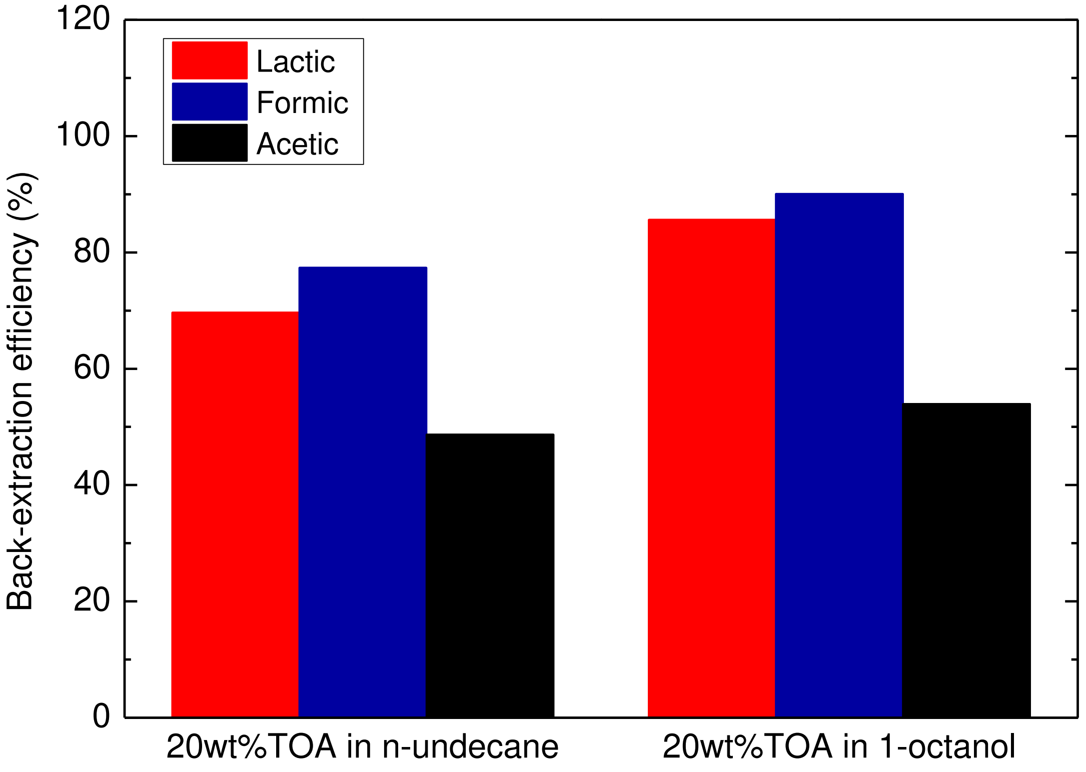

Fig. 6-13 Back-extraction efficiency with 1 mol/L $NaHCO_3$ of lactic acid, formic acid and acetic acid. solvent composition: 20 wt% TOA in *n*-undecane and 20 wt% TOA in 1-octanol; T= 25°C; ambient pressure

6.2.5 Transfer to liquid membrane permeation unit

In the present chapter, the transfer of gained data to supported liquid membrane permeation for lactic acid recovery was studied. A microporous polyethylene sheet was impregnated with the solvent (liquid membrane) and then put between the aqueous and stripping solution to allow simultaneous extraction and back-extraction. This chapter summarizes the results from optimization of liquid membrane composition targeting maximum lactic acid mass transfer. Mass transfer coefficients were calculated and compared among the different liquid membrane used.

6.2.5.1 Optimization of liquid membrane

In liquid membrane permeation the solvent provides the liquid membrane phase. From phase equilibrium measurements, discussed in section 6.2.2, the solvent consist of a reactive extractant (TOA), a modifier (1-octanol) and a diluent (*n*-undecane) provide high extraction efficiency of lactic acid from aqueous solution. Therefore, the effect of TOA concentration in the presence of 1-octanol and *n*-undecane in liquid membrane on mass transfer was studied. The feed solution consisted of 1 mol/L lactic acid solution for all experiments and the stripping phase was 1 mol/L $NaHCO_3$.

The dependence of the diffusion coefficient as a function of TOA concentration is depicts in

Fig. 6-14. The results show that with increasing TOA concentration the diffusion coefficient increases until it reaches a maximum of 4.09×10^{-10} m^2/s. This diffusion coefficient corresponds to a liquid membrane composition of 60 wt% TOA in *n*-undecane. According to Zidi et al.(2010) at low reactive extractant concentration, the diffusion of the acid-amine complex across the liquid membrane is the rate-determining step. By increasing the TOA concentration increased extraction of lactic acid is expected. However, the increase of the diffusion coefficient is not proportional to the increase in the TOA concentration beyond 60 wt% TOA. This is due to increasing viscosity with increasing TOA concentration, seen therefore in Tab. 6-6. The viscosity of the liquid membrane leads to an increase of the liquid membrane resistance to the diffusion of the amine salt species (Garcia-Valls et al., 1999). An increase of the TOA concentration beyond 60 wt% does not compensate the increasing membrane viscosity which hinders mass transfer.

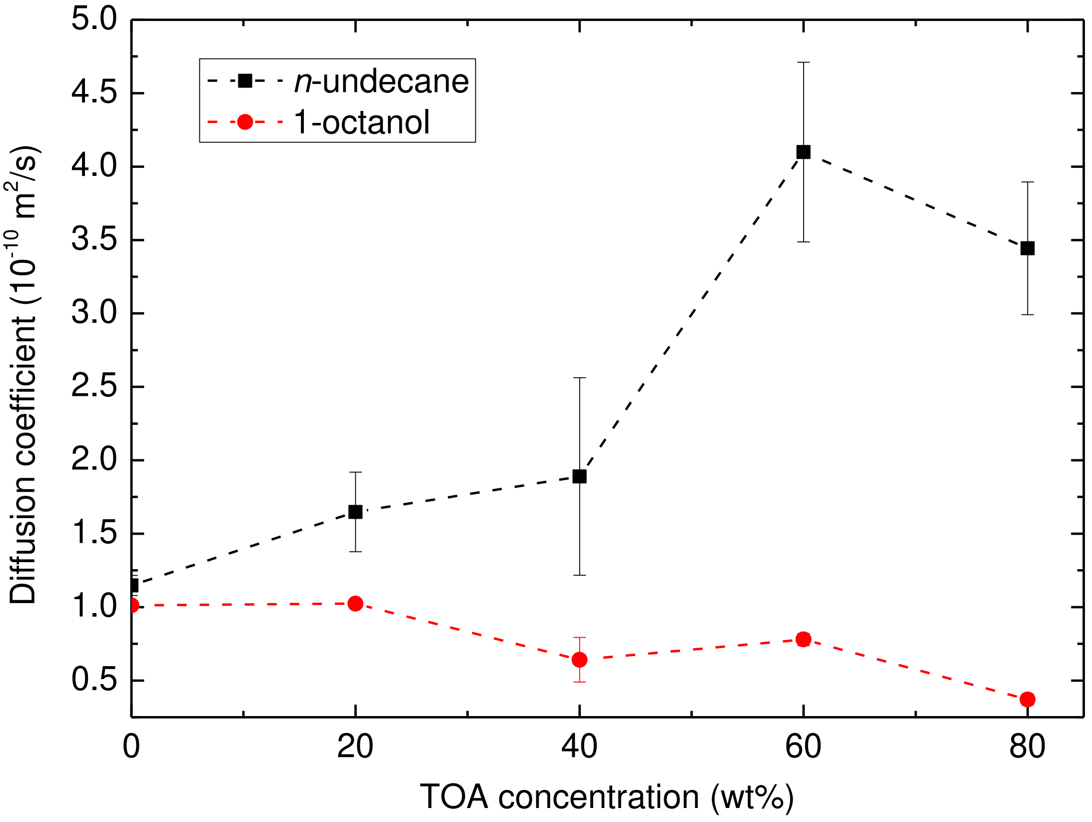

Fig. 6-14 Effect of TOA concentration on the diffusion coefficient of lactic acid. c_{feed} = 1 mol/L; c_{strip} = 1 mol/L $NaHCO_3$; T=25 °C; ambient pressure

Tab. 6-6 Summary of density, viscosity, and diffusion coefficient in lactic acid transport

TOA (wt%)	*n*-undecane (wt%)	1-octanol (wt%)	Viscosity (mPas)	Density (g/cm^3)	Diffusion coefficient ×10^{-10}(m^2/s)
-	100	-	1.18	0.74	1.15±0.07
20	80	-	1.65	0.75	1.65±0.27
40	60	-	2.31	0.77	1.89±0.67
60	40	-	3.49	0.78	4.10±0.61
80	20	-	5.53	0.80	3.44±0.45
100	-	-	9.61	0.81	3.46±0.36
-	-	100	9.00	0.83	1.01±0.10
20	-	80	9.56	0.83	1.02±0.12
40	-	60	9.91	0.82	0.64±0.15
60	-	40	10.24	0.82	0.78±0.04
80	-	20	10.20	0.82	0.37±0.04
30	40	30	3.50	0.79	0.41±0.06

Fig. 6-14 also points out the influence of 1-octanol and *n*-undecane on lactic acid diffusion. Different to phase equilibria measurements, where in reactive extraction, 1-octanol which has higher polarity compared to *n*-undecane increases solvation and stability of lactic acid in the solvent phase, leading to higher extraction efficiency. In liquid membrane permeation the diffusivity of the salt is inversely proportional to the viscosity of the liquid membrane as explained by Stokes–Einstein equation. The liquid membrane consist of TOA-octanol has higher viscosities than the TOA-undecane pairs. Since, 1-octanol has a viscosity of 9 mPas, TOA has 9.6 mPas and *n*-undenace has1.2 mPas, smaller diffusion coefficients were found.

Further, the balance of TOA concentration and the liquid membrane viscosity was investigated. The liquid membrane consisting of 60 wt% TOA in *n*-undecane which has shown the best extraction of lactic acid. In order to clarify the influence of the TOA-concentration on the mass transfer, the liquid membrane composed of 60 wt% TOA in *n*-undecane and 30 wt% TOA: 30 wt%1-octanol in *n*-undecane were compared. Both liquid membrane have a similar viscosity of 3.5 mPas and 3.49 mPas at 20°C, respectively. Tab. 6-6 summarizes the diffusion coefficient for the variation of the liquid membrane composition. The results signify the influence of the TOA concentration on the viscosity. The double TOA-concentration of 60 wt% leads to a diffusion coefficient that is 10 times higher compared to liquid membrane composed of 30 wt% TOA: 30 wt%1-octanol in *n*-undecane. It is due to the fact that the diffusion in the supported liquid membrane takes place after the reaction between TOA and lactic acid hence, the higher the concentration of the reactive extractant in the liquid membrane phase, the better the mass transfer is. The data indicate that a certain concentration is needed, but when having a high concentration of TOA at the interface the diffusion is as expected the rate determining step.

6.2.5.2 Mass transfer in supported liquid membranes

Mass transfer coefficient is the parameter used to define the acid mass transfer between the phases. Yang et al.(2003) determined the rate-controlling step in supported liquid membrane by comparing the mass transfer coefficient across feed boundary layer, membrane mass transfer coefficient, the interfacial mass transfer coefficient and the overall mass transfer coefficient. They found out that the overall mass transfer coefficient is nearly the same as the membrane mass transfer coefficient, which indicates that the rate-determining step of supported liquid membrane is controlled by the diffusion in the microporous support sheet. In the present work the overall mass transfer coefficients of the liquid membrane used to extract lactic acid were calculated and compared in this work.

Fig. 6-15 show the time dependency of the concentration change of lactic acid in the feed phase and the stripping phase. It is obvious that lactic acid concentration decreases in the feed phase whereas the concentration of lactic acid in the stripping phase increases in the same manner. Nearly 20% of lactic acid was recovered in the stripping phase after 24 h of transport through the used set up. Similar results have been found from the transport of phenol through supported liquid membrane using tributyl phosphate (Zidi et al., 2010)

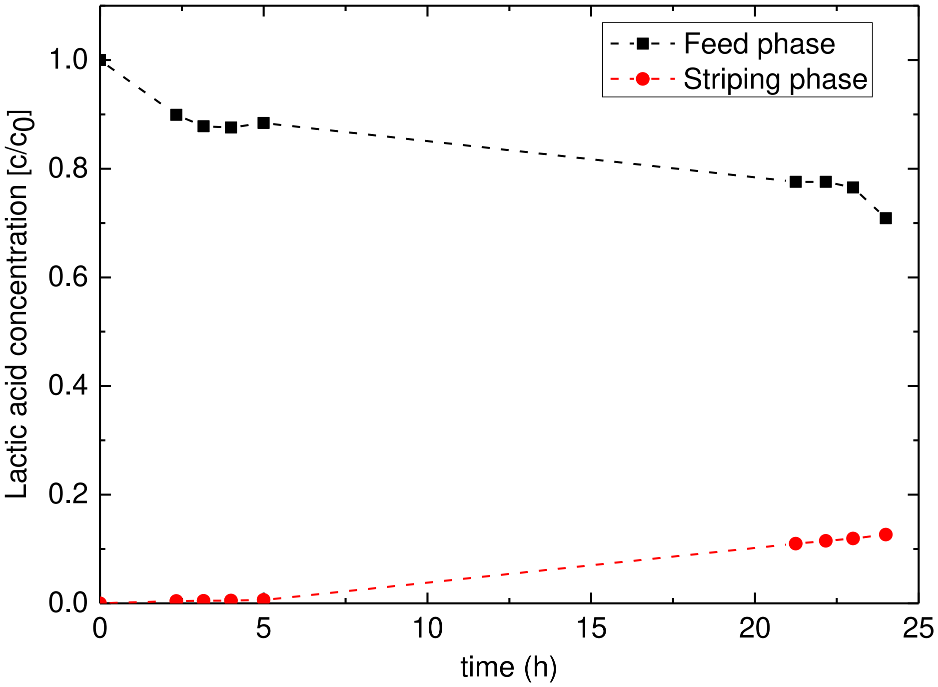

Fig. 6-15 Time course of lactic acid concentration in feed phase and stripping phase. Liquid membrane composition: 60 wt% TOA in *n*-undecane. c_{feed} = 1 mol/L; c_{strip} = 1 mol/L $NaHCO_3$; T=25 °C; ambient pressure

The overall mass transfer coefficient of lactic acid can be calculated according to Equation 4-24 as explained in section 4.2.1.1. A model is prepared by plotting the experimental values of (-ln c/c_0) against time. With the specific membrane area and volume, the trend line slope interprets the overall mass transfer coefficient. Mass transfer coefficients were compared for liquid membranes consisting of 60 wt% TOA in *n*-undecane or 1-octanol and 30 wt% TOA: 30 wt% 1-octanol in *n*-undecane. The modeled plot for the results obtained is shown in Fig. 6-16. A gradually increase in the extent of permeation of lactic acid from feed phase to stripping phase was observed with the variation of liquid membrane compositions. The slope of the modelled data provides the overall mass transfer of 7.2 $\times 10^{-6}$, 3.1$\times 10^{-6}$ and 9.9 $\times 10^{-7}$ for 60 wt%TOA in *n*-undecane or 1-octanol and 30 wt% TOA: 30wt% 1-octanol in *n*-undecane, respectively.

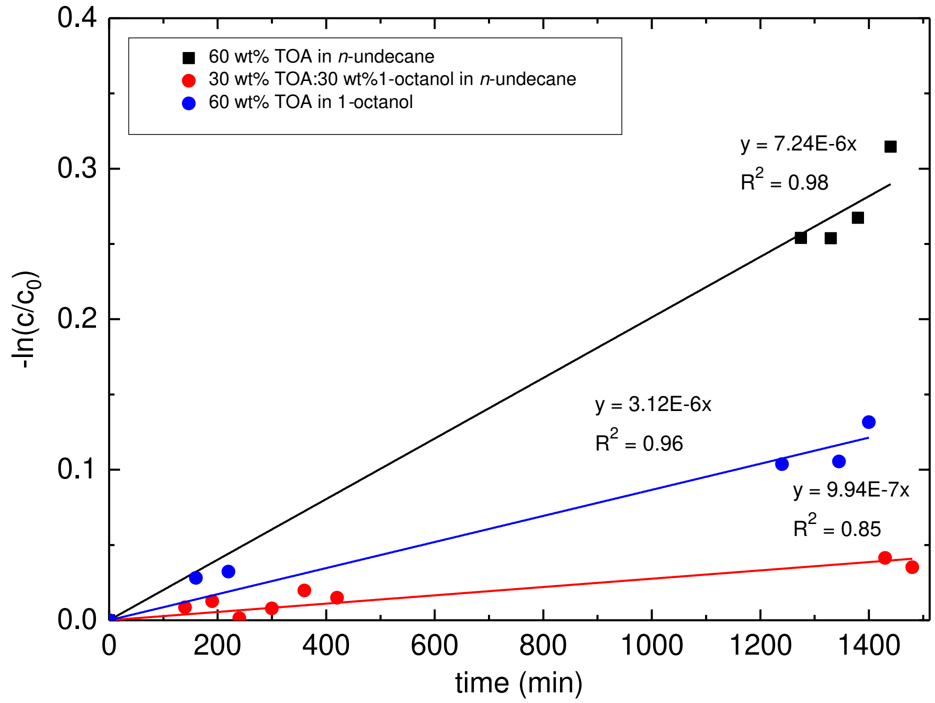

Fig. 6-16 Plot of (-ln c/c_0) vs time for estimate of the overall mass transfer coefficient; c_{feed} = 1 mol/L; c_{strip} = 1 mol/L $NaHCO_3$; T=25 °C; ambient pressure

The results are in agreement with the calculated diffusion coefficients. As expected, the highest mass transfer was found for 60 wt% TOA in *n*-undecane. This results also confirm the role of 1-octanol on lactic acid recovery by supported liquid membrane as mentioned in section 6.2.5.1, that 1-octanol does not improve lactic acid mass transfer. Further, the decrease of viscosity by decreasing the TOA concentration does reduce acid mass transfer too. Therefore, it can be concluded that it is necessary to find the best compromise between the TOA concentration and the viscosity in the liquid membrane.

The overall mass transfer coefficients were then compared to determine the influence of the different single feed phase substances, lactic acid, formic acid and acetic acid, on mass transfer in the supported liquid membrane set up. The initial concentration of the three acids was constant at 1 mol/L in this experiment. The liquid membrane consisted of 60 wt% TOA in *n*-undecane and the stripping solution was 1 mol/L $NaHCO_3$.

Fig. 6-17 shows the comparison of the mass transfer coefficient of lactic acid, formic acid and acetic acid. The overall mass transfer coefficient were found in the order of appearance of formic>lactic>acetic at 7.59×10^{-6} m/s, 7.24×10^{-6} m/s and 6.11×10^{-7} m/s, respectively. The results are in agreement with the reactive extraction study in section 6.2.3. Acids mass transfer coefficients are found to depend on the pK_a value. The results indicate that the selective separation of lactic acid form the acid mixture solution with the liquid membrane composed of TOA is not possible. Therefore, the selective separation of lactic acid was not further investigated.

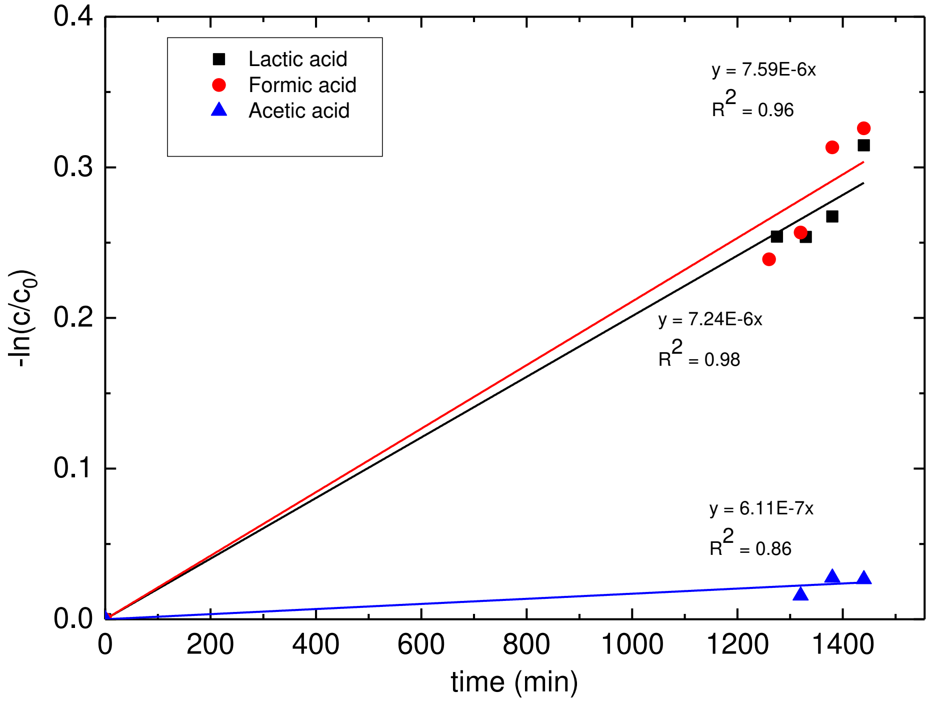

Fig. 6-17 Plot of (-ln c/c_0) vs time for estimation of the overall mass transfer coefficient. Liquid membrane composition: 60 wt% TOA in *n*-undecane. c_{LA}= 1 mol/L; c_{FA}= 1 mol/L; c_{AA}= 1 mol/L; $c_{strip\ phase}$= 1 mol/L $NaHCO_3$

6.3 Reactive extraction of lactic acid from alkaline solution

This chapter targets the isolation of lactic acid from highly alkaline process effluents such as the black liquor from Kraft pulping process. Due to the pH of ~13, the acids are present as dissolved anions. Liquid/liquid extraction may be used to selectively isolate lactic acid, however the common amine reactive extractant follows a salt-formation mechanism. Applying this mechanism to highly alkaline solutions will not succeed. Recently, ionic liquids have been studied as extractants in hydrometallurgical processing. They also show potential performance for carboxylic acid extraction (Marták and Schlosser, 2006). Therefore, the ionic liquid Aliquat 336, Cyphos 101 and Cyphos 104 were chosen as solvent for lactic acid extraction in this work. Section 6.3.1 shows the results from phase equilibrium measurement by liquid/liquid extraction. The implementation of ionic liquid as liquid membrane for lactic acid recovery will be discussed in the section 6.3.2

6.3.1 Phase equilibrium measurement using ionic liquids

In this section, an experimental study of lactic acid extraction from a highly alkaline aqueous solution using Aliquat 336 and the carbonated form thereof is presented. In section 6.3.1.1 the comparison of the commercial ionic liquids Cyphos 101 (trihexyltetradecylphosphonium chloride) and Cyphos 104 (trihexyltetradecylphosphonium bis (2,4,4-trimethylpentyl) phosphinate) will be presented. The extraction equilibrium was measured depending on the solvent composition. In section 6.3.1.2, three solvent categories were used: non-polar, polar-protic and polar-aprotic solvents. The extraction efficiency was examined as a measure of the ability of each group to improve lactic acid extraction. The solvent composition was varied in binary and ternary solvent mixtures, and the comparison thereof is discussed in section 6.3.1.3 and 6.3.1.4. Subsequently, the back-extraction process of the laden solvent was investigated in dependence on the stripping agent, the results are discussed in section 6.3.1.5.

6.3.1.1 Extraction of lactic acid with Aliquat 336 and the carbonated form of Aliquat 336

In this study, the extraction of lactic acid from an aqueous solution using commercially available Aliquat 336 and the carbonated form of Aliquat 336 was investigated. The solvent phase consisted of either Aliquat 336 or its carbonate form diluted in MIBK at a fixed ratio of 1:3, Aliquat:MIBK by weight. Since the dissociation of the acid is essential for the extraction with a quaternary amine, and specifically Aliquat 336, to take place (Kyuchoukov et al., 2005), the pH in the aqueous solution was adjusted by means of the addition of sodium hydroxide at pH 13.

The mechanism of lactate extraction follows an ion exchange mechanism, whereby chloride or carbonate is exchanged by lactate. The lactate is then transferred into the solvent phase. The anion exchange reaction can be described with the following equations:

$$[R_4NCl]_{sol} + [A^-]_{aq} \leftrightarrow [(R_4N)A]_{sol} + [Cl^-]_{aq} \qquad \text{Equation 6-2}$$

$$[(R_4N)_2CO_3]_{sol} + 2[A^-]_{aq} \leftrightarrow 2[(R_4N)\,A]_{sol} + [CO_3]^{2-} \qquad \text{Equation 6-3}$$

where R_4N represents Aliquat 336 and A^- represents the anion of lactic acid.

Tab. 6-7 summarizes data of the distribution coefficient and extraction efficiency of Aliquat 336 and the carbonated form. The data show that the use of the latter leads to an extraction efficiency of 62%, whereas the use of the commercially available, chlorinated form leads to an extraction efficiency of 46%. This result indicates that the lactate anion replaces the carbonate anion better than the chloride anion. Furthermore, the results are in line with those presented in the study of Kyuchoukov et al.(2004) which found that carbonated form of Aliquat is more efficient than the classical chloride in the extraction of lactic acid. The replacement of chloride by mono-acid anion leads to the formation of hydrochloric acid in the aqueous phase, leading to a drop of pH-value which in turn limits extraction of the target acid (Kyuchoukov et al., 2004).

Tab. 6-7 Summary of the distribution coefficient and extraction efficiency for lactic acid. solvent composition: 33 wt% Aliquat 336 or the carbonated Aliquat 336 diluted in MIBK. $c_{\mathrm{LA,ini}}$= 0.2 mol/L ; pH 13; T= 25°C; ambient pressure.

Solvent	$c_{\mathrm{LA,ini}}$ (mol/L)	$c_{\mathrm{LA,aq}}$ (mol/L)	$c_{\mathrm{LA,sol}}$ (mol/L)	K_d	E (%)
Aliquat 336	0.22	0.12	0.10	0.9	45.8
Carbonated Aliquat 336	0.21	0.08	0.13	1.6	62.2

The commercially-available ionic liquids Cyphos 101 and Cyphos 104 are known to extract carboxylic acids (Marták and Schlosser, 2006),(Magnin et al., 2017) and were compared to the carbonated form of Aliquat 336.

Fig. 6-18 shows the comparison of the extraction efficiency of lactic acid when the different reactive extractants were used. The use of the carbonated form of Aliquat 336 led to the highest extraction efficiency at 62%. The use of Aliquat 336 and Cyphos 101 led to similar extraction efficiencies of 46% and 48%, respectively. Since the anion of both extractants is the chloride anion, similar behavior was expected. The difference observed in the extraction efficiency between Aliquat 336 and Cyphos 101 may be due to the steric hindrance related to the different alkyl chains present in the reactants.

The extraction efficiency of Cyphos 104 was determined with 19%. The difference between Cyphos 101 and Cyphos 104 is the counterion; while Cyphos 101 has a chloride anion, Cyphos 104 has the (bis-2,4,4,-trimethylpentyl) phosphinate anion as counterion. The phosphinate anion is able to form hydrogen bonds with the non-dissociated lactic acid (Marták and Schlosser, 2006),(Matsumoto et al., 2011) while the lactate anion assumingly results in poor extraction efficiency.

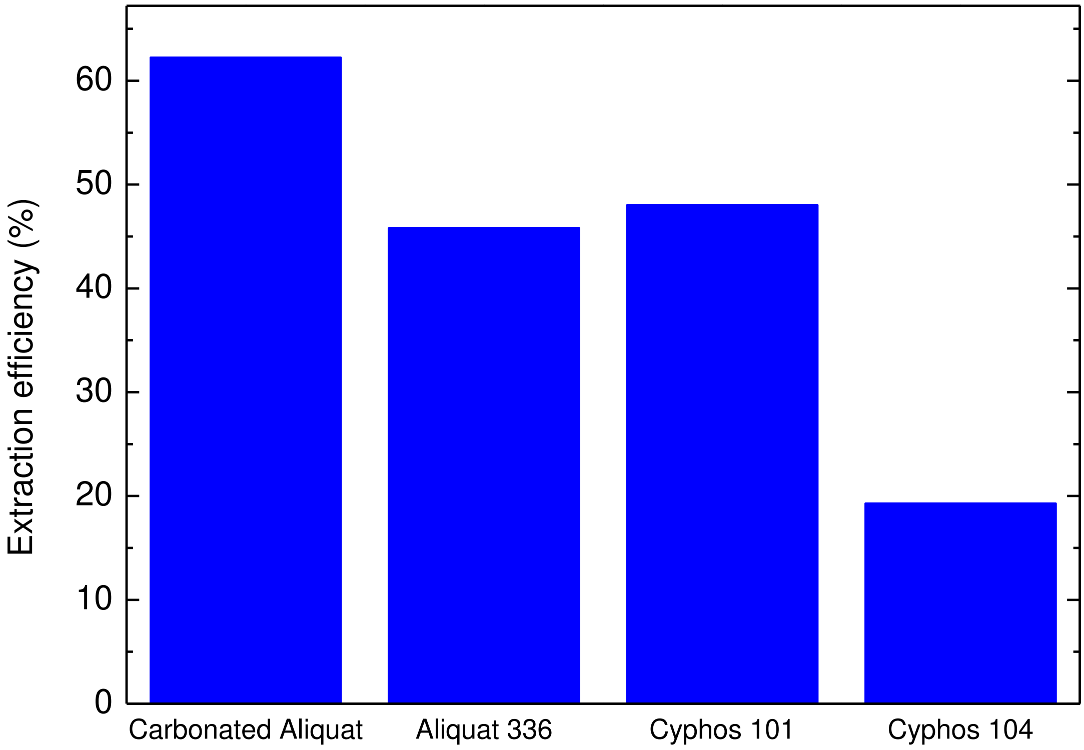

Fig. 6-18 Effect of the reactive extractant (33 wt% diluted in MIBK) on the extraction of lactic acid. $c_{LA,ini}$= 0.2 mol/L ; pH 13; T= 25°C; ambient pressure.

6.3.1.2 Effect of the solvent on the extraction of lactic acid

In this chapter, the influence of different polar solvent classes on the extraction efficiency of lactate using an initial lactic acid concentration of 0.2 mol/L and a pH of 13 was investigated. To be able to select the appropriate solvent and attain the highest extraction efficiency, three solvent categories were considered: non-polar, polar-protic and polar-aprotic solvents. In each category, two representatives were investigated. The solvents chosen were toluene and *n*-hexane (non-polar), MIBK and anisole (polar-aprotic) and 1-heptanol and 1-octanol (polar-protic). The phase ratio of the extractant to the solvent was kept constant at 1:3 by weight.

Due to its electrostatic affinity, aprotic solvents are expected to improve the solubility and the extraction efficiency of lactate. The highest extraction efficiency was observed for the group of polar aprotic solvents (see

Fig. 6-19).The difference in the extraction efficiency of MIBK and anisole can be attributed to their polarity; they dissolve the lactate anions as nucleophiles. While Van der Waals forces and electrostatic affinity applies in a polar aprotic solvent, only Van der Waals forces are present in non-polar solvents, and both increase the solubility of the organic lactate salt. Polar-protic solvents are able to increase the solubility of substances that are able to dissociate and, obviously, this effect is small compared to the effects of the Van der Waals and electrostatic forces. The polar-protic diluents increase stabilization of the lactate due to solvation. More stable lactate ions are less reactive and therefore the overall efficiency has the lowest value for polar-protic diluents. Similar observations have been obtained by Wasewar et al. (2011). They found that the higher dipole moment of ethyl acetate compared to kerosene and hexane raises solvation of the itaconic acid-amine salt.

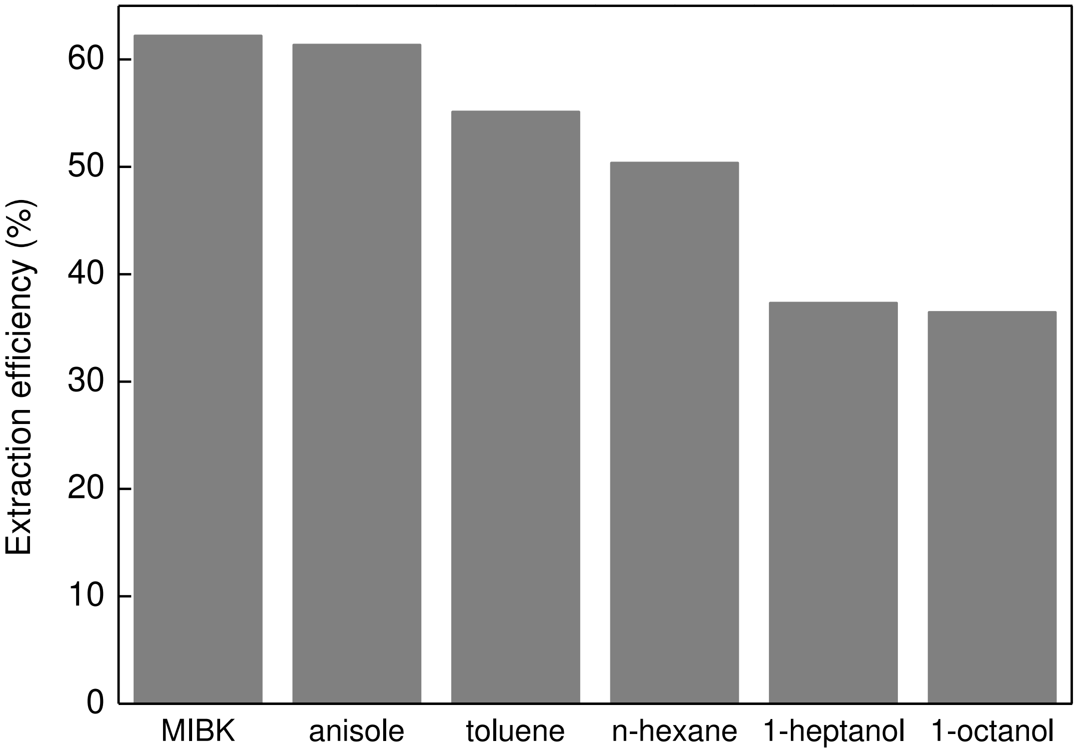

Fig. 6-19 Effects of polar-aprotic (MIBK, anisole), non-polar diluents (toluene, *n*-hexane) and polar-protic (1-heptanol,1-octanol) on the extraction efficiency of lactic acid. Reactive extractant: carbonated Aliquat 336, c_{Aliquat} =33 wt%. $c_{\mathrm{LA,ini}}$ = 0.2 mol/L; pH 13; T= 25°C; ambient pressure.

Considering to the lactic acid extraction by a tertiary amine from acidic solutions, where a polar-protic solvent such as 1-octanol improves the phase transfer more than non-polar solvents (*n*-undecane). the result is in contrast. The polarity of the solvent, influenced by the alcohol side groups, promotes the solubility of the acid-amine salt and leads to higher extraction efficiency. The extraction mechanism of lactic acid from acidic solutions involves the proton transfer of non-dissociated acid, which forms ion pairs in acidic environment or, more precisely, the acid-base reaction. The polar solvent affects the amine basicity and, thus, the stability of the acid-amine salt and its solvation (Kislik, 2012).

6.3.1.3 Effect of carbonated form of Aliquat 336 concentration on lactic acid extraction

The influence of the extractant concentration on the extraction efficiency of the lactate isolation is discussed in the present chapter. Therefore, the initial lactate concentration was 0.2 mol/L and the pH was adjusted to 13. Based on the previous results, the carbonated form of Aliquat 336 was diluted in MIBK. The concentration of carbonated form of Aliqut 336 was varied between 0 wt% and 100 wt%. Fig. 6-20 depicts the influence of the carbonated form of Aliquat 336 concentration on the extraction efficiency. The extraction efficiency increased from 28.5% when pure MIBK was used to 77.5% when the pure carbonated form of Aliquat 336 was used. It clearly shows that the extraction efficiency increases with increasing the carbonated form of Aliquat 336 concentration, however, as known from the extraction from acidic solutions the extraction efficiency passes a maximum. Increasing the reactive extractant concentration leads to an increase in the amount of lactate distributed. However, the distribution coefficient was significantly higher at low the carbonated form of Aliquat 336 concentrations when MIBK was applied. The solvent composition affects the hydrodynamic conditions.

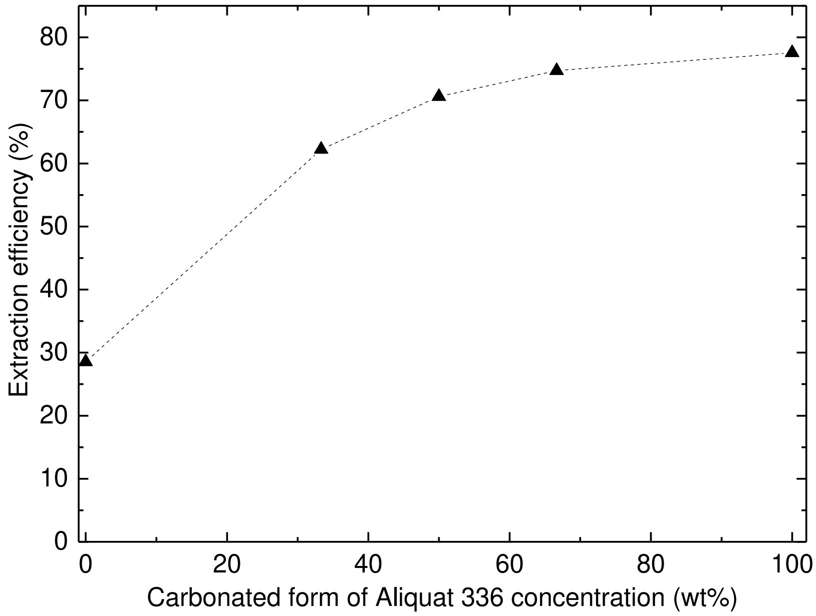

Fig. 6-20 Effect of carbonated form of Aliquat 336 concentration (0-100 wt%), diluted in MIBK, on the extraction efficiency. $c_{\mathrm{LA,ini}}$ = 0.2 mol/L; pH = 13; T= 25°C; ambient pressure

6.3.1.4 Optimized solvent phase

All the reactive extractants had high viscosities and densities. The viscosity of carbonated form of Aliquat 336 is 1450 mPa·s at 30°C. In order to reduce the viscosity and increase the diffusive mass transfer in reactive extraction processes, diluents are usually used. The diluent affects the viscosity, the density and surface tension and, hence, it may influence the reactions that take place at the interphase. This chapter provides data for the optimized composition of the solvent phase, whereby all three components are present. The results presented in chapter 6.3.1.2 shows that the polar-aprotic solvent (MIBK) is able to increase the extraction efficiency of lactic acid in comparison to the polar-protic and nonpolar solvents. Therefore, the polar-aprotic solvents could be considered as modifiers instead of diluents. In order to decrease the viscosity, carbonated form of Aliquat 336 mixed with MIBK in equal mass concentration, was diluted with *n*-hexane. The concentration of the carbonated form of Aliquat 336 was varied in the range of 25-37.5 wt%. The feed solution consisted of lactic acid with an initial concentration of 0.2 mol/L and a pH-value of 13. The phase ratio of the feed phase and the solvent phase was kept constant at one by weight in all experiments.

Fig. 6-21 compares the extraction performance for lactic acid using a binary mixture of carbonated form of Aliquat 336 mixed with MIBK with a ternary mixture of carbonated form of Aliquat 336 and MIBK diluted in *n*-hexane.

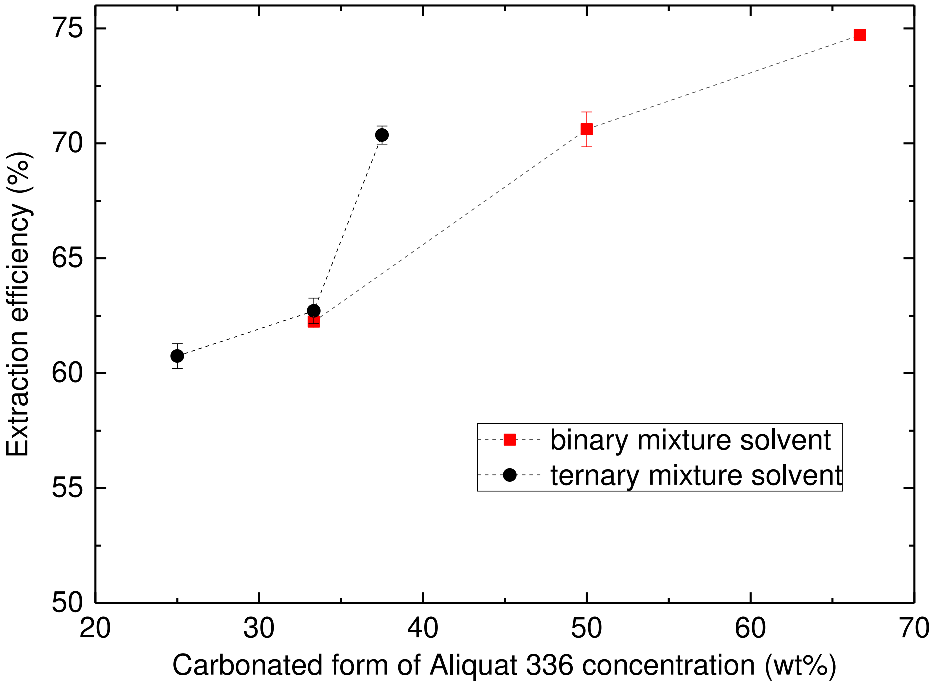

Fig. 6-21 Influence of the solvent composition on the extraction efficiency. Binary and ternary mixture solvent; the binary mixture solvent refers to carbonated form of Aliquat 336 diluted in MIBK. Ternary mixture solvent refers to an equal amount of carbonated form of Aliquat 336 and MIBK by weight diluted in *n*-hexane; $c_{LA,ini}$= 0.2 mol/L; pH = 13;T= 25°C; ambient pressure.

The results show that increasing the carbonated form of Aliquat 336 concentration leads to an increase in the extraction efficiency for the binary and the ternary mixture solvent. However, a significant difference in the extraction efficiency was observed above a concentration of 30 wt% carbonated form of Aliquat 336. The extraction efficiency was 62% for the binary and the ternary mixtures with an extractant concentration of 33 wt%. With an extractant concentration of 37.5 wt% in the ternary mixture, the same extraction efficiency of 70% as for the ternary mixture having a carbonated form of Aliquat 336 concentration of 50 wt%. In terms of costs, the results are promising, as the reactive extractants are more expensive than the modifier and diluents.

6.3.1.5 Back-extraction

To liberate the lactic acid from the laden solvent, back-extraction is needed. Three different stripping agents, de-ionized water, sodium hydrogen carbonate and hydrochloric acid, with a concentration of 1 mol/L were tested. The three stripping agents provide different pH-value and anions available for the ion exchange. The stripping solution was mixed with the laden carbonated form of Aliquat 336 obtained from the extraction experiments. The phase ratio of both phases was kept constant at one by mass for all experiments. The back-extraction efficiency was calculated based on the lactate concentration released into the stripping solution during back-extraction.

Fig. 6-22 summarizes the back-extraction efficiency for the three stripping agents. The results clearly show that the use of $NaHCO_3$ led to the highest amount of back-extraction compared to H_2O and HCl. These results are in accordance with what is predicted by Equation 6-3. Back-extraction respectively regeneration of the reactive extractant requires an ionic exchange. According to the results described in section 6.3.1.1 the ionic exchange obtained using carbonated form of Aliquat 336 was more effective than using Aliquat 336 in the chlorinated form. The results from the back-extraction confirm the data obtained during the lactate extraction.

The basic properties of $NaHCO_3$ lead to an enhancement of the dissociation of lactic acid and promotes the solubility of the lactate in the stripping solution. Water, on the other hand, offers OH^- ions for the ionic exchange reaction, but these are not able to act as counterions. Furthermore, the back-extraction efficiency using HCl was found to be 60% lower than that with $NaHCO_3$. This confirms the results described in section 6.3.1.1, namely, that a carbonate anion replaces a lactate anion more easily than a chloride anion.

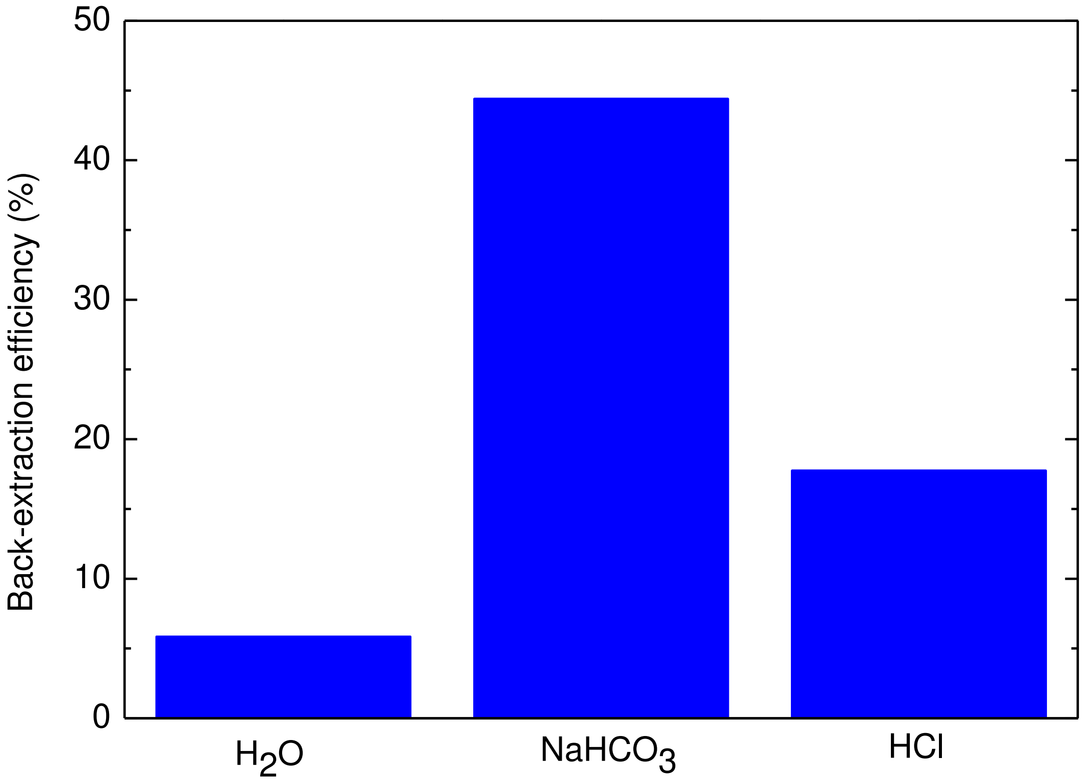

Fig. 6-22 Back-extraction efficiency of lactic acid using H_2O, $NaHCO_3$ and HCl. The solvent composition 33 wt% carbonated form of Aliquat 336 in MIBK. $c_{LA,ini}$ = 0.13 mol/L; pH = 13: T = 25°C; ambient pressure

6.3.2 Carbonated form of Aliquat 336 as liquid membrane

According to the results obtained in section 6.3.1, carbonated form of Aliquat 336 shows the best efficiency for lactic acid extraction, hence, it was implemented as the liquid membrane for lactic acid recovery using liquid membrane permeation. To be able to determine the most effective stripping agent to be used in further experiments, the first experiments were carried out using both stripping phases, water and sodium hydrogen carbonate. Fig. 6-23 shows that the lactic acid concentration in the feed phase decreases exponentially at the beginning of the experiment for both stripping solutions used. At the beginning of the experiment, there was no lactate concentration in the stripping phase. Lactic acid in the stripping phase can be measured after 2 hours.

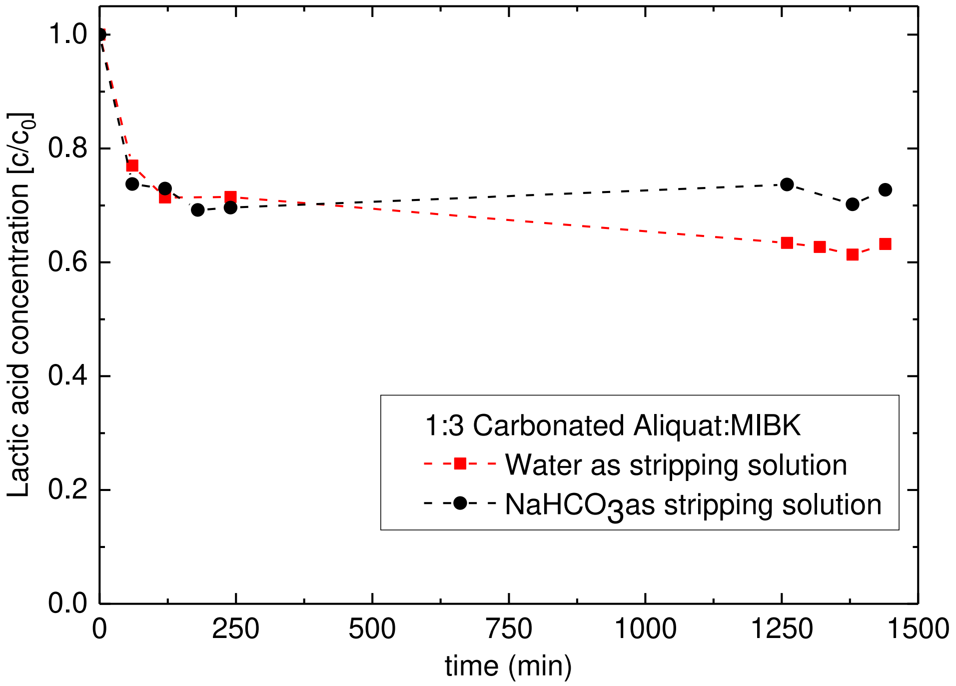

Fig. 6-23 Time course of lactic acid concentration in feed phase. Liquid membrane composition: 1:3 Carbonated Aliquat:MIBK. c_{LA}= 0.25 mol/L; pH=13; T=25 °C; ambient pressure

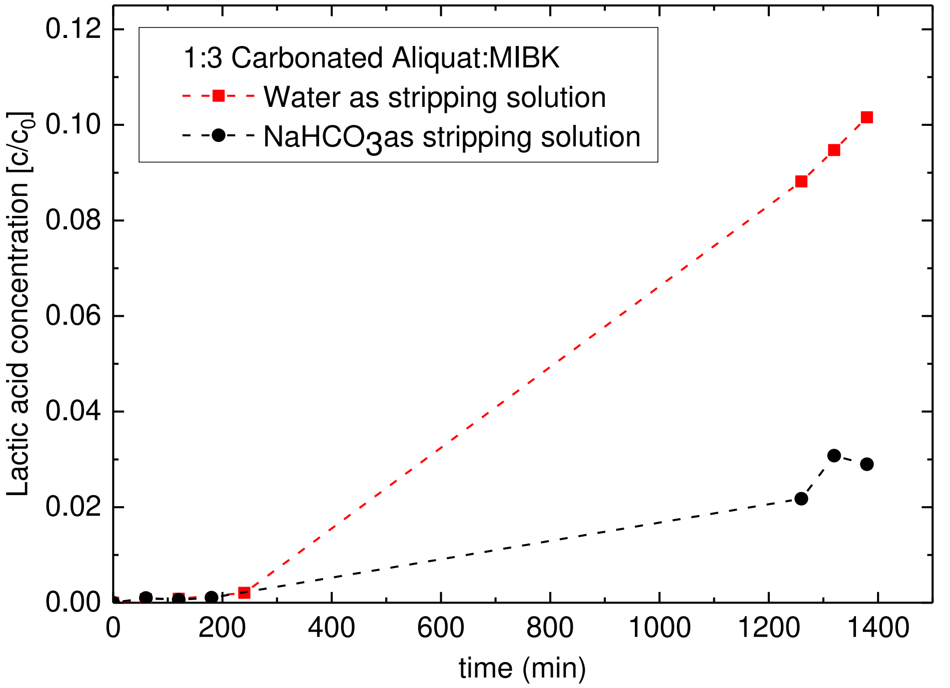

Fig. 6-24 Time course of lactic acid concentration in the stripping phase. Liquid membrane composition: 1:3 Carbonated Aliquat:MIBK. c_{LA}= 0.25 mol/L; pH =13; T=25 °C; ambient pressure

Fig. 6-24 shows the standardized concentration of lactate in dependence on the time. As can be seen, water is a more effective stripping agent leading to significantly higher concentration in the stripping phase after 24 h than sodium hydrogen carbonate. Fig. 6-25 depicts the effect of carbonated form of Aliquat 336 concentration on the water flux. Due to high osmotic pressure in the feed phase, an osmotic water flux is induced in the direction of the feed phase and hence a pre-concentration of the stripping phase occurs. Since the stripping agent used was pure water, there is a concentration gradient in the system. The water strives for equilibrium and balance the concentrations on either side of the membrane.

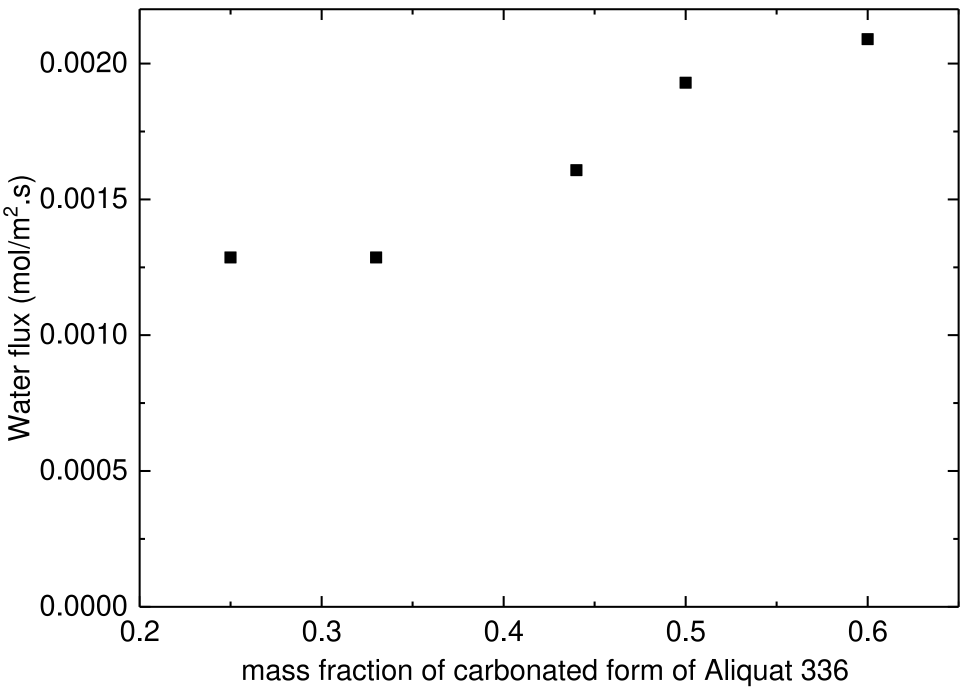

Fig. 6-25 Water flux from stripping phase to feed phase versus mass fraction of carbonated form of Aliquat 336. $c_{LA,ini}$ = 0.2 mol/L; pH = 13: T = 25°C; ambient pressure

Another explanation of the water transport from stripping phase to feed phase is, that water is involved in extraction process. Marták et al.(2008) suggest another mechanism, they stated that water transfers to the reverse micelles in the ionics liquid and establishes a hydrophilic microenvironment, which enables the unspecific transport of solute base on hydrophilic interaction. Their studies also showed that the water transport was vastly different depending on the ionic liquid used.

6.3.2.1 Influence of liquid membrane composition on mass transfer

The influence of liquid membrane on lactic acid mass transfer coefficient using binary and ternary liquid membrane was investigated with the similar method explained in section 6.2.5.2. Fig. 6-26 depicted the plot of -ln(*c*/*c*₀) against time. The slope indicates the overall mass transfer coefficient according to Equation 4-24. It can clearly be seen that the ternary mixture composed of carbonated aliquat:MIBK:*n*-hexane is more effective and shows a higher overall mass transfer coefficient compare to the binary mixture, which is the desired outcome. Whereas the pure carbonated form of Aliquat 336 leads to the lowest mass transfer coefficient. The solubility of lactic-Aliquat salt in the membrane phase increases with increasing carbonated Aliquat concentration, which improves the mass transfer. However, the diffusivity of lactic-Aliquat salt decreases as the viscosity of membrane phase increases. These results confirm the advantage of using ternary liquid membrane mixture as mentioned in section 6.3.1.4, that is, the liquid membrane cost saving as the reactive extractants are more expensive than the modifiers and diluents.

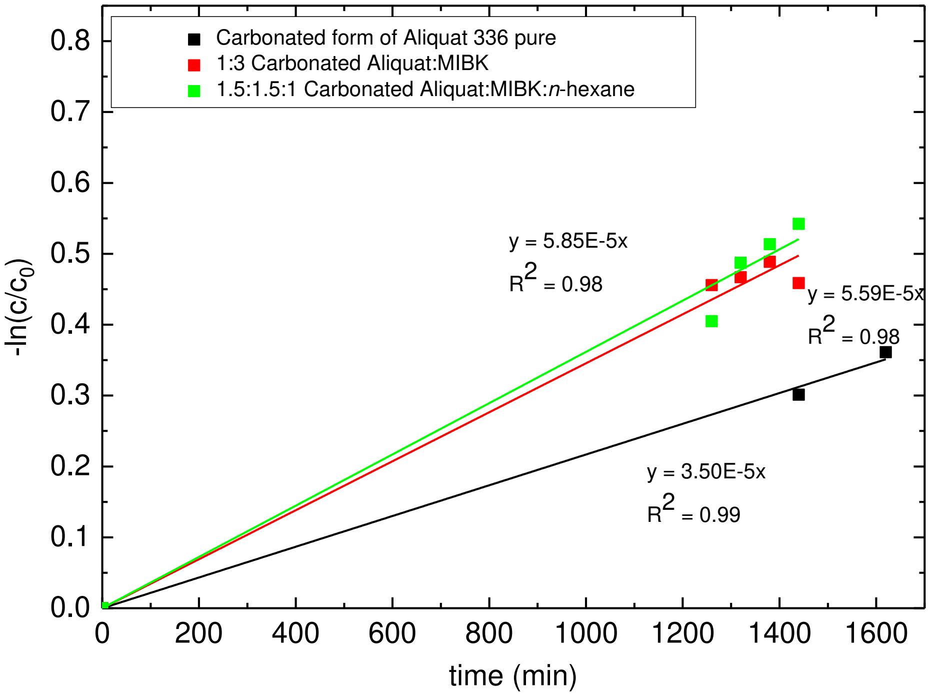

Fig. 6-26 Plot of (-ln c/c_0) vs time to estimate of the overall mass transfer coefficient. $c_{LA,ini}$ = 0.2 mol/L; pH = 13: T = 25°C; ambient pressure

7 Summary

Due to the environmental protection aspects, the substitution of fossil fuel-based substance by bio-based substance is of interest. The demand of lactic acid as monomer for the poly lactic acid production, has been rising currently. The conventional production of lactic acid by fermentation requires a costly and complex downstream processing. More efficient technologies respectively process intensification is hence required. Besides the use of fermentation for lactic acid production, lactic acid is present in process streams for example from the pulping industry. Isolation from this complex matrix is challenging but targeted in the present work. Curd formation prevented the use of liquid-liquid extraction as isolation technology, but liquid membrane permeation is a promising approach to overcome crud- or emulsion formation in a complex matrix.

This work focuses on the isolation of lactic acid from fermentation broth and pulping effluent by using liquid membrane permeation. In liquid membrane permeation the solvent provides the liquid membrane, by optimization of the liquid membrane a high degree of separation can be reached. Two approaches for lactic acid isolation were studied. In the first approach, phase equilibrium study on physical and reactive extraction of lactic acid from the acidic solution targets the acid isolation from fermentation broth. Physical extraction uses 1-octanol and *n*-undecane as solvent and reactive extraction uses tri-n-octylamine (TOA) in 1-octanol and *n*-undecane as solvent. Physical extraction shows disadvantages in terms of extraction efficiency and selectivity compared to reactive extraction. In reactive extraction 1-octanol acts as modifier and influences the extraction equilibrium by its polarity leading to an enhanced solubility of the acid-amine salt in the solvent phase. *n*-undecane is used as diluent to decrease the solvent viscosity. Thus, a ternary solvent mixture of TOA/1-octanol/*n*-undecane was used to increase the extraction efficiency and lower the solvent viscosity. The phase equilibria data suggest an increasing acid affinity toward solvent with increasing TOA and 1-octanol concentration. Further, lower acid concentration in the feed phase lead to higher extraction efficiency.

The stoichiometric extraction equilibrium constant was evaluated by applying the law of mass action. The highest equilibrium constant of lactic acid was found at a solvent composition of 40:40 TOA:1-octanol by weight diluted in *n*-undecane. However, this solvent composition lead to the formation of a third phase at the interface. Third phase formation was found for solvents consisting a TOA greater than 40 wt%. The tendency to form a third phase increases with increasing acid concentration in the feed phase.

The extent of extraction of the single carboxylic acids lactic acid, formic acid and acetic acid were compared. The extraction equilibrium constant decreased in the order of formic > lactic > acetic acid. This order is identical with the order of the decreasing pK_a. Back-extraction from the laden solvent phase was performed with sodium hydrogen carbonate, and it was found to depend, in the same way as the extraction, on the acid $pK_{a.}$

After the equilibrium measurement, the transfer to supported liquid membrane permeation was investigated. The mass transfer of lactic acid was found inversely proportional to the viscosity of the liquid membrane at the specific liquid membrane composition. The liquid membrane composed of 1-octanol does not increase mass transfer in liquid membrane permeation. The highest mass transfer coefficient of lactic acid was found with 7.2×10^{-6} m/s for the liquid membrane composted of 60 wt% TOA in *n*-undecane.

Different to fermentation broth, pulping effluent from Kraft pulping are highly alkaline, the second part of the present work deals hence with the study on the reactive extraction of lactic acid from highly alkaline aqueous solution using a carbonated form of Aliquat 336. The results show that a carbonated form of Aliquat 336 was found to be the most promising reactive extractant leading to an extraction efficiency of 62%. The polarity of diluent affects the separation of lactic acid. A polar-aprotic solvent like MIBK increases the extraction efficiency of lactic acid in comparison to polar-protic and nonpolar solvents. The use of a ternary mixture made from a carbonated form of Aliquat 336/MIBK/*n*-hexane led to the highest extraction efficiency of 70%. As stripping agent sodium hydrogen carbonate was used leading to a back extraction efficiency of 44%.

The transfer to liquid membrane permeation was studied in a U-tube set up. Water was found to be more effective as stripping agent then $NaHCO_3$, reason therefore is the osmotic water flux or the involving of water in extraction mechanism. The mass transfer coefficient of lactate was found highest at 5.8×10^{-5} m/s for the ternary mixture composted of carbonated Aliquat:MIBK:*n*-hexane.

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9 List of abbreviation

General symbol

BLM	Bulk liquid membrane
ELM	Emulsion liquid membrane
FDA	Food and drug administration
GRAS	Generally recognized as safe
HPLC	High Performance Liquid Chromatography
LAB	Lactic acid bacteria
MIBK	Isobutyl methylketone
PE	Polyethylene
PLA	Polylactic acid
PVC-U	Polyvinylchloride – rigid
SLM	Supported liquid membrane
TOA	Tri-*n*-octylamine

Symbol	**Description**
A	Area [cm^2]
A^-	Dissociated acid
c	Concentration [mol/L]
D	Dimerization constant
D_{eff}	Diffusion coefficient [m^2/s]
D_m	Diffusion coefficient in membrane phase [m^2/s]
D_a	Diffusion coefficient in aqueous phase [m^2/s]
E	Extraction efficiency [%]
HA	Non-dissociated acid
J	Molar flux [mol/m^{2}s]
K_a	Dissociation constant
K_d	Distribution coefficient
K_{st}	Equilibrium constant
K_{diss}	Dissociation constant,
$k_{overall}$	Overall mass transfer coefficient [m/s]

k_f	Mass transfer coefficient in the feed phase [m/s]
k_{mf}	Mass transfer coefficient at membrane phase[m/s]
k_o	Mass transfer coefficient in stripping phase[m/s]
n	Association factor
V	Volume [mL]
α	Degree of dissociation
δ_{fb}	Thickness of boundary layer feed and membrane
ε	Porosity (%)
$\Tau$	Tortuosity

Subscripts	**Description**
0	Entry value
aq	Aqueous phase
AA	Acetic acid
eq	Equilibrium
f	Feed phase
FA	Formic acid
HA	Carboxylic acid
ini	Initial value
LA	Lactic acid
nondiss	Non-dissociation
org	Organic phase
sol	Solvent phase
strip	Stripping phase

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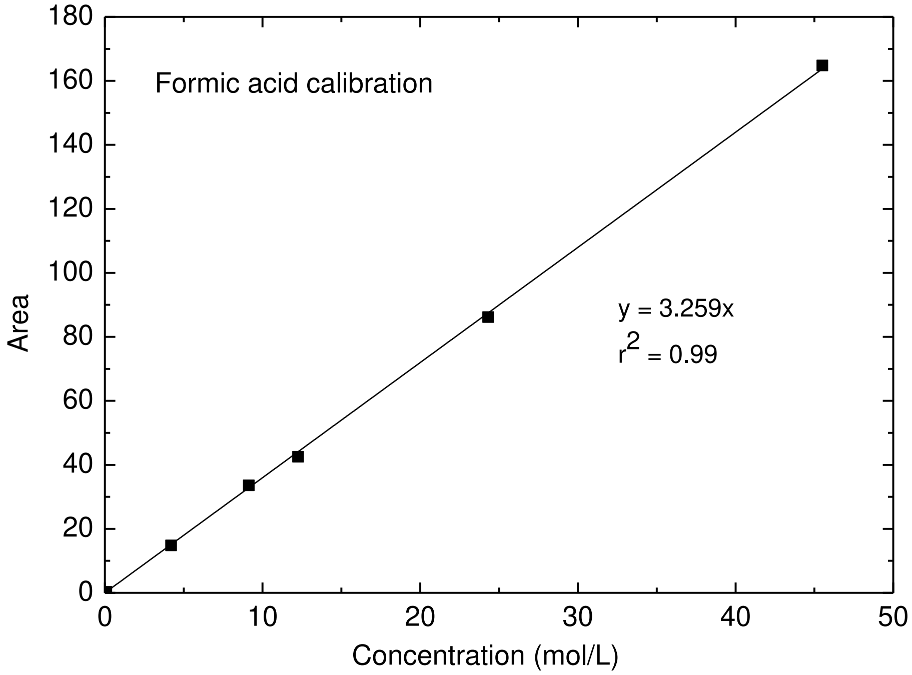
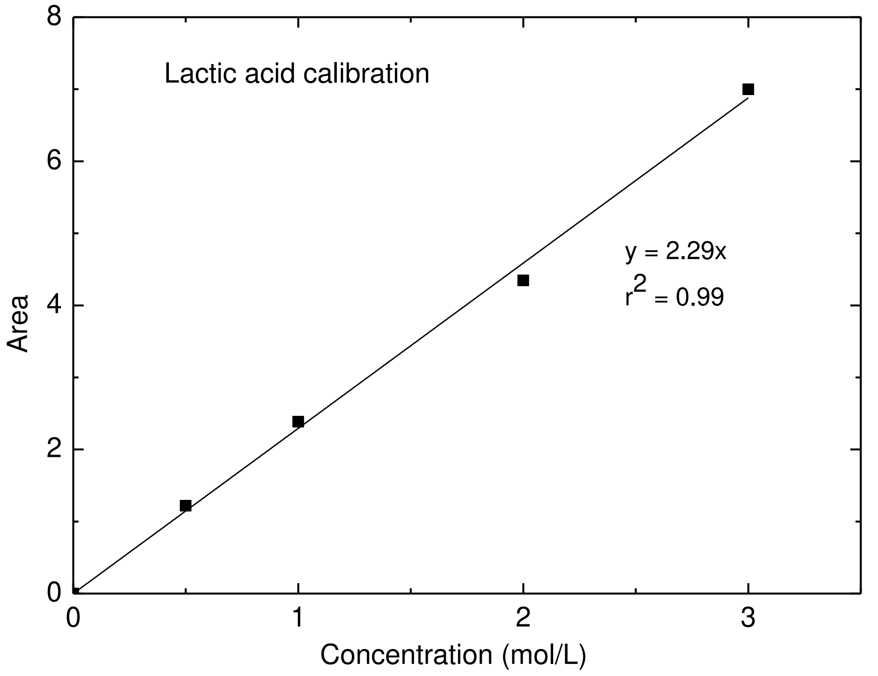
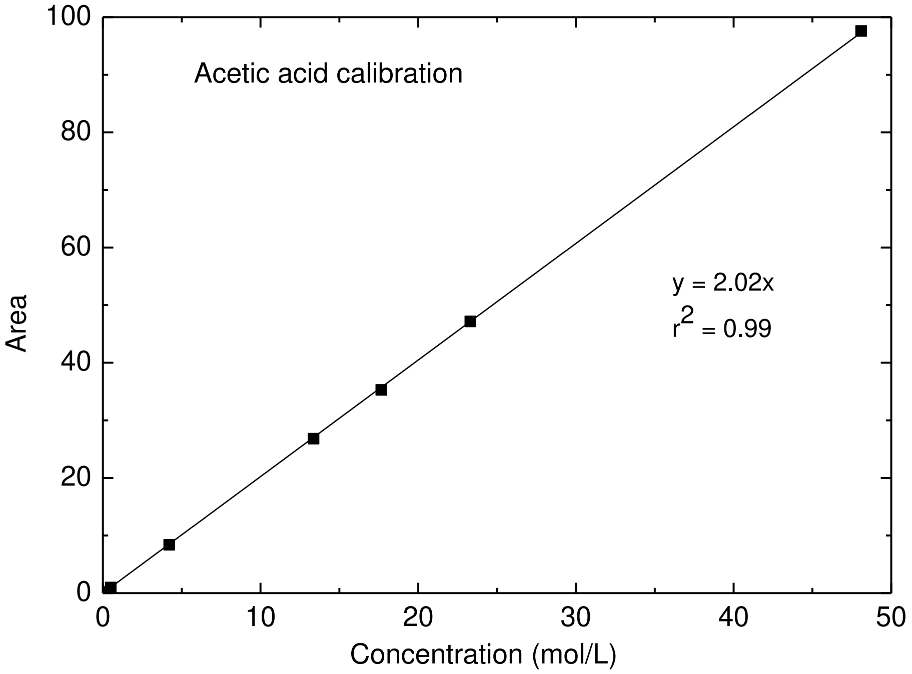
11 Appendix

11.1 Calibration curve for HPLC






Acetic acid calibration
y = 2.02x
$r^2 = 0.99$
Area
Concentration (mol/L)
0
20
40
60
80
100
0
10
20
30
40
50

11.2 Process development strategies for lactic acid isolation evaluations

Tab. 11-1 Mechanical unit operation evaluation

Properties of target substance									
Properties	**Value**	**Sedimentation**	**Flocculation**	**Filtration**	**Mechanical sieving**	**Chromatography**	**Hydro cyclone**	**Centrifuge**	**Electrophoresis**
MW [g/mol]	90.08	-	-	-	-	+	-	-	+
MP [°C]	16.8	-	-	-	-	-	-	-	-
BP [°C]	122	-	-	-	-	-	-	-	-
Acidity (pK_a)	3.86	-	-	-	-	-	-	-	+
Density [g/cm^3]	1.209	-	-	-	-	-	-	-	-
Dielectric constant	19.4	-	-	-	-	-	-	-	+
Solubilty in water	Very soluble	-	-	-	-	-	-	-	-
Enthalpy [kJ/mol]	1361.9	-	-	-	-	-	-	-	-
pH value	2	-	-	-	-	-	-	-	+
Flash point [°C]	113	-	-	-	-	-	-	-	-
Vapor pressure[mmHg] at 25 °C	0.0813	-	-	-	-	-	-	-	-
Heat of combustion [kJ/mol]	1361	-	-	-	-	-	-	-	-
Heat capacity[J/kg.K]	2.3	-	-	-	-	-	-	-	-
Entropy [kJ/mol.K)	192.05	-	-	-	-	-	-	-	-
Viscosity [Pa.s] 88.6%sol	0.037	-	-	-	-	-	-	+	+
Henry constant [atm-m ^{3} /mol]	9.6×10^{-9}	-	-	-	-	-	-	-	-
Freezing point [°C]	16.8	-	-	-	-	-	-	-	-
Molecular size [A]	7.5	-	-	-	-	+	-	-	+
Total		0	0	0	0	2	0	1	6

Tab. 11-2 Mass transfer unit operation evaluation

Properties of target substance (Lactic acid)		**Sorption**	**Desorption**	**Distillation**	**Flash vaporization**	**Extraction**	**Drying**	**Crystallization**	**Evaporation**	**Permeation**	**Pervaporation**	**Lyophilisa tion**	**Electrodialysis**	**Molecular sieve**
Property	**Value**													
MW [g/mol]	90.08	+	+	-	-	-	-	-	-	+	+	-	+	+
MP [°C]	18	-	-	-	-	-	-	-	-	-	-	-	-	-
BP [°C]	122	-	-	+	+	-	-	-	+	-	+	-	-	-
Acidity (pKa)	3.86	+	+	-	-	+	-	+	-	+	-	-	+	+
Density [g/cm^3]	1.209	+	+	-	-	+	-	+	-	+	-	-	-	+
Dielectric constant	19.4	-	-	-	-	-	-	-	-	-	-	-	+	-
Solubility in water	Very soluble	-	-	-	-	-	-	-	-	-	-	-	-	-
Enthalpy [kJ/mol]	69.1	-	-	+	+	-	-	-	+	-	-	-	-	-
pH value	2	+	+	-	-	+	-	+	-	+	+	-	+	+
Flash point [°C]	113	-	-	-	-	-	-	-	-	-	-	-	-	-
Vapor pressure [mm.Hg] at 25 °C	0.0813	-	-	+	+	-	-	-	+	-	+	-	-	-
Heat capacity [J/kg.K)	2.3	-	-	+	+	-	-	-	+	-	-	+	-	-
Entropy [kJ/mol.K]	192.05	-	-	+	+	-	-	+	+	-	+	-	-	-
Viscosity [Pa.s] 88.6%sol	0.0369	-	-	-	-	+	-	+	-	+	-	-	+	+
Freezing point [°C]	16.8	-	-	-	-	-	-	-	-	-	-	+	-	-
Molecular size [A]	7.5	+	+	-	-	-	-	-	-	+	+	-	+	+
Total		5	5	5	5	4	0	5	5	6	6	2	6	6

11.3 Purchased chemicals

Chemical	Purity	CAS	Supplier
Acetic acid	≤99	64-19-7	Sigma-Aldrich
Anisole	99	100-66-3	Fluka
Formic acid	≤99	64-18-6	Chem-Lab
Hydrochloric acid	37	7647-01-0	Carl Roth
Heptanol	99	111-70-6	Fluka
Isobuthylmethyl ketone (MIBK)	99	108-10-1	Merck
Lactic acid	80	50-21-5	Carl Roth
n-hexane	95	110-54-3	JT Baker
n-undecane	99	1120-21-4	Sigma-Aldrich
Sodium carbonate	99.8	497-19-8	Fluka
Sodium hydrogen carbonate	99.5	144-55-8	Carl Roth
Sodium hydroxide	99	1310-73-2	JT Baker
Tri-*n*-octylamine	97	1116-76-3	Sigma-Aldrich
Trioctylmethylammonium chloride (Aliquat 336)	88.2-93	5137-55-3	Sigma-Aldrich
Trihexytetradecyllphosphonium chloride (Cyphos 101)	≤95	258864-54-9	Sigma-Aldrich
Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate (Cyphos 104)	≤95	465527-59-7	Sigma-Aldrich
Toluene	99.5	108-88-3	Sigma-Aldrich
1-Octanol	98	111-87-5	Sigma-Aldrich

11.4 Model parameters of lactic acid

Solvent	$c_{\mathrm{LA,ini}}$	$c_{\mathrm{LA,aq}}$	K_{diss}	α	$c_{\mathrm{LA,aq,nondiss}}$	$c_{\mathrm{LA,solvent}}$	n	$1/c^{n}_{\mathrm{aq}}$	$1/c_{\mathrm{sol}}$	R^2	Slope	$c_{\mathrm{sol,ini}}$	Cal.K_{st}
A	0.166123	0.157688	0.000138	0.02841	0.153208	0.006363	1.42	14.35159	157.1506				
	0.349161	0.323874	0.000138	0.019684	0.317499	0.019076	1.42	5.099472	52.42236				
	0.515162	0.483209	0.000138	0.016234	0.475365	0.024105	1.42	2.874889	41.48525				
	0.701574	0.60697	0.000138	0.013927	0.598516	0.071369	1.42	2.072775	14.01161				
	0.978435	0.823956	0.000138	0.011806	0.814229	0.116538	1.42	1.338875	8.580865	0.9995	11.5781	0.46	0.13
B	0.166123	0.011521	0.000138	0.02841	0.011194	0.128799	0.99	85.40978	7.764056				
	0.349161	0.019216	0.000138	0.019684	0.018838	0.274876	0.99	51.01671	3.637998				
	0.515162	0.0272	0.000138	0.016234	0.026758	0.406521	0.99	36.04293	2.459896				
	0.701574	0.064605	0.000138	0.013927	0.063706	0.530658	0.99	15.27087	1.884452	0.9924	0.10962	0.46	20.03
	0.978435	0.194127	0.000138	0.011806	0.191835	0.653407	0.99	5.127451	1.53044				
C	0.215051	0.092289	0.000138	0.025013	0.089981	0.122761	0.81	7.032957	8.145879				
	0.472185	0.236102	0.000138	0.01695	0.2321	0.236083	0.81	3.264395	4.235803				
	0.740413	0.413992	0.000138	0.013559	0.408379	0.326421	0.81	2.065564	3.063531				
	1.007607	0.599957	0.000138	0.011635	0.592977	0.40765	0.81	1.527002	2.453084	0.9999	1.030007	0.34	3.525298
D	0.215051	0.036595	0.000138	0.025013	0.035679	0.178456	0.97	25.36034	5.603619				
	0.472185	0.099398	0.000138	0.01695	0.097713	0.372787	0.97	9.544365	2.682494				
	0.740413	0.189365	0.000138	0.013559	0.186797	0.551048	0.97	5.090623	1.814723				
	1.007607	0.324079	0.000138	0.011635	0.320308	0.683528	0.97	3.017163	1.462998	0.9999	0.185881	0.57	9.730135
E	0.215051	0.006086	0.000138	0.025013	0.005934	0.208965	0.85	78.10049	4.785499				
	0.472185	0.020407	0.000138	0.01695	0.020061	0.451778	0.85	27.73265	2.213479				
	0.740413	0.045132	0.000138	0.013559	0.04452	0.695281	0.85	14.08396	1.438268				
	1.007607	0.079302	0.000138	0.011635	0.07838	0.928305	0.85	8.708162	1.077233	0.9999	0.05282	0.91	24.4761

11.5 Model parameters of acetic acid

Solvent	$c_{LA,ini}$	$c_{LA,aq}$	K_{diss}	α	$c_{LA,aq,nondiss}$	$c_{LA,solvent}$	n	$1/c^{n}_{aq}$	$1/c_{sol}$	R^2	**Slope**	$c_{sol,ini}$	**Cal.**K_{st}
C	0.205777	0.126672	1.76E-05	0.009206	0.12551	0.079104	1.11	10.01076	12.64152	0.9998	1.223607	0.34	2.165489
	0.401643	0.23057	1.76E-05	0.006598	0.22905	0.171073	1.11	5.134254	5.845458				
	0.60696	0.349316	1.76E-05	0.00537	0.34744	0.257643	1.11	3.233132	3.881336				
	0.801349	0.480821	1.76E-05	0.004675	0.47857	0.320528	1.11	2.266003	3.119852				
	1.009948	0.616567	1.76E-05	0.004166	0.614	0.393381	1.11	1.718435	2.542065				
D	0.205777	0.089991	1.76E-05	0.009206	0.089163	0.115785	1.55	42.3852	8.636682	0.9975	0.215277	0.57	5.257699
	0.401643	0.169818	1.76E-05	0.006598	0.168697	0.231825	1.55	15.77547	4.313603				
	0.60696	0.246026	1.76E-05	0.00537	0.244705	0.360933	1.55	8.863473	2.770593				
	0.801349	0.347142	1.76E-05	0.004675	0.345519	0.454207	1.55	5.192398	2.201642				
	1.009948	0.407615	1.76E-05	0.004166	0.405917	0.602332	1.55	4.045034	1.660213				
E	0.205777	0.03945	1.76E-05	0.009206	0.039087	0.166327	1.09	34.25237	6.012257	0.9945	0.155627	0.91	6.478102
	0.401643	0.083059	1.76E-05	0.006598	0.082511	0.318584	1.09	15.17061	3.138893				
	0.60696	0.146904	1.76E-05	0.00537	0.146115	0.460056	1.09	8.137366	2.173648				
	0.801349	0.184003	1.76E-05	0.004675	0.183142	0.617346	1.09	6.361507	1.619837				
	1.009948	0.248742	1.76E-05	0.004166	0.247705	0.761206	1.09	4.577308	1.313705				

11.6 Model parameters of formic acid

Solvent	$c_{\mathrm{LA,ini}}$	$c_{\mathrm{LA,aq}}$	K_{diss}	α	$c_{\mathrm{LA,aq,nondiss}}$	$c_{\mathrm{LA,solvent}}$	n	$1/c^{n}_{\mathrm{aq}}$	$1/c_{\mathrm{sol}}$	R^2	Slope	$c_{\mathrm{sol,ini}}$	Cal.K_{st}
C	0.230854	0.067267	0.000177	0.027309	0.06543	0.16846	1.55	68.47759	5.936127	0.997	0.06828	0.34	27.79031
	0.434162	0.122206	0.000177	0.019988	0.119763	0.32255	1.55	26.82864	3.100295				
	0.640731	0.194613	0.000177	0.016483	0.191405	0.45597	1.55	12.97096	2.193127				
	0.83432	0.271229	0.000177	0.01446	0.267307	0.57079	1.55	7.729182	1.751958				
	1.014461	0.341511	0.000177	0.013122	0.337029	0.683716	1.55	5.396532	1.462596				
D	0.230854	0.049402	0.000177	0.027309	0.048053	0.181452	1.99	420.1183	5.51111	0.9949	0.011111	0.57	79.3471
	0.434162	0.07107	0.000177	0.019988	0.06965	0.363092	1.99	200.7210	2.75412				
	0.640731	0.097348	0.000177	0.016483	0.095743	0.543383	1.99	106.5599	1.840324				
	0.83432	0.141144	0.000177	0.01446	0.139104	0.693175	1.99	50.67074	1.442636				
	1.014461	0.185863	0.000177	0.013122	0.183424	0.828598	1.99	29.22284	1.206858				
E	0.230854	0.029445	0.000177	0.027309	0.028641	0.201409	1.99	1176.511	4.965022	0.9985	0.003867	0.91	142.798
	0.434162	0.046867	0.000177	0.019988	0.04593	0.387296	1.99	459.6506	2.58200				
	0.640731	0.054746	0.000177	0.016483	0.053843	0.585985	1.99	335.004	1.706528				
	0.83432	0.062827	0.000177	0.01446	0.061919	0.771493	1.99	253.6733	1.296189				
	1.014461	0.081318	0.000177	0.013122	0.080251	0.933143	1.99	151.4047	1.071648				

*A = 20 wt% TOA in *n*-undecane , B = 20 wt% TOA in 1-octanol , C = 15:15:70wt% TOA:1-octanol:*n*-undecane,

D = 25:25:50wt% TOA:1-octanol:*n*-undecane, E = 40:40:20wt% TOA:1-octanol:*n*-undecane

12 Publication

Oral presentation

Kienberger, M., Mungma, N. & Siebenhofer, M. Supported liquid membrane permeation for selective lactic acid recovery, 21st International Solvent Extraction Conference,Miyazaki, Japan ,November, 2017

Mungma, N., Kienberger, M. & Siebenhofer,M. Reactive extraction of lactic acid with Trioctylamine/Octanol/n-Undecane, AIChE annual Meeting, Minneapolis, United States, October 2017

Mungma, N., Kienberger, M. & Siebenhofer,M.Reactive extraction of lactic acid,formic acid and acetic acid using liquid membrane permeation,The 7th International TIChE conference, Bangkok, Thailand, August ,2017

Poster presentation

Mungma, N., Kienberger, M. & Siebenhofer,M. Isolation of carboxylic acids and hydroxycarboxylic acids by liquid-liquid extraction, 13th Minisymposium Chemical and Process Engineering, Innsbruck, Austria, March,2017

Mungma, N., Kienberger, M. & Siebenhofer,M.Process development strategies: Lactic acid isolation, 12th Minisymposium Verfahrenstechnik, Graz, Austria , March , 2016

Journals

Jantasee, S., Kienberger, M., Mungma, N. & Siebenhofer, M.Potential and assessment of lactic acid production and isolation – a review, : Journal of chemical technology & biotechnology, March, 2017

Mungma, N., Gil, M. & Kienberger,M. A study of supported liquid membrane to isolate carboxylic and hydroxyl carboxylic acid, CEET konkret 2017, p. 12-13

Mungma, N. & Kienberger,M .Separation of carboxylic and hydroxy-carboxylic acids from dilute aqueous feed, CEET konkret 2016, p. 20-21