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Mass Transfer Investigation of Organic Acid Extraction with Trioctylamine and Aliquat 336 Dissolved in Various Solvents

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1. Introduction

Organic acids have been used in producing biodegradable polymeric materials (polylactate) and they are also being considered for manufacture of drugs, perfumes and flavours as raw materials. Therefore the production of high purity organic acids is very important. They can be produced by chemical methods. However, fermentation technology has proven to be the best alternative being more energy efficient and having potential. To allow production and separation simultaneously. The major part of the production cost accounts for the cost of separation from very dilute reaction media where productivity is low due to the inhibitory nature of many organic acids. The current method of extraction/separation is both expensive and environmentally unfriendly. Therefore, there is great scope for development of an alternative technology that will offer increased productivity, efficiency, economic and environmental benefits. One of the promising technologies for recovery of organic acids from fermentation broth is reactive liquid-liquid extraction (Tamada and King, 2001, Dutta et al., 2006). However, common organic solvents when used alone show low distribution coefficients and do not give efficient separation. Reactive liquid-liquid extraction (RLLE) utilizes a combination of an extractant (also known as carrier) and diluents to intensify the separation through simultaneous reaction and extraction. Thus this method provides high selectivity and enhances the recovery. RLLE has been applied in many analytical, industrial, environmental and metallurgical processes (Parthasarathy et al., 1997; Klassen, et al., 2005; Kumar et al., 2001; Urtiaga et al., 2005; Carrera et al., 2009). In most of these applications one of these following solvents: kerosene, toluene/mixtures of kerosene and methyl isobutyl ketone (MIBK), hexane/decanol/octanol or any solvent system with similar toxic characteristics have been examined. These solvents have been proven to separate the “target” component from the aqueous solutions containing it. However, they have the issues of sustainability, health and safety, operator-friendliness and environmental impact. Therefore, efforts are devoted to determine a solvent that will partially or fully address these issues. In this chapter, a new, non-traditional solvent is examined for its ability to separate a specific component by applying the reactive extraction. Lactic acid (an organic acid) is chosen as the specific component (as a model for all other organic acids), experiments are presented to show its capacity and finally the analysis is extended to include the mass transfer processes in microporous hollow-fiber membrane module (HFMM). In the next few paragraphs lactic acid is described with the processes of production and ongoing research in
the development of techniques to separate it from the production media. From the methods one is selected (i.e. RLLE) and the new solvent system that has the potential to overcome the disadvantages of the currently practiced solvent, is examined.

Lactic acid (2-hydroxypropanoic acid, CH$_3$CHOHCOOH) is a colorless, organic liquid. It has a variety of applications in the food, chemical, pharmaceutical and cosmetic industries [Hong, et al., 2002]. The Food and Drug Administration (FDA) have approved lactic acid and its salts to be GRAS (Generally Recognized as Safe) [Lee, et al., 2004]. It can be converted to a polylactic acid used for the synthesis of biodegradable materials [Coca, et al., 1992]. As well as being environmentally friendly, there is a growing demand; due to strict environmental laws being legislated for biodegradable polymers as a substitute for conventional plastic materials. Biodegradable copolymers are also used for the production of new materials with biomedical applications such as drug delivery systems [Choi, and Hong, 1999].

Lactic acid is typically produced via either chemical synthesis or the fermentation of whey or another in-expensive carbon source [Lee, et al., 2004]. Due to the increasing cost of the common raw material for the chemical synthesis, the efficient production of lactic acid through fermentation has become increasingly important [Han, et al., 2000; Heewsink, et al., 2002; Drioli, et al., 1996; Hano, et al., 1993; Siebold, et al., 1995]. As mentioned earlier, an economical and efficient method for the recovery from fermentation broth is vital as the overall cost of production is dominated by the cost of recovery [Han, et al., 2000; Drioli, et al., 1996].

The production of most organic acids from fermentation media are subject to product inhibition as the reaction proceeds [Hano, et al., 1993; Hong and Hong, 1999; Yuchoukov, et al., 2005]. Hence, the separation of the organic acid as it is being produced is highly desirable. The extractive fermentation, in situ application of the solvent extraction technique, keeps the product concentration in the broth at a low level and suppresses the product inhibition by continuously removing them from a fermentation broth [Siebold, et al., 1995; Yankov et al., 2005; Frieling and Schugerl, 1999].

Various methods for the extraction of lactic acid have been reported such as precipitation, ion exchange process, adsorption, diffusion dialysis, microcapsules, esterification and hydrolysis, reactive extraction as well as a simulated moving bed process (Hong, et al., 2002; Tik, et al., 2001; Tong, et al., 1999; Ju, and Verma, 1994; Gong, et al., 2006; Sun et al., 2006). These methods have several disadvantages including high cost, and they produce large volumes of waste, require multiple steps, and operate with low efficiency under practical conditions. As mentioned earlier, the RLLE method using microporous Hollow Fibre Membrane Contactor (HFMC) may potentially overcome many of the disadvantages and provide a better alternative for the recovery of lactic acid (Wasewar, et al., 2002; Datta and Henry, 2006; Schlosser, 2001; Lin, and Chen, 2006). In a recent review, a process based on RLLE in HFMM has been found to be competitive from the process, economic and environmental points of view (Sun, et al., 2006; Joglekar, et al., 2006; Datta, et al., 2006). The advantages of the membrane mass transfer process over the conventional systems are (Lin, and Chen, 2006; Sun, et al., 2006; Joglekar, et al., 2006; Datta, et al., 2006):

- Selectivity and flexibility of extraction
- In situ application to reduce any inhibitory effect
- Reduction of number of steps (improved productivity)
- Use of operator and environmentally-friendly organic system
- Minimal dispersion of phases (less contamination)
- Recycle of extracting media and generation of smaller wastes
Mass Transfer Investigation of Organic Acid Extraction with Trioctylamine and Aliquat 336 Dissolved in Various Solvents

- Lower temperature operation requiring less energy
- Ability to operate on identical density systems
- Availability of large-scale module (i.e. easy scale up methods).

Amine compounds have been found useful as extractants for the separation of organic acids (Tamada and King, 2000; Kertesz, and Schlosser, 2005). They provide high efficiency and selectivity. Secondary, tertiary and quaternary amines and their mixtures have been employed for this purpose. An organic solvent is required to dissolve the reaction product, and a diluent is required to control the viscosity and to stop formation of any third phase. Active polar and proton-donating diluents as alcohols have been shown to be the most suitable diluents for amines as they show high distribution coefficient. The reaction mechanism changes with the combination of the extractant and solvent type. But the mass transfer equations and analysis of the processes involved are similar to those developed in the following section.

To understand and explore more of this process the main aims were set
- to determine a less toxic, environmentally-friendly solvent and a carrier or a mixture of carriers for extraction of lactic acid and the effect of conditions (temperature and pH) similar to the fermentation,
- to discuss the results of the experiments on liquid-liquid extraction
- to develop a mathematical model for the mass transfer processes in a small pilot-scale contactor
- to evaluate the performance of the less toxic solvent for extraction under fermentation conditions (i.e. in presence of salts and lactose).
- to compare the results of the hollow-fibre experiments.

The results show that the new system has the potential to overcome some of the disadvantages mentioned above. More research is required to optimise the experimental conditions, to develop a more comprehensive mathematical model including extraction and re-extraction and obtain performance data with “real” (rather than synthetic system) system.

In the next section, mathematical modelling is presented for liquid-liquid extraction and mass transfer processes in a commercially available membrane module (i.e. HFMM). Rather than a comprehensive approach a simple analysis is proposed to provide an understanding of the mass transfer phenomena in a small pilot-scale module.

2. Modeling of equilibrium and mass transfer

2.1 Liquid-liquid extraction

The reaction of undissociated lactic acid (HLA) with a carrier (B) dissolved in the solvent gives a reaction complex (BHLA) which remains largely in the organic phase and may be represented by (Juang and Huang, 1997; Datta, et al., 2006; Yuchoukov, et al., 2005):

$$\text{(HLA)}_{aq} + \text{(B)}_{org} \rightleftharpoons \text{(BH + LA)}_{org}$$  (1)

A simple 1:1 stoichiometry (the molar ratio of organic acid to that of extractant) has been proposed. However, this depends on the type of the organic acid and its ionic state, the type of the extractant and the type of the solvent (Uslu et al., 2009). The reaction mechanism does not change the mass transfer processes.

For reactive extractions microporous hollow fiber membrane contactors, in various configurations have been evaluated (Klassen et al., 2005; Yang, and Cussler, 2000; Ren et al.,
Typically two modules are used, one for the extraction and the other for the re-extraction or stripping process. These are commercially available modules, e.g. a module with catalogue No. 5PCM-218, obtained from Separation Products Division, Hoechst Celanese Corporation, Charlotte, NC, USA, have been extensively used for mass transfer operation. The contactor has a shell-and-tube configuration with a total of 10,000 polypropylene hollow fibers (Celgard X-30, 240 µm ID, 300 µm, OD, length 15 cm) potted in polyethylene in a polypropylene case of 6 cm ID. The surface area of the contactor is 1.4 m$^2$. The hollow fiber module is usually set up as

Fig. 1. A schematic diagram of the mass transfer operation of the hollow-fibre membrane contactor.
shown in Figure 1. When these modules are used, aqueous and organic solutions flow continuously, one through the lumen side of the fibre and the other through the shell side. The both the solutions get into contact through the pores of the wall. Phase entrainment is avoided by applying a little higher pressure on the aqueous side. The pressure difference between the phases is between 0.2 – 0.3 bar and it has been reported that it has no influence on the mass transfer processes.

These contactors have been used in various process configurations such as hollow fibre contained liquid membranes, HFCLM (Yang et al., 2003; Dai et al., 2000), hollow fibre supported liquid membrane, HFSLM, (Yang and Kocherginsky, 2006; Rathore, et al., 2001), non-dispersive solvent extraction, NDSX, Ortiz, et al., (2004) and hollow fibre renewal liquid membranes, HFRLM, (Ren et al., 2008). The main difference between these configurations is that the contacting pattern of the liquid phases are different. In a newly developed mass transfer operation known as emulsion pertraction, PERT, a single module is used for extraction and stripping simultaneously (Klaassen and Jansen, 2001; Klassen et al., 2005). The emulsion consists of an organic solvent with a dissolved extractant phase with droplets of strip liquid dispersed in it. The phases are separated by the hydrophobic membrane surface. The contact between the water phase and emulsion phase occurs at the pore mouth. The organic acid-extractant complex diffuses through the pores and on the other side of the membrane the extractant is regenerated by strip liquid. The analysis below is not applicable to the PERT process, it is devoted to extraction in a single module.

2.2 Mass transfer in a hollow fibre membrane contactor

A schematic of the transport mechanism of solute molecules from an aqueous feed side to the organic side through hollow-fibre wall is shown in Figure 2 (Hossain and Mysuria, 2008). The mass transfer processes can be described by the solute transport through the resistances from the aqueous feed (inside the fibre) to the organic phase (shell side). The steps considered for the mass transport and reactive extraction, the solute (lactic acid) molecules:

- are transported from the feed solution to the feed-pore interface and can be expressed by Eq. (2).
- at the interface the reaction between the solute and the carrier takes place (Eq.1) to form a solute-carrier complex. The equilibrium concentrations at the interface in the aqueous and organic phases can be related by an apparent distribution coefficient (DE), given by Eq. (3).
- The diffusion of the solute-carrier complex through the pores of the hollow-fibers filled with the organic phase and this can be expressed by Eq. (4).
- The final step is the transport through the solvent boundary layer at the outer end of the pore mouth and this step can be expressed as in Eq. (5).

The following assumptions have been considered for writing the model equations:

- The system works at isothermal conditions.
- Equilibrium is reached at the interfaces of the aqueous and organic phases.
- The curvature of the interfaces does not affect significantly the processes.
- The distribution coefficient of the solute is considered to be constant with the conditions used
- Uniform pore size along the entire length of the contactor.
- The mass transfer processes in the boundary layer is described by the diffusion model.
- The phases are immiscible and the pores are wetted by the organic phase only.

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The interfacial reaction:

\[(\text{HLA})_{\text{aq}} + \text{(B)}_{\text{org}}^- \rightleftharpoons (\text{BH}^+\text{LA}^-)_{\text{org}} \]

\[\text{(BH}^+\text{LA}^-) \] diffuses through the wall to the shell side (the diffusive flux)

\[\text{Flux} = -K_{\text{of}} \left( \frac{c_{\text{LAf}}^m}{D_E} - \frac{c_{\text{LAr}}^m}{D_E} \right)\]

Convective flux = \(-u_{\text{f}} \left( \frac{V}{A_{\text{in}}} \right) \frac{\partial c_{\text{LAf}}^m}{\partial z}\)

Fig. 2.(a) A schematic of the mass transfer processes in the membrane module.

Fig. 2.(b) Concentration profiles of lactic acid in the feed phase (fibre side), in membrane wall and in the organic phase (shell side).
The transport equations are

\[ N_{LAf} = k_f(C_{LAf} - C_{LAf}) \]  
\[ D_E = C_{LAOi} / C_{LAf} \]  
\[ N_{LAmf} = k_{mf}(C_{LAfi} - C_{LAOi}) \]  
\[ N_{LAo} = k_o(C_{LAO} - C_{LAO}) \]

where \( k_f, k_{mf} \) and \( k_o \) are the mass transfer coefficient in the feed side, on the membrane and in the organic side, respectively. The concentrations \( C_{LAf} \) and \( C_{LAfi} \) are the total lactic acid concentrations in the bulk and at the interface, respectively. The concentrations \( C_{LAOi} \) and \( C_{LAO} \) are the concentration of lactic acid at the membrane-organic interface and in the bulk organic phase, respectively.

Combining the above equations the flux in the system at the steady state is obtained as:

\[ \frac{1}{K_{of}} = \frac{1}{k_f} + \frac{1}{D_E k_{mf}} + \frac{1}{k_o D_E} \]

In order to calculate the overall mass transfer coefficient from the above equation the individual mass transfer coefficients have to be known in addition to the distribution ratio of lactic acid between the aqueous-organic solutions. There are many correlations available in the literature for calculating the individual mass transfer coefficients (Lin, and Chen, 2006; Bringas, et al., 2009; Coelho et al. 2000). Each of the correlation is based on the specific experimental conditions and equipment set-up used to develop the correlation. So the assumption of the correlation needs to be matched for its appropriateness before applying to any other system. The calculations from the correlations will be discussed later. In the section below an approximate solution is presented for hollow-fibre membrane modules to evaluate the overall mass transfer coefficient from an analysis of concentration versus time data.

2.3 Approximate solution for the mass transfer model

The membrane modules are operated in recycling mode as the percentage extraction in once-through operation is small. In the recycling mode, it is considered that the feed and the organic solutions are circulated through the fiber side and shell side of the module, respectively.

The mathematical model consists of two mass balance equations, Eq. (8) and (9) that defines the change in solute concentration (i) in the module and (ii) in the feed tank, where aqueous solution is continuously circulated.

\[ \left( \frac{V}{A} \right)_{in} \frac{\partial C_{LAf}^{in}}{\partial t} = -u_f \left( \frac{V}{A} \right)_{in} \frac{\partial C_{LAf}^{in}}{\partial Z} - K_{of} \left( C_{LAf}^{in} - \frac{C_{LAO}}{D_E} \right) \]
\[ \frac{dc_{LAf}^m}{dt} = \frac{q_f}{V} \left( C_{LAf}^m |_{z=L} - C_{LAf}^m |_{z=0} \right) \]  

(9)

where \( \left( \frac{V}{A} \right)_{in} \) is the ratio of the volume to inner area of mass transfer in the fibers, \( L \) is the length of the fiber, \( u_f \) is the linear velocity, \( q_f \) is the feed flow rate and \( v^T \) is the tank volume. The superscripts \( m \) and \( T \) refer to the membrane module and tank, respectively.

The ratio, \( \left( \frac{V}{A} \right)_{in} \), for the feed solution circulating along the inside of the fiber is equal to \( \frac{d_i}{4} \), where \( d_i \) is the inner radius of each fiber. The factor, \( \left( \frac{V}{A} \right)_{in} L \), is a small number for this type of contactor, i.e. approx. \( 4 \times 10^{-4} \). Using this and assuming a slow rate of change of solute concentration in the module, Eqn (8) can be simplified to

\[ \frac{dc_{LAf}^m}{dZ} = -\frac{1}{u_f \left( \frac{V}{A} \right)_{in}} \frac{K_{gf}}{1} \left( C_{LAf}^m / L - C_{LAf}^m / D_E \right) \]  

(10)

An approximate solution of the model equations form is given by

\[ L_{Hf} \left( \frac{C_{LAi}}{(1 + 1/D_E)C_{LAf} - C_{LAf}^m} \right) = \frac{q_f}{V} \left[ 1 - \exp \left( -BK_{gf} \right) \right] \]  

(11)

where \( B \) has been defined by the following equation:

\[ B = \left( \frac{V}{A} \right)_{in} u_f \]  

(12)

The overall mass transfer coefficient (\( K_{oa} \)) can be determined from the value of the slope of the linear plots of the left hand side (LHS) of equation (11) versus \( t \) (time). The LHS of equation (11) requires (i) the experimental values of the concentrations and (ii) the partition coefficient of the solute. We also need to calculate \( B \) from equation (12) which requires the velocity inside the fibre, module characteristics (volume, mass transfer area) and the partition coefficient.

As mentioned earlier in Equation (7), the overall mass transfer coefficient can be calculated using the individual mass transfer coefficients: mass transfer coefficient in the aqueous side (\( k_0 \)), membrane mass transfer coefficient (\( k_{mO} \)) and the mass transfer coefficient in the organic side (\( k_o \)). In most of the hollow fibre systems, the aqueous phase containing the “target” component is allowed to flow (under laminar conditions) through the inside of the hollow fibres. The mass transfer coefficient in the aqueous side can be calculated using an equation of the following form (Skelland, 1974):

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\[ Sh = (1.5 \text{ or } 1.62) \times (G_\varepsilon)^{0.33} \]  
(13)

where \( Sh \) and \( G_\varepsilon \) are, respectively the Sherwood and Graetz numbers. The values of \( k_d \) reported (Bringas et al., 2009) within the Reynolds number range, \( Re (0.08-200) \) are \( 1.8 \times 10^{-6} \text{ m/s to } 9.5 \times 10^{-4} \text{ m/s} \). It is noted that the equation will be different (if the organic flow is allowed through the fibres) as used in Lin and Chen (2006).

For the membrane mass transfer coefficient (\( k_{mf} \)), the following equations have been suggested (Schlosser, 2001; Prasad and Sirkar, 1988):

\[ k_{mf} = \frac{D_m \varepsilon}{\sigma \tau} \]  
(14)

where \( \sigma \) is the thickness of the hollow fibre, \( \tau \) is the membrane totuosity, \( \varepsilon \) is the membrane porosity and \( D_m \) is the molecular diffusivity of the carrier-solute complex. The values estimated (Bringas et al., 2009) using the reported values of \( D_m \) are: \( 1.1 \times 10^{-8} \text{ m/s to } 1.5 \times 10^{-5} \text{ m/s} \). Other equations have also been used by researchers in this field (de Haan, et al., 1989; Hu and Wiencek, 1998).

For the organic phase flowing through the shell side of the contactor, the value of \( (k_o) \) can be estimated using the following equation (Yang and Cussler, 1986):

\[ Sh = 1.25 \left( Re \frac{d_h}{L} \right)^{0.03} \left( Sc \right)^{0.33} \]  
(15)

Where \( d_h \) is the hydraulic diameter, \( L \) is the effective length of the fibres. The dimensionless numbers: \( Re \) and \( Sc \) represent the Reynolds and Schmidt numbers, respectively. The values of \( k_o \) reported (Bringas et al., 2009) are in the range \( 7.4 \times 10^{-7} \text{ m/s to } 6.5 \times 10^{-5} \text{ m/s} \).

A detailed discussion of various systems and the estimated values of the mass transfer coefficients are available in Bringas et al. (2009). It is concluded that the estimation by any empirical correlation mentioned in the literature require a description of the specific system, the characteristics of the fibres and contactor, the physical and transport properties of the system under study, the operating conditions and the assumption that the specific system is at least similar to the one where the correlation was developed.

The degree of extraction, \( E(\%) \), for the HFM experiments is measured by the extraction efficiency which is defined by the following equations:

\[ E(\%) = \frac{C_{LAI} - C_{LAf}}{C_{LAI}} \times 100 \]  
(16)

where \( C_{LAI} \) and \( C_{LAf} \) are the initial and final concentration values of the feed solution in the recirculation system, respectively.

### 3. Equilibrium experiments

#### 3.1 Effect of organic solvent

In the mass transfer analysis of the process the value of the distribution coefficient (DE) is required. It is worthwhile to know the range of values obtained for the extraction of organic acids. The physical extraction of lactic acid with pure solvent (no carrier added) is less and these values for various organic phases are listed in Table 1.
Solvent Distribution Coefficient, DE(-)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Distribution Coefficient, DE(-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tri-butyl phosphate (TBP)</td>
<td>0.82</td>
</tr>
<tr>
<td>Oleyl Alcohol (OLA)</td>
<td>0.25</td>
</tr>
<tr>
<td>Decanol (D)</td>
<td>0.43</td>
</tr>
<tr>
<td>Hexane (H)</td>
<td>0.25</td>
</tr>
<tr>
<td>Dodecane (DD)</td>
<td>0.25</td>
</tr>
<tr>
<td>Shellsol TK (STK)</td>
<td>0.11</td>
</tr>
<tr>
<td>Oleic Acid (OA)</td>
<td>0.67</td>
</tr>
<tr>
<td>Sunflower oil</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Table 1. The values of the distribution coefficient of lactic acid at pH 2.4.

The data in Table 1 suggest that TBP is the optimum solvent for extraction of lactic acid. TBP is followed by oleic acid, decanol, oleyl alcohol, hexane, dodecane. Shellsol TK and sunflower oil gave the lowest distribution ratio of lactic acid. It is evident that active solvents (with functional groups), e.g. TBP, oleic acid have greater extraction power than the inactive solvents, e.g. shellsol TK, dodecane. The active solvent can assist the solvation of the lactic acid molecules and enhance the solubility of the lactic acid complex (Wasewar, et al., 2002). The complex formed with the functional group of the active solvent may be more stable and soluble in the organic phase and thus allow greater extraction compared to those solvents without any functional groups (Tamada, and King, 2000). Although this result with active solvent is good, other points like solvent loss (due to solubility in the aqueous phase) and environmental effects should also be considered before the final selection of the solvent. It has been reported that the solvents containing phosphorus-bonded oxygen atoms (like tributyl phosphate) are not favourable from the points of water solubility and environmental considerations (Matsumoto, et al., 2003).

As mentioned earlier that the reaction with the carrier molecules can enhance the values of DE. The values of DE increased when extraction is performed with adding carrier in the solvent phase. These values at natural pH (2.4) of lactic acid and at room temperature are presented in Table 2 for the extraction using tributyl phosphate as solvent. At this low pH the values of the distribution coefficient were moderate to high for all the carriers. The organic system of 10 wt% TOA – 90 wt% TBP gave a distribution coefficient as 4.88. This value increased with the increase in the concentration of TOA for a fixed feed concentration.

<table>
<thead>
<tr>
<th>10 wt% Carrier in TBP</th>
<th>Distribution Coefficient, DE (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-octyl amine</td>
<td>4.26</td>
</tr>
<tr>
<td>Trioctyl amine</td>
<td>4.88</td>
</tr>
<tr>
<td>Aliquat 336</td>
<td>1.22</td>
</tr>
</tbody>
</table>

Table 2. Effects of carrier in tri-butyl phosphate on lactic acid extraction at pH 2.4.

Oleic acid, a component of sunflower oil, did not perform as well when carrier was added to it. However, the best organic solvent, TBP, is expensive and is not recognized as a GRAS (generally regarded as safe) solvent. Sunflower oil is a non-toxic, cheap and can be regarded as an environmentally friendly solvent. It is worth mentioning that the solvents used in this study are less toxic to the fermentation media compared to those reported in the study of organic acid extraction (Wasewar, et al., 2002).
Fig. 3. Effect of feed solution pH on reactive extraction of lactic acid.

Fig. 4. Effect of temperature on the extraction of lactic acid with sunflower oil.

The values of the distribution coefficient also depend on the extraction condition such as feed solution pH (Canari and Eyal, 2003) and temperature. The values for extraction of 0.2M lactic acid with sunflower oil (as diluent) and Aliquat 336/TOA (as carriers) is shown in Figure 3. The distribution ratio decreased considerably with the increase in aqueous solution pH range 4-6 (Kyuchoukov, et al., 2006). The magnitude of the distribution ratio was greater with Aliquat 336 than for TOA at higher pH. The two extractants when combined also gave considerably higher distribution ratios than the individual extractant. The synergistic effect
is apparent in these results, as reported in the literature (Hong, and Hong, 1999; Kyuchoukov, et al., 2001; Yankov, et al., 2005). However, this synergistic effect is much more apparent at lower pH (pH 4) than at higher pH (pH 6). The organic phase which comprised of 15% Aliquat 336 and 15% TOA give the highest distribution ratios at all pH values. Since pH used for fermentative production of lactic acid is approx. 6, the values at high pH are useful in the analysis of mass transfer processes. This will determine their applicability in the in situ recovery of lactic acid and thus reduce its inhibitory effect to enhance its productivity.

The values of DE also depend on the operating temperature. As shown in Figure 4 the temperature (both phases at the same temperature) increased the value of distribution coefficient. Hence, better extraction could be expected at temperatures higher than the room temperature (Martak, J. and Schlosser, 2004). This trend is a positive result, as the optimal temperature for lactic acid fermentation could be in the range 30-38°C.

### 3.2 Hollow fibre experiments

For the analysis of the mass transfer processes the experiments in hollow-fibre were chosen and a typical base case of the operating conditions are presented in Table 3. The effects of the flow rate, the fermentation media, the carrier, the operating temperature with the solvents: TBP and sunflower oil are discussed below.

<table>
<thead>
<tr>
<th>Feed Solution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of lactic acid (M):</td>
<td>0.2</td>
</tr>
<tr>
<td>Volume (L):</td>
<td>0.5</td>
</tr>
<tr>
<td>pH (-):</td>
<td>2.4-4.5</td>
</tr>
<tr>
<td>Flow rate (L/h):</td>
<td>12-13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Organic solution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of carrier in the solvent (%w/w):</td>
<td>5,10</td>
</tr>
<tr>
<td>Volume (L):</td>
<td>0.5</td>
</tr>
<tr>
<td>Flow rate (L/h):</td>
<td>9-10</td>
</tr>
</tbody>
</table>

Table 3. The operating conditions for mass transfer experiments in the HFMC.

#### 3.2.1 Effect of flow rate

The maximum extraction percentage of approx. 93% was obtained with 10% TOA-TBP organic phase within a processing time of 2 - 3 h (Figure 5). The extraction profiles for three different flow rates were identical except for the profile of 8.33 mL/s that attained lower than the other two organic systems. This could be due to the experimental error (as is observed in Figure 5) that occurred during the initial period of monitoring. The effect of flow rate in the tested range is small and suggests that the overall extraction is not significantly affected by the external mass transfer of lactic acid (i.e. the aqueous side resistance).

#### 3.2.2 Effect of solvent type

Oleyl alcohol (OA) is non-toxic to acid producing bacteria and the results for extraction of lactic acid with this solvent are presented. The percentage extraction increased with time.
and then attained a plateau at approx. 93% within 2-3 h (Figure 6). With OA the extraction rate was initially slower, increased with time and finally attained approx. 84% (which is within 10% of that for TBP). The lower efficiency and slower rate could be attributed to the high viscosity of oleyl alcohol resulting in a decreased mass transfer rate and requiring longer time to complete the process compared to the less viscous solvent systems viscous.

Fig. 5. Effect of flow rate on the extraction of lactic acid with TOA-TBP system.

Fig. 6. Effect of the solvent type with TOA as a carrier in the extraction of lactic acid.

3.2.3 Effect of fermentation media
The synthetic fermentation broths (containing lactose and salts) and the pure lactic acid solution gave nearly the same extraction efficiency of about 90% as shown in Figure 7. The variation of the solution pH, i.e. a pH of 4.5 for the synthetic fermentation broth (compared to pH 2.4 for pure lactic acid) and presence of salts did not significantly affect the extraction efficiency. These results compare well with those in the literature (Tik, et al., 2001; Yankov, et al., 2005).
Because the above-mentioned solvents are not considered suitable (although many studies in the literature have used them) for large scale applications due to cost, health and safety and environmental reasons, further hollow-fibre experiments were conducted with sunflower oil.

### 3.3 Hollow-fibre extraction with sunflower oil

#### 3.3.1 Effect of carrier

The presence of carrier (either as a single solvent or combination with others) in the solvent had a large effect on the efficiency of the extraction. All of the trials reached steady state after a period of 45-60 mins. The run with no carrier (only sunflower oil) performed poorly with only 9% extraction efficiency (Figure 8). The experimental run with 30% carrier, which consisted of half Aliquat 336 and half TOA, performed the best, and reached an extraction efficiency of 33%. This percentage extraction is low but was obtained at conditions similar to the
fermentation conditions; so selective separation of lactic acid from the fermentation can be achieved without addition of any chemicals to adjust the pH of the broth. Thus in situ application would be possible without interruption of the fermentation. This continuous removal of lactic acid is expected to reduce its inhibitory effect and eventually the productivity of lactic acid can be increased.

3.3.2 Comparison with other solvent (TBP)
The extraction results of lactic acid at pH 6 with sunflower oil and TBP are compared in Figure 9. The carrier used was a mixture of 15% Aliquat 336 and 15% TOA. As expected TBP performed better; TBP achieved 50% extraction efficiency compared to 33% with sunflower oil. It is surprising to see that sunflower oil, having a much lower distribution coefficient than TBP, achieved a moderately good performance. Comparing the cost, industrial acceptability and environmental benefits sunflower oil could be a very good candidate as a single solvent or in combination with other high performing solvents.

![Fig. 9. Comparison of Extractions: sunflower oil vs. TBP.](image)

3.3.3 Effect of temperature on extraction with sunflower oil
The temperature has an effect on the extraction. This is observed in Figure 10, the experiment performed at room temperature reached 24%, whereas the run at 30.5 °C reached 28% extraction using a 10% TOA in sunflower oil (lactic acid feed pH 6). The increase in temperature increased the distribution of the organic phase and the diffusivity of the carrier-acid complex (as the viscosity of the two phases are decreased at higher temperature). These effects allowed faster mass transport through the pores (Frieling & Schugerl, 1999) and achieved greater percentage extraction. Therefore, the amount of extracted lactic acid can be further increased, by applying (i) higher temperature, (ii) lower aqueous solution pH, (iii) increased TOA concentration, and (iv) a mixed solvent system of sunflower oil and TBP. It is to be noted that temperatures more than 45 °C is not allowable in the hollow-fibre contactors used in these experiments. Also, fermentation of lactic acid is usually carried out below 40 °C as higher temperatures may make bacteria ineffective.
3.3.4 Optimal operating conditions
The results of extraction at the optimal operating parameters are presented in Figure 11. The conditions are: pH 5.0, at 35 °C, with an organic phase: a mixture of 15% Aliquat 336 and 15% TOA and a binary solvent system of 35% TBP and 35% sunflower oil. It is seen in Figure 11 that approx. 70% of lactic acid was extracted within 4h of contact time. The extraction rate was still increasing gradually and would have reached higher value at a longer operating time. It is also observed (from the comparison of the profiles in Figure 10 and 11) that the extraction rate decreases at these conditions (higher pH and larger composition of carrier and solvents). This could be because the distribution of lactic acid decreases at higher pH and at with larger composition of other solvents the diffusivity decreases (because of higher viscosity). But the extraction process goes on continuously. This is the effect of the mixed carrier being used in this experiment.

Fig. 10. Effect of temperature on extraction with 10% TOA in sunflower oil.

Fig. 11. Extraction (%) with a mixed carrier and mixed solvent system.
3.4 Overall mass transfer coefficient

The overall transfer coefficient \( (K_{\text{oa}}) \) was calculated from the slope of the plot of the left-hand side of Eq. (11) versus time. The value of the distribution coefficient obtained experimentally for each organic phase was used in the calculation. The experimental data during the initial period (approx. 60-70 mins) showed good correlation \( (R^2 = 0.9 \text{ at least}) \) and were considered for the calculation. A plot of the LHS of Eq. (11) versus the extraction time with various organic phases is shown in Figure 12. From the best fit line of the plot of LHS versus time, the slope was calculated and with the value of \( B \) from Eq. (12), the overall mass transfer coefficient has been calculated.

\[
y = 0.032x \\
R^2 = 0.975
\]

\[
y = 0.035x \\
R^2 = 0.973
\]

\[
y = 0.014x \\
R^2 = 0.912
\]

\[
y = 0.030x \\
R^2 = 0.938
\]

\[
y = 0.011x \\
R^2 = 0.913
\]

Fig. 12. A plot of LHS of Eqn. (11) versus time (min) for the overall mass transfer coefficient.

The values of the mass transfer coefficients are in the range \((0.4 - 2.3) \times 10^{-5} \text{ cm/s}\) (shown in Table 3). This is in consistent with the values of the distribution coefficient (Figure 9), i.e. the mass transfer rate is much faster in tributyl phosphate than in the other two organic phases. The values of overall mass transfer coefficient reported in the literature are range: \((0.2 - 5) \times 10^{-5} \text{ cm/s}\) (Juang and Huang, 1997; Coelho et al., 2000; Frielingsdorff and Schugerl, 1999). Considering the fact that this analysis is based on the extractions only (simultaneous re-extraction was not considered in this analysis), the values obtained in this study compare very well. The other advantage of the approximate method used in the present analysis is that the estimation of the mass transfer coefficient is based on semi-analytical equation and requires no correlation and additional data from any other experiments or literature. The model is based on many assumptions such as plug flow in both the aqueous feed and the organic phase, this has been reported in the literature in many extraction processes.

The knowledge of the analysis of results in terms of mass transfer coefficient could be useful in estimating the membrane area for a large-scale fermentative production process (as a preliminary exercise) where lactic acid can be removed as it is produced and thus enhancing the productivity.

In order to test the prediction capability of the model, more experimental results are required in a wide range of conditions with a variety of process solutions (especially with real process solutions obtained under industrial conditions). This is left for future work.
Table 4. The values of the overall mass transfer coefficient ($K_{ol}$) for lactic acid extraction.

<table>
<thead>
<tr>
<th>Organic phase</th>
<th>Feed solution</th>
<th>Overall mass transfer coefficient ($K_{ol}$) cm/s x 10^5</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% TOA in TBP (250 ml/min)</td>
<td>Aqueous lactic acid (0.2M)</td>
<td>1.82</td>
</tr>
<tr>
<td>10% TOA in TBP (750 ml/min)</td>
<td>Aqueous lactic acid (0.2M)</td>
<td>2.30</td>
</tr>
<tr>
<td>10% TOA in OA (250 ml/min)</td>
<td>Aqueous lactic acid (0.2M)</td>
<td>0.52</td>
</tr>
<tr>
<td>10% TOA in TBP (250 ml/min)</td>
<td>Synthetic fermentation broth</td>
<td>1.57</td>
</tr>
<tr>
<td>15% TOA + 15% Aliquat 336 in sunflower oil</td>
<td>Aqueous lactic acid (0.2M)</td>
<td>0.4</td>
</tr>
</tbody>
</table>

4. Conclusions

- The values of the distribution coefficient of lactic acid with solvents such as tri-butyl phosphate (TBP, the best), oleic acid, oleyl alcohol, shellsol TK and sunflower oil are small for physical extraction (solvent only).
- These values can be increased by reactive extraction with tri-octylamine (TOA/Aliquat 336 as the carrier) dissolved in any of the above solvents. The best organic system TOA-TBP gave a high distribution ratio at the natural pH 2.4. An extraction of approx. 93% can be achieved in the hollow fibre module within 2-3 h using 10% (w/w) TOA-TBP.
- The use of less toxic solvents such as oleyl alcohol (instead of TBP or its mixture with TBP) would give a lower percentage extraction with the final value around 83%.
- The presence of the components of the fermentation media, such as, lactose and salts do not significantly affect the percentage extraction in the membrane module.
- Extractions with these two organic systems are considered less suitable for large scale production because of cost, toxicity and potentially harmful environmental effects.
- For industrial application an organic phase with sunflower oil, is more attractive because of its cost (cheaper by an order of magnitude), non-toxicity and environmental benefits. It has proven to be effective at operating conditions (pH and temperature) similar to the fermentative production of lactic acid and shows stability with the commercially available hollow fibre modules.
- With sunflower oil-TOA/Aliquat 336 as the organic phase the percentage extraction is lower (30-35%) at room temperature. The extraction can be enhanced by operating at higher temperature.
- The percentage removal at this rate (at feed flow rate of approx. 12-13 L/h) from the fermentation media should reduce the product inhibition (lactic acid) effects and would improve the productivity by allowing the process over a longer period of time.

Notation

- A  surface area (m²)
- B  defined in Equation (12)
- C  concentration of lactic acid (mmol/L)
- $d_i$, $d_o$  inner diameter, outer diameter of a hollow fiber (cm)
- $D_E$  distribution coefficient of lactic acid defined in Eq. (3)
- $D_m$  diffusion coefficient of lactic acid defined in Eq. (14)
- $d_h$  hydraulic radius of lactic acid defined in Eq. (15)
Mass Transfer Investigation of Organic Acid Extraction with Trioctylamine and Aliquat 336 Dissolved in Various Solvents

E (%) percent of extraction of lactic acid, defined in Eq. (17)
H+ hydrogen ion
HLA undissociated lactic acid
Gz Graetz number defined in Eq. (13)
Km mass transfer coefficient in Equation (6), (cm/s)
L length of the fiber (cm)
N number of fibers
N steady state flux, defined in Equation (6)
Re Reynolds number defined in Eq. (15)
Sc Schmidt number defined in Eq. (15)
Sh Sherwood number defined in Eq. (13)
t time, s
v flow rate, L/s
u linear velocity in the hollow fibers (cm/s)
V volume (L)
Z axial distance in the module (cm)

Subscripts
aq aqueous phase
f feed solution
fi feed side at aqueous-organic interface
fo organic side at aqueous-organic interface
in based on inside fibre diameter
LAf final lactic acid concentration
LAi initial lactic acid concentration
oi organic side interface
o, org organic phase

Superscripts
m module
T tank

Greek symbols
e membrane porosity
σ thickness of the hollow fibres
τ tortuosity of the pores

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This book covers a number of developing topics in mass transfer processes in multiphase systems for a variety of applications. The book effectively blends theoretical, numerical, modeling and experimental aspects of mass transfer in multiphase systems that are usually encountered in many research areas such as chemical, reactor, environmental and petroleum engineering. From biological and chemical reactors to paper and wood industry and all the way to thin film, the 31 chapters of this book serve as an important reference for any researcher or engineer working in the field of mass transfer and related topics.

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