Supported Liquid Membrane Composed of Tertiary or/and Quaternary Amine for the Extraction of Lactic Acid

B.S. Chanukya and Navin K. Rastogi*

Academy of Scientific and Innovative Research India, Department of Food Engineering, Central Food Technological Research Institute, Mysore-570 020, India. A Constituent laboratory of Council of Scientific and Industrial Research, New Delhi, India

Abstract: The present work deals with the extraction of lactic acid from aqueous solution, fermentation broth and buttermilk by supported liquid membrane. The mixed amine extractant system of tertiary amine (Tri-octyl-amine) and quaternary amine (Aliquat^{TM} 336) in xylene was used in the supported liquid membrane The parameters such as effect of mixed amine extractant system, its ratios and concentration, stirring speed, strip: feed phase volume, and solute permeability as well as extraction efficiencies were calculated. The extraction of lactic acid from fermentation broth using standardised supported liquid membrane conditions showed 17.3% and 31.9% extraction with deionized water and Na_2CO_3 solution as the strip phase respectively and from buttermilk: 67 and 65.9% extraction with deionized water and Na_2CO_3 solution as the strip phase, respectively. The present study demonstrates the potential of supported liquid membrane composed of a combination of tertiary amine and quaternary amine as carriers for lactic acid extraction from aqueous and real systems.

Keywords: Supported liquid membrane, Mixed amine extractant, Lactic acid extraction, Fermentation broth.

1. INTRODUCTION

Lactic acid ($CH_3CHOHCOOH$) is one of the most frequently occurring hydroxycarboxylic acid and it is widely used in the food, pharmaceutical, cosmetics, and chemical industries [1]. Lactic acid production by fermentation has gained much interest because optically pure lactic acid is the raw material of biodegradable polymer [2]. A number of processes for lactic acid recovery from fermentation broth, such as reactive extraction, solvent extraction, adsorption, distillation, membrane technology, ion exchange and electrodialysis, have been studied [3-8]. Electrodialysis is considered to be an effective technique, but not economical [9]. Precipitation fails to remove the major impurities such as the residual sugar and the nitrogenous materials [1]. Solvent extraction suffers from environmental problems caused by excess volatile organic solvent usage [10] and toxicity to the micro-organism [1]. Also, simultaneous removal of the lactic acid during the process can improve the productivity of the product-inhibited fermentation process [1].

Supported liquid membrane (SLM) is a promising technology for recovering lactic acid from mixtures, as it potentially offers high flux, selective separation, low energy consumption, simplicity of operation and regeneration [11]. The process is considered economical for the aqueous feed in the concentration range of 100-2000 mol/m^3 [12]. Supported liquid membrane is a type of liquid membrane in which the liquid membrane (organic solvent containing the carrier) phase is immobilised unto a solid microporous support which is retained by capillary forces, between the feed and stripping phases. Since very small amounts of solvent and carrier are used in the supported liquid membrane, toxicity to the feed solution is negligible. Amine based supported liquid membrane has earlier been studied for the separation and recovery of citric acid [13-15], lactic acid [16-21], Salicylic acid [22], Fumaric acid [23] and Acetic acid [24]. Primary amines are highly soluble in water to be used with aqueous solutions and secondary amines are subject to amide formation upon regeneration [25]. Consequently, long-chain tertiary and quaternary amines (Figure **1**) have received the most attention. A large amount of work has been earlier carried out on the recovery of organic acids, such as lactic and citric acids, using tertiary and quaternary amines by liquid membranes [25, 12]. Since the separation and purification steps account for up to 50% of the production costs [26], the research is focused on effective, efficient and economical downstream processes for recovering lactic acid from fermentation broth.

The objectives of the present work, was to investigate the effect of supported liquid membrane composed of individual and combination of carriers such as tertiary amine (Tri-octyl-amine) and quaternary amine (Aliquat^{TM} 336), on the extraction of lactic acid. To standardise the experimental parameters that

---

[*] Address correspondence to this author at the Academy of Scientific and Innovative Research India, Department of Food Engineering, Central Food Technological Research Institute, Mysore-570 020, India. A constituent laboratory of Council of Scientific and Industrial Research, New Delhi, India
Tel: +91 821 2513910; Fax: +91 821 2517233;
E-mail: nkrastogi@cftri.res.in or nkrastogi@yahoo.com

E-ISSN: 2410-1869/15

influence the rate of lactic acid extraction from aqueous solution and use the standardized conditions for extraction of lactic acid from fermentation broth and buttermilk.

2. MATERIALS AND METHODS

2.1. Materials

2.1.1. Chemicals

Quaternary ammonium salt (Methyltricaprylammonium chloride or Aliquat^{TM} 336$C_{25}H_{54}ClN$, Mw 404.15 g/mol, density 0.884 g/ml) was of Himedia Laboratories Pvt Ltd, Mumbai, India. Tertiary ammonium salt (Tri-octyl-amine (TOA)$C_{24}H_{51}N$, Mw 353.68 g/mol, density 0.81 g/ml), organic phase xylene (C_8H_{10}, Mw 106.16 g/mol) and indicator phenolphthalein was procured from Merck Specialties Pvt Ltd. Stripping agent sodium carbonate (anhydrous) (Na_2CO_3, Mw 105.99 g/mol) was procured from Ranbaxy Fine Chemicals Ltd, New Delhi, India. Sodium hydroxide (NaOH, Mw 39.99 g/mol) was purchased from Qualigens Fine Chemicals, Mumbai, India. Extra pure lactic acid (Mw 90.08 g/mol) was purchased from Lobal Chemie Pvt Ltd, Mumbai, India. All reagents were used directly as received from the manufacturer.

2.1.2. Membrane

Polytetrafluroethelene (PTFE) membrane (pore size 0.45 micron, diameter 47 mm) manufactured by *Sartorius AG*, Goettingen, Germany was used in the study. Upon assembling onto the apparatus, the effective membrane surface area was 38.46 cm^2.

2.2. Methods

2.2.1. Feed Solutions

Aqueous lactic acid solution (3%) was prepared by dissolving 3.0 g anhydrous lactic acid crystals in 100 ml double distilled water and used as model feed solutions for the study. Fermentation broth was prepared in MRS media by addition of *Lactobacillus plantarum* NCIM 2083 at 1% to the broth and allowed to ferment at 37°C for 24 hours. The broth was centrifuged to remove suspended particles and stored at -20°C until usage. The final fermented product had lactic acid concentration of 1.16% and pH of 5.11, the broth was used without further pH adjustments. Buttermilk (*Nandini* Dairy Products Ltd., Mysore) was brought from local market and centrifuged at 5000 rpm (rotations per minute). The supernatant was used for the extraction studies. The lactic acid content in buttermilk was 0.85% and pH was 3.31 and was used without further pH adjustments.

2.2.2. Carrier and Strip Solutions

15% Tri-octyl-amine or Aliquat^{TM} 336 or a combination of [7.5% each (v/v)] both were dissolved in xylene to prepare the carrier solution. Carrier solution was freshly prepared for each experiment. Strip phase was either double distilled water or a solution of 0.5 M Na_2CO_3 in double distilled water.

2.2.3. Membrane Preparation for Supported Liquid Membrane

The PTFE membrane was soaked in carrier solution overnight before using for the extraction experiments. After experimentation, the membrane was washed with mild soap and re-soaked in the carrier solution until next use.

2.2.4. Supported Liquid Membrane Setup

The custom-made supported liquid membrane set-up consisted of upper (35 mm ID X 110 mm length) and the lower glass chambers, placed one inside the other, respectively. The effective volume of each cell was 100 ml. The carrier soaked PTFE membrane was inserted in-between the two chambers. The set-up was placed in a glass beaker with stripping solution in it. The lower and the upper glass chambers were filled with stripping solution and feed solution, respectively, separated by the PTFE membrane. Stirring was maintained in both chambers to avoid concentration polarization. Magnetic bead was placed on the perforated platform just above the membrane surface. The unit was placed on a magnetic stirrer. All experimentations were carried out in batch mode, at room temperature (26±2℃) and atmospheric pressure.

2.2.5. Determination of Lactic Acid Content

Lactic acid content in case of model solutions was estimated by acid-base titration method [27] using 0.05N NaOH solution as basic titrant and phenolphthalein as the indicator. Lactic acid content in case of real systems was estimated by high performance liquid chromatography (HPLC) analysis as per the procedure described in Zeppa *et al*, [28].

The percentage extraction (%E) was calculated from the following equation [29],

$$\%E = \frac{C_O - C_t}{C_O} \text{X } 100 \tag{1}$$

Where, C_0 and C_t are the lactic acid concentration at time 0 and t, respectively

2.2.6. Estimation of pH

pH of the samples was measured using a pH meter (*Eutech instruments,* Singapore).

2.2.7. Estimation of Total Soluble Solids

The total soluble solids (TSS) of the samples was measured as % °Brix using 0-32% hand held sugar refractometer (*ERMA,* Japan) at 25 ± 2.0 °C.

2.2.8. Estimation of Viscosity

The viscosities of the samples were measured using *Ostwald* viscometer (capillary diameter 1.0 mm) using water as the reference (0.890 mPa s) at 25.0 ± 2.0 °C.

2.2.9. Estimation of Density

The densities of the samples were determined using a specific gravity bottle (25ml), using weight of water as a reference (988 kg m^{-3}) at 25.0 ± 2.0 °C.

2.2.10. Estimation of Color

The *L*, a*, b** values of the samples were measured using a spectrophotometer (*Konica Minolta spectrophotometer CM-5, Konica Minolta optics Inc.,* Japan). *L** represents lightness of the sample (100: white, 0: black) *a** indicates redness when positive and greeness when negative; *b** represents yellowness when positive and blueness when negative. 10 ml of the sample was placed in the color measuring instrument and transmittance measurements were carried out at wavelength between 300 and 800nm, with illuminant D65 and observer placed at 10°.

2.2.11. Statistical Analysis

Significant difference between means were determined by t-test (two samples assuming unequal variance) using Microsoft Excel. The significance of differences was defined at p< 0.05.

2.2.12. Permeability

Lactic acid permeability during the experimental course was calculated based on the following equation. The flux (*J*) of the equation is given as:

$$J = P \cdot C \qquad (2)$$

Where P is the permeability coefficient (m/s) at the feed–membrane interface and C is the concentration of lactic acid (g/100ml) at the feed side.

$$PC = -V\frac{1}{A}\frac{dc}{dt} \qquad (3)$$

V is the volume of the feed solution (m^3), A the membrane area. After combining the equations (2) and (3), and integration within the appropriate limits:

$$\int_{C_0}^{C_t}\frac{dC}{C} = \int_0^t -\left(\frac{PA}{V}\right)dt \qquad (4)$$

Where, C_0, C_t are the initial and final concentrations of lactic acid in feed. Equation (4) can also be rearranged as:

$$ln\left(\frac{C_t}{C_0}\right) = -\left(\frac{P}{V}A\right)t \qquad (5)$$

The permeability co-efficient of lactic acid transport in supported liquid membrane can be inferred by equation (5) [30, 31]

3. RESULTS AND DISCUSSION

3.1. Mechanism of Lactic Acid Extraction by Supported Liquid Membrane

In supported liquid membrane extraction process, the solute (lactic acid) separation is facilitated by the carrier mixed in organic solution and impregnated in the pores of polymeric membrane support. This membrane separates the aqueous feed and the stripping solutions. Lactic acid transfer takes place from the feed with the help of carrier molecules into the strip solution in the following stages as shown schematically in Figure **1**:

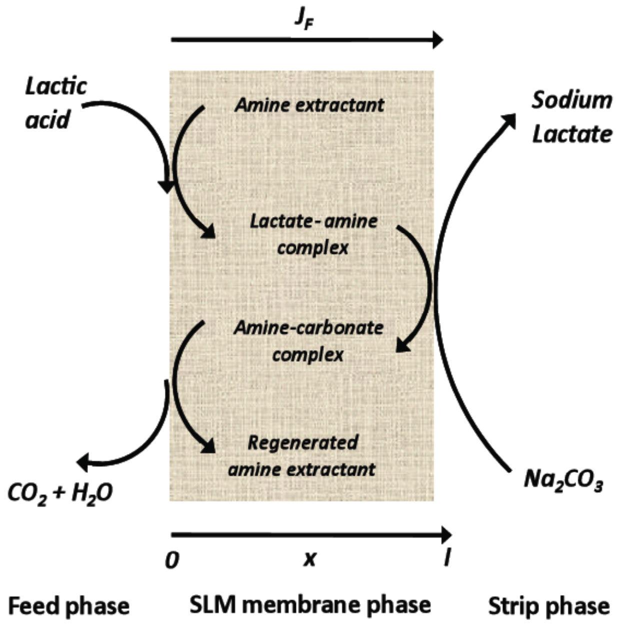

Figure 1: Schematic representation of the mechanism of lactic acid extraction by supported liquid membrane.

1) Diffusion of lactic acid in the feed phase towards the membrane interface (0) followed by reversible reaction of lactic acid with the amine extractant to form the lactate-amine complexes at the feed-membrane interface. 2) Diffusion of the acid-amine complexes through the supported liquid membrane (J_F) and 3) reaction of the acid-amine complexes with the strip agent at the membrane-strip interface (l), the reaction that occurred at the feed-membrane interface is now reversed causing the decomposition of the acid-amine complexes, consequently expelling the acid into the strip phase as sodium lactate (The solute does not diffuse back to the membrane due to conversion of the solute to sodium lactate form and the driving force is maintained). The free amine is left to diffuse back to the feed-membrane interface (0), thus completing the cycle.

3.2. Effect of Tertiary and Quaternary Amine Carrier on Lactic Acid Extraction

The experimental data plotted as a function of time against lactic acid extraction (Figure **2**) shows higher lactic acid extraction with tri-octyl-amine as carrier, reaching 51.3% extraction in 6h, compared to Aliquat^{TM} 336 (17.5%). Combination of tri-octyl-amine and Aliquat^{TM} 336 in the ratio of 1: 1 in the organic phase shows highest lactic acid extraction of 54.5% as compared to use of individual carriers (Figure **2**). The efficiency of these two carriers for extraction varies with the feed conditions, especially the pH. The structures of tertiary and quaternary amine salts used in the present work are shown in Figure **3**. Tertiary and quaternary amines extract acids from the aqueous phase by forming acid-base complex with the undissociated acid [25]. Weak acids such as lactic acid sparingly dissociate in water. Hence, the initial lactic acid feed solution has higher concentration of undissociated acid. Tertiary amines are more efficient in extracting undissociated acid [25].

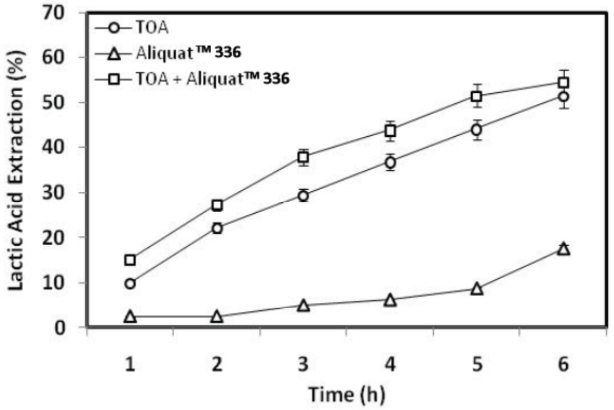

Figure 2: Percentage extraction of lactic acid by supported liquid membrane using tri-octyl-amine, Aliquat^{TM} 336, and combination of Tri-octyl-amine + Aliquat^{TM} 336 as carriers xylene. Experimental Conditions; feed concentration = 3% (v/v), volume of feed: strip phase (deionized water) = 25: 75ml, and stirring speed = 150 rpm.

This means less extraction would take place at basic pH conditions when tertiary amine is used as carriers. However, weak acids coexist in both dissociated and undissociated state. Quaternary amines such as Aliquat^{TM} 336 can extract acid under both acidic and basic conditions (undissociated and dissociated forms of the acid). Aliquat^{TM} 336 is composed of an organic cation associated with a chloride ion, it can function as an anion-exchange reagent under both acidic and basic pH conditions [25]. As the pH value decreases the hydrogen ions remain in the system, while the lactate ions are replaced by the corresponding anions of the quaternary ammonium salt [32].

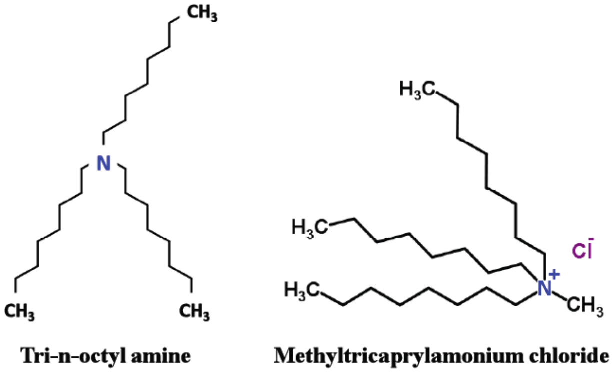

Figure 3: Structure of tertiary (Tri-n-octyl amine) and quaternary (Methyltricaprylamonium chloride or Aliquat^{TM} 336) amines.

Since the pH conditions in the feed vary with extraction of acid content and affect the efficiency of carrier, especially in case of real systems such as fermentation broth. As the distribution coefficient of the mixed extractant is greater than the sum of distribution coefficients of the two individual components for each pH value. The use of a combination of Tri-octyl-amine and Aliquat^{TM} 336 may have a synergistic effect on the lactic acid extraction at both acidic and basic feed conditions.

The process can be expressed in the following reactions: For reversible dissociations in a chemical equilibrium, the equation is given as:

$$AB \leftrightarrow A + B$$

The reaction of an acid in water where the proton acid *HA* dissociates to form ions H^+ (hydronium ions) and A^- (aqueous anions) is given by the below equation. Weak acids have both dissociated state (A^-) and undissociated state (*HA*) that coexist according to the equation:

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

The double arrow means that this is an equilibrium process, with dissociation and recombination occurring at the same time. The equation can also be expressed as:

$$HA(aq) + H_2O(l) \leftrightarrow H_3O^+(aq) + A^-(aq)$$

In the presence of a weak acid in water, the acid molecules *HA* (aq), react with water to form anions, (aq). The latter are produced when the acid molecules lose H+ ions to water.

In writing a constant expression for this homogeneous equilibrium, we leave out the concentration of the water. The equilibrium constant for this expression is called the acid dissociation constant, K_a. (Dissociation constant K_a, is the ratio of dissociated to undissociated ions or radicals per mole in water) K_a is defined by the following equation

$$K_a = \frac{[H^+][A^-]}{HA}$$

The square brackets indicate the concentration of respective components. K_a values can be used to describe the relative strength of the acids. A stronger acid will generate more hydronium ions in solution. A larger K_a indicates a greater ratio of ions (including hydronium ions) to uncharged acid.

Lactic acid is a weak acid, which means that it only partially dissociates in water. Lactic acid dissociates in water resulting in ion lactate and H^+.

K_a of lactic acid 1.38×10^{-4} Depending on the environmental pH, lactic acid is present either in its undissociated form at low pH (at pH 3.8, over 90% exist as lactic acid molecules in the feed) or as ion salt at higher pH (at pH 5.8, over 90 % exist as lactate ions)

The following reactions occur in the reactive extraction of lactic acids with tertiary amine.

$$R_3N + HA \leftrightarrow R_3N{-}HA$$

The acid extracted into an amine-containing organic phase is no longer regarded as an acid, but as ammonium salt, Hence recombination of ammonium salt is given by the reaction:

$$R_3N{+}H^+ + A^- \leftrightarrow R_3NH^+A$$

Thus, the overall reaction can be given as:

$$R_3N + HA \leftrightarrow R_3NHA$$

The reaction of lactic acid with quaternary amine is given as:

$$R_4NH^+X^- + A^- \leftrightarrow R_3NH^+A^- + X^-$$

Where the anions of lactic acids are replaced with anions of quaternary ammonium salt

Rate equations for the formation and dissociation of the lactic acid (HC) - carrier (Tri-octyl-amine) complexes, R_1 and R_{-l}, are given by

$R_1 = k_1\,[HC][TOA]^2$

$R_{-1} = k_{-1}\,[HC]^{-1}[TOA]^{-1}[HC]$; with water as a strip phase

$R_{-1} = k_{-1}[TOA]^{-1}[HC]$; with Na_2CO_3 as a strip phase

Where k_1 is 1.67×10^{-11} $m^7/(mol^2s)$, and k_{-1} is 3.73×10^{-4} $mol^2/(m^5\ s)$ and 4.90×10^{-4} $mol/(m^2\ s)$ with water and 100 mol/m^3 Na_2CO_3 as a strip phase, respectively [12]

Tri-octyl-amine + Aliquat^{TM} 336 were varied at ratios of 3:1, 1:1, 1:3, respectively. At Tri-octyl-amine + Aliquat^{TM} 336 ratio of 1:1, the lactic acid extraction and permeability is highest at 54.5% and 6.83×10^{-6} m/s, respectively (Figure **4a**, Table **1**), due to the synergistic effect caused by a combination of carriers on percentage extraction. The increase in the ratios to 1:3 resulted in reduced lactic acid extraction, due to increased viscosity of the membrane phase caused by the higher viscosity of the Aliquat^{TM} 336, reducing mass transfer across the liquid membrane [14, 25, 31]. Maximum lactic acid extraction was observed (54.5%) with 15% (1:1 Tri-octyl-amine: Aliquat^{TM} 336) carrier concentration (Figure **4b**, Table **1**). Further increase in the carrier concentration (>15%) resulted in reduction in rate of extraction and permeability due to higher concentration of viscous Aliquat^{TM} 336 in the organic membrane phase. Although the percentage increase in lactic acid extraction with the use of a combination of Tri-octyl-amine and Aliquat^{TM} 336 is very small compared to the use of individual carriers, the present work is aimed at showing that improvement in rate of lactic acid extraction is possible with the use of a combination of tertiary and quaternary amines.

3.3. Effect of Stirring Speed

Stirring of the feed and stripping phases during the extraction process enlarges the tangent velocity and facilitates disturbances of the boundary layers at the interfaces resulting in decrease in the thickness of boundary layer facilitating effective permeation of targeted molecule [33]. From the experimental results over a stirring range of 100-250 rpm, it was observed that, with lower stirring speed, *i.e*. 100 and 150 rpm, the lactic acid permeability and % extraction increased (Table **1**, Figure **4c**) and reached maximum of 5.69 × 10^{-6}m/s and 50.7%, respectively at 150 rpm. Increase in the stirring speed beyond 150 rpm showed reduction in the lactic acid extraction and permeation. The increase in the mass transfer at lower stirring speeds indicates that the thickness of the diffusion layer is decreased and is minimum [34]. As stirring speed is increased to 200 rpm and beyond, aqueous boundary layer thickness is diminished continuously with increasing stirring speed, resulting in displacement of the carrier molecules form the membrane pores due to turbulence [33], leaving lesser amounts of carrier molecules in the membrane to transport the lactic acid. This reduced the lactic acid extraction efficiency from 44-50% at 100 and 150 rpm, respectively to 37-35% at 200-250 rpm, respectively. Stirring speed of 150 rpm was found to be optimum and was chosen for further experiments.

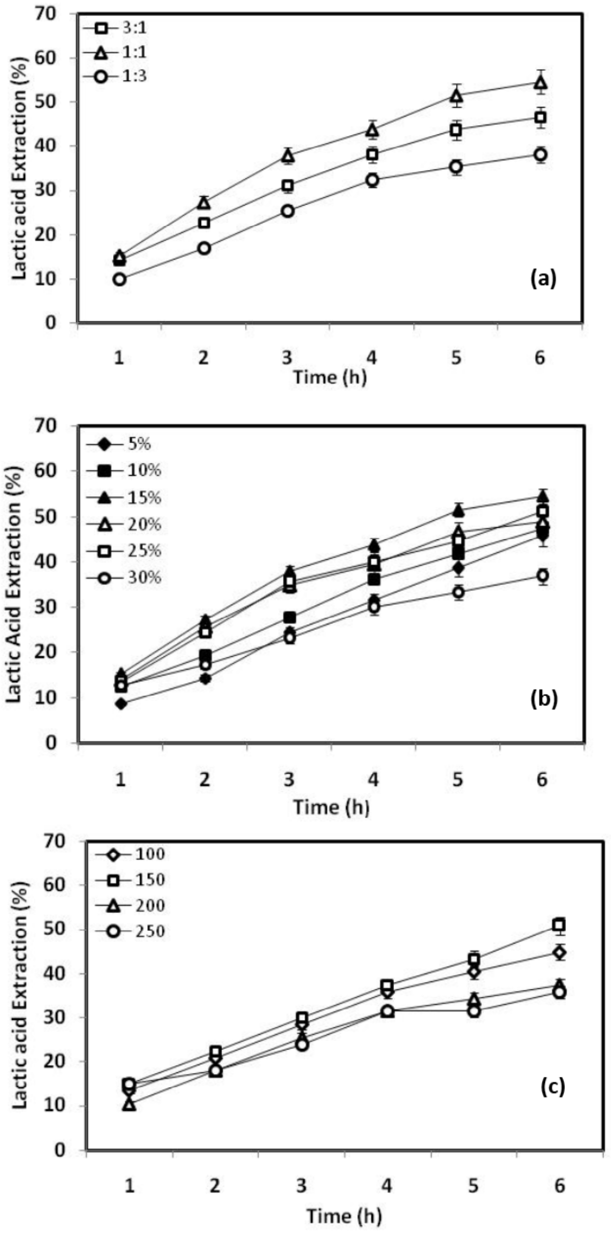

Figure 4: Percentage extraction of lactic acid (**a**) for varying ratios of Tri-octyl-amine and Aliquat^{TM} 336 in supported liquid membrane. (Carrier concentration 15%, Stirring speed 150 rpm) (**b**) using various concentrations of carrier (Tri-octyl-amine + Aliquat^{TM} 336), (ratio of tri-octyl-amine and Aliquat^{TM} 336 1:1, Stirring speed 150 rpm) (**c**) at different stirring speeds (rpm) of the feed and the stripping phase (ratio of tri-octyl-amine and Aliquat^{TM} 336 1:1, Carrier concentration 15%,). Feed concentration = 3% (v/v).

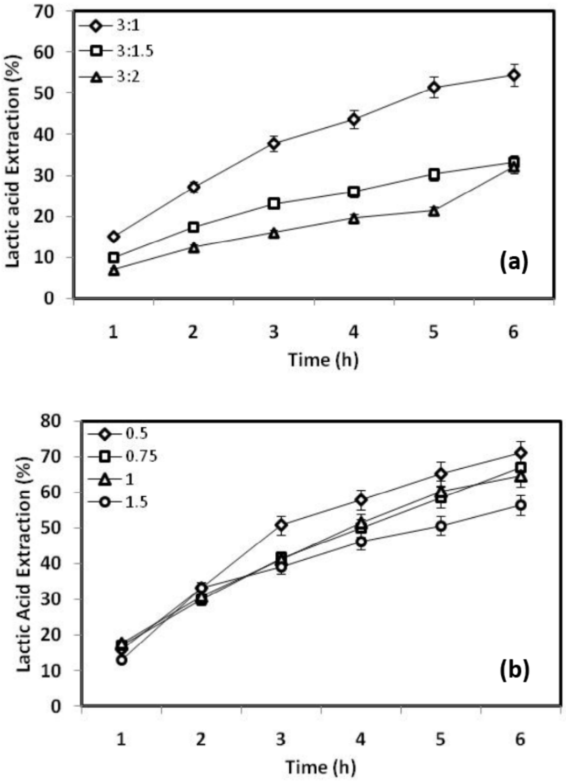

Figure 5: Percentage extraction of lactic acid (**a**) for different volume ratio of strip (deionized water) to feed phase, (**b**) for varying strip (Na_2CO_3) concentrations (Molar). Experimental conditions: feed concentration = 3% (v/v), carrier concentration = 15% (v/v), stirring speed = 150 rpm.

3.4. Effect of Strip to Feed Phase Volume Ratio

From the graphical plot of % extraction against time (Figure **5a**), highest extraction was achieved with strip to feed phase volume ratio (V_s:V_f) of 3:1 resulting in 54.5 % extraction in 6 hours. The permeability was found to be 6.83 × 10^{-6} m/s (Table **1**). At V_s:V_f ratio of 3:1.5, 33.3% lactic acid extraction was observed with mass transfer rate of 4.49 × 10^{-6} m/s. A specific concentration of carrier would transfer the same amount of lactic acid molecules across supported liquid membrane without being affected by the volume of feed. Thus, the process is affected by the concentration of lactic acid in the feed phase. However, at V_s:V_f ratio of 3:1.5, with higher volume of the feed solution, the concentration of amine-acid complex available per concentration of strip solution is higher. Since a given volume of strip solution has limitations to the amount of amine-acid it can strip, it results in inefficient stripping of the amine-acid complex and build up of the amine-acid complex at the membrane-strip interface resulting in resistance to mass transfer and reduced rate of extraction. Hence, V_s:V_f of 3:1 were used for further experiments.

3.5. Effect of Strip Phase Concentration

Sodium carbonate solution as strip phase was varied in the concentration range of 0.5-1.5 M. 0.5 M resulted in maximum lactic acid extraction and permeability of 71% (Figure **5b**) and 10.39 X 10^{-6} m/s, respectively (Table **1**). Increase in sodium carbonate concentrations (>0.5 M) showed no major change in % extraction. Sodium carbonate as stripping agent for liquid membrane extraction of lactic acid from

Table 1: Permeability and % Extraction of lactic acid at Different Supported Liquid Membrane Conditions

Parameter	Range	Permeability (× 10^{-6} m/s)	Extraction (%)
Tri-octyl-amine: Aliquat™ 336 ratio (v/v)	1:0	5.17	51.3
	3:1	5.44	46.4
	1:1	6.83	54.5
	1:3	4.21	38.0
	0:1	1.18	17.5
Feed Concentration (v/v), (%)	1	6.38	50.0
	2	7.86	47.8
	3	6.58	44.0
	4	5.04	43.0
	5	4.92	31.2
Stirring speed, (rpm)	100	5.03	44.7
	150	5.69	50.7
	200	4.1	37.3
	250	3.82	35.8
	500	4.82	45.7
Carrier concentration (v/v), (%)	10	5.27	47.2
	15	6.83	54.5
	20	5.89	48.8
	25	5.98	51.1
	30	3.93	36.7
Volume of Strip: feed (V_s: V_f), (ml)	3:2	5.64	32.1
	3:1.5	4.49	33.3
	3:1	6.83	54.5
Strip (Na_2CO_3) conc. (M)	0.5	10.39	71.0
	0.75	8.82	67.0
	1	8.73	64.7
	1.5	7.11	56.5

(v/v: volume/ volume, rpm: rotations per minute, V_s: V_f: volume of strip phase: volume of feed phase, M: Molar concentration) fermentation broth has been reported by Demirci *et al.* [16] and for extraction of salicylic acid by Kouki *et al.* [22]. Sodium carbonate shows higher stripping efficiency as compared to the use of water, as sodium carbonate solution gives faster dissociation reaction of the complexes [35]. Also, sodium carbonate interacting with lactic acid would form sodium lactate salt and thus, retain lactic acid within the strip phase. This removes the lactic acid liquid mass-transfer resistance across supported liquid membrane. With water as stripping agent, the un-complexed carrier-solute molecules may saturate the membrane reducing extraction efficiency. Hence, 0.5 M sodium carbonate solution was used as the stripping phase for lactic acid extraction from real systems. Stripping phase consisting of either sodium carbonate or deionized water for the extraction of citric acid [14] and lactic acid [35] from aqueous solutions has been earlier reported.

3.6. Lactic acid Extraction from Fermentation Broth and Buttermilk

The mixed extractant supported liquid membrane systems and the standardised extraction conditions were applied for lactic acid extraction from fermented product containing various organic acids. The usage of a combination of carriers as extractants can find its advantage in the extraction of lactic acid from real systems as the presence of carriers which works at both basic and acidic pH can enhance the rate of lactic acid extraction. The lactic acid concentration in the fermentation broth reduced from 1.16 to 0.79 (31.9% extraction) with Na_2CO_3 based strip system and 0.96 (17% extraction) with water based strip solution system (Table **2** (**a**)). Analysis of the physical properties such as TSS, density and viscosity did not show substantial change from the crude, whereas increase in pH was observed in the Na_2CO_3 based strip solution treated fermentation broth. A comparison of the color characteristics showed changes in *a** and *b** of the crude broth and the supported liquid membrane treated samples (Table **2** (**b**)).

Similarly, extraction of lactic acid from buttermilk was carried out. The extraction resulted in lactic acid reduction from 0.85 to 0.29 (65.8% extraction) with Na_2CO_3 based strip solution system and 0.28 (67%

Table 2(a): HPLC Analysis of Crude and Supported Liquid Membrane Processed Fermentation Broth/ Buttermilk Systems with Na_2CO_3 or Water as the Strip Solutions

	Crude	SLM Processed		Crude	SLM Processed	
		Na_2CO_3 as strip	Water as Strip		Na_2CO_3 as Strip	Water as Strip
Fermentation Broth				Buttermilk		
Lactic acid conc. (mg/ml)	1.16	0.79	0.96	0.85	0.29	0.28
Extraction (%)	-	31.9	17.3	-	65.8	67

Table 2(b): Changes in the Physical and Color Characteristics of Fermentation Broth/ Buttermilk before and after Supported Liquid Membrane Process

Conditions before SLM Extraction			Conditions after SLM Extraction			
	Fermentation Broth	Buttermilk	Fermentation Broth		Buttermilk	
			Water (strip)	Na_2CO_3 (strip)	Water (strip)	Na_2CO_3 (strip)
pH	5.11	3.31	5.31	5.94	3.31	5.51
TSS (°Brix)	10.1	7.45	9.9	9.25	7.3	7.2
Density (Kg/m³)	999	1002	1008.6	1007.1	1001.4	1001.6
Viscosity (mPas)	1.105	0.886	1.103	0.905	0.870	0.882
*L**	69.36	95.9	74.36	79.67	95.16	97.32
*a**	19.2	0.85	14.48	8.98	1.03	0.78
*b**	75.14	5.62	50.34	57.48	6.66	5.57

extraction) with water based strip solution system, as calculated from the retention peaks of the lactic acid (Table **2** (a)). The physical properties of the treated broth such as TSS, density and viscosity did not vary much from the crude sample, whereas increase in pH was observed in the Na_2CO_3 based strip solution treated buttermilk. A comparison of the color characteristics of the crude and the processed buttermilk showed changes in the *a** and *b** of the water based strip solution supported liquid membrane processed samples as compared to the crude (Table **2** (**b**)).

4. CONCLUSION

The supported liquid membrane in the present work was composed of a combination of tertiary (Tri-octyl-amine) and quaternary amine (Aliquat^{TM} 336) carriers in xylene as the liquid membrane phase. The mixed amine extractant system (Tri-octyl-amine + Aliquat^{TM} 336) was observed to be marginally effective in terms of percentage lactic acid extraction compared to usage of individual carriers. The standardised experimental conditions resulted in maximum lactic acid extraction of 71, 31.9 and 65.8% from aqueous systems fermentation broth and buttermilk, respectively.

ACKNOWLEDGEMENT

The Author B.S. Chanukya acknowledges the Council of Scientific and Industrial Research, New Delhi, Government of India, for providing financial support in the form of Senior Research Fellowship to carry out this research. The authors wish to thank Dr. K.A. Anu Appaiah, Department of Food Microbiology, Central Food Technological Research Institute for his help in preparation of fermentation broth.

REFERENCES

[1] Choudhury B, Basha A, Swaminathan T. Study of lactic acid extraction with higher molecular weight aliphatic amines, J. Chem Technol Biotechnol 1998; 72; 111-116. http://dx.doi.org/10.1002/(SICI)1097-4660(199806)72:2<111::AID-JCTB878>3.0.CO;2-O

[2] Vijayakumar J, Aravindan R, Viruthagiri T. Recent trends in the production, purification and application of lactic acid, Chem Biochem Eng Quart 2008; 22: 245-264.

[3] Baniel AM, Eyal AM, Mizarahi J, Hazan B, Fisher R.Lactic acid production, separation and recovery process, 2001 US Patent. No. 6 187,951.

[4] Eyal AM, Starr JN, Fisher R., Hazan B, Canari R, Witze DR.Lactic acid processing methods arrangements and products. 2001 US Patent No. 6,229,046.

[5] Kulprathipanja S, Separation of lactic acid from fermentation broth with an anionic polymeric absorbent, 1991 US Patent No. 5,068,418.

[6] Russo LJ, Kim H. Membrane-based process for the recovery of lactic acid by fermentation of carbohydrate substrates containing sugars, 1996 US Patent No. 5,503,750.

[7] Nispen VJGM, Jonker R. Process for the fermentative preparation of organic acids, 1991 US Patent No. 5,002,881.

[8] Datta R. Recovery and purification of lactate salts from whole fermentation broth by electrodialysis, 1989 US Patent. No. 4,885,257.

[9] Matsumoto M, Hasegawa W, Kondo K, Shimamura T, Tsuji M. Application of supported ionic liquid membranes using a flat sheet and hollow fibers to lactic acid recovery, Desal. Water Treat. 2010; 14: 37-46. http://dx.doi.org/10.5004/dwt.2010.1009

[10] Keshav A, Wasewar KL, Chand S, Recovery of propionic acid by reactive extraction – 1. Equilibrium, effect of pH and temperature, water co-extraction, Desal. Water Treat. 2009; 3: 91-98. http://dx.doi.org/10.5004/dwt.2009.442

[11] Yang Q, Chung TS. Modification of the commercial carrier in supported liquid membrane system to enhance lactic acid flux and to separate L, D-lactic acid enantiomers, J Membr Sci 2007; 294: 127-131. http://dx.doi.org/10.1016/j.memsci.2007.02.021

[12] Juang RS, Huang RH, Wu RT. Separation of citric and lactic acids in aqueous solutions by solvent extraction and liquid membrane processes, J Membr Sci 1997; 136: 89-99. http://dx.doi.org/10.1016/S0376-7388(97)00176-2

[13] Park SW, Choi BS, Kim SS, Lee JW. Facilitated transport of organic acid through a supported liquid membrane with a carrier, Desal 2006; 193: 304-312. http://dx.doi.org/10.1016/j.desal.2005.06.066

[14] Juang RS, Chen LJ. Transport of citric acid across a supported liquid membrane containing various salts of a tertiary amine, J Membr Sci 1997; 123: 81-87. http://dx.doi.org/10.1016/S0376-7388(96)00205-0

[15] Rockman JT, Kehat E, Lavie R. Thermally enhanced extraction of citric acid through supported liquid membrane, AIChE J 1997; 43(9): 2376-2380. http://dx.doi.org/10.1002/aic.690430924

[16] Demirci A, Cotton JC, Pometto III AL, Harkins KR, Hinz PN. Resistance of lactobacillus casei in plastic-composite-support biofilm reactors during liquid membrane extraction and optimization of the lactic acid extraction system, Biotechnol. Bioeng.2003; 83(7): 749-759. http://dx.doi.org/10.1002/bit.10722

[17] Ju LK, Verma A. Characteristics of lactic acid transport in supported liquid membranes, Sep Sci Technol 1994; 29(17): 2299-2315. http://dx.doi.org/10.1080/01496399408003180

[18] Yahaya GO, Brisdon BJ, England R. Facilitated transport of lactic acid and its ethyl ester by supported liquid membranes containing functionalized polyorganosiloxanes as carriers, J Memb Sci 2000; 168: 187-201. http://dx.doi.org/10.1016/S0376-7388(99)00312-9

[19] Juang RS, Huang RH. Kinetic studies on lactic acid extraction with amine using a microporous membrane-based stirred cell. J Membr Sci 1997; 129: 185-196 http://dx.doi.org/10.1016/S0376-7388(96)00338-9

[20] Harington T, Hossain MM. Extraction of lactic acid into sunflower oil and its recovery into an aqueous solution, Desal. 2013; 218: 287-296. http://dx.doi.org/10.1016/j.desal.2007.02.024

[21] Matsumoto M, Takagi T, Kondo K. Separation of lactic acid using polymeric membrane containing a mobile carrier, J. Ferm. Bioeng. 1998; 85(5): 483-487 http://dx.doi.org/10.1016/S0922-338X(98)80066-4

[22] Kouki N, Tayeb R, Zarrougui R, Dhahbi M. Transport of salicylic acid through supported liquid membrane based on ionic liquids, Sep Purif Technol 2010; 76: 8-14.

http://dx.doi.org/10.1016/j.seppur.2010.09.013

[23] Li SJ, Chen HL, Zhang L. Recovery of fumaric acid by hollow-fiber supported liquid membrane with strip dispersion using trialkylamine carrier, Sep Purif Technol 2009: 66; 25-34. http://dx.doi.org/10.1016/j.seppur.2008.12.004

[24] Narayanan J, Palanivelu K. Recovery of acetic acid by supported liquid membrane using vegetable oils as liquid membrane, Indian J. Chem. Technol. 2008; 15: 266-270.

[25] Yang ST, White SA, Hsu ST, Extraction of carboxylic acids with tertiary and quaternary amines. Effect of pH, Ind Eng Chem Res 1991; 30: 1335-42. http://dx.doi.org/10.1021/ie00054a040

[26] Wasewar KL. Separation of lactic acid: recent advances, Chem. Biochem. Eng. Quart. 2005; 19: 159-172.

[27] AOAC. Official methods of analysis, fifteenth edition, In K. Helrich (Ed.), Arlington, VA, USA, 1990.

[28] Zeppa G, Conterno L, Gerbi V. Determination of organic acids, sugars, diacetyl, and acetoin in cheese by high-performance liquid chromatography, J Agric Food Chem 49 (2001) 2722-2726. http://dx.doi.org/10.1021/jf0009403

[29] Zidi C, Tayeb R, Boukhili N, Dhahbi M. A supported liquid membrane system for efficient extraction of vanillin from aqueous solutions, Sep Purif Technol 2011; 82: 36-42. http://dx.doi.org/10.1016/j.seppur.2011.08.013

[30] Gaikwad AG. Studies of anion transport through supported liquid membrane, Anal Lett 2009; 42: 3018-3030. http://dx.doi.org/10.1080/00032710903202063

[31] Biswas S, Pathak PN, Roy SB. Carrier facilitated transport of uranium across supported liquid membrane using dinonyl phenyl phosphoric acid and its mixture with neutral donors, Desal 2012; 290: 74-82. http://dx.doi.org/10.1016/j.desal.2012.01.006

[32] Yankov D, Molinier J, Kyuchoukov G, Albet J, Malmary G. Improvement of the lactic acid extraction from aqueous solutions and simulated fermentation broth by means of mixed extractant and TOA, partially loaded with HCl, Chem Biochem Eng Q 2005: 19(1): 17-24.

[33] Badgujar V, Rastogi NK. Extraction of phenol from aqueous effluent using triglycerides in supported liquid membrane, Desal Water Treat 2011; 36(1-3): 187-196. http://dx.doi.org/10.5004/dwt.2011.2406

[34] Gaikwad AG. Transport studies of lactic acid through supported liquid membrane, Chem Biochem Eng Q 2004; 18 (3): 285-293.

[35] Juang RS, Lee SH, Shiau RC. Mass-transfer modeling of permeation of lactic acid across amine-mediated supported liquid membranes, J Membr Sci 1997; 137: 231-239.

Received on 31-08-2015 Accepted on 08-10-2015 Published on 30-11-2015

http://dx.doi.org/10.15379/2410-1869.2015.02.02.03