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Batch and dynamic study of lactic acid extraction using emulsion liquid membrane

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Abstract. The extraction of lactic acid by an emulsion liquid membrane (ELM), in batch and continuous mode, has been reported. On the basis of preliminary experiments, the optimum composition of the organic phase (membrane) is determined. When the SPan 80 is used as surfactant, the emulsion breakage exceeds 50%, but only 10% is obtained when the ECA4360 is used. The effects of surfactant, carrier and solute concentrations, phase volume ratio, and stirring speed on the extraction yield were examined and optimized. Surfactant, carrier and diluent used were ECA4360, trilaurylamine (TLA) and dodecane, respectively; 2-ethylhexane-1,3-diol (EHD) is used as a co-surfactant. Under optimal conditions, emulsion breaking is very low and the swelling is kept at its lowest level. Under the pH conditions of fermentation medium, the extraction yield is lower. A mixer-settler continuous system was used for testing these conditions. The residence time, the number of extraction stages and the stability of the emulsion were studied and optimized. The extraction yield obtained exceeds 90%.

Keywords: lactic acid; emulsion liquid membrane; continuous extraction; mixer-settler; whey effluent

1. Introduction

Cheese whey is a byproduct of the dairy industry obtained by separating the coagulum from whole milk, cream, or skim milk. About 30 million tons of liquid whey is produced annually in the United States. Cheese whey represents about 85-90% of the milk volume and retains 55% of the milk nutrients, including lactose with a composition of 4.5-5.0% (w/v). (Gonzalez 1996). This byproduct is traditionally treated as a waste because of its low nutrient value, low concentration, and limited market (Yang and Silva 1995). But, its use as a substrate for the fermentative production of chemicals can solve part of the environmental problem (Chiarini *et al.* 1992). Whey lactose can be fermented into some products, such as lactic acid ($CH_3CHOHCOOH$) (Reddy et al. 2008). It is an organic liquid; its field of application is constantly expanding, as the manufacture of food products, chemicals, and pharmaceuticals (Li et al. 2010). The biodegradable poly-lactic acid (PLA) is an alternative to plastics derived from petrochemicals (Drumright *et al.* 2000); it can be

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used in products, such as flower pots, disposable diapers, textile fabrics (Huang *et al.* 2004) and plastics derived from petrochemicals (Drumright *et al.* 2000). Lactic acid is the first commercially successful biotechnological product (Hujanen and Linko 1996). It is produced either via the chemical route (petrochemical synthesis) or the biological pathway (fermentation of whey) or another source of cheap carbon (Tay and Yang 2002). The chemical method can only produce racemic mixtures of lactic acid, whereas fermentation can produce optically pure isomer. Fermentation utilizes renewable resources that make it more attractive (Huang *et al.* 2004).

For lactic acid recovery from fermentation broth, solvent extraction (Tik *et al.* 2001), adsorption (Aljundi *et al.* 2005), direct distillation (Choi and Hong 1999), precipitation (Min *et al.* 2011), esterification-hydrolysis (Sun *et al.* 2006) and the membrane techniques (Pal *et al.* 2009) are the most methods cited in the literature.

Since its discovery in 1968 by N.N. Li, emulsion liquid membrane method has shown a considerable potential application in various areas such as hydrocarbon separation (Kim *et al.* 1997), recovery of metal ions (Goyal *et al.* 2011, Ahmad *et al.* 2013) and rare-earths metals (Hasan *et al.* 2009), elimination of trace contaminants from wastewater (Datta *et al.* 2003, Agarwal *et al.* 2010), recovery of biochemical products (Thien and Hatton 1988) and biomedical fields (Razo-Lazcano *et al.* 2014), recovery of vegetal growth promoter used in agriculture (Berrios *et al.* 2010).

In the emulsion liquid membrane (ELM) process, water in oil (w/o) emulsion containing a carrier (extractant) is dispersed in an aqueous solution to cause mass-transfer between the external and internal aqueous phases through the oil layer (membrane). The emulsion is stabilized by adding an emulsifier (surfactant). This method enables to perform in one step both extraction and back-extraction. The extraction yield depends on a number of operating parameters as well as the composition and the nature of the membrane.

The development of modern biotechnology is strongly related not only to the advancement of microbiological synthesis but also in choosing the best method for the separation of manufactured products, to achieve this goal, ELM technique is one of the methods that can be used. Few studies are devoted to the lactic acid extraction using ELM technique. In these works, the membrane used contains either a secondary amine (Amberlite LA-2) as carrier and ECA 11522 (Reisinger and Marr 1992) or Paranox 100 (Mok and Lee 1994) as surfactant, but when the carrier is a tertiary amine (tri-N-octylamine or Hostarex A327), the surfactant used is the Span 80 (Chaudhuri and Pyle 1992a, b, Manzak and Tutkun 2011, Yuanli et al. 2001, Demirci et al. 1999, Thakur et al. 2008). No studies have tested a membrane containing a tertiary amine as carrier and a surfactant other than Span 80. For contribute to the implementation of a lactic acid recovery process, obtained by converting the lactose contained in whey, the present work aims firstly to study, in batch mode, optimizing operating parameters, namely, the organic extraction phase composition, initial acid concentration and pH of the external phase. Then, the feasibility of the extraction process in continuous mode has been evaluated by performing experiments in a multistage mixer-settler system. The emulsion used is stabilized by ECA 4360 as surfactant, and containing a tertiary amine (tridodecylamine).

2. Experimental

2.1 Materials

Lactic acid is a product of Merck, it has a purity of about 90%. Tri-dodecylamine or trilaurylamine (TLA), 2-ethylhexane-1,3-diol (EHD) and sodium hydroxide are procured, also, from Merck. Span-80 and ECA4360 are obtained from Fluka and EXXON, respectively. Dodecane and octanol-1 are supplied by Prolabo.

2.2 Method

The membrane phase is consisted of dodecane, TLA, EHD, 1-octanol and Span 80 or ECA 4360. The internal aqueous phase is a NaOH solution. Water in oil emulsion is prepared by slow addition of the internal aqueous phase to the organic membrane phase using a high speed homogenizer (Ultra-Turrax T 25, Janke & Kunkel, IKA- Labortechnik, Staufen, Germany). The external feed solution of lactic acid is prepared separately into the agitated vessel (capacity 200 cm^3), in which emulsion is dispersed at a constant stirring speed. The stirring speed is measured by a digital non-contact type tachometer. Adjusted solutions of external phase are obtained by adding NaoH. All experiments are conducted at room temperature.

Lactic acid and lactate concentration are measured in aqueous solution by acid-base titration using an automatic titrator (Metrohm Herisau E 536), in conjunction with an automatic syringe buret (655 Dosimat). Sodium concentrations in the external phase are measured by atomic absorption spectroscopy (VARIAN A300). The samples are drawn from the vessel at the end of the test; all parameters are analyzed like described above.

Changes in the volume of internal phase are estimated by volume balance after breaking the emulsion at the end of the experiments. The emulsion is broken by thermal demulsification.

3. Theory

3.1 Emulsion breakage

The membrane breakage includes the leakage of the internal reagent and the extracted solute through the membrane phase to the external phase during the transfer, as a result, a decrease of driving force for mass transfer; thereby lowering the extraction efficiency (Wan and Zhang 2002). This phenomenon still considered as one of the most serious obstacles in the successful application of liquid membrane to industrial application, and then it is necessary to minimize it. The main factors affecting the emulsion stability encompass the membrane formulation; the method of emulsion preparation, and the condition under which the emulsion is contacted with a reactant phase (Djenouhat *et al.* 2008). The emulsion breakage is determined using tracer method. It is based on the introduction a compound (tracer) soluble in the internal phase, and which cannot diffuse or be transported across the membrane. The sodium ion (Na$^+$) of internal phase (NaOH) is used as a tracer; its presence in the external phase is a proof of emulsion breakage. The breakage ratio (B) is calculated using Eq. (1).

$$B(\%)=\frac{C_{e,T}.V_{e,t}}{V_{i,0}.C_{i,0}}.100 \qquad (1)$$

B: membrane breakage (dimensionless, %)

$C_{e,T}$: Concentration of the tracer in external phase after mixing operation (mol.L^{-1}).

$V_{e,t}$: the volume of the external phase after mixing operation (L).

$V_{i,0}$: the initial volume of the internal phase (L).

$C_{i,0}$: the initial concentration of the tracer in the internal phase (mol/L).

3.2 Emulsion swelling

During the membrane swelling, water is transported from the external phase to the internal phase, leading to the change in the volume of emulsion, and then the solute dilution of internal phase, where it has been extracted. Swelling is considered as an undesirable phenomenon, so must be minimized. Membrane swelling can be classified into two types. (1) Permeation (or osmotic) swelling, occurs when there exists a difference of electrolyte concentration between the internal and external aqueous phases. (2) Entrainment swelling, takes place in the initial dispersion process (Zihao *et al.* 1996). Usually, emulsion swelling is evaluated by the emulsion swelling ratio, which can be calculated by the ration of the change in volume of the internal phase after dispersion operation to the initial volume, but according to (Wan and Zhang 2002) work, two emulsion swelling ratios can be defined, the apparent swelling ratio (S_{ap}) and the actual swelling ratio (S_{ac}) expressed by Eqs. (2)-(3), respectively.

$$S_{ap}(\%) = \frac{V_i - V_{i,0}}{V_{i,0}}.100 \tag{2}$$

$$S_{ac}(\%) = \frac{\Delta V_{i,s}}{V_{i,0}}.100 \tag{3}$$

Where V_i is the volume of the internal phase after dispersion operation, $V_{i,s}$ the change in the internal phase volume caused only by emulsion swelling and $V_{i,0}$ is the initial volume of the internal phase. The actual swelling can be expressed by Eq. (4) as the combination of the osmotic swelling ratio (S_{os}) and the entrainment swelling ratio (S_{en}).

$$S_{ac}(\%) = S_{os}(\%) + S_{en}(\%) \tag{4}$$

According to definition given above, the (S_{ac}) can be expressed by Eq. (5)

$$S_{ap}(\%) = S_{ac}(\%) - B(\%) \tag{5}$$

3.3 Extraction of acid

The yield of acid recovery (E) may be calculated, either as the ratio of the difference between initial and final solute concentration to the initial concentration in external phase, taking into account the percentage of emulsion breakage (Eq. (6)), or as the ratio of the final concentration of the solute in the internal phase to the initial concentration of solute in the external phase (Eq. (7)). The concentration factor (Fc) is the degree of solute concentration in the internal phase, at a time "*t*", compared to the initial concentration in the external phase; it is calculated according to Eq. (8).

$$E(\%)=\frac{C_{e,0}.V_{e,0} - C_{e,t}V_{e,t} + C_{e,T}.V_{e,m}}{C_{e,0}.V_{e,0}}.100 \tag{6}$$

$$E(\%)=\frac{C_{i,t}.V_{i.t}}{C_{e.0}.V_{e,0}}.100 \tag{7}$$

E: yield of extraction (%).
$C_{e,0}$: Initial concentration of the solute in external phase (mol.L^{-1}).
$V_{e,t}$: Volume of the external phase after mixing operation (L).
$V_{e,0}$: Initial volume of the external phase (L).
$C_{e,T}$: Concentration of the tracer in the external phase after mixing operation (mol.dm^{-3}).

$$F_c = \frac{C_{i,t}}{C_{e,0}} \tag{8}$$

$C_{i,t}$: the lactic acid concentration in the internal phase after mixing operation (mol.L^{-1}).

4. Results and discussion

4.1 Determination of membrane phase composition

To determine the composition of the organic phase to be used in the membrane phase, solvent extraction experiments were carried out, separately. Aqueous solutions of lactic acid (HLa) are brought into contact with different organic phases, each containing TLA in various diluents (dodecane, dodecane/octanol and dodecane/ethyhexanediol (EHD) / octanol). When n-dodecane is used as diluent; a third phase appeared instead of two phases normally existing in the case of solvent extraction. The best extraction efficiency is obtained with organic phase consisted of dodecane/octanol and/or EHD. The extraction is favored at pH<pKa (=3.9), where the predominant form of lactic acid is the non-dissociated molecule (HLa); in this case the extraction reaction is given by Eq. (9).

$$\mathrm{HLa} + \overline{\mathrm{R_3N}} \leftrightarrow \overline{\mathrm{R_3NH^{+}La^{-}}} \tag{9}$$

Where HLa and La^{-} are the lactic acid and lactate, respectively, and R_3N is TLA. The bar over the symbols denotes species in the organic phase.

This organic phase is then used to make the membrane. Two surfactants to stabilize the emulsions, namely, the SPAN 80 and ECA 4360 are tested separately. The composition of the phases is given in Table 1.

The concentration of the EHD will vary between 0 and 5% (w/w) and that of the surfactant between 1 and 5 (%w/w). Fig. 1 shows the breakage kinetics; when Span 80 is used as surfactant, the predominant phenomenon is the emulsion breakage with a ratio exceeding 50%; however when membrane containing the ECA 4360, the emulsion breakage does not exceed 10%.

To minimize the breakage of the emulsion stabilized by Span 80, a parametric study (not presented here) was performed, unfortunately, no improvement is obtained. Consequently, this

Table 1 Phases composition

	External phase (I)	Organic phase (II)	Internal phase (III)
Composition	Lactic acid 0.56 mol/L	TLA 5%(w/w) EHD SPAN80 or ECA 4360 Dodecane	NaOH 3.7 mol/L
Volume (mL)	100	10	10

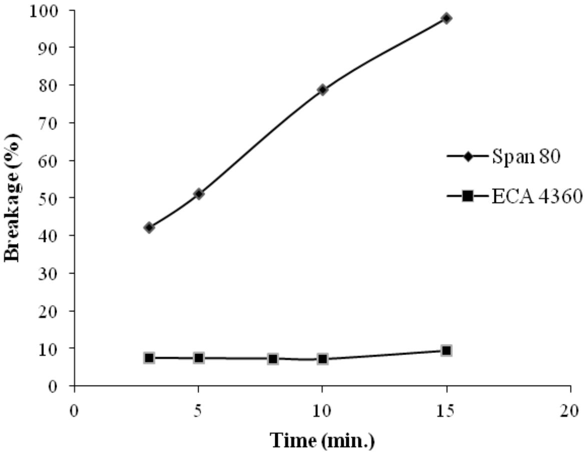

Fig. 1 Breakage emulsion kinetics

surfactant is not retained for further study. When ECA 4360 is used, extraction yield is low (20%), but the emulsion swelling is relatively high (100%). The first concern is, then, to find operating conditions to improving the yield of extraction and to reduce the emulsion swelling.

4.2 Optimization of lactic acid extraction conditions

4.2.1 Effect of ECA 4360 concentration

The effect of surfactant concentration on extraction yield is examined. Figs. 2 and 3 show the effect of surfactant concentrations on the swelling of emulsion and the extraction yield, respectively.

Extraction yield and emulsion swelling increase with contact time regardless of the concentration of surfactant, but they decrease when the time is fixed and the surfactant concentrations increase. These results show that water transfer through the membrane has the same

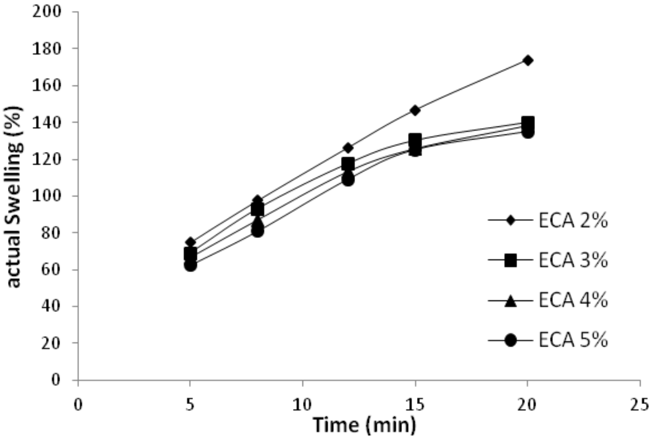

Fig. 2 Effect of surfactant concentrations on actual swelling

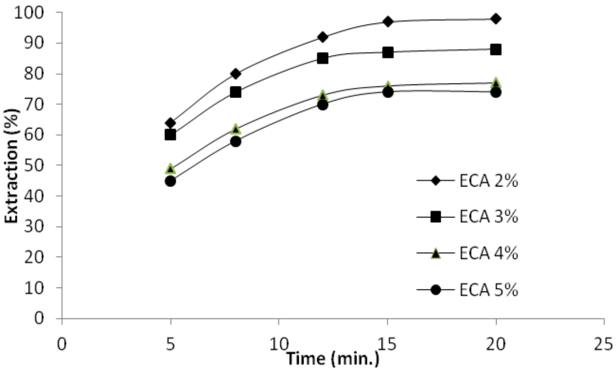

Fig. 3 Effect of surfactant concentrations on yield extraction

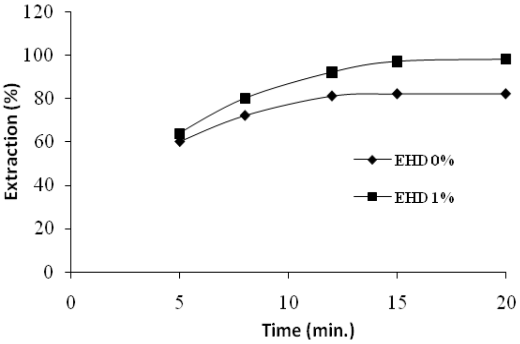

Fig. 4 Effect of the EHD concentration on the extraction

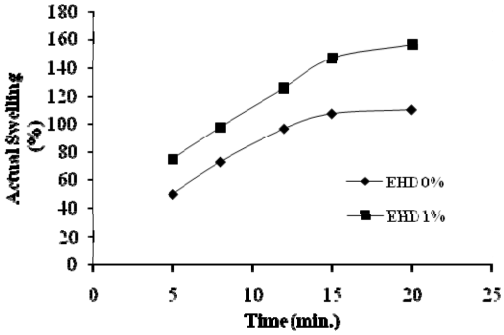

Fig. 5 Effect of the EHD concentration on the emulsion swelling

behavior as the acid transfer that causes an increase of the difference in ionic strength between the two aqueous phases. At higher surfactant concentrations, the emulsion becomes more stable, but an increase in the mass transfer resistance occurs in the membrane phase (Gu *et al.* 1992), which produces a decrease in extraction efficiency. The concentration factor ranges from 1.3 to 1.6 when the concentration of surfactant decreases from 5% to 2%, respectively. In all cases, the emulsions produced under these conditions show a good stability, and a maximum breakage does not exceeding 3%. On the basis of these results, the optimal concentration of the surfactant is 2% (w/w).

4.2.2 Effect of EHD concentration

To examine the effect of this parameter, experiments are performed with an emulsion containing EHD (1% w/w) and free of EHD; the yield of extraction (E = 95%) is better when membrane contains EHD (Fig. 4); the swelling is more important too (Fig. 5), showing that the EHD may contribute to water transport. One might also note that the membrane stability is affected when it does not contain the EHD, therefore EHD can be considered as co-surfactant that can contribute to emulsion stability.

4.2.3 Effect of carrier concentration

The carrier (TLA) concentration effect is studied in range of 0-5% (w/w); the other factors were held constant. As shown in Fig. 6, an increase in the TLA concentration implies an increase in the extraction, therefore a better transfer through the membrane; this suggests that the extraction reaction (carrier-solute) seemed be one of the limiting steps. The carrier concentration in the membrane phase could increase the interfacial concentration of lactic acid, hence the driving force for extraction providing an increased extraction rate. In addition, swelling of emulsion increases by increasing the carrier concentration, thereby diluting the stripping phase also causes an increase in diffusion distance in the membrane (Chaudhuri and Pyle 1992a). It has been suggested that the swelling phenomena during lactic acid extraction could be explained by the surfactant solubilization-diffusion mechanism combined with the carrier-solute and reactionsolubilization-diffusion mechanism (Chaudhuri and Pyle 1992b, Yuanli *et al.* 2001).

Although the membrane does not contain extractant, low extraction can be observed; certainly this is due to the surfactant, because it is protonated. It must be noted that a relatively large breakage of emulsion occurs when membrane does not contain TLA, this seems to confirm the protonation of the ECA 4360. This protonation would be minimal in the presence of TLA, which is a stronger base.

4.2.4 Effect of stirring speed

As shown in Fig. 7, at low stirring speed (270 rpm), transfer of lactic acid increases during

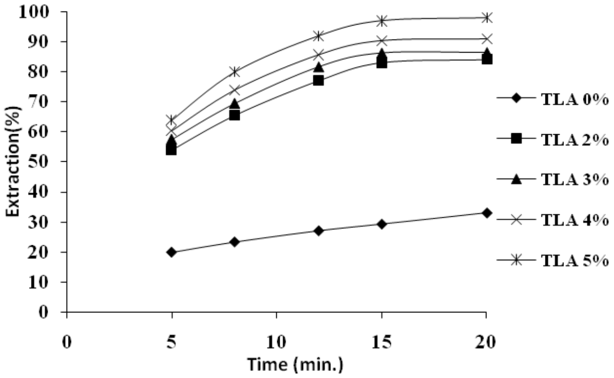

Fig. 6 Effect of the TLA concentration on the extraction

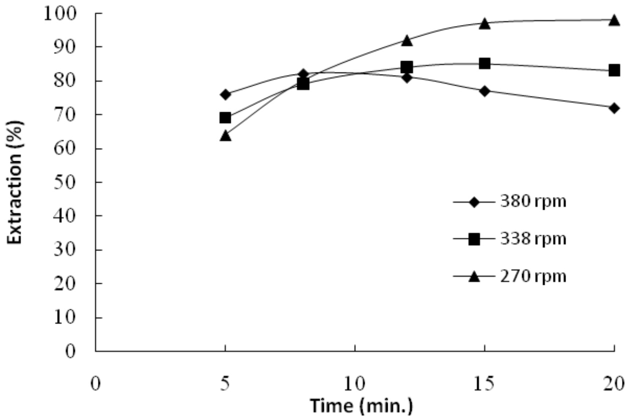

Fig. 7 Effect of the stirring speed on the extraction

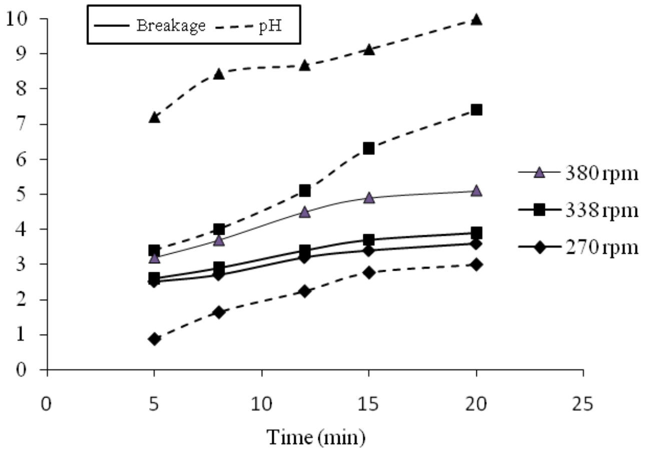

Fig. 8 Effect of the stirring speed on the emulsion breakage and pH of external phase

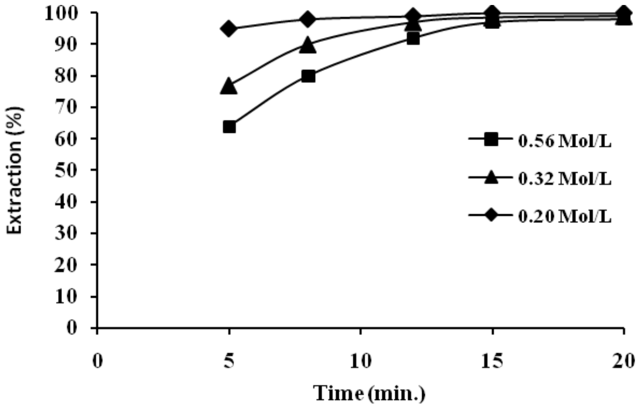

Fig. 9 Effect of the initial lactic acid concentration on the yield of extraction ([NaOH] in internal phase = 3.7 M, $r = V_{i,0} / V_{0,\mathrm{org}} = 1$, $R = V_{e,0} / V_{em} = 2$)

mixing, due to reduction of the emulsion globule size, thereby providing a high interfacial contact area between the external and membrane phases. However, at stirring speed (338 and 380), undesirable phenomena can appear, the emulsion is partially destroyed by shear forces, and breakage may take place; then lactic acid in the external phase is neutralized by NaOH, an increase of pH is observed (Fig. 8).

4.2.5 Effect of phase volume ratios

The concentration of the stripping agent (NaOH) in the internal phase is related to that of the solute in the external phase. To examine the effect of the concentration of lactic acid in the feed phase, tests are performed at different initial concentrations. Fig. 9 shows that the extraction yield increases with the increase of $[HLa]_0$, the solute transport rate may increase largely due to the important capacity of the internal phase to strip it. At 0.2 mol/L of acid in the external phase, a complete extraction is achieved after 10 minutes of contact; then the pH of the external phase becomes alkaline (= 11), which makes the process difficult to control in the acid range.

This problem is not encountered when $[HLa]_0 = 0.32$ M, furthermore, the transfer is faster than the case of 0.56 M, consequently in the following experiments, 0.32 Mol/L is retained. In this case, swelling of emulsion, main phenomenon causing acid dilution in the internal phase, becomes important. The reduction of this phenomenon improves the concentration factor, for this purpose r and R have been varied between 1-2 and 2-5, respectively. In any case studied, the extraction yield exceeds 90%. In the Fig. 10, are plotted the maximum actual swelling and the concentration factor against the phase volume ratios. The highest acid concentration in the internal phase is obtained when $r = 1$ and $R = 2.5$; it should be noted that the increasing of the external phase volume causes an improvement of concentration factor, and that of the organic phase causes its decreasing, this can be explained by the fact that the increasing of acid transfer induces an increasing in the difference of ionic strength, and that the increasing of ECA4360 concentration induces increasing emulsion swelling.

For further study, the phase volume ratios adopted are $r = 1$ and $R = 2.5$.

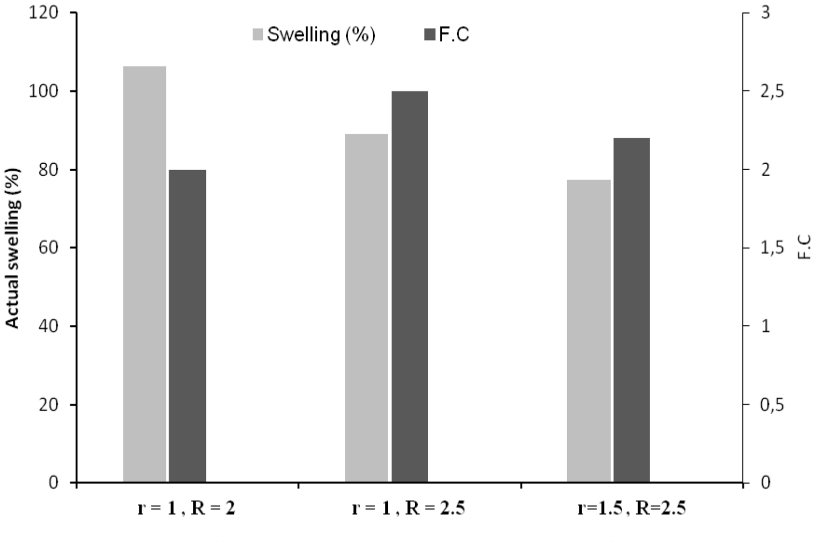

Fig. 10 Maximum swelling and concentration factor versus the phase volume ratios

4.3 Extraction of lactic acid under the actual conditions of pH

Some studies are reported that the pH of the lactic acid production by fermentation is above 4.0 (Wildenauer and Winter 1985, Ferrari *et al.* 2001), and the pH value close to 5 is found to be optimal for acid production (Fu and Mathews 1999). Experiments are performed in these conditions of pH. The acid dissociation occurs according to Eq. (10); the constant dissociation "Ka" and the final relationship between species of dissociation process are given by Eqs. (11) and (12), respectively.

$$\mathrm{HLa} \Leftrightarrow \mathrm{H}^+ + \mathrm{La}^- \tag{10}$$

$$K_a = \frac{[\mathrm{H}^+].[\mathrm{A}^-]}{[\mathrm{HA}]} \Leftrightarrow \frac{[\mathrm{H}^+]}{K_a} = \frac{[\mathrm{HA}]}{[\mathrm{A}^-]} \tag{11}$$

$$\mathrm{pKa} - \mathrm{pH} = \ln\frac{[\mathrm{HA}]}{[\mathrm{A}^-]} \tag{12}$$

When pH > pKa, according to Eq. (12), the main species in solution is the lactate ion ($\mathrm{A}^- > \mathrm{HA}$), the extraction yield is low (17%) and the final pH is 5.5. To maintain the pH around the adjusted value (4.5) during mixture, sulfuric acid is added. Fig. 11 shows the kinetic of HLa extraction, lactate ion prevails (less extractable species) and the undissociated acid form (HLa) is low, which explains the low extraction efficiency.

This result shows that the lactic acid extraction at the pH of fermentation medium is, however, possible.

4.3.1 Acid extraction study in continuous mode

Experiments are performed in continuous mixer-settlers as schematically illustrated in Fig. 12. One or two stages can be used. The fresh emulsion and the external phase feed the system in countercurrent flow. The pH is adjusted during mixing by H_2SO_4 addition. The loaded emulsion is

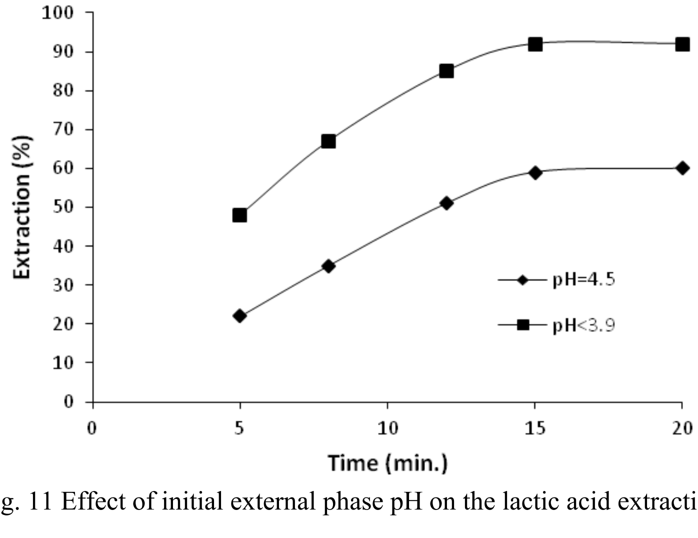

Fig. 11 Effect of initial external phase pH on the lactic acid extraction

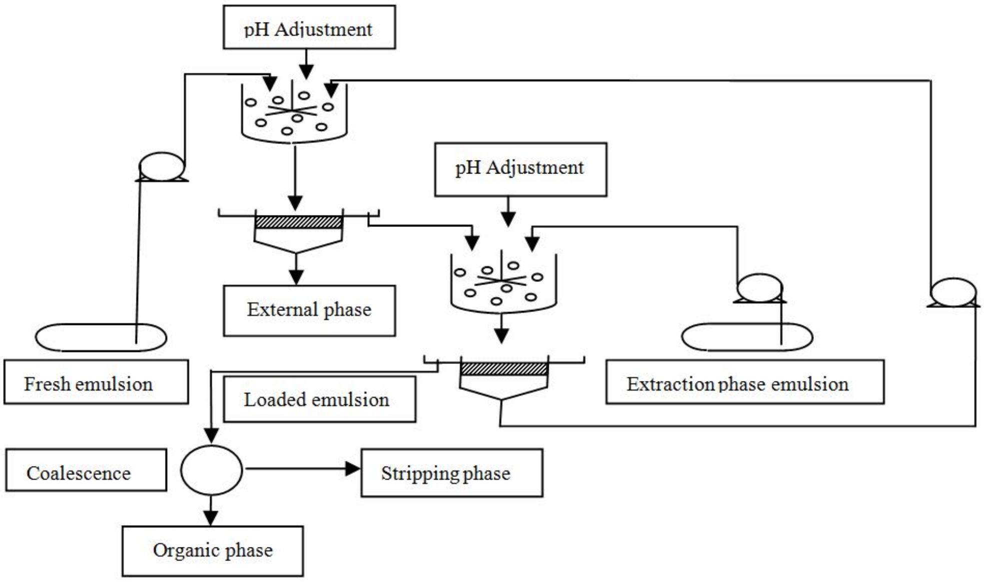

Fig. 12 Countercurrent continuous experiments with two stages

separated, coalesced, the internal and external phase are recovered and analyzed separately.

To optimize the parameters affecting the extraction efficiency and identify process data, the effect of residence time (θs) in the mixer and the number of stages (N) required for the separation are studied. When the residence time is relatively high, the stability of the emulsion could be affected, therefore it is necessary to take into consideration an important parameter that is directly related to the stability of the emulsion, and that may play a role in the extraction process, namely the speed of homogenization (ω_{em}).

Table 2 gives the values of the main experimental variables and the calculation of performance parameters of extraction. Runs (No. 1 and 2) show that for a given residence time, a single contacting stage gives a slightly better extraction efficiency compared to two extraction stages. An improvement of the transfer can be obtained (run No. 3) using two stages, and thus a higher residence time; however, the emulsion stability is compromised, yielding a breakage of 18%. The emulsion stability is improved by increasing the homogenizer speed (Run No. 4). The yield of extraction can exceed 90%, when the homogenizer speed of emulsion and residence time (run No. 5) increase. The results obtained are plotted in the Figs. 13 and 14.

Table 2 Experimental conditions

Run No.	ω_{em} (rpm)	N	θ_s (min.)	E (%)	S_{ac} (%)	B (%)	F_c
1	10000	1	13.4	60.0	57.7	9.0	1.8
2	10000	2	6.7 × 2	51.0	37.0	7.0	1.7
4	24000	1	10.4	64.0	59.4	4.0	1.9
5	24000	2	10.4 × 2	93.7	63.9	9.0	2.5

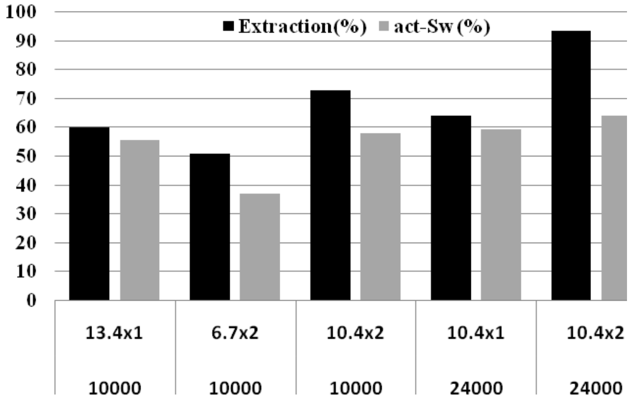

Fig. 13 Maximum values of the extraction yield and actual swelling versus time residence and homogenizer speed

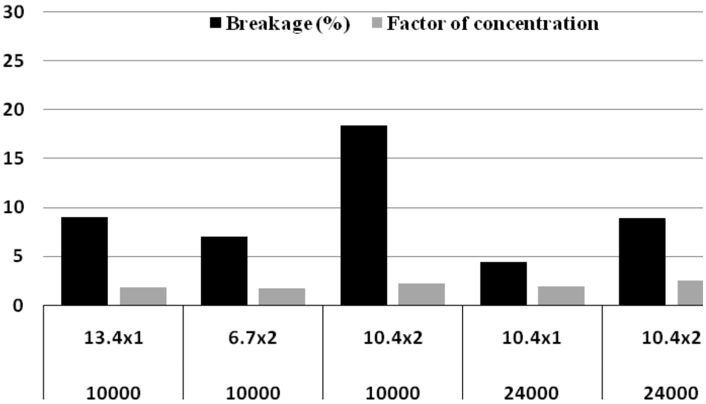

Fig. 14 Maximum values of the emulsion breakage and concentration factor versus time residence and homogenizer speed

5. Conclusions

The extraction using an emulsion liquid membrane is a very interesting tool in the separation process, however the phenomena that may occur during its implementation, namely swelling and rupture of the emulsion, are the main disadvantages. Through this study, it has been shown that it is possible to reduce these phenomena. The using ECA 4360 as surfactant to stabilize the emulsion and TLA (tertiary amine) as extractant, with only 2% (w/w) and 5% (w/w), respectively, in the membrane, allow to attain a concentration factor of 1.6 and a high extraction yield, exceeding 95%. The EHD can being an essential component in the composition of the emulsion, at only 1% (w/w), it can effectively contribute to the stabilization of the emulsion. The choice a low stirring speed is favorable to reducing the effects of shear forces on the emulsion globules; 270 rpm is the optimal value. The ratios of phase volume can substantially improve the concentration factor, a value of 2.5 is obtained under the optimal conditions of $r = 1$ and $R = 2.5$. If the initial pH of the solution is greater than the pKa of lactic acid, extraction was possible, although the yield is relatively low.

This ELM system, established in the optimal conditions, appears to be effective for the recovery of lactic acid from a synthetic fermentative medium. The feasibility of continuous process has been demonstrated. Using two-stages of mixer-settler, with 10.7 min. of residence time, in each; and an emulsion prepared at a maximal homogenizer speed, the yield of extraction exceeds 90%.

References

Ahmad, A.L., Kusumastuti, A., Derek, C.J.C. and Ooi, B.S. (2013), "Emulsion liquid membranes for cadmium removal: Studies of extraction efficiency", *Membr. Water Treat.*, *Int. J.*, **4**(1), 11-25.

Agarwal, A.K., Das, C. and De, S. (2010), "Modeling of extraction of dyes and their mixtures from aqueous solution using emulsion liquid membrane", *J. Membr. Sci.*, **360**(1-2), 190-201.

Aljundi, I.H., Belovich, J.M. and Talu, O. (2005), "Adsorption of lactic acid from fermentation broth and aqueous solutions on Zeolite molecular sieves", *Chem. Eng. Sci.*, **60**(18), 5004-5009.

Berrios, J., Pyle, D.L. and Aroca, G. (2010), "Gibberellic acid extraction from aqueous solutions and fermentation broths by using emulsion liquid membranes", *J. Membr. Sci.*, **348**(1-2), 91-98.

Chaudhuri, J.B. and Pyle, D.L. (1992a), "Emulsion liquid membrane extraction of organic acids – I. A theoretical model for lactic acid extraction with emulsion swelling", *Chem. Eng. Sci.*, **47**(1), 41-48.

Chaudhuri, J.B. and Pyle, D.L. (1992b), "Emulsion liquid membrane extraction of organic acids – II. Experimental", *Chem. Eng. Sci.*, **47**(1), 49-56.

Chiarini, L., Mara, L. and Tabacchioni, S. (1992), "Influence of growth supplements on lactic acid production in whey ultrafiltrate by *Lactobacillus helveticus*", *Appl. Microbiol. Biotechnol.*, **36**, 461-464.

Choi, J. and Hong, W.H. (1999), "Recovery of lactic acid by batch distillation with chemical reactions using ion exchange resin", *J. Chem. Eng. Jpn.*, **32**(2), 184-189.

Datta, S.P., Bhattacharya, K. and Verma, N. (2003), "Removal of aniline from aqueous solution in a mixed flow reactor using emulsion liquid membrane", *J. Membr. Sci.*, **226**(1-2), 185-201.

Demirci, A., Pometto, A.L. and Harkins, K.R. (1999), "Rapid screening of solvents and carrier compounds for lactic acid recovery by emulsion liquid extraction and toxicity on Lactobacillus casei (ATCC 11443)", *Bioseparation*, **7**(6), 297-308.

Djenouhat, M., Hamdaoui, O., Mahdi Chiha, M. and Samar, M.H. (2008), "Ultrasonication-assisted preparation of water-in-oil emulsions and application to the removal of cationic dyes from water by emulsion liquid membrane: Part 1: Membrane stability", *Sep. Sci. Technol.*, **62**(3), 636-641.

Drumright, R.E., Gruber, P.R. and Henton, D.E. (2000), "Polylactic acid technology", *Adv. Mater.*, **12**(23), 1841-1846.

Ferrari, M.D., Bianco, R., Froche, C. and Loperena, M.L. (2001), "Baker's yeast production from molasses/cheese whey mixtures", *Biotechnol. Lett.*, **23**(1), 1-4.

Fu, W. and Mathews, A.P. (1999), "Lactic acid production from lactose by Lactobacillus plantarum: Kinetic model and effects of pH, substrate, and oxygen", *Biochem. Eng. J.*, **8**(3), 163-170.

Gonzalez, S.M.I. (1996), "The biotechnological utilization of cheese whey: A review", *Bioresour. Technol.*, **57**(1), 1-11.

Goyal, R.K., Jayakumar, N.S. and Hasshim, M.A. (2011), "A comparative study of experimental optimization and response surface optimization of Cr removal by emulsion ionic liquid membrane", *J. Hazard. Mater.*, **195**, 383-390.

Gu, Z., Ho, W.S.W. and Li, N.N. (1992), *Emulsion Liquid Membrane*: *Design Considerations*, (W.S. Winston Ho, Sirkar K.K. Eds.), Membrane Handbook; Chapman and Hall, New York, NY, USA.

Han, D.H., Hong, Y.K. and Hong, W.H. (2000), "Separation characteristics of lactic acid in reactive extraction and stripping", *Korean J. Chem. Eng.*, **17**, 528-533.

Hano, T., Matsumoto, M. and Ohtake, T. (1993), "Recovery of lactic acid by extraction from fermentation broth", Proceedings of ISEC93; *Solvent Extraction in the Process Industries*, Elsevier Applied Science for SCI, London, UK, **3**, pp. 1353-1361.

Hasan, M.A., Aglan, R.F. and El-Reefy, S.A. (2009), "Modeling of gadolinium recovery from nitrate medium with 8-hydroxyquinoline by emulsion liquid membrane", *J. Hazard. Mater.*, **166**(2-3), 1076-1081.

Huang, H., Yang, S.T. and Ramey, D.E. (2004), "A hollow-fiber membrane extraction process for recovery and separation of lactic acid from aqueous solution", *Appl. Microbiol. Biotechnol.*, **114**(1-3), 671-688.

Hujanen, M. and Linko, Y.Y. (1996), "Effect of temperature and various nitrogen sources on L (+)-lactic acid production by Lactobacillus casei", *Appl. Microbiol. Biotechnol.*, **45**(3), 307-313.

Kim, S.J., Kim, S.C. and Kawasaki, J. (1997), "Separation of hydrocarbons by liquid surfactant membrane with a batch stirred vessel", *Sep. Sci. Technol.*, **32**(7), 1209-1221.

Li, Z., Han, L.U., Ji, Wang, Y.X. and Tan, T. (2010), "Fermentative production of lactic acid from hydrolysate of wheat bran by Lactobacillus rhamnosus", *Biochem. Eng.*, **49**(1), 138-142.

Manzak, A. and Tutkun, O. (2011), "The extraction of lactic acid by emulsion type of liquid membranes using alamine 336 in escaid 100", *Can. J. Chem. Eng.*, **89**(6), 1458-1463.

Min, D.J., Choi, K.H., Chang, Y.K. and Kim, J.H. (2011), "Effect of operating parameters on precipitation for recovery of lactic acid from calcium lactate fermentation broth", *Korean J. Chem. Eng.*, **28**(10), 1969-1974.

Mok, Y.S. and Lee, W.K. (1994), "Water transport in water-in-oil-in-water liquid emulsion membrane system for the separation of lactic acid", *Sep. Sci. Technol.*, **29**(6), 743-764.

Pal, P., Sikder, J., Roy, S. and Giorno, L. (2009), "Process intensification in lactic acid production: A review of membrane based processes", *Chem. Eng. Process.*, **48**(11-12), 1549-1559.

Razo-Lazcano, T.A., Stambouli, M., González-Muñoz, M.D., Pareau, D. and Ávila-Rodríguez, M. (2014), "Emulsion liquid membranes for recovery of ibuprofen from aqueous solutions", *J. Chem. Technol. Biotechnol.*. **89**(6), 890-898.

Reddy, G., Altaf, Md., Naveena, B.J., Venkateshwar, M. and VijayKumar, E. (2008), "Amylolytic bacterial lactic acid fermentation", *Biotechnol. Adv.*, **26**(1), 22-34.

Reisinger, H. and Marr, R. (1992), "Multicomponent membrane permeation of organic acid", *Chem. Eng. Technol.*, **15**(6), 363-370.

Sun, X., Wang, Q., Zhao, W., Ma, H. and Sakata, K. (2006), "Extraction and purification of lactic acid from fermentation broth by esterification and hydrolysis method", *Sep. Purif. Technol.*, **49**(1), 43-48.

Tay, A. and Yang, S.T. (2002), "Production of L(+)-lactic acid from glucose and starch by immobilized cells of Rhizopus oryzae in a rotating fibrous bed bioreactor", *Biotechnol. Bioeng.*, **80**(1), 1-12.

Thakur, A., Panesar, P.S. and Singh, M. (2008), "Parametric optimization of lactic acid extraction from aqueous solution in a mixed flow reactor using emulsion liquid membrane by response surface methodology", *Chem. Biochem. Eng. Q.*, **22**(2), 157-167.

Thien, M.P. and Hatton, T.A. (1988), "Liquid emulsion membrane and their applications in biochemical processing", *Sep. Sci. Technol.*, **23**(8-9), 819-853.

Tik, N., Bayraktar, E. and Mehmetoglue, U. (2001), "In-situ reactive extraction of lactic acid from fermentation media", *J. Chem. Techol. Biotechol.*, **76**(7), 764-768.

Wan, Y. and Zhang, X. (2002), "Swelling determination of W/O/W emulsion liquid membrane", *J. Membr. Sci.*, **196**(2), 185-201.

Wildenauer, F.X. and Winter, J. (1985), "Anaerobic digestion of high-strength acidic whey in a pH-controlled up-flow fixed film loop reactor", *Appl. Microbiol. Biotechnol.*, **22**(5), 367-372.

Yang, S.T. and Silva, E.M. (1995), "Novel products and new technologies for use of a familiar carbohydrate, milk lactose", *J. Dairy Sci.*, **78**(11), 2541-2562.

Yuanli, J., Fuan, W., Hyun, K.D. and Sook, L.M. (2001), "Modeling of the permeation swelling of emulsion during lactic acid extraction by liquid surfactant membranes", *J. Membr. Sci.*, **191**(1-2), 215-223.

Zihao, W., Yuanli, J. and Jufu, F. (1996), "The entrainment swelling of emulsion during lactic acid extraction by LSMs", *J. Membr. Sci.*, **109**(1), 25-34.

CC

Appendix

B : membrane breakage (dimensionless, %)
$C_{e,T}$: Concentration of the tracer in external phase after mixing operation (mol/L)
$C_{i,0}$: the initial concentration of the tracer in the internal phase (mol/L)
$C_{e,0}$: Initial concentration of the solute in external phase (mol/L)
$C_{e,T}$: the concentration of the tracer in the external phase after mixing operation (mol/dm^3)
$C_{i,t}$: the lactic acid concentration in the internal phase after mixing operation (mol/L)
E : yield of extraction
F_c : concentration factor (dimensionless)
pKa : logarithmic measure of the lactic acid dissociation constant (dimensionless)
R : the ratio of external phase – membrane phase (dimensionless)
r : the ratio of volume emulsion (dimensionless)
S_{ap} : the apparent swelling ratio (dimensionless, %)
S_{ac} : the actual swelling ratio (dimensionless, %)
$V_{e,0}$: the initial volume of the external phase (L)
$V_{e,t}$: the volume of the external phase after mixing operation (L)
$V_{i,0}$: the initial volume of the internal phase (L)
$V_{e,t}$: the volume of the external phase after mixing operation (L)
$V_{\mathrm{org},0}$: the initial volume of the organic phase (L)
V_i : the volume of the internal phase after dispersion operation (L)
$V_{i,s}$: the change in the internal phase volume (L).
θ_s : residence time (min.)
N : Number of stages
ω_{em} : the homogenizer speed (rpm)