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Separation and Recovery of Low Molecular Weight Organic Acids by Emulsion Liquid Membranes

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Abstract

Emulsion liquid membrane (ELM) extraction of low molecular weight organic acids resulting from whey fermentations was investigated. Rates of removal of lactic, acetic, propionic, and acrylic acids decreased as pH and concentration were increased. An ELM process for selective removal of acrylic acid from acrylic acid-propionic acid mixtures was developed through incorporation of a cosolvent (cyclohexanone) in the membrane phase of the emulsion. Degree of removal for each acid and, hence, selectivity among the acids appears to be determined by the water-membrane phase partition coefficient.

INTRODUCTION

Since their technological development by Li (*1*) twenty years ago, emulsion liquid membranes (ELMs) have found application in mass transfer operations as diverse as metal removal from waste streams (*2*), transport and enzymatic hydrolysis of amino acid esters (*3*), and recovery of amino acids from aqueous fermentation broths (*4*). Reviews of liquid membranes technology (*5*) and industrial applications (*6*) have been published.

For the aqueous systems to be considered herein, an emulsion liquid membrane is defined as a water-immiscible phase which separates two aqueous phases, thus preventing direct contact of the aqueous phases. A water-in-oil emulsion is created and dispersed throughout a continuous, aqueous (feed) phase in an appropriate reactor. A characteristic of most ELM systems is the rapid, effective separation of the emulsion and feed phases under quiescent conditions. A schematic diagram of an ELM system is presented in Fig. 1.

Interest in ELMs for biochemical separations has focused on their potential for cocurrent product removal in fermentation processes through reduced product inhibition of the fermenting organism(s). In this study, application of ELMs to the separation and recovery at low concentrations of low molecular weight organic acids resulting from whey fermentations was investigated.

Compounds under consideration were acetic and propionic acids (the predominant end products of heterofermentative lactobacillus fermentations), lactic acid, and acrylic acid. Biological production of acrylic acid from whey-derived propionic acid via *Clostridium propionicum* as described by Sinskey (*7*) could be greatly increased by cocurrent acrylic acid removal because this reaction is severely product inhibited. As separation

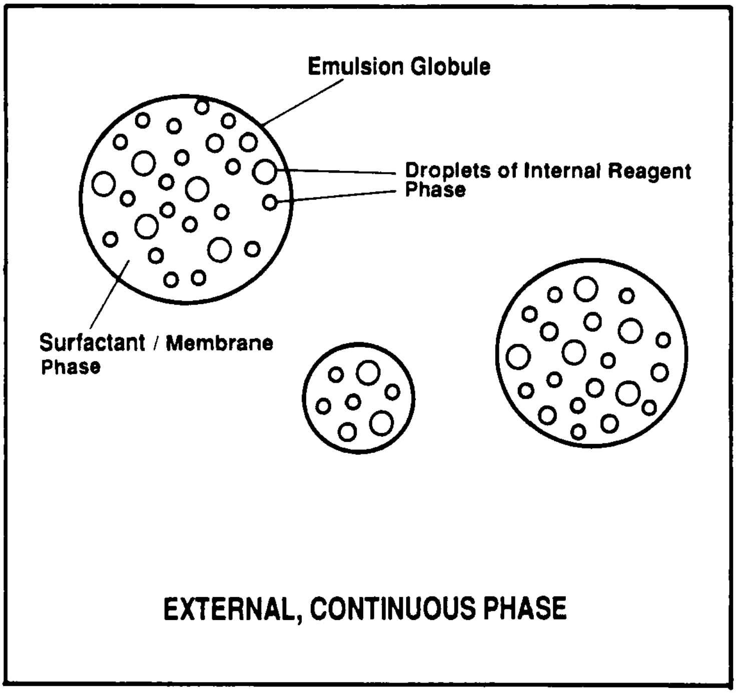

FIG. 1. Schematic diagram of an emulsion liquid membrane system.

TABLE 1
ELM Physical and Chemical Characteristics

Property	Value
Membrane composition	96% Solvent 100 Neutral 4% Paranox 100
Membrane viscosity	45 mPa · s at 23°C
Internal reagant phase	5 *M* NaOH or KOH
Emulsion composition	64/36 membrane/internal reagent (v/v)
Globule diameter (av)	0.167 ± 0.005 cm (Sauter mean diameter)

of acrylic and propionic acids is extremely difficult by conventional methods, techniques for introducing selectivity for acrylic acid into an ELM extraction process were explored. Specific objectives of the present study were: 1) evaluation of acetic and propionic acid recovery from sweet whey fermented by a coculture of *Lactobacillus bulgaricus* and *Propionibacterium shermanii* and 2) development of an ELM process for the selective removal of acrylic acid from acrylic acid–propionic acid mixtures.

EXPERIMENTAL

ELM Characteristics

Table 1 lists the properties of the ELM used throughout this study (except where noted). Solvent 100 neutral, a middle distillate paraffinic solvent with average molecular weight of 386.5, and Paranox 100, a nonionic surfactant, were obtained from Exxon, Inc.* Membrane viscosity was measured with a calibrated Ubbelohde Dilution Type Capillary Viscometer, No. 200 (Cannon Instrument Co., State College, Pennsylvania). The globule diameter was measured photographically under conditions identical to those of a typical experiment. The Sauter mean diameter, $\bar{d}s = \Sigma d^3/\Sigma d^2$, was calculated from measurements of 30 globules on each of seven photographs.

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*Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

The emulsion was prepared by adding the internal reagent (IR) phase to the membrane phase in three equal volumes equally spaced over 6 min in a commercial Waring-type blender on the "whip" setting. Emulsification was continued for an additional 5 min.

Experimental Procedures

ELM batch extraction experiments were conducted in a 2-L beaker with agitation provided by a laboratory shaft mixer equipped with a three-bladed 45° pitch propeller. The treat ratio, the volume ratio of feed phase to emulsion phase, was fixed at 5:1. The shaft speed of the mixer was measured stroboscopically and was maintained at 500 ± 20 rpm in all experiments. In experiments to determine the effects of pH and concentration on ELM extraction of organic acids, feed solutions were buffered with phosphate or pyrophosphate buffers (100 m*M*), adjusted to the desired pH with H_2SO_4. During experiments, samples for pH and organic acid analysis were taken from the feed phase after emulsion/feed phase separation.

In some experiments the emulsion was broken in order to determine the IR phase composition or the extent of emulsion swelling (water transport to the IR). Demulsification was effected by a filtration-centrifugation technique in which a volume of emulsion is forced through a hydrophilic disk filter (Durapore type GVWP, .22μ, Millipore Corp., Bedford, Massachusetts) in a custom-built stainless steel syringe. The partially demulsified mixture was then centrifuged at 15,000 rpm in a high speed centrifuge.

Whey Fermentation

Cultures of *Lactobacillus bulgaricus* (NRRL B-548) and *Propionibacterium shermanii* (*Propionibacterium freudenreichii,* subsp. *shermanii,* NRRL B-3569) were obtained from the Northern Regional Research Center, USDA, Peoria, Illinois. These organisms constitute an effective coculture for the fermentation of sweet whey to propionic and acetic acids in a 2/1 molar ratio. Fermentation conditions were as follows: media, 67 g/L spray dried sweet whey powder (Lehigh Valley Farms/ Atlantic Processing, Allentown, Pennsylvania), 10 g/L yeast extract (Difco), 15 g/L calcium carbonate, adjusted to pH 7.1; inocula, 5% (v/v) for each organism grown on fermentation media for 24 h prior to inoculation; temperature, 33°C. Fermentations were conducted in a 2-L bench fermentor (LH Fermentation, Hayward, California) with automatic pH and temperature control under a nitrogen atmosphere.

Analytical

Acetic, propionic, and acrylic acid concentrations were determined by gas chromatography or HPLC. The gas chromatographic method consisted of ethyl ether extraction of an acidified aqueous sample, sample analysis, and quantitation with the aid of a valeric acid internal standard added to all samples. Chromatography was performed on a Varian 5700 chromatograph utilizing a glass column packed with 0.3% carbowax 20M/0.1% H_3PO_4 on 60/80 mesh Carbopak C. In samples requiring lactic acid analysis, all concentrations were determined by HPLC on a Spectra-Physics SP 8700 liquid chromatograph with a refractive index detector. Samples were injected through a 10-μL sample loop onto an Aminex HPX-87H strong cation exchange column (Bio-Rad Laboratories, Richmond, California) and eluted with a 0.013 *N* sulfuric acid mobile phase at a flow rate of 0.7 mL/min.

RESULTS AND DISCUSSION

ELM Breakage and Swell

The phenomena of membrane breakage and membrane swelling are important operational considerations in ELM processes. Under the conditions employed in the batch extraction studies, membrane breakage was minimal, approximately 0.6% (volume basis), at 60 min extraction time. Breakage was calculated from measurements of a K^+ tracer in the continuous phase in experiments in which KOH was the base in the membrane IR. Membrane breakage was found to be a strong function of the membrane surfactant concentration, increasing to greater than 7% when the Paranox 100 concentration was one-half of the 4% level used in this study.

Membrane swell can lead to changes in the chemical and physical properties of ELMs. Although not an area of study in this investigation, the extent of membrane swell under the conditions of the batch extraction experiments was quantified by direct measurement of K^+ in the IR to which KCl was added as a tracer. Values of membrane swell were found to be between 20 and 83% and were in the range reported by other investigators (*4*, *8*) using similar membrane formulations.

Extraction of Low Molecular Weight Organic Acids

Batch experiments were conducted to determine appropriate conditions for extraction of acetic, propionic, lactic, and acrylic acids from aqueous solution. The effect of pH in the range 2.2 to 6.8 is demonstrated in Fig. 2. Concentrations are reported as the ratio C/C_0, where C_0 is the initial concentration. Lactic acid was not removed by ELM extraction. Analysis of these data indicate that for each acid, the initial extraction rate is a function of the undissociated acid concentration. The pK_as of acetic, propionic, and acrylic acids are 4.75, 4.87, and 4.25, respectively. Concentration effects are presented in Fig. 3. The initial extraction rate falls off sharply as the initial concentration of each acid increases from 2

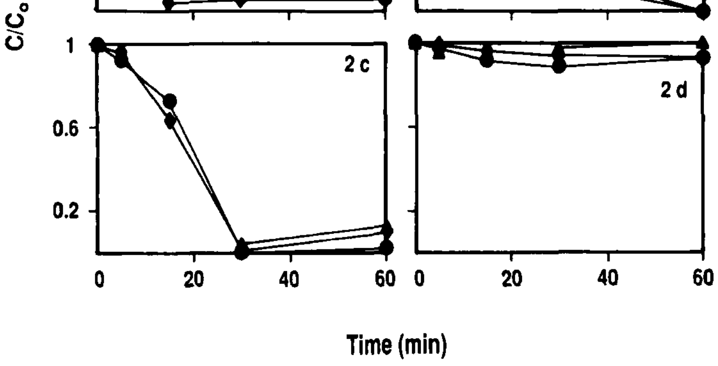

FIG. 2. Effect of pH on batch ELM extraction of organic acids. (2a) pH = 2.2; (2b) pH = 3.9; (2c) pH = 5.6; (2d) pH = 6.8. Initial concentrations: Acetic acid (▲), propionic acid (●), and acrylic acid (♦) were 1.6–3.5 m*M*.

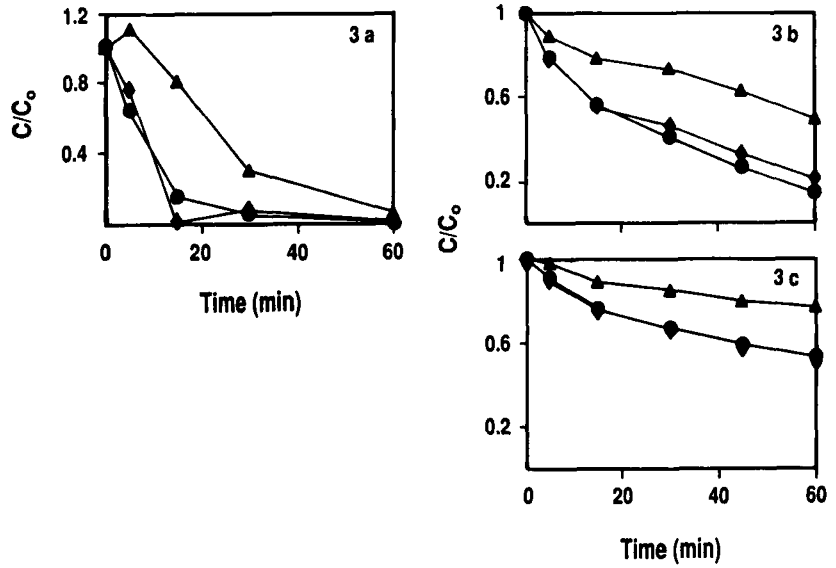

FIG. 3. Effect of initial concentration on batch ELM extraction of organic acids, pH = 4.0. Initial concentrations of organic acids: (3a) 2 m*M*; (3b) 10 m*M*; (3c) 200 m*M*. Symbols same as in Fig. 2.

to 200 m*M*. In this nonselective, nonfacilitated transport ELM system, there is no selectivity between propionic and acrylic acids.

Mass transport in ELMs can be considered a five-step process of diffusion in the feed phase to the membrane interface, transport across the interface (driving force:phase equilibria) diffusion in the membrane phase, reaction at the droplet surface, and diffusion in the IR. In many mathematical models of mass transfer in ELM systems, e.g., that of Ho et al. (*9*), diffusion in the membrane phase is assumed to control mass transfer. However, the acids under consideration here are hydrophilic in nature and their behavior in ELM extraction processes is probably governed by the phase equilibria between the aqueous and membrane phases. The fact that lactic acid is not removed is undoubtedly due to its extremely low solubility in organic solvents. Further evidence for this view is the effect of concentration on the initial extraction rate (Fig. 3); for poorly membrane soluble compounds the extraction rate would be expected to decrease with increasing concentration (*5*), as observed. A further effect at the 200-m*M* concentration level is IR saturation as extraction proceeds, which would cause further slowing of the extraction

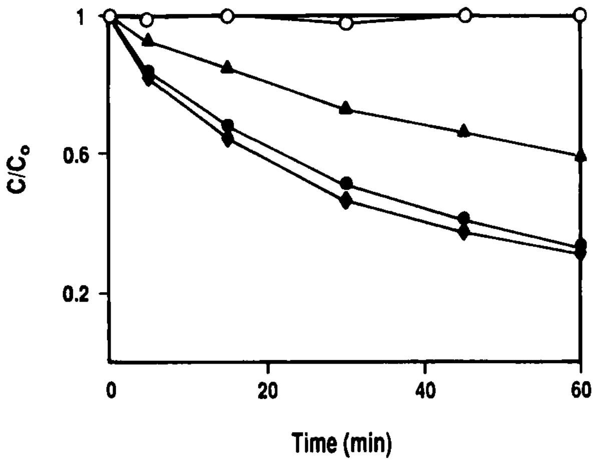

FIG. 4. Removal of organic acids from simulated whey fermentation broth, pH = 3.9. Initial concentrations: Acetic acid (▲), 120 m*M*; propionic acid (●), 300 m*M*; acrylic acid (♦), 10 m*M*; lactic acid (○), 20 m*M*.

rate. For example, in Fig. 3(c) the capacity of the IR of the ELM was 360 mmol of acid and the initial acid present in the feed was 620 mmol.

ELM selectivity among acetic, propionic, lactic, and acrylic acids is not affected by differences in concentrations in mixtures of these compounds, as illustrated in Fig. 4. The concentrations of acetic, propionic, and lactic acids are roughly equivalent to those found in sweet whey broth fermented to acetic and propionic acids by a coculture of *L. bulgaricus* and *P. shermanii*. The similar pattern of selectivity regardless of concentration is consistent with the interpretation that the partition coefficient of the individual acids between the aqueous and membrane phases is the primary determinant of membrane selectivity. This finding is in agreement with the results of Li (*10*) and Terry et al. (*8*).

The coupling of an ELM product removal process to an actual fermentation is illustrated in Fig. 5. In this fermentation of sweet whey by a *L. bulgaricus–P. shermanii* coculture in which propionic and acetic acids are produced in an approximately 2/1 ratio at 75–85% yield (based on lactose), lactose is fermented to lactic acid by *L. bulgaricus* which is then utilized (preferably over lactose) by *P. shermanii* for acid production. Results demonstrate that the emulsion did not affect the activity of the fermenting organisms and that the product removals of 60 and 51% for propionic and acetic acids, respectively, are in general agreement with results of controlled batch experiments (Fig. 4). The availability of lactic

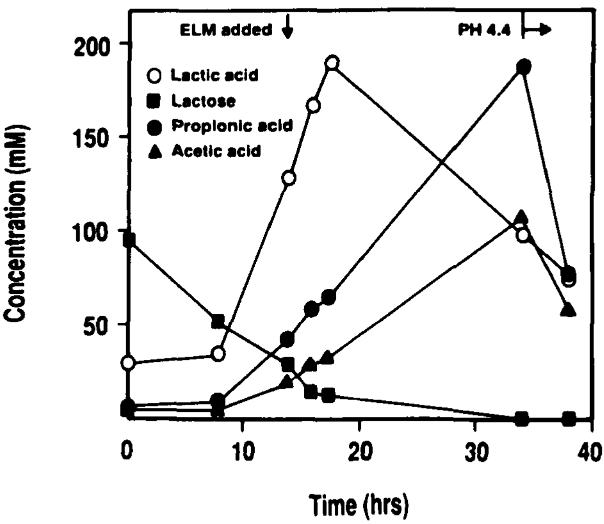

FIG. 5. Cocurrent removal of acetic and propionic acids from sweet whey media fermented by a coculture of *L. bulgaricus* and *P. shermanii*. At 34 h, pH was lowered to 4.4 with H_2SO_4. Treat ratio = 5:1.

acid for fermentation was not impaired by the presence of the ELM, as direct analysis of the IR revealed that a maximum of only 1.3% of the lactic acid produced was removed by the ELM during the course of the fermentation-extraction. However, for truly cocurrent removal of these organic acids, a fermentation pH of approximately 5.5 or lower would be necessary.

Selective Removal of Acrylic Acid from Acrylic Acid/Propionic Acid Mixtures

The similarity in chemical structures and boiling points make separation of acrylic acid and propionic acid extremely difficult (see Table 2). As has already been shown, the conventional ELM formulation utilized in this study exhibits no selectivity for acrylic acid. Selective removal of acrylic acid from acrylic/propionic mixtures was investigated in conjunction with research on the biological production of acrylic acid from sweet whey.

The approach taken was to increase the membrane phase solubility of acrylic acid relative to propionic acid by the addition of a cosolvent to the

TABLE 2
Chemical Properties of Acrylic and Propionic Acids

Compound	Structure	bp (°C)	pK_a
Propionic acid	CH_3-CH_2-COOH	141.1	4.87
Acrylic acid	$CH_2=CH-COOH$	141.6	4.25

TABLE 3
Partition Coefficients[a] for Low Molecular Weight Carboxylic Acids in Cyclohexanone-Water Systems
(conditions: equal volumes of cyclohexanone and water, pH = 3.1, T = 23°C)

Compound	$C_{w,t=0}$	$C_{w,\mathrm{equil}}$	Partition coefficient
Acetic acid	9.8	4.4	1.23
Propionic acid	10.6	2.3	3.43
Acrylic acid	8.6	1.1	6.82

[a] Partition coefficient = $C_{c,\mathrm{equil}}/C_{w,\mathrm{equil}}$, where $C_{c,\mathrm{equil}}$ = concentration of acid in cyclohexanone at equilibrium, mM; $C_{w,\mathrm{equil}}$ = concentration of acid in water at equilibrium, mM; $C_{c,\mathrm{equil}} = C_{w,t=0} - C_{w,\mathrm{equil}}$.

membrane phase. The cosolvent, in addition to possessing desirable solubility characteristics, could not adversely affect ELM performance through increased breakage or reduced stability. Trioctylamine, methyl isobutyrate, cyclohexanone, decane, toluene, xylene, and diisobutylketone were chosen for screening based upon their low water solubility and their use as entrainers or liquid-liquid extraction solvents in industrial processes for acrylic acid manufacture. Of these solvents, cyclohexanone has the most desirable phase equilibrium data (Table 3). From these data, the acrylic acid/propionic acid selectivity or separation factor* was calculated to be 2.0.

ELMs with membrane phases incorporating cyclohexanone at levels of 2–30% (by weight) were prepared. All emulsions were stable, and pH measurements indicated that there was no additional breakage. Results

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*[(C_1/C_2) cyclohexanone/(C_1/C_2) water], where subscript 1 refers to acrylic acid and subscript 2 represents propionic acid.

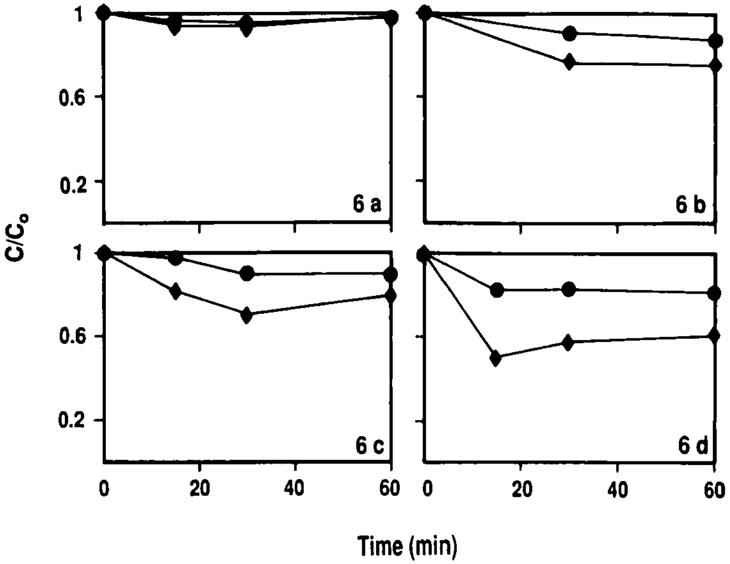

FIG. 6. Effect of cyclohexanone addition to membrane phase of ELM on selectivity between propionic (●) and acrylic (♦) acids. pH = 7.0. Weight % cyclohexanone in membrane phase: (6a) 2%; (6b) 10%; (6c) 20%; (6d) 30%.

of batch extraction experiments at pH 7 are shown in Fig. 6. At levels of 10% or higher, cyclohexanone addition to the menbrane phasse improved removal of propionic and acrylic acids and caused selective removal of acrylic acid over propionic acid. These effects can be explained by the increased solubility of these acids in the cyclohexanone/solvent 100 neutral membrane phase. Selectivity for acrylic acid relative to propionic acid is due to the higher cyclohexanone/water partition coefficient of acrylic acid.

CONCLUSIONS

This paper has reported the results of an investigation of the removal of whey fermentation-derived organic acids by ELMs in which a high strength base was the internal reagent trapping agent. The major conclusions are:

(1) Selectivity of the ELM system among the acids was found to be in the order (lowest to highest degree of removal): lactic acid, acetic acid, propionic and acrylic acids (equal).

(2) Selective removal of acrylic acid over propionic acid can be accomplished through addition of a cosolvent (cyclohexanone) to the membrane phase, thereby increasing the solubility of acrylic acid in the membrane phase relative to that of propionic acid.

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