Separation of Butyric Acid through agitated Bulk Liquid Membrane

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ABSTRACT
Biotechnological production of butyric acid can be achieved if a successful method for separation is implemented. Therefore, in the present study reactive separation process has been employed in Bulk liquid membrane for the separation of butyric acid from dilute aqueous solutions where the tributyl phosphate has been used as an extractant dissolved in diluent toluene. The results of the study show that this can be utilized for the separation of acid from fermentation media if the process is developed further.

Keywords— reactive separation process, bulk liquid membrane, butyric acid, tributyl phosphate, toluene

I. INTRODUCTION

Butyric acid is one of the important carboxylic acid used for the manufacture of its esters that are used as food additives. Conventionally its production is by petroleum feed stock and new improved method that is environment friendly is required. Fermentation in this regard, offers new way for the production of butyric acid[1]. However, the recovery from the fermentation media is a challenging task. There are different ways to recover organic acids from fermentation media of which reactive extraction is a simple technique that can be used for the downstream recovery of butyric acid[2–4]. Reactive extraction has been utilized for the separation of butyric acid from dilute solutions[5]. The acid from the acid laden organic phase has to be extracted with the contact with base solution termed as back extraction. In bulk liquid membrane the two processes can be carried out simultaneous[6–8]. Therefore, in view of the recovery of butyric acid, in the present work the bulk liquid membrane study of butyric acid from dilute aqueous solution through proper selection of parameters such as strip phase and its concentration, membrane composition and agitation.

II. THEORY

A bulk liquid membrane is a very simple kind of liquid membrane which consists of a feed, stripping and membrane phase. The acid within the feed phase when reaches the interphase between the feed and membrane, it reacts with the extractant present within the membrane to forms a chemical complex. This chemical complex then diffuses through the membrane phase and reaches the membrane and stripping interphase, here the chemical complex breaks down and thus releases the acid into the stripping phase while the extractant diffuse back through the membrane phase to reach the feed/membrane interphase. The initial acid flux through the extraction surface is given as (JF0) (mol cm^{-2} min^{-1}) is given by the equation: -

$J_{F0} = - (V_F /A_F)*(dC_{A,F}/ dt)$
(1)

The maximum acid flux through the stripping interface (J_S.), (mol cm^{-2} min^{-1}), which indicates the total flux of acid through the liquid membrane, is given by the equation

$$J_{S0} = - (V_S /A_S)*(dC_{A,S}/ dt)$$

(2)   In these equations, V_F and V_S are the volume of feed and stripping solutions, and A_F and A_S are the surface area of feed phase/membrane phase interface and stripping membrane/ stripping phase interface, respectively.

III. MATERIAL AND METHOD

All chemicals used were of analytical grade of very high purity (>99%). Butyric acid and tri butyl phosphate (TBP) were obtained from LobaChemie. Toluene was procured from Pallav. Phenolphthalein obtained from Fisher Scientific was used as an indicator.

Solutions for the experiments were prepared - 0.5N Butyric acid concentration was prepared in 200ml distilled water also 0.1N, 0.3N, 0.5N NaOH concentration solutions were prepared in 500ml distilled water. Solutions for titrations were prepared- 0.05N NaOH and 0.05N Oxalic acid were prepared in 500 ml distilled water each. The transport experiments were performed at room temperature approximately 298.15K using the BLM glass cell setupas shown in Figure 1.
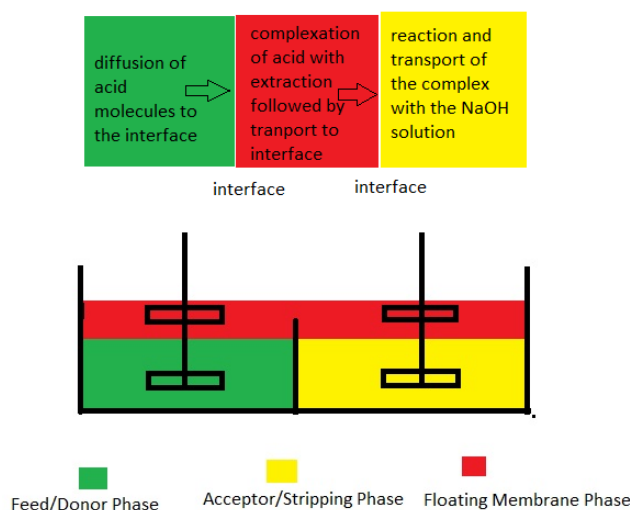

Figure 1: The setup and the mechanism of transfer of acid

BLM glass cell consists of two equal-volume compartments (feed and stripping phases) at the bottom, in contact with a liquid organic phase (membrane phase) above. The surface areas of extraction (feed phase/membrane phase (F/M)) and stripping (membrane/stripping phase (M/S)) interface were 56.25 cm^2 each for both the phases. Next the feed solutions (180 ml each) were poured into the cell's compartments. Above it the membrane solution (180ml) was poured. The membrane solution was made of toluene and TBP (10% of the total solution). The cell compartment solutions were agitated by two mechanical stirrers. The stirring speed was maintained at 80 RPM. The F/M/S phase ratio used was 1:1:1 (v/v). The samples from feed and stripping phases were taken at regular time intervals until equilibrium was reached. The concentration of acid in aqueous feed and stripping phases was determined by the volumetric NaOH titration method. When the stripping phase was NaOH solution, the concentration of acid in the stripping phase was determined by the volumetric Oxalic acid titration method. Both the titrations were done using phenolphthalein as an indicator. The above steps were repeated with various concentrations of NaOH (0.1N, 0.3N, 0.5N) at a constant stirring of 80 RPM. And the results were recorded. The above steps are repeated but with constant NaOH concentration and varying stirring speed from 0 to 80 RPM and the results were recorded. The above experiment is also performed by keeping the NaOH

concentration and stirring constant while changing the membrane phase volume to double of the previous one so that the F/M/S phase ratio is 1:2:1(v/v).

IV. RESULTS AND DISCUSSIONS

The different parameters had a different effect on the rate of flux of acid that are transferred first from the acid solution to membrane and then from membrane to strip solution. These are discussed here one by one.

A. Effect of Concentration of NaOH in the Strip Phase

The mass transfer process is governed by concentration gradient and therefore this parameter is one of the most significant parameters. The NaOH concentration was varied in three steps: 0.1 N, 0.3 N and 0.5 N at fixed stirring speed of 80 RPM for all the phases and fixed initial acid concentration of 0.5N. The F:M:S ratio was 1:1:1. It was observed that the concentration of NaOH had a very big impact on the rate of mass transfer of acid. With 0.1 N NaOH in the strip phase there was dominant transfer of acid from feed phase to membrane phase in comparison to the transfer of acid from membrane phase to strip phase. The concentration of acid rises with time in the membrane phase and then there is slowly transfer of acid in the strip phase.

When stoichiometric amount of NaOH in the strip phase to that of acid in the feed phase (both butyric acid and NaOH concentration = 0.5 N) the transfer of acid to that to the strip phase was very fast and the membrane acted merely as a carrier with very less containment. The transfer of acid when concentration of butyric acid in the feed phase was 0.5N and NaOH concentration was 0.3 N exhibited a characteristic different to the cases of 0.1 N and 0.5N NaOH. Initially the transfer process is fast up although decaying to a certain time after which very less transfer took place. The reason for such a behavior could be the neutralization of base for initial time and after that no further NaOH base is available for the reaction and therefore the transfer process was slow. Since the transfer is maximum in the case where the acid and base concentrations are equal in the feed and the strip phase, further all the experiments were conducted in this condition only.

B. Effect of agitation speed of Feed, Membrane and Strip phases

The agitation speed of the stirrer had a profound effect on the flux transferred. The agitation speed was varied from 0 to 80 RPM for all the three phases and it was observed that flux rate drastically improves (nearly 1000 times) from the case of no agitation to that of 40 RPM. Further increase in the agitation increase from 40 to 80 RPM had significant effect though not of that order that was observed in the case of increase as for 0-40 RPM. The interfacial turbulence was not observed till 80 RPM and therefore all the further experiments were carried out in 80 RPM only.

C. Effect of the extractant concentration in the Membrane

Extractant concentration is a very important factor in batch reactive extraction equilibrium studies. Tributyl phosphate works well with inactive diluents and therefore in the present study the TBP was used in the range of 0-20% v/v in toluene. In the batch equilibrium studies, increasing the TBP concentration increases the distribution coefficient. However, in the present case of BLM study of butyric acid, it was observed that the extractant concentration up to 10 % had significant effect and after that only marginal increase in the fluxes was observed if the concentration of extractant is increased. The reason for such a behavior can be attributed to the fact that the stirring speed was fixed at 80 RPM (as it the maximum agitation speed at which no interfacial turbulence was observed) and stirring at

such speed also restricts the number of acid molecules that are available at the interphase for complexation with the extractant molecules.

D. **Effect of Feed/Membrane/Strip phase volume ratio**

To observe the effect of volume ratio of three phases i.e., Feed (F), Membrane (M) and Strip(S) phase two different experiments were conducted. In the first experiment the F/M/S was set at 1/1/1 and the fluxes of acid transferred was observed. In the second experiment the membrane volume was doubled so that the ratio becomes 1/2/1. In both the cases the extractant concentration was taken as 10% v/v in toluene. It was observed from the results that the flux increased as the volume of membrane phase was increased.

Figure 2 shows the variation of concentration of butyric acid in the feed, membrane and strip phase for the optimum conditions i.e., 0.5 N butyric acid, 0.5 N NaOH, 10% TBP v/v in toluene, F/M/S ratio of 1/1/1. The mass flux transferred for the process were calculated using equation (1) and equation (2) and the data is presented in the table 1.
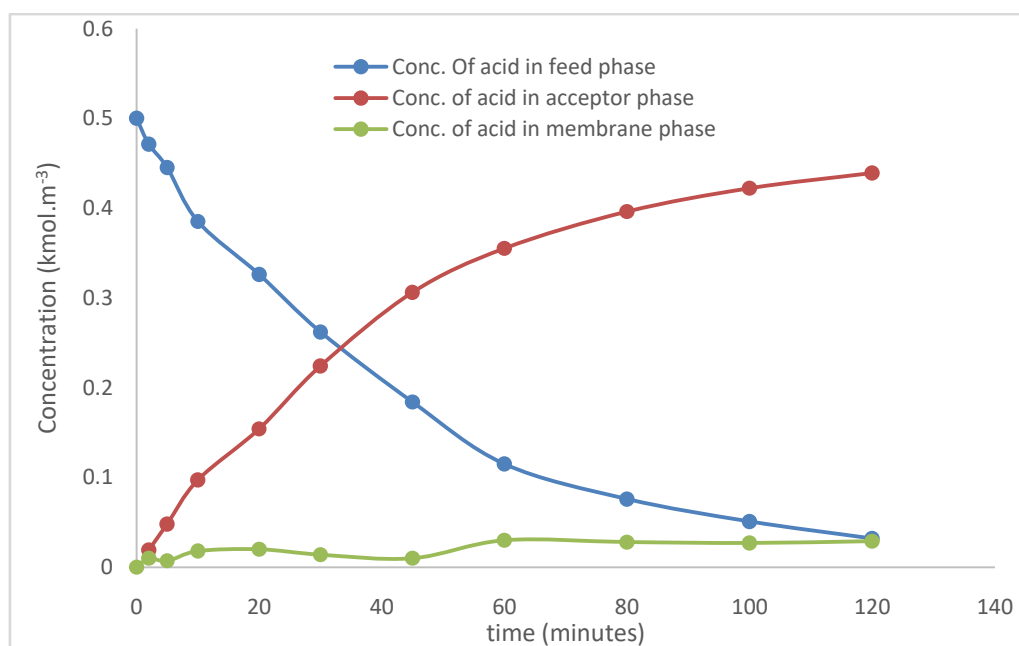

Figure 2:Concentration of acid in different phases with time

Table 1: Concentration of acid in feed, membrane and acceptor phase and resulting mass fluxes

time (min)	Conc. Of acid in feed phase (N)	Conc. Of NaOH Acceptor (N)	Conc. of acid in acceptor phase(N)	Conc. of acid in membrane phase (N)	dC_A/dt (mol min^{-1})	dC_B/dt (mol min^{-1})	Jf_0 (mol cm^{-2} min^{-1})	Js_0 (mol cm^{-2} min^{-1})
0	0.5	0.5	0	0	-0.0115	0.007917	0.040889	-0.14538
2	0.471	0.481	0.019	0.01	-0.01098	0.007916	0.039051	-0.1388

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5	0.445	0.452	0.048	0.007	-0.01025	0.007913	0.036447	-0.12959
10	0.385	0.403	0.097	0.018	-0.00914	0.00791	0.032488	-0.11551
20	0.326	0.346	0.154	0.02	-0.00726	0.007906	0.025812	-0.09178
30	0.262	0.276	0.224	0.014	-0.00577	0.0079	0.020509	-0.07292
45	0.184	0.194	0.306	0.01	-0.00409	0.007894	0.014525	-0.05164
60	0.115	0.145	0.355	0.03	-0.00289	0.007891	0.010287	-0.03658
80	0.076	0.104	0.396	0.028	-0.00183	0.007888	0.006494	-0.02309
100	0.051	0.078	0.422	0.027	-0.00115	0.007886	0.004099	-0.01458
120	0.032	0.061	0.439	0.029	-0.00073	0.007884	0.002588	-0.0092

V. CONCLUSION

Butyric acid production by the bio route has taken a leap forward. However, its separation from fermentation media remains a challenging task. Bulk liquid membrane studies carried in the present work suggest that through proper selection of parameters such as strip phase and its concentration, membrane composition and agitation the daunting task of separation of acid could be achieved. The present work suggests that for a feed phase concentration of 0.5N butyric acid following parameters could be used such as strip phase concentration (0.5 N NaOH) and agitation speed of 80RPM and F/M/S of 1/1/1 at the extractant concentration of 10% v/v in toluene.

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