

Separation of Biobutanol from Fermentation Solutions by Perstraction using $[P_{6,6,6,14}][Tf_2N]$ as Receiving Phase: Phase Temperature Analysis

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In this work, the perstraction process was implemented to separate butanol, acetone and ethanol from a model fermentation aqueous solutions using $[P_{6,6,6,14}][Tf_2N]$, which is a highly hydrophobic phosphonium based ionic liquid as receiving phase. Perstraction assays were carried out using a flat sheet dense membrane of polydimethylsiloxane (PDMS) to quantify the extraction percentage, transmembrane fluxes of butanol, water and butanol/water selectivity focused on the effect of the temperature difference between the feed and extractant phase. The results indicate that the fluxes of butanol were particularly high considering the PDMS membrane used in the experiments was relatively thick (160 μm). The highest average flux of butanol was obtained when the temperature of the aqueous phase was 60 °C and the temperature of the organic phase was 30 °C reaching a value of $6.3 \cdot 10^{-3} \text{ kg h}^{-1} \text{ m}^{-2}$, showing a butanol-water selectivity of 58.2, generated by the different sensitivity to temperature of the vapor pressure of both compounds. Finally, this disruption technique combined with ILs could allow the design of a wide range of separation processes for purify a wide variety of molecules. In addition to this, the perstraction process could be considered as a good alternative for the selective separation of fermentation or reaction products with high commercial value.

1. Introduction

Several types of microbial processes were developed before the First World War, to obtain butadiene and acetone. One of the first process was the so-called ABE fermentation. This process uses *clostridium* bacteria and starch among other types of biomasses as raw material to produce volatile organic compounds (Lauri et al., 2021). This fermentation produces the acetone/butanol/ethanol compounds in an approximate ratio of 3:6:1 respectively (Arregoitia-Sarabia et al., 2020). With typical concentrations of 6,000, 12,000, 2,000 ppm for acetone, butanol and ethanol, respectively. In general, a maximum concentration of butanol is reported at 13,000 ppm for the *Clostridium acetobutanicum* strain, since concentration of butanol above that number inhibits the fermentation process. (Cabezas et al., 2015).

Currently, this fermentation has gained new importance due to the production of biobutanol, which is a biofuel with a higher energy density than the gasoline-ethanol mixtures and, it has a lower vapor pressure and a greater tolerance to water contamination when mixed with gasoline (Segovia-Hernández et al., 2020). Butanol is getting attention among the possible biofuels as an alternative to bioethanol. Compared to bioethanol, biobutanol shows less miscibility with water, less flammability and corrosivity, and it has the advantage of being able to directly replace gasoline in the car engines without any modifications (Segovia-Hernandez et al., 2021).

There are several separation technologies to recover alcohols from fermentation broths such as adsorption (Collins et al., 2020), membrane distillation (Diban et al., 2009), vacuum flash distillation, gas stripping (Chen et al., 2019), pervaporation (Cabezas et al., 2021), or liquid-liquid extraction. However, these techniques have drawbacks (Pietrelli et al., 2022) such as high energy requirements, toxicity of solvents, loss of extractant agents, need of sterilization, adsorption of microorganisms on the surfaces, among others (Claes et al., 2012). The use of membrane separation processes stands out for being efficient, versatile and environmentally friendly. (Reinoso-Guerra et al., 2021), from these membrane separation technologies, perstraction arises as a viable process because of the moderate energy requirement and the indirect contact between the feed solution and the extractant phase (Olea et al., 2021).

The principle of this operation combines the permeation with the liquid-liquid extraction process. Thus, butanol as the compound of interest is transferred from an aqueous phase through a dense polymeric membrane to an extractant where the butanol is absorbed. Separation performance in perstraction could be improved with the right choice of receiving phase. Nowadays, Ionic Liquids (ILs) appear as a "green" alternative to organic solvents, and they may be used as solvents to increase extraction and/or selectivity. as they may also be regenerated and reused selecting the proper strategy (Olea et al., 2021)., ILs are also an attractive alternative for the perstraction process. Even so hydrophobic ILs reduce energy consumption in regeneration because of the decrease of the water content. The perstraction alongside silicone-based membrane may allow extending the applicability of ILs, therefore, hydrophilic ILs could be implemented in this kind of process, since the silicone-based membrane to some extent rejects the water fluxes through the membrane. Therefore, perstraction can lessen the energy consumption used in recovery processes like distillation, due to the lower water content (Oliveira et al., 2012).

Looking for an effective butanol separation, Merlet and co-workers (Merlet et al., 2017) developed the perstraction process to separate butanol, acetone and ethanol from aqueous solutions using four different commercial hydrophobic ILs as receiving phase: [bmin][PF₆], [bmim][Tf₂N], [omim][Tf₂N] and [P_{6,6,6,14}][DCA]. Perstraction assays were carried out using a symmetric membrane made in polydimethylsiloxane (PDMS). Where the highest average flux of butanol was obtained using [P_{6,6,6,14}][DCA] as the extractant reaching a value of $5.5 \cdot 10^{-3} \text{ kg h}^{-1} \text{ m}^{-2}$. Nevertheless, the IL with the best separation performance was [omim][Tf₂N] with a low flux of butanol ($4.3 \cdot 10^{-3} \text{ kg h}^{-1} \text{ m}^{-2}$) but with the highest butanol/water selectivity value equal to 64.25 (Merlet et al., 2017).

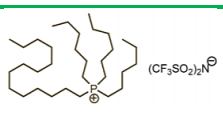
The aim of this work is to study the temperature effect in the performance extraction of Butanol from ABE solutions in order to optimize butanol extraction and, considering the effect that the temperature has on the transport properties of the aqueous solution and ionic liquid, as well as the effect on the thermodynamic equilibrium at the aqueous solution/ membrane and membrane / ionic liquid. In addition, to test the performance of an ionic liquid with a cation very similar to butanol and a very hydrophobic anion

2. Experimental

2.1. Materials and reagents

Trihexyltetradecyl phosphonium bis(trifluoromethyl sulfonyl)imide [P_{6,6,6,14}][Tf₂N] purity 98%, were supplied by lolitec. acetone, butan-1-ol and ethanol with analytical grade were purchased from Sigma Aldrich. On the other hand, PDMS membranes were purchased from Kolm®, Chile. These membranes were selected from their organophilic character and as one of the most used materials in pervaporation membranes. The model ABE solutions were prepared by mixing acetone, butanol and ethanol with deionized water (>18 MU) obtained from a Purelab Classic Co. Water System. The properties of the IL tested in this study are summarized in Table 1

Table 1. properties of the ionic liquid used in this work

Name	Nomenclature	Structures	Density/ viscosity	Melting point	Molecular weight	Water saturati on 25°C
Trihexyltetradecyl phosphonium Bis(trifluoromethylsulfonyl)imide	[P _{6,6,6,14}][Tf ₂ N]		1260 kg m ⁻³ / 209 mPa s	16°C	497.50 gmol	>200 ppm

2.2. Perstraction assays

Perstraction process were carried out in a system (shown in Figure 1) with two streams: an aqueous feed solution (fs) containing acetone, butanol and ethanol with a concentration of 6,000, 12,000 and 2,000 ppm

respectively and $[P_{6,6,6,14}][Tf_2N]$ as receiving phase of the ABE compounds, separated by a flat sheet membrane of polydimethyl siloxane (PDMS) with thickness of 160 μm , a surface area of 0.015 m^2 and a density of 1,200 kg m^{-3} . The experimental runs were performed in a total time of 6 h, where the decrease in concentration of each solute of the ABE solution was measured as a function of time by gas chromatography in a Perkin Elmer® Clarus 500 GC with a Carbowax column and FID. The concentration changes of butanol, acetone and ethanol were monitored as a function of time collecting 1 μL samples from the feed solution vessel, the measures were realized in triplicate. The water content of the extractant phase was quantified using a Metrohm KF 831 Karl Fischer titrator.

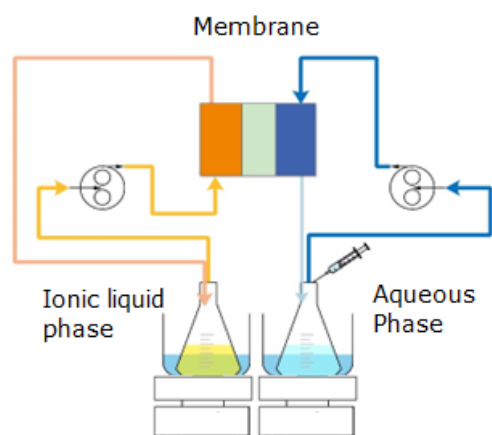


Figure 1: Experimental setup for perstraction process

Experimental responses

The experimental responses were the extraction percentage ($E\%$), the transmembrane flux (N_t) in $\text{kg m}^{-2} \text{h}^{-1}$ of the solute i and the selectivity ($\alpha_{i/w}$) which can be estimated by the following equations:

$$E\% = \frac{(C_{i,t=0} - C_{i,t+\Delta t})}{C_{i,t=0}} \cdot 100 \quad (1)$$

$$N_t = -\frac{V}{A} \frac{dC}{dt} = -\frac{V}{A} \frac{(C_{i,t+\Delta t} - C_{i,t})}{\Delta t} \quad (2)$$

$$\alpha_{i/w} = \frac{C_i^{IL}/C_i^{aq}}{C_w^{IL}/C_w^{aq}} \quad (3)$$

In this study, the performance of the perstraction process was assessed as a function of the temperature of the feed solution (fs) and the ionic liquid (IL) phase, with four sets of experimental runs: i) fs 0 $^{\circ}\text{C}$ - IL 30 $^{\circ}\text{C}$, ii) fs 30 $^{\circ}\text{C}$ - IL 30 $^{\circ}\text{C}$, iii) fs 60 $^{\circ}\text{C}$ - IL 30 $^{\circ}\text{C}$, iv) fs 30 $^{\circ}\text{C}$ - IL 60 $^{\circ}\text{C}$, that were controlled through two thermostats. The flow rates of both phases were constant and equal to 0.9 L min^{-1} and the total volume of both phases was 125 mL each.

3. Results and discussion

Extraction percentage of solutes

The perstraction tests described in Section 2.2 were carried out for all four conditions described previously. Thus, Figure 2 shows an example of the results obtained in these experiments.

Figure 2 shows an example of one of the extraction kinetics obtained in the experiments where the concentration of each compound in the feed ABE solution decreases as a function of time. From this figure the clearest decreases in the concentration of butanol and acetone. Meanwhile, the concentration of ethanol could be considered practically constant during the time of the perstraction process. Thus, the lower transfer rate of ethanol, which is the smallest molecule among these solutes, could be explained by a smaller solubility of this alcohol in the PDMS layer membrane and the affinity between ethanol and IL. With the analysis of the extraction kinetics is

possible to obtain the experimental responses 2.2, The extraction percentage values of butanol for each temperature combination are reported in Table 2.

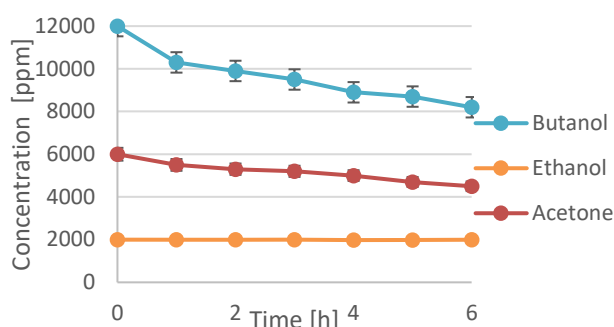


Figure 2: Concentration of butanol, acetone, and ethanol in the feed solution as a function of time, fs 30°C-IL 30°C

Table 2: Extraction percentage values of butanol as a function of temperature difference between phases.

Temperature combination	E%
fs 0°C – IL 30°C	12.3
fs 30°C – IL 30°C	26.6
fs 60°C – IL 30°C	44.9
fs 30°C – IL 60°C	32.4

Table 2 shows the extraction percentage observed for butanol, evidencing how the temperature of the feed phase governs the butanol mass transfer process, obtaining the best result for the feed phase circulating at 60 °C, which is mainly explained by the change in the transport properties in the PDMS membrane, which is known to be the controlling phase in the processes of perstraction (Merlet et al., 2017) and Pervaporation (Cabezas et al., 2021) as well.

Transmembrane Flux

Table 3 shows the total transmembrane flux obtained according to equation 2, also including the value obtained for water, which, presents an almost constant concentration in the feeding phase and, as water does not have an extraction kinetics, but rather the value of the transmembrane flux is obtained directly by determining the amount of water in the IL phase after the perstraction process.

Table 3: Average values of transmembrane flux of butanol and water for different phase temperature combination

Temperature combination	Butanol Flux [Kg·m ⁻² ·h ⁻¹]	Water Flux [Kg·m ⁻² ·h ⁻¹]
fs 0°C – IL 30°C	1.5 · 10 ⁻³	3.9 · 10 ⁻³
fs 30°C – IL 30°C	4.2 · 10 ⁻³	8.1 · 10 ⁻³
fs 60°C – IL 30°C	6.3 · 10 ⁻³	16 · 10 ⁻³
fs 30°C – IL 60°C	4.9 · 10 ⁻³	37 · 10 ⁻³

From the results presented in Table 3, it can be corroborated that the change in the temperature of the aqueous feed phase generates the greatest effect on the mass transfer of butanol, following a clear trend that with a higher feed phase temperature, a greater transmembrane flux of butanol is observed, which responds directly to an Arrhenius-type behaviour of the butanol/PDMS diffusion coefficient, a variable that governs the transfer phenomenon of the process. This effect is not observed when it is the organic-organic extraction phase that increases its temperature, which also indicates that it is the butanol/PDMS interaction in the contact surface from the feeding phase to the membrane, the variable that is seen enhanced with an increase in temperature and that corresponds to the solution-diffusion model that governs the phenomena of permeation in a dense membrane. For water, the same trend as for butanol can be observed, thus indicating how both diffusion coefficients are affected in a similar way by a change in temperature. The resulting water flow that presents an unexpected value is 37 · 10⁻³ kg m⁻² h⁻¹ for the condition fs 30 °C – IL 60 °C, which can be explained by the

increase in the solubility of water in the ionic liquid phase, considered highly hydrophobic, then losing its hydrophobic character in part, due to the increase in temperature, being an effect also observed for the viscosity and density variables mainly, where small changes in temperature generate a significant effect on the ionic liquid.

Selectivity

From equation (3) it is possible to obtain the selectivity of butanol over water, these results are presented in Table 4.

Table 4: Average values of the selectivity calculated for perstraction assays

Temperature combination	$\alpha_{B/w}$
fs 0 °C – IL 30 °C	52.0
fs 30 °C – IL 30 °C	58.3
fs 60 °C – IL 30 °C	41.3
fs 30 °C – IL 60 °C	12.3

The selectivity analysis allows us to corroborate much more clearly, the effect of the temperature between both compounds (the one of interest and the undesired one), being able to observe how, despite having a relatively high transmembrane flux of butanol, the condition for fs 60 °C — IL 30 °C also has a high water flux, which limits the transfer process, not necessarily due to a competitive mass transfer, but simply, the water value increases more when the temperature of the aqueous phase does, considering its greater potential for transfer by concentration, as well as the increase in the vapor pressure of this phase.

Finally, the best selectivity result is found when the temperature of both compound is 30 °C. This is the best result operationally speaking as well, since it is a temperature close to the ABE fermentation temperature and that would allow obtaining an IL current with a smaller amount of water, where a later distillation step of butanol would be much more efficient.

4. Conclusions

In this work the separation of ABE fermentation products was achieved by means of perstraction using [P_{6,6,6,14}][Tf₂N], a commercial hydrophobic ionic liquid as extractants. This process showed good permeability and selectivity to recover butanol from ABE solutions. From the perstraction assays, seemed to be the best ionic liquid. A feed phase temperature of 30 °C for both the feed solution and extractant phase was the best operational temperature, since it shows the highest butanol/ water selectivity with values equal to 58.3.

The results obtained in this study related to the mass transfer rates of specific compounds are promising, since the synthesis of task-specific ionic liquids and temperatures could allow to design a perstraction process to selectively obtain a great variety of molecules with high commercial value from fermentation or reaction products.

Nomenclature

$E\%$ – extraction percentage, -

N_t – transmembrane flux, $\frac{kg}{m^2h}$

$\alpha_{i/w}$ – selectivity, -

$C_{i,t=0}$ – initial concentration of the specie i in the aqueous phase, $\frac{kg}{m^3}$

$C_{i,t}$ – concentration of the specie i in the aqueous phase at time t, $\frac{kg}{m^3}$

$C_{i,t+\Delta t}$ – concentration of the specie i in the aqueous phase at time t+ Δt , $\frac{kg}{m^3}$

V – the volume of the feed solution, m^3

A – surface area available for mass transfer, m^2

C_i^{IL} – concentration of the specie i in the collected permeate (p), $\frac{kg}{m^3}$

C_i^{aq} – concentration of the specie i in the feed solution (fs), $\frac{kg}{m^3}$

C_w^{IL} – concentration of water in the collected permeate (p), $\frac{kg}{m^3}$

C_w^{aq} – concentration of water in the feed solution (fs), $\frac{kg}{m^3}$

i – compound butanol (B), acetone (A) or ethanol (E), -

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