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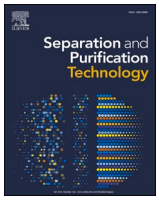

Recovery of ionic liquids from aqueous solutions using membrane technology

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ABSTRACT

Ionic liquids (ILs) have great potential as solvents and catalysts in the most diverse areas of the chemical industry. However, the need for a process that allows the recycling and purification of ILs in an efficient and economically viable manner is restricting the practical application of these solvents. The recycling processes most used to recover ILs are distillation and evaporation, followed by extraction and crystallization. However, most of these processes demand high energy consumption, or temperatures that may compromise the structural and chemical stability of the ILs. This work focuses on understanding the separation of ionic liquid from aqueous solution using membranes, a technique widely used in industry. The separation of eleven ILs (([C_4mim][AOc], [C_4mim][SCN], [C_4mim][CF_3SO_3], [C_4mim][CF_3CO_2], [C_4mim][Cl], [C_8mim][Cl], [P_{4444}][Cl], [N_{4444}][Cl], [C_4mpip][Cl], [C_4mpyr][Cl] and [$C_{4\text{-}2}$-mpy][Cl]) was studied using a nanofiltration (NF270) and a reverse osmosis (BW30LE) membrane. The influence of cation and anion, pressure, IL concentration, and temperature, on the separation of ILs, was evaluated. The Donnan exclusion mechanism was found to be the limiting factor for the reverse osmosis, while the combination of concentration polarization and sieving mechanism was the limiting factor for nanofiltration membrane. The increase of temperature and pressure leads to an increase in the volumetric flux at the cost of a decrease of the IL retention. On the other hand, the increase in the concentration of the IL solution resulted in an increase in the osmotic pressure and, consequently, a decrease in the volumetric flow and a decrease in the rejection of the IL.

1. Introduction

Ionic liquids (ILs) have become very prominent in recent years for their ability to dissolve a wide variety of materials, including hydrophobic, hydrophilic, polymeric compounds, and applications in the most diverse areas have been reported [1–3]. They are defined as low-melting salts, that in addition to their non-volatile nature, have other advantages such as the possibility of adjusting their properties through different cations/anions combinations that define them as “designer solvents” [4]. This characteristic makes it possible to develop new processes that are environmentally and technologically advantageous [5–7].

One of the main constraints that are restricting the large-scale application of ILs is their purification and recyclability, which directly impacts process economic viability and the environment [8,9]. The recyclability of ILs, especially those hydrophilic, is a bit more difficult than usual, given their nonvolatile nature. For the separation of ionic liquids from aqueous solutions, evaporation (often wrongly described as distillation) is generally used due to the negligible vapor pressure of the ILs. While the evaporation processes require, by its nature, a vast amount of energy, the evaporation of mixtures containing ionic liquids, presents increased energy penalties and temperature profiles that increase exponentially with the IL concentration, temperatures at which most ILs degrade, preventing or limiting the separation and recovery of the ILs [10]. Moreover, the low volatility of the ILs is also a problem in separating them from other low-volatile solutes (polymers, salts, carbohydrates) and thermal-sensitive products [11].

In the literature, different technics for the recovery/separation of ILs were proposed [12–14]. It is possible to highlight the extraction using water, organic solvents, aqueous biphasic system, supercritical CO_2 ($scCO_2$), distillation/evaporation, adsorption by activated carbon, resin, soils or sediments, crystallization, centrifugal solvent-extraction contactors, and membranes (pressure-driven, pervaporation, membrane distillation) [15–17].

Among these technologies, membrane filtration has gained acceptance because of its numerous advantages over other techniques, namely remarkable reduction in energy consumption, space efficiency, and low

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capital cost [18].

Several works report the application of membrane technology, either by pressure-driven (Table S1), pervaporation, or membrane distillation, as an efficient methodology to purify/concentrate ILs [11,19,20]. Nanofiltration is common applied to separate ILs due to the elevated purity of the permeates and cost-effective operation. Kröckel and Kragl [15] studied the application of nanofiltration membrane to separate bromophenol blue from an aqueous solution of $[C_4C_1im][BF_4]$ and lactose from an aqueous solution of $[C_1C_1im][CH_3SO_4]$. In both cases, the IL aqueous solution permeated the membrane while the remaining compounds were retained. In another study, nanofiltration membranes (STARMEM^{TM} 120 and 122) were used to recover ionic liquids from synthetic post-reaction mixtures [21]. The authors report an IL rejection of 95% for the tetradecyl(trihexyl)phosphonium chloride and the PEG-5 cocomonium methosulfate from ethyl acetate and methanol solutions. In another more detailed study, Hazarika et al [22] studied the effect of pressure and solution concentration on the 1-butyl-3-methylpyridinium tetrafluoroborate rejection from lignocellulose aqueous solutions with a nanofiltration membrane (NF270-400, FilmTech). The membrane retained most of the IL (>50%), and the solvent flux increased with increasing pressure. Abels et al [23] reported that higher IL concentrations decreased permeate flux due to low IL permeability and osmotic pressure differences.

In the study conducted by Haerens et al [24] reverse osmosis membranes (FilmTec 102,326 and BW30XLE) and nanofiltration membranes (FilmTec NF90, NF207 and Desal DK) were used to concentrate an aqueous solution of ChCl:Ethylene glycol. The authors reported that the rejection of ChCl:Ethylene glycol by the NF90 and NF207 membranes was low, <20%. As for the reverse osmosis membranes, a minimum rejection of 88% was obtained. Therefore, only a five-fold ionic liquid concentration was possible for a maximum concentration of 25% (V/V) of ionic liquid. Sosa et al.[20] observed the same behavior in their study, for the serial filtration tests, a three-fold ionic liquid concentration was achieved using a combination of nanofiltration and reverse osmosis membranes.

In general, the properties of membranes are unique and depend mainly on the membrane functional groups. The rejection mechanisms combine several factors, such as electrical exclusion, steric hindrance, and hydration mechanism dielectric effect. However, these mechanisms are unclear, and many solution factors contribute to membrane rejection.

This work is aimed to understand the separation of ionic liquids aqueous solutions in nanofiltration (NF) and reverse osmosis filtration (RO). For that purpose the separation from water of eleven widely used ILs ([C_4mim][AOc], [C_4mim][SCN], [C_4mim][CF_3SO_3], [C_4mim][CF_3CO_2], [C_4mim][Cl], [C_8mim][Cl], [P_{4444}][Cl], [N_{4444}][Cl], [C_4mpip][Cl], [C_4mpyr][Cl] and [$C_{4\text{-}2}$mpy][Cl]) was studied under different conditions. These ILs were selected to allow understanding the effect of the cation and anion of the IL on the membrane permeation. In addition, the retention, flow, pressure effect, and IL concentration in the IL rejection and permeate flux were evaluated.

2. Experimental

2.1. Chemicals

The 1-butyl-3-methylimidazolium acetate - [C_4mim][AOc], 1-butyl-3-methylimidazolium thiocyanate - [C_4mim][SCN], 1-butyl-3-methylimidazolium trifluoromethanesulfonate - [C_4mim][CF_3SO_3], 1-butyl-3-methylimidazolium trifluoroacetate - [C_4mim][CF_3CO_2], 1-butyl-3-methylimidazolium chloride - [C_4mim][Cl], 1-methyl-3-octylimidazolium chloride - [C_8mim][Cl], tetrabutylphosphonium chloride - [P_{4444}][Cl], tetrabutylammonium chloride - [N_{4444}][Cl], 1-butyl-1-methylpiperidinium chloride - [C_4mpip][Cl], 1-butyl-1-methylpyrrolidinium chloride - [C_4mpyr][Cl], 1-butyl-2-methylpyridinium chloride - [$C_{4\text{-}2}$mpy][Cl] were purchased from Iolitec. All ILs used have a stated supplier purity of at least 98 wt%. The molecular structures of all the ILs are presented in Table 1. The water content of the ILs was measured using a Metrohm 831 Karl-Fischer coulometer, with the analyte Hydranal®–Coulomat AG from Riedel-de Haën. The ultrapure water used to prepare the ILs aqueous solution was double-distilled, passed through a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus.

2.2. Filtration procedure

Filtration experiments were carried out in a dead-end stirred cell from Sterlitech (HP4750). A polyamide-TFC nanofiltration membrane from FilmeTec (NF270) and a reverse osmosis membrane from Dow-Filmtec (BW30LE) were used. Membrane specification details are shown in Table S2, in supporting information. The experimental conditions and the respective IL are presented in Table 2. The methodology used was described and optimized on a previous publication [20]. Briefly, the membrane is placed on top of the porous metallic support, the cell is loaded with 50 mL of the IL aqueous solution and pressurized (10 – 50 bar). During the test, the permeate solution is collected and the permeate mass is measured using a semi-analytical balance (Sartorius LA2000P, $d \pm 0.001$ g). To prevent excessive concentration of the solution and maintain optimal filtration performance, a strict limit was set during the filtration process. Specifically, no>25 wt% of the feed solution's mass was collected. This precautionary measure ensures that the concentration of the solution remains within an acceptable range, minimizing any potential negative effects on the filtration process.

Each experiment is repeated in duplicate with a cleaned membrane. The membrane cleaning procedure consists of permeating the membrane with an aqueous solution of sulfuric acid (0.2 wt%), an aqueous solution of sodium hydroxide (0.1 wt%), and posteriorly ultrapure water.

The volumetric flux was determined using equation (1).

$$J = \frac{v}{tA} \tag{1}$$

where J is the flux, v is the volume collected over the permeation time, t, and A is the active membrane area.

The resistance happening during permeate transport through porous membranes (NF270) can be determined using the Darcy's law (equation (2).

$$J = \frac{\Delta P}{\mu_p R_t} \tag{2}$$

where ΔP is transmembrane pressure (Pa), μ_p the viscosity of the permeate (Pa.s) and R_t the total resistance (m^{-1}). The total filtration resistance (R_t) is the sum of the membrane filtration resistance caused by the membrane itself (R_m) and the resistance to filtration due to cake formation, fouling and concentration polarization [25] (R_f), as described by equation (3).

$$R_t = R_m + R_f \tag{3}$$

The R_m can be determined using the water flux and viscosity of filtration o ultrapure water. Combining equations (2) and (3) it is possible to determine the R_f for each IL solution through equation (4).

$$R_f = \frac{\Delta P}{\mu_p J} - R_m \tag{4}$$

The IL concentration in permeate and retentate solution was determined using an Anton Paar Abbemat 5010 refractometer, at 303.2 K, with an uncertainty of $2 \cdot 10^{-5}$ nD. The IL rejection (R_{IL}) can be determined by equation (5):

$$R_{IL} = \left(1 - \frac{c_{IL_p}}{c_{IL_f}}\right).100\% \tag{5}$$

Table 1
Molecular formula, chemical structure, molar mass, cation volume and anion volume of tested Ionic liquid.

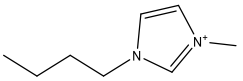
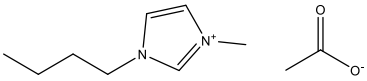
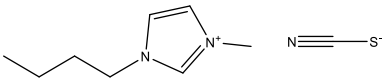
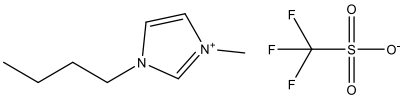
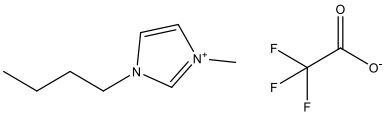
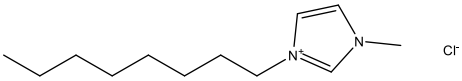
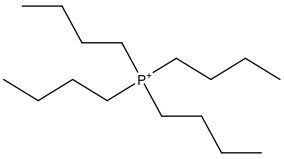
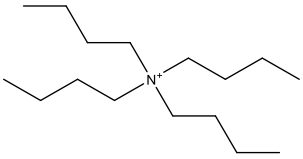
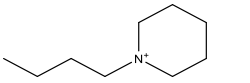
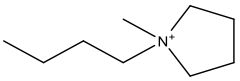
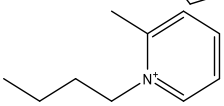
Ionic Liquid	Chemical Structure	Molar Mass(g/mol)	Cation Volume (nm^3)	Anion Volume(nm^3)
[C_4mim][Cl		174.67	0.1965	0.0410
[C_4 mim][AOc]		198.26	0.1965	0.0784
[C_4 mim][SCN]		197.30	0.1965	0.0754
[C_4mim][CF_3SO_3]		288.28	0.1965	0.1261
[C_4mim][CF_3CO_2]		252.24	0.1965	0.1024
[C_8mim][Cl]		230.78	0.2912	0.0410
[P_{4444}][Cl]		294.89	0.4099	0.0410
[N_{4444}][Cl]		277.92	0.3926	0.0410
[C_4mpip][Cl]		191.74	0.2319	0.0410
[C_4mpyr][Cl]		177.72	0.2122	0.0410
[$C_{4\text{-}2}$.mpy][Cl		185.69	0.2110	0.0410

Table 2
Membranes, initial IL concentration, experimental conditions and respective ILs evaluated.

Membrane	Conditions	Ionic Liquids
BW30LENF270	1 wt% at 10 bar298.2 K	[C_4mim][AOc], [C_4mim][SCN], [C_4mim][CF_3SO_3], [C_4mim][CF_3CO_2], [C_4mim][Cl], [C_8mim][Cl], [P_{4444}][Cl], [N_{4444}][Cl], [C_4mpip][Cl], [C_4mpyr][Cl], [$C_{4\text{-}2}$.mpy][Cl]
	1 wt% at 10, 20, 30, 40 and 50 bar298.2 K 1, 5, 10, 15 and 20 wt% at 30 bar298.2 K 20 wt% at 30 bar 298.2 and 313.2 K	[C_4mim][AOc] and [P_{4444}][Cl]

where is the rejection of IL, c_{ILp} is the concentration of IL in the permeate solution and c_{ILf} is the concentration of IL in the feed solution.

2.3. Osmotic pressure

Osmotic pressure of the aqueous solution of Ionic liquid, at 298.2 K, was determined using water activity meter (Novasinahygrometer LabMaster). The methodology used to measure the water activity was described and optimized in previous publications [26,27]. Briefly, known compositions of aqueous solutions of IL (4–5 mL) were placed in the air-tight equilibrium chamber and maintained at 298.2 K until reaching thermal and chemical equilibria and the water activity determined (*aw*). The instrument was calibrated with seven standard solutions of $MgCl_2$ ($0.3278 < aw < 1.000$) prior to the measurements. The measured *aw* was used to calculate the osmotic pressure (π) using the following equation:

$$\pi(MPa) = -\frac{R \bullet T \bullet \ln aw}{V_{water}} = \frac{1 - aw}{\frac{M_{water}}{\rho_{water}}} RT$$

where R is the gas constant (8.314462 $cm^3 \cdot MPa \cdot K^{-1} \cdot mol^{-1}$), T is the temperature (K) and V_{water} is the partial molar volume of water in the IL aqueous solution at 298.2 K. M_{water} is the molecular weight of water ($g \cdot mol^{-1}$), and ρ_{water} is the density of pure water ($g \cdot cm^{-3}$) at 298.2 K.

2.4. Statistical analysis

All the statistical analysis was performed using the Jamovi program

version 1.6.6 [28]. All the results were expressed as mean ± standard deviation of the mean. To investigate possible correlations between molar mass, molecule volume, anion volume and ionic liquid rejection, the Pearson coefficient was performed (or Spearman correlation to heteroscedastic data) considering a significance level of 95%.

3. Results

The adequate integration of an efficient IL recovery process can bridge the gap between economics and sustainability. Membrane filtration has shown to be a promising technique to achieve that purpose but the separation of ILs from aqueous solutions using membrane technologies is nontrivial, with the membrane performance highly dependent on several process operating parameters, such as feed concentration, feed flow, temperature, particle size, osmotic pressure, and pressure, besides the nature of the IL itself [29,30].

Considering the importance of recovering ILs from aqueous solutions using membrane technology, the influence of IL cation and anion, IL concentration, pressure, and temperature in nanofiltration (NF270) and reverse osmosis filtration (BW30LE) was evaluated.

3.1. The IL effect

Eleven ILs, comprising 7 different cations and 5 different anions, were selected aiming at evaluating the filtration in two membranes with different characteristics. Fig. 1 shows the experimental volumetric fluxes and ILs rejection for mixtures containing 1 wt% of IL, at 10 bar and 298.2 K. The volumetric fluxes followed the order of [C_4mim][SCN] > [C_4mpyr][Cl] > [C_4mim][Cl] > [C_4mim][CF_3SO_3] > [P_{4444}][Cl] > [C_4mim][AOc] > [C_4mpip][Cl] > [C_4mim][CF_3CO_2] > [N_{4444}][Cl] > [C_8mim][Cl] > [$C_{4\text{-}2}$mpy][Cl] at the same pressure applied to the nanofiltration membrane (NF270). As for the reverse osmosis membrane (BW30LE), the volumetric flow values followed the following order [P_{4444}][Cl] > [C_4mim][AOc] > [C_4mim][SCN] > [N_{4444}][Cl] > [C_4mim][Cl] > [C_4mpip][Cl] > [C_4mpyr][Cl] > [$C_{4\text{-}2}$mpy][Cl] > [C_4mim][CF_3CO_2] > [C_8mim][Cl] > [C_4mim][CF_3SO_3].

In the case of the nanofiltration membrane, the highest volumetric flux was observed for [C_4mim][SCN] (148.1 $L{\cdot}m^{-2}{\cdot}h^{-1}$) and the lowest for [$C_{4\text{-}2}$mpy][Cl] (43.2 $L{\cdot}m^{-2}{\cdot}h^{-1}$), while for the reverse osmosis membrane, the highest volumetric flux was observed for [P_{4444}][Cl] (36.0 $L{\cdot}m^{-2}{\cdot}h^{-1}$) and the lowest for [$C_4$mim][$CF_3CO_2$] (5.4·$L/m^{-2}$(−|-)·$h^{-1}$).

In general, permeation through the membrane will be more difficult for large molecules than for smaller ones, so the membrane cut-off directly impacts the separation efficiency of the membrane. The NF270 membrane presents a molecular weight cut-off around 300 Da (200–400 Da), so in theory, the NF270 membrane removes>90% of compounds with molecular weights of 300 Da or bigger. The molecular weight of the studied ILs varies between 174.67 and 294.89 Da (Table 1). As the molecular weight of the ILs is lower than the average cut-off of the membrane, it was expected that the IL rejections would be low, mainly for the small molecular weight ILs. However, it was possible to retain>55% of the [C_4mpip][Cl], that presents a molecular weight lower than the minimum cut-off value of the membrane. As for reverse osmosis membranes, the sieving process does not occur, but the separation is instead dominated by the diffusion process since they are dense membranes. The diffusion process is usually slower, resulting in a lower volumetric flow.

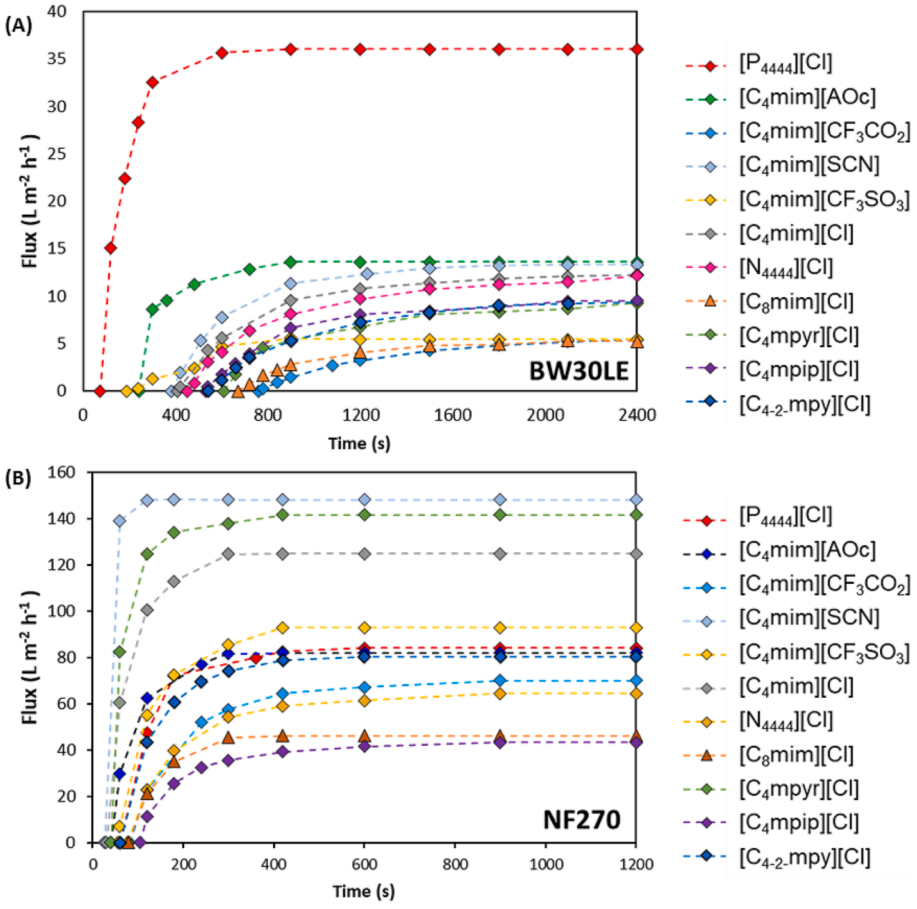


Fig. 1. Volumetric flux over the time of ionic liquid solution in the **(A)** NF270 and **(B)** BW30LE filtration. Conditions: solution of 1 wt% of 10 bar, 200 rpm at 298.2 K.

For all studied systems, the volumetric flow profile was determined. As can be seen in Fig. 1, the volumetric permeation flux has an exponential increase in the beginning ($t > 200$ s) and then the flux tends to remain constant for a specific time ($t > 1000$). This behavior is related to concentration polarization, a natural consequence of membrane selectivity [31]. Dissolved molecules accumulated on the surface of the membrane obstruct the transport of water, which in turn limits or even decreases the membrane flux. Another factor that affects the flow is the blockage of the pores during the filtration process, which, depending on the characteristics of the IL, such as molecular weight, affects the sieving and adsorption mechanisms of the IL on the internal surface or within the membrane pores [32,33].

Therefore, other effects than sieving, or a combination of these effects, such as concentration polarization and pore blockage, may be occurring in the membrane filtration. Differences in the molecular structure of IL, such as cation volume, anion volume, and molecular weight, are key factors for IL permeation across membranes. These effects will be discussed in detail below.

For both membranes, a fraction of the IL was retained (IL rejection > 13%), while water permeated the membrane (Fig. 2). The highest rejections were obtained for the reverse osmosis membrane (BW30LE), mainly for the ILs with the chloride anion. Generally, membranes with high permeability to water, as in the case of BW30LE, also have a higher permeability to salts. However, the permeability of solutes decreases with increasing molecular mass, ion charge, and mainly with degree of hydration.

In the case of ILs aqueous solution, the MD simulations show a formation of the H_2O–Cl complex (hydrated [Cl]) and then a particular interaction between hydrated-[Cl] and the imidazolium ion [34,35]. Consequently, in chloride-based ionic liquids hydration is expected, consequently, a large number of water molecules associated with it, which makes it more difficult for the ion to pass through the membrane because of its larger size compared with less hydrated ILs such as $[C_4mim][CF_3CO_2]$ and $[C_4mim][CF_3SO_3]$ [36,37]. Furthermore, increasing the number of carbons in the IL cation alkyl chain (C_4 to C_8) resulted in an increase in IL rejection by the membrane due to the difficulty for the larger molecule to permeate the membrane [30].

Remarkably, the nanofiltration membrane (NF270) showed rejection rates for some ILs comparable to the reverse osmosis membrane (BW30LE). For example, the rejection rate of $[P_{4444}][Cl]$ is 85.5% and 87.5% for NF270 and BW30LE membranes, respectively. This implies that, at these conditions, it is possible to obtain a volumetric flow rate about 2.3-fold higher, with the same rejection rate, providing greater efficiency for the filtration process.

In order to better understand the IL retention, the IL rejection results were correlated with IL molecular weights, osmotic pressure, and anion volume.

The correlation between IL rejection and IL volume or IL molecular weights are shown in Fig. 3 and Figure S1, respectively. To investigate potential correlations between IL volume (cation + anion) and IL rejection, the Pearson coefficient ($r_{pearson}$) was determined. For the NF270 membrane, it is possible to observe a significant trend ($p < 0.05$) towards increased IL rejection with increasing molecular weight. As for the BW30LE membrane, this dependency was not statistically significant ($p > 0.05$) (Table S3). The same behavior was observed for the correlation of IL molecular weight and IL rejection (Figure S1). This behavior is related to the adsorption of IL on the surface of the membrane and the sieving mechanism, which causes a blockage of the pore of the membrane during the filtration process, adding resistance to the IL permeation, especially for ILs with higher molecular weight. Avram et al. [38] reported the same trend. They failed to separate IL and low molecular weight sugars using modified nanofiltration membranes, revealing that the separation based on the sieving mechanism is ineffective for this type of solvent. The maximization of sugar rejection was effective with the control of the thickness of the layer formed on the membrane and the filtration resistance.

As reported by Choi et al. [25], the total filtration resistance is not related only to the membrane, but to a sum of other various factors, such as the resistance caused by cake formation, incrustation, and concentration polarization. Fig. 4 presents the relationship between the total resistance to filtration (R_f) and the volumetric flow in the NF270 membrane.

The increase in filtration resistance results in an exponential decrease of flux. The impact of increasing the filtration resistance is

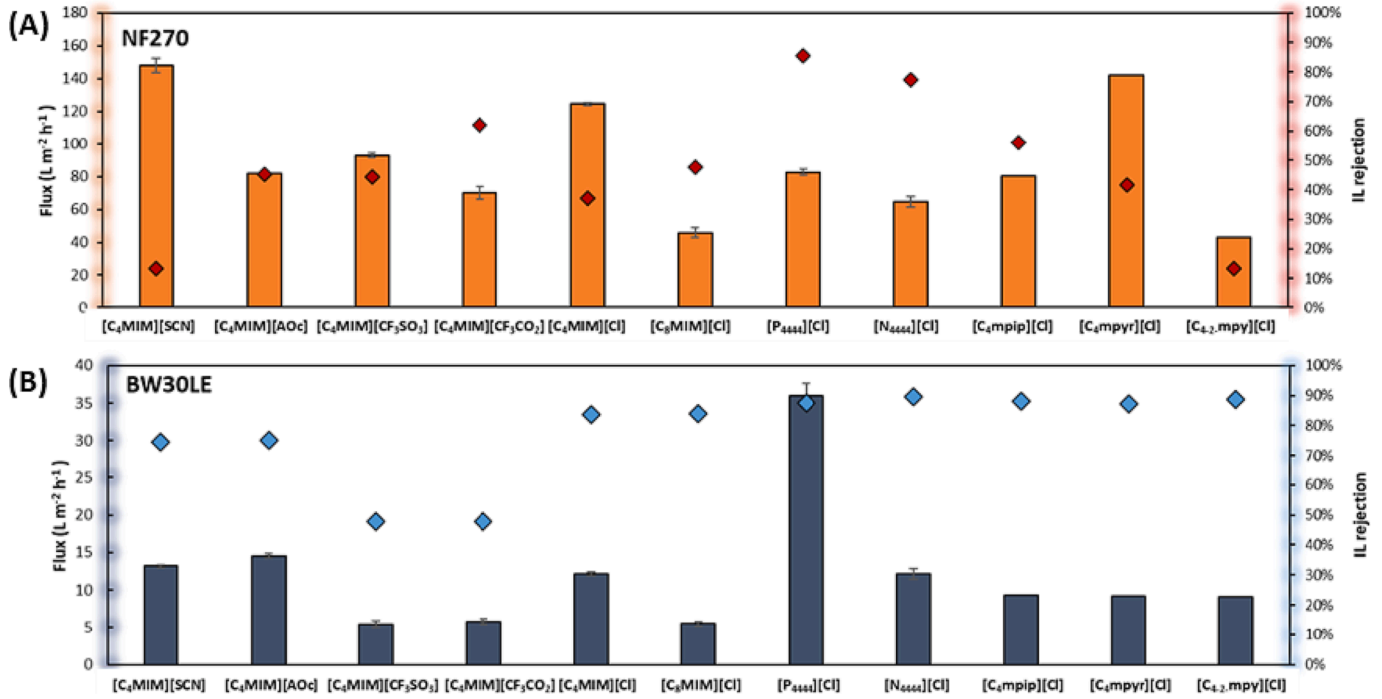


Fig. 2. Effect of ionic liquid on the **(A)** volumetric flux (■) IL rejection (◆) using NF270 and **(B)** volumetric flux (■) IL rejection (◆) using BW30LE. Conditions: solution of 1 wt% of 10 bar, 200 rpm at 298.2 K.

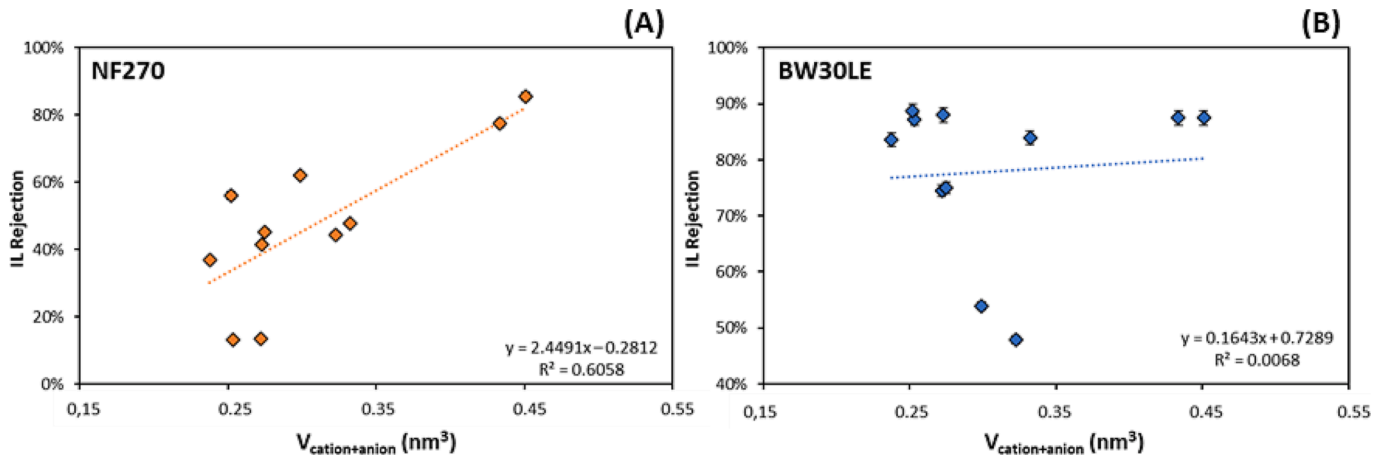


Fig. 3. Relationship between IL rejection of **(A)** NF270 (◆) and **(B)** BW30LE (◆) and IL volume. Conditions: solution of 1 wt% of 10 bar, 200 rpm at 298.2 K.

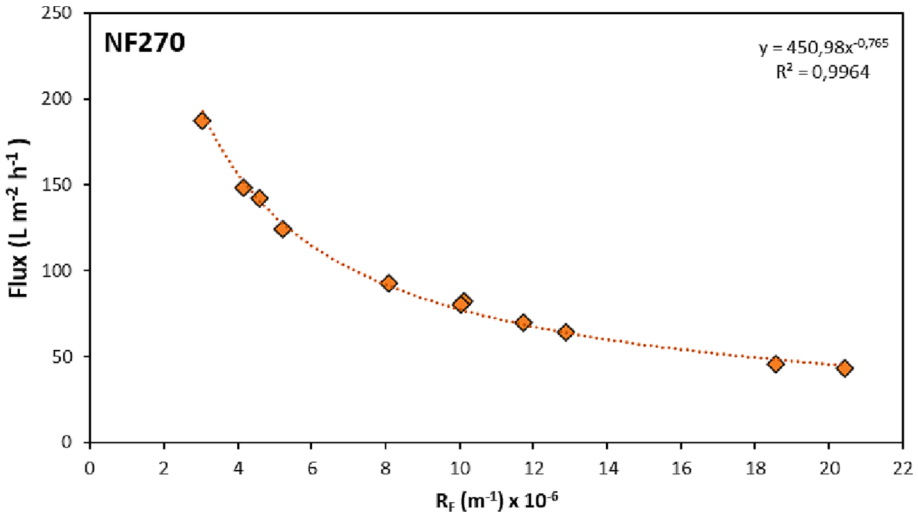


Fig. 4. Relationship between the volumetric flux of NF270 and filtration resistance (R_f). Conditions: solution of 1 wt% of 10 bar, 200 rpm at 298.2 K.

greater for high flows (>100 L $m^{-2}h^{-1}$). As for the region with a lower flow (<50 L $m^{-2}h^{-1}$), the increase in resistance is less significant.

Another determining factor for filtration efficiency is the osmotic pressure of the feed solution, which is dependent on the solute and solution concentration. When the osmotic pressure of the solution is high, it requires more pressure to force the water molecules through the membrane, which can lead to a lower efficiency of the filtration process. Haerens et al. [24] reported that the osmotic pressure was the restrictive factor for separating IL and water using RO and NF membranes.

In this study, the solute concentration was set at 1 wt%, so that it was

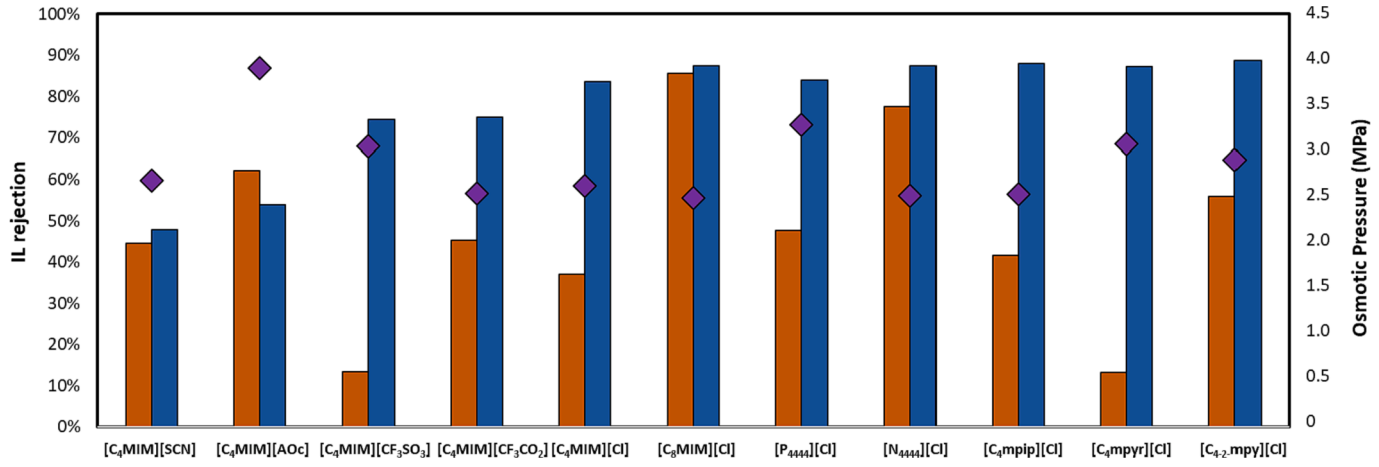


Fig. 5. IL rejection of (■) NF270 and (■) BW30LE, and (◆) omsotic pressure of IL solutions. Conditions: solution of 1 wt% of 10 bar, 200 rpm at 298.2 K.

possible to assess the influence of different cations and anions on the osmotic pressures of the ILs as shown in Fig. 5 (and Table S4).

In general, a trend has been noticed, where solutions with lower osmotic pressure tend to yield higher IL rejection values. As these are dilute solutions, the effect of type and IL is not prominent. It is important to note that the osmotic pressure of the solution is just one factor that can affect the efficiency of membrane filtration. Other non-sieving factors, such as the ionic charge density on the Donnan exclusion mechanism, can also affect the membrane efficiency. Furthermore, other contaminants in the solution may clog or damage the membrane. For this reason, the effect of the non-sieving mechanism was evaluated, specifically the Donnan exclusion, in the filtration of the different ILs, since the non-sieving mechanisms play an essential role for the charged solute, mainly in non-porous membranes, and there is the ionic charge interaction between IL (cation and anion) and the membrane [39,40].

Fig. 6 shows the correlation between membrane rejection rate and the IL anion volume. For the BW30LE membrane, there is a significant correlation ($p < 0.0001$) between IL anion volume and rejection. The larger the volume of the anion, the smaller the observed rejection.

This behavior is related to Donnan's exclusion mechanism. Since the BW30LE membrane is negatively charged (Table S2), it tends to repulse negative ions and allow positive ions to pass through [41]. Seidel et al. [42] evaluated the effect of loading saline solutions (NaCl, $CaCl_2$, Na_2SO_4). The authors found that ion rejection increased with co-ions with higher charges, and decreased with counter-ions with higher charges.

As the electrical charge of the IL anions is (-1), the volume of the anion is a controlling factor, as it impacts the charge density of the molecule. The greater the volume, the lower the charge density, that is, the lower the repulsion by the membrane.

As for the nanofiltration membrane (NF270), it was not possible to identify any trend. This behavior is related to the fact that, as discussed above and shown in Fig. 2, the membrane separation mechanisms of NF270 is dominated by the blockage of the pores during the filtration process. [43].

3.2. The effect of the pressure

To evaluate the effect of pressure on the filtration of aqueous solutions of IL two IL were selected: [C_4mim][AOc] and [P_{4444}][Cl]. This choice was made due to the distinct rejection behavior of these IL in membrane filtration, [C_4mim][AOc] (IL rejection > 47.7%) and [P_{4444}][Cl] (IL rejection > 85.5%) and a series of filtrations at different pressures (10, 20, 30, 40, and 50 bar) were performed. All tested systems showed a linear relationship between permeate flux and applied pressure as depicted in Fig. 7. The increase in pressure led to an increase in permeate flux. The rate of increase in flux with increasing pressure was predominantly limited by membrane type (NF or OR), while IL type having effect in the IL rejection, as will be discussed below. No irreversible fouling was observed during the experiments, as there was no change in the water flow measurements before and after filtration (Figure S3).

Regarding the IL rejection, it was observed, for both membranes, that it tends to increase with pressure, reaches a maximum around 30 bar and then tends to stabilize (formation of a plateau) (Fig. 7). This behavior, at first sight atypical, has already been reported by other authors [20,44,45]. The literature attributes this to the shielding phenomenon: part of the solute is adsorbed on the membrane, inducing the formation of a concentration polarization layer, which decreases the flow since, at low pressure, the surface forces are more intense than the drag forces [46,47]. Therefore, the IL flux remains low while the water flux increases with the pressure, increasing IL retention. Above 30 bar drag forces are likely to exceed surface forces. Consequently, solute transfer increases, and IL retention decreases. Furthermore, the concentration polarization phenomenon leads to additional resistance to transfer across the membrane due to an increase in the osmotic pressure of the solution [48].

Abels et al.[23] pointed out that the effect of pressure depends on the concentration of the IL solution. In evaluating the filtration of IL solutions (0 to 80 wt%) using nanofiltration membranes (Starmem 240, Desal DK, and Desal DL), the authors observed that increased pressure had a more significant effect at low concentrations of IL. As in the filtration of diluted solutions, the effect of the shielding phenomenon is more pronounced since the differences between the concentration of IL in the solution and the formed layer on the membrane is more significant in these cases. However, the effect of decreasing IL rejection cannot be seen only as a disadvantage. For example, for the filtration of [P_{4444}][Cl] using the NF270, the maximum IL rejection was 86.4% at a pressure of 30 bar. When the pressure was increased to 50 bar, the IL rejection was slightly reduced to 82.7%. But, on the other hand, the volumetric permeate flux increased about 1.5 times for the pressure of 50 bar. Therefore, even if there is a decrease in IL rejection, the increase in the permeate fluxes compensates this, making the process more efficient.

3.3. The effect of ionic liquid concentration

The separation of compounds by reverse osmosis and nanofiltration membranes depends on several factors (osmotic pressure, concentration polarization, membrane resistance, steric hindrance, Donnan effect, and dielectric effects) originating in a complex mechanism [49,50].

As shown in section 3.2, transmembrane pressure plays a significant role in separating IL and water at low IL concentrations, particularly in permeate flux. Since the water permeates the membrane more easily than the IL, an increased pressure leads to a greater water flow and

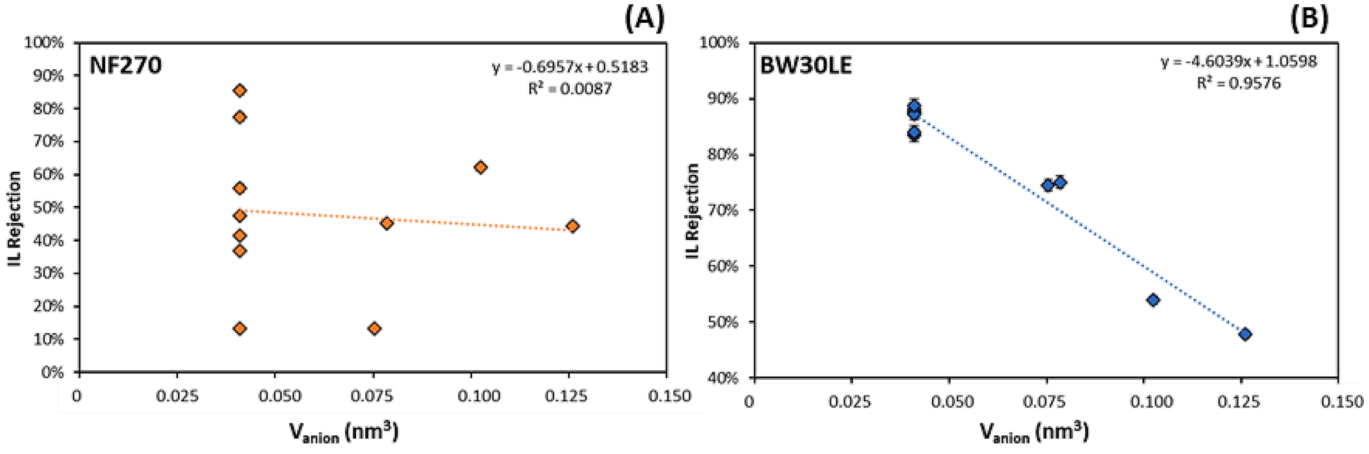


Fig. 6. Relationship between IL rejection of **(A)** NF270 (◆) and **(B)** BW30LE (◆) and IL cation volume. Conditions: solution of 1 wt% of 10 bar, 200 rpm at 298.2 K.

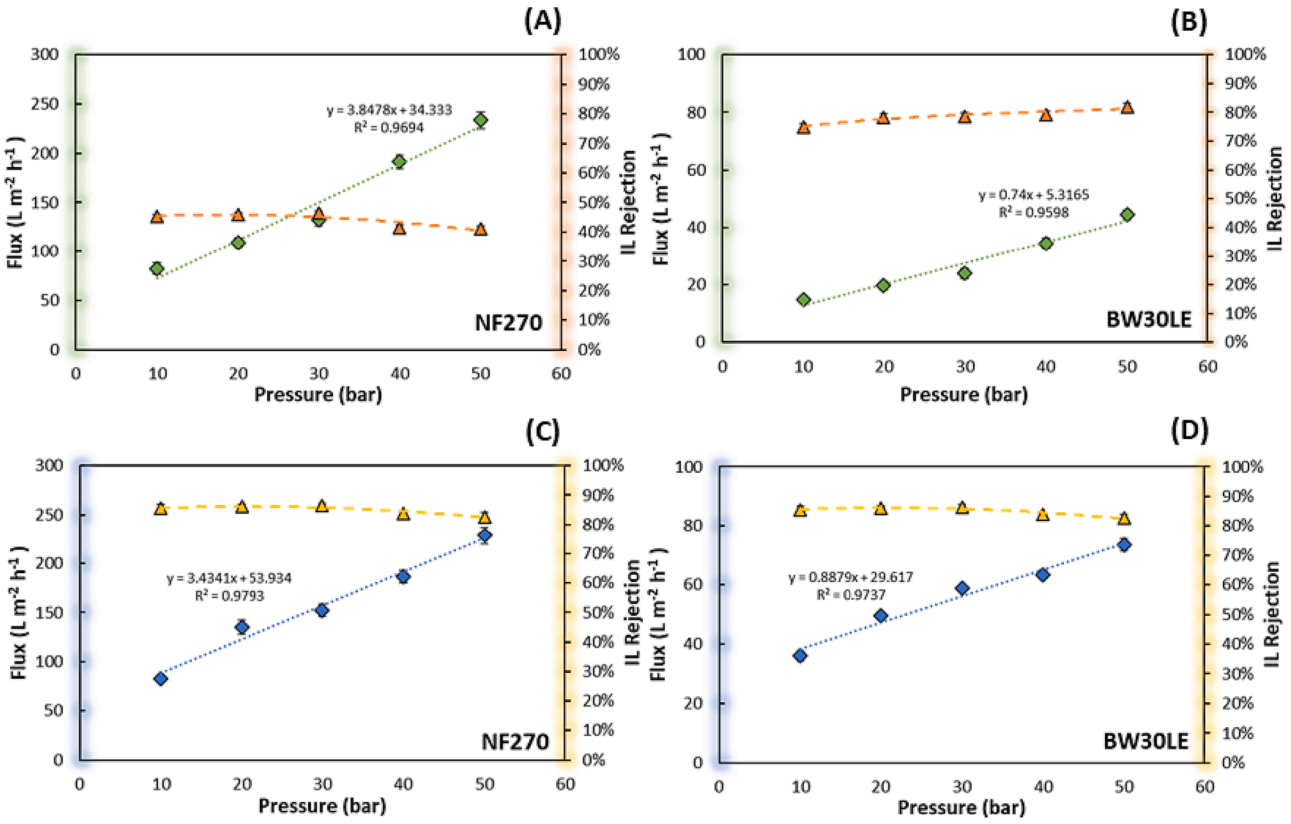


Fig. 7. Effect of pressure on the performance of [C_4mim][AOc] using **(A)** NF270 and **(B)** BW30LE, volumetric flux (◆) and IL rejection (▲), and [P_{4444}][Cl] using **(C)** NF270 and **(D)** BW30LE, volumetric flux (◆) and IL rejection (▲). Conditions: 1 wt% [mTBDH][OAc] or [mTBNH][OAc], 10, 20, 30, 40, 50 bar, 200 rpm at 298.2 K. Dashed lines are visual guides.

improved separation. However, the literature reports that the separation of IL from water depends little on the applied feeding pressure for high concentrations of IL [23].

In order to evaluate this effect on the studied membranes, the same two ILs ([C_4mim][AOc] and [P_{4444}][Cl]) were selected, and the effect of IL concentration on membrane performance (IL rejection and volume flow) is reported on Fig. 8. The increase in the IL concentration results in a decrease in the permeate flux, with non-permeation being observed in some cases ([C_4mim][AOc] 20 wt% - BW30LE).

When the [C_4mim][AOc] concentration was increased from 1 wt% to 10 wt%, a flux reduction from 186.4 L $m^{-2}h^{-1}$ to 22.6 L $m^{-2}h^{-1}$ was observed. Abels et al. [23] observed a reduction in permeate flux of the same order of magnitude for 1,3-dimethylimidazolium dimethylphosphate ([C_1mim][DMP]) in nanofiltration membranes (Desal DL and Desal DK) with an approximately five-fold reduction in flux being reported when the concentration of [C_1mim][DMP] was similarly increased from 1 wt% to 10 wt%.

The increase in the viscosity of the feeding solution can explain this behavior [51]. In addition, the high concentration causes the solute to be adsorbed onto the membrane, accumulating in the pores, thus inducing a more significant concentration polarization layer and lower permeate flux [52]. This phenomenon is characteristic of this type of membrane and is known as the shielding phenomenon [53]. Furthermore, the higher the concentrations of the IL solutions, the more significant the difference between the feed and permeate concentrations. The increase in IL concentration increases the osmotic pressure of the IL solution (Figure S2). The higher osmotic pressure of the IL solution entails the requirement to apply higher transmembrane pressure to overcome the difference in osmotic pressure between the feed and permeate solutions.

Regarding the IL rejection, a decrease was observed with increasing concentration. On the other hand, an increase in IL rejection for the 5 wt % solutions was observed. This phenomenon has been reported before [20,54] for other ionic liquids and different membranes. The authors also attributed this behavior to the shielding phenomenon.

The shielding phenomenon tends to be weak at low concentrations (<5 wt%), so a high IL rejection is expected. However, the volumetric permeate flux obtained for the 1 wt% IL solution is much higher (≈2x for NF270 and ≈3x for BW30LE). In this case, the drag forces overcome the surface forces, reducing the rejection of IL [45]. For high concentrations of IL, the volumetric flow is smaller, the drag forces do not overcome the surface forces, and therefore the potential of the membrane weakens [20]. These results show that the IL concentration plays a key role in the membrane performance, changing the membrane characteristics, resulting in a significant decrease in permeate flux and reducing the IL rejection.

3.4. Temperature effect

Previous studies have demonstrated that some factors of nanofiltration and reverse osmose membrane can affect the targeted compound rejections [55]. The use of additional forces to aid filtration has recently gained increasing attention [56]. This study evaluated so far the effect of IL cation, anion, IL concentration, and transmembrane pressure effect. In addition, another significant factor is the temperature of the solution, since the temperature of the feed solution plays an important role in the viscosity of the solution, water flux and pore size of membranes [57,58].

The temperature effect on nanofiltration and reverse osmose filtration of [C4mim][AOc] and [P_{4444}][Cl] solution are shown in Fig. 9. It is possible to observe an increase in the flux with the increase of temperature from 298.2 K to 313.2 K. This flux increase is related to the expansion of the membrane pore in addition to the reduction of solvent viscosity and increasing ion diffusivity [20]. Hai et al. [59] reported a 13% increase in the pore size of the NF270 membrane (from 0.39 nm to

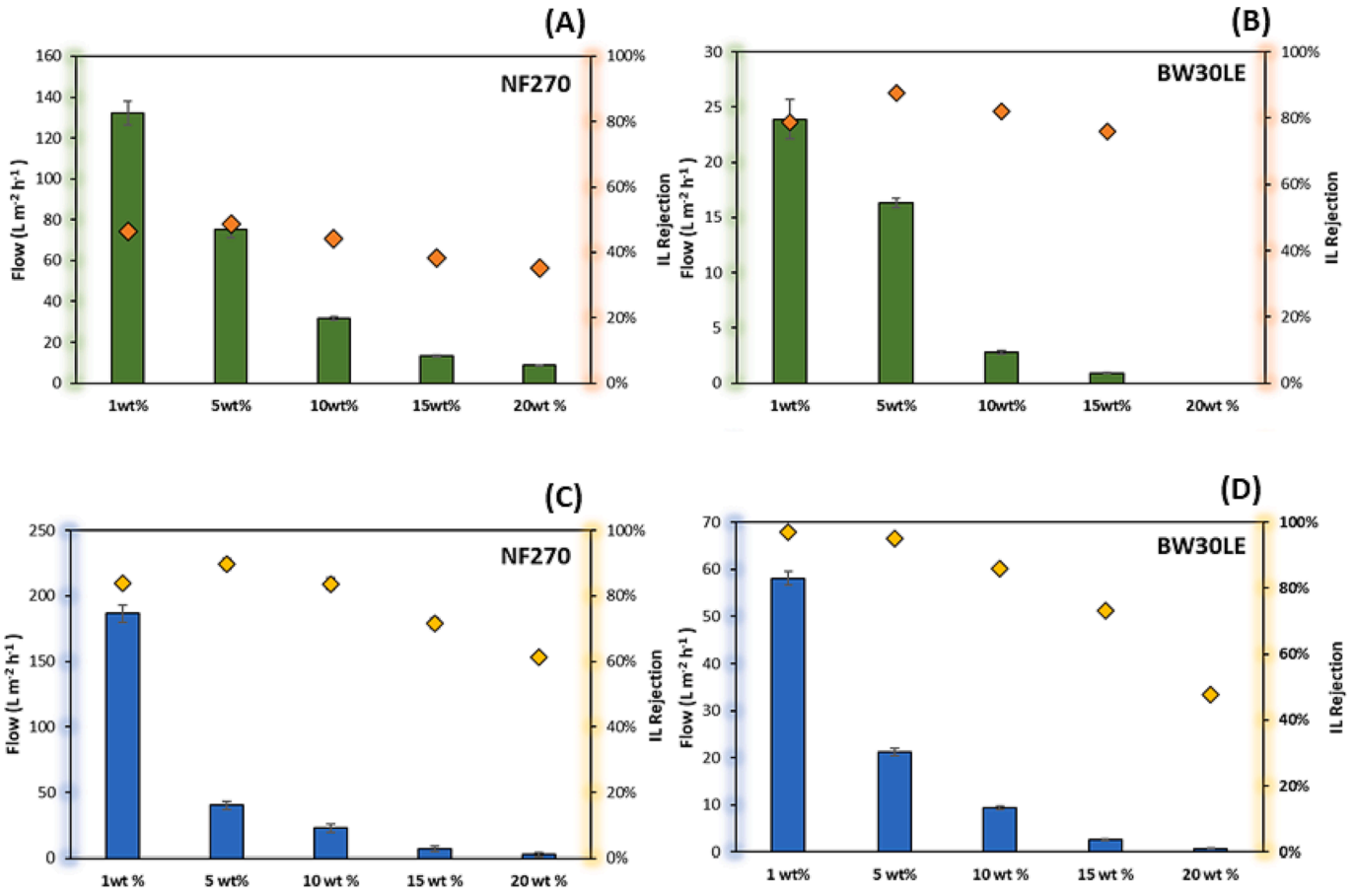


Fig. 8. Effect feed IL concentration on the performance of [C_4mim][AOc] using **(A)** NF270 and **(B)** BW30LE, volumetric flux (■) and IL rejection (◆), and [P_{4444}][Cl] using **(C)** NF270 and **(D)** BW30LE, volumetric flux (■) and IL rejection (◆). Conditions: 1, 5, 10, 15, 20 wt [C_4mim][AOc] or [P_{4444}][Cl] 200 rpm at 30 bar and 298.2 K.

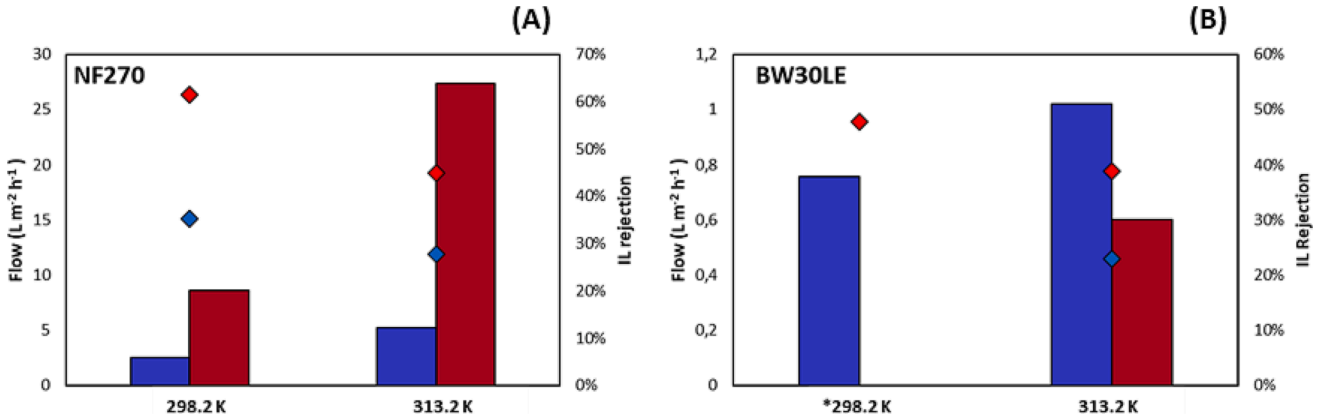


Fig. 9. Effect temperature on the performance of **(A)** NF270 and **(B)** BW30LE (right): volumetric flux (■) [C_4mim][AOc] and (■) [P_{4444}][Cl],and IL rejection (◆) [C_4mim][AOc] (◆) [P_{4444}][Cl]. Conditions: 20 wt% [C_4mim][AOc] or [P_{4444}][Cl] 200 rpm at 40 bar and 298.2 or 313.2 K.*No flux was observed under these conditions.

0.44 nm) with increasing temperature from 293.2 K to 313.3 K.

Typically, an increase in temperature leads to an increase in permeate flux, as observed. However, the increased flux at higher temperature may lead to a potential obstruction of the membrane pores (by fouling), and reduce the membrane's hydrophobicity, which affects its wetting behavior [60,61]. It is, therefore, important to follow the manufacturer's guidelines and not expose the membrane to temperatures above the recommended limit.

On the opposite, the IL rejection decreases with increasing temperature. This behavior is also related to the increase in the membrane's pore size, allowing greater permeation of the IL and consequently reducing rejection. Studies reported in the literature have also shown that membrane surface charge densities change substantially with increasing temperature. [41,59] Xu et al. [62] observed that relatively more negative surface charge densities of membranes with increasing temperature might also cause less electrostatic repulsion between

positively and neutrally charged compounds and the membrane surface, thus resulting in lower rejections. In addition, the diffusion coefficients increased with increasing temperature (278.5 K to 298.2 K), which leads to an increase in the diffusion capacity through the membranes and, consequently, a reduction in rejection [59].

In general, the temperature favors the flow but decreases IL rejection, mainly in the high concentrated samples (20 wt%) [20]. These effects are related to the modification of the membrane properties in combination with changes in the properties of the solution.

4. Conclusions

Two membranes, a nanofiltration (NF270) and a reverse osmosis (BW30LE), were investigated for separating eleven ionic liquids from aqueous solutions. The influence of cation and anion on the separation of ILs was evaluated, and relationships were found to describe the filtration behavior of aqueous solutions of ILs. For the reverse osmosis membrane, it was possible to correlate the IL rejection with the IL anion volume, the Donnan exclusion mechanism being identified as the limiting factor. As for the nanofiltration membrane, the limiting factor was identified as a combination of sieving and adsorption of IL in the membrane surface, which can be related to the size of the molecule, and it was possible to correlate the IL rejection with the IL molecular mass and IL volume.

For both membranes, the permeate volumetric flux increased linearly with increasing pressure, however, the rate of increase depends on the type of membrane. A flux reduction was observed at high IL concentrations. This drop in the permeate flux is related to the greater permeability of the IL as well as the increase in the osmotic pressure of the solution. It was found that an increase in temperature provided an increase in the permeate volumetric flux. However, it affected the IL rejection. Again, the presence of osmotic pressures prevented a higher permeation rate.

When selecting a filtration method, various factors come into play, including rejection, flow rates, economic efficiency, and other application-specific requirements. These factors collectively determine the most suitable filtration method for a given system. Understanding the nature of the contaminants, desired flow rates, and economic considerations is crucial in making a right decision about the filtration method that best aligns with your specific needs. Ultimately, considering all these factors ensures the selection of an appropriate filtration method that optimally meets the requirements of your application.

The results obtained in this work highlight the challenges in recovering ILs from aqueous solutions, mainly hydrophilic ILs. Furthermore, it presents a set of data and information that contribute to designing the best process to recover them.

CRediT authorship contribution statement

Filipe H.B. Sosa: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft, Visualization. **Pedro J. Carvalho:** Conceptualization, Methodology, Writing – review & editing. **João A.P. Coutinho:** Conceptualization, Data curation, Writing – review & editing, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2023.124341.

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