Bulgarian Chemical Communications, Volume 54, Issue 2 (pp. 141-146) 2022 *DOI: 10.34049/bcc.54.2.5461*

Flux and separation efficiency in nanofiltration with mixed solvents

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Received: November 30, 2021; Revised: May 11, 2022

Membrane processes meet the requirements for efficient and cost-effective separation methods, although they still have to solve challenges such as insufficient selectivity. The quality of separation is a problem particularly relevant to mixed solvents (ex. water-alcohol mixtures) given their numerous applications such as: extraction of bioactive molecules from renewable sources (plants, seaweed, by-products from the agro-food industry); separation of ethanol from water-ethanol systems. Achieving high flux and rejection is a major challenge for the membrane separation in view of alcohol recovery, production of low-alcohol beverages and others.

This article presents a brief overview of research in the field of mixed solvents nanofiltration, experimental evidence and theoretical interpretation of the observed effects. Own results with NADIR NP030 P membrane are presented. Model water-alcohol mixtures, as well as red wine (Mavrud) nanofiltration are investigated in view of flux and separation behavior relative to ethanol. Lower flux is observed with water-ethanol mixtures as compared to water. Improved separation efficiency towards ethanol and higher permeate flux is observed with increasing transmembrane pressure.

Keywords: nanofiltration, mixed solvents, ethanol separation.

INTRODUCTION

Solute concentration and solvent recovery are among the most important implementations of membrane separation. The traditional practice in this field requires an essential energy input (up to ~50% of the energy required in the production process) [1, 2], while membrane filtration, used either alone or in combination with traditional processes, results in significantly reduced energy consumption. Furthermore, the target molecules, extracted from natural sources, or involved in the pharmaceutical production are often thermally labile, which allows to take advantage of membrane technologies that do not require elevated temperatures. In the field of extraction of bioactive compounds, the use of mixed solvents benefits from their high selectivity, but has to be considered together with the problem of their subsequent separation and the requirements for green technologies.

The transport of neutral and charged molecules across membranes (nanofiltration, reverse osmosis) in hydro-organic media has been poorly studied, both experimentally and theoretically. The effect of the solvent composition and its subsequent separation, as well as the achievable flux and rejection of other organic substances from such solvents, are matters of essential importance. A solution to the problem of membranes selectivity towards mixed solvents is sought in the direction of: new membranes; membrane processes; integration of several membrane processes [2].

As for the membrane material, the introduction of polymers and hybrid materials with improved permeability, selectivity, and long term stability are regarded as promising. Examples for synthesis and optimization of membranes for highly selective separations can be found, focused on solvent-resistant nano- and reverse osmosis membranes (OSN and OSRO) treatment of mixed solvents. In [3] a polyketone-supported polyamide was proposed with highly improved separation factor towards methanol/toluene solvents. Another successful membrane for binary solvent mixtures separation is proposed, based on the glassy amorphous copolymer (perfluoro-2,2-dimethyl-1,3-dioxole copolymerized with tetrafluoroethylene, (PDD-TFE), supported on an e-PTFE) [4].

Commercial OSN membranes (MPF, StarMem, DuraMem) were studied in view of separation capability towards a number of binary solvent mixtures with different physical and chemical properties [5, 6]. The membrane behavior (flux, contact angle, Hansen solubility parameter) was studied for a number of polyimide membranes in presence of a mixed solvent (hexane-isopropanol, hexane-ethanol) and compared to the pure ones (hexane, i-propanol, ethanol) [7]. A recent study compared the behavior of the NF 270 membrane (polypiperazine-amide) when filtering water-alco-

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holic (methanol, ethanol, isopropanol) mixtures over a wide range of alcohol content and physicochemical characteristics: molecule size, hydrophobicity, Hansen-Hildebrand solubility parameters [8]. Fluxes and rejections were studied for binary mixtures, showing that hydrophilicity/ hydrophobicity and porosity of the membrane have greatest importance with respect to solvent permeability, as well as viscosity and polarity of the solvent mixture [9].

Some successful results have been reported for selective separations of binary and ternary solvent systems, such as water-alcoholic mixtures (methanol, ethanol, isopropanol) [8, 9]; binary alcoholic mixtures - methanol–ethanol [9]; ethanol–NMP, ethanol–DMSO; methanol–DMSO, methanol–NMP, toluene–methanol, toluene–NMP, toluene–DMF [4], methanol, toluene, pentanol, hexane binary and ternary mixtures [3], etc.

Regarding the separation mechanism, the size exclusion has to be considered together with several other important factors resulting from the physico-chemical properties of the solute, the solute-membrane and solvent-membrane interactions, the membrane structure, etc. [1]. The important parameters are dielectric constant, surface tension, Hansen solubility and viscosity of the solvent. Concerning the dielectric constant and the Hansen solubility parameter, some authors report larger differences between the two solvents and smaller differences between the membrane and one of the solvents as favorable for a preferential permeation, resp. an improved separation to be observed [5]. Hydrophobic membranes, corresponding to low values of surface tension, are expected to have a small flux for solvents with high surface tension values and *vice versa* [5].

Nanofiltration from a hydro-organic solvent usually results in a lower permeate flow and a lower rejection of the target compounds compared to their values in aqueous medium. The explanation is sought in factors such as different viscosity, molar volume, surface tension, change in the polarity and the dielectric constant of the solvent and swelling of the membrane. In a binary solvent mixture, a preferential solvation results in different surroundings of the molecule, the effect being dependent on the relative amounts of the two solvents. The solvation of the solute and of the pore wall (swelling) affects solute rejection and the partial permeabilities of the components [9]. Polarity changes the solvation of the solutes and their size, while swelling can affect the effective pore size of the membrane.

A number of publications have considered the extraction of biologically active compounds from mixed solvents [10, 11], but the role of the latter in the membrane separation is rarely commented on. Example of such research, where several membranes (based on polyamide and polypiperazine-polyamide) are studied, is given in [12]. Nanofiltration and reverse osmosis of water-ethanolic solutions containing glucose, proline, tyramine and tartaric acid have been performed. Solvent recovery from micro algae oil-solvent miscellas using OSN membranes was also concerned in view of its potential for industrial application in the oleochemistry [7]. Measured rejections of microalgae oil dissolved in different pure or mixed solvents are presented, highest values being obtained for hexane and hexane-i-propanol (3:2) mixtures depending on the membrane type. In [13] purification of omega-3 by nanofiltration was performed and the membrane behavior towards phospholipids and triglycerides from herring roe extract was studied, where dry extract was dissolved in a solvent with different water/ethanol ratio. Another field of membrane application to water-alcoholic systems is focused on the correction of the ethanol content in alcoholic beverages such as wine and beer. According to the properties of the different membranes, membrane technologies are applied both for wine concentration and for reduction of its alcohol content [14, 15]. Thin-film polypiperazine membrane XN45 has been used for red wine concentration [15]. RO98pHt M20 and NF M20 membranes were found suitable for red wine content and aroma enhancement or correction [14]. Reported results after NF or RO treatment are found successful with respect to the whole bouquet of flavors, antioxidants and other biologically active substances.

The effect of the alcoholic content in membrane filtration from water-alcoholic solvents is related both to the observed permeate flux and rejection. The significance, as well as the direction of this effect depends on the affinity of the alcohol for the membrane as compared to water. Polar solvents show lower permeate flux with hydrophobic membranes and higher when using hydrophilic ones; observed rejection coefficients of neutral molecules in organic solvents are usually lower than in aqueous media.

The impact of alcohol presence in water/alcohol mixtures affects the concentration polarization through viscosity and osmotic pressure; the observed mass transfer coefficients are of the order of 10^{-5} m/s [8] and decrease with increasing alcohol content. Commonly used are diffusion coefficients for highly dilute aqueous media, while knowledge of their actual values often remains outside the scope of the study. The thickness of the concentration polarization layer when filtering with water-alcoholic solvent is estimated at 1–2 µm to 6–8 µm depending on the method used. Fluid viscosity and osmotic pressure influence the concentration polarization in opposite directions.

When nanofiltrating mixed solvents, mutually compensating phenomena may occur. For instance, at higher alcohol content (above 20-30%) the observed resistance of the membrane remained constant because of the simultaneous increase of the pore size and the thickness of the membrane [8]. The latter is due to swelling of the polymer membrane and a changed mobility of the polymer chains. The calculation of the diffusion coefficients in solvent swollen membranes must be approached with care, accounting for the effects of the frame of reference and thermodynamic non-idealities. This also applies to the possibility for development of structure-property correlations and the design of membranes [1].

From a theoretical point of view these phenomena are poorly described. The final effect on permeate flux and selectivity can be observed, but is difficult to model and predict. Experimental observations for binary solvents separation with a number of membranes (MPF, StarMem and DuraMem) and solvent mixtures with different physical and chemical properties were modelled, the Hansen solubility parameters and polarity of membranes and solvents being the main factors affecting the separation [5, 16]. The modelling approach most often referred to the classical solution-diffusion theory [3, 4, 16]. Improved solution-diffusion model, specifically for solvent separation process in OSN, integrating the Hansen solubility parameter and the dielectric constant were proposed [5, 16]. Specific models for pure and mixed solvent flux, allowing the prediction of solute rejection in pure and mixed solvents were developed and tested with a number of experimental data and commercial OSN membranes (Puramem) [17, 18]. The filtration of water-alcoholic mixtures was satisfactorily modelled by the model of Spiegler and Kedem combined with the film theory [8]. The Spiegler – Kedem approach for multicomponent systems works with the differences in chemical potential on both sides of the membrane and does not directly involve interactions such as solute-membrane, or diffusion across the membrane.

The aim of this study is to present a brief overview of research in the field of mixed solvents nanofiltration, as well as own results for nanofiltration of model water-alcohol mixtures and red wine (Mavrud) with membrane NADIR NP030 P.

EXPERIMENTAL

The present investigation is focused on water-ethanol separation with model solutions, as well as preliminary experiments with red wine (Mavrud) nanofiltration. Flux behavior and separation ability of the membrane relative to the ethanol is studied.

A laboratory membrane filtration unit, (MaxiMem, Prozesstechnik GmbH) with a rectangular flat-sheet membrane of 215 cm^2 active area was used, Fig. 1. The experimental conditions for operating pressure, temperature, permeate flux, were precisely controlled and recorded for further analysis. Temperature regime with cooling was applied for red wine and ethanol-water model solutions.

The membrane (Microdyn Nadir™ NP030 with MWCO 500 Da) was subjected to previous adaptation with the solvent until constant flux. Cross-flow velocity of 1.2 l/min and transmembrane pressure of 10 bar was used as initial set of experimental conditions. The same initial feed volume ($V_f = 750$) and final permeate volume ($V_p = 0.6\ V_f$) were kept in all experiments. Samples were taken after every 10 ml permeated volume.

Feed concentration (C_f), final average concentration in the retentate (C_r) and in the cumulative permeate volume (C_p) were measured in order to estimate the final ethanol distribution C_p/C_r between the retentate and the permeate.

Fig. 1. MaxiMem membrane filtration unit

Ethanol-water model solutions with different ethanol concentrations in the range of 0 to 80% were subjected to nanofiltration. Dry red wine Mavrud was used in a preliminary set of experiments to check the separation ability in the presence of a complex composition and a number of biologically active substances. The red wine composition before nanofiltration is certified as follows: Specific gravity - 1.0495; Alcohol - 13.0 vol.% EtOH; Sugar - 0.99

g/l; Total dry extract - 29 g/l; Total acidity - 4.58 g/l, Citric acid - less than 1.0 g/l; Volatile acidity - 0.41 g/l; Free SO_2 - 30.99 mg/l; Total SO_2 - 91.0 mg/l; Metals harmful to health - Iron - 0.01mg/l.

Ethanol concentration was quantified by HPLC analysis. Samples were analyzed on a chromatographic system consisting of a pump Smartline S-100 Knauer, refractometric detector - Perkin-Elmer LC- 25RI, column Aminex HPX-87H, Biorad, 300 × 7.8 mm and specialized software EuroChom, Knauer. 0.01 N H_2SO_4 was used as mobile phase, at a flow rate of 0.6 ml/min. The temperature of the column was maintained at 65 °C. The standard deviation of the analysis didn't exceed 1.5%.

RESULTS AND DISCUSSION

The experimental results with model water-ethanol solutions prove a pronounced decrease in the permeate flux (J, l $m^{-2}\cdot h^{-1}$) up to 20% ethanolic content, afterwards an increase is observed; however the flux remains much lower than the one in water, Fig. 2. Similar observations in the same concentration range are reported in [8]. The concentrations of ethanol in the permeate (C_p) and the retentate (C_r) in the model solutions remain close to each other, the ratio C_p/C_r being lower than 1. A trend to slight increase of the observed retention with the ethanol content is noticed (Fig. 3).

It was further investigated how this behavior is changing when filtering a complex multicomponent water-alcohol system.

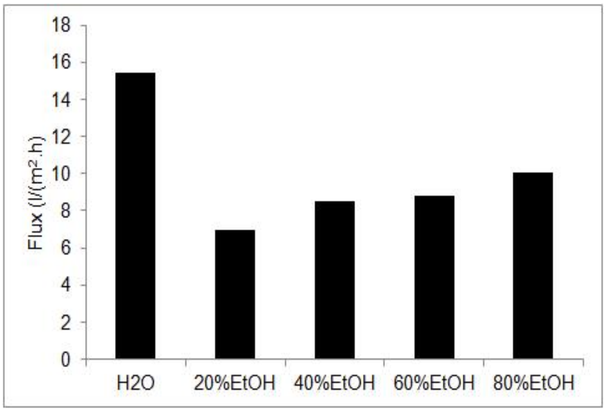

Fig. 2. Permeate flux *vs* ethanol content in the model solutions.

Wine filtration experiments show a much lower permeate flux as compared to the model solutions, so the effects of transmembrane pressure and cross-flow velocity were explored in order to improve the flux behavior, Figs. 4a and 4b.

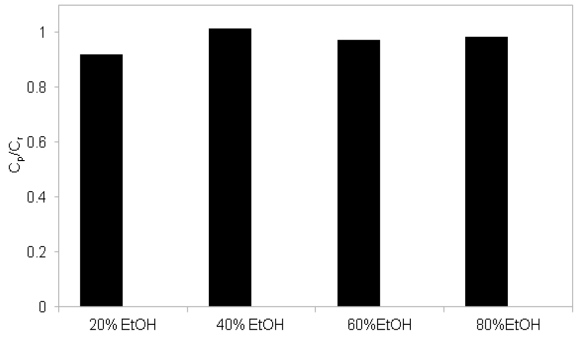

Fig. 3. Ethanol concentration ratio in permeate and retentate depending on the ethanol content in the model solutions.

Effect of transmembrane pressure

In wine filtration at 10 bar, the observed low permeate flux tends to decrease during the experiment due to progressive membrane fowling. The value 0.63 l/(m^2.h), obtained for 10 bars refers to a much lower filtered volume (V_p/V_f=0.08) as compared to the rest of the data. For this reason, higher transmembrane pressures were preferred.

Wine filtration in the range of 10 to 50 bar has shown about a fivefold increase of the permeate flux, the dependence being linear (Flux= 0.053×Pressure, R^2=0.99). No effect of membrane compressing at higher transmembrane pressure is observed. These results together with the observed linear time evolution of the permeated volume - R^2>0.99 for transmembrane pressures 20 to 50 bar - confirm that favorable hydrodynamic conditions are assured in all filtration experiments. Fouling effect was observed at lower pressure (10 bar) and was reversible. The membrane regains its characteristics after washing and good reproducibility of the measured flux is observed on repeated experiment. This is illustrated in Fig. 4a with the measured permeate fluxes at 20 bars.

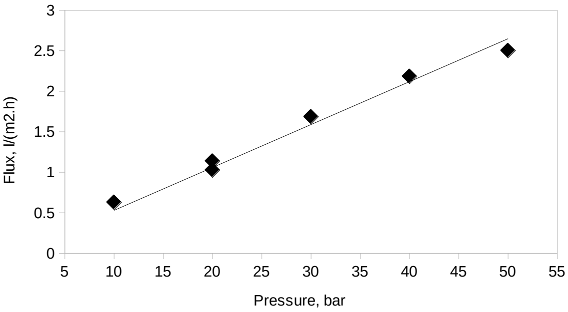

Fig. 4a. Permeate flux *vs* transmembrane pressure

Effect of cross-flow velocity

Cross-flow velocity can effectively influence the filtration process by reducing possible concentration polarization and fouling and improving the conditions for higher and stable permeate flux. Three different cross-flow velocities were applied – 1.2, 2 and 3 l/min. The rest of the conditions were transmembrane pressure 30 bar and permeated volume $V_p=0.6V_f$ (V_f=750 ml). The observed flux is less sensitive to change in the cross-flow velocity. A more significant increase is observed at 3 l/min, but the improvement of the permeate flux does not exceed 15%. An illustration of the flux behavior with different cross-flow velocities is given in Fig.4b.

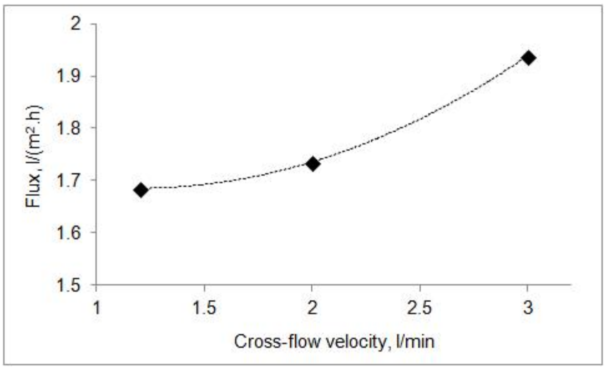

Fig. 4b. Permeate flux vs cross-flow velocity

The tendency of the membrane to retain ethanol is more pronounced in the multicomponent medium than in the model solutions and increases with applied pressure. No noticeable effect of the cross-flow velocity on the C_p/C_r ratio is observed. Fig. 5 illustrates the ethanol distribution between retentate and permeate, where C_p and C_r are average permeate and retentate concentrations.

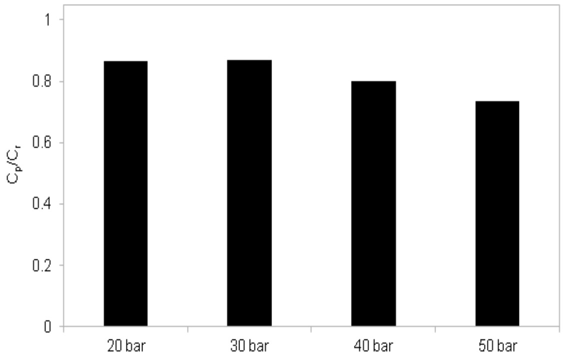

Fig. 5. Ethanol concentration ratio in permeate and retentate for wine filtration.

Results on wine concentration towards ethanol using a membrane with a similar MWCO and separation behavior have been published in [15]. The resulting permeate and retentate have been found useful in the alcohol industry. The observation that both permeate flux and ethanol retention increase with the operating pressure was found in [19].

As a compromise between energy input for pressure and cross-flow velocity on the one hand and flux and membrane separation efficiency on the other, we preferred the following set of experimental conditions to be maintained in the studies: transmembrane pressure 30 bar, cross-flow velocity 1.2 l/min, temperature 19 °C. The check of the material balance for the before mentioned experimental conditions was fulfilled, the error being 0.24%. It was calculated as a percentage of the initial ethanol mass following the equation: $V_fC_f=V_pC_p+V_rC_r$. In general, there are two sources of error in the experiments performed - retention of a small part of the retentate volume in the system (check of $V_f=V_p+V_r$) and insufficient prevention of alcohol loss during the experiment due to its volatile nature. Our experience showed errors up to 10-12% if these considerations are not taken into account.

CONCLUSIONS

Water-ethanol separation of model solutions with nanomembrane Microdyn Nadir™ NP030 showed lower permeate flux as compared to water and a retention tendency, which is slightly increased with the ethanolic content. In the presence of higher viscosity and complex multicomponent composition, the permeate flux is essentially reduced. However, it can be significantly improved by applying higher pressure and/or cross-flow velocity. The former has stronger effect on both permeate flux and ethanol retention. Their increase with operating pressure, as well as with cross-flow velocity is shown in nanofiltration of red wine Mavrud. The obtained results have to be interpreted in the context of the rest bouquet of biologically active substances contained in the wine, including their antioxidant activity.

Acknowledgement: *The authors acknowledge with gratitude the financial support from the Bulgarian Science Fund, Ministry of Education and Science under Contract No KP-06-N47/1/26.11.2020.*

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