



Solvent resistant nanofiltration for acetonitrile based feeds: A membrane screening



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ABSTRACT

A range of commercially available and lab-made membranes was screened for use in feeds containing acetonitrile (ACN). ACN was selected as it is one of the most widely used solvents in pharmaceutical industry and surprisingly absent in earlier studies on solvent resistant nanofiltration (SRNF). The selected membranes ranged from the tight nanofiltration range to the lower end ultrafiltration range, prepared from different membrane chemistries and with different membrane preparation methods. Multiple dyes were tested as probe molecules to study the retention behavior of the membranes in ACN. Gel content measurements were conducted on the membranes and interaction parameters with ACN, the dyes and the membranes were calculated to link physico-chemical properties to separation performances. ACN was found to be a very appropriate solvent for SRNF applications, as most membranes reached high fluxes and retentions, comparable to those obtained in most other solvents. As most membrane polymers did not dissolve in ACN, membrane crosslinking is not even strictly necessary to ensure stability of the membranes when applied in these feeds. This study thus showed that for ACN-based solutions, many different types of SRNF membranes can potentially be selected to achieve the aimed separations.

1. Introduction

Solvent resistant nanofiltration (SRNF), also known as organic solvent nanofiltration (OSN), is an emerging technology that performs separations between molecules in organic media. This technique has great potential as an energy-efficient and waste-free separation method [1–3]. Research is ongoing in various fields that require separations in organic solvents, such as in petrochemistry [4,5], food processing [6,7] and catalysis [8–12]. Most membrane tests are still run on lab-scale, but some are already operational on pilot-scale and even on industrial, full-scale [13,14].

SRNF membranes show varying performances when used in different solvents [15,16]. One of the solvents that has not yet been investigated thoroughly for SRNF is acetonitrile (ACN), a very common solvent in pharmaceutical and chemical industry. ACN is a polar aprotic solvent, considered as key solvent for industry [17]. It is commonly used as extraction solvent, HPLC-eluent and in organic synthesis. ACN has a medium polarity, high solubility in water and is relatively inert. One of the best known, large-scale applications of ACN is its use in the purification of 1,3-butadiene where it extracts this diene from crude butadiene mixtures [18]. It is used for several organic synthesis pathways as it is a very good solvent for many chemicals. ACN is most

widely used in the pharmaceutical industry, which accounts for 70% of the total ACN use. It is believed that consumption of ACN for pharmaceuticals will continue to grow during the next years [19]. Since the market is vulnerable to fluctuations, as shown by the shortage a decade ago following the shutdown of Chinese production [20], and aiming at the reduction of waste streams, recycling the solvent is recommended.

Many of the recycling methods for ACN proposed in patents involve distillation by mixing with hexane to achieve a favorable azeotrope [21], a combination of solvent extraction and distillation [22] or other distillation approaches [23,24]. It is opportune to consider SRNF membranes to recover the solvent by retaining the products or catalysts while letting ACN pass, considering the energy- and waste efficiency of SRNF.

With this in mind, a wide range of nanofiltration membranes were tested in ACN to get an overview of their behavior and suitability for use in this solvent. Membrane literature on ACN mainly focuses on pervaporation, which has been applied on multiple occasions to separate ACN from water. Dense PDMS, PVDF and PTFE membranes [25] as well as thin film composites [26], zeolite-filled [27] and nanocomposite [28] membrane systems have been screened for this application. As for SRNF membranes, little research has been reported

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using ACN-based feeds. Inorganic ceramic membranes [29] and carbon nanosheets [30] have been used for ACN nanofiltration, as well as polyimide, polyaniline and commercial thin film composite (TFC) membranes [31,32]. A thorough screening of several solutes and membranes has nonetheless not yet been performed.

For current study, the DuraMem® commercial membrane series (DuraMem150®, DuraMem200®, DuraMem300® and DuraMem500®) was tested together with other commercial membranes from SolSep (NF 080105, NF 070706, NF 030705, NF 090801 and NF 090101) along with a few lab-made membranes of diverse nature that are stable in ACN. These include membranes based on poly electrolyte complexes (PEC) [33,34], poly (ether ether ketone) (PEEK) [35], polysulfone [36] and polyamide TFC membranes [37]. To test the SRNF performance of these membranes, 6 dyes of varying molecular weight (from 314 to 1018 g/mol) and charge were dissolved in ACN. All membranes were screened in a high-throughput mode [38]. All membranes were also tested in pure ACN to obtain the pure solvent fluxes and gain more fundamental insight in the membrane behavior.

2. Experimental

2.1. Materials

The dyes that were used for filtration experiments are listed in Table 1. All dyes were dissolved in ACN (HPLC-grade, VWR) in a 35 μM concentration.

The materials used to prepare the lab-made membranes are listed per membrane in the following section. All water was deionized.

2.2. Membrane preparation

The lab-made membranes were prepared via commonly used methods, namely phase inversion, dip coating and interfacial polymerization (IP) [39,40]. Some relevant properties of these and the commercial membranes are shown in Table 2.

2.2.1. TBPEEK

These membranes were prepared from poly (ether ether ketone) modified with a tertiary-butyl group [35]. Solvents used in the polymer solution are N-methyl-2-pyrrolidinone (NMP, Acros) and tetrahydrofuran (THF, Acros). The polymer is dissolved in NMP/THF in a 50/50 ratio. The casting solution is stirred until homogeneous, kept overnight to degas and cast on a polypropylene/polyethylene (PP/PE) non-woven backing with a 250 μm thickness, kindly provided by Freudenberg (Germany). The cast film was left to evaporate for 30 s and transferred to a water bath at room temperature for coagulation. The membrane will be referred to as ‘TBPEEK’.

2.2.2. PEC

Two types of PEC membranes were prepared as described in Joseph et al. [34] following the layer-by-layer (LBL) method, with an automatic dipcoater.

Poly(diallyldimethylammonium chloride) (PDDA, Sigma-Aldrich, 20 wt% aqueous solution) as polycation and poly(sodium styrene

Table 1
Commercially available dyes used for ACN filtrations

Dye	Abbreviation	Origin	Absorption maximum in ACN [nm]	Charge
Disperse Red	DR	Fluka	487.5	Zwitterion
Methyl Orange	MO	Fluka	419.0	-1
Safranin O	SO	Acros	518.5	+1
Crystal Violet	CV	UCB	588.5	+1
Acid Fuchsin	AF	Fluka	549.0	Zwitterion
Rose Bengal	RB	Fluka	558.0	-2

sulfonate) (PSS, Sigma-Aldrich, 30 wt% aqueous solution) as polyanion are deposited on a hydrolyzed polyacrylonitrile (PAN, Scientific Polymer Products) support in 20 bilayers via the LBL method [34] and is referred to as ‘PDDA/PSS’, referring to the two polyions that are used for its synthesis.

The second PEC membrane consists of sulfonated poly (ether ether ketone) (sPEEK) as polycation and PSS as polyanion. Again, 20 bilayers were deposited on a hydrolyzed PAN support [33]. This membrane will be referred to as ‘sPEEK/PSS’.

2.2.3. PA

Psf support – Psf ultrafiltration membranes were prepared via phase inversion [39]. A homogeneous solution of 18.3 wt% Psf (dried overnight at 110 °C) in NMP was cast on a PE/PP non-woven, which was first impregnated with NMP. Spreading of the polymer solution was done at constant speed (77 mm/s) with an automatic casting device (Braive Instruments, Belgium). After casting, the 200 μm thick wet polymer film was immersed in distilled water. Membranes were rinsed and stored in distilled water.

Thin film composite – A thin PA layer was synthesized on top of the Psf support via interfacial polymerization (IP). A support layer was impregnated with a solution of 2 wt% *m*-phenylenediamine (MPD, Acros), 2 wt% triethylamine (TEA, Sigma-Aldrich) and 0.1 wt% sodium dodecyl sulfate (SDS, Acros) in water for 30 min. Before IP, excess aqueous solution was removed from the Psf membrane with a rubbery wiper. A solution of 0.1 (w/v)% trimesoyl chloride (TMC, Acros) in hexane was then gently poured on the impregnated support layer. The hexane solution was drained off after 60 s of polymerization and the synthesized TFC membranes were stored at room temperature to dry overnight, while kept in dark. Post treatment was done by putting the membranes 10 min in an oven at 50 °C. Finally, the membranes were stored in distilled water and in dark. The membrane will be referred to as ‘PA’.

2.2.4. Polysulfone

Polysulfone Udel P1835 (Solvay) pellets were dissolved in N,N-dimethylformamide (DMF, Sigma-Aldrich) and THF in a 70/30 ratio and with 21 wt% concentration. Thin films (250 μm) of membrane casting solutions were coated on top of a polyester non-woven support (Hirise 05TH100) at a speed of 2 m/min. After a 30 s evaporation step, the polymer films were transferred to a coagulation bath containing deionized water at room temperature [36].

2.2.5. Matrimid-based PI

The Matrimid-based PI membrane was prepared by making a casting solution of 22 wt% Matrimid in 50.4 wt% NMP as solvent and 25.2 wt% THF as a volatile co-solvent. As a low boiling point additive, 2.5 wt% acetone was added. The solution was stirred until homogenous and kept overnight to degas. A 250 μm thick polymer film was cast at a constant speed of 20 mm/s on a PP/PE non-woven support impregnated with NMP. After an evaporation time of 30 s, the film was immersed for 30 min in a coagulation bath containing 6 wt% 1,6-hexanediamine (HAD, Sigma-Aldrich) in distilled water for crosslinking. The membrane was post-treated in isopropyl alcohol (IPA) for 1 day and in IPA:glycerol (60:40) for 3 days. Long-term storage of the membrane took place in plastic containers containing distilled water [41].

2.2.6. Commercial membranes

Four types of membranes from the DuraMem series were kindly provided by Evonik. These membranes are DuraMem 150, 200, 300 and 500, for which the number stand for the MWCO value of polystyrene in toluene. These are crosslinked PI membranes, based on P84 polyimide. NF270 is a commercially available PA-based TFC membrane with a MWCO of 270, kindly provided by Dow.

SolSep recommended five membranes suitable for ACN filtrations. These are NF 080105, NF 070706, NF 030705, NF 090801 and NF

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