Hybrid ceramic membranes for organic solvent nanofiltration: State-of-the-art and challenges

Renaud B. Merlet, Marie-Alix Pizzoccaro-Zilamy, Arian Nijmeijer, Louis Winnubst

Inorganic Membranes, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE, Enschede, the Netherlands

Abstract

Uniquely suited to organic solvent nanofiltration (OSN) are hybrid, ceramic-based membranes. The stability of these membranes in the harsh solvents and conditions of industrial process streams is due to the sturdy and inert architecture of the ceramic, while the organic functionalization is responsible for surface and pore properties of the membrane, and hence its performance. Recently, this kind of inorganic-organic union has produced a plethora of stable and high-performance membranes in a variety of OSN conditions - the topic of this review. This work details and compares the surface modification methods used to fabricate these membranes and their resulting performance. Also, we discuss the capabilities and shortcomings of both the characterization tools and the transport models used to describe this class of membranes. Throughout we aim to provide insight into the challenges awaiting the researcher of hybrid, ceramic-based membranes for OSN.

1. Introduction

Membrane technology is the application of a selective barrier to separate components of interest, creating a product of added value for the user. A driving force, such as a pressure difference, separates the product from the feed mixture. Much of the research in membrane technology has focused on aqueous-based separations, for example, desalination or wastewater treatment [1,2]. However, upon exposure to organic solvent solutions most of these membranes do not possess the required durability or performance. Development of a new class of membranes destined for such harsh conditions has been spurred by in

Received 16 September 2019; Received in revised form 28 December 2019; Accepted 11 January 2020
Available online 15 January 2020

https://doi.org/10.1016/j.memsci.2020.117839

E-mail address: a.j.a.winnubst@utwente.nl (L. Winnubst).
alkoxylation compounds onto a γ-alumina support layer increased hexane permeability from 0.0 to 6.1 L m$^{-2}$ h$^{-1}$ bar$^{-1}$, while the same treatment reduced water permeability from 4.0 to 0.0 L m$^{-2}$ h$^{-1}$ bar$^{-1}$. Ever since, a plethora of existing chemistries have been ingeniously adapted to modify porous ceramic membranes for OSN, resulting in hybrid membranes which can maintain excellent permeation and retention properties.

Not only do we detail the fabrication, characterization methods and transport modeling of these membranes in this review, we have also analyzed and identified, to the best of our ability, the advantages and constraints of each, as well as the challenges that await the field of OSN as a whole. Both precise pore modification and the prediction of membrane performance remain challenging to the researchers of hybrid ceramic-based membranes for OSN. Specifically, there are two main obstacles: i) obtaining a consistently low (<400 Da) and specific molecular weight cut-off (MWCO) despite the limited pore size selection of unmodified ceramic membranes, and, ii) understanding the relations between membrane, solvents and solutes to accurately predict membrane performances. The formulation of a predictive transport model would enable a facile starting point for custom membrane fabrication; reaching a target retention would become a matter of fine-tuning the graft. Complicating this is the increased demand to be able to process solvent-containing aqueous streams such as produced water from natural gas fields. This emerging topic in OSN is called organic solvent-resistant nanofiltration (OSRNF). Treating mixed water-solvent streams combines the requirements of both water-based and OSN applications. There are no publications specifically on this topic, though several academic research groups have recently become involved. Similarly nascent fields, which are not discussed in this review, are organic solvent ultrafiltration (OSUF), dealing with larger solutes, or organic solvent reverse osmosis (OSRO), dealing with smaller solutes such as salts.

Naturally, the wide field of OSN has been examined in years past, either in a broader context than this review, or focusing on another subfield of OSN. The reader is invited to the following for an exhaustive overview of past research in this field. Marchetti et al. [3] thoroughly described advances from 2008 until 2014 in all of OSN, including the various efforts to model transport across these membranes. A review by Cheng et al. [10] reported the advances until 2014 of polymeric OSN membranes; Hermans et al. [11] covered a narrower subset of these, TFC membranes, in 2015. A different subset, polymeric OSN membranes embedded with inorganic fillers, was reviewed in 2018 [12]. OSN membranes having found use in the pharmaceutical industry were detailed by Buonomenna et al. [13] in 2014. Catalysis reactions aided by OSN membranes (as either product or catalysis isolators) were also reviewed recently [14]. A review by Szekely et al. [5] evaluated the sustainability of OSN technology including aspects related to membrane fabrication (preparation of NF ceramic support and conventional OSN membranes) and utilization. Ahmad et al. [15] reviewed the preparation of hydrophobic membranes for diverse applications, while Amirilargani et al. [16] reviewed the various ways to modify and functionalize both polymeric and ceramic membrane surfaces for OSN in 2016. Relevant to this review are two reviews by Buekenhoudt et al. [17,18], published in 2012 and 2014, respectively, detailing the methods used to diversify ceramic surfaces and their performance in OSN, gas separation and pervaporation applications.

As stated, the aim of this review is to provide a summary of the state-of-the-art of ceramic-based hybrid OSN membranes and insights into promising avenues of research. First presented in Sections 3 are the methods used to modify porous ceramic and the resulting OSN membranes. The characterization techniques and tools of both graft and membrane follows in Section 4. Section 5 reviews the mathematical models that attempt to describe and predict the transport behavior of solvent and solute through OSN membranes.

2. From conventional NF membranes to hybrid ceramic-based membranes for OSN

The composition of a membrane, from the selective layer – the most discriminating layer of the membrane – to the support layer(s), can be divided into one of three material classes: either polymer (organic), ceramic (inorganic), or a hybrid consisting of both. Polymers commonly used in polymeric OSN include polyamide-imides [19], poly(dimethylsiloxane) (PDMS) [20], poly(ether ether ketone) (PEEK) [22], polysulfones [23], polyacrylonitrile (PANI) [24], polybenzimidazole (PBI) [25] and blends [26] of the above. The cited examples have all shown some degree of resistance to organic-solvent-induced degradation, although additional enhancements, such as crosslinking or doping, are often required [27-29]. Polymeric membranes have generally shown the most success, in terms of permeability and retention, with polar organic solvents such as alcohols or THF. However, solutions of non-polar solvents can be more troublesome, liable to either chemically degrade the membrane or physically distort the membrane geometry [3,10,11,30]. These disadvantages can be avoided altogether with ceramic membranes.

The porous ceramics for nanofiltration are composed of oxide materials, with either a symmetric or asymmetric architecture, various pore size distributions, porous structures and overall different geometries (e.g. tubular, Fig. 3). Depending on the material and preparation method, porous oxide ceramics can present surface hydroxyl groups and acidic sites, enabling surface modification with a linking function, as found for instance in either gas separation or heterogeneous catalysis [31,32].
Porous ceramic membranes are typically multi-layered structures. These layers are classified according to their pore diameter (IUPAC): microporous (<2 nm), mesoporous (2–50 nm) and macroporous (>50 nm) [33]. Generally, macroporous support will provide structural strength to a thinner, selective, meso- or microporous layer (Fig. 3a). For more in-depth information on the stability, preparation and industrial applications in pressure-driven processes of porous ceramic membranes, the reader is referred to the work of respectively Buekenhoudt et al. [34], Larbot et al. [35], and Luque et al. [36]. Ceramics are an ideal material to withstand harsh environments due to their resilience to high operating temperatures and common industrial organic solvents [34], especially when compared against polymeric membranes. However, the filtration of non-polar solvents through these hydrophilic membranes is challenging. This was evident as early as the turn of the century: a 90% retention of 1200 Da polyolefin was reported, slightly above the wetting properties of porous ceramic membranes are easily altered by grafting a molecule or a polymer of the correct type [47]. However, there is also a need for pore size alteration to make ceramic membranes pertinent to a broad range of nanofiltration applications. As shown in Table 1, the commercial availability of ceramics with pores between 0.9 nm and 5 nm is discontinuous, i.e. only a few sizes are available in the nanofiltration range. The multitude of potential OSN applications requires alteration of the membrane to fit the circumstances. It is then evident that there is not only a need to alter the surface properties (i.e. hydrophilic nature) but also the size of the pores. Both of these changes can be achieved by grafting a molecule or a polymer of the correct type and size onto the pore wall. In this review, grafting is defined as the formation of strong chemical bonds (i.e. covalent and coordination bonds) between an inorganic substrate and an organic compound.

Table 1

| Tradename/Manufacturer | Material    | Pore sizes [nm] |
|------------------------|-------------|-----------------|
| Inopor GmbH/Rauschert   | TiO₂        | 10.0, 5.0, 1.0, 0.9 |
| Inopor GmbH/Rauschert   | SiO₂        | 5.0            |
| Inopor GmbH/Rauschert   | ZrO₂        | 3.0            |
| Membralox/Pall Corporation | TiO₂    | 5.0            |
| Pervatech B.V [50].    | γ-Al₂O₃    | 0.9, 3.5        |
| Media and Process Technology Inc. | γ-Al₂O₃ | 4.0, 10.0     |

Reliable fabrication methods have evolved for ceramic membranes. Listed below is a partial list manufacturers marketing aqueous nanofiltration ceramic membranes and their standard pore sizes.
3. Surface modification of ceramic oxides

3.1. Pore surface modification: chemisorption vs. physisorption

The term surface modification refers to the deliberate attachment or deposition of (macro)molecules to the surface of a ceramic oxide to change its physical or chemical properties [51]. It is important to distinguish deposition by physisorption from attachment by chemisorption. Physisorption (Fig. 4, right) corresponds to the physical deposition of species to the surface by electrostatic or van der Waals interaction, such as polyelectrolyte layering [52]. For a physisorbed species to have a stable, strong attachment – a bonding strength comparable to covalent or coordination bonds – there must be multiple electrostatic interactions per molecule. Practically, this means employing high molecular-weight polyelectrolytes (>30 k Da). The minimum pore size these large polyelectrolytes can enter is no smaller than 200 nm in diameter [53], far outside the nanofiltration range. Layering polyelectrolyte on a support with smaller pores results in a membrane performance similar to coated membranes [53]. Therefore, neither polyelectrolyte nor coated membranes will be covered; the focus will be on surface modification of nanofiltration membranes by chemisorption. Attachment by chemisorption, i.e. grafting (Fig. 4, left) implies the formation of covalent or coordinated bonds between the support surface and the organic compound. Surface modification by grafting offers a multitude of possible functionalization, finer control over the pore size, and a sturdy covalent attachment, yet is more challenging. The chemical reaction at the support surface requires the optimization of reaction conditions to control surface and pore coverage (i.e., grafting density, monolayer), and to avoid unwanted secondary reactions (i.e., clustering due to polymerization) [51].

Grafting can be roughly categorized according to two approaches: either grafting-to or grafting-from (Fig. 5). Grafting-to refers to a one-step reaction in which an already-synthesized molecule or polymer, containing an inorganic-organic “linking” function, is directly bonded to the support surface. The main advantage of grafting-to is the control over the graft, since the graft is fabricated beforehand. Grafting-from, also termed graft polymerization, occurs when polymerization begins from a grafted initiator at the pore surface. In this second category, the presence of the initiator on the pore surface implies the use of the grafting-to procedure in first step. In contrast to grafting-from, grafting-to of ready-made polymer chains can lead to a lower graft density, as polymer chains attach and sterically hinder neighboring linking sites. Conversely, grafting-from can provide a more uniform and denser coverage due to the ease of diffusion of smaller monomers. Grafting-from at a mesoporous length scale implies the use of a specialized polymerization technique that can exercise a high degree of control over the degree of polymerization, as covered in Section 3.5. A series of grafting-to reactions is also possible, this approach is described in Section 3.5. Step-by-step grafting.

Many of the grafting chemistries and methods presented in the following sections were first adapted from developments in other fields (e.g. sensors, coatings, polymer chemistry). Due to the extensive reach of these fields, this review will not be covering those associated publications. If the reader wishes a broader overview of grafting chemistries, focused on flat and particle geometries, we recommend the review of Pujari and co-workers [51]. The following sections focus on grafted porous ceramic oxide surfaces used as membrane to purify organic solvents. Specialized grating techniques, their advantages and disadvantages, as well as the performances of the resulting membranes, are all covered.

3.2. Inorganic-organic linking functions

A linking function is the chemical group which allows the chemical attachment of (macro)molecules onto oxides. As represented schematically in Fig. 6, the linking function bonds to the ceramic surface, and the functional group. The functionalized surface is either the final modification or the starting point for further modification. Many classes of linking functions have been shown to create covalent bonds between a metal oxide surface and a functional group [51]. Among the different attachment chemistries that have been used to graft (macro)molecules onto oxides, only few have been employed to prepare grafted-ceramic membranes: organosilanes, organophosphonates, and organometallic Grignard reagents. Each attachment chemistry and their combability with various ceramic oxides are detailed below.

3.2.1. Organosilanes: alkoxysilane and silyl halide linking functions

Within organosilane linking functions, both alkoxysilanes and silyl
halides are routinely employed. A general formula for an organosilane linking agent is as follows: \((\text{R})_4\text{Si}(\text{X})_n\), where \(n\), the number of linking groups, ranges from 1 to 3, and \(\text{X}\) represents either the alkoxy leaving group, typically a methoxy or ethoxy group, or a halide, typically a chloride. The functional group \(\text{R}\) will drive the interaction of the membrane with the solute and solvent or be used as a starting point for further modification. The formation of bonds between the OH-bearing surface of the ceramic oxide and the linking function occurs via hydrolysis (for alkoxysilanes) and condensation, resulting in the formation of M-O-Si covalent bonds. It must be noted that the number and type of hydrolysable groups (\(n\)) impacts both the grafting density, attachment strength, and the ability of the alkoxysilane to polycondensate. For instance, silyl halide linking functions are usually employed for their high reactivity, and consequently restricted to one link per functional group (\(n = 1\)), lest polycondensation and subsequent pore blockage occur [54]. On the other hand, alkoxysilanes can provide multiple attachment (\(n = 2,3\)) per functional group, although in that case water content has to be regulated. The presence of water is necessary, though a maximum of 1–3 pre-adsorbed monolayers of water on the pore surface is ideal for the formation of a dense monolayer [55]. An excess of water causes the formation of Si–O–Si bonds, leading to the formation of organosilane multilayers [56–60]. Other factors found to have an influence are the temperature, solvent, reaction time, and the size and concentration of the linker, among others, which must be tuned for best coverage [61–65].

Grafting of alkoxysilane and silyl halide can be achieved via solution phase deposition (SPD), where an (anhydrous) solvent serves as a reaction medium. Toluene has resulted in high density coverage for a variety of silanes in this role [66]. An alternate method is to employ vapor phase deposition (VPD), bypassing the need for a solvent. This method has proven effective in suppressing the formation of multilayers while yielding uniform, dense grafts, and is usually performed at higher temperatures than SPD [67–69]. Fig. 7 shows a representation of the commonly-grafted (3-aminopropyl)triethoxysilane (APTES) onto a hydroxyl-terminated surface.

3.2.2. Organophosphorus linking functions

Phosphonic acids \([\text{R}-\text{P(O)(OH)}_2]\) and their phosphonate derivatives \([\text{R}-\text{P(O)(OR)}_2]\) (\(\text{R} = \text{alkyl, aryl or trimethylsilyl groups}\)) are increasingly being used for controlling surface and interface properties in hybrid or composite materials [70] (Fig. 6B). The fourth component (\(\text{R}'\)) is an organic carbonated moiety linked to phosphorus with a P–C bond. Organophosphorus linking agents are famous for their versatile coordination chemistry, allowing them to react with different metal ions via P–O-metal ionocovalent bonds. Furthermore, unlike organosilane linking functions, phosphonic acids and their phosphonate derivatives are not subjected to homocoordination reactions. This allows the controlled formation of organic monolayers of grafted phosphonate molecules on the surface of inorganic supports [70,71].

When using an organophosphonic acid, the reaction may easily be
performed in water, and the resulting monolayer is also stable in aqueous conditions, unlike many silane-grafted ceramics [71]. Some organophosphorus-modified surfaces have also shown high temperature stability, up to 400 °C, due to the strength of the M-O-P and P–C bond while the alkoxysilanes usually decompose around 200–250 °C [58,71].

3.2.3. Organometallic Grignard linking functions

Grignard reagents (alkyl, vinyl, or aryl magnesium halides, e.g. Fig. 6C, have long been used to form carbon-carbon bonds. They can also form a M–C bond when M is part of a titania or zirconia matrix, as was demonstrated by Buekenhoudt and co-workers [72,73] with the grafting of 1 and 3 nm pore sizes. The Grignard linking function has not been demonstrated on other porous ceramic substrates. The reaction requires oxygen, water-free conditions, and several days, to yield a partially covered surface, i.e. not a full hydrophobization [73]. Their thermal stability has not been reported, though they are stable in water [74] and a range of polar, aprotic and apolar solvents [75].

3.2.4. Strengths and weaknesses

Compatibility, advantages and disadvantages of the organosilane, organophosphorus and organometallic Grignard linking functions are summarized in Table 2. As it can be seen, not all porous ceramic oxide are compatible with these linking functions. For example, phosphorous-based linking agents have yielded uniform monolayers on porous zirconia, alumina [58,76,77] and titania [74,78], while organosilanes have been widely used on silica and alumina [51,79–82]. Silylation on γ-alumina or silica surfaces has overwhelmingly been chosen as the first, and sometimes only, grafting step. Comparatively to organosilanes, relatively few examples of organophosphorus grafting exist [83,84]. The authors believe this can be attributed to the non-reactivity of phosphonates towards silica surfaces [71,78,78], which is a common material in many other research areas, such as microfluidics or electronics. However, organophosphorus compounds continue to be an attractive yet relatively unapplied linker chemistry for alumina membranes [85–87]. The grafting of organometallic Grignard linking agents has

![Proposed 3-step mechanism for alkoxysilane. Unregulated conditions can result in multi-layering of the silane (bottom left), whereas optimized conditions will promote monolayer formation (bottom right). Adapted from Ref. [51] with permission.](image-url)
only been reported on titania and zirconia porous ceramic support.

Thus during the selection of the linking function, one should refer not only to the compatibility with the metal oxide ceramic support but also to the surface bonding (number of possible bonds), the yielding grafting density, and the possibility to form a monolayer. The attachment strength, beyond compatibility, extends to the number and type of bonds the linking function can exhibit. Strong bonds, for instance with high bonding energy, are usually more stable (e.g. covalent vs. hydrogen bonds). However, even covalent bonds can be unstable under specific conditions, this is why the linkage stability should be investigated before filtration. More bonds per linking function can, in certain cases, boost the overall attachment strength while sacrificing or increasing the potential grafting density, and decreasing the free surface hydroxyl groups. This is important when trying to impart a customizable functionality to the selective layer, as covered in the following sections. First grafting-to membranes are detailed, then grafting-from and its potential as a tunable OSN membrane production method, and also membranes modified by step-by-step grafting. Finally the merits and disadvantages of these three membrane modification methods are compared to one another.

Existing fabrication processes for porous silica, titania and zirconia can yield stable layers with a pore diameter equal to or less than 3 nm [88,89]. Since grafting in these small mesopores or micropores is sterically hindered, it is generally the only modification step. However, with mesopores of at least 5 nm in diameter, there can be further modification via the functional group of the linker, either by grafting-from or grafting-to.

3.3. Grafting-to

Grafting-to refers to a one-step reaction in which an already-synthesized molecule or polymer is directly bonded to the support surface. A well-known grafting-to functionalization is the attachment of perfluoroalkylsilanes (FAS), a fluorinated alkyl molecule terminated with an organosilane linking function. It has been grafted onto various substrates for a variety of separation applications: emulsion separation [47], membrane distillation [91] and pervaporation [3], among others [92,93]. The draw of the FAS grafted molecules is the ability to impart hydrophobicity in one, simple grafting step. Tuning the fluorinated alkyl chain length (from 1 to 12 carbons), degree of fluorine substitution, and reaction conditions have all shown an impact on performance [94]. Studies appear to be limited to a chain length of 12 or fewer carbons; this reflects the range of commercially available FAS. However, one-step surface tuning, i.e. when the (macro)molecule already contains a linking function, is not always achievable or practical. Oftentimes, the functional group of the linking agent (see Fig. 6) is purposed to react with a second reagent, which will in turn dictate the pore size and surface properties. Together, these two reactions are also referred to as grafting-to.

The following sections explore the advances in grafting-to as applied to OSN ceramic membranes. First presented are various hybridizations of the alumina membrane mesopores, followed by Grignard-grafted titania and zirconia membranes. We emphasize that linking functions [70], the authors believe phosphonate-grafted ceramic membranes to be an unexplored approach for the treatment of mixed aqueous-solvent or ‘wet’ gas streams, as often found in the oil and gas industry.

3.3.1. Alkoxysilane grafted-to membranes

Gamma alumina (γ-Al₂O₃) is a mesoporous phase of alumina. When used as the membrane selective layer, it is typically deposited on an alpha alumina support. Pinheiro et al. and Tanardi et al. used organosilanes as the linking agents between γ-Al₂O₃ of a 5 nm native pore size and chains of mono-functional-terminated PDMS with an average degree of polymerization (n) equal to 10 or 29, as shown in Fig. 8. The PDMS rendered the surface hydrophobic, shifting the contact angle from \( \sim 0 \) to 30 to 90–99° [95]. High fluxes and dye retentions were found for these PDMS-grafted membranes as shown in Table 3. The permeability of the PDMS n = 10 membrane was found to be stable for at least 170 days in toluene, showing no significant change in permeability [96,97], though no retention tests were conducted over this time-frame.

A follow-up study explored the introduction of crosslinking PDMS inside the pores of the alumina. Di-functional PDMS (n = 10) mixed with a tetra-functional crosslinker were grafted onto 5 nm γ-Al₂O₃ organosilane-functionalized surface [96,97]. As shown in Table 3, the resulting membranes demonstrated higher retentions with reasonable permeabilities [99].

The studies detailing and testing PDMS-grafted alumina membranes found that permeability and retention were dependent on graft swelling, i.e. the swollen graft constrained the pore, reducing permeability and increasing retention [99,100]. This swelling was constrained to the individual pores of the ceramic architecture, as the overall membrane size and shape remained stable. No evidence was found for compaction of the swollen graft under the pressures tested, as solvent fluxes remained linear with respect to the applied pressure [101]. Localized swelling and no compaction distinguish the PDMS-grafted membranes from other PDMS-based OSN membranes, whose performance suffers from these effects, especially in nonpolar solvents such as toluene [102].

Further research by Tanardi et al. investigated the grafting of polyethylene glycol (PEG), with an organosilane linking function into the same γ-Al₂O₃ 5 nm pores. The organosilanes linker and PEG chain were bonded together before grafting, and subsequently as a whole, into the membrane pores and surface. These membranes were hydrophilic as evidenced by the water contact angle of 38° [103]. Only the PEG-grafted membrane with the highest graft density was selected for performance testing. Results are shown in Table 3.

3.3.2. Phosphonate-grafted ceramic membranes

Though no phosphate-grafted membranes exist for OSN, the use of this linking chemistry has begun to be applied in other membrane separation fields. The treatment of titania with phosphoric acid terminated alkyls was found impart fouling resistance during the ultrafiltration of BSA proteins in water in the form of longer consistent fluxes and retentions [105]. Similar fouling resistance was witnessed found when grafting porous titania or zirconia with phosphate or phosphinate terminated alkyl or phenyl groups [73]. Ionic liquids grafted via a phosphonate linking function onto gamma-alumina for CO₂ selective-membranes have demonstrated potential in gas separation applications with a high ideal CO₂/N₂ selectivity (∼144) yet low flux (130 Barrer) [31]. As the hydrolytic stability of phosphate-based coupling has been demonstrated to be greater than alkoxysilane-based linking functions [70], the authors believe phosphate-grafted ceramic membranes to be an unexplored approach for the treatment of mixed aqueous-solvent or ‘wet’ gas streams, as often found in the oil and gas industry.

3.3.3. Grignard-grafted ceramic membranes

Buskenhoudt et al. recently introduced Grignard-grafted membranes [72,84]. The eponymous reaction to fabricate these membranes requires a strictly inert, water-free atmosphere and yields membranes showcasing direct M – C bonds, M representing a titanium or zirconium ceramic surface atom and C representing the terminal carbon atom of an alkyl chain or phenyl group, as shown in Fig. 9. Although Grignard-grafting bypasses the need for a separate linker, it results only in partial surface coverage of the ceramic, imparting an amphiphilic
character to the membrane [106]. A continued investigation of these membranes [107] evaluated membrane performance in either acetone or toluene solutions, the solutes were either polystyrene (PS) chains, PEG chains or 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) ligands. The membranes were grafted with varying n-alkyl groups (n = 1, 5, 8, or 12); selected results are shown in Table 4. The authors attributed the high retentions of solutes in acetone to a high solvent-membrane affinity [107]. The low retention differences between

![Fig. 8. Two-step process for the grafting-to of PDMS onto an alumina pore surface, as in Refs. [95–97]. (A) the linking agent 3-aminopropyltriethoxysilane (APTES) is grafted. (B) Mono-epoxy terminated PDMS is reacted with the amine functional group to further modify the pore.](image)

**Table 3**

Permeability in various solvents and retention (R) of Sudan Black B (neutral dye, Mw = 457 Da) across various organically-grafted γ-Al₂O₃ membranes (WCA: water contact angle).

| Membrane       | WCA | Solvent (polar) | Permeability [L m⁻² h⁻¹ bar⁻¹] | R 457 Da [%] | Solvent (apolar) | Permeability [L m⁻² h⁻¹ bar⁻¹] | R 457 Da [%] | Ref. |
|----------------|-----|-----------------|--------------------------------|--------------|-----------------|--------------------------------|--------------|------|
| PDMS n = 10    | 94° | Isopropanol     | 0.9                            | 55           | toluene         | 3.1                            | 72           | [100]|
| PDMS n = 39    | 95° | Isopropanol     | 0.75                           | 66           | toluene         | 2.1                            | 83           | [100]|
| Crosslinked PDMS | 108° | Isopropanol     | 0.4                            | 80           | toluene         | 1.3                            | 95           | [99] |
| PEG n = 10     | 38° | Ethanol         | 0.78                           | 89           | hexane          | 3.7                            | 54           | [103]|
| p(MA-alt-1-decene) | 74° | Ethyl acetate   | 1.7                            | 90           | toluene         | 1.8                            | 98           | [104]|

![Fig. 9. Grignard functionalization of a ceramic oxide surface showing partial surface coverage [106].](image)

**Table 4**

Permeability and retention of solutes across Grignard-modified (8-carbon alkyl chain) 1-nm diameter TiO₂ membranes [107].

| Solvent | PS Permeability [L m⁻² h⁻¹ bar⁻¹] | Retention 580 Da [%] | Retention 1500 Da [%] | PEG Permeability [L m⁻² h⁻¹ bar⁻¹] | Retention 600 Da [%] | Retention 1500 Da [%] |
|---------|----------------------------------|----------------------|----------------------|-----------------------------------|----------------------|----------------------|
| Acetone | 9.5                              | 85                   | 92                   | 5.0                               | 55                   | 81                   |
| Toluene | 3.0                              | 55                   | 63                   | 1.5                               | -5                   | 46                   |
the different molecular weights of PS (580 Da & 1500 Da) indeed suggest that pore size is not the most important factor in solute retention, at least when membrane-solute affinity is low. On the other hand, when dealing with high solute-membrane affinities (PEG), it appears that the effect of solute size on retention is more pronounced.

Negative retentions of PEG in toluene have been previously observed and explained as stemming from a raised PEG concentration at the membrane surface due to a high membrane-solute affinity (hydrogen bonding) [75]. Negative rejection can occur when the solute-membrane affinity is stronger than the solvent-membrane affinity, as is the case with PEG in toluene. Size exclusion effects are then readily apparent, as is the case with PEG retention in toluene. As shown in Table 4, the PEG rejection in toluene jumps from −5% to 46% as the PEG increases in molecular weight. As described by Hosseinabadi and co-workers [107], size exclusion in Grignard membranes could be a combination of pore-shrinkage and pore entrance blockage. As the alkyl chain length increased, pore entrances may become obstructed, yet less of the inside of the pore is modified due to reduced graft penetration by steric hindrance, thereby explaining the relative difference in permeabilities: unmodified > C12 > C10 > C8 > C5.

3.3.4. Maleic anhydride copolymer grafts

Amirilargani et al. [104] have bypassed the need for a traditional linker. Instead, the maleic anhydride (MA) ring opening moieties of an alternating copolymer, poly(MA-alt-1-alkene) directly bond to the surface hydroxyl groups of γ-Al₂O₃, as shown in Fig. 10. This pre-synthesized polymer was found too bulky (Mₙ: 17–23 kDa) to significantly penetrate into the 5.0 nm pores of the γ-alumina, meaning a new selective layer was formed on the external surface of the support. While the MA provides the linking functionality, the alkane chains were found to dictate the performance of the membrane. When varying the length of the 1-alkene monomer n = 6 to n = 18 carbons, the solvent permeabilities peaked at n = 10 (toluene, 1.8 L m⁻² h⁻¹ bar⁻¹; ethyl acetate, 1.9 L m⁻² h⁻¹ bar⁻¹), double that of the second-best sample. Retentions of Sudan Black B (Mw = 450 g mol⁻¹) did not depend on alkene monomer length, staying remarkably high and constant, between 90 and 94%. The results are shown in Table 3.

Swelling of the graft did not seem to be an issue, likely due to the multiple attachment points per chain grafted. Noted was the significant adsorption of solute onto the un-grafted pore surface sites. As this membrane is a recent development, its long-term graft stability is yet unreported. The authors of this review speculate that the MA linking function is stable in the long-term in most organic solvents, although the ester linkage may be vulnerable to nucleophilic attack, making it unsuitable for a minority of environments, for example, extreme-pH aqueous mediums.

3.4. Step-by-step grafting

Step-by-step grafting is the modification of a selective layer by the stepwise addition of monomers, i.e. a series of grafting-to reactions. In each separate reaction, the monomers supplied react to form covalent bonds with the previous layer of monomer applied, forming chains extending away from the substrate. Attachment to the substrate is typically done beforehand by grafting a monomer as the functional group of a linking agent. Described below are two examples of step-by-

---

Fig. 10. Schematic representation of maleic anhydride (MA) ring opening of an alternating copolymer, poly(MA-alt-1-alkene) directly bond to the surface hydroxyl groups of porous γ-Al₂O₃ support [104].
step grafting.

Pinheiro [108] grafted, step-by-step, one of each the following polyanime monomers onto 5 nm or 9 nm pores of γ-alumina: benzo-phenonetetracarboxylic acid and 3,3′-diaminodiphenyl ether. The 9 nm γ-alumina showed a pore shrinkage to 2.4 nm, and permeabilities of 1.7 L m⁻² h⁻¹ bar⁻¹ in toluene and 3.9 L m⁻² h⁻¹ bar⁻¹ in hexane. For these membranes, a MWCO of 850 Da was determined by the filtration of polysibutylene solutions. However, the membrane degraded after 29 days, becoming impermeable to hexane and decreasing its toluene permeability. The blocking of solvent transport was attributed to capillary condensation of water inside the pores. Fluorinated monomer equivalents were also grafted in the same manner [108]. However, the only permeable membranes obtained were those grafted on α-alumina pores of 70 nm, resulting in membranes with toluene permeabilities of 8–9 L m⁻² h⁻¹ bar⁻¹ and untested, though likely poor, retentions.

Amelio et al. [109] cyclcd the addition of monomers trimersoy chloride and m-phenylenediamine to an APTES-functionalized annelized-alumina substrate. The resulting membranes were only tested for salt retention, retention peaking at 5 layers with 76% NaCl retention with a water permeability of 0.6 L m⁻² h⁻¹ bar⁻¹. However, layer growth was observed only on the external surface of the membrane, not in the pores. The external layer did not extend from the surface uniformly after at 3.5 cycles of monomer addition. This membrane type has not yet been tested on organic solvents, though without improvements its performance will likely fall short of its chemical equivalent prepared by interfacial polymerization (IP) on polymeric supports [110].

3.5. Grafting-from

Grafting-from is a newly developed approach for the functionalization of nanofiltration mesopores [111]. It is the process of growing polymer chains from a porous substrate, via a grafted molecule which contains both the linking function and polymerization initiator. Only recent advances in controlled polymerization techniques have made such synthesis approachable to material scientists and engineers, as well as tunable at the nanoscale [112]. Grafting-from has been mainly used to fabricate polymer brushes – chains grown in high density – from flat or convex geometries (e.g., sheets, nanoparticles), and less from concave surfaces, such as the inside of a tube or pore [113]. Accordingly, there exists few examples of grafting-from inside membrane pores. More common are polymer brushes on the external membrane surface for added functionalization [16].

Brushes on ceramic oxide membranes have mainly been used as a means to create a new layer or to modify large macropores. In one instance, acrylic acid was polymerized into polyacrylic acid brushes on the surface of alpha alumina membranes (3 μm pore diameter) to reduce fouling during the ultrafiltration of aqueous solutions. These brushes were pH responsive, compacting at a pH smaller than 1.1 and extending at pH 5.5. Compacted brushes increased the flux ~15 times [114,115]. In another example, the free-radical polymerization of vinylpyrrolidone or vinyl acetate on top of silica surfaces was performed to make a pervaporation membrane for the separation of methanol and methyl tert-butyl ether. The polyvinyl acetate (PVAc) and polyvinyl pyrrolidone (PVP) brushes were found to be 39 nm thick and 26 nm, respectively [116]. The molecular weight of each brush was claimed to depend roughly on monomer concentration and temperature, though no tuning of brush height was demonstrated [117,118].

The two examples listed in the previous paragraph are dealing with brushes much larger than the mesopores of ceramic oxides destined for nanofiltration. Comparing the starting pore size of ceramic oxides mesopores (Øpore≈5 nm) with the backbone length of vinyl polymers (C-Cn=0.25 nm), we can understand the need for a brush whose degree of polymerization can be controlled in the range of 4–20 monomers. Conventional radical polymerization yields polymers with hundreds or thousands of repeating units, so controlled polymerization techniques are needed to achieve precise control over the degree of polymerization of the graft.

For this reason, controlled polymerization techniques such as atom-transfer radical polymerization (ATRP) or nitroxide-mediated polymerization (NMP) are now used to grow polymers of low specific molecular weights [119]. This can be done from ceramic surfaces by immobilizing an initiator on the surface (e.g., with a peroxy carbonate initiator onto silica nanoparticles [120], an azo initiator on ferrite, titania and silica particles [121], or an ATRP initiator onto the 5 nm pores of γ-alumina [111]).

The ATRP-initiator of [111] was composed of an organosilane linking function, and was used to grow polystyrene chains from the pore surface (Fig. 12). This resulted in shrunken and hydrophobic membrane pores, which gave a toluene permeability of 2.0 L m⁻² h⁻¹ bar⁻¹ while reaching 90% retention of diphenylanthracene (Mw = 330 g mol⁻¹). This membrane needed plasma etching, post-initiator and pre-polymerization, to remove external-facing initiator not in the pore. Chain length control, and thus the tuning of effective pore size, was achieved by varying the reaction time as well as the monomer:initiator ratio of the reaction, activators-regenerated-by-electron-transfer (ARGET)-ATRP.

The Surface-Initiated, Activators-Regenerated-by-Electron-Transfer, Atom Transfer Radical Polymerization (SI-ARGET-ATRP) method was used to grow polystyrene brushes inside the mesoporous of a γ-Al₂O₃ support (%o≈5 nm) [111].

ARGET-ATRP is ATRP with the incorporation of a reducing agent, allowing for (ppm) levels of catalyst, as well as easier maintenance of oxygen-free conditions. This enables practical implementation of grafting-from on surface areas larger than laboratory wafers, such as a membrane [122,123]. Its ease-of-use is depicted in Fig. 11. Though Merlet and coworkers [111] reported the first use of ATRP to shrink and modify nanofiltration pores, it was also used to grow ultrafiltration membranes [124] and free-floating, 14 nm mesopores [125]. Using surface-initiated ATRP, Chu et al. [124] polymerized poly (3-(N-2-methacryloyloxyethyl-N,N-dimethylammonio)propanesulfonate) (PMAPS) from an initiator bonded on the surface of 200 nm diameter pores of anodic aluminum oxide. The study reported no impact on chain growth due to the concave geometry, though the retardation of monomer to growing chains in the center of the pores was noted. In Ref. [125] mesoporous silica particles of diameter ~15 nm were grafted, with polyacrylonitrile (PAN) of varying lengths. These silica mesopores were however free-standing porous structures, not aligned and packed together as a membrane.

3.6. Evaluation & comparison

The potential of grafting-to has been realized across a variety of ceramic oxides. The advantages and disadvantages of several grafting-to methods and grafting-from are summarized in Table 5.

The PDMS-grafted alumina membranes developed by Tanardi and Pinheiro [96,97] exhibit competitive separation properties for non-polar organic solvent solutions, whereas the amphiphilic character of the Grignard-grafted membranes developed at VITO [107] renders them competitive when dealing with separations of polar organic solvents with solutes which are less polar than the solvent. The grafting-from membranes of [111] are easily tuned and have demonstrated a MWCO down to 300 Da. In each case, swelling of the polymeric graft is not an issue, as it is attached to a rigid, solvent-resistant, ceramic architecture. In the PDMS-grafted alumina membranes swelling is localized to the pores, actually increasing the selectivity, whereas swelling was not observed in Grignard-grafted membranes, since the graft only partially covers the surface. Just as the Grignard-grafted membranes, the p (MA-df-1-decene) membranes of [104] are linkerless. They also show promise for both the filtration of polar and non-polar organic solvents.

There is now one instance of grafting-from used to make an OSN membrane. An advantage of this method is that there is no need for ex-situ polymer synthesis. This step can consume more time and resources.
than the membrane grafting-to itself, as in the work of Amirilargani et al. [104]. However, reducing the number of synthesis steps is not the biggest advantage. There are many other monomers, polymer architectures, as well as other controlled polymerization techniques, available to fabricate OSN membranes via grafting-from. Developing these, using [111] as a starting point, would realize the potential of grafting-from: a highly tunable membrane modification method. Dictating the pore size and surface properties of the membrane would allow to target specific applications. A disadvantage of grafting-from is that the graft is much harder to characterize. Whereas the grafting-to polymer can be analyzed prior to attachment, no such information can be obtained beforehand for grafting-from. The characterization of brushes in mesopores is difficult; traditional methods such as light scattering (for particles geometry) or ellipsometry (for planar substrates) are incompatible with the pore geometry. Additionally, comparing chains grown from ungrafted and grafted initiator, in otherwise the same conditions, yields unequal results [126]. Characterization of the graft and resulting membrane is further discussed in the following section.

Step-by-step grafting for OSN has been used to make two different membranes. The approach taken by Pinheiro [108] is difficult within narrow 5 nm mesopores because of the bulky, rigid polyamide monomers used. Though the macropores in the α-alumina are large enough to accommodate these monomers, no data was published on either the retention or stability of such membranes. The work presented by Amelio...
et al. [109] shows scant evidence of pore modification but is instead focused on the creation of a layer on top of the alumina support, which is likely to suffer from the same problems of polyimides layers that are exposed to non-polar solvents. In a broader context, the step-by-step approach has several drawbacks compared to grafting-from or grafting-to. Step-by-step grafting has also not demonstrated the performance of membrane washing, and thermal treatment, take time and resources.

So far, only three distinct grafting-to methods and one grafting-from method have yielded well performing membranes. The performance of the membranes discussed in this section can be found in Table 6. As it can be seen, the difficulty in the evaluation and comparison reside in the lack of comparable and uniform performance data which renders screening and discussion difficult. Many approaches have yet to be tried. The advantages of grafting onto ceramic membranes have been shown: tunability of the graft, versatile grafts, and a sturdy architecture. Combined with the wealth of unexplored grafting chemistries, hybrid ceramic-based membranes for OSN continue to be a promising research avenue. With the aim to conduct cross-comparison of the hybrid ceramic-based membranes and conventional OSN membranes, future research should consider the use of the standard method to characterize the performance of the membranes as described by Marchetti et al. [127] (e.g. a broad class of solvents and solutes should be tested).

4. Graft & pore characterization

In the previous sections, the effect of surface modification of porous ceramic supports was suggested based on the results from water contact angle (e.g., modification in the hydrophilic character), cyclohexane permoporometry (e.g., active pore shrinkage), and, most importantly, membrane performance (e.g., increase of apolar solvent flux, increase in retention of low molecular weight solutes). The combination of these results does not actually confirm the formation of an hybrid ceramic membrane composed of (macro)molecules chemically bond to the porous ceramic support. Indeed, a host of other valuable information is absent, such as grafting density and homogeneity into the pores as well as the local chemical environment (the nature and number of chemical bond between the grafted species and the metal oxides). These are useful data which could serve to understand, predict and improve the membrane performance and stability. Thankfully, several analytical techniques are available for the direct evaluation of the (macro)molecule concentration on a metal oxide surface. However, these characterization methods are challenging or ill-suited to hybrid ceramic membranes due to two factors: i) the relatively low amount of grafted species, ii) the porous structure of the ceramic support [99,111]. Indeed, the grafted species which are confined in the mesopores represent less than 1% by weight or volume of the total sample. The macroporous support layer makes up the majority of the support (99.5+ %, by weight or volume), and is generally unreactive, with a low specific surface area [38]. This section aims to explore the characterization techniques currently used or applicable to hybrid ceramic-based membranes.

4.1. Spectroscopic characterisation methods

X-ray photoelectron spectroscopy (XPS) has proven to be useful to estimate the grafting density at the surface of the ceramic support [128]. However, due to the rough and porous nature of the support, the results are less accurate compared to a flat and dense support. To circumvent these issues, porous particles of the same material as the selective layer can be used as a model system. This method eliminates the inactive substrate that otherwise diminishes the sample signal and allows the estimation of grafting density by coupling TGA and N2 sorption analysis [99,111]. Another method is to cyclically measure and etch from the surface of the membrane to obtain atomic depth profiles by XPS. Difficulties associated with this method include imprecise etching rates, the contamination of the pores underneath by etched material, and the destruction of the sample [128]. Complementary to XPS, LEIS and ToF-SIMS could be considered to cross-link the results from multi-instrument surface analyses [129,130].

In many cases, IR spectroscopy can be useful to demonstrate and distinguish between the presence of physiosorbed or grafted species on

| Membrane composition | Grafting method | Support | Solvent | Permeability [L m⁻² h⁻¹ bar⁻¹] | Solute (Mw) | Retention [%] | Ref. |
|-----------------------|----------------|---------|---------|-------------------------------|-------------|--------------|-----|
| PDMS-oligomer (n = 10) Alkoxysilane Grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Isopropanol | 0.9 | SBB (457) | 55 [100] |
| PDMS-oligomer (n = 10) Alkoxysilane Grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Toluene | 3.1 | SBB (457) | 72 [100] |
| PDMS-oligomer (n = 39) Alkoxysilane Grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Isopropanol | 0.75 | SBB (457) | 66 [100] |
| PDMS-oligomer (n = 39) Alkoxysilane Grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Toluene | 2.1 | SBB (457) | 83 [100] |
| Cross-linked PDMS Alkoxysilane Grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Isopropanol | 0.4 | SBB (457) | 80 [99] |
| Cross-linked PDMS Alkoxysilane Grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Toluene | 1.3 | SBB (457) | 95 [99] |
| PEG oligomer (n = 39) Alkoxysilane Grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Ethanol | 0.78 | SBB (457) | 89 [103] |
| PEG oligomer (n = 39) Alkoxysilane Grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Hexane | 3.7 | SBB (457) | 54 [103] |
| p(MA-alt-1-decene) | Single-step grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Ethyl acetate | 1.7 | SBB (457) | 90 [103] |
| p(MA-alt-1-decene) | Single-step grafting-to | γ-Al₂O₃ (Øpore = 5 nm) | Toluene | 1.8 | SBB (457) | 98 [104] |
| Octadecane | Grignard reaction | TiO₂ (Øpore ≈ 1 nm) | Acetone | 9.5 | PS (580) | 85 [107] |
| Octadecane | Grignard reaction | TiO₂ (Øpore ≈ 1 nm) | Acetone | 9.5 | PS (1500) | 92 [107] |
| Octadecane | Grignard reaction | TiO₂ (Øpore ≈ 1 nm) | Acetone | 5.0 | PEG (600) | 55 [107] |
| Octadecane | Grignard reaction | TiO₂ (Øpore ≈ 1 nm) | Acetone | 5.0 | PEG (1500) | 81 [107] |
| Octadecane | Grignard reaction | TiO₂ (Øpore ≈ 1 nm) | Acetone | 3.0 | PS (580) | 55 [107] |
| Octadecane | Grignard reaction | TiO₂ (Øpore ≈ 1 nm) | Acetone | 3.0 | PS (1500) | 63 [107] |
| Octadecane | Grignard reaction | TiO₂ (Øpore ≈ 1 nm) | Acetone | 1.5 | PEG (600) | -5 [107] |
| Octadecane | Grignard reaction | TiO₂ (Øpore ≈ 1 nm) | Acetone | 1.5 | PEG (1500) | 46 [107] |
| PS brushes | Grafting-from | TiO₂ (Øpore ≈ 1 nm) | Acetone | 2.0 | DPA (330) | 90 [111] |
| microporous SiO₂ layer | In-situ modification | TiO₂ (Øpore ≈ 1 nm) | Acetone | 7.2 | Polyethel (1200) | 90 [45] |
or near the external surface of modified membranes. For example, the degree of protonation of the phosphonate linking function can be, as a first attempt, investigated by IR spectroscopy [71,76,86,131]. In the case of Grignard-functionalized membranes, Micro-ATR/FTIR spectroscopy was used directly on the external surface of the membrane to demonstrate the presence of alkyl groups [106]. Compared to standard FTIR spectroscopy, this technique has an increased signal to noise ratio because more reflected light is received by the detector. A less considered alternative, Raman spectroscopy can also be used as a complementary tool to assess the local environment of the grafted species. Raman spectroscopy may detect other bonds not clearly shown by FTIR [132], and has the ability to scan for organic species as a function of depth (micrometers) into the porous ceramic support [133].

In addition, solid state NMR is one of the techniques which can provide detailed information on the grafting mode of the linking function. For example, after a grafting-to reaction with an alkoxysilane linking function, the degree of silanol attachment to the metal oxide surface can be determined by measuring the 29Si chemical shift by performing 29Si – 1H cross-polarization (CP) MAS experiments [104]. Furthermore, it has been shown that 13C-CP/MAS NMR experiments can directly prove the formation of C–O–Ti bonds between alkyl Grignard reagent and TiO2 [72]. Recently, the bonding of phosphate-based ILs with only surface hexacoordinated aluminum nuclei of a γ-alumina powder was established using both solid-state 31P, 27AL-HMQC and 31P NMR experiments [134]. Unfortunately, given either to the poor abundance of the nuclear nuclei (e.g. 29Si: 4.7%, 13C: 1.1%) and/or the relatively low amount of grafted species compared to the bulk, such experiments have only been carried out so far on richly-grafted, model mesoporous particles. Recently, 1H, 13C, 19F and 31P one pulse High Resolution MAS NMR experiment on a phosphate-based ionic liquid ceramic membrane was conducted directly on pieces of ceramic support immersed in D2O [76]. Using this technique, the authors were able to detect and evidence the presence of both grafted and physisorbed species in the hybrid ceramic membrane. This confirmed that significant spectra resolution of HR-MAS NMR experiments can be obtained even at moderate spinning rates, hence providing valuable information on the local chemical environment of the membrane [135]. As HR-MAS NMR was only recently (successfully) adapted to the study of grafted ceramic membrane, we expect the use of this technique to become more accessible in the future.

4.2. Pore characterization techniques

Equally important is the characterization of the pores to determine the impact of graft on the pore size distribution, general surface properties and, also, the presence of defects. Small mesopores and micropores exclude pore-sizing techniques long used in membrane technology: scanning electron microscopy (SEM), bubble point test method, mercury intrusion porosimetry, and permoporometry. Each of these techniques has its limitation. The magnification capability of standard SEMs will not, for example, display 3 nm TiO2 pores, nor the molecules grafted inside. The lower detection limits of the bubble point method and mercury intrusion porosimetry do not reach down to small mesopores. The pore diameters of conventional mesoporous ceramic supports can be determined by permoporometry only down to 2 nm and up to 50 nm [136,137]. The 2 nm diameter detection limit of this technique restrict its use in the characterization of grafted pores [136,137]. These methods can however often detect the following information: i) the presence of a graft, if the change from support to grafted sample is noticeable, ii) the properties of the ungrafted sample and, importantly, iii) the presence of defects. Less considered, the nanopermoporometry technique can measure nanosized pores ranging from 0.6 to 30 nm, though both the accuracy and lower detection limit are dependent on the solvent and the properties of the membrane surface [138].

Another new accurate technique was developed for the analysis of micropores <1 nm to expand the range of conventional adsorption isotherm analysis [139]. This technique combines the information from thermogravimetry and pycnometry data. Thermogravimetric data is employed to assess the uptake of solvent vapors into the microporous structures of the sample at room temperature. Together with qualitative information on surface chemistries, quantitative micropore volumes and minimum pore entrance sizes are derived. In conjunction, the pycnometer is employed to measure the uptake and adsorption of inert gas into the structure at room temperature. From these data, semiquantitative surface-to-volume ratios, surface areas and micropore cavity sizes are derived as well as qualitative information on surface chemistry of the sample. This technique, until now only used on zeolite is very promising for grafted ceramic membrane pore characterization.

Together, graft and pore characterization provide crucial insights and parameters which help the membrane researcher to predict membrane performance via transport models, allowing for the tuning of graft, solvent, and solute interactions. Inversely, the membrane performance can also yield information about the membrane structure. A model is then needed to translate permeability and retention measurements into pore size and other parameters the model may call for, such as tortuosity. The following section studies OSN models for ceramics and grafted ceramics.

5. Transport through ceramic membranes

Membrane performance is defined by two main metrics: its throughput, expressed as permeability, and its selectivity, expressed as retention. The permeability, P (L m-2 h-1 bar-1), is equal to the pressure-normalized flux through a unit area of the membrane, as shown in Equation (1). The retention of a solute, also referred to as rejection, is usually expressed as a percentage, R (%), as shown in Equation (2).

\[
P = \frac{J}{\Delta p}
\]

\[
R = \left(1 - \frac{c_p}{c_f}\right) \times 100
\]

where \(J\) is the flux and \(\Delta p\) is the pressure applied across the membrane (trans-membrane pressure, TMP), and where \(c_p\) and \(c_f\) are the permeate and feed concentrations, respectively, of the solute. A common metric ascribed to membranes is the molecular weight cut off (MWCO), defined as the molecular weight that reaches 90% retention across the membrane. In the field of OSN, this metric does not accurately describe the retention capability of a given membrane, as the MWCO is often different when examining retention of the same solute in different solvents, and also varies across different solutes of the same molecular weight [140,141]. Regardless of the non-specific nature of the MWCO in OSN, a sharp difference in the retention of two molecules of similar molecular weight is advantageous, as it enables the separation of multi-solute mixtures. This ability allows a nanofiltration membrane to compete with traditional separation processes such as distillation.

Many solutes have been proposed and advocated as model testing solutes. Due to the simplicity of light absorption testing and the molecular weight range of nanofiltration solutes, dyes are often used in retention tests. Their advantage is also their disadvantage, as their overlapping absorption spectrums makes testing of multiple dyes at once impossible. Commonly used dyes and their properties are listed in Table 7. Besides dyes, at least three separate studies have advocated the use of various polymers as “model solutes” for testing membranes in organic solvents. These polymers include polyethylene glycol (PEG) [142], polystyrene (PS) [143], and polypropylene glycol (PPG) [144] as ideal testing solutes, also listed in Table 7.

Though each solute has its merits, it remains difficult to translate molecular weight across solvents, as changing the solvents will change...
Table 7
Commonly used solutes, their molecular weight, or repeat unit molecular weight (n), along with notable properties. HPLC = high performance liquid chromatography, ELSD = evaporative light scattering detector, TOC = total organic carbon [142-144].

| Solute                | Molecular weight [g mol⁻¹] | Selected properties                                      |
|-----------------------|----------------------------|----------------------------------------------------------|
| Rose Bengal, dye      | 974                        | Neutral, insoluble in hexane, toluene                    |
| Methyl Orange, dye    | 327                        | (-) charge, insoluble in diethyl ether                   |
| Sudan Black B, dye    | 457                        | Neutral, widely soluble                                  |
| Bromothymol, blue, dye| 624                        | Neutral, limited solubility in nonpolar solvents         |
| Brilliant Blue R, dye | 826                        | Zwitterionic, limited to no solubility in nonpolar solvents |
| Orange II, dye        | 350                        | (-) charge, limited solubility in nonpolar solvents      |
| Saffronin O, dye      | 350                        | (+) charge, limited solubility in nonpolar solvents      |
| 9,10-Diphenyl anthracene | 330              | Nonpolar UV-visible aromatic hydrocarbon                 |
| Alkane oligomers (C₆H₄) | <400                       | Limited solubility in polar solvents, availability is impr > 400 ha detected via gas chromatography |
| PS oligomers          | n • 104                    | Expensive, limited solubility in polar solvents, measured via HPLC |
| PEG oligomers         | n • 44                     | Insoluble in many non-polar solvents, limited accuracy, measured via GPC or HPLC with ELSD or TOC analysis |
| PPG oligomers         | n • 58                     | Soluble in a wide range of solvents, limited accuracy, measured with HPLC with ELSD |

the retention of the same oligomer. Predicting the retention of other solutes from the retention of one, even in the same solvent, has not yet been achieved. In short, rather than proposing an ideal solute class, it is our view that new membranes should be evaluated by a class of solutes representative of the target application rather than by any semiarbitrary standard.

If there were a single predictive model for all OSN membranes, such as the solution-diffusion model for reverse osmosis membranes, a standardized testing method would make sense. However, this ideal has yet to be formulated. The models describing transport through aqueous-application membranes are not directly applicable to OSN, as retention is a function of not only the membrane but also of complex membrane-solute-solvent interactions [140, 141]. For instance, polymers, either as part of the membrane or as a solute, are susceptible to solvent effects. They have been shown to change their size and conformation based on the solvent(s) present [145, 146]. These effects can, for example, create, restrict, or enlarge pores [96, 147]. Other interactions between the solvent, solute and membrane have led to negative retentions, as reported in several publications [19, 148, 149]. The search for a single model is naturally continuing, recent or notable models for OSN ceramic membranes are listed in Table 8, each described in the following section.

5.1. Transport through porous ceramic membranes

There are generally three types of models describing transport through membranes, defined below.

a) Models based on irreversible thermodynamics, treating the membrane as a “black box”, meaning membrane properties are excluded.

b) Pore-flow models (for porous membranes) which incorporate membrane properties.

c) Solution-diffusion models, for dense membranes.

Model types (a) and (b) can describe transport through porous ceramics. Model type (c) aptly describes dense membranes [150] and is hence not reflective of the transport mechanics through porous ceramics.

The transport model by Kedem and Katchalsky [151] is one of the first of the thermodynamic models for membrane transport and is still used in various forms today. This model excludes any membrane-specific properties such as tortuosity or porosity, and was later expanded upon by Spiegler and Kedem [152] to Equations (3) and (4).

\[
R = \sigma(1 - F) \left( \frac{1}{F} - F \right) \tag{3}
\]

\[
F = \exp\left( - \left(1 - \frac{1}{F} \right) \right) \tag{4}
\]

Table 8
Models used to interpret or predict solvent and solute transport across OSN ceramic-based membranes.

| Reference         | Capability          | Model basis                  | # of fitted variables | Parameters                                                                 | Model agreement with experimental data |
|-------------------|---------------------|------------------------------|-----------------------|---------------------------------------------------------------------------|----------------------------------------|
| Darvishmanesh et al. [164] | Pure solvent permeability | SD with pore-like imperfections | 2                     | Solvent viscosity, dielectric constants of solvent & reference solvent, surface tension of solvent & reference solvent | Overall agreement with 3 membranes tested, Koch MPP-50, Solsep-030505, HITK 27, of which alone HITK is ceramic Agreement with 2 ceramic membranes tested, HITK 275 and HITK2750. |
| Darvishmanesh et al. [165] | Pure solvent permeability | Coupled resistances          | 3                     | Solvent viscosity, dielectric constants of solvent & reference solvent, surface tension of solvent & reference solvent, solvent size pore size | Agreement except for acetonitrile/water mixtures. Membranes tested Inopor Nano 450, Inopor Nano 750, Sulzer 1000, Inopor Ultra 2000 |
| Marchetti et al. [166] | Solvent (pure & mixtures) permeability | Modified pore flow           | 3                     | Solvent surface tension, contact angle between membrane and solvent, solvent dipole moment, polarizability of the membrane as calculated by Carré’s theory of surface polarizability, solvent size, pore size | Agreement with 3 Inopor membranes (pore sizes 0.9, 1 and 5 nm) |
| Buekenhoudt et al. [167] | Pure solvent permeability | Empirical fit to Hansen solubility parameters | 1                     | Hansen solubility parameters of solvent and reference liquid (water) | Agreement with PDMS-grafted membranes (2 sizes of PDMS, n = 10, 39) |
| Tanardi et al. [101] | Pure solvent permeability | Modified pore flow with swelling parameter | 1                     | Swelling degree for PDMS in solvent, swelling degree for PDMS in reference solvent, solvent viscosity | Agreement with PDMS-grafted membranes (2 sizes of PDMS, n = 10, 39) |
| Merlet et al. [100] | Permeability & retention | Modified Spiegler Kedem model | 2                     | Pore size, diffusion pore size, solute size, membrane thickness | Agreement with PDMS-grafted membranes (2 sizes of PDMS, n = 10, 39) |
| Hosseinabadi [73] | Permeability & retention | Spiegler Kedem model | 2                     | None | Fitted to Grignard-grafted membranes, better agreement for high polarity solvents and at higher pressures |
| Blumenschein [168] | Permeability & retention | Modified Bowen-Welfoot        | 0                     | Solvent viscosity, Solvent size, solvent size, pore size, solute molecular weight | No agreement except for retention of polystyrenes in THF |
where the volumetric flux, $J_v$, and retention, $R$, are related through two constants: the membrane reflection coefficient, $\sigma$, and the solute permeability, $P_s$. The reflection coefficient is a measure for the retention of a solute under purely convective influence. $P_s$ is the diffusion-driven permeability of solute across the membrane, and thus varies with the solute-solvent combination [153]. This model has explained the behavior of aqueous-applications membranes well, such as salt retention, and has been used to predict the effect of operating parameters such as trans-membrane pressure [154].

One of the first models describing the size-exclusion mechanism across porous membranes was the “Theory of Sieving” proposed by Ferry [155] in 1936 for ultrafiltration. Its underlying concept is that there is a statistical distribution of retained solutes that are smaller than the pores of a given membrane. Assuming spherical solutes, an isoporous membrane, cylindrical pores oriented normal to the membrane surface, and a homogenous (bulk) solution at the pore entrance, retention was expressed in the following way, where $d_s$ is the solute diameter and $d_p$ the membrane pore diameter, for $d_s \leq d_p$:

$$R = \left( \frac{d_s}{d_p} \right)^{\frac{d_s}{d_p} - 2}$$

(5)

Though filtration by steric hindrance, i.e. sieving, undeniably plays a role in the retention of solutes through pores, affinity and membrane surface effects play an increasingly important role as mesopores shrink to nanofiltration range. Interactions are further complicated when water is replaced with organic solvents or a mixture of liquids, and different solutes are studied. This was witnessed by Tsuru et al. [156] when filtering alcohols and alkanes in ethanol through porous ceramic reverse osmosis (RO) membranes. The permeability and retentions at different temperatures could be modeled by including both a diffusion and a pore-flow contribution through via a bilayer model. Marchetti et al. [157] studied the retention of solutes which are significantly smaller than the pore and similar in size to the solvent (e.g. salts). The retention is determined by the preferential affinity of the membrane surface to either the solute or solvent, as illustrated in Fig. 13. The same work showed that if no preferential affinity exists, the retention is near zero (if $d_s < d_p$). It was also shown that the addition of water to an organic solvent can change the interaction as preferential solvation of the solute can change its interaction with the membrane surface. These findings, among others, helped qualitatively explain observed negative retentions in terms of membrane-solute-solvent interactions in a number of studies [107,158,159]. It has become clear that any comprehensive model describing nanofiltration through pores should include both bulk and surface effects.

Qualitative evaluation and performance prediction of porous, non-swelling membranes was undertaken using Hansen solubility parameters (HSPs) [160]. The relative affinity between solvent and membrane (SM) and the difference in the relative affinities between solvent-membrane and solute-membrane (SM-SoM) were calculated and visualized by employing ternary HSP plots. The membranes used were the 0.9 nm TiO$_2$ Grignard-grafted membranes from VITO described in section 2.3.2. A clear relationship was shown between the SM parameter and relative solvent flux, when corrected for viscosity. Visually, it is seen as the lower the affinity, the higher the distance on the ternary plot, and therefore the lower the expected flux. It was also claimed that a low SM-SoM (i.e. stronger solute-membrane than solvent-membrane affinity) indicated an increased likelihood of low or even negative retentions. The HSP method [160] presents a useful tool for maximizing the performance for non-swelling porous membranes. It should be considered when modifying the surface hydrophilicity of a porous ceramic for a given application. However, the retention indication parameter (SM-SoM) has no input from the relative size of the solute to the membrane pore, and should therefore be carefully applied.

Other solute-membrane interaction terms have been used besides HSPs. For the nanofiltration of aqueous solutions, solute-membrane interaction terms are found in porous models, for example in sieving models modified by empirically-determined correction factors [161, 162], and also in the Donnan-Steric Pore Model (DSPM) [163]. These and other models have been adapted from aqueous membrane applications to describe the transport of organic solvent solutions through

![Fig. 13. a) Membrane surface effects in nanofiltration versus ultrafiltration b) In nanofiltration, higher solute or solvent flux due to either preferential solute–membrane or solvent–membrane affinity, respectively. Adapted from Ref. [157].](image-url)
nanofiltration membranes; they are described in the next two sections. The first section describes OSN models for transport through unmodified ceramic membranes. These models have been derived from transport studies across hydrophilic (unmodified) ceramic membranes, nonetheless their behavior can be used as a basis to understand transport through modified ceramics. The second section describes models for grafted ceramics. Many of the models presented focus only on explaining or predicting solvent permeability and do not include solute transport.

5.1.1. Ungrafted ceramic membranes

The models used to describe the transport of organic solvent solutions through porous ceramics have generally been derived from existing models for aqueous applications. This section, begins with models describing the passage of solvent and solute through porous ceramics. The following section continues with those models generated to describe transport through grafted ceramics.

The unique permeation characteristics of organic solvents passing through a ceramic nanofiltration membrane were detailed by Tsuru et al. in two papers published at the outset of OSN in 2000 [38,169]. A set of alcohols permeating through SiO₂/ZrO₂ membranes (pore diameters 1–5 nm) was found to deviate from the Hagen-Poiseuille model. Though viscosity was still the major solvent parameter impacting flux, permeability was facilitated by an increase in temperature (after correcting for viscosity) while negatively affected by solvent size. The study concluded that permeation through pores of 1–5 nm required a higher activation energy for larger molecules [38]. Next, permeation of alcohols and sugars at different temperatures was analyzed by the Spiegler-Kedem model and corroborates the proposition of a size-dependent activation energy [169]. These studies established the different character of porous nanofiltration membranes from their ultrafiltration counterparts.

In 2009, Darvishmanesh et al. [164] published a solution-diffusion model with imperfections adapted to pure solvent permeability. In addition to diffusive transport within the membrane, an extra term takes into account the viscous transport through the imperfections located in the membrane itself:

\[
J_{\text{imper}} = \frac{a_0 \alpha}{\mu \exp (1 - \beta)} (\Delta p - \Delta p_s) + \frac{b_0}{\mu \exp (1 - \beta)} (\Delta p)
\]  

(6)

where \( a_0 \) and \( b_0 \) are fitted diffusivity and permeability parameters, respectively, for a given membrane, \( \mu \) is the viscosity, \( p \) is the pressure, \( p_s \) is the osmotic pressure, \( \alpha \) is the dielectric constant ratio (relative to water for hydrophilic membranes, and to hexane for hydrophobic membranes) and \( \beta \) is either the surface tension ratio of the solvent to the hydrophilic membrane or the surface tension ratio of the hydrophobic membrane to the solvent’s. A range of organic solvents was tested on two commercial membranes, a hydrophilic ceramic membrane, HTK 275 (TiO₂), and a hydrophobic PDMS polymeric membrane, MPF 50. The fitted parameters of the model were reported to agree within 5% error. This model confirmed earlier findings showing the inverse relation between single-solvent permeability and viscosity as well as molar volume [20,38,169,170], and also continued to emphasize the impact solvent-membrane affinity has on permeability [171,172].

Shortly following the previously discussed study, Darvishmanesh et al. published a coupled series-parallel resistance model (CSR) specific to inorganic membranes [165]. The model was tested on HTK275 (0.9 nm diameter, TiO₂) and HTK2750 (3.0 nm, ZrO₂) only with pure solvents. The three resistances consisted of a surface resistance, \( R_s \), connected in series to two parallel resistances: the membrane resistance, \( R_m \), and the pore resistance, \( R_p \). The \( \alpha \) and \( \beta \) parameters are the same as Equation (8). The \( t_s \) and \( t_p \) are solvent and pore radius, respectively, and \( k_s \), \( k_m \) and \( k_p \) are parameters to be fitted for each membrane. These resistances are combined to give flux equation (13).

\[
R = k_s \left( \frac{t_s}{t_p} \right)^2 \exp (1 - \beta); \quad R_m = k_m \left( \frac{t_m}{t_p} \right)^2; \quad R_p = k_p \left( \frac{t_p}{t_p} \right)^2
\]  

(7)

\[
J = \frac{\Delta P}{R_{\text{total}}}
\]  

(8)

This model again gives fitting results with a reported error of less than 5%. Here the surface affinity between solvent and membrane are taken into account by incorporating the dielectric constants and surface tensions of both the solvent and membrane as parameters. Unfortunately, neither of these models were tested on solvent mixtures or solutions. Marchetti et al. [166] proposed in 2012 a corrected pore-flow model, which has four parameters to be fitted. Only three, \( K_{\text{hp}}, k_{\text{capillary}} \) and \( f_{\text{steric}} \) were found necessary for model validity.

\[
J = \frac{K_{\text{hp}} \Delta p}{\mu} (1 + f_c)
\]  

(9)

\[
f_c = f_{\text{capillary}} + f_{\text{dipole}} + f_{\text{steric}} = C_1 \frac{2 \mu L \cos \theta}{t_p} + C_2 (k_s - k_{\text{pol}}) + C_3 \left( \frac{t_s}{t_p} \right)^2
\]  

(10)

where \( \theta \) is the contact angle between membrane and solvent, \( \delta_i \) is the solvent’s dipole moment, \( k_{\text{pol}} \) is the polarizability of the membrane as calculated by Carré’s theory of surface polarizability [173]. The dipole moment was chosen over the dielectric constant as a better indicator of molecular (versus bulk) properties. This model was tested on a range of TiO₂ and ZrO₂ membranes with solvent and solvent mixtures and compared against the classic Hagen-Poiseuille equation and coupled resistances model [165]. The Hagen-Poiseuille equation failed to accurately predict some solvent permeabilities through microporous membranes, while the coupled resistance model suffered the same shortcoming for mesoporous membranes. The corrected pore flow model was found to be accurate (within 5%) through pore sizes of 0.9 nm–3 nm, and the parameters taken to vary linearly with composition for most solvent mixtures.

A model derived by Bukenhoudt et al. [167] in 2013 uses the empirically determined linear relation between the Hansen solvent solubility parameter and its viscosity-corrected flux. The derived equation is shown below,

\[
\frac{J \mu}{J_{\text{water}} \mu_{\text{water}}} = \frac{S_{\text{Hansen, water}}}{S_{\text{Hansen, solvent}}} C (1 - C)
\]  

(11)

where \( S_{\text{Hansen}} \) is the total Hansen solubility parameter and \( C \) is the only parameter to be fitted. The product of viscosity and flux is normalized to that of water, just as the Hansen solubility parameter of the solvent is normalized to water. When tested on inorganic membranes, it was shown that for the given material (TiO₂) the \( C \) parameter has an exponential relationship with the pore diameter and found to be valid from 0.9 nm to 100 nm, using different solvents and solvent mixtures. This model that accurately describes solvent flow through both ultrafiltration and nanofiltration pores is remarkable, however, no effort has been made to describe retention using this model or its ‘C’ parameter. This publication tentatively proposes that the observed affinity difference between the membrane and solvent is in fact between the membrane and a thin water layer adsorbed onto the hydrophilic membrane surface. Extension of this simple model to modified hydrophobic surfaces may prove to be more complex, as the Hansen solubility parameter at the membrane surface would depend on the solvent or solute preferentially adsorbed to the membrane surface.

A transport analysis [168] of in-situ modified membranes whose fabrication method [46] is described in Section 2 was published in early 2016. The membrane selective layer was composed of hydrophobic 1.0 nm diameter pores of ZrO₂. The retentions of styrene oligomers of low molecular weight with varying endgroup polarities were tested. The authors modified the model of Bowen and Welfoot [174] to include a
pore size dependent viscosity, due to the presence of an absorbed layer at pore surface, and a pore size distribution to accommodate defects in the top layer. The applicability of the resulting model is poor, as it is only valid for the retentions of polystyrene in one solvent, THF. When using other solvents, such as ethanol or n-heptane, retentions are significantly over-predicted. The model also over-predicts solvent fluxes by at least an order of magnitude, and fails to accommodate membrane defects. A purely theoretical model with no fitted parameters is ideal, however, this attempt falls short. Though the applicability of pore size dependent viscosity as applied in Ref. [168] is probably not applicable to the “soft surface” of grafted ceramic pores, it may still be possible to incorporate, in another way, the impact of defects on retention and permeability.

5.1.2. Grafted ceramic membranes

Now described are the few models that have attempted to describe mass transport through grafted ceramic membranes. As detailed in the previous sections, numerous grafted membrane types have been developed, differing in both chemical makeup and structure. The pores of the selective layer, if indeed still present, have shrunk to microporous dimensions and may be subject to effects such as swelling. With hybridization, complexity increases: the selective layer may not be well-defined (characterization shortcomings are discussed in Section 4) and surface interactions from one or more materials dominate (as opposed to bulk interactions, Fig. 11). As a result, the applicability of either a (a) thermodynamic or a (b) pore-flow models is made even less straightforward than it was for unmodified meso- or microporous ceramic membranes.

Nevertheless, the models reviewed here have each been used to gain an understanding of the transport phenomena occurring through the grafted membranes and to then predict general behavior. First described are two PDMS-grafted membrane studies [100,101], particularly dealing with the effect of a presence of a polymer brush in the pore, followed by a study detailing transport through Grignard-grafted membranes [75], seeking to generally classify membrane retention by solvent class.

Tanardi et al. [101] developed an organic solvent permeability model specific to grafted ceramic membranes. Derived from the pore flow (Hagen-Poiseuille) model, this approach equates the swelling degree of the grafted moiety, assumed to be responsible for mass transport through grafted ceramic membranes. As detailed in the present section, numerous grafted membrane types have been developed, differing in both chemical makeup and structure. The pores of the previous sections, numerous grafted membrane types have been developed, differing in both chemical makeup and structure. The pores of the selective layer, if indeed still present, have shrunk to microporous dimensions and may be subject to effects such as swelling. With hybridization, complexity increases: the selective layer may not be well-defined (characterization shortcomings are discussed in Section 4) and surface interactions from one or more materials dominate (as opposed to bulk interactions, Fig. 11). As a result, the applicability of either a (a) thermodynamic or a (b) pore-flow models is made even less straightforward than it was for unmodified meso- or microporous ceramic membranes.

Nevertheless, the models reviewed here have each been used to gain an understanding of the transport phenomena occurring through the grafted membranes and to then predict general behavior. First described are two PDMS-grafted membrane studies [100,101], particularly dealing with the effect of a presence of a polymer brush in the pore, followed by a study detailing transport through Grignard-grafted membranes [75], seeking to generally classify membrane retention by solvent class.

Tanardi et al. [101] developed an organic solvent permeability model specific to grafted ceramic membranes. Derived from the pore flow (Hagen-Poiseuille) model, this approach equates the swelling degree of the grafted moiety, assumed to be responsible for shrinking the pore. A linear relationship between graft swelling and solvent class.

The permeability of the reference solvent, hexane, was obtained along with values of $V_i'$, as determined through simple sorption experiments of free-standing PDMS [101]. Equation (16) correctly predicted the permeabilities of six other solvents, as shown in Table 9. Expanding this model to multi-solvent mixtures should be straightforward, as permeability would likely remain a function of solvent sorption, to be determined by further simple sorption experiments on those multi-solvent mixtures.

\[
\frac{P_i}{P_{ref}} = \left( A - BV_i \right) \Delta \rho
\]

where $P_{ref}$ is the permeability of a reference solvent, $V_{ref}$ is the amount of sorbed reference solvent per gram of grafted moiety, $P_i$ and $V_i$ are the permeability and sorbed solvent per gram of graft of the solvent in question, respectively, and $P_i '$ and $V_i' $ are the normalized values of these, and are equal to 1 when $P_i = P_{ref}$ and $V_i = V_{ref}$. The membrane-specific constants $A$ and $B$ are empirically determined by the linear relationship between $P_i'$ and $V_i'$. This model was tested on 2 different PDMS-grafted $(n = 10, 39)$ γ-alumina membranes in a temperature range of 20°C–70°C. Noting that the linear relationship between $P_i'$ and $V_i'$ always passes through the point (1,1) implies the possible reduction of this model to 1 fitted constant:

\[
J_i \times \mu = P_{ref} \left( B - BV_i' + 1 \right) \Delta \rho
\]

The points are experimental data and the lines from the modified Spiegler-Kedem model of [100].

**Table 9**

Permeabilities (P) of PDMS (n = 10) grafted membranes for each solvent, with permeabilities corrected for viscosity ($P' \mu$) and permeabilities corrected for viscosity and PDMS swelling ($P' \mu/(B-V_i' + 1)$). Correcting for both swelling and viscosity gives a uniform permeability. B = 0.68 for PDMS n = 10 grafted membrane [101].

| Solvent       | $\mu$ (mPa s) | $V_i'$ | Permeability [L m-2 h-1 bar-1] | $P' \mu$ | $P' \mu/(B-V_i' + 1)$ |
|---------------|---------------|--------|-------------------------------|-----------|-----------------------|
| Isopropanol   | 2.39          | 1.00   | 0.9                           | 2.2       | 2.2                   |
| Ethyl acetate | 0.45          | 1.02   | 4.6                           | 2.1       | 2.1                   |
| Octane        | 0.54          | 1.12   | 3.4                           | 1.8       | 2.0                   |
| Toluene       | 0.59          | 1.15   | 3.1                           | 1.8       | 2.0                   |
| p-xylene      | 0.64          | 1.34   | 2.7                           | 1.7       | 2.2                   |
| Hexane        | 0.31          | 1.40   | 4.8                           | 1.5       | 2.0                   |
| Cyclooctane   | 2.13          | 1.48   | 0.6                           | 1.3       | 2.0                   |

![Solute-induced swelling](Image)
Merlet et al. [100] modeled the retention performance of these same PDMS-grafted membranes with a modified Spiegler-Kedem (SK) model. The retention of neutral dyes of molecular weights ranging from 322 g mol\(^{-1}\) to 973 g mol\(^{-1}\) in a variety of solvents were reported, as shown in Fig. 14. Building upon previous work [175], the Ferry sieving model, Einstein-Stokes diffusion equation and Renkin equation (hindered diffusion in a cylinder) were used to make the original model parameters, \(\alpha\) and \(P\) (Equations (3) and (4)), a function of the ratio of the solute size to the pore size. This alteration to the SK model allowed for the diffusion of solutes through the graft by introducing a “diffusion pore size”, equal to the original diameter minus the monolayer of organosilane linker on the \(\gamma\)-alumina pore, resulting in a diffusion pore size of 4.1 nm. The end result is a model that requires two fitted parameters, one obtained from a permeation and retention experiment through a given solvent-membrane pair, the second being membrane-dependent and easily obtainable by permoporometry. This model does not include any specific affinity interactions between the solute and either the membrane or solvent, yet still correctly predicts permeation because in this work it tests only one class of solutes, namely neutral dyes. Despite this limited scope of this model, it shows the need to consider the diffusion of solutes through the graft when evaluating or modeling these types of membranes.

While solvents clearly swelled and changed the performance of the PDMS-grafted membranes described in the model above, solutes with a high or low graft affinity may influence their own retention as well. Besides the pronounced surface effects in the nanofiltration pore that influence solute retention [157], it is possible for the solute to affect the graft swelling. Postel et al. [176] as well as Ogiglio et al. [177] have determined that solutes with an affinity for PDMS, as determined by Hansen solubility parameters, will additionally swell PDMS that was already saturated with a given organic solvent. Further studies of PDMS-grafted membranes with different types of solutes, not only neutral dyes, would elucidate this relationship.

A different behavior is seen for TiO\(_2\) Grignard-grafted membranes, as the graft partially covers the surface and has not been observed to swell. In a comprehensive study of these membranes [75], the permeabilities in a range of solvents, from polar to nonpolar, was obtained. Retention was also measured, both by PEG chains of similar molecular weight but with endgroups of varying polarity, and by a series of PS oligomers. Results were analyzed via the Spiegler-Kedem model and in terms of the affinity of the solvent and solute, as measured by Hansen solubility parameters. Observed were two classes of solvents: high polarity solvents, where solute retention is independent of pressure, and low polarity solvents, where retention shows a pressure dependence. As observed in previous studies of Grignard-grafted membranes [107], these polar solvents also had higher fluxes (DMF: 2.6 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\), THF: 2.7 L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)). This was likely due to the partial graft coverage, which imparts only an amphiphilic character to the membrane surface. The membrane surface then prefers polar compounds over non-polar ones, which translates into higher fluxes for polar solvents. When analyzed through the Spiegel Kedem model, solutions of polar solvents were found to be in a convection-dominated regime. While in this regime, diffusion of solutes through the membrane is negligible. The study concludes that the retention mechanism in these polar solvents is therefore intrinsic to a size exclusion mechanism, i.e. by the reflection coefficient of the Spiegler-Kedem model (Equations (3) and (4)), while those solutions of solvents below a certain affinity, as measured by Hansen solubility parameters, will show lower retentions. These retentions especially decreased with an increase in solute polarity or a decrease of applied pressure. Through Hansen solubility parameters and the Spiegler-Kedem model this study gains an understanding of the performance Grignard-grafted membranes in the context of solvent-solute-membrane affinities.

5.2. Evaluation & applicability of transport models

Both PDMS-grafted and Grignard-grafted ceramic membranes are similar in many respects, as each is a grafted ceramic designed as an OSN membrane. Upon comparison of their transport studies via the Spiegler-Kedem model we perceive that their different graft styles lead to different transport behaviors. The best performance of PDMS-grafted membranes in non-polar solvents can largely be explained by examining the graft swelling, which is maximized in non-polar solvents, while the amphiphilic character imparted by the partial surface coverage of the Grignard-graft makes those membranes especially suitable for polar solvent nanofiltration. Both PDMS-grafted and Grignard-grafted ceramic membranes show competitive separation in organic solvents, yet transport through either is not yet fully understood. For the PDMS-grafted membranes the effect of solute type was not studied nor modeled as only one type of solute has been used [180]. For Grignard-grafted membranes, the effect of solute affinity is only qualitatively understood, by either placing the solute in an affinity-independent regime (polar solvents) or in an affinity-dependent regime (less polar solvents) and identifying trends in each region [75]. In each case a qualitative, predictive model is missing, which would allow for confident estimations of membrane performance than the informed guesses we can currently make.

Before thinking of a single OSN model for both ceramic and polymeric membranes, a logical, prior step is one that fits hybrid ceramic-based membranes. The two models discussing PDMS-grafted membranes [100,101] explored the impact of the grafted pore-brush on transport through two phenomena: (1) solvent-dependent swelling and (2) diffusion of solute through the brush itself. These were necessary studies undertaken before what must logically follows: the quantification and mathematical description of the effect of the brush on not only different solvents, but also different solute types. Further modification of the Spiegler-Kedem model is limiting, as more system-specific parameters would need to be introduced, and would strain compatibility with the Grignard-grafted membranes [75]. On the other hand, a model based on physical parameters appeals to the abundance of solvent-solute-membrane surface effects during filtration.

A recurring theme of the transport models described in the last two sections is choosing solvent properties as baselines to normalize various parameters. Examples include the dielectric constant of either water or n-hexane [164], the flux and solubility parameters of water [167] and the swelling degree of PDMS in cyclooctane [101]. Choosing water as a baseline is not logical for the filtration of organic solvents through hydrophobic membranes. A rational alternative is to normalize properties to a representative hydrophobic solvent, such as hexane. Besides the ambiguity of the term “representative hydrophobic solvent,” this approach prevents the formulation of a unified transport theory for both hydrophilic and hydrophobic membranes. It also raises the question of how to model those membranes termed amphiphilic, as determined either by their water contact angle (70–90°) or by their varied functional surface groups (e.g. a mixture of hydroxyl and alkyl groups). Since it is the relative affinities of the solvent, solute and membrane to one another that influence performance, a better approach is to use the membrane properties to normalize various parameters, as with the corrected pore flow model [166], where the solvent’s dipole moment is normalized to the surface charge of the membrane, possible to determine by streaming zeta potential measurement.

As discussed in this section, the research, development and production of polymeric membranes outnumbers that of ceramic membranes. Naturally, models describing polymeric membranes also exceed models for ceramic membranes. However, no model has proven superior for both membrane types. Different models work best for different combinations of solvent, solute, and membrane [171, 178–181]. The few models tailored to ungrafted or grafted ceramic OSN membranes are either descriptive, i.e. not predictive, or do not adequately predict performance across several types of membranes. The
complexity of a theory that can cover both types of membranes may be too unwieldy and complicated, or existing in different forms depending on the membrane structure. Additionally, if any model describing ceramics OSN membranes makes use of physical characteristics of the membrane, such as pore size, hydrophobicity, etc., then it will likely not be applicable to most polymeric membranes. From this we conclude that the focus should shift towards finding models describing a set of membranes with a similar structure, such as a single model well-describing porous ceramics.

6. Conclusions

Grafted ceramics are a promising class of materials for OSN. While to-date much research is focused on polymeric membranes, the advantages of tailoring porous ceramics with polymers are clear. The inherent chemical and mechanical resistance of ceramics coupled with the multitude of possible grafts translates into three major benefits: long membrane lifetimes, suitability to harsh conditions, and the ability to be tailored to a large range of applications. This potential, the facile tuning of separation properties, has started to be realized. A sharp and low MWCO in the range of 250–450 Da would potentially enable solvent-solute discrimination, opening up new applications. This challenge can be overcome by exploring and expanding the many grafting chemistries and techniques available, notably surface-initiated polymerization. Recent developments, such as one-step, direct grafting of an alternating copolymer [104] and the grafting-from of polystyrene [111], show how known chemistries can be applied to the fabrication of ceramic-based hybrid membranes.

Developing performance-predicting models valid for a range of grafted ceramics would allow for facile membrane customizations, as grafts could then be tailored to target applications with a reasonable expectation of success. Currently, only a partial grasp of the complex solvent-solute-membrane relationship is present. Research efforts to quantitatively model these interactions could yield the much needed greater understanding needed for predictive modeling as well as naturally attract further interest from industry. OSN technology is young yet advancing rapidly, and the sub-field of grafted ceramics for OSN even more so, propelled by its recent advancements that encourage further development.

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.

Acknowledgements

This work is part of the research program titled ‘Modular Functionalized Ceramic Nanofiltration Membranes’ (BL-20-10), which is taking place within the framework of the Institute for Sustainable Process Technology (ISPT, the Netherlands) and is jointly financed by the Netherlands Organization for Scientific Research (NWO, the Netherlands) and ISPT.

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi.org/10.1016/j.memsci.2020.117839.

References

[1] M.M. Pendergast, E.M.V. Hoek, A review of water treatment membrane nanotechnologies, Energy Environ. Sci. 4 (2011) 1946–1971, https://doi.org/10.1039/c0ee00541j.

[2] N. Hillal, H. Al-Zoubi, N.A. Darwish, A.W. Mohamma, M. Abu Arabi, A comprehensive review of nanofiltration membranes: Treatment, pretreatment, modelling, and atomic force microscopy, Desalination 170 (2004) 281–308, https://doi.org/10.1016/j.desal.2004.01.007.

[3] P. Marchetti, M.F. Jimenez Solomon, G. Szekely, A.G. Livingston, Molecular separation with organic solvent nanofiltration: a critical review, Chem. Rev. 114 (2014) 10735–10806, https://doi.org/10.1021/cr500006.

[4] P. Van den Abeele, L.E.M. Gevers, I.P.J. Vankelecom, Solvent resistant nanofiltration: separating on a molecular level, Chem. Soc. Rev. 27 (2008) 365–405, https://doi.org/10.1039/b618048m.

[5] G. Szekely, M.F. Jimenez-Solomon, P. Marchetti, J.F. Kim, A.G. Livingston, Sustainability assessment of organic solvent nanofiltration: from fabrication to application, Green Chem. 16 (2014) 4440–4473, https://doi.org/10.1039/c4gc00701h.

[6] P. Aptel, J. Armor, R. Audinos, R.W. Baker, R. Bakish, G. Belfort, B. Bilko, R. G. Brown, M. Bryk, J.J. Burke, I. Cabasso, R. T. Cher, M. Cheryan, E.L. Cussler, R. H. Davis, Terminology for membranes and membrane processes (IUPAC Recommendations 1996), J. Membr. Sci. 120 (1996) 149–159, https://doi.org/10.1016/0376-7388(96)82864-1.

[7] J. Großeheilmann, T. Fahrmeinert, U. Kragl, Organic solvent nanofiltration-supported purification of organocatalysts, ChemCatChem 8 (2015) 322–325, https://doi.org/10.1002/cctc.201500902.

[8] K. Werth, P. Kaupenjohann, M. Kniebein, M. Skiborowski, Solvent recovery and deacidification by organic solvent nanofiltration: experimental investigation and mass transfer modeling, J. Membr. Sci. 528 (2017) 369–380, https://doi.org/10.1016/j.memsci.2020.117839.

[9] N. Hilal, H. Al-Zoubi, N.A. Darwish, A.W. Mohamma, M. Abu Arabi, R.B. Merlet et al., Supplementary data to this article can be found online at https://doi.org/10.1016/j.memsci.2020.117839.
A. Asadi-Tavigh, T.S. Chung, Robust polybenzimidazole (PBI) hollow fiber membranes for organic solvent nanofiltration, J. Membr. Sci. (2019) 580–587, https://doi.org/10.1016/j.memsci.2018.11.048.

G. Ignacz, F. Fei, G. Szekely, Ion-Stabilized membranes for demanding applications, Prog. Polym. Sci. 38 (2013) 874–896, https://doi.org/10.1016/j.progpolymsci.2012.11.001.

J.C. Jansen, S. Darvishmanesh, F. Tasselli, F. Bazzarelli, P. Bernardo, E. Tocci, M. Khemakhem, S. Khemakhem, R. Ben Amar, Emulsion separation using poly (styrene-co-maleic anhydride), J. Membr. Sci. 243 (2004) 125–132, https://doi.org/10.1016/j.memsci.2004.05.031.

S.P. Pujari, L. Scheres, A.T.M. Marcelis, H. Zuilhof, Covalent surface modification of oxide surfaces, Angew. Chem. Int. Ed. 53 (2014) 6322–6356, https://doi.org/10.1002/anie.201306709.

M.L. Bruening, D.M. Dottzauer, P. Jain, L. Ouyang, G.L. Baker, Creation of functional membranes using poly (styrene-co-maleic anhydride) and poly (styrene-co-maleic anhydride) functionalized polyvinylidene fluoride, J. Membr. Sci. 118, https://doi.org/10.1016/j.memsci.2001.07.050.

S. Zeidler, P. Puhlfürst, J. Campbell, R.P. Davies, D.C. Braddock, A.G. Livingston, Improving the performance of crosslinked polyimide organic solvent nanofiltration (OSN) membranes, J. Membr. Sci. 470 (2014) 421–430, https://doi.org/10.1016/j.memsci.2014.07.051.

S.R. Hoseinabad, K. Wyns, V. Meynen, A. Buekenhoudt, B. Van der Bruggen, Influence of the blend composition on the fouling resistance of Inorganic Membranes by Grafting with Organic Moieties, J. Membr. Sci. 118, https://doi.org/10.1016/j.memsci.2001.07.050.

J. Caro, M. Noack, P. Kölsch, Chemically modified ceramic membranes, Microporous Mesoporous Mater. 22 (1998) 321–332, https://doi.org/10.1016/S1387-1811(98)00107-2.

K.V. Vancanen, P. Van Der Voort, I. Gilles-D’Hamers, E.F. Vansant, P. Grobet, Influence of water in the reaction of gamma-aminopropyltriethoxysilane with silica gel. A Fourier-transform infrared and cross-polarization magic-angle spinning nuclear magnetic resonance study, J. Chem. Soc. Faraday. Trans. 88 (1992) 3197, https://doi.org/10.1039/ft9882803197.

E. Tocci, A. Asadi-Tavigh, T.S. Chung, Membrane separation processes and units, appendix II: definitions, terminology and symbols in colloid and interface science, J. Membr. Sci. 181 (2001) 3–26.

S.P. Pujari, L. Scheres, A.T.M. Marcelis, H. Zuilhof, Covalent surface modification of oxide surfaces, Angew. Chem. Int. Ed. 53 (2014) 6322–6356, https://doi.org/10.1002/anie.201306709.

10.1002/anie.201306709.
CR. Tanardi, I.F.J. Vankelecom, A.F.M. Pinheiro, K.K.R. Teta, A. Nijmeijer, L. Winnubst, Solvent permeation behavior of PDMs grafted γ-alumina membranes, J. Membr. Sci. 495 (2015) 216–225, https://doi.org/10.1016/j.memsci.2015.08.004.

L. Leitner, C. Haroscht-Schlaivo, C. Vallieres, Experimental contribution to the understanding of transport through polydimethylsiloxane nanofiltration membranes: influence of swelling, compaction and solvent on permeation properties, Polym. Test. 33 (2014) 88–96, https://doi.org/10.1016/j.polymertesting.2013.10.016.

C.R. Tanardi, R. Catera, M. Barbou, A. Ayral, I.F.J. Vankelecom, A. Nijmeijer, L. Winnubst, Polyethylene glycol grafting of γ-alumina membranes for solvent resistant nanofiltration, Micro porous Mesoporous Mater. 229 (2016) 106–116, https://doi.org/10.1016/j.micros.2016.04.024.

D.H. Park, N. Nishiyama, Y. Egashira, K. Ueyama, L.P.C.M. de Smet, E.J.R. Sudholter, Poly (maleic anhydride-alt-1-alkenes) directly grafted to γ-alumina for high-performance organic solvent nanofiltration membranes, J. Membr. Sci. 564 (2018) 259–266, https://doi.org/10.1016/j.memsci.2017.08.042.

J. Randon, P. Blanc, R. Paterson, Modification of ceramic membrane surfaces using phosphonic acid and alkyl phosphonic acids and its effects on ultrafiltration of BSA protein, J. Membr. Sci. 98 (1995) 119–129, https://doi.org/10.1016/0376-7388(94)00185-Y.

S. Rezaei Hoseinabadi, K. Wyns, V. Meynen, R. Carleen, P. Adriaensens, A. Buekenhoudt, B. Van der Bruggen, Organic solvent nanofiltration with Grignard functionalised ceramic nanofiltration membranes, J. Membr. Sci. 454 (2014) 496–504, https://doi.org/10.1016/j.memsci.2013.12.032.

C.R. Tanardi, A. Nijmeijer, L. Winnubst, Polymerization of functional groups on titania particles, Angew. Chem. Int. Ed. 45 (2006) 3660–3664, https://doi.org/10.1002/anie.200600276.

K. Zarkadakis, S. Banting, M. Keep, H. Jope, A. Gogos, N. Boulard, Grafting of polymeric materials onto ceramic oxide membranes, Ceram. Int. 35 (2009) 4370–4377, https://doi.org/10.1016/j.ceramint.2009.04.007.

K. Zarkadakis, S. Banting, M. Keep, H. Jope, A. Gogos, N. Boulard, Grafting of polymeric materials onto ceramic oxide membranes, Ceram. Int. 35 (2009) 4370–4377, https://doi.org/10.1016/j.ceramint.2009.04.007.

A. F.M. Pinheiro, D. Hoogendoorn, A. Nijmeijer, L. Winnubst, Development of a polyethylene glycol grafted ceramic nanofiltration membrane, J. Membr. Sci. 392 (2012) 1–10, https://doi.org/10.1016/j.memsci.2011.11.023.

A. F.M. Pinheiro, D. Hoogendoorn, A. Nijmeijer, L. Winnubst, Development of a polyethylene glycol grafted ceramic nanofiltration membrane, J. Membr. Sci. 392 (2012) 1–10, https://doi.org/10.1016/j.memsci.2011.11.023.

A. F.M. Pinheiro, D. Hoogendoorn, A. Nijmeijer, L. Winnubst, Development of a polyethylene glycol grafted ceramic nanofiltration membrane, J. Membr. Sci. 392 (2012) 1–10, https://doi.org/10.1016/j.memsci.2011.11.023.

A. F.M. Pinheiro, D. Hoogendoorn, A. Nijmeijer, L. Winnubst, Development of a polyethylene glycol grafted ceramic nanofiltration membrane, J. Membr. Sci. 392 (2012) 1–10, https://doi.org/10.1016/j.memsci.2011.11.023.

A. F.M. Pinheiro, D. Hoogendoorn, A. Nijmeijer, L. Winnubst, Development of a polyethylene glycol grafted ceramic nanofiltration membrane, J. Membr. Sci. 392 (2012) 1–10, https://doi.org/10.1016/j.memsci.2011.11.023.

A. F.M. Pinheiro, D. Hoogendoorn, A. Nijmeijer, L. Winnubst, Development of a polyethylene glycol grafted ceramic nanofiltration membrane, J. Membr. Sci. 392 (2012) 1–10, https://doi.org/10.1016/j.memsci.2011.11.023.

A. F.M. Pinheiro, D. Hoogendoorn, A. Nijmeijer, L. Winnubst, Development of a polyethylene glycol grafted ceramic nanofiltration membrane, J. Membr. Sci. 392 (2012) 1–10, https://doi.org/10.1016/j.memsci.2011.11.023.
[172] J. Geens, B. Van der Bruggen, C. Vandecasteele, Transport model for solvent permeation through nanofiltration membranes, Separ. Purif. Technol. 48 (2006) 255–263, https://doi.org/10.1016/j.seppur.2005.07.052.

[173] A. Carré, Polar interactions at liquid/polymer interfaces, J. Adhes. Sci. Technol. 21 (2007) 961–981, https://doi.org/10.1163/156856107781393875.

[174] W.R. Bowen, J.S. Welfoot, Modelling the performance of membrane nanofiltration—critical assessment and model development, Chem. Eng. Sci. 57 (2002) 1121–1137, https://doi.org/10.1016/S0009-2509(01)00413-4.

[175] B. Van der Bruggen, C. Vandecasteele, Modelling of the retention of uncharged molecules with nanofiltration, Water Res. 36 (2002) 1360–1368, https://doi.org/10.1016/S0043-1354(01)00318-9.

[176] S. Postel, C. Schneider, M. Wessling, Solvent dependent solute solubility governs retention in silicone based organic solvent nanofiltration, J. Membr. Sci. 497 (2016) 47–54, https://doi.org/10.1016/j.memsci.2015.09.014.

[177] W. Ogieglo, H. van der Werf, K. Tempelman, H. Worneester, M. Wessling, A. Nijmeijer, N.E. Benes, n-Hexane induced swelling of thin PDMS films under non-equilibrium nanofiltration permeation conditions, resolved by spectroscopic ellipsometry, J. Membr. Sci. 437 (2013) 313–323, https://doi.org/10.1016/j.memsci.2013.04.039.

[178] J. Robinson, Solvent flux through dense polymeric nanofiltration membranes, J. Membr. Sci. 230 (2004) 29–37, https://doi.org/10.1016/j.memsci.2003.10.027.

[179] M.F.J. Dijkstra, S. Bach, K. Ebert, A transport model for organophilic nanofiltration, J. Membr. Sci. 286 (2006) 60–68, https://doi.org/10.1016/j.memsci.2006.09.012.

[180] L. Hesse, J. Mičovič, P. Schmidt, A. Görak, G. Sadowski, Modelling of organic-solvent flux through a polyimide membrane, J. Membr. Sci. 428 (2013) 554–561, https://doi.org/10.1016/j.memsci.2012.10.052.

[181] D.R. Machado, D. Hasson, R. Semiat, Effect of solvent properties on permeate flow through nanofiltration membranes. Part I: investigation of parameters affecting solvent flux, J. Membr. Sci. 163 (1999) 93–102, https://doi.org/10.1016/S0376-7388(99)00158-1.