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Review: Membrane Materials for the Removal of Water from Industrial Solvents by Pervaporation and Vapor Permeation

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Abstract

Organic solvents are widely used in a variety of industrial sectors. Reclaiming and reusing the solvents may be the most economically and environmentally beneficial option for managing spent solvents. Purifying the solvents to meet reuse specifications can be challenging. For hydrophilic solvents, water must be removed prior to reuse, yet many hydrophilic solvents form hard-to-separate azeotropic mixtures with water. Such mixtures make separation processes energy intensive and cause economic challenges. The membrane processes pervaporation (PV) and vapor permeation (VP) can be less energy intensive than distillation-based processes and have proven to be very effective in removing water from azeotropic mixtures. In PV/VP, separation is based on the solution-diffusion interaction between the dense permselective layer of the membrane and the solvent/water mixture. This review provides a state-of-the-science analysis of materials used as the selective layer(s) of PV/VP membranes in removing water from organic solvents. A variety of membrane materials, such as polymeric, inorganic, mixed matrix, and hybrid, have been reported in the literature. A small subset of these are commercially available and highlighted here: poly(vinyl alcohol), polyimides, amorphous perfluoro polymers, NaA zeolites, chabazite zeolites, T-type zeolites, and hybrid silicas. The typical performance characteristics and operating limits of these membranes are discussed. Solvents targeted by the U.S. Environmental Protection Agency for reclamation are emphasized and ten common solvents are chosen for analysis: acetonitrile, 1-butanol, *N,N*-dimethyl formamide, ethanol, methanol, methyl isobutyl ketone, methyl tert-butyl ether, tetrahydrofuran, acetone, and 2-propanol.

Keywords

Solvent reclamation; membrane materials; dehydration; pervaporation; vapor permeation; membrane-based separation

Introduction

Organic solvents serve a variety of functions in the manufacture of chemicals and materials in the worldwide economy. Industries that use organic solvents provide economic opportunity in their communities, but the life cycles of industrial solvents – encompassing the production, transportation, use, and ultimate disposal/destruction of the solvent – introduce sources of emissions that potentially impact human health and the environment in

those communities^{1, 2}. According to the principles of Green Chemistry and Green Engineering, designing (or redesigning) products and processes to avoid the need for solvents is the preferred means of preventing pollution associated with solvent use^{3–5}. If solvent use cannot be avoided in a process, the Green Chemistry/Engineering principles advocate employing the least amount of the safest solvent that delivers the requisite performance. In many situations, the life cycle impact of using even the safest solvents can be reduced by recovering and reusing the solvents². For example, the Green Engineering Program of the United States Environmental Protection Agency (USEPA) identified solvents used in four industrial sectors as a potential opportunity to obtain large environmental benefits should those solvents be reclaimed and reused⁶. The solvents were used in high volumes and the production and disposal of these solvents were determined to require large amounts of energy^{7, 8}. In 2015, the USEPA finalized a new *Definition of Solid Waste Rule* intended, in part, to encourage the reuse/re-processing of 18 higher-value hazardous spent industrial solvents used in four manufacturing sectors: pharmaceuticals, paints and coatings, plastics and resins, and basic organic chemicals⁹. The 18 solvents targeted for reclamation are listed in Table 1, grouped as non-polar, polar aprotic, and polar protic types of solvents. Although these 18 solvents are only a small fraction of the many organic solvents used in industry, they represent a cross-section of many *types* of organic solvents: aliphatic and aromatic hydrocarbons, chlorinated aromatic and aliphatic hydrocarbons, ethers, ketones, amides, nitriles, and alcohols.

The technical challenge to solvent reuse/reprocessing is the application of suitable separation technologies to recover those solvents from mixtures with other processing materials and to purify them to quality specifications. Contaminants to be removed may include suspended solids, dissolved solids (salts, higher molecular weight soluble species), other solvents or oils, and water¹⁰. This review is focused on the reduction of water contamination in selected industrially-important solvents. Water may become part of the spent solvent in a variety of ways: added intentionally to alter the property of the solvent system, introduced in a washing step, produced via an intentional/unintentional reaction, or simply absorbed from the atmosphere.

Despite the wide range of solvent types represented in Table 1, most of these solvents, 15 of the 18, form difficult-to-separate azeotropic binary mixtures with water, as indicated by an asterisk next to the name of the solvent in the table. An azeotrope exists when a vapor phase in equilibrium with a liquid phase has the same composition as the liquid phase¹¹. Under normal circumstances, the vapor phase will have a different composition than the liquid phase – the property that enables separation by evaporation and condensation. As a result, concentrating solvents beyond an azeotropic composition by simple evaporation/condensation, the basis for batch solvent stills and conventional distillation processes, becomes impossible. Fortunately, water is sparingly soluble in low polarity solvents, making it less likely that water will contaminate such solvents. Due to the partial miscibility found in many solvent/water systems, the liquid phases at azeotropic compositions often consist of two phases. In such cases, the azeotrope is referred to as “heterogeneous.” If the azeotropic liquid is a single phase, then it is referred to as a “homogeneous” azeotrope. In fact, 10 of the 18 targeted solvents solubilize less than 0.2 wt% water, as detailed in Table 2. In this group, the water solubility in the solvents ranges from only 0.0090 wt% water for n-hexane

up to 0.18 wt% water for dichloromethane¹². Also shown in Table 2 are the solubilities of these solvent in water.

The remaining 8 solvents from Table 1 are more hydrophilic than those in Table 2, dissolving 1 wt% or more of water, with five being fully miscible with water (see Table 3). Even in this subset of more hydrophilic solvents, 6 of the 8 form azeotropes with water. Thus, the solvents in Table 3 are both prone to accumulating water and form mixtures with water that are challenging to separate. As a result of these features, the Table 3 solvents were selected for further analysis with regard to the types of materials and processes that are suitable for removing water. Additionally, acetone and 2-propanol will be considered because they are representative of the types of solvents in Table 3 and data for their dehydration is often reported alongside those of the other solvents. Acetone, like MIBK, is a ketone, but, unlike MIBK, acetone does not form a water azeotrope and is fully miscible with water. 2-propanol adds a branched azeotrope-forming lower alcohol to the group of alcohols.

In 2008, this author reviewed the types of separation technologies that could be used to recover alcohols from water and then dry those alcohols in the production of alcohol-based biofuels from dilute fermentation broths¹³. The categories of technologies applicable to drying alcohol biofuels described in that review also apply here to the drying of hydrophilic industrial solvents, namely:

- Distillation
- Adsorption
- Liquid-liquid Extraction
- Pervaporation
- Vapor Permeation

Separation processes and separating materials take advantage of the chemical and structural differences between the compounds to be separated. As noted above, the vapor-liquid equilibrium (VLE) behavior is the primary chemical difference used in distillation-based processes to drive the separation utilizing single or successive evaporation/condensation step(s). Subcategories of distillation applicable to solvent drying include fractionation, azeotropic distillation, extractive distillation, and pressure swing distillation. Several of these involve modifying the conditions or solution components to alter the normal VLE behavior of the solvent/water mixture. The VLE behaviors for binary mixtures of three lower alcohols with water (methanol, ethanol, and 2-propanol) are shown in Figure 1. At low alcohol concentrations, the vapor phase is significantly enriched in the alcohol relative to the liquid phase for all three of the alcohols – as indicated by the VLE curves lying above the no-VLE-separation diagonal line. As alcohol concentration increases, the distance between the VLE curves and the diagonal line decreases and, in the cases of ethanol and 2-propanol, the VLE curves cross the diagonal line. The point of intersection is the azeotropic concentration. According to Table 3, at 25 °C, the ethanol/water and 2-propanol/water azeotropes occur at 4.0 and 12.6 wt% water, respectively. As indicated in Figure 1 and Table 3, the methanol/

water system exhibits no azeotrope, although the VLE difference becomes small at high alcohol concentrations.

Two additional parameters that can be leveraged in separation processes are molecular size and solvent characteristics, the latter represented by solubility parameters. The kinetic diameters of water and several solvents are listed in Table 4. By this measure, water is the smallest of the molecules considered here, allowing it to pass through sieving structures more readily than the larger solvent molecules. The interaction of a solvent with another material is frequently characterized based on solubility parameters, particularly for prediction of sorption, swelling, and miscibility. Hansen solubility parameters provide a three-dimensional description of the interaction properties of a solvent: a dispersion contribution (δ_d), polar contribution (δ_p), and hydrogen bonding contribution (δ_h)¹⁴. The more dissimilar the properties of two solvents, the more likely it is that a third material could be introduced to preferentially interact with one of the solvents relative to another and affect a separation. This additional material, termed a mass separating agent, could be an adsorbent, liquid absorbent, or membrane.

The solubility parameters for water and the hydrophilic solvents listed in Table 3 are plotted in Figure 2 and the values are provided in Table S3. The solubility parameters for the more hydrophobic solvents listed in Table 2 are included at the bottom of Table S3 for comparison. As is clear from Figure 2, the largest difference between water and the hydrophilic solvents of Table 3 is observed in the hydrogen bonding contribution parameter. Methanol is the most similar to water in this parameter. Therefore, methanol/water mixtures are more difficult to separate utilizing molecular size and chemical differences than other organic solvents. The Hansen solubility parameter with the smallest range for the Table 3 solvents and water is the dispersion contribution parameter, suggesting this molecular aspect has the least separation leverage. Overall, mass separating agents that possess a high hydrogen bonding contribution and a high polar contribution are likely to preferentially interact with water relative to the organic solvents.

For drying hydrophilic solvents, distillation and adsorption are the most established processes^{10, 16, 17}. To separate azeotropic mixtures using distillation, a third solvent or compound can be added as an entrainer to alter the VLE behavior. In the separation of ethanol/water mixtures, benzene was once used as an entrainer in azeotropic distillation, but has since been replaced by less hazardous solvents such as cyclohexane^{10, 18}, ethylene glycol^{19, 20}, hyperbranched polymers²¹, and glycerol²². Adsorption with molecular sieves supplanted azeotropic distillation for drying ethanol in the U.S. ethanol biofuel industry decades ago²³. In adsorption, the solvent/water mixture, either as a vapor or liquid, is contacted with a hydrophilic solid adsorbent with water selectively sorbing to the solid, leaving a water-laden adsorbent and a water-depleted solvent stream. The spent sorbent would then undergo regeneration, utilizing a swing in temperature or pressure, or both, possibly combined with the introduction of a sweep stream, to desorb the water from the sorbent. Thus, adsorption is a cyclic process. As a result, if continuous operation is desired, then multiple adsorbent beds/columns are required so that regeneration of one bed can occur while another bed is being loaded. The most recent advances in adsorbents have come in the areas of metal-organic framework (MOF) materials (including the subcategory of zeolitic

imidazolate frameworks (ZIFs)), carbon molecular sieve (CMS) materials, and in the fabrication of molecular sieves into more efficient structures^{24–28}. For water adsorption from solvents, however, zeolite-based molecular sieve particles, particularly sodium A-type (“NaA” or “4A”) and potassium A-type (“KA” or “3A”) aluminosilicates, are still the primary materials used^{10, 17, 29, 30}.

Other drying processes that may be suitable for industrial solvents are: reacting, salting out, coalescing, and fractional freezing¹⁰. For smaller scale drying applications, hydrate formation through contact with salts has been used^{10, 15}. For example, solid calcium chloride removes water from hydrophobic ethers, esters, and hydrocarbons, but the salt is too soluble in alcohols, amines, and ketones to work effectively as an adsorbent¹⁰. Similarly, a significant challenge for liquid-liquid extraction is finding an extractant with a high selectivity toward water relative to the hydrophilic solvent.

Unlike most of the other drying processes, the membrane technologies of pervaporation and vapor permeation (PV and VP) operate on principles that leverage differences in both molecular size and solubility properties to separate miscible mixtures. This feature enables PV and VP to separate mixtures that might not be easily separated otherwise. The remainder of this paper will focus on the principles of PV/VP separations and the membrane materials that have proven effective at removing water from hydrophilic solvents.

Solvent/Water Separation by Pervaporation and Vapor Permeation

The emerging membrane technologies of PV and VP have been investigated for separating a variety of mixtures of volatile liquids, most often involving solvent/water mixtures. PV and VP operate under very different principles than filtration-type membrane processes (i.e. particle filtration, microfiltration, ultrafiltration). For filtration, the membrane is constructed with a porous top layer to allow fluid to flow under an applied pressure gradient through the membrane. However, the membrane in PV and VP is constructed with a dense top layer material such that molecules can only pass through that layer by a sorption-diffusion mechanism, often referred to as “solution-diffusion” transport. Molecules in the feed fluid sorb into the dense layer material, diffuse through that layer, and then desorb from the opposite side of the dense layer. As noted earlier, solubility parameters can be used to identify differences in solvent characteristics. Dense layer materials can be chosen based on the solubility parameters of the membrane material and the solvents to leverage these differences to yield a sorption selectivity^{31–40}.

By selecting a dense layer material that exhibits a sorption-diffusion selectivity towards one component of the feed fluid, PV and VP are able to selectively separate that component from the other component(s) in the feed fluid. The material that passes through the membrane, the “permeate” fluid, would then be enriched, relative to the feed fluid, in the preferentially transported component. Thus, while filtration membranes cannot separate simple miscible solvent/water solutions, PV and VP membranes can. The other difference is the driving force for transport through a PV or VP membrane is the chemical potential gradient across the membrane, as compared to the applied pressure gradient that controls fluid filtration. The chemical potential gradient is usually represented by the partial pressure gradient of a

species. As a result, to cause a component of the feed fluid to pass through a PV/VP membrane, the partial pressure of the species in the feed fluid must be higher than the partial pressure of that species in the permeated downstream fluid. Thus, PV and VP operate under the same fundamental principles. The difference between them is the feed fluid in PV is a liquid while the feed fluid in VP is a vapor. The permeate in both cases is a vapor. A simplified illustration of a PV/VP separation unit is shown in Figure 3. The permeate vapor is typically recovered via cooling to yield a permeate condensate.

The objective of this project is to analyze the state of the science of PV and VP in the field of water removal from the hydrophilic solvents identified in Table 3. For a more complete overview of PV/VP processes, a number of references are suggested reading including the works of Néel⁴¹, Baker⁴², Brüscke⁴³, Bowen *et al.*⁴⁴, and Vane⁴⁵. Many operating and design parameters affect the performance of a PV/VP system. As noted above, the properties of the dense layer material of a PV/VP membrane are often the most consequential to system performance. As is the case with most material-based technologies, numerous membrane materials have been developed and evaluated for solvent drying, but only a few are commercially available. A search of the SCOPUSTM abstract and citation database using the words “pervaporation/pervapouration and dehydration and solvent” yields over 5000 documents in the scientific literature and over 1700 patents, with most activity since 1980. The emphasis of this paper is the state of selective materials development for PV/VP for the dehydration of hydrophilic solvents, providing a synopsis rather than an in-depth review of each type of material. Both commercial and research materials will be discussed although emphasis will be given to materials that are commercially available. The membrane materials will be further differentiated into organic, inorganic, and mixed matrix material categories.

Terminology and Fundamentals

In this section, to establish a common frame of reference for the discussion of membrane material performance, the terminology used in reporting the performance of PV/VP membranes will be outlined. In typical PV/VP experiments, the compositions of the feed and permeate fluids are measured, as are the amount of permeate collected per unit time, the permeate pressure, and the temperature of the feed fluid. For VP experiments, the total pressure of the feed vapor must be known in addition to the parameters measured for PV experiments. The total flux is calculated as the mass of permeate collected per unit time divided by the active membrane area.

The preferred method of reporting the separation performance of a PV/VP membrane material is in terms that have been normalized by the partial pressure driving force and the thickness of the dense layer (ℓ): the molar permeability of each species (P_i) and the molar permselectivity (α). In cases where ℓ is unknown or difficult to discern, the permeance (Π_i), the ratio of permeability to thickness, may be reported instead of permeability. For commercial membranes, permeance is the most appropriate measure of performance since ℓ may not be reported and is not an experimental variable as in research studies. These parameters are calculated as:

$$P_i = \frac{w_i^V J \ell}{(p_i^F - p_i^V) MW_i} \text{ and } \Pi_i = \frac{P_i}{\ell} \quad \text{Equation 1}$$

Where J is the total flux ($\text{kg}/\text{m}^2 \cdot \text{s}$), w_i^V is the mass fraction of species i in the permeate vapor, MW_i is the molecular weight of species i (kg/kmol), and where p_i^F and p_i^V are the partial pressures (kPa) of species i in the feed fluid and permeate vapor, respectively. SI units for permeance are $\text{kmol}/\text{m}^2 \cdot \text{s} \cdot \text{kPa}$ and those for permeability are $\text{kmol} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{kPa}$. Common units for permeance are gas permeation units (GPU), with $1 \text{ kmol}/\text{m}^2 \cdot \text{s} \cdot \text{kPa} = 2.99 \times 10^9 \text{ GPU}$ and 1 GPU defined as $10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$. Common units for permeability are Barrer with $1 \text{ kmol} \cdot \text{m}/\text{m}^2 \cdot \text{s} \cdot \text{kPa} = 2.99 \times 10^{15} \text{ Barrer}$ and 1 Barrer defined as $10^{-10} \text{ cm}^3(\text{STP}) \cdot \text{cm}/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}$.

For VP calculations, the feed and permeate partial pressures are simply calculated as the product of the mole fraction of a species in the feed or permeate (x_i or y_i) times the total observed pressure for that stream (i.e. $p_i^F = x_i p^F$ and $p_i^V = y_i p^V$). For PV, the permeate partial pressure is calculated in the same manner as for the permeate in VP. However, the partial pressures for components of the PV feed liquid are calculated as the partial pressure of a given species in a hypothetical vapor phase that is in equilibrium with the feed liquid phase (i.e. $p_i^F = x_i \gamma_i p_i^{\text{sat}}$). Such a calculation requires either experimental VLE data or thermodynamic models to calculate the activity coefficient (γ_i) and the saturated vapor pressure (p_i^{sat}).

Molar permselectivity (i.e. “selectivity”) is the ratio of the molar permeabilities or permeances of two species through the membrane:

$$\alpha_{12} = \frac{P_1}{P_2} = \frac{\Pi_1}{\Pi_2} \quad \text{Equation 2}$$

Although the driving force-normalized performance parameters defined in Equations 1 and 2 are preferred, PV and VP results are often reported in terms of individual fluxes and the separation factor (β), where the latter is calculated from mass fractions or mole fractions in the feed fluid and permeate as:

$$\beta_{12} = \frac{(J_1/J_2)}{(w_1^F/w_2^F)} = \frac{(w_1^V/w_2^V)}{(w_1^F/w_2^F)} = \frac{(y_1/y_2)}{(x_1/x_2)} \quad \text{Equation 3}$$

(It should be noted the literature contains a variety of symbols and terms for what are defined here as permselectivity and separation factor and the definition and notation of “selectivity” in each article should be carefully assessed.) For VP experiments with

negligible permeate pressure, the separation factor is equal to the permselectivity. However, for PV, the two terms differ at least by the relative VLE selectivity due to the need for the activity coefficient and saturated vapor pressure terms in Equation 1. In other words, the PV separation factor is determined by both the membrane selectivity and the VLE selectivity. As a result, it is possible to have a membrane that shows no molar permselectivity (i.e. $\alpha = 1$), but would still register an appreciable PV separation factor. Further, some materials are reported as being “selective” for one compound over another based on a PV separation factor greater than 1, but which are actually permselective for the other compound. The separation of ethanol from dilute aqueous solutions with silicone rubber membranes is a case in point with ethanol/water separation factors greater than 1 observed but molar permselectivity values less than 1 calculated after accounting for the favorable enrichment of ethanol in the vapor by VLE^{46, 47}. Thus, on a molar permselectivity basis, silicone rubber is modestly water selective.

The reason for the water selectivity of silicone rubber goes to the properties that determine permeability. Permeability is defined as the product of solubility and diffusivity (i.e. $P_i = S_i \times D_i$)⁴⁸. Thus, the molar permselectivity is the product of the ratio of solubilities and the ratio of diffusivities as:

$$\alpha_{12} = \frac{S_1}{S_2} \times \frac{D_1}{D_2} \quad \text{Equation 4}$$

Ideally, both the solubility and diffusivity ratios in Equation 4 favor one of the species. However, in some cases, including the separation of ethanol/water by silicone rubber, the diffusion selectivity and solubility selectivity are antagonistic. The size of the penetrant primarily dictates diffusion. Due to the small size of water relative to organic solvents, diffusion selectivity usually favors water. As a result, a membrane material would have to exhibit a high solubility selectivity toward the organic compound in order for the solvent/water selectivity to be greater than one. Thus, membranes have an uphill battle being more permselective for an organic solvent relative to water. However, the reverse objective, selectively removing water from an organic solvent, has the advantage of a favorable water/solvent diffusion selectivity. Pairing that advantage with a favorable water/solvent solubility selectivity makes for a truly water-selective membrane.

Mass Transfer

A molecule migrating from the bulk feed fluid to the bulk permeate vapor encounters several resistances to migration: a boundary layer of feed fluid on the upstream face of the membrane, sorption from the feed fluid into the dense membrane layer, diffusion through the dense layer, desorption out of the dense layer, diffusion/convection through the support layers of the membrane (if present), and a boundary layer of permeate vapor on the downstream face of the membrane^{48–50}. These “resistances-in-series”, along with the partial pressure driving forces, determine the observed throughput and separation performance of the membrane. Ideally, the permeance of the dense layer represents the dominant mass transfer resistance, since it is the most selective step in the series. However, as the thickness

of the dense layer is reduced to decrease the resistance of this layer and, thereby, increase the flux through the membrane, the other resistances become more consequential. In laboratory testing with thick films, the behavior of the dense selective layer is more easily discerned than from testing of thin, supported films such as the typical commercial membrane. When the membrane is packaged into a module, bulk feed maldistribution and total pressure gradients in vapor streams complicate the assessment of the properties of the dense membrane layer. Considering all the parameters that can affect mass transfer in membrane testing, care should be taken when comparing PV/VP data sets from different sources evaluated under dissimilar conditions.

Membrane Materials for Solvent Drying by Pervaporation and Vapor Permeation

In this section, the types of materials that are currently used or have been evaluated as the selective dense membrane layer for the drying of hydrophilic solvents will be reviewed. Commercially available materials will be emphasized.

1. Organic Polymeric Materials

1.1 Poly(vinyl alcohol)—The benchmark polymeric membrane material for solvent drying is poly(vinyl alcohol) (PVA)^{42, 51–73}. The repeat unit of PVA is relatively simple compared to most performance polymers, consisting of two carbon atoms in the backbone of the polymer with one pendant hydroxyl group attached to every second carbon atom (see Figure 4A). PVA is produced through the hydrolysis of poly(vinyl acetate) and can be obtained with different degrees of hydrolysis, indicating the fraction of acetate groups that have been converted to alcohol groups⁷⁴. Hydrophilicity increases with increasing degree of hydrolysis. PVA has a glass transition temperature of about 80 °C, but melts above 200 °C and will begin to decompose before melting⁷⁴. PVA membranes are cast from aqueous solution and the films are usually crosslinked in some fashion to reduce swelling of the membranes in PV/VP feed streams with high water activities. Swelling usually results in an increase in permeance, which is favorable, but a decrease in selectivity, which can be unfavorable. Excessive swelling may cause irreversible changes in the membrane, such as delamination from the support layer or defect formation. Crosslinking of PVA can be accomplished via an added functional component or post-casting thermal, chemical, and/or radiation treatment^{62, 69, 75–79}. Common crosslinking agents include dianhydrides, dialdehydes, and multifunctional acids. Depending on the type of bonds formed, the crosslinks can introduce chemical stability issues. For example, the hemiacetal bonds formed when a dialdehyde, like the commonly studied glutaraldehyde, is the crosslinking agent can be hydrolytically labile⁸⁰. Thus, operation under high water activities and at elevated temperatures can lead to a loss of crosslinks. Commercial PVA-based membranes have a sensitivity to certain impurities in the solvent/water mixture, including aldehydes, organic acids, amines, acetals/ketals, mineral acids, and peroxides⁸¹.

PVA-based membranes were among the first to be commercialized for PV/VP applications and are still commercially available from DeltaMem AG (Switzerland) as part of their PERVAPTM product line of flat sheet membranes. Although the PERVAPTM membranes have

been available for many years, DeltaMem AG was only recently formed from a management buy-out of the membrane technology business of Sulzer Chemtech. Sulzer had previously acquired the membrane product line that dates to GFT Ingenieurbüro für Industrieanlagenbau^{57, 58, 82}. CM Celfa Membrantrenntechnik AG (Switzerland), which is now a special products unit in The Folex Group⁸³, is mentioned as manufacturing composite membranes with a crosslinked PVA dense layer⁸⁴. Similarly, AzeoSep™–2002 membranes from PetroSep Membrane Research (Canada) are said to be PVA on a poly(acrylonitrile) (PAN) support⁸⁵. The longevity of PVA in the PV/VP industry reflects the functional stability and performance of this polymer. While the nature of the polymers used by a company in the manufacture of PV/VP membranes might be openly disclosed or deduced from patent or scientific literature, it is common for the companies to alter the materials over time and/or hold this information as a trade secret. For example, the selective layer in the Azeo Sep™ membranes offered by Petro Sep Corporation (and KmX Membrane Technology) for solvent dehydration is not disclosed and may no longer be based on PVA^{86–88}.

1.2 Cellulose Polymers—Cellulose-based polymers have an even longer history in the PV literature than PVA, with nitrocellulose collodion containers being used in the 1917 article credited with first using the word “pervaporation”^{89, 90}. Many membranes with a permselective layer prepared from cellulose, cellulose esters, or cellulose ethers have been reported for PV/VP applications^{58, 91–98}. Cellulose acetate membranes are seen as the benchmark material in the field of gas separation for the removal of carbon dioxide from carbon dioxide/methane mixtures^{42, 99}. In some situations, cellulose acetate filtration membranes can be used as a physical support material for thin permselective layers of another polymer¹⁰⁰. It is likely there are commercial cellulose-based membranes available despite the lack of any specific mention of such membranes in descriptions of membrane offerings. For example, Membrane Technology and Research, Inc. (USA) recently reported on the performance of a cellulose ester-based membrane custom manufactured for them⁹³. The structure of one type of cellulose, carboxymethyl cellulose (CMC), is shown in Figure 4B.

1.3 Polyimides—Polyimides represent another class of polymeric membrane materials that were developed for solvent dehydration decades ago and are commercially available today. The hydrophilicity of polyimides is attributed to hydrogen bonding interaction between water molecules and imide functional groups¹⁰¹. Early patents on the subject were assigned to Ube Industries, Ltd. (Japan) and the company continues to produce polyimide membranes^{102–111}. More recently, Whitefox Technologies Limited (United Kingdom) has emerged to offer polyimide membranes for ethanol dehydration and solvent/chemical drying^{112–114}. Polyimide polymer chemistry was also the basis for SifTek™ VP membranes developed by Vaperma Inc. for ethanol dehydration^{115–117}. Despite successful field demonstrations for the drying of biofuel ethanol and expansion of their membrane production line, Vaperma did not survive the worldwide economic downturn that began in 2008 and the resulting pause in investment in what was expected to be a rapid rise in infrastructure to produce cellulosic ethanol. Several membrane-related patents originally assigned to Vaperma are now assigned to Parker Filtration BV (The Netherlands). Although

some of the literature reports and patents from companies producing polyimide dehydration membranes mention application to liquid streams, the commercial applications have been limited to VP with superheated vapor feeds. This may be associated with the reported reaction of water with imide groups in polyimides and hydrolytic scission reactions at high water activities and temperatures^{101, 118}.

The scientific literature contains a variety of reports of polyimide materials for PV/VP dehydration of solvents. Some of these have been experimental polyimide/polyetherimide materials, while others have been commercially available polymers, such as P84™ (Evonik, Austria) and Matrimid™ (Huntsman Chemical, USA)^{119–125}. The chemical structure of Matrimid™ 5218 is shown in Figure 4C. In some cases, the polyimide is used in the preparation of the porous support layer for a dense selective layer of another polymer^{126, 127}. Thermally rearranged (TR) polymers have recently been reported for solvent dehydration^{128, 129}. TR polymers are formed when ortho-functional polyimides are thermally treated at temperatures up to about 450 °C, causing a condensation reaction to yield a heterocyclic, aromatic structure that is both thermally stable and resistant to swelling¹³⁰. Classes of TR polymers include poly(benzoxazole), poly(benzimidazole) (PBI) (see Figure 4D), and poly(benzothiazole)^{128–131}. Whitefox Technologies Limited has been developing PBI-based membranes for gas separation applications¹³². A 2017 blog post from Lux Research indicates that Whitefox Technologies also offers PBI membranes for the removal of water from solvents¹¹⁴.

1.4 Other hydrophilic polymers—Aside from PVA, cellulose, and polyimides, the scientific and patent literature discloses numerous polymers for PV/VP solvent drying applications. Chitosan- and alginate-based polymers have received significant attention over several decades of research, but do not appear to be commercially available at present^{133–135}. Other polyelectrolyte materials have been widely studied for PV/VP applications, including those formed using a layer-by-layer deposition method^{136–142}. Blends of polymers, interpenetrating networks, and copolymers provide opportunities to synergistically combine properties of individual polymers. Example blends and copolymers for dehydration applications include PVA/hydroxyethyl cellulose¹⁴³, PVA/CMC¹⁴⁴, PVA/poly(acrylic acid)^{60, 145–149}, PVA/sodium alginate¹⁵⁰, and PVA/poly(allylamine)-hydrochloride^{151, 152}.

1.5 Amorphous Perfluoropolymers—Most, if not all, of the permselective polymer materials mentioned above exhibit some sorption selectivity toward water relative to the targeted organic solvents. This sorption of water often results in the swelling of the polymer matrix and a change in the permeability and selectivity. A newer class of polymers, amorphous perfluoropolymers (APFPs), shows little, if any, change in permeability or selectivity due to contact with water, or even most solvents, because of minimal swelling in water¹⁵³. Examples of APFPs that have been studied for solvent dehydration include Teflon™ AF polymers (e.g. AF2400 and AF1600, Chemours, USA), Cytop™ (Asahi Glass, Japan), and Hyflon™ AD polymers (e.g. AD60 and AD40, Solvay Specialty Chemicals, Italy). These are random copolymers of tetrafluoroethylene and bulky dioxolenic units such as the poly(2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole-co-tetrafluoroethylene) used in

the Teflon™ AF polymers (see Figure 4E). The dioxole groups disrupt the crystallinity normally found in poly(tetrafluoroethylene) (PTFE) to yield amorphous polymers possessing high fractional free volumes that enable permeation¹⁵⁴. The glass transition temperatures of most APFPs are in the range of 110 to 240 °C, meaning they are in a glassy state at most PV/VP operating temperatures¹⁵⁵. APFPs are insoluble in organic solvents apart from perfluorinated solvents, such as perfluoropolyethers. As with perfluorinated polymers like PTFE, APFPs are more chemically stable than most polymers. Some membrane research groups and companies, such as Compact Membrane Systems and Membrane Technology and Research, are developing APFPs tailored for permselective membrane applications^{156–158}.

APFP materials are described as being hydrophobic¹⁵⁵, however, they are permeable to water due to the high fractional free volume they possess. The lack of interaction with both water and solvents yields APFP membranes with stable PV/VP performance characteristics over a wide range of solvent/water compositions and conditions¹⁵⁹. The nature of the free volume elements in APFPs favors the transport of water molecules compared to the larger solvent molecules. In addition, for gas separation, the clustering of water molecules in the free volume elements has been proposed as a hindrance to transport of permanent gas molecules¹⁶⁰. Huang *et al.* reported the permeances of water, methanol, ethanol, acetic acid, 2-propanol, and 1-butanol from binary solvent/water mixtures decreased dramatically with increasing molecular size of the compounds (reported as critical volume) in Hyflon™ AD60^{84, 159}. For example, for composite membranes with a ~0.5 µm thick layer of Hyflon™ AD60, permeances of water, methanol, ethanol, 2-propanol, and 1-butanol measured during PV testing were on the order of 1100, 100, 16, 10, and 7 GPU, respectively, resulting in water/alcohol permselectivities on the order of 11, 70, 110, and 160 for the 1-, 2-, 3-, and 4-carbon alcohols, respectively. Smuleac *et al.* reported water/ethanol and water/2-propanol permselectivities for an APFP material (CMS-3, Compact Membrane Systems, USA) that was stable for water concentrations ranging from 10 wt% to over 90 wt%. The water/ethanol and water/2-propanol permselectivities for the CMS-3 material were 20 and 60, respectively¹⁵⁷. Separately, Compact Membrane Systems reported water/ethanol permselectivities for PV and VP conditions of 25 and 18, respectively,¹⁵⁸ and a water/THF PV permselectivity of 164¹⁶¹. Tang *et al.* reported on the ability of CMS-3 membranes to separate water from polar organic compounds, including acetone, 1-butanol, ethanol, DMF, *N,N*-dimethylacetamide (DMAc), and *N,N*-dimethylsulfoxide (DMSO)^{153, 162, 163}. The permeability of water through the CMS-3 material was about 1000 Barrer (3.34×10^{-13} kmol·m/m²·s·kPa). Huang *et al.* studied three APFP materials and reported performance differences between the Cytop™, Hyflon™ AD60, and Teflon™ AF1600 APFP materials for water/ethanol separation with the following trend in permselectivity: Cytop™ > Hyflon™ AD60 > Teflon™ AF1600 (110 > 70 > 27)^{84, 159}. The trend in water permeance was the opposite of permselectivity, demonstrating a trade-off between permeability and selectivity that is common in permselective membranes. The permeability of these APFP increases with increasing polymer glass transition temperature (T_g)¹⁵⁵ with Teflon™ AF2400 exhibiting both the highest T_g and highest gas/vapor permeability of the commercially available Cytop/Hyflon/Teflon AF polymers.

1.6 Emerging organic materials—Carbon molecular sieves (CMSs) are a class of amorphous materials exhibiting molecular sieving characteristics and have been developed for membrane-based separations¹⁶⁴. CMS materials are the microporous carbon skeleton remaining after pyrolysis of an organic polymer precursor material. Despite their origin as organic polymers and the retention of a carbon backbone, CMS materials have more in common, from a permselective transport perspective, with inorganic molecular sieves. CMS membranes have received significant research attention in the last several decades though there is limited information available on their use for PV/VP dehydration applications^{165–168}. Nevertheless, Media and Process Technology, Inc. (USA) markets a ceramic-supported CMS membrane for solvent drying and claims a water/solvent separation factor of up to about 2,000 – likely for a water/acetone mixture (water/methanol and water/ethanol mixtures are mentioned under the same heading)¹⁶⁹.

Graphene and graphene oxide are additional carbon-based materials with molecular sieving capabilities that show promise as permselective membrane materials^{170–172}. These graphene materials are two-dimensional, atomically thin platelets that have the potential to create layers that are thinner than typical polymeric membranes. A few applications of graphene/graphene oxide membranes have involved the separation of water/solvent mixtures^{173–181}. For example, in a recent paper, a graphene oxide membrane was reported to deliver a water/2-propanol separation factor of over 800 and a flux of over 4 kg/m²·h in PV experiments with a feed stream of 5 wt% water at 70 °C¹⁷³, indicating both good permselectivity and throughput.

Polymers that have received significant research attention lately, and show promise for solvent dehydration, are the TR polymers and polymers of intrinsic microporosity (PIMs). PIMs, such as PIM-1, possess a molecular structure that imparts microporosity enabling them to exhibit permselective behavior that is similar to that of conventional microporous materials, like zeolites, but with greater ease of preparation¹⁸². PIM-1 has been described as being ethanol-selective based on observed ethanol/water separation factors greater than 1¹⁸³. However, as was previously described for silicone rubber membranes, the ethanol/water separation factors for PIM-1 membranes were less than that of natural ethanol/water VLE, indicating the PIM-1 membranes were modestly permselective for water under the conditions evaluated.

All three of these types of emerging materials (CMS, graphene, and PIM) have found more application as fillers in polymers than as standalone films. Such mixed matrix materials will be explored in a later section.

1.7 Layering of polymeric permselective materials—The majority of commercial polymeric membranes are layered composites with a dense permselective layer coated on a porous mechanical support structure that usually consists of a microporous material coated on top of a non-woven support. This allows the dense permselective layer to be very thin – on the order of 1 µm. In some cases, several thin layers of the same material are overcoated to build up the dense permselective layer. A number of reports describe the potential advantages of stacking layers of *different* polymeric permselective materials to form the dense permselective layer of the composite membrane^{93, 127, 159, 184–187}. For example,

Membrane Technology and Research, Inc. described a multilayer membrane consisting of a layer of APFP on top of a cellulose ester layer⁹³. As noted above, APFPs do not swell in water or in solvents while cellulose-based polymers are hydrophilic and will swell in water. Thus, the cellulose ester layer, by itself, would exhibit a wide swing in selectivity and permeance as a function of water activity in the feed liquid it contacted - with low permselectivity and high permeance when water activity was high. Huang *et al.* reported that the PV water/ethanol permselectivity of the bare cellulose ester membrane dropped two orders of magnitude as water content in the feed increased, from almost 1,000 under low water conditions (5 wt% water) to less than 10 when the feed contained 86 wt% water⁹³. The water permeance increased by a factor of four over the same water concentration range, while ethanol permeance surged almost three orders of magnitude. Adding the APFP layer on top of the cellulose ester membrane caused a reduction in water activity in the cellulose ester layer due to the added mass transfer resistance between the feed fluid and the cellulose ester, resulting in an improved selectivity for water - at the expense of permeance. In fact, for much of the water concentration range, the APFP/cellulose ester layered composite delivered a permselectivity higher than that of either of the two permselective layers individually. The order of the layers is important, however. If the cellulose ester layer had been on top of the APFP layer (and, thus, in contact with the feed fluid), the performance of the composite under high water activities would be similar to that of the APFP layer alone due to high water activities and swelling throughout the cellulose ester layer. Hua *et al.* confirmed the synergistic behavior of multi-layered membranes by coating APFP Teflon™ AF2400 onto a hydrophilic poly(etherimide) hollow fiber and using them for the VP separation of mixtures of water with 2-propanol, ethanol, and 1-butanol^{187, 188}.

The behavior of membranes composed of multiple permselective layers is determined by the complex interrelationship between the activities of the permeating molecules and the activity-dependent transport properties of the membrane materials. In addition to membranes prepared with multiple permselective layers, there are other multilayer applications where an additional layer is added to aid in mass transfer rather than as a specific permselective layer. In some cases, a protective or a high permeability “gathering” or “gutter” layer is added to improve properties of the composite such as overall lifetime, selectivity (by filling pinhole defects and reducing the impact of support porosity), or throughput (by allowing thinner permselective layers)⁴². Development of any multi-layer membrane is complicated by adhesion issues that naturally develop when materials of different thermal expansion and swelling properties are layered together. Such issues can lead to defect formation and delamination.

2. Inorganic materials

2.1 Zeolites – microporous crystalline inorganic materials—As noted earlier, zeolite-based molecular sieve adsorbent particles are used to remove water from solvents and bioethanol. The same types of zeolite crystals that are effective in adsorbent particles have been utilized to fabricate permselective membrane materials. Making a zeolite membrane is much more challenging than making an adsorbent particle because the membrane requires growth of a thin, defect-free zeolite crystal layer on a porous support. The mechanical support is usually made by depositing layers of ever finer particles of γ -

and/or α -Alumina onto a base ceramic filter, although porous metal supports have also been used^{189, 190}. Zeolites are classified as microporous TO_2 crystals with uniform pore sizes, where T represents tetrahedral framework atoms such as Si, Al, B, Ge, Fe, and P^{44, 191}. The specific repeating crystal lattice atoms determine the dimensions and interconnectivity of pores and cavities as well as the sorption characteristics. Because of the types of atoms and bonds involved, zeolite crystals used for membranes are chemically and thermally stable and do not swell in either water or most organic solvents, imbuing them with stable performance characteristics over a wide range of conditions.

2.1.1 Linde Type A (LTA) Zeolites: Linde Type A (LTA) zeolites, aluminosilicates with a 1:1 ratio of silicon to aluminum, are the most common type of zeolite used in PV/VP membranes. The lattice structure of an LTA zeolite is shown in Figure 5A. When a tetravalent silicon atom in SiO_2 is replaced by trivalent aluminum atom, a positive charge deficiency is created¹⁹². An increase in the aluminum content results in an increase in hydrophilicity and decreases in both hydrothermal and acid resistances¹⁹³. The charge introduced by aluminum atoms is balanced by introducing monovalent or divalent cations, such as sodium, potassium, calcium, and magnesium ions. These “counterions” affect the sorption and diffusion properties of the zeolite material. When sodium ions are the counter ions in an LTA lattice, the aluminosilicate is referred to as “NaA” or “4A” zeolite and the maximum pore size is 0.42 nm¹⁹¹. NaA zeolites are the benchmark inorganic membrane material for PV/VP dehydration applications¹⁹⁴. If potassium ions are the counterions, then the resulting “KA” or “3A” LTA zeolite possesses a pore size of roughly 0.3 nm. As noted in Table 4, the kinetic diameter of water is 0.296 nm⁴⁴. As a result, water molecules are able to pass through the pores of both KA and NaA zeolites. Of the solvents listed in Table 3, the solvent with the smallest kinetic diameter, at 0.38 nm, is methanol^{44, 195}. Because both water and methanol are theoretically small enough to enter the pores of NaA zeolites, separation based on molecular sieving is limited. However, at 0.42 nm, ethanol is slightly, but meaningfully, larger than methanol and about the same size as the pores of a NaA zeolite membrane. All the other solvents in Table 3 are larger than ethanol, thus restricting their entry into the pores of both KA and NaA zeolites relative to water. There are a variety of estimates and measures of molecular dimensions, some of which yield larger sizes for the solvent molecules than the kinetic diameters referred to here¹⁹⁶.

Since the molecular shape is more complicated than a single dimensional parameter and since both molecules and zeolite lattices are somewhat flexible, kinetic diameters and pore sizes should only be used as rough indicators of molecular sieving characteristics. Fortunately, molecular sieving is just one of the separation actions taking place with zeolite membranes. Sorption and diffusion within the zeolite pores also factor into the selectivity of zeolite membranes¹⁹⁷. In addition, Bowen *et al.* described how each species in a multicomponent feed can impact the transport of other species through the constrained environment within a zeolite channel⁴⁴. The net result can be water/solvent permselectivities that are surprisingly large compared to the size difference. For example, water/ethanol permselectivities for NaA zeolite membranes are consistently over 1,000 and commonly over 10,000 in both VP and PV modes^{194, 198–200}. Selectivities for solvents larger than

ethanol are at least as high as those for ethanol²⁰¹. Even for water/methanol, separation factors over 1,000 have been reported with NaA membranes^{198–200}.

While NaA zeolites do not undergo significant swelling due to water sorption, hydrothermal stability issues have been reported for NaA LTA zeolites in PV of water/ethanol mixtures at high water levels in the feed, specifically 50 or 80 wt% water at 70 °C and 80 wt% water at lower temperatures²⁰². Exposure of aluminosilicates to steam can cause hydrolysis of Si–O–Al bonds in the zeolite framework resulting in dealumination and the formation of aluminum oxide or aluminum hydroxide species outside of the framework²⁰³. Better stability in VP mode relative to PV was reported, possibly due to lower water activity in the superheated vapor²⁰². NaA zeolites can also undergo dealumination in strong acid environments (pH<6), compromising the cage structure and molecular sieving character^{194, 204}. Damage to NaA membranes under alkaline conditions (pH>8) has also been reported, indicating the need to operate NaA membranes under neutral pH conditions²⁰⁵. Thermal stability issues have been described for zeolite membranes, not due to changes in the zeolite framework, but due to thermal expansion differences between the zeolite layer and the porous support layer²⁰⁶.

Compared to hydrophilic polymeric membranes, LTA membranes are considered to have a greater operating range with respect to water concentration and temperature as well as a longer average lifetime. However, early zeolite membranes suffered from low permeance (low water flux) due to thick zeolite layers, low water selectivity due to grain boundary/intercrystalline defects, and high cost to manufacture due to the many steps involved in the formation of a zeolite membrane. These issues have been resolved through the deposition of a uniform layer of zeolite seed crystals onto the porous support followed by hydrothermal secondary crystal growth treatment that yields a thinner defect-free zeolite layer^{194, 203, 207}. Grain boundary defects that cannot be eliminated through seeding/secondary growth may be addressed via post-crystallization treatment(s)^{203, 208, 209}. The majority of zeolite membranes are in single-channel tube form, although multi-channel tubes and monoliths, as well as hollow fibers, are emerging^{194, 210–213}.

Reports of zeolite PV membranes began to appear in the patent and scientific literature several years after polymeric PV membranes. One informal measure of the timing of the emergence of zeolite PV membranes relative to polymeric PV membranes can be found in the papers presented at the International Conference on Pervaporation Processes in the Chemical Industry, a conference held from 1986 through 1995. The first paper on zeolite membranes, specifically NaA membranes for solvent dehydration, was presented at the seventh of these conferences in 1995 jointly by Yamaguchi University and Mitsui Engineering & Shipbuilding Co., Ltd. (Japan)²¹⁴. A U.S. patent for NaA membranes assigned to Mitsui was granted in the following year and Mitsui claims their first commercial installation of zeolite membrane was in 1998^{215, 216}. Over the ensuing 20+ years, several companies have marketed NaA zeolite membranes. Based on internet searches, literature references, and other information sources, NaA membranes and related PV/VP systems are available from at least nine sources in 2018, indicating a competitive market for this type of membrane. A list of commercial suppliers of NaA membranes and systems known to the author along with contact/website information is included in Supporting Information.

Firm costs for PV/VP membranes and modules are difficult to obtain, but zeolite membranes are consistently described as being about ten times more expensive than polymeric membranes, per unit active area²¹⁷. The largest portion of the cost of zeolite membranes is attributed to that of the ceramic support²¹⁸. The costs for both polymeric and inorganic materials should decrease as fabrication methods become more efficient and scale of production increases. In a crude simplification, inorganic membranes offer a longer lifetime that partially offsets the higher per unit area cost. The thermal stability of inorganic materials enables them to be used at temperatures that might not be appropriate for most polymeric materials. Higher temperatures translate into higher partial pressure driving forces which, in turn, results in lower membrane areas required. Finally, for some PV/VP systems, the cost of the membrane system can be a minor component of the overall capital and operating costs, especially if compressors, vacuum pumps, large heat exchanger areas, and, if a hybrid process, distillation columns are involved^{219, 220}. All factors considered, the higher cost per unit area of inorganic membranes may not translate into a significantly higher total system cost, if at all²²¹.

2.1.2 T-type and Chabazite Zeolites: As noted above, NaA-type membranes can be degraded by dealumination when contacted with feed fluids exhibiting a high water activity or acidic condition. To extend the operating range of zeolite membranes for solvent dehydration, more stable zeolite frameworks than LTA have been developed. At least two of these, T-type (or “Zeolite T”) and chabazite (CHA), are commercially available. T-Type zeolites are an intergrowth structure of erionite and offretite crystals with a silicon to aluminum ratio of 3:1 to 4:1 vs. the 1:1 ratio of LTA zeolites²²². The lower aluminum content is believed to make T-type zeolites less hydrophilic and more acid-stable than LTA zeolites. In this regard, T-type membranes were found to be stable in 50 wt% acetic acid, but experienced dealumination in 0.1 M HCl¹⁹³. Ji *et al.* recently reported stable performance over 20 days of operation for a T-type membrane module removing water from an ethanol solution containing 9.3 wt% water and 6.9 wt% acetic acid (pH ~3) at 70 °C²¹². The framework of T-type zeolite yields pores that are slightly larger (effectively 0.36 nm × 0.51 nm) than those of NaA^{223, 224}. As a result, T-type zeolites have demonstrated a lower selectivity for water than NaA, particularly for methanol and ethanol^{193, 198}. T-type zeolite membranes are manufactured by Mitsui Engineering & Shipbuilding Co., Ltd. and were disclosed in the patent literature for PV/VP applications a few years after NaA membranes^{198, 225}.

CHA membranes have emerged more recently in the PV/VP arena and are manufactured by both Mitsubishi Chemical Corporation (Japan)^{226–229} and Hitachi Zosen Corporation (Japan)^{230–232}. Chabazite is a naturally occurring zeolite exhibiting a pseudohexagonal unit cell with ellipsoidal cages interconnected via 8-member ring windows in the form of rhombohedral crystals^{192, 233, 234}. The maximum pore size of the 3-dimensional pore matrix for dehydrated CHA zeolites is 0.38 nm, falling between that of KA and NaA LTA zeolites^{44, 191, 234}. The lattice framework is shown in Figure 5B. Like LTA zeolites, CHA can be ion exchanged to yield a variety of forms with slightly different pore sizes, including CHA-Na, CHA-K, and CHA-Ca²³³. CHA-type zeolites can be prepared with different silicon to aluminum ratios, with a ratio as high as 11:1 reported, and using various

crystallization conditions^{213, 229, 235, 236}. CHA membranes with higher Si:Al ratios are claimed to impart resistance to organic acids that cannot be treated with NaA membranes^{213, 229}. A CHA-type zeolite membrane with a Si:Al ratio of about 3 was reported to have a water/ethanol separation factor of over 270,000 for an 8 wt% water feed liquid at 77 °C²³⁷. The maximum calculable separation factor was constrained by the 50 ppm analytical detection limit for ethanol in the permeate. The water/2-propanol separation factor for the same membrane type was similarly high. The separation factor for water/methanol was not as high as that of ethanol or 2-propanol, but was still about 600 for feeds containing between 15 and 65 wt% water. For all three alcohols, the separation factor dropped at low water levels, particularly when less than 1 wt% water, falling to about 100 for methanol and 2-propanol and to about 5,000 for ethanol. The decline in water/alcohol separation factor was attributed to freer movement of the alcohols through zeolitic channels and non-zeolitic grain boundaries due to the relative absence of adsorbed water molecules that would block alcohol transport²³⁷.

As mentioned previously, a higher silicon to aluminum ratio is expected to impart improved hydrothermal and acid stability in zeolites. A high silica CHA-type zeolite (Si:Al of 7.5) was reported to achieve a water/ethanol PV separation factor of 500 for 86 wt% water at 70 °C²²⁹. Separation factors for larger solvents including 2-propanol, THF, acetone, and *N*-methyl-2-pyrrolidone (NMP) were higher than for ethanol, ranging from around 3,000 for water/THF to over 30,000 for water/2-propanol. As with all membranes, these separation factors vary with membrane fabrication methods and similar high silica CHA-type membranes were reported to have lower water/2-propanol separation factors of about 1,600 (molar permselectivity of 1,500) for 10 wt% water at 75 °C²³⁵. The water/methanol separation was not reported, but is expected to be of low selectivity because the high silica CHA was able to selectively permeate methanol from a mixture with acetone²²⁹. Thus, it appears the CHA-type membranes with higher Si:Al ratios have a lower water selectivity than CHA-type membranes with lower Si:Al ratios, an attribute that is most noticeable with the smaller alcohols.

2.2 Microporous amorphous inorganic materials—Microporous hydrophilic silica membranes, formed from tetraethyl orthosilicate (TEOS) using a sol-gel deposition method onto a porous alumina support, showed early promise for PV/VP solvent dehydration applications^{238–241} but were eventually found to suffer from poor hydrothermal stability^{242–244}. Fortunately, researchers discovered that adding an organic linkage in the structure improved stability while still yielding a water-selective microporous material^{242, 245, 246}. This type of material is referred to as “hybrid silica” or “organosilica”. The general structure of silica formed from TEOS and a hybrid silica prepared using bis(triethoxysilyl)ethane (BTESE) are shown in Figure 5C. The chemical composition and pore structure can be fine-tuned through alteration of sol components and cure conditions^{247–252}. Hybrid silica membranes are commercially available as the HybSi™ product line from Pervatech BV (The Netherlands)^{253, 254}.

Hybrid silica materials have been reported to yield water/solvent separation factors that are generally lower than benchmark NaA zeolites - with water permeances/fluxes that are of the same order of magnitude than those of NaA membranes, under comparable conditions²⁵⁵.

For example, BTESE-derived hybrid silica membranes have shown water/2-propanol PV separation factors between 210 and 4,400 for 10 wt% water at 75 °C²⁵⁵. Under similar feed conditions (10 wt% water at 70 °C), Moriyama *et al.* recently observed somewhat higher water/2-propanol separation factors of 1,000 and 7,000 for BTESE-derived membranes prepared with high and low sol acid molar ratios²⁵². They also reported the performance of these BTESE-derived membranes for several other alcohol/water and solvent/water systems. The water/ethanol separation factors were 170 and 1,120 for the high and low acid molar ratios, respectively, with 10 wt% water at 50 °C. Water permeance for the lower selectivity membrane (~6,800 GPU) was several times greater than that of the higher selectivity membrane (~3,000 GPU). When hybrid silica membranes were prepared using a sol based on bis(triethoxysilyl)methane (BTESM), a water/ethanol separation factor of 890 was reported while that of water/1-butanol was 10,500²⁴⁵. The water/methanol separation factor was markedly lower, only 23. The water permeance of BTESE-based membranes was observed to increase with increasing water concentration and with decreasing temperature in tests with water/2-propanol mixtures^{252, 255}. Kreiter *et al.* prepared hybrid silica membranes based on BTESE, BTESM, and a mixture of BTESE and methyltriethoxysilane, testing them using 5 wt% water in binary mixtures with four alcohols: methanol, ethanol, 1-propanol, and 1-butanol²⁵⁶. They reported the water permeance decreased with increasing alcohol chain length. However, the tests were not performed at the same temperature. In fact, the test temperature was increased as alcohol chain length increased, from 55 °C for methanol to 95 °C for 1-butanol. Based on the dependency of water permeance on temperature reported by Nagasawa *et al.*, it is likely that much, if not all, of the change in water permeance with alcohol chain length observed by Kreiter *et al.* can be attributed to differences in the PV temperature²⁵⁵. This is borne out in the results of Moriyama *et al.* in that the water permeances observed for methanol and 1-butanol solutions, both tested at 50 °C, differed by only about 20%²⁵².

Considering the known instability of microporous silica membranes, the developers of hybrid silica membranes carried out a wide range of long-term stability tests with the new hybrid silica membranes^{256–258}. For example, van Veen *et al.* subjected HybSi™ membranes to acidic conditions (concentrated acetic acid and dilute nitric acid), high temperatures (up to 190 °C), and strong aprotic solvents (e.g. NMP), some tests for as long as 1,000 days²⁵⁸. The main limitation reported was the need to maintain the pH between 2 and 8. Although the membranes were stable under acidic conditions, the organic linkages provide no improvement to the standard silica deterioration under alkaline conditions²⁵⁸. In the long-term tests, water/solvent selectivity of the membranes increased for a few weeks before stabilizing. Water flux for most membranes declined initially and took longer than selectivity to stabilize, requiring 1–12 months, when the flux had declined by about 50%. Pervatech BV notes limitations of use for their HybSi™ AR membranes as temperatures up to 150 °C and pH values between 0.5 and 8.5²⁵³.

2.3 Other Inorganic and Hybrid Materials—Researchers continue to develop and evaluate zeolite materials that offer the separation performance of NaA zeolites, but with greater stability under PV/VP conditions. Faujasite (FAU) type zeolites, claimed to have excellent durability, heat resistance, acid resistance, and water resistance, have been reported

for solvent dehydration, although commercial availability is not apparent at this time^{259, 260}. Hydroxy sodalite has also been proposed as a more stable alternative to NaA zeolites^{261, 262}. As with polymers, zeolite blends and layering of zeolites is possible. For example, Mitsubishi Chemical Corporation was recently issued a patent for zeolite membranes fabricated from multiple zeolite crystals, either consisting of a mixture of zeolite crystals in one layer or two layers of different zeolites²⁶³.

As mentioned earlier, MOF materials are emerging as sorbents. These hybrid organic-inorganic structures are also being evaluated as permselective membranes, but reports of MOF-only membranes for solvent dehydration is limited. Most PV applications of MOF materials involve mixed matrix materials as described below.

3. Mixed Matrix Materials

Fabrication of high surface area, thin, defect-free membranes at a large-scale from molecular sieving materials such as zeolites, graphenes, CMSs, and MOFs can be quite challenging. One alternative is to disperse nanoscale or microscale particles of the sieving materials into a polymeric continuous phase to form a “mixed matrix membrane” (MMM)^{170, 264, 265}. The objective in creating a MMM is to combine the desirable molecular sieving separation characteristics of the particulate dispersed phase with the desirable film-forming characteristics of the polymeric continuous phase. The final permeability properties are expected to fall between those of the two matrices, often mathematically described using empirical relationships^{42, 266, 267}.

The number of MMM systems that have been studied for water removal from organic solvents is roughly equal to the number of organic polymeric materials (and polymer blends) studied for that separation multiplied by the number of particulate materials that are sorption-selective for water. Since both material categories are large, the number of applicable MMM systems is even larger. As might be expected, MMMs prepared from the two benchmark hydrophilic materials, PVA and NaA zeolite particles, have been studied for solvent dehydration by PV and VP^{265, 268–272}. As anticipated, the performance of a PVA/NaA zeolite MMM falls between that of 100% PVA and 100% NaA membranes. More recently, the emerging molecular sieving materials of CMS, MOF, and graphene have been used as the dispersed phase in water permselective MMMs^{273–277}.

Despite the promising performance characteristics of MMMs, they are not without limitations. As with the adage “a chain is only as strong as its weakest link,” the most prominent weakness of a specific MMM is generally that of either of the materials. For example, adding particles of an NaA zeolite to a continuous phase of PVA does not impart additional acid resistance to the NaA or additional water swelling resistance to the PVA. Despite the wide array of research publications on the topic of MMMs for water removal from organic solvents, it is not apparent that any water-selective MMM is commercially available for PV/VP applications - possibly due to the additive weaknesses in MMMs and the added complexity of MMM fabrication. Historically, the most commonly studied commercial MMM for PV, the Sulzer Chemtech PERVAP™ 1070 membrane, was actually designed to be solvent-selective for the recovery of organic compounds *from* water, containing hydrophobic ZSM-5 zeolite particles dispersed in silicone rubber²⁷⁸.

4. Other Materials in Membrane Modules

While the permselective membrane is the most important material in determining PV/VP separation performance, other materials in a membrane module must properly function under process extremes for the membrane to operate as intended. A critical material for all membrane formats is the porous support. Adhesion between the selective layer and the support must be maintained even when dimensional changes occur in either material due to swelling, thermal expansion, and pressure swings. At the same time, the support should present a low mass transfer resistance relative to that of the selective layer. As thinner selective layers are produced, the resistance of the support can become an important factor²⁷⁹. Membrane modules come in a variety of formats: hollow fiber, tubular, multichannel monolith/tube, plate & frame, and spiral wound. A set of materials are inherent to each type of modules and may include housings, adhesives (glues/tapes), sealants, gaskets/seals, turbulence enhancers, and feed or permeate flow spacers⁴². When considering whether an existing PV/VP module or system can be used under different operating conditions or even with a different solvent, the integrity of all materials of construction must be reviewed.

Overview of Performance and Operational Restrictions for Common PV/VP Membrane Materials

The commercially available materials and many of the emerging materials have proven to be effective in removing water from most, if not all, of the targeted solvents listed in Table 3. Each material will have limitations to the range of conditions under which they can be used. The known general limitations of common commercially available dehydration membrane materials are provided in Table 5. Seven types of dense layer materials are included in the table: PVA, polyimide, APFP, NaA zeolite, CHA zeolite, Zeolite T, and Hybrid Silica. A list of commercial suppliers of these materials/systems along with contact/website information is included in Supporting Information. Also provided in Table 5 are representative water permeance and water/ethanol permselectivity values based on PV performance reported for ethanol/water mixtures containing 5 to 15 wt% water at between 50 and 80 °C. The water/ethanol system was chosen because it is one of the most widely studied solvent/water systems in the PV/VP literature owing to the need for drying ethanol biofuels beyond the VLE azeotrope and because it is one of the second-most challenging permselective dehydration separation for the solvents in Table 3. As noted above, the most challenging permselective water/solvent separation is that of the water/methanol system. Water/methanol permselectivities for the seven materials listed in Table 5 are listed in the last column for comparison with those for water/ethanol. The water/solvent permselectivity for Table 3 solvents other than ethanol and methanol will be higher than that of ethanol. The water permeances for dilute water/ethanol solutions are reasonably representative of other water/solvent solutions. This is particularly true for those mixtures with water activities in the same region as those of 5–15 wt% water in ethanol or for materials that are insensitive to water activity, like the APFPs.

All told, these seven commercially available membrane materials may be used to remove water from practically all the solvents of interest. Of the Table 3 solvents, only DMF has

been reported as being problematic and only for two of the membranes listed in Table 5: PVA and APFP. This is most likely a limitation of the support materials employed in these composite membranes rather than of the PVA or APFP dense layers. For PVA membranes with a PAN microporous support layer, the PVA layer may be compatible with DMF, but the PAN support can be swelled by DMF, negatively impacting membrane integrity. The most significant limitation, particularly for hydrophilic polymers, is the maximum water content of the feed fluid. As indicated in Table 5, the reported limitation for water in the feed for PVA is 30–50 wt% with that limit dependent on the nature of the crosslinking in the PVA matrix. For polyimides, up to 70 wt% water has been demonstrated, but that was for a superheated vapor feed, liquid feeds are not advised. APFP membranes have the greatest water tolerance of the polymeric materials, with no reported limit on the water concentration in the feed. For zeolite materials with low Si:Al ratios, like NaA zeolites, high water activities and non-neutral pH values can cause hydrolysis and dealumination. As a result, NaA zeolites are limited to feeds containing less than 20 wt% water and to a pH range of 6–8. CHA and T-type zeolites have no stated limits on the feed water content, with reports of CHA membranes used at up to 50 wt% water and Zeolite T membranes at up to 100 wt% water. These two zeolites are also more acid resistant than the NaA materials. Hybrid Silica has no stated limit on the water content in the feed and is more acid tolerant than the zeolites. However, Hybrid Silica can break down under alkaline conditions, so 8.5 is reported as the maximum pH.

The stated long-term maximum operating temperature for commercial PVA membranes is 100 °C - all the other materials listed in Table 5 can be operated at higher temperatures. For commercial NaA zeolite and Hybrid Silica membranes, the stated long-term maximum operating temperature is 150 °C. For APFP, CHA zeolite, and Zeolite T, experimental results have been reported for temperatures as high as 130–135 °C, but the actual temperature limit has not been explicitly stated. Overall, PVA appears to be the most sensitive of the membrane materials, particularly to temperature and secondary compounds/contaminants. APFP, CHA, Zeolite T, and Hybrid Silica are the least sensitive to operating conditions and feed constituents. This feature not only defines the useful operating range for the membrane, but also factors into the risk of membrane damage due to process upsets or process shutdowns/startups.

As for separation performance, there is higher variability between the materials covered in Table 5 in terms of water/ethanol permselectivity than in terms of water permeance. The lowest water/ethanol selectivity of 20 was observed for a “CMS3” APFP material. Cytop™ APFP was reported to have a higher water/ethanol selectivity of 110. The water/ethanol selectivity of polyimides in PV mode is observed to be somewhat higher than that of the APFPs, in the 57 to 280 range. Hybrid silica is in this same range, yielding a water/ethanol selectivity of 230. Commercial PVA membranes deliver the highest water/ethanol selectivities of the polymeric membranes, well over 1,000 ($\alpha=4,800$ for DeltaMem AG PERVAP™ 4101). As for the zeolites, Zeolite T is reported to have a water/ethanol selectivity in the same range as that of the PVA membranes while the selectivity increases to 10,000 for NaA membranes and up to 120,000 for CHA.

The water permeances for the membranes chosen as representative of the common membrane materials are in a tighter range than the respective selectivities, at least for the conditions selected in preparing Table 5. This is noteworthy given that permeance is roughly inversely proportional to the thickness of the dense layer and the dense layers of these assorted types of membranes can be quite different. The polymeric membranes are at the lower end of the range, with water permeances of between about 1,000 to 3,000 GPU. Zeolite T, NaA, and Hybrid Silica membranes delivered water permeances in the 3,500 to 6,500 GPU range. A CHA zeolite membrane exhibited water permeance of 35,000 GPU, far exceeding the other materials in Table 5. The amount of publicly disclosed data on CHA zeolite membranes with ethanol/water systems under the conditions outlined in Table 5 is limited. Additional testing is needed to determine if the high water/ethanol selectivity ($\alpha=120,000$) and high water permeance ($\Pi_w=33,000$ GPU) reported for experimental CHA membranes is routinely observed with commercial-grade CHA membranes. For example, results reported by Mitsubishi for a CHA membrane with Si:Al of 3.5, tested at a higher temperature of 100 °C with an ethanol/water mixture containing 15 wt% water, delivered a slightly reduced performance ($\alpha=75,000$ and $\Pi_w=5,600$ GPU) compared to the CHA membrane referenced in Table 5²²⁸. Since permeances are inversely related to the thickness of the dense layer, it is likely that permeances of future membranes of these same materials will be higher than those reported previously as manufacturers and researchers find ways to make thinner selective layers. Gains in permeance may come at the expense of lower selectivities as thinner dense layers become harder to make without defects and the mass transfer resistance of the support layer has a greater impact on overall mass transfer.

The ethanol/water separation performance characteristics of the seven membrane types listed in Table 5 are presented in Figure 6 in a pseudo-Robeson log-log plot of water/ethanol selectivity vs. water permeance. Each material is shown as a region in the graph. For PVA, NaA, T-type zeolite, Hybrid Silica, and CHA the regions are rectangles representing the selectivity and permeance values given in Table 5 for commercial or pre-commercial membranes with a $\pm 50\%$ span added to represent future improvements or losses in either selectivity or permeance. For APFP and Polyimide, the results from two versions of commercial or pre-commercial membrane materials were included in Table 5 and are shown in Figure 6 as extended rectangles. Additional details regarding the specific membranes, references, and performance data used to generate Figure 6 are provided in Table S2 of Supporting Information. The intention of Figure 6 is to qualitatively capture the typical performance differences between commercially available PV/VP membrane materials. Similar trends in performance have been reported through direct comparisons of two or more of these types of materials for water/solvent separations^{68, 280–283}.

As noted previously, methanol is more similar to water than is ethanol, in both size and chemical properties, making the selective removal of water from methanol more challenging than from ethanol. This is reflected in the significantly lower water/methanol permselectivities reported in Table 5 relative to those for water/ethanol, about 1–2 orders of magnitude lower. The CHA and NaA zeolite membranes captured in Table 5 were found to deliver the highest water/methanol selectivities of 2,000 to 2,100, but those are much smaller

than the 120,000 and 10,000 selectivities reported for the water/ethanol separation. The lowest water/methanol selectivities, 5 to 11, were reported for APFP materials.

Status of, and Near-Term Prospects for, Dehydration Membrane Materials

In a 2013 PV/VP tutorial article, this author noted two large-scale PV/VP applications, alcohol biofuel drying and gasoline desulfurization, that held the near-term potential to enable these technologies to graduate from “emerging technology” status. While desulfurization by PV/VP is still in development, PV/VP technologies have gained a foothold as accepted options in the drying of bioethanol, either as a replacement for the molecular sieve system or to increase the capacity of an existing distillation-molecular sieve system. This acceptance is exemplified by several recent retrofits involving Whitefox Technologies Ltd. hollow fiber membranes systems in U.S. ethanol plants and in a recently announced marketing collaboration between ICM Inc., a developer of fuel ethanol technologies and a designer of many U.S. ethanol plants, and Mitsubishi Chemical Corporation to utilize Mitsubishi’s zeolite membranes in the fuel ethanol drying process^{227, 284–287}.

Overall, a robust and varied PV/VP membrane industry has developed. The membrane material with the greatest number of manufacturers and suppliers appears to be NaA zeolite (see Supporting Information). However, over the last decade or so, membranes made with several “newer” materials have become commercially available, including CHA and T-type zeolites, APFP, and hybrid silica. Membrane manufacturers are working to improve performance and stability while reducing the cost of their products. Thus, it is expected that the selectivity vs. permeance performance regions depicted in Figure 6 will shift over time to the right (i.e. higher throughput/flux) and up (higher selectivity). No doubt one or more of the emerging materials outlined in earlier sections will eventually become commercially available and warrant placement in Figure 6, joining PVA, polyimide, APFP, NaA zeolite, CHA zeolite, Zeolite T, and Hybrid Silica. Fortunately, as outlined in Table 5, the available PV/VP membrane materials can be used under a wide range of conditions to dry the hydrophilic solvents of interest outlined in Table 3. The design of batch and continuous solvent drying processes based on the PV/VP membrane materials detailed herein will be the subject of a future paper.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations/Nomenclature

APFP	amorphous perfluoropolymer
BTESE	bis(triethoxysilyl)ethane
BTESM	bis(triethoxysilyl)methane
CHA	chabazite
CMC	carboxy methyl cellulose
CMS	carbon molecular sieve
DMAc	<i>N,N</i> -dimethylacetamide
DMF	<i>N,N</i> -dimethylformamide
DMSO	<i>N,N</i> -dimethylsulfoxide
FAU	faujasite
GPU	gas permeation unit ($10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \cdot \text{s} \cdot \text{cmHg} = 3.344 \times 10^{-10} \text{ kmol}/\text{m}^2 \cdot \text{s} \cdot \text{kPa}$)
IPA	isopropyl alcohol, 2-propanol
LTA	Linde Type A
MIBK	methyl isobutyl ketone
MMM	mixed matrix membrane
MOF	metal-organic framework
MtBE	methyl tertiary-butyl ether
NaA	sodium Linde Type A zeolite
NMP	<i>N</i> -methyl-2-pyrrolidone
PAN	poly(acrylonitrile)
PBI	poly(benzimidazole)
PIM	polymer with intrinsic microporosity
PTFE	poly(tetrafluoroethylene)
PV	pervaporation
PVA	poly(vinyl alcohol)
STP	standard temperature and pressure
THF	tetrahydrofuran, oxolane
TR	thermally rearranged

USEPA	United States Environmental Protection Agency
VLE	vapor-liquid equilibrium
VP	vapor permeation
ZIF	zeolitic imidazolate framework

Roman symbols

D_i	diffusivity of species i in membrane material, m^2/s
J	total mass flux through membrane, $\text{kg}/\text{m}^2\cdot\text{s}$
l	membrane thickness, m
MW_i	molecular weight of species i , kg/kmol
p_i^{sat}	saturated vapor pressure of species i at system temperature, kPa
p_i^F	partial pressure of species i in the feed vapor or feed liquid, kPa
p_i^V	partial pressure of species i in the permeate vapor, kPa
P_i	permeability of species i in membrane material, $\text{kmol}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{kPa}$
S_i	solubility of species i in membrane material, $\text{kmol}/\text{m}^3\cdot\text{kPa}$
w_i^F	mass fraction of species i in the feed vapor or feed liquid
w_i^V	mass fraction of species i in the permeate vapor
x_i	mole fraction of component i in the feed vapor or feed liquid
y_i	mole fraction of component i in the permeate vapor

Greek symbols

α	molar permselectivity (“selectivity”)
β	separation factor
γ_i	activity coefficient of species i
δ	overall Hansen solubility parameter, $\text{MPa}^{1/2}$
δ_d	dispersion contribution to solubility parameter, $\text{MPa}^{1/2}$
δ_h	hydrogen bonding contribution to solubility parameter, $\text{MPa}^{1/2}$
δ_p	polar contribution to solubility parameter, $\text{MPa}^{1/2}$
Π_i	permeance of species i through membrane, $\text{kmol}/\text{m}^2\cdot\text{s}\cdot\text{kPa}$

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Figure 1.
Vapor-liquid equilibrium of three alcohol/water mixtures of interest. Curves based on NRTL thermodynamic model at 101.3 kPa system pressure (see Table S1).

Figure 2.
Hansen solubility parameters for solvents listed in Table 3.

Figure 3.
Schematic diagram of a pervaporation or vapor permeation membrane process. Molecules are depicted as circles.

Figure 4.

Chemical structures of several polymers used to prepare the dense layer of PV/VP dehydration membranes: A) Poly(vinyl alcohol); B) Poly(carboxy methyl cellulose); C) Polyimide (Matrimid™ 5218 shown); D) Poly(benzimidazole); E) Teflon™ AF.

Figure 5.

Structures of several inorganic materials used as the dense layer in PV/VP dehydration membranes: A) LTA zeolite lattice structure (e.g. NaA zeolite); B) CHA zeolite lattice structure; C) Microporous silica (left) and Hybrid Silica (right). (Figures A and B from Database of Zeolite Structures²³³. Figure C reproduced from Chang *et al.*³⁰⁰ with permission from The Royal Society of Chemistry.)

Figure 6.

Rough performance comparison of membranes prepared from the seven common PV/VP membrane materials listed in Table 5 removing water from ethanol/water mixtures by pervaporation for feeds containing 5–15 wt% water at temperatures of 50–80 °C. See text for explanation of the location and size of the region shown for each type of membrane.

Table 1.

Solvents covered by remanufacturing exclusion of the 2015 USEPA Definition of Solid Waste Rule.

Non-Polar Solvents	Polar Aprotic Solvents	Polar Protic Solvents
n-Hexane ^{*†}	Methyl tert-butyl ether (MtBE) ^{*†}	1-Butanol [*]
Cyclohexane [*]	Chlorobenzene ^{*†}	Methanol [†]
1,2,4-Trimethylbenzene [*]	Chloromethane [†]	Ethanol [*]
Toluene ^{*†}	Dichloromethane ^{*†}	
Ethylbenzene ^{*†}	Chloroform ^{*†}	
Xylenes ^{*†}	Methyl isobutyl ketone (MIBK) ^{*†}	
	Tetrahydrofuran (THF) [*]	
	Acetonitrile ^{*†}	
	N,N-Dimethylformamide (DMF) [†]	

^{*} Solvent forms an azeotrope with water (azeotrope information from Handbook of Organic Solvent Properties²⁸⁸ and Nishikawa *et al.*²⁸⁹)

[†] Considered a Hazardous Air Pollutant (HAP) by the USEPA²⁹⁰

Table 2.

Properties of solvents that exhibit sparing solubility in water and sparing solubility of water in the solvent, listed in general order of increasing polarity.

Solvent	CAS No.	MW [£] (g/mol)	Boiling Point [£] (°C)	Density @ 25°C [£] (g/mL)	Water in Azeo- trope @ 1 atm [§] (wt %)	Temp. of Azeo- trope @ 1 atm [§] (°C)	Solubility of water in solvent at 25°C [‡] (wt%)	Solubility of solvent in water at 25°C [‡] (wt%)
n-Hexane	110-54-3	86.18	68.7	0.656	6	62	0.0090	0.00095
Cyclohexane	110-82-7	84.16	80.7	0.773	9	70	0.016	0.0067
1,2,4-trimethylbenzene (pseudocumene)	95-63-6	120.19	168.9	0.859	23.4 [£]	97 [£]	0.038	0.0057
Toluene	108-88-3	92.14	110.6	0.865	20	85	0.054	0.057
Ethyl benzene	100-41-4	106.17	136.2	0.865	33	92	0.044	0.018
Xylenes (mixed)	1330-20-7	106.17	140	0.862	37	93	0.045	0.011
Chlorobenzene	108-90-7	112.56	131.7	1.101	28	90	0.033 [§]	0.054
Chloromethane	74-87-3	50.49	-24.2	N/A			N/A	0.54 ^{**}
Dichloromethane	75-09-2	84.93	39.8	1.318	1	38	0.18	1.3
Chloroform (trichloromethane)	67-66-3	119.4	61.2	1.480	3	56	0.087	0.78

[£]From Nishikawa *et al.*²⁸⁹

[£]Yaws' Critical Property Data for Chemical Engineers and Chemists, Knovel²⁹¹, accessed via <https://app.Knovel.com> on 01/10/2018

[§]Handbook of Organic Solvent Properties via Knovel²⁸⁸

[‡]Yaws' Handbook of Properties for Aqueous Systems via Knovel¹²

^{**}
At 1 atm partial pressure of solvent

Table 3.

Physical properties of solvents targeted for reclamation that are miscible with water or exhibit a solubility of water in the solvent of 1 wt% or greater.

Solvent	CAS No.	MW [‡] (g/mol)	Boiling Point [‡] (°C)	Density @ 25°C [‡] (g/mL)	Water in Azeo- trope @ 1 atm [§] (wt %)	Temp. of Azeo- trope @ 1 atm [§] (°C)	Solubility of water in solvent at 25°C [‡] (wt%)	Solubility of solvent in water at 25°C [‡] (wt%)
Acetonitrile	75-05-8	41.05	81.6	0.779	16	76.0	Miscible	
1-Butanol	71-36-3	74.12	117.7	0.806	42.0	93.0	20.2	7.34
N,N-Dimethyl formamide (DMF)	68-12-2	73.10	153.0	0.945	No Azeotrope		Miscible	
Ethanol	64-17-5	46.07	78.3	0.787	4.0	78.0	Miscible	
Methanol	67-56-1	32.042	64.7	0.787	No Azeotrope		Miscible	
Methyl Isobutyl Ketone (MIBK), 4-methyl-2-pentanone	108-10-1	100.16	117.7	0.796	24.0	88.0	2.15	1.85
Methyl <i>tert</i> -Butyl Ether (MtBE)	1634-04-4	88.15	55.2	0.735	3.0	52.0	1.0	3.25
Tetrahydrofuran (THF), Oxolane	109-99-9	72.11	64.9	0.880	5.3	64.0	Miscible	
Commonly used solvents similar to those above								
Acetone, Propan-2-one	67-64-1	58.08	56.3	0.786	No Azeotrope		Miscible	
2-Propanol (isopropanol, IPA)	67-63-0	60.10	82.3	0.783	12.6	80.0	Miscible	

[‡]Yaws' Critical Property Data for Chemical Engineers and Chemists, Knovel²⁹¹, accessed via <https://app.Knovel.com> on 01/10/2018

[§]Handbook of Organic Solvent Properties via Knovel²⁸⁸

[†]Heterogeneous azeotrope

[‡]Yaws' Handbook of Properties for Aqueous Systems via Knovel¹²

Table 4.

Kinetic diameters of common solvents, including several from Table 3⁴⁴.

Solvent	Kinetic Diameter (nm)
Water	0.296
Methanol	0.380
Ethanol	0.430
Acetic acid	0.436
Acetone	0.469
2-Propanol	0.470
Methyl acetate	0.478
Trichloromethane	0.483
THF	0.486
Pyridine	0.496
2-Butanol	0.504
Methyl ethyl ketone	0.504

Table 5.

Performance and Limitations of Common PV/VP Dehydration Membrane Materials⁷.

Material	Reported PV Water Permeance $\frac{1}{\text{cm}^2 \text{ s bar}}$ (J_w) (GPU)	Water/Ethanol PV Selectivity ⁷ (α)	Source of membrane for ethanol/water performance data	General Limitations of Membrane Material				Water/Methanol PV Selectivity ⁸
				Excluded Table 3 Solvents	Max. Water Conc. ^{7,8} (wt%)	Max. Temperature ^{7,8} (°C)	Other	
PVA	1,100 ²⁹⁴	4,800 ²⁹⁴	DeltaMem PERVAP TM 4101 tested by Clausthal Univ. of Technol. ²⁹⁴	DMF ⁸¹	30–50 ⁸ (depends on x-linking) ⁸¹	100 ^{8,81}	pH range: 5–8, Avoid (conditional): Aldehydes, mineral acids, sulfonates, peroxides, acetals, amides, amines ⁸¹	30 (PERVAP 2201) ²⁹⁵ to 250 (PERVAP 1510) ²⁹⁶
Polyimide	1,100 ²¹⁵ to 3,700 ²⁹⁷	57 ²⁹⁷ to 280 ²¹⁵	Experimental, Yamaguchi Univ. ²⁹⁷ and Mitsui Engg. & Shipbldg. ²¹⁵	None stated	70 ^{7,102}	None stated, at least 150 ^{7,110} , Vapor feed	Polyimides generally limited to vapor feed for long-term applications ¹¹⁰	≈10x lower than ethanol (e.g. 6 to 30) ⁸
APFP	930 ¹⁵⁸ to 2,900 ¹⁵⁹	20 ¹⁵⁸ to 110 ¹⁵⁹	Compact Membrane Sys. CMS3 ¹⁵⁸ and experimental Cytos and Teflon AF1600 ¹⁵⁹	Possibly DMF (may depend on support)	None stated, 100 ^{7,158}	None stated, at least 130 ^{7,158}	None stated	5 ¹⁵⁸ to 11 ¹⁸⁴
NaA	4,500 ¹⁹⁸	10,000 ¹⁹⁸	Experimental, Mitsui Engg. & Shipbldg. <i>et al.</i>	None	20 ^{8,298}	150 ^{8,298}	pH range: 6–8, Avoid: Mineral & organic acids	2,100 ¹⁹⁸
CHA	35,000 ²³⁷	120,000 ²³⁷	Experimental, National Inst. of Advanced Industrial Sci. and Technol. (AIST)	None	None stated, at least 50 ^{7,235}	None stated, at least 130 ^{7,235}	None stated	2,000 ²³⁷
Zeolite T	3,500 ¹⁹⁸	2,500 ¹⁹⁸	Experimental, Mitsui Engg. & Shipbldg. <i>et al.</i>	None	None stated, 100 ^{7,193}	None stated, at least 135 ^{7,198}	Avoid mineral acids at low pH (e.g. pH<2)	27 ¹⁹⁸

Material	Reported PV Water Permeance $\frac{1}{2}$ (J_w) (GPU)	Water/Ethanol PV Selectivity $\frac{3}{4}$ (α)	Source of membrane for ethanol/water performance data	General Limitations of Membrane Material				Water/Methanol PV Selectivity $\frac{5}{6}$
				Excluded Table 3 Solvents	Max. Water Conc. $\frac{7}{8}$ (wt%)	Max. Temperature $\frac{9}{10}$ ($^{\circ}\text{C}$)	Other	
Hybrid Silica	6,500 ²⁹⁹	230 ²⁹⁹	Experimental, Energy Research Centre of the Netherlands <i>et al.</i>	None	None Stated	150 ^{2,253}	pH range: 0.5–8.5 ²⁵³	59 ²⁹⁹

¹Information in this table is a rough overview, losing some of the finer nuances of material compatibility and range of feed conditions, the reader is urged to contact a vendor or access the original literature reference to obtain more detailed information on a material for specific applications.

²Water permeance and water/ethanol permselectivity – as reported or calculated from flux data obtained, if possible, with commercial or pre-commercial membranes for ethanol/water mixtures containing 5–15 wt% water at between 50–80 °C. The values in the table were from tests covering the narrower operating range of 5 to 10 wt% water and 60 to 77 °C. 1 GPU = 3.34×10^{−10} kmol/m²·s·kPa

³Based on the maximum tested in literature reports, not necessarily the limit of the material.

⁴Based on a product description from the commercial supplier for long term use applications

⁵Water/methanol permselectivity – as reported for methanol/water mixture containing 5–15 wt% water in the range of 40–65 °C

⁶Based on reported vapor permeation permselectivities for ethanol/water and methanol/water mixtures¹⁰².