Facile Preparation of a Laponite/PVA Mixed Matrix Membrane for Efficient and Sustainable Pervaporative Dehydration of C1–C3 Alcohols
Asmaa Selim, András Jozsef Toth, Daniel Fozer, Karoly Süvegh, and Péter Mizsey*

ABSTRACT: The exfoliation method was applied for the preparation of high-water selective mixed matrix membranes (MMMs), especially for the dehydration of C1–C3 alcohol–water solutions. Herein, a facile and easy method was employed to fabricate physically cross-linked Laponite nanosilicate clay–PVA MMMs without additional cross-linking by a one-step synthesis route for water dehydration from methanol, ethanol, and isopropanol aqueous solutions. The morphologies, chemical structures, thermal stabilities, and surface hydrophilicity of Laponite–PVA MMMs were investigated properly by different characterization techniques. The Laponite concentration has affected the fractional free volume of the membranes, as proven by positron annihilation lifetime spectroscopy analysis. The MMMs displayed both a significant improvement in the separation factor and remarkable enhancement in the permeation fluxes for the three alcohol systems. The influence of the operating temperature on the MMM performance was investigated for the methanol/water solution. The methanol permeability was 100-fold lower than that of the water, indicating that the membranes are more water selective. Particularly, the Laponite–PVA membrane with 5 mg/mL Laponite loading exhibits excellent separation efficiency for C1–C3 dehydration having water permeabilities higher than most other polymeric membranes from the other literature studies of 2.82, 2.08, and 1.56 mg m−1 h−1 kPa−1 for methanol, ethanol, and isopropanol/water systems, respectively. This membrane development allows a more efficient and sustainable separation of aqueous alcoholic mixtures.

1. INTRODUCTION
In recent years, the extensive use of fossil fuel results in increase in global warming. Therefore, finding clean and green energy has received full attention. Biofuels are reported to be a promising alternative for fossil fuel representation.1 Recently, the production of renewable alcohols from the biomass process is not only essential in numerous chemical industries but has also received attention as biofuels. Methanol has great importance in the CO₂ capture processes and the transformation process.2 For the biofuel production through the fermentation broth, the cost of the separation process is the highest. Consequently, finding an economical alternative for the traditional separation process is an essential issue.

In this regard, pervaporation (PV) has been reported as a portentous process for alcohol separation and dehydration either from the fermentation broth or from the reaction products, especially in the case of azeotropic mixtures.3–5 PV is vital to improve the alcohol composition from 80–85 to 99 wt %. However, the traditional distillation works efficiently up to the same concentration and above. The process becomes prohibitively expensive, especially near an azeotropic composition. Therefore, a significant share of the production cost goes to alcohol purification.6,7 Additionally, based on the literature, PV operating cost could be 50% less compared to the conventional distillation with a relatively higher separation efficiency.8 Therefore, PV is considered to be one of the most promising candidates in the bio-fuel purification field. Additionally, PV has attained much attention because of its properties of lower energy consumption and higher efficiency, as well as its merit as being eco-friendly and economically undisputed.9,10

PV is vastly accounted for liquid separation in different ways, such as the dehydration of the chemical solvents, the
concentration of volatile organic compounds, or the separation of two organic solvents using hydrophilic, hydrophobic, and organoselective membranes, respectively.\textsuperscript{11−13} In the PV process, the well-known solution–diffusion model of mass transport is approved. The driving force is generated on the membrane sides; mainly, the feed mixture is heated up to a specific temperature, then penetrates through the membrane to be converted to gas, and leaves from the permeate side. By maintaining the vacuum, the collected vapors are condensed by cold medium.\textsuperscript{14} Hence, the membrane is the core of the PV process, its type, material, and intrinsic properties are the most critical factors to achieve high separation performance.

For the dehydration process, usually, hydrophilic polymers are used, which are mostly polymers with a high affinity toward water, such as poly(vinyl alcohol) (PVA), chitosan, and alginate, increasing the PV performance. However, these materials were reported having low mechanical stability in aqueous solutions. This is credited to their high sorption

*Figure 1. Schematic figure of CM-Celfa P-28 Membrantechnik AG in PV mode.*
affinity toward water and low rigidity of these polymers, which results in lowering the water selectivity and increasing the permeability in a trade-off trend.\textsuperscript{12} In an attempt to inhibit this phenomenon, different modifications are reported, such as chemical cross-linking, heat treatment, blending with another polymer, grafting,\textsuperscript{16–18} as well as mixing with inorganic fillers.\textsuperscript{14,19}

Mixed matrix membranes (MMMs) consisting of a polymer matrix filled with inorganic fillers were first reported by Kulprathipanja et al. to combine the advantages of both polymeric and inorganic membranes.\textsuperscript{20} The most reported polymer for PV dehydration technology is the well-studied hydrophilic PVA, followed by other polymeric materials such as chitosan and alginate.\textsuperscript{21} Among the variety of inorganic fillers, nanosilicate clays for PVA membranes, such as clinoptilolite, montmorillonite, and bentonite, are perceived as promising fillers for the dehydration process because of their unique characteristics of exceptionally high surface area and biocompatibility.\textsuperscript{22–24}

Laponite is a relatively new nanosilicate clay which has a disc structure with 30 nm diameter and 1 nm in thickness with the empirical formula Na\textsuperscript{0.7}[(Mg\textsubscript{0.8},Li\textsubscript{0.2})Si\textsubscript{4}O\textsubscript{10}(OH)\textsubscript{4}].\textsuperscript{0.7} Laponite clay has a high affinity toward water and forms a clear dispersion easily in water. Laponite is reported for enhancing the mechanical and the physical stability of polymer nanocomposite and hydrogels.\textsuperscript{25–28} Whereas, silicate nanoclay has been extensively reported for biochemical and biological applications such as wound healing and drug delivery.\textsuperscript{29,30} However, to the best of our knowledge, no research has studied the impact of implementing Laponite clay as a nanofiller in PV MMMs for dehydration applications.

This work endeavors to investigate the tenor of designing PV-based MMMs with Laponite nanoclay for alcohol dehydration. The suggested MMMs consist of PVA as a polymer matrix and different nanoclay concentrations. The nanoclay incorporation is believed to increase the overall performance of the PV dehydration process because of their hydrophilicity and excellent surface area. Moreover, this work aims to observe the effect of the nanoclay content on alcohol dehydration and to compare their influence on the separation of three different alcohols, namely, methanol, ethanol, and isopropanol at 85 wt % solutions, and different operating temperatures. Additionally, the basic characterizations of the MMMs have been examined as a function of the nanofiller concentration such as solvent uptake, surface hydrophilicity (contact angle measurements), density, surface morphology (scanning electron microscopy (SEM), transmission electron microscopy (TEM), and surface analysis (scanning electron microscopy (SEM))), thermal stability (thermogravimetric analysis (TGA)), and positron annihilation lifetime spectroscopy (PALS) analyses.

2. RESULTS AND DISCUSSION

2.1. Characterization of MMMs. 2.1.1. Morphology. The scanning electron micrograph, along with the transmission electron microscopy (TEM) image, shown in Figure 2a,b, show Laponite nanoclay before the dispersion in water. The SEM images present that the clay is formed from large agglomerates with different sizes and shapes, and the disc structure clearly appears in the TEM image. On the other hand, Figure 2c displays the surface of the pristine cross-linked membrane with a smooth and dense structure. Figure 2 also shows the surface morphologies of MMMs consisting of different Laponite concentrations in the casting solution. First at a concentration of 1 mg/mL, as shown in Figure 2d, the Laponite nanoclay shows even dispersion in the polymer chain with no recognized voids or cracks. However, increasing the concentration to 2.5 mg/mL led to apparent nanodisc agglomeration, as seen in Figure 2e, and the further loading of Laponite results in the assembly of the nanodiscs together forming a separate phase inside the polymer matrix, as shown in Figure 2f. However, it is observed that compared to the thermally cross-linked membrane, the surface of the MMMs with the different nanoclay concentrations is denser, and on the other hand, it has higher roughness. Additionally, from Figure 2g,h, it could be observed that increasing the Laponite content in the casting solution results in the formation of an agglomeration layer inside the polymer matrix. Moreover, the EDX analysis, as shown in Figure 2i, shows that the agglomeration layer is from the Laponite nanoclay. Similar behavior of the Laponite nanoclay has been reported by Selim et al.\textsuperscript{31}

2.1.2. Thermogravimetric Analysis. Figure 3 shows the TGA curves of Laponite nanoclay, thermally cross-linked membrane, and MMMs in the temperature range of 34–700 °C under a nitrogen atmosphere. Hence, the dihydroxylation process of Laponite is above 700 °C; Laponite shows total thermal stability up to the end of the temperature range.
For all membranes, the water dehydration process at approximately 5% weight loss can be recognized at around 100–150 °C. It can also be seen in the DTG curves that the temperature of the dehydration is shifted slightly with increasing the Laponite concentration, this could be assigned to the decrease of the –OH group in the PVA matrix because of the interaction with Laponite through the H-bond.

The thermally cross-linked PVA, PVA-1, and PVA-2.5 membranes exhibit a second failure between 200 and 350 °C, which is attributed to the decomposition of the side chain of the PVA matrix. However, for PVA-5, this failure is shifted from ∼250 to 420 °C. This can be due to the fact that at higher concentrations of the nanoclay compared to the polymer nanodiscs promote the intercalated membrane formation by assembling and forming a separated layer, resulting in a stronger interaction between the polymer and the nanofiller.

All the membranes then show the last degradation step between 380 and 550 °C, which can be attributed to the carbonated residue decomposition, such as the PVA backbone. Although the change in the weight residue when adding 1 mg/mL of Laponite is obsolete, PVA-2.5 and PVA-5 show ∼90% higher compared to PVA. Additionally, with the addition of Laponite, the thermal degradation temperature of the PVA-5 membrane increased by ∼100 and ∼74 °C for 10 and 30% weight loss compared to the PVA membrane, respectively.

2.1.3. Chemical Interaction. The Fourier transform infrared (FT-IR) spectra of the Laponite XLG powder, PVA, and Laponite-loaded PVA MMMs are depicted in Figure 4. The Laponite spectrum showed a multicomponent wide band between 3700 and 3000 cm⁻¹, which is assigned to the stretching and bending of surface hydroxyl groups (Si–OH and Mg–OH), and at 1630 cm⁻¹ it is related to adsorbed water on Laponite XLG. The stretching of Si–O and Si–O–Si bonds appeared as a strong band at 950 cm⁻¹, and the stretching of Mg–O is ascribed by a band at 640 cm⁻¹.

The bands between 2940 and 2900 cm⁻¹ are due to C–H stretching vibration alkyl groups of PVA chains. The vibration peaks attributed to the C–O chain, the angular deformation outside the plan of the O–H bond, and C–C in the PVA chain are identified at 1085, 920, and 831 cm⁻¹, respectively. Compared to the PVA membrane, Laponite-loaded PVA membranes’ FT-IR spectrum displayed the same peaks but changing in intensity. Moreover, the bands between 2940 and 2900 cm⁻¹ are due to C–H stretching vibration alkyl groups of PVA chains.

Figure 3. TGA and DTG curves of Laponite clay (black), PVA membrane, and Laponite-loaded PVA MMMs.

Figure 4. FT-IR spectrum of Laponite XLG powder, PVA, and Laponite-loaded PVA MMMs.
between the PVA polymer and the clay through Si–OH groups.

2.2. Fraction Free Volume Measurements. In order to investigate the free volume size in the MMMs, PALS has been employed. PALS is considered the most advanced direct method to observe the free volume parameters in polymers. In PALS, the measurement of the free volume and its distribution is based on the positron lifetime \( \tau \) and lifetime intensity \( I_\tau \), respectively. Using the values of the lifetime and its intensity, the fractional free volume (FFV) can be estimated using eq 6. Table 1 displays the \( \tau \), \( I_\tau \), \( R \), and FFV values. All the values show significant structural modifications in the PVA structure upon the incorporation of Laponite. At first glance, the small amount of nanoclay modifies the structure of PVA by increasing the free volume. However, after the addition of 2.5 mg/mL of the nanodiscs, a decrease in the FFV is noticed, and a phase change appears as long as a further increase in the Laponite concentration on the thermally cross-linked PVA and Laponite–PVA MMMs on solvent uptake percentage of water, methanol, ethanol, and isopropanol. The results show that increasing the Laponite concentration results in increasing the water uptake % during the reduction of the three alcohols. This indicates that the incorporation of the nanoclay enhanced the membrane affinity toward water but decreased the alcohol solubility.

Additionally, it could be recognized that the water uptake ratio is much higher than all the alcohol uptake ratios. This could be attributed to the hydrophilic behavior of the Laponite nanodiscs as well as the high affinity toward water of the PVA polymer itself. Moreover, it can be observed that the water uptake increases up to 211% upon the incorporation of 2.5 mg/mL Laponite and then practically remains constant, or slightly decreases with increasing the Laponite concentration to 5.0 mg/mL. The increase might be associated with the high hydrophilic feature of the membrane, while the trivial dwindling could be attributed to the fact that the clay can act as a physical cross-linker which delimits the PVA solubility in the water and shrinks the available space in the polymer matrix as proved by PALS analysis.

Moreover, the results demonstrate also that the solvent uptake follows the order of EtOH > IPA > MeOH. In order to understand the interactions between the PVA membrane and alcohols during the solvent uptake test Hansen solubility parameters are introduced, and the affinity of PVA toward methanol, ethanol, and isopropanol is determined by the distance (Ra) between a polymer and solvent in the Hansen parameter.27 While the trivial cross-linking could be attributed to the fact that the clay can act as a physical cross-linker which delimits the PVA solubility in the water and shrinks the available space in the polymer matrix as proved by PALS analysis.

The Hansen solubility parameter (Ra) and RED calculated according to eqs 1 and 2 are shown in Table 3. The results show that methanol and ethanol have the highest solubility parameter, while isopropanol has the lowest. This indicates that the incorporation of the nanoclay enhanced the membrane affinity toward water but decreased the alcohol solubility.

### Table 1. PALS Parameter for Thermally Cross-Linked PVA and PVA–Laponite MMMs

| membrane | Laponite concentration (mg/mL) | \( \tau \) (ns) | I\(_\tau\) (%) | R (Å) ± 0.003 | FFV (%) ± 0.001 |
|----------|--------------------------------|----------------|---------------|---------------|----------------|
| PVA      | 0                              | 1.17 ± 0.002   | 12.20 ± 0.141 | 1.844         | 0.320          |
| PVA-1    | 1.0                            | 1.283 ± 0.015  | 11.65 ± 0.212 | 2.077         | 0.437          |
| PVA-2.5  | 2.5                            | 1.066 ± 0.001  | 10.55 ± 0.071 | 1.766         | 0.244          |
| PVA-3.5  | 3.5                            | 1.081 ± 0.007  | 11.15 ± 0.071 | 1.790         | 0.268          |
| PVA-5    | 5.0                            | 1.093 ± 0.005  | 11.85 ± 0.212 | 1.808         | 0.293          |

### Table 2. Solvent Uptake Analyses for the PVA Cross-Linked Membrane and MMMs

| membrane | water uptake (%) | methanol uptake (%) | ethanol uptake (%) | isopropanol uptake (%) |
|----------|------------------|---------------------|--------------------|-------------------------|
| PVA      | 191.98 ± 0.04    | 9.04 ± 0.02         | 25.40 ± 0.05       | 10.45 ± 0.07             |
| PVA-1    | 200.90 ± 0.20    | 8.48 ± 0.05         | 9.74 ± 0.04        | 9.02 ± 0.10              |
| PVA-2.5  | 211.47 ± 0.15    | 8.68 ± 0.06         | 9.82 ± 0.04        | 7.58 ± 0.05              |
| PVA-3.5  | 210.85 ± 0.17    | 8.01 ± 0.08         | 8.90 ± 0.19        | 7.31 ± 0.04              |
| PVA-5    | 209.01 ± 0.24    | 7.26 ± 0.03         | 8.46 ± 0.04        | 6.35 ± 0.02              |

### Table 3. Hansen’s Solubility Parameters for Pure C1–C3 Alcohols and PVA and Distance Parameter (Ra) and RED Calculated According to eqs 1 and 2

| solvent/polymer | \( d_1 \) [MPa\(^{0.5}\)] | \( d_2 \) [MPa\(^{0.5}\)] | \( d_3 \) [MPa\(^{0.5}\)] | \( d_4 \) [MPa\(^{0.5}\)] | \( R_{a,PVA} \) [MPa\(^{0.5}\)] | RED |
|-----------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|---------------------------------|-----|
| PVA             | 17.00                       | 9.00                        | 18.00                       | 26.34                       |                                 |     |
| methanol        | 15.10                       | 12.30                       | 22.30                       | 29.61                       | 6.62                            | 1.65|
| ethanol         | 15.80                       | 8.80                        | 19.40                       | 26.52                       | 2.79                            | 0.70|
| IPA             | 15.80                       | 6.10                        | 16.40                       | 23.58                       | 4.09                            | 1.02|
| water           | 15.50                       | 16.00                       | 42.40                       | 47.90                       | 25.56                           | 6.39|

\[
R_{a} = 4(d_{12} - d_{14})^2 + (d_{24} - d_{44})^2 + (d_{32} - d_{13})^2
\]

where \( d_{14} \) and \( d_{34} \) are the dispersion solubility parameter, polar solubility parameter, and hydrogen bond solubility.
respectively. Additionally, comparing the solubility parameter distance between the polymer and solvent with the radius of the solubility sphere of polymer \( R_p \), the result is the relative energy difference (RED), which indicates the affinity of the polymer toward the different solvents. The RED number is calculated by eq 2. Where the RED number lower than 1 indicates high affinity and higher than 1 is the low affinity of the polymer toward the solvent, the 0 RED number is found for no different energy case.

\[
\text{RED} = \frac{R_a}{R_p}
\]

(2)

where \( R_a \) is the radius of the interaction sphere in the Hansen space or interaction radius, and its value is 4 for PVA.46 The data in Table 3 demonstrate that the affinity of the PVA toward ethanol is the highest, followed by isopropanol and methanol. However, isopropanol and methanol are not solvents for PVA, but the RED values are close to 1, which indicates that the solvent could cause swelling for the PVA, and the degree of swelling is decreased with a higher RED number far away from 1.47,48

The hydrophilicity of the surface of all the membranes is elaborated by using the sessile drop method for contact angle measurements. The results in Table 4 show that the water contact angle decreases with increasing the Laponite concentration. The reason could be the hydrophilic nature of the nanoclay surface.28 Consequently, the water permeability through the membrane will be improved because of the increase of hydrophilicity. The contact angle measurements for the PVA0 membrane have a higher error than those of the others because it swells quickly within less than a minute.

Additionally, Table 4 shows that the density of the membrane increased by both thermally cross-linking of PVA and the incorporation of the Laponite nanofiller leading to formation a more compact membrane structure compared to PVA0 and PVA.49

| membrane   | contact angle (deg) | density (g/cm³) |
|------------|---------------------|-----------------|
| PVA0       |                     | 0.835 ± 0.24    |
| PVA        | 54.58 ± 1.26        | 1.245 ± 0.21    |
| PVA-1      | 42.57 ± 1.66        | 1.205 ± 0.22    |
| PVA-2.5    | 39.17 ± 1.39        | 1.313 ± 0.23    |
| PVA-3.5    | 37.06 ± 2.01        | 1.705 ± 0.29    |
| PVA-5      | 32.72 ± 1.62        | 1.905 ± 1.35    |

2.4. PV Dehydration of Alcohol Solutions. 2.4.1. Effect of the Laponite Concentration on Dehydration Performances of C1–C3 Alcohol Solutions. Hence, the pristine PVA membrane swells quickly; therefore, all the PV tests are done using the thermally cross-linking membrane PVA as 0% clay. The performance of dehydration separation of 85 wt % methanol, ethanol, and isopropanol solutions at 40 °C as a function of the nanoclay concentration in the casting solution have been investigated and presented in Figure 5a–c, respectively. Both the permeation flux and the separation factor of all alcohol solutions follow a similar trend. Both separation factor and permeation flux increase with increasing the Laponite concentration in the casting solution. The increment of the flux could be attributed to the increase of the hydrophilicity of the membrane because of the incorporation of the hydrophilic Laponite clay. While the increase in the separation factor is due to (1) the decrease in the free volume in the polymer matrix upon the Laponite loading and (2) the lower diffusivity of the solvent in the membrane compared to water diffusivity. However, the flux is rather constant then slightly decreases with the further addition of Laponite at 5 mg/mL. The reason for that could be the agglomeration of the nanoclay and the formation of the nanoclay layer between the polymer matrix as reported.32,33 Additionally, as the PALS analysis showed, increasing the Laponite concentration results in the decrease of the FFV in the membrane. The same reason results in increasing the separation factor significantly after increasing the Laponite content in the beginning solution as the Laponite separated layer works as an additional filter inside the polymer matrix.

2.4.2. Effect of Operating Temperature on Methanol PV Performance. Although the membrane material and characterization are the most crucial factors in the PV process. Nevertheless, the operating temperature could be considered as a predominant feature in the PV process.50 Hence, changing the temperature can directly affect the driving force, the permeation flux, water permeability, and diffusivity through the membrane. The influence of operating temperature and concentration of Laponite in the casting solution on methanol dehydration performance is investigated and shown in Figure 6. Additionally, it can be seen that changing the temperature...
fugacity as a function of temperature are observed and separation factor, selectivity, and methanol permeability). Such as activity coefficients (continuous line, dotted line, separation factor, selectivity, and methanol permeability). Figure 6. Methanol dehydration performance of the PVA membrane and MMMs with different Laponite concentrations, as function of temperature vs (A) total flux and separation factor, (B) total permeability and selectivity, and (C) water and ethanol permeability (continuous line, flux, permeability, and water permeability; dotted line, separation factor, selectivity, and methanol permeability).

has a considerable impact on solvent and water vapor pressures, which also affects the thermodynamic properties of the feed. The thermodynamic properties of the feed mixture such as activity coefficients $\gamma_i$, saturation pressures $P_i^\text{sat}$, and fugacity as a function of temperature are observed and presented in Table 5.

Table 5. Effect of Operating Temperature on Thermodynamic Properties of the Feed Mixture

| $T$ (°C) | $\gamma_{\text{MeOH}}$ | $\gamma_{\text{water}}$ | $P_i^\text{sat}$ (kPa) | $P_i^\text{MeOH}$ (kPa) | MeOH fugacity (kPa) | water fugacity (kPa) |
|---------|----------------|----------------|----------------|----------------|----------------|----------------|
| 40      | 1.060          | 1.557          | 35.413          | 7.409          | 28.569         | 2.754          |
| 50      | 1.059          | 1.530          | 55.624          | 12.382         | 44.835         | 4.524          |
| 60      | 1.058          | 1.504          | 84.701          | 19.979         | 68.210         | 7.176          |
| 70      | 1.057          | 1.479          | 125.425         | 31.228         | 100.911        | 11.030         |

Generally, the Laponite–PVA MMMs show enhanced performance for both the permeation flux and separation factor. From Figure 6A, for all the membranes, the flux shows an increasing behavior with a higher operating temperature, while the separation factor shows a slight decreasing tendency. Additionally, the flux values varied remarkably with increasing the temperature, while the separation factor shows a slight contraction even at elevated temperatures. The flux accretion could be assigned to (1) the increase in the methanol/water feed solution fugacity, as shown in Table 5, and (2) increasing the temperature led to increasing the free volume in the polymer chain mobility resulting in the increased permeation flux. Meanwhile, the separation factor shows counteractive behavior. However, all the membrane separation factor values are nearly close at all the temperatures, yet as discussed in the previous section, the highest separation factor and flux is achieved when the MMM contains 5.0 and 3.5 mg/mL of Laponite in the casting solution, respectively.

Alternatively, the intrinsic properties of the membranes are estimated such as permeability ($P$) and selectivity ($\alpha$) for the feed component with respect to the operating temperature to demonstrate the PV performance of the MMMs, and the results are shown in Figure 6B,C. Distinctly, the intrinsic properties ($P$ & $\alpha$) have the same tendency as the flux and separation factor when increasing the Laponite content in the casting solution. Clearly, both $P$ and $\alpha$ follow an increasing trend with increasing the Laponite in the MMMs. Moreover, the selectivity of all membranes has the same decreasing behavior as the separation factor with an increase of the operating temperature. On the contrary to the flux trend, the total permeability follows a downward trend at elevated temperatures.

Based on the solution—diffusion theory, at higher temperatures, the diffusivity of the membranes increases while the solubility decreases. However, as the PVA–Laponite MMMs have a more compact and denser structure, the membranes swell barely at elevated temperatures, which led to decreasing the diffusivity of the membranes. Furthermore, increasing the inter- and intramolecular hydrogen bonds between the PVA chain and the Laponite nanoclay at higher temperatures could result in decreasing the diffusivity of the feed solution in the MMMs. Consequently, both the solubility and diffusivity of the membranes curtailed, which results in the decreasing trend of the total permeability at higher temperatures. Figure 6C shows the membrane swelling and selectivity, clearly demonstrates that the individual permeabilities of methanol and water are following the same order as the total permeability. As shown, the water permeability is 100-fold higher compared to the methanol. Additionally, the water permeability almost coincides with the total permeability of all the membranes at all temperatures, whereas, methanol permeability is negligible, yet it augments trivially with the increasing the Laponite concentration up to 3.5 mg/mL, and then decreases dramatically when the Laponite reaches 5 mg/mL. This is attributed to the decrease in the free volume with a higher Laponite concentration besides diminishing the free volume of the MMMs because of performing the nanoclay as a cross-linker, which allows only smaller molecules like water to pass through the membrane. This manifests that the membrane has a higher affinity toward water.

Hence, it was proved that the temperature has a significant influence on the dehydration performance of the MMMs. Further understanding is generally expressed by Arrhenius equations (eq 3)

$$J = J_0 \exp \left( -\frac{E_f}{RT} \right)$$

(3)

where, $J$ is the flux of the membranes, $J_0$ is the pre-exponential factor, $E_f$ is the apparent activation energy (kJ/mol), $R$ is the gas constant (kJ/mol-K), and $T$ is the temperature (K). A typical agreement with the model has been recognized for all the membranes. The apparent activation energies for thermally cross-linked PVA membrane MMMs with different nanoclay concentrations are calculated from the slope of the Arrhenius
of the nano membrane, and the amalgamation of the appropriate amount of water molecules require less energy for penetrating through the membrane. This indicates that the membrane and ease the permeation again. Furthermore, the separated layer of the nanodiscs helped to free more volume in permeation through the membranes. Afterward, forming a small agglomeration, which hinders water permeation through the membrane and as a consequence more energy is required. Therefore, increasing the Laponite concentration in the casting solution dramatically upon the addition of Laponite from 12.37 to 9.65 and then increases to 13.53 kJ/mol when 2.5 mg/mL is added. This is due to the excellent dispersion of the Laponite nanodiscs at the low concentration, while the nanoclays start to form a small agglomeration, which hinders water permeation through the membrane and as a consequence more energy is needed. Therefore, increasing the Laponite concentration to 3.5 mg/mL led to the reduction of both water and methanol permeation through the membranes. Afterward, forming a separated layer of the nanodiscs helped to free more volume in the membrane and ease the permeation again. Furthermore, one could recognize that all the activation energy values for water are lower than that for methanol. This indicates that water molecules require less energy for penetrating through the membrane, and the amalgamation of the appropriate amount of the nanofiller enhances the permeability of water across the membrane.

### Table 6. Activation Energies (kJ/mol) of Permeation Flux for Thermally Cross-Linked PVA Membrane and Laponite-Loaded PVA MMMs

| membrane | $E_J$ | $E_{jw}$ | $E_{jp}$ |
|----------|-------|----------|---------|
| PVA      | 18.32 | 12.37    | 22.48   |
| PVA-1    | 16.82 | 9.65     | 21.90   |
| PVA-2.5  | 15.46 | 13.53    | 17.23   |
| PVA-3.5  | 19.28 | 18.33    | 20.34   |
| PVA-5    | 16.82 | 15.50    | 20.81   |

required for each feed component to permeate through the membrane. The lower the energy required, the easier the permeation is.

In Table 6, obviously, the oscillation in the activation energies between the PVA membrane and the MMMs can be seen that is, the total activation energy decreases with increasing the Laponite concentration in the casting solution up to 2.5 mg/mL, which could be attributed to the hydrophilic behavior of the nanoclay which eases the permeation of both feed components (water and methanol) through the membrane; while, the water activation energy decreases dramatically upon the addition of Laponite from 12.37 to 9.65 and then increases to 13.53 kJ/mol when 2.5 mg/mL is added. This is due to the excellent dispersion of the Laponite nanodiscs at the low concentration, while the nanoclays start to form a small agglomeration, which hinders water permeation through the membrane and as a consequence more energy is needed. Therefore, increasing the Laponite concentration to 3.5 mg/mL led to the reduction of both water and methanol permeation through the membranes. Afterward, forming a separated layer of the nanodiscs helped to free more volume in the membrane and ease the permeation again. Furthermore, one could recognize that all the activation energy values for water are lower than that for methanol. This indicates that water molecules require less energy for penetrating through the membrane, and the amalgamation of the appropriate amount of the nanofiller enhances the permeability of water across the membrane.

#### 2.4.3. Comparison of Dehydration Performance for Methanol, Ethanol, and Isopropanol

Figure 7a shows the fluxes and the water concentration in the permeate versus carbon number in alcohols for the binary system with water. While the overall performance of the PV dehydration processes (PV separation index) is displayed in Figure 6b. The permeate water concentration follows the size exclusion theory; isopropanol has the highest separation factor followed by ethanol and ended by methanol. This is due to the fact that isopropanol has the biggest size and the most nonlinear structure, so it is the easiest to separate. However, the flux values do not follow the same order. The flux of the isopropanol system is a bit higher than the ethanol system, this is due to the significant increase in the separation factor for the isopropanol system, which is accompanied by an increase in the water flux resulting in the increase in the total flux of the isopropanol-water system compared to the ethanol–water system flux. Additionally, ethanol tends to form a cluster with the water molecules, which has a bigger molecular size and, therefore, reduces the flux a bit compared to isopropanol. The fluxes for the 5 mg/mL Laponite loading follows the size order, and this is due to the decrease in the free volume of the membranes. Therefore, all three alcohol-water systems have lower fluxes and higher separation factors. From Figure 6B, it could be recognized that PVA-5 has the best performance for alcohol dehydration, and its performance is improved with a higher number of carbon atoms in the alcohol compound.

#### 2.5. Comparison of PV Performance with Different Membranes

With the aim of clarification, the PV performance of the PVA–Laponite MMMs are compared with other PV membranes Tables 7–9 present a benchmarking of the PVA-2.5, PVA-3.5, and PVA-5 MMMs for methanol, ethanol, and isopropanol dehydration, respectively. The fabricated MMMs with different Laponite concentrations in this work display not only outstanding fluxes and water permeability, which are much higher than most of the other PV membranes, but also have comparable separation factors and selectivities. More specifically, compared to the PVA membrane, PVA-5 exhibits the highest performance and could be promising for the industrial scale.

Until now, using polymeric PV membranes for methanol dehydration has not been widely studied because of the lack of a suitable membrane material, which combines good economic availability and antiswellling toward methanol. However, in this work, we demonstrate that PVA-5 shows the highest fluxes and water permeabilities of 314 g/m²·h and 2.82 mg/m²·h·kPa, as well as comparable selectivity and separation factors for methanol dehydration. Moreover, for ethanol dehydration performance PVA-5 disclosed exceptional flux, separation factor, and water permeability of 301.2 g/m²·h, 347.3, and 2.08 mg/m²·h·kPa respectively, in addition to the high comparable value of selectivity of 185, which is higher than most of the others except the H-PESU membrane. On the other hand, for isopropanol dehydration, PVA-3.5 shows the highest water permeability of 1.6 mg/m²·h·kPa, while the highest selectivity of 208 is achieved by the PVA-5 membrane. Comparing PVA-5 for isopropanol dehydration performance with other membranes shows that it has the highest water permeability through the membrane and a selectivity higher than most of those reported in other published works except polyimide/UiO-6 MMM.

### 3. CONCLUSIONS

In this work, MMMs were produced and tested for the pervaporative separation of alcohol-water mixtures. The MMMs consist of Laponite nanoclay as a nanofiller and PVA as the polymer chain has been fabricated. The PV dehydration performance of the developed MMMs shows a promising...
Table 7. Comparison of PV Performance for 85% Methanol Dehydration

| membrane | δ (μm) | T (°C) | flux (g/m²·h) | separation factor (β) | water permeability (mg/m·h·kPa) | selectivity (α) | refs |
|----------|--------|--------|---------------|-----------------------|-------------------------------|----------------|------|
| polyimide/UiO66-NH₂ (10%) | 34 | 60 | ~176.5 | 13.22 | 0.413 | 24.20 | 57 |
| 5%-µPPSU | 16 | 60 | 33.03 | 11.1 | 0.033 | 19.01 | 54 |
| PPSU | 23 | 60 | ~49.3 | 28.7 | 0.089 | 46.12 | 56 |
| H-PESU | 36 | 60 | ~59.3 | 31.3 | 0.171 | 50.45 | 56 |
| PVA-2.5 | 25–45 | 40 | 290.5 | 5.5 | 1.63 | 10.68 | this study |
| PVA-3.5 | 25–45 | 40 | 341.7 | 6.5 | 2.09 | 12.63 | |
| PVA-5 | 25–45 | 40 | 314.3 | 18.88 | 2.82 | 37.62 | |

(5) The MMMs of all concentrations exhibit higher PV performance for the dehydration of C1–C3 alcohols compared to the thermally cross-linked PVA membranes. PVA-5 discloses the highest separation factor for alcohol separation with an order of isopropanol > ethanol > methanol/water, while the higher fluxes achieved by PVA-3.5 comply with the reverse order.

As a summary, our development with the production of MMMs guarantees a significant step forward toward the development of the dehydration of the problematic C1–C3 alcohols with PV. The new MMMs may find interest in industrial applications.

4. EXPERIMENTAL SECTION

4.1. Materials. PVA (85,000–124,000 g/mol, 99%+ hydrolyzed) is purchased from Sigma-Aldrich Chemie GmbH. (Schnelldorf, Germany). Laponite XLG (ρ = 2.53 g/cm³, CEC = 0.55 mequiv/g, d = 25–30 nm, h = 0.92 nm) is purchased from Byk Additives and Instruments (Wesel-Germany). Ethanol (EtOH), methanol (MeOH), and isopropanol (IPA) absolute alcohols are provided by VWR Chemicals (Budapest, Hungary). All chemicals are used as such without further purification.

4.2. Membrane Fabrication. The flat, dense MMMs are prepared using the solution casting method followed by the solvent evaporation phase inversion method. The 5% wt PVA solution is first prepared by dissolving a certain amount of the PVA powder in DI water (18 MΩ cm) at 90 °C under vigorous stirring. In parallel, a certain amount of Laponite
nanoclay is sonicated in DI water for 3 h in order to form a clear dispersion. After that, the two solutions are mixed for 24 h using a magnetic stirrer. The final casting solutions have nanoclay concentrations of 0, 1.0, 2.5, 3.5, and 5.0 mg/mL. After pouring a certain amount of the solutions, all of the membranes are totally dried at room temperature for 48 h. The final dry membranes are picked up and named PVA0, PVA-1, PVA-2.5, PVA-3.5, and PVA-5 respective to the above-mentioned nanoclay concentrations. For better performance, the only pristine membrane is thermally cross-linked at 60 °C for 3 h, and the PVA membrane was designed.

4.3. Membrane Characterization. 4.3.1. Thermogravimetric Analysis. Perkin Elmer TGA-6 is used to analyze the thermal properties and degradation temperatures of the nanoclay and all of the MMMs. The temperature range is set between 35 and 700 °C with a heating rate of 10 °C/min⁻¹. The weight of all the samples is varied from 10–13 mg. The thermal degradation process is performed under a nitrogen atmosphere.

4.3.2. Contact Angle. KRÜSS, DSA 30, is assigned for measuring the contact angle of all the samples at room temperature. A drop of deionized water is placed onto the membrane, and immediately the contact angle is measured. For all the samples, five points are measured, and their average is used.

4.3.3. Density. The densities of pristine cross-linked and uncross-linked membranes, as well as MMMs with different nanoclay loadings, are estimated by a weight measurement method using an analytical balance and Pycnometer. The membrane density is measured at least three times for each type of sample, and the average values are obtained. Subsequently, the membrane density is calculated by eq 4:

\[
ρ_{\text{m}} = \frac{(M_pM_m)}{V(M_p + M_s + M_m - M_i)} \tag{4}
\]

In this method, a pycnometer with well-known volume \( V \) (mL) and weight of \( M_p \) (g) is used, then the pycnometer is filled with the solvent, and the weight of the solvent is \( M_s \) (g). After the pycnometer is emptied, cleaned, and dried, the sample with a weight of \( M_m \) is placed in it then filled with the solvent and the total weight of the pycnometer, solvent, and membrane of weight \( M_i \) (g) is measured.

4.3.4. Morphology. Laponite nanodiscs have been analyzed using a JEOL JSM-6380 scanning electron microscope and FEI Morgagni-268D transmission electron microscope FEI Inspect S50 is used to determine the surface morphology of the pristine membrane as well as the MMM. Prior to the analysis, all SEM samples had been sputter-coated with gold with 35 mA sputter current for 1:30 s, and all the images are secondary electron micrographs created by an Evenhart–Thornley detector.

4.3.5. Chemical Interaction. A FT-IR spectroscopy (ATR mode of FT-IR, BRUKER Tensor-37) is utilized to analyze the chemical linking of the powder Laponite, PVA membrane, and MMMs in the range of 500–4000 cm⁻¹.

4.4. Positron Annihilation Lifetime Spectroscopy. Positron annihilation lifetime of all the membranes is determined using a fast–fast coincidence system based on BaF₂/XP2020Q detectors and Ortec electronics. The positron source is \(^{22}\text{Na}\), carrier-free, and the sample is kept between two Kapton foils with a thickness of 2 mg/cm². The activity of the source is around \( 5 \times 10^3 \) Bq. Each spectrum contained approximately 2 million counts, and every spectrum is recorded in 4096 channels of an analyzer card, and each contained 105 coincidence events. The spectra are evaluated into 3-lifetime components (\( \tau_1, \tau_2 \), and \( \tau_3 \)). Hence, \( \tau_1 \) is the most extended lifetime, it is used along with its intensity \( I_1 \). The mean free volume radius \( R \) (Å) is estimated from the following empirical equation: \(^{60,61}\) (eq 5)

\[
τ_1^{-1} = 2 \left[ 1 - \frac{R}{R + \Delta R} + \frac{1}{2π} \sin \left( \frac{2πR}{R + \Delta R} \right) \right] \tag{5}
\]

where \( \Delta R \) is the thickness of the electron layer, and it is constant of 1.66 Å. Additionally, the FFV is estimated from the values of \( R \) and \( \sigma\)-Ps intensity, \( I_3 \) (%), using an empirical formula: \(^{60,61}\) as follows (eq 6)

\[
\text{FFV} = \frac{4π}{3} \times 10^3 R^2 I_3 \tag{6}
\]

4.5. Solvent Uptake. In order to measure the sorption capacity of the MMMs toward the different organic solvents, solvent uptake measurements are done in different absolute alcoholic solutions at room temperature and pure water. The circularly cut MMMs are totally dried in an oven overnight before starting the experiments to make sure that all the absorbed moisture is removed. Thereafter, the weighted MMMs are immersed in water, methanol, ethanol, and isopropanol. Subsequently, the membranes are taken out, and with the aid of filter paper, all the surface solution is completely removed, and then it is weighed and immediately returned to the solutions. This process has been repeated at different time intervals until no vital difference in the weight can be recognized, which means the MMMs had sorption equilibrium. The membrane solvent uptake is elaborated as the ratio between the amounts of the solvent and the dry membrane, where the amount of the solvent is the weight difference between swollen (\( M_s \)) and dry (\( M_d \)) membranes using the following equation (eq 7)

\[
\text{solute uptake} = \frac{M_s - M_d}{M_d} \tag{7}
\]

4.6. PV Tests. All the PV experiments are performed using a multifunction lab-scale P-28 apparatus supplied by CM—Celfa Membranetechnik AG, as shown in Figure 1 and described elsewhere. \(^{62}\) The membrane with a 28 cm² effective area is kept secure on a sintered disc, which works as a mechanical support in the membrane cell. Alcohol/water mixture (500 mL, 85/15 wt %) is loaded in a double jacketed feed tank stirred and circulated through the system by a flow rate of ~3 L/min to diminish the concentration and temperature polarization.

The downstream side is maintained at a low pressure of 2 Torr (0.27 kPa) by applying a vacuum to ensure that the required driving force is achieved across the membrane. On the permeate side, a liquid nitrogen cold trap is used to collect the condensed vapor in the liquid form. Before conducting experiments, the membrane is swollen in the feed solution for an hour. Additionally, the circulation system is turned on until reaching the required temperature and stabilized for another hour to ensure the constant condition prior to sample collection. The temperature is maintained by a water thermostat and checked using a thermometer on the inlet and outlet of the apparatus. The permeate samples are analyzed when collecting enough condensate after condition-
ing the membrane for at least 2 h. The concentration of the feed and permeate is measured by the RA-620 (accuracy ±0.00002, KEM Kyoto Electronics, Japan) refractometer.

All experiments are repeated three times to ensure reproducibility. To evaluate the PV performance, total flux ($J$) and separation factor ($\beta$) are employed. The flux, $J$ (g/m²·h), depended on the permeate weight, $W$ (g), effective area of the membrane, $A$ (m²), and experiment duration, $t$ (h), and is obtained using eq 8.

$$J = \frac{W}{A \times t} \tag{8}$$

The separation factor ($\beta$) is calculated using eq 9.

$$\beta_{ij} = \frac{X_i/Y_i}{X_j/Y_j} \tag{9}$$

where $Y_i$ and $X_i$ are permeate and feed mass fractions of component $i$, while $i$ and $j$ refer to water and alcohol, respectively. The PV overall separation index is expressed by eq 10.

$$\text{PSI} = J(\beta - 1) \tag{10}$$

For evaluating the intrinsic properties of the MMs, both water and alcohol permeabilities are calculated using the following equation (eq 11):

$$P_i = \frac{J_i \delta}{(x_iP_i^{\text{sat}} - x_iP_i)} \tag{11}$$

where $P_i$ (g/(m²·h·kPa)) represents component $i$ permeability, $\delta$ (m) is the thickness of the membrane, $J_i$ (g/m²·h) is the individual flux, $x_i$ is the activity coefficient, $P_i^{\text{sat}}$ (kPa) is the saturated vapor pressure, $x$ and $y$ are the mole fractions in the feed and permeate sides, respectively. $P_i$ (kPa) represents the downstream pressure. The activity coefficients are calculated using the Wilson equation, while the $P_i^{\text{sat}}$ is calculated from the Antoine equation, using ChemCAD software. The selectivity ($\alpha_{ij}$) is calculated from the ratio between $i$ and $j$ permeability (eq 12), where $i$ and $j$ are the water and alcohol, respectively.

$$\alpha_{ij} = \frac{P_i}{P_j} \tag{12}$$

## AUTHOR INFORMATION

### Corresponding Author

Peter Mizsey — Environmental and Process Engineering Research Group, Department of Chemical and Environmental Process Engineering, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, H-1521 Budapest, Hungary; Institute of Chemistry, University of Miskolc, H-351S Miskolc, Hungary; orcid.org/0000-0002-6976-6210; Email: mizsey@mail.bme.hu

### Authors

Asmaa Selim — Environmental and Process Engineering Research Group, Department of Chemical and Environmental Process Engineering, Faculty of Chemical Technology and Biotechnology, Budapest University of Technology and Economics, H-1521 Budapest, Hungary; Chemical Engineering Department, National Research Centre, 12622 Cairo, Egypt; orcid.org/0000-0001-9012-0038

### References

(1) Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Lieto, C. L.; Mielcz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The path forward for biofuels and biomaterials. J. Membr. Sci. 2013, 444, 285–317.

(2) Balat, M.; Balat, H. Recent trends in global production and utilization of bio-ethanol fuel. Appl. Energy 2009, 86, 2273–2282.

(3) Bahaj, A.; Karalis, G.; Tascioglu, C. The thermodynamic support. J. Membr. Sci. 2013, 444, 285–317.

(4) Suhas, D. P.; Aminabhavi, T. M.; Jeong, H. M.; Raghu, A. V. Hydrogen peroxide treated graphene as an effective nanoassert filter for separation application. RSC Adv. 2015, 5, 100984–100995.

(5) Dharupadeedi, S. P.; Anjanapura, R. V.; Han, J. M.; Aminabhavi, T. M. Functionalized Graphene Sheets Embedded in Chitosan Nanocomposite Membranes for Ethanol and Isopropanol Dehydration via Pervaporation. Ind. Eng. Chem. Res. 2014, 53, 14474–14484.

(6) Jiang, L. Y.; Wang, Y.; Chiou, T.-S.; Qiao, X.-Y.; Lai, J.-Y. Polyimides membranes for pervaporation and biofuels separation. Prog. Polym. Sci. 2009, 34, 1135–1160.

(7) Feng, X.; Huang, R. Y. M. Liquid separation by membrane pervaporation. Ind. Eng. Chem. Res. 1997, 36, 1048–1066.

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04380

Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The first author is grateful to Dr. Hurtony Tamás for performing SEM analysis. This publication was supported by the Varga Jozsef Scholarship, the János Bolyai Research Scholarship of the Hungarian Academy of Sciences, UNKP-19-4-BME-416 New National Excellence Program of the Ministry for Innovation and Technology, OTKA 112699, 128543, and 131586. This research was also supported by the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, aimed to promote the cooperation between the higher education and the industry and the National Research, Development and Innovation Fund (TUDFO/51757/2019-ITM, Thematic Excellence Program).

[ACS Omega](http://pubs.acs.org/journal/acsofd)
Polym.-Plast. Technol. Eng. on the Pervaporation Performance of Crosslinked Poly (Vinyl Alcohol) (PVA) by activated natural clay clinoptilolite. J. Membr. Sci. 2005, 210, 123–132.

Valler, L. C. Membrane Systems for the Separation of Ethanol/Water (Azeotropic Mixture). J. Membr. Sci. 2015, 492, 162–173.

M.; Khorasani, S. N. Nanohybrid hydrogels of laponite: PVA-Alginate composite hydrogels at high clay concentrations. Mater. Sci. Eng., C 2015, 49, 1–7.

Wang, S.; Zheng, F.; Huang, Y.; Fang, Y.; Shen, M.; Zhu, M.; Shi, X. Encapsulation of amoxicillin within laponite-doped poly (lactic-co-glycolic acid) nanofibers: Preparation, characterization, and antibacterial activity. ACS Appl. Mater. Interfaces 2012, 4, 6395–6401.

Polotskaya, G.; Pulyalina, A.; Goikhman, M.; Podeshvo, I.; Polonskii, G.; Rostovtseva, V.; Shugurov, S.; Gulii, N.; Prokhorov, E.; Sanchez, I. C.; Luna-Bárcenas, J. G.; Manzano-Ramírez, A.; González-Hernández, J.; López-Castro, Y.; Río, R. E. d. Molecular Dynamics Analysis of PVA-AgNP Composites by Dielectric Spectroscopy. J. Nanomater. 2012, 2012, 925750.

Mansur, H. S.; Sadahira, C. M.; Souza, A. N.; Mansur, A. A. P. FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde. Mater. Sci. Eng., C 2008, 28, 539–548.

Hasimi, A.; Stavropoulou, A.; Papadokostaki, K. G.; Sanopoulou, M. Transport of water in polyvinyl alcohol films: Effect of thermal treatment and chemical crosslinking. Eur. Polym. J. 2008, 44, 4098–4107.

Gohil, J. M.; Bhattacharya, A.; Ray, P. Studies on the Cross-linking of Poly(Vinyl Alcohol). J. Polym. Res. 2006, 13, 161–169.

Karthekeyan, B. Spectroscopic studies on Ag-polyvinyl alcohol nanocomposite films. Physica B 2005, 364, 328–332.

Ghanipour, M.; Dorranian, D. Effect of Ag-Nanoparticles on the Structural and Optical Properties of PVA Films. J. Nanomater. 2013, 2013, 897043.

Dong, A. W.; Pascual-Izarra, J.; Prokhorov, E.; Sanchez, I. C.; Luna-Bárcenas, J. G.; Manzano-Ramírez, A.; González-Hernández, J.; López-Castro, Y.; Río, R. E. d. Molecular Dynamics Analysis of PVA-AgNP Composites by Dielectric Spectroscopy. J. Nanomater. 2012, 2012, 925750.
Loretsyan, N.; Toikka, A. Novel Polyheteroarylene Membranes for Separation of Methanol−Hexane Mixture by Pervaporation. Sci. Rep. 2018, 8, 17849−17861.

(50) Schaetzel, P.; Vauclair, C.; Nguyen, Q.; Bouzerar, R. A simplified solution − diffusion theory in pervaporation : the total solvent volume fraction model. J. Membr. Sci. 2004, 244, 117−127.

(51) Liang, B.; Zhan, W.; Qi, G.; Lin, S.; Nan, Q.; Liu, Y.; Cao, B.; Pan, K. High performance graphene oxide/polyacrylonitrile composites pervaporation membranes for desalination applications. J. Mater. Chem. A 2015, 3, 5140−5147.

(52) Nigiz, F. U.; Hilmioglu, N. D. Bentonite-loaded carboxy methylcellulose membrane for pervaporative desalination. Desalin. Water Treat. 2017, 92, 20−26.

(53) Liu, G.; Shen, J.; Liu, Q.; Liu, G.; Xiong, J.; Yang, J.; Jin, W. Ultrathin two-dimensional MXene membrane for pervaporation desalination: J. Membr. Sci. 2018, 548, 548−558.

(54) Tang, Y.; Widjojo, N.; Shi, G. M.; Chung, T.-S.; Weber, M.; Maletzko, C. Development of flat-sheet membranes for C1−C4 alcohols dehydration via pervaporation from sulfonated polyphenylsulfone(sPPSU). J. Membr. Sci. 2012, 415−416, 686−695.

(55) Jiang, L. Y.; Chung, T.-S.; Rajagopalan, R. Dehydration of alcohols by pervaporation through polyimide Matrimid® asymmetric hollow fibers with various modifications. Chem. Eng. Sci. 2008, 63, 204−216.

(56) Xu, Y. M.; Tang, Y. P.; Chung, T.-S.; Weber, M.; Maletzko, C. Polyarylether membranes for dehydration of ethanol and methanol via pervaporation. Sep. Purif. Technol. 2018, 193, 165−174.

(57) Xu, Y. M.; Japip, S.; Chung, T.-S. Mixed matrix membranes with nano-sized functional UiO-66-type MOFs embedded in 6FDA-HAB/DABA polyimide for dehydration of C1-C3 alcohols via pervaporation. J. Membr. Sci. 2018, 549, 217−226.

(58) Wang, Y.; Jiang, L.; Matsuura, T.; Chung, T. S.; Goh, S. H. Investigation of the fundamental differences between polyamide-imide (PAI) and polyetherimide (PEI) membranes for isopropanol dehydration via pervaporation. J. Membr. Sci. 2008, 318, 217−226.

(59) Xie, Z.; Hoang, M.; Ng, D.; Doherty, C.; Hill, A.; Gray, S. Effect of heat treatment on pervaporation separation of aqueous salt solution using hybrid PVA/MA/TEOS membrane. Sep. Purif. Technol. 2014, 127, 10−17.

(60) Peng, F.; Lu, L.; Hu, C.; Wu, H.; Jiang, Z. Significant increase of permeation flux and selectivity of poly(vinyl alcohol) membranes by incorporation of crystalline flake graphite. J. Membr. Sci. 2005, 259, 65−73.

(61) Selim, A.; Valentinyi, N.; Mizsey, P. Influence of double-network interpenetration on ethanol dehydration performance of PVA-based pervaporation membranes. Chem. Pap. 2019, 73, 1069−1081.