pH-Triggered Membrane in Pervaporation Process
Alessandro Angelini,† Csaba Fodor,† Wilfredo Yave,*‡ Luigi Leva,‡ Anja Car,‡ and Wolfgang Meier*‡

†Department of Chemistry, University of Basel, Mattenstrasse 24a, BPR1096, 4002 Basel, Basel-Stadt, Switzerland
‡DeltaMem AG, Rothausstrasse 61, 4132 Muttenz, Basel-Land, Switzerland

ABSTRACT: Dehydration of binary methyl acetate–water mixtures under neutral, acidic, and basic conditions was carried out by using PERVAP composite membranes based on polyvinyl alcohol and poly(1-vinylpyrrolidone-co-2-(dimethylamino)ethyl methacrylate) P(VP-co-DMAEMA). The effects of an acid (HCl) and a base (NaOH) on the separation performance of the membrane during the pervaporation process were investigated. The pH-responsive nature of membranes has been confirmed by swelling tests and analysis of the chemical structure of polymeric membranes. In addition, a mechanism of ring-opening of VP units is proposed and correlated to the changes of membrane separation performance.

INTRODUCTION

In the last decades, great attention has been dedicated to developing and scaling up novel and advanced membrane materials.1−12 However, only few polymers are used to produce membranes at large scale.3,4 Lack of understanding of material properties and its correlation with membrane behavior under real operating conditions are usually the reasons for failing.

One of those novel materials are the so-called stimuli-responsive polymers. Such polymers as membranes are also known as intelligent or smart membranes5,6 as they allow intelligent control of separation when the environment changes. Because they exhibit trigger behavior predictably to pH,8 temperature,9 different fields,10 or ionic strength,9 new applications can be developed based on these polymeric membranes. In fact, by introducing pH-responsive groups and controlling ionic strength, the membranes were able to release drugs,10 improve the separation performance in water treatment11 and perform as chemical sensor and flow regulator.12

The commonly available pH-responsive functional polymers are weak polyelectrolytes with carboxyl, pyridine, or amino groups.13−15 The presence of acidic groups in polymers (e.g. carboxyl groups, pyridine) at low pH induces the intermolecular hydrogen bonding formation, thus leading to shrinkage of the polymer chains. While at high pH, carboxyl groups dissociate into carboxylate ions, resulting in a high charge density, which trigger the swelling of the polymer. Polymers containing basic groups (e.g. amino groups) show opposite behavior compared to polyacids. At low pH, the amino group is protonated, and the material exhibits hydrophilic character and at high pH, hydrophobic properties are pronounced. As a result of protonation/deprotonation, swelling properties of these polymeric materials are changed.8

A typical polymer containing amino groups used to prepare stimuli-responsive membranes is poly(2-(dimethylamino)ethyl methacrylate) P(DMAEMA). The interesting feature of this polymer and derivatives (copolymers) is their pH- and temperature-responsive nature.16 These polymers were used as graft material in the membrane and as a blend with other polymers to obtain dual stimuli-responsive properties.17,18 P(DMAEMA) was also used as membrane material for gas separation,19−22 nanofiltration,23 and microfiltration.18,24 In addition, P(DMAEMA) copolymers were synthesized and investigated as micelles for drug delivery.15,25,26 Despite the overall high number of references discussing pervaporation membranes,27 up to date there are only few works about pH-triggered membranes for pervaporation and their behavior under variable and industrial separation conditions.28−30

In the present work, pervaporation membranes based on poly(1-vinylpyrrolidone-co-2-(dimethylamino)ethyl methacrylate) P(VP-co-DMAEMA) with pH-trigger behavior are investigated. These membranes are the commercial PERVAP membranes for alcohol removal from other solvents. Although these membranes are already applied for dehydration of various solvents and methanol removal from neutral mixtures,31,32 the feature as pH-responsive pervaporation membrane in acidic and basic mixtures has not been reported yet. In the industry, during the dehydration processes and methanol removal from other solvents, many mixtures have acidic and/or basic nature, depending on impurities present in the streams. Thus, understanding the membrane behavior under triggered conditions is extremely important for the
membrane process and scale up. In addition, the new insight into these membranes might extend their use to other applications.

**EXPERIMENTAL SECTION**

**Materials.** For the pervaporation tests, commercial pervaporation membranes PERVAP 4155-30 and PERVAP 4155-70 from DeltaMem AG, Switzerland were used. For the dense film preparation, the P(VP-co-DMAEMA) and polyvinyl alcohol (PVA) were supplied by DeltaMem AG. Polyvinylpyrrolidone (PVP) with average molecular weight of around 55 kDa, methyl acetate (MeAc, 99%) and sodium hydroxide (NaOH, 90%, flakes) were purchased from Sigma-Aldrich. P(DMAEMA) with a molecular weight of 98 kDa and hydrochloric acid (HCl, 37%) were obtained from Polymer Source Inc. and VWR, respectively. Deuterated chloroform (CDCl₃, D 99.8%) with 0.05 v/v % TMS was obtained from Cambridge Isotope Laboratories. Distilled water was used for the experiments, unless stated otherwise.

**Polymer Dense Film Preparation.** For copolymer characterization, freestanding dense films from P(VP-co-DMAEMA) were prepared in Teflon molds by solution casting (5.0 wt % aqueous solutions). The drying of the films was performed in two steps: first the solvent was slowly evaporated (two days) under atmospheric pressure at room temperature, and then, the drying is completed at 40 °C under vacuum (400 mbar) for one day. For the membrane characterization, free-standing dense films from PVA and P(VP-co-DMAEMA) were obtained by casting on Teflon sheets. Polymer solutions with the same composition as the commercial composite membranes (PERVAP 4155-30 and 4155-70) were used. The wet film thickness was adjusted with a knife blade to 500 μm. The procedure of drying and crosslinking is described elsewhere.

**Pervaporation Experiments.** The pervaporation tests were performed with binary MeAc/water mixtures, neutral and containing 2 mmol/L of HCl and 2 mmol/L of NaOH, respectively. The setup includes two pervaporation cells, which allows testing simultaneously two different types of membranes. The effective membrane area in each cell is 38 cm². The mixture is filled into a feed tank and recirculated by a pump with a feed flow parallel to the membrane surface. The feed goes to the membrane cells, and then, the product from the cells is returned to the feed tank as retentate. A heating system maintains constant the feed/retentate temperature at 85 °C. In the permeate side, a vacuum of 10 mbar is maintained by a vacuum pump. Permeate samples are collected in a cold trap with dry ice and ethanol mixture. For each measurement point, the amount of permeate, time, as well as the feed/retentate samples are collected.

**Instrumental Methods.** The chemical structure of the (co)polymer systems was confirmed by nuclear magnetic resonance spectroscopy (NMR). NMR spectra were obtained at room temperature by using a Bruker Ascend 500 spectrometer operated at 500 MHz for ¹H nucleus. Deuterated CDCl₃ was used as the solvent with a sample temperature of 298 K. Chemical shifts (δ) are reported in ppm, and chemical shifts are referenced with respect to residual solvent peaks and quoted with respect to TMS (δ 0.00). The collected spectra were analyzed using MestReNova (v12.0) (Mestrelab Research S.L.).

Background corrected attenuated total reflection–Fourier transform infrared spectroscopy (ATR–FTIR) spectra were recorded on a Bruker spectrophotometer in the range of 4000–400 cm⁻¹, using 128 scans at a nominal resolution of 4 cm⁻¹ using a diamond single reflection ATR. Atmospheric compensation and offset correction were applied on the collected spectra with the use of OPUS spectroscopy software (v7.0) (Bruker Optics).

The membrane swelling measurements were performed on free-standing dense films prepared in the laboratory. The solvent uptake ratios of the dense film were determined gravimetrically in water and MeAc/water mixtures, under neutral, acidic, and basic conditions, respectively. Dried films were used and placed in the selected solvent mixture at room temperature and then left to swell until constant weight. The samples were removed from the mixture between times, wiped with a filter paper and weighed, and placed back into the mixture until the equilibrium swelling ratios is obtained. Three parallel measurements were carried out for each sample and average values as well as standard deviation were calculated.

The wetting properties of membranes were investigated with static contact angle (CA) measurements performed with a CA goniometer, CAM 100 (LOT quantum design) based on a CDD camera with 50 mm optics. Droplets of ultrapure water were placed on the membrane substrates with a micro syringe, and the CA was automatically recorded and analyzed by the instrument software by fitting the curve with the Young–Laplace equation. The drop volume was kept constant for all measurements, each sample was measured 6 times, and average values as well as standard deviation were calculated.

During pervaporation tests, the water concentration in the feed/retentate samples was determined by coulometer Karl Fischer titration (737 KF Coulometer, Metrohm). The compositions of permeates were measured by using an Agilent 6890 gas chromatography equipped with a thermal conductivity detector and HP-PLOT Q column.

The scanning electron microscope (SEM) images of the membranes were processed and analyzed using a Hitachi S-4800 SEM (Hitachi High-Technologies Corporation, Japan) with a cold field-emission electron source. Electrically conducting surfaces were achieved by sputtering the surface with gold layer of 5 nm thickness.

**RESULTS AND DISCUSSION**

According to DeltaMem AG, the two tested membranes are fabricated from PVA and P(VP-co-DMAEMA). The copolymer content in PERVAP 4155-30 and PERVAP 4155-70 is 70 and 30 wt %, respectively. NMR and ATR–FTIR were performed to verify the molecular structure of used P(VP-co-DMAEMA). Homopolymers of PVP and P(DMAEMA) were also analyzed to correlate with the copolymer.

Figure 1 displays the ¹H NMR spectra, where the observed peaks fit to the expected chemical structure of the copolymers. The peaks also agree with those reported in the literature for similar copolymers. The characteristic peaks of the copolymer backbone related to the VP units appeared between 1.80 to 2.50 ppm and between 3.00 and 3.40 ppm. Peaks from the copolymer backbone related to the VP units appeared between 1.3 and 1.78 ppm, and between 3.00 and 3.40 ppm. Peaks from the DMAEMA units in the copolymer structure were placed on the membrane substrates with a micro syringe, and the CA was automatically recorded and analyzed by the instrument software by fitting the curve with the Young–Laplace equation. The drop volume was kept constant for all measurements, each sample was measured 6 times, and average values as well as standard deviation were calculated.

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The characteristic absorption bands of P(DMAEMA) homopolymer as well as the C–N stretching vibrations of the secondary amine functional group at 2773–2790 cm\(^{-1}\), and the stretching vibration of C=N bond at 1120–1170 cm\(^{-1}\), related to the DMAEMA content in the structure. The band around 1640 cm\(^{-1}\) arising from the C=O stretching vibration mode, the C=N stretching vibrations appear around 1410 cm\(^{-1}\) due to the VP units in the copolymer.

The membrane structure of PERVAP 4155-30 and PERVAP 4155-70 was analyzed by SEM, and the cross-section of the membranes is shown in Figure 3. The PVA and copolymer-based selective layer is at the upper part of membrane tightly adhered to the polyacrylonitrile porous support (bottom), and neither of the PERVAP 4155-30 and 4155-70 samples have voids, indicating a good compatibility between the porous support and the selective layer. In both cases, the membrane thickness is around 2 μm. These representative SEM images are tilted, and thus, in addition to the membrane cross-section, the surfaces of the composite membranes are also visible, which are uniform.

Unlike other reports on membranes with pH-responsive nature, where the membranes are first treated with acidic and basic aqueous solutions before testing, here the membranes are not pretreated and are continuously contacted by different mixtures. The pervaporation tests are performed by using MeAc/water mixtures containing HCl and NaOH, and in both cases, the concentration is controlled (2 mmol/L). We have controlled the HCl and NaOH concentration because the pH measurement in organic mixtures is not reliable due to the unstable readings, long response time, measurement errors, and because pH is a measure of H\(^+\) concentration in aqueous solutions.

The pervaporation operating conditions were identical for all tests, that is neutral, acidic, and basic condition. Therefore, the comparison of flux and permeate concentration as separation performance data is possible. Two set of pervaporation tests were performed. On one hand, for each mixture and for each test, a new membrane sample was used. On the other hand, the same membrane was tested in all conditions to see the reversibility of separation performance. The order of tests was as follows: neutral, acidic, neutral, basic, and neutral.

The water flux and permeate concentration as a function of feed water concentration for both membranes are shown in Figure 4. The permeate concentration values (red circle data) for PERVAP 4155-30 (Figure 4a) are slightly lower than those for PERVAP 4155-70 (Figure 4b). These results are expected due to the cross-linking degree of the membranes. PERVAP 4155-30 has 70 wt % of copolymer and 30 wt % of PVA, and because of PVA content in the membrane, this membrane is less cross-linked than PERVAP 4155-70. The content of PVA in the polymer matrix is directly correlated with the degree of cross-linking, that is, the higher the PVA content in the membrane, the higher the cross-linking degree (information received from DeltaMem AG). Because PERVAP 4155-30 is less cross-linked than PERVAP 4155-70, it swells more (see Figure 5) and presents slightly lower values of water permeate concentration.

The permeate concentration values in PERVAP 4155-70 are not dependent on feed nature (acidic, neutral or basic). While for PERVAP 4155-30 in acidic condition, they are shifted to

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**Figure 1.** Phase and baseline-corrected \(^1\)H NMR spectra of the neat polymers (P(DMAEMA) and PVP) and the P(VP-co-DMAEMA) copolymer (solvent: CDCl\(_3\), temperature: RT, number of transients (\(n\)): 256 and relaxation time (\(t\)): 1.5).

**Figure 2.** ATR–FTIR spectra of both homopolymers and P(VP-co-DMAEMA) copolymer, depicted in Figure 2, were found to be consistent with the corresponding macromolecular structures. The absorption bands at 1465 and 1425 cm\(^{-1}\) are characteristic absorptions of the pyrrolidinyl group, and the bands at 1654 and 1024 cm\(^{-1}\) are attributed to the carbonyl group as well as the C=N stretching vibrations in PVP. The characteristic absorption bands of P(DMAEMA) homopolymer can be assigned to the C=O stretching vibration at 1730 cm\(^{-1}\), (C=\((-\text{N(CH}_3)_2\)) stretching vibrations between 2770–2940 cm\(^{-1}\) as well as the N(CH\(_3\))\(_2\) deformational stretching vibrations around 1459 cm\(^{-1}\).
higher values (Figure 4a). The water permeate concentration increase in this membrane is due to the presence of the pH-responsive copolymer and its high content; hence, under acidic condition, this membrane swells less and is more hydrophilic (discussed later), and thus, the selectivity of the membrane is improved.

Pervaporation tests performed with neutral mixture show that PERVAP 4155-30 exhibits higher water flux than PERVAP 4155-70 (compare open red circle in Figure 4a,b). This difference is also explained by the content of PVA in the membrane (cross-linking degree and swelling of membrane, described above). As PERVAP 4155-30 has 70 wt % of copolymer, the shifting of water flux to lower values is more pronounced than that in PERVAP 4155-70, when the pervaporation tests are performed in acidic conditions (compare the red and black experimental points). The decrease of water flux and the increase of permeate concentration are interesting results, and they are attributed to the DMAEMA units in the copolymer. As described above, the P(DMAEMA) is a pH-responsive polymer, and thus, this segment of copolymer is protonated in acidic mixture. Because of amine protonation and the presence of PVA (containing −OH) and Cl− ions (from HCl), the free movement of copolymer segment containing the protonated amine is slowed down, and the material as such does not swell or slightly shrinks (PERVAP 4155-30, Figure 5). This makes the material less flexible and decreases the fractional free volume of polymer that results in a water flux decrease through the membrane and selectivity improvement.

Under basic conditions, the pervaporation tests gave even more interesting results. At the beginning, at higher water concentration in the mixture, the water flux is higher than in the neutral condition (see the open green triangle at >2.5 wt % of water in feed, Figure 4). After the mixture is dehydrated, the water flux drops to lower values like in acidic conditions. These results can be partially explained by the decreased swelling of the membrane (Figure 5) and by the hydrophilic nature of the material under basic conditions (Figure 6). High water content in the mixture under basic conditions and the hydrophilic nature of material seem to increase the swelling of the membrane. However, it happens only at the beginning of tests. Later, once the MeAc is dehydrated, a pronounced decrease of flux is observed. This behavior can be explained by the gradual deprotonation of amine groups and simultaneous hydrogen bonding between deprotonated amine and OH− groups present in PVA. At the end, the material (membrane) becomes less swollen because of the lower water content in the mixture, the membrane shrinks, and consequently the water flux drops. Because of a complex mechanism of deprotonation and formation of hydrogen bonds, the PVP segment present in the copolymer may also play a certain role on water flux decrease.

As discussed above, the swelling and hydrophilicity of the selective layer play important roles in the pervaporation
The degree of swelling of the membranes depends on the composition and the structure of the polymer matrix. Thus, PERVAP 4155-30 and 4155-70 should exhibit different behavior in terms of swelling. This investigation is carried out by using dense films in pure water and mixtures used for pervaporation tests, that is, binary mixtures of MeAc and water in neutral, acidic, and basic conditions.

The swelling degree of these films is presented in Figure 5. In general, it is observed that the degree of swelling of PERVAP 4155-30 is higher than PERVAP 4155-70. This is due to the cross-linking degree of the membrane (less content of PVA means less degree of cross-linking) and hydrophilic nature of the copolymer. The swelling of films in binary (MeAc/water) mixtures is less than that in water, and this can be explained by the wettability properties of polymer system itself. In mixtures containing acid, the swelling of membrane PERVAP 4155-30 decreases compared to neutral mixtures. Thus, this result agrees with the water flux decrease. However, PERVAP 4155-70 does not show remarkable changes in swelling degree between tests in water, neutral and acidic mixture. This result may be due to the high content of PVA in the membrane (high degree of cross-linking).

In basic conditions, both types of membranes do not swell at all (Figure 5). This observation supports the pervaporation results well (Figure 4), where a decrease of water flux is observed once the MeAc is dehydrated.

The hydrophilicity of the PERVAP 4155 membrane surface with different PVA content was studied by static CA with water as a probe liquid. As shown in Figure 6, the CA of the liquid decreased with increasing PVA content in the membrane. This means that the PERVAP 4155-70 is more hydrophilic than PERVAP 4155-30 because of more hydroxyl group in the membrane (higher PVA content) as well as because of the slightly different roughness of membrane surface, derived from the different composition. In other words, higher PVA content in the membrane produces a smoother, continuous hydrophilic surface.

PERVAP 4155-30 samples exhibit slightly different CA when they are treated with different liquid mixtures. In basic conditions, this membrane becomes more hydrophilic, while PERVAP 4155-70 does not show notable changes.

It should be noted that during the pervaporation tests at different conditions (basic and acidic) random ring-opening of the pyrrolidone ring in the copolymer may occur, which can facilitate the polymer chain reconfiguration and constructs hydrogen bonding with the DMAEMA units in the polymer system. The presence of opened ring VP units were analyzed by ATR−FTIR and confirmed by the appearance of the characteristic band at around 1732 cm$^{-1}$, corresponding to the carboxyl acid group in the ring-opened VP. To prove the structural rearrangement and the ring-opening, the cross-linked free-standing dense films made from P(VP-co-DMAEMA) and PVA were exposed to the acidic and basic mixtures under the same conditions used in pervaporation tests. A slight color change was observed in the case of acidic treatment.

Figure 7a shows the ATR−FTIR spectra of the neutral and the acid and base treated samples at 85 °C. A characteristic peak at around 1650 cm$^{-1}$ represents the carbonyl moiety present in the VP unit, and after treatment, a new characteristic peak of carboxylic acid group appeared at around 1720 cm$^{-1}$, revealing that ring opening occurred during the treatment of the samples in acidic and basic conditions. The treated samples were used for swelling measurements in pure water and in binary MeAc/water mixtures (Figure 7b); this was done to investigate the possible self cross-linking of the polymeric material. After the samples are treated in both acidic and basic conditions, the PERVAP 4155-30 sample exhibited lower equilibrium swelling degree, especially in MeAc/water mixtures, and thus, because of high amount of the P(VP-co-DMAEMA) in this sample, the additional self cross-linking due to the ring-opening can be confirmed by these tests. The PERVAP 4155-70 sample also showed an evidence of the ring-opening VP (Figure 7a), but according to the swelling measurements, the additional self cross-linking could not be noticed (Figure 7b). Contrary to PERVAP 4155-30, this result can be explained by the PVA content in this sample, which might suppress this effect and act as a stabilizing matrix.

The appearance of the new characteristic band of the carboxyl acid group in the treated samples and the swelling tests corroborate the separation performance change during the pervaporation tests under different conditions, that is, it contributed to water flux decrease, which can be due to the self cross-linking and hydrogen bonding between the carboxylic acid group and amine from P(DMAEMA) segment and PVA.

By last, to confirm the responsive nature of these membranes and their reversibility, additional pervaporation tests were performed with the same membrane sample by using different mixtures, as follows: neutral−acid−neutral−basic−neutral.

Figure 8 shows the results for this set of experiments. The trend and range of water flux and permeate concentration are like previous experiments, this means the measurements are highly reproducible and the membranes show a responsive behavior. However, the water flux with neutral mixture after...
the experiments with acidic and basic mixture, does not recover as the initial values. This phenomenon could be explained as follows: (i) the cleaning of membrane may require multiple steps (long-term washing) to remove the remaining H+ from the membrane after the tests with acidic mixture, and (ii) the separation property of membrane is not entirely reversible, suggested because of the chemical changes. As ring-opening might occur during the pervaporation test in acidic and basic conditions, the amine and carboxylic acid moieties can further react to lead to an amide moiety, inducing self cross-linking of the material.41 Therefore, although the membranes have pH-responsive nature, the separation performance in terms of water flux could not be recovered once the membrane is exposed to acidic and basic mixtures. So, the results show that chemical changes and self cross-linking could have happened in the polymer system, that is, the polymer matrix is more cross-linked and is responsible for the water flux decrease.

The change of separation performance in pervaporation processes (in this case the water flux and permeate concentration) is very important during the process design and industrial plant sizing. Thus, the information got from this work is profitable for membrane developers and end users. In addition, the observed membrane behavior can be used in a useful way, especially in mixtures where acidic and basic compounds are present, for example, for obtaining higher water flux at higher water concentration in basic mixtures, for enhancing the selectivity or for preventing the separation performance change, that is, by neutralizing the acidic and basic mixtures before the streams go to the membrane modules.

■ CONCLUSIONS

Two commercial pervaporation membranes containing P(VP-co-DMAEMA) were investigated as pH-responsive membranes. The copolymer itself, the composite membrane, and dense films were characterized in detail to understand the pH-responsive nature of these membranes.

By changing the MeAc/water mixture nature from neutral to acidic and from neutral to basic mixture, the water permeate concentration was enhanced. This membrane behavior was attributed to swelling and shrinking of the polymer matrix because of the presence of DMAEMA units in the copolymer.

Pervaporation tests carried out with the same membrane sample under neutral, acidic, and basic conditions showed that the membrane performance (water flux) change is irreversible once the conditions changed. As proposed, the chemical structure changes occurred in the polymer system. Ring opening of VP units and self cross-linking has been hypothesized and later confirmed by the sample analyses.

Because these membranes are commercial and they are industrially applied for neutral mixtures, stability tests under acidic and basic conditions are needed to confirm if subsequent changes occur for a longer period. Thus, depending on the stability of these membranes, one could be able to use them for the separation of acidic and basic mixtures.

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Figure 7. (a) ATR−FTIR spectra of the treated free-standing dense films (scan number: 128, nominal resolution: 4 cm⁻¹) and (b) equilibrium swelling ratio (%) of the original (O), basic (B), and acidic (A) treated free-standing dense films (in water and neutral binary MeAc/water mixture).

Figure 8. Separation performance of membranes (a) PERVAP 4155-30 and (b) PERVAP 4155-70 for dehydration of binary MeAc/water mixtures from neutral to acidic and from neutral to basic condition at 85 °C and 10 mbar (black square: acidic, red circles: neutral (various stages), green triangle: basic).
on the application and impurities present in the mixture, the pH-responsive nature of these membranes can be advantageous.

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: wilfredo.yave@deltamem.ch.*

*E-mail: wolfgang.meier@unibas.ch.*

**ORCID**

Anja Car: 0000-0002-0168-3662

Wolfgang Meier: 0000-0002-7551-8272

**Notes**

The authors declare no competing financial interest.

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