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pH-Triggered Membrane in Pervaporation Process

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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 (PVA) and poly(1-vinylpyrrolidone-co-2-dimethylaminoethyl 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.¹⁻² 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 behaviour 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 membranes^{2, 5} as they allow intelligent control of separation when the environment changes. Because they exhibit trigger behaviour predictably to pH,⁶ temperature,⁷ different fields⁸ 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 polymer. Polymers containing basic groups (*e.g.* amino groups) show opposite behaviour 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.²

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3 A typical polymer containing amino groups used to prepare stimuli-responsive membranes is
4 poly(2-(dimethylamino)ethyl methacrylate) P(DMAEMA). The interesting feature of this
5 polymer and derivatives (copolymers) is their pH-and temperature-responsive nature.¹⁶ These
6 polymers were used as graft material in membrane and as a blend with other polymers to
7 obtain dual stimuli-responsive properties.¹⁷⁻¹⁸ P(DMAEMA) was also used as membrane
8 material for gas separation,¹⁹⁻²² nanofiltration²³ and microfiltration.^{18, 24} In addition,
9 P(DMAEMA) copolymers were synthesized and investigated as micelles for drug delivery.^{13, 25-}
10 ²⁶ Despite the overall high number of references discussing pervaporation membranes,²⁷ up
11 to date there are only few works about pH-triggered membranes for pervaporation, and their
12 behaviour under variable and industrial separation conditions.²⁸⁻³⁰
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17 In the present work, pervaporation membranes based on poly(1-vinylpyrrolidone-*co*-2-
18 dimethylaminoethyl methacrylate) P(VP-*co*-DMAEMA) with pH-trigger behaviour are
19 investigated. These membranes are the commercial PERVAP™ membranes for alcohol
20 removal from other solvents. Although these membranes are already applied for dehydration
21 of various solvents and methanol removal from neutral mixtures,³¹⁻³² the feature as pH-
22 responsive pervaporation membrane in acidic and basic mixtures has not been reported yet.
23 In the industry, during the dehydration processes and methanol removal from other solvents,
24 many mixtures have acidic and/or basic nature, depending on impurities present in the
25 streams. Thus, understand the membrane behaviour under triggered conditions is extremely
26 important for the membrane process and scale up. In addition, the new insight into these
27 membranes might extend their use to other applications.
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Materials. For the pervaporation tests, commercial pervaporation membranes PERVAP™
4155-30 and PERVAP™ 4155-70 from DeltaMem AG, Switzerland were used.³³ 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. PDMAEMA with molecular weight of 98kD 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

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3 was adjusted with a knife blade to 500 micrometers. The procedure of drying and crosslinking
4 is described elsewhere.³⁴
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6 **Pervaporation experiments.** The pervaporation tests are performed with binary MeAc/water
7 mixtures, neutral and containing 2 mmol/l of HCl and 2 mmol/L of NaOH, respectively. The
8 setup includes two pervaporation cells, which allows testing simultaneously two different type
9 of membranes. The effective membrane area in each cell is 38 cm². The mixture is filled into a
10 feed tank and recirculated by a pump with a feed flow parallel to the membrane surface. The
11 feed goes to the membrane cells, and then, the product from the cells is returned to the feed
12 tank as retentate. A heating system maintains constant the feed/retentate temperature at
13 85°C. In the permeate side, a vacuum of 10 mbar is maintained by a vacuum pump. Permeate
14 samples are collected in a cold trap with dry ice and ethanol mixture. For each measurement
15 point, the amount of permeate, time, as well as the feed/retentate samples are collected.
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20 **Instrumental Methods.** The chemical structure of the (co)polymer systems was confirmed by
21 nuclear magnetic resonance spectroscopy (NMR). NMR spectra were obtained at room
22 temperature by using a Bruker Ascend 500 spectrometer operated at 500 MHz for ¹H nucleus
23 and 125 MHz for ¹³C nucleus. Deuterated CDCl₃ was used as solvent with sample temperature
24 of 298 K. Chemical shifts (δ) are reported in ppm, and chemical shifts are referenced with
25 respect to residual solvent peaks and quoted with respect to TMS (δ 0.00). The collected
26 spectra were analyzed using MestReNova (v12.0) (Mestrelab Research S.L).
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30 Background corrected attenuated total reflection-Fourier transform infrared spectroscopy
31 (ATR-FTIR) spectra were recorded on a Bruker spectrophotometer in the range of 4000-400
32 cm⁻¹, using 128 scans at a nominal resolution of 4 cm⁻¹ using a diamond single reflection ATR.
33 Atmospheric compensation and offset correction were applied on the collected spectra with
34 the use of OPUS spectroscopy software (v7.0) (Bruker Optics).
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37 The membrane swelling measurements were performed on free standing dense films
38 prepared in the laboratory. The solvent uptake ratios of the dense film were determined
39 gravimetrically in water and MeAc/water mixtures, under neutral, acidic and basic conditions,
40 respectively. Dried films were used and placed in the selected solvent mixture at room
41 temperature and then left to swell until constant weight. The samples were removed from the
42 mixture between-times, wiped with a filter paper and weighed, and placed back into the
43 mixture until the equilibrium swelling ratios is obtained. Three parallel measurements were
44 carried out for each sample and average values as well as standard deviation were calculated.
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48 The wetting properties of membranes were investigated with static contact angle (CA)
49 measurements performed with a contact angle goniometer, CAM 100 (LOT quantum design)
50 based on a CDD camera with 50 mm optics. Droplets of ultrapure water were placed on the
51 membrane substrates with a micro syringe, and the contact angle was automatically recorded,
52 analyzed by the instrument software by fitting the curve with the Young-Laplace equation.
53 The drop volume was kept constant for all measurements and each sample was measured 6
54 times and average values as well as standard deviation were calculated.
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58 During pervaporation tests, the water concentration in the feed/retentate samples was
59 determined by coulometer Karl Fischer titration (737 KF Coulometer, Metrohm). The
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compositions of permeates were measured by using an Agilent 6890 gas chromatography equipped with a Thermal Conductivity Detector (TCD) and HP-PLOT Q column.

The Scanning Electron Microscope (SEM) images of the membranes were processed and analyzed using a Hitachi S-4800 scanning electron microscope (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).³⁴ The copolymer content in PERVAP™ 4155-30 and PERVAP™ 4155-70 is 70 wt. % 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 PDMAEMA 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.³⁵ The characteristic peaks of the copolymer backbone related to the VP units appeared between 1.3 ppm and 1.78 ppm, and between 3.00 ppm and 3.40 ppm. Peaks from 1.80 ppm to 2.50 ppm and between 3.00 ppm and 3.40 ppm are assigned with the protons of the heterocyclic ring in the VP units. The signals of the DMAEMA units in the copolymer structure appear in the region of 1.05 ppm to 1.23 ppm and 1.80 ppm to 2.10 ppm, corresponding to the methyl and methylene protons in the backbone. The methyl protons of the DMAEMA units appear at around 2.30 ppm, and the characteristic peaks around 2.56 ppm and 4.08 ppm are assigned with the methylene groups in the DMAEMA units.

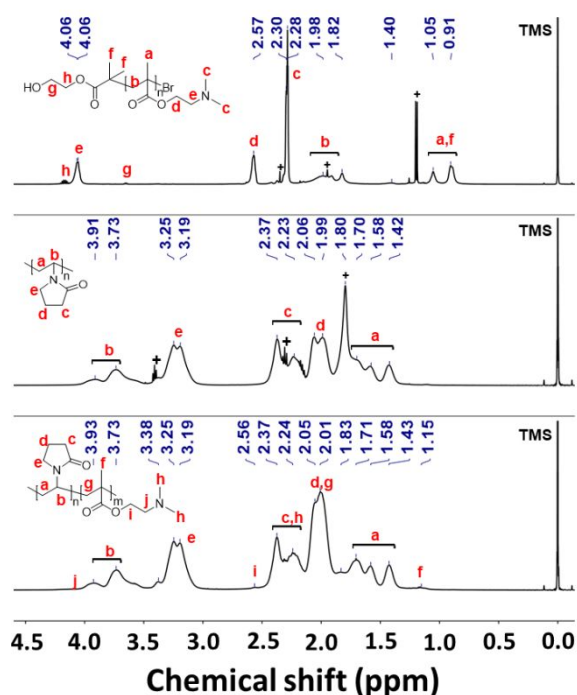


Figure 1. Phase and baseline-corrected ^1H NMR spectra of the neat polymers (PDMAEMA and PVP) and the P(VP-co-DMAEMA) copolymer (solvent: CDCl_3 , temperature: RT, number of transients (nt): 256 and relaxation time ($d1$): 1.5).

The 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.³⁵⁻³⁶ The absorption bands at 1465 cm^{-1} and 1425 cm^{-1} are characteristic absorptions of the pyrrolidiny group, and the bands at 1654 cm^{-1} 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 PDMAEMA homopolymer can be assigned to the C=O stretching vibration at 1730 cm^{-1} , (C–H(-N(CH₃)₂)) stretching vibrations between $2770\text{--}2940\text{ cm}^{-1}$ as well as the N(CH₃)₂ deformational stretching vibrations around 1459 cm^{-1} . The characteristic bands of the copolymer can be noted to stretching vibration of the carbonyl group at 1732 cm^{-1} , the deformational stretching vibrations of the secondary amine functional group at $2773\text{--}2790\text{ cm}^{-1}$ and the stretching vibration of C–N bond at $1120\text{--}1170\text{ cm}^{-1}$, 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.

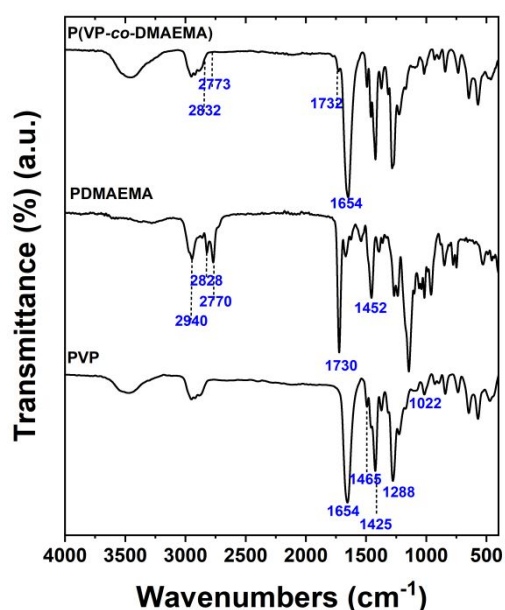


Figure 2. ATR-FTIR spectra of the neat polymers (PDMAEMA and PVP) and the P(VP-co-DMAEMA) copolymer (scan number: 128, nominal resolution: 4 cm^{-1}).

The membrane structure of PERVAP™ 4155-30 and PERVAP™ 4155-70 was analyzed by SEM, and the cross-section of the membranes are shown in Figure 3. The PVA and copolymer based selective layer is at the upper part of membrane tightly adhered to the polyacrylonitrile (PAN) 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 two micrometers. 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.

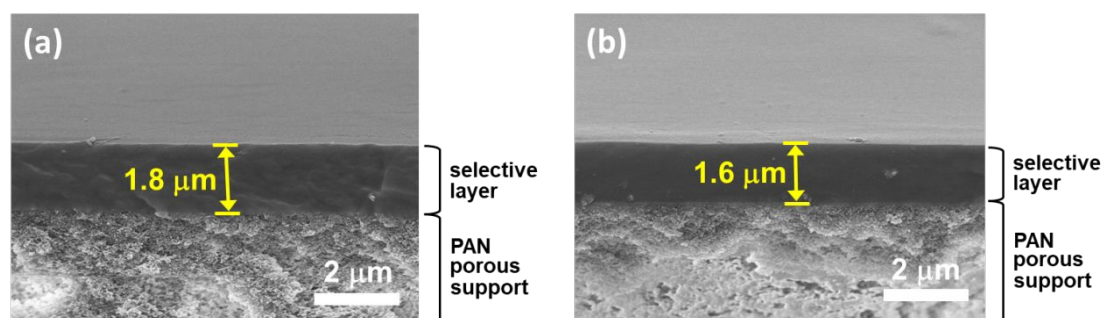


Figure 3. Representative SEM images of membrane cross-section and surface (a) PERVAP™ 4155-30 and (b) PERVAP™ 4155-70.

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 the 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, *i.e.* 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 the 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 follow: 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, *i.e.* 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.

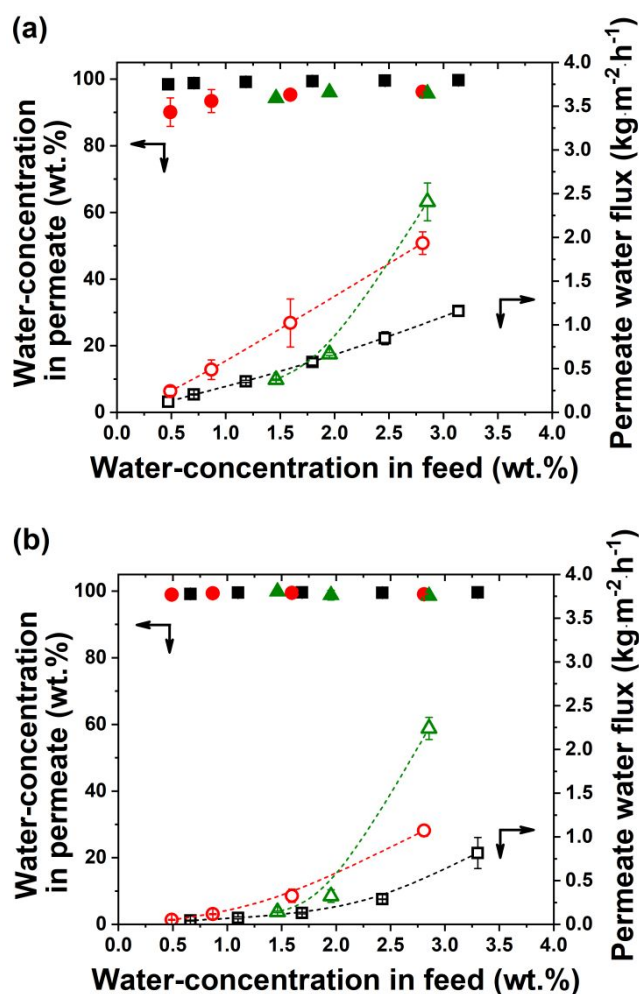


Figure 4. Separation performance of membranes (a) PERVAP™ 4155-30 and (b) PERVAP™ 4155-70 for dehydration of binary MeAc/water mixtures at 85 °C and 10 mbar under different conditions (black square: acidic, red circle: neutral, green triangle: basic).

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 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 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 and 4b). 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 PDMAEMA is a pH-responsive polymer, and thus, this segment of copolymer is protonated in acidic mixture. Because of amine protonation and the presence of

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3 PVA (containing -OH) and Cl⁻ ions (from HCl), the free movement of copolymer segment
4 containing the protonated amine is slowed down, and the material as such does not swell or
5 slightly shrinks (PERVAP™ 4155-30, Figure. 5). This makes the material less flexible and
6 decreases the fractional free volume of polymer, that results in a water flux decrease through
7 the membrane and selectivity improvement.
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10 Under basic conditions, the pervaporation tests gave even more interesting results. At the
11 beginning, at higher water concentration in the mixture, the water flux is higher than in
12 neutral condition (see the open green triangle at >2.5 wt. % of water in feed, Figure. 4). After
13 the mixture is dehydrated, the water flux drops to lower values like in acidic conditions. These
14 results can be partially explained by the decreased swelling of the membrane (Figure. 5) and
15 by the hydrophilic nature of the material under basic conditions (Figure. 6). High water
16 content in the mixture under basic conditions and the hydrophilic nature of material seem to
17 increase the swelling of the membrane. However, it happens only at the beginning of tests.
18 Later, once the MeAc is dehydrated, a pronounced decrease of flux is observed. This behavior
19 can be explained by the gradual deprotonation of amine groups and simultaneous hydrogen
20 bonding between deprotonated amine and OH⁻ groups present in PVA. At the end, the
21 material (membrane) becomes less swollen due to the lower water content in the mixture,
22 the membrane shrinks, and consequently the water flux drops. Due to a complex mechanism
23 of deprotonation and formation of hydrogen bonds, the PVP segment present in the
24 copolymer may also play certain role on water flux decrease.
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30 As discussed above, the swelling and hydrophilicity of the selective layer play important roles
31 in pervaporation process. The degree of swelling of the membranes depends on the
32 composition and the structure of the polymer matrix. Thus, PERVAP™ 4155-30 and 4155-70
33 should exhibit different behavior in terms of swelling. This investigation is carried out by using
34 dense films in pure water and mixtures used for pervaporation tests, *i.e.* binary mixtures of
35 MeAc and water in neutral, acidic and basic conditions.
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39 The swelling degree of these films are presented in Figure 5. In general, it is observed that the
40 degree of swelling of PERVAP™ 4155-30 is higher than PERVAP™ 4155-70. This is due to the
41 cross-linking degree of membrane (less content of PVA means less degree of cross-linking) and
42 hydrophilic nature of copolymer. The swelling of films in binary (MeAc/water) mixtures is less
43 than in water, and this can be explained by the wettability properties of polymer system itself.
44 In mixtures containing acid, the swelling of membrane PERVAP™ 4155-30 decreases
45 compared to neutral mixtures. Thus, this result agrees with the water flux decrease. However,
46 PERVAP™ 4155-70 does not show remarkable changes in swelling degree between tests in
47 water, neutral and acidic mixture. This result may be due to the high content of PVA in the
48 membrane (high degree of cross-linking).
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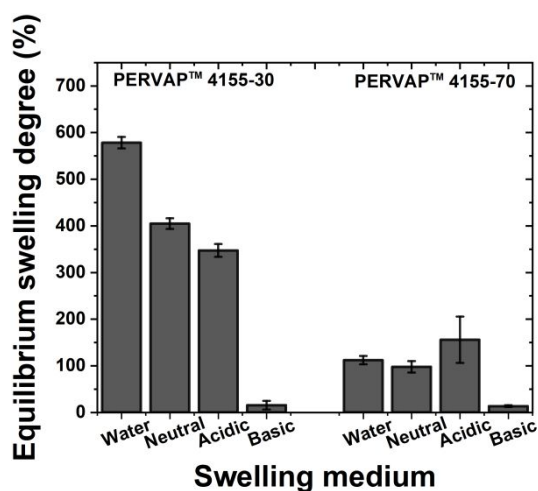
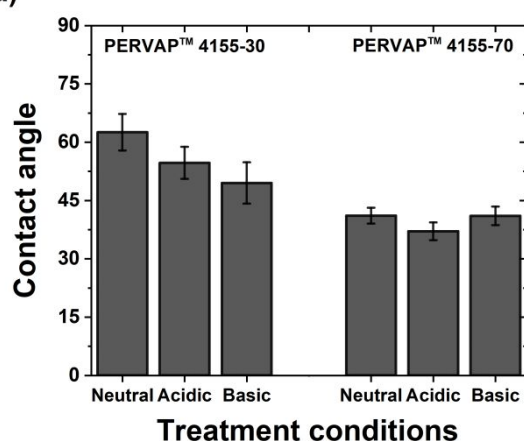


Figure 5. Equilibrium swelling ratio (%) of the free standing dense films with different P(VP-co-DMAEMA) and PVA ratios in water and various binary (MeAc/water) mixtures.

In basic conditions, both type 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 contact angle with water as a probe liquid. As shown in Figure 6, the contact angle of the liquid decreased with increasing PVA content in the membrane. This means that the PERVAP™ 4155-70 is more hydrophilic than 4155-30 due to more hydroxyl group in the membrane (higher PVA content) as well as due to 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.

(a)



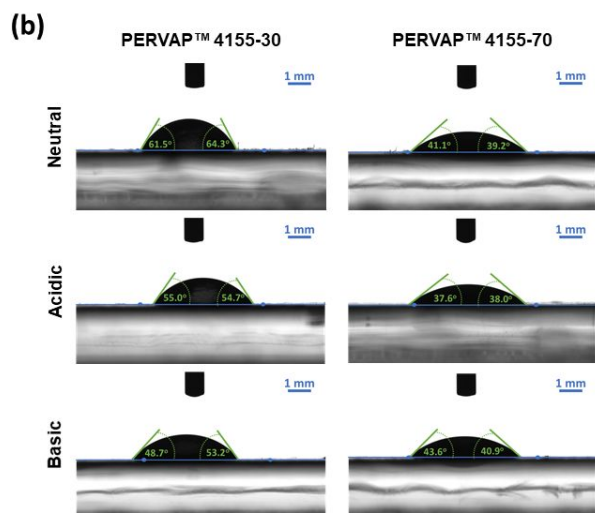


Figure 6. PERVAP™ 4155-30 and PERVAP™ 4155-70 composite membranes (a) contact angles after different treatments and (b) their representative shapes of water drops.

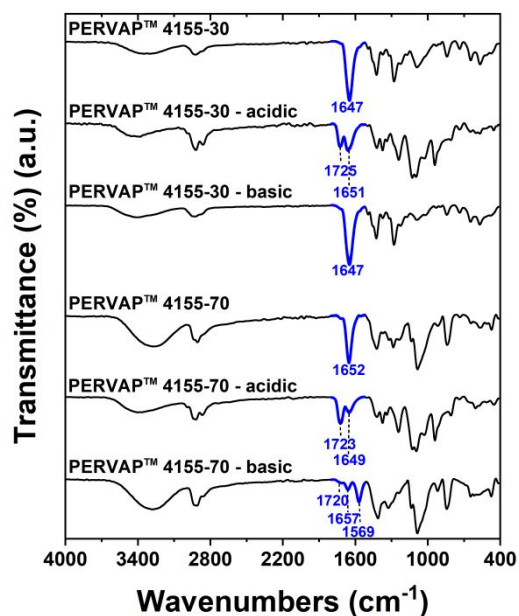
PERVAP™ 4155-30 samples exhibit slightly different contact angle when they are treated with different liquid mixtures. In basic conditions, this membrane becomes more hydrophilic, while PERVAP™ 4155-70 does not show notable changes.

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.³⁷⁻⁴¹ 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.⁴² 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 7(a) 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 also used for swelling measurements in pure water and in binary MeAc/water mixtures (Figure 7(b)), 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 (Fig. 7(a)), but according to the swelling measurements, the additional self cross-linking could not be noticed (Fig. 7(b)). 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.

(a)



(b)

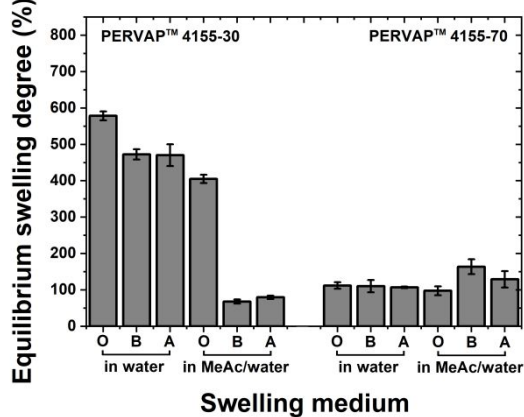
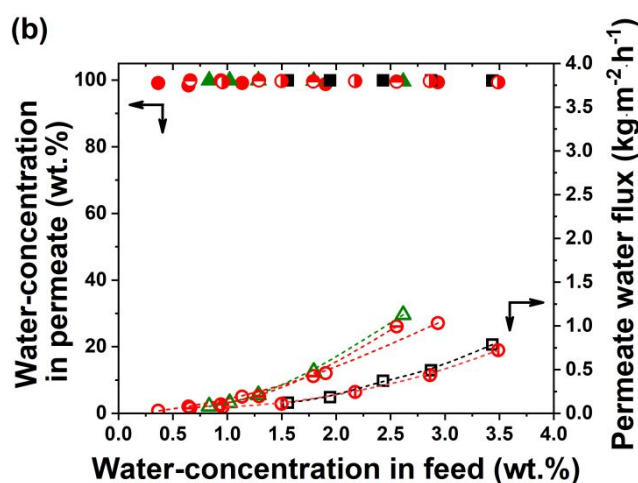
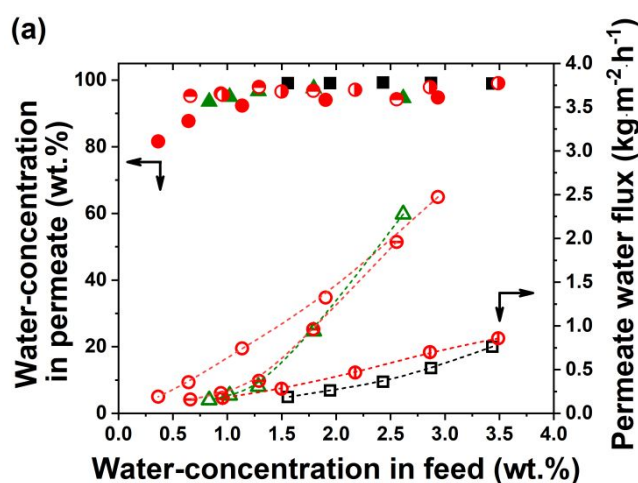


Figure 7. (a) ATR-FTIR spectra of the treated free standing dense films (scan number: 128, nominal resolution: 4 cm^{-1}) and (b) equilibrium swelling ratio (%) of the original (O), basic (B) and acidic (A) treated free standing dense films (in water and neutral binary MeAc/water mixture).

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, *i.e.* it contributed to water flux decrease, which can be due to the self cross-linking and hydrogen bonding between carboxylic acid group, and amine from PDMAEMA 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 due to 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-crosslinking 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, *i.e.* the polymer matrix is more cross-linked and is responsible for the water flux decrease.



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3 **Figure 8.** Separation performance of membranes (a) PERVAP™ 4155-30 and (b) PERVAP™
4 4155-70 for dehydration of binary MeAc/water mixtures from neutral to acidic and from
5 neutral to basic condition at 85 °C and 10 mbar (black square: acidic, red circles: neutral
6 (various stages), green triangle: basic).
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11 The change of separation performance in pervaporation processes (in this case the water flux
12 and permeate concentration) is very important during the process design and industrial plant
13 sizing. Thus, the information got from this work is profitable for membrane developers and
14 end users. In addition, the observed membrane behavior can be used in a useful way,
15 especially in mixtures where acidic and basic compounds are present, *e.g.* for obtaining higher
16 water flux at higher water concentration in basic mixtures, for enhancing the selectivity or for
17 preventing the separation performance change, *i.e.* by neutralizing the acidic and basic
18 mixtures before the streams go to the membrane modules.
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23 24 **CONCLUSION**

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26 Two commercial pervaporation membranes containing P(VP-*co*-DMAEMA) were investigated
27 as pH-responsive membranes. The copolymer itself, the composite membrane and dense films
28 were characterized in detail to understand the pH-responsive nature of these membranes.
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31 By changing the MeAc/water mixture nature from neutral to acidic and from neutral to basic
32 mixture, the water flux through the membrane dropped during the dehydration of MeAc by
33 pervaporation. In PERVAP™ 4155-30, the water permeate concentration was enhanced. This
34 membrane behavior was attributed to swelling and shrinking of polymer matrix due to the
35 presence of DMAEMA units in the copolymer.
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38 Pervaporation tests carried out with the same membrane sample under neutral, acidic and
39 basic conditions showed that the membrane performance (water flux) change is irreversible
40 once the conditions changed. As proposed, chemical structure changes occurred in the
41 polymer system. Ring-opening of VP units and self-cross-linking has been hypothesized and
42 later confirmed by the sample analyses.
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45 Because these membranes are commercial, and they are industrially applied for neutral
46 mixtures, stability tests under acidic and basic conditions are needed to confirm if subsequent
47 changes occur for a longer period. Thus, depending on the application and impurities present
48 in the mixture, the pH-responsive nature of these membranes can be advantageous.
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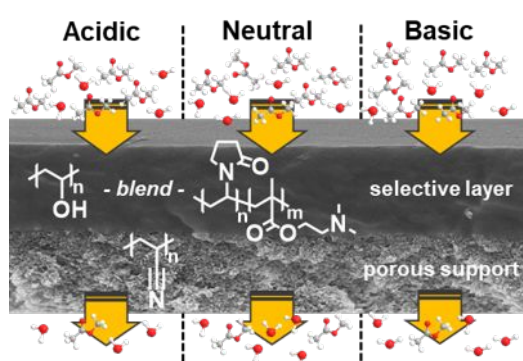
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38 Dehydration of binary methyl acetate-water mixtures under pH-triggered conditions. The
39 effects of an acid and a base on the separation performance of the membrane during the
40 pervaporation process.
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