Weak polyelectrolyte multilayers as tunable membranes for solvent resistant nanofiltration

CrossMark

Shazia Ilyas [a,b], Nithya Joseph [b], Anthony Szymczyk [c], Alexander Volodin [d], Kitty Nijmeijer [a],
Wiebe M. de Vos [a,*], Ivo F.J. Vankelecom [b]

[a] Membrane Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, Faculty of Science and Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands
[b] Centre for Surface Chemistry and Catalysis, Faculty of Bioengineering Sciences, Katholieke Universiteit Leuven, Celestijnenlaan 200F - Box 2461, 3001 Leuven, Belgium
[c] Institut des Sciences Chimiques de Rennes, CNRS, UMR 6226, Université de Rennes 1, 35042 Rennes, France
[d] Laboratory of Solid-State Physics and Magnetism, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, 3001 Leuven, Belgium

ARTICLE INFO

ABSTRACT

This manuscript encompasses the investigation into the solvent resistant nanofiltration (SRNF) performance of multilayer membranes prepared from weak polyelectrolytes. These weak polyelectrolytes are unique in that the charge density is not fixed and depends on the coating pH, adding an extra variable as tuning parameter for SRNF performance. The weak polyelectrolyte based multilayers (PEMs) were prepared on a hydrolyzed PAN support membrane from poly(allylamine hydrochloride) (PAH) as polycation and poly(acrylic acid) (PAA) as polyanion. Detailed investigations on the role of the pH of the coating solution on the performance of the prepared SRNF-membranes were carried out with organic dyes of different size ($\sim$300–1000 Da) and charge. Variation in pH of the coating solutions was found to lead to a large degree of control over the separation performance of the prepared SRNF-membranes for the different dyes. The solvent permeabilities and the dye retentions were measured and correlated to variations in the PEM membrane structures, with more dye adsorption being found for membranes with more free acid and amine groups. The membranes were also found to be stable for long term-filtrations in solvents such as isopropyl alcohol (IPA), acetonitrile (ACN), tetrahydrofuran (THF) and in the challenging polar aprotic solvent, N,N-dimethylformamide (DMF). Results of this study clearly demonstrate the potential of using pH as tuning parameter for weak PEMs to prepare SRNF-membranes optimized for specific applications.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Nanofiltration (NF) is among the pressure-driven membrane processes which have gained a lot of attention recently, with separation characteristics falling in the range between RO and UF membranes. This makes the technology especially promising for separations on a molecular level. One of the key current challenges for NF is to broaden the range of applications from aqueous to organic feeds in the form of solvent-resistant nanofiltration (SRNF) membranes [1]. As SRNF separation does not involve an energy demanding phase transition, it has drawn considerable attention as an alternative separation technique to alleviate the energy costs and related environmental problems caused by conventional separation methods such as distillation [2,3]. SRNF has potential applications in strategic fields, such as the petrochemical industry, pharmaceutical industry and food industry to separate desired molecules from solvents and/or to recover solvents and solutes from waste streams [4–8]. However, there is lack of membranes that are thermally and chemically stable, that have a high permeability and that provide effective separation of molecules in the range of 200–1000 g mol^{-1} in various organic solvents over long time-scales [1,3,9–11]. Polymers are an interesting material for SRNF related applications but very few polymeric membranes are stable: swelling and/or dissolution of the polymeric matrix often results in a loss of membrane selectivity.

In membrane technology, layer by layer (LbL) based self-assembly of charged polyelectrolytes (PEs) on an oppositely charged porous support has recently emerged as one of the simplest, most versatile, and most environmentally benign techniques to fabricate membranes with selective top-layers [12]. Fig. 1 shows schematically the LbL process to create membranes with a polyelectrolyte multilayer (PEM) top layer. A key strength of the PEM membranes
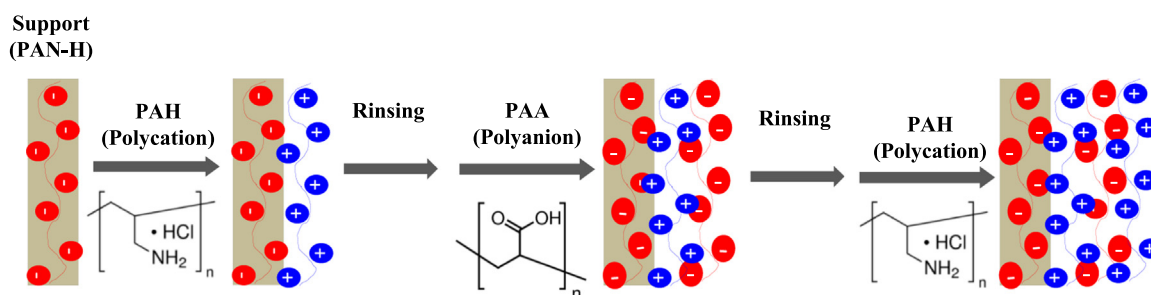
Fig. 1. Overview of the LbL assembly of PEMs of PAH/PAA on a charged membrane support.

is their versatility as the layer properties, and thus the separation properties, can be controlled via the types of PEs used, the number of deposited layers and the pH and ionic strength during coating [13]. PEMs have already been used to make different kinds of membranes such as reverse osmosis [14,15], ion selective [13,16–19], nanofiltration [14,20–26] and SRNF membranes [27–32].

Tetrahydrofuran (THF), N,N-dimethylformamide (DMF), acetonitrile (ACN), dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP) and dichloromethane (DCM) are some of the important industrial solvents that are still problematic for most of the currently available SRNF membranes [1]. These aprotic solvents demand an extremely high chemical stability from any membrane they come into contact with. Recently, PEM-based SRNF-membranes were reported to have promising and stable performance for some of these solvents [27–31]. Furthermore, PEM-based membranes typically possess a highly charged top layer allowing the possibility for Donnan based exclusion of similarly charged molecules [33]. However, all previous studies utilized at least one strong PE, making their systems relatively insensitive to the pH at which the layers are formed. With such a combination of PEs, salt addition to the PE dipping solutions best controls the thickness and morphology of the adsorbed layer. With the addition of salt the polymer chains become more coiled due to the screening of the charges along the polyelectrolyte chain. Furthermore, the ionic strength can determine the structure of the formed polyelectrolyte complex. To describe this, Schlenoff et al., [34] defined two types of charge compensations in polyelectrolyte complexation, intrinsic and extrinsic. In the former, a polymeric charge is balanced by an opposite charge of the other polyelectrolyte, while in the later most the polymeric charge is balanced by a counter ion. Increasing the ionic strength shifts the equilibrium from intrinsic to extrinsic charge compensation which leads to thicker, more mobile and more swollen layers [34]. Thicker layers on a membrane lead to lower membrane permeabilities, whereas more open layers can increase the permeability [35]. However, the effectiveness of this parameter is often limited to a small range of salt concentrations because of either solubility problems or decomposition of the multilayer films when increasing the ionic strength [36,37].

The use of two weak PEs (both the polycation and the polyanion) can provide the opportunity to use the pH during coating to allow a large degree of control over membrane performance [38]. Unlike strong PEs, which remains charged over the entire pH range, the degree of ionization of weak PEs depends greatly on the deposition solution pH. So the resulting charge density of PEs and the thickness of deposited PEMs can be affected by both the pH and the salt concentration of the PE solutions [39–42]. SRNF-membranes fabricated by the LbL deposition of weak PEs thus have an obvious advantage: the molecular structure inside of the PEM and the charge on the outside of the PEM can be controlled by an additional parameter, the pH. An added advantage of using weak PEs based membranes is that after fouling their cleaning can be made very easy using a sacrificial layer approach [43,44].

In this work, the first example of a PEM-based SRNF-membrane is presented prepared from weak PEs, a system where variation in pH can be used to tailor the membrane performance for specific solutes. More specifically, poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH) based PEMs were used, as this system has already shown itself promising in traditional NF-applications [38,43]. The pH of the coating solution was used as a parameter to control the layer thickness and the molecular organization of the multilayers, which in turn leads to different separation behavior for different solutes. PEMs were prepared under three pH combinations (PAH/PAA: 7.5/7.5, 7.5/3.5 and 3.5/3.5) and were characterized on model surfaces in order to understand the effect of coating pH on their resulting multilayer composition. The PEMs were then prepared on a hydrolyzed PAN support membrane under the same coating conditions and were characterized in terms of surface roughness, contact angle and IPA permeance. The performance of these multilayered membranes was characterized in terms of their ability to retain different organic solutes of varying size and charge from IPA in order to understand the effect of coating pH on membrane performance. Finally, the multilayered membranes were tested for their stability towards aprotic solvents such as acetonitrile (ACN), dimethylformamide (DMF) and tetrahydrofuran (THF) for long periods of time (> 50 h).

2. Experimental

2.1. Chemicals

Polyacrylonitrile (PAN, MW = 150,000 Da) was purchased from Scientific Polymer Products Inc., Ontario, New York. Isopropyl alcohol (IPA), acetonitrile (ACN), tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were obtained from VWR, Leuven, Belgium, and were used as solvents. Rose bengal (RB), acid fuchsin (AF), bromothymol blue (BTB), methylene blue (MB) and methyl orange (MO) were purchased from Sigma–Aldrich and used as solutes (see Table 1 for more details). The PEs used in this study were poly(allyl amine) hydrochloride (PAH; $M_w = 15,000$ g mol^{-1}) and poly(acrylic acid) (PAA; $M_w = 15,000$ g mol^{-1}). Sodium nitrate (NaNO$_3$) was used to adjust the ionic strength in all solutions. Sodium hydroxide

Table 1
Properties of solutes used in this study.

Solute	Mol. weight (Dalton)	Charge	Molar volume (cm^3 mol^{-1})
Rose Bengal (RB)	1017	−2	273
Methyl Orange (MO)	327	−1	160
Bromothymol Blue (BTB)	624	0	281
Methylene Blue (MB)	320	+1	242
Acid Fuchsin (AF)	585	−2	247

(NaOH) and hydrochloric acid (HCl) were used to adjust the pH.

PE solutions always contained 0.1 g l^{-1} of polymer at various pH conditions and always with 50 mM of background electrolyte. Deionized water (Milli Q, 18.2 MΩ cm) was used to rinse the membranes and to prepare polyelectrolyte solutions. All solutions were used within eight days after preparation.

2.2. Membrane support preparation and LbL coating

The charged PAN-H support was prepared using a procedure reported earlier [27], but a short summary is given here. 15 wt% PAN in DMSO was cast on a polypropylene/polyethylene support (FO 2471, Viledon) and then immersed in deionized water. The PAN film was subsequently immersed in 10 wt% NaOH at 50 °C for 45 min for hydrolysis. The remaining NaOH was removed by copious rinsing with water. The PEM-based membranes were prepared by means of an automated dip-coater (HTML, Belgium). The dip-coater comprises four separate compartments, two for PE solutions and two for background electrolyte solutions for rinsing. PEs were dissolved in background electrolyte solutions at a concentration of 0.1 g l^{-1}. To adsorb the PEs, the PAN-H support was first immersed in the solution of the cationic PE (PAH) for 15 min, followed by rinsing with background electrolyte of same ionic strength and pH as that of the PAH solution for 10 min, then immersed in the solution of the anionic PE (PAA) and rinsed with background electrolyte of same ionic strength and pH as that of the PAA solution. Three different pH combinations for PAH/PAA were used to coat the membranes and resulting membranes are [7.5/7.5], [7.5/3.5] and [3.5/3.5]. For example, [7.5/3.5] represents membranes with multilayer films (PAH/PAA) alternately assembled with the PAH layers deposited at pH 7.5 and the PAA layers at pH 3.5. The rinsing step removes any loosely bound or excess polyelectrolyte from the membrane surface and prevents complex formation in bulk solution. The described procedure was repeated to deposit the desired number of bilayers. The final membranes were then stored in Milli Q water for further use.

2.3. Preparation of PEMs on glass slides and silicon wafers

For ellipsometry studies, the PEMs were assembled on silicon wafers using a similar procedure as for the membrane support. For MB adsorption studies, PEMs were assembled on glass slides. Before assembly, the silicon wafers and glass slides were pre-treated with piranha solution (3:1 mixture of 98% H_2SO_4 and 30% H_2O_2; caution: piranha is a strong oxidizer and should not be stored in closed containers) for 2 h and rinsed in de-ionized water. Wafers and glass slides were used within 1 h after piranha treatment. PEMs were then deposited on wafers and glass slides [32,45], and were dried with a nitrogen stream and stored at ambient conditions for characterization.

2.4. Characterization

2.4.1. Thickness of PEMs by ellipsometry

The dry thickness of PEMs deposited on polished silicon wafers under different pH conditions were measured using an ellipsometer (Woolam EC-400, M-2000V) at ambient conditions. All samples were dried at room temperature with a nitrogen stream prior to measurements.

2.4.2. Methylene blue adsorption on PEMs

Methylene blue (MB) staining technique was used to gain information on the charge of the surface layer (terminal layer) of PEMs. PEMs were assembled on glass slides, dried with a nitrogen stream, and subsequently immersed in aqueous 10^{-3} M, pH 7.0 MB aqueous solutions for 10 min. With an immersion time of 15 min or less the dye can only diffuse into the outer most layers, making the results independent of the layer thickness [39,40]. After immersion in the dye solution, the multilayer films were soaked in demi-water for 1 min to remove unbound dye and dried with a mild air flow. UV/Vis spectroscopy was used to determine the amount of MB adsorption on multilayer films. Absorbance was measured at a wavelength of 600 nm.

2.4.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of membranes were acquired using a spectrometer (Varian 670-IR, Varian Inc., USA) in absorbance mode. The samples were dried at room temperature for 24 h prior to FTIR measurement to minimize the influence of water.

2.4.4. Scanning electron microscopy (SEM)

SEM (Philips XL FEG30) was used to study the surface structure and cross section of the membranes. Before use, the SEM samples were first gold coated.

2.4.5. Atomic force microscopy (AFM)

The surface morphology and roughness of dry membranes were measured by AFM (Agilent 5500) operating in tapping mode at ambient conditions (relative humidity ∼30%). Commercial AFM cantilevers (PPP-NCSTR AFM probes from NanoAndMore GmbH) made of Si with a nominal spring constant of 7.4 N m^{-1} and with a typical tip radius of less than 7 nm were used. AFM measurements were performed with scan areas of 1×1 μm^2 at 3 different locations for each of the samples. The average roughness (R_a) and the root-mean-square roughness (R_{rms}), which is given by the standard deviation of the topography height measurement data (Z values), were calculated using Eq. (1)

$$R_a = \frac{1}{N} \sum_{i=1}^{N} |Zi - \bar{Z}|; \; R_{rms} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} |Zi - \bar{Z}|^2} \tag{1}$$

where $\bar{Z}$ is the average of the height values within the given area, Z_i is the current height, and N is the number of data points taken within the given area.

2.4.6. Contact angle

Optical contact angle measurements of a DI water droplet on the membrane surface were performed using a Krüss goniometer (drop shape analysis system DSA 10 Mk2). For contact angle measurements, the membranes were dried overnight at room temperature. The contact angle of the sessile drop of 3 μL of water on the membrane was measured three times for each membrane at 20 °C in static mode, and the average value and standard deviation are reported. The contact angles were measured 5 s after the droplet was placed on the surface.

2.5. Membrane performance

2.5.1. Filtration and rejection

Five dyes (Fig. 2) were selected for the rejection experiments. The dye molecular weight range was chosen to be between 319 and 1100 Da. The selection of dyes was made such that it covers neutral, positive, negative, but also small and large molecular sizes. Filtration of membranes with dye solutions was performed using a stainless steel dead-end high-throughput apparatus (HTML, Belgium) [45] with 8 filtration cells, all with a membrane surface area of 1.77 cm^2. The filtration setup was pressurized with nitrogen to 25 bar. To minimize concentration polarization during filtration, the feed solution was constantly stirred at 500 rpm. Dye rejections were calculated based on the differences between permeate and concentrate concentrations. The retention values were calculated from concentrations of the permeate and of the
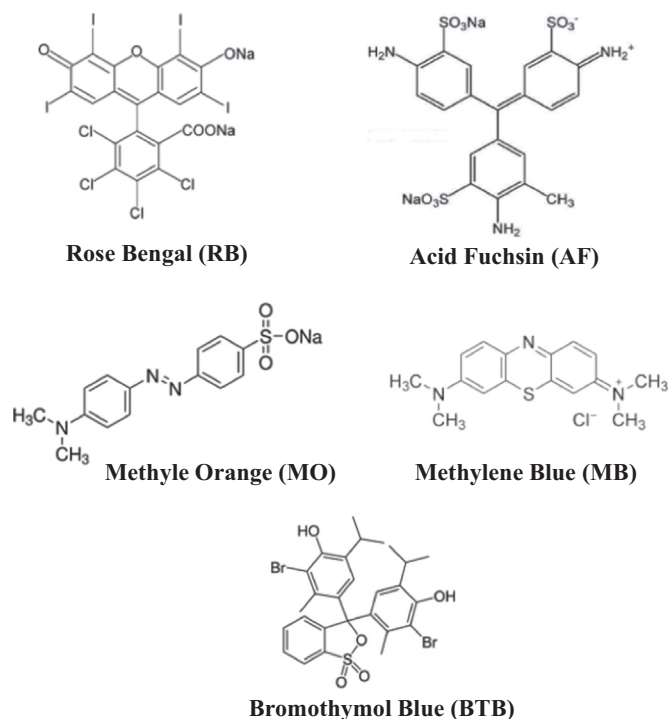
Rose Bengal (RB)

Acid Fuchsin (AF)

Methyle Orange (MO)

Methylene Blue (MB)

Bromothymol Blue (BTB)

Fig. 2. Chemical structures of solutes used for rejection experiments.

original feed solutions according to Eq. (2):

$$R\ (\%) = 1 - \frac{C_p}{C_f} \times 100 \qquad (2)$$

where C_p and C_f are solute concentration in the permeate and the feed, respectively. The permeation was stopped when the retention reached a constant value. All measurements were based on at least three samples, and the average values were used. The standard deviation on the measurements was about 5%. All were used in a 35 μM concentration, with most experiments performed in IPA.

2.5.2. Long term filtration studies

To further demonstrate the chemical stability of these weak PEM-membranes for different solvents and for longer time-scales, ACN, THF and DMF were selected for long-term filtrations. Table 2 gives the physico-chemical properties of these solvents. Membranes prepared with 5 bilayers [7.5/3.5] were subjected to filtration with RB in IPA, THF, ACN and DMF separately for more than 50 h.

3. Results and discussion

The results and discussion section is divided into three major parts. The first part deals with the characterization of PEMs by

Table 2
Physico-chemical properties of solvents used [46].

Solvent	Molar volume (cm³ mol⁻¹)	Viscosity (cP)	Molar volume/viscosity (cm³ mol⁻¹ cP⁻¹)	Dielectric constant
IPA	76.92	2.00	38.46	18.30
DMF	77.43	0.82	94.43	36.70
ACN	52.86	0.38	139.10	37.50
THF	81.08	0.55	147.42	7.60

Table 3
Average thickness of PEMs with 5 bilayers of PAH/PAA (prepared at three pH combinations with 0.1 g l⁻¹ polymer and 50 mM salt).

	pH [PAH/PAA]		
PEMs	[7.5/7.5]	[7.5/3.5]	[3.5/3.5]
Thickness (nm)	10 ± 1	83 ± 1	61 ± 2

ellipsometry and MB absorption to study their structure and composition. In the second part, the characterization of the support and the prepared multilayered membranes is given. The third part reports on the SRNF-membrane performance, with membranes prepared under different pH conditions, being tested for their retention of different organic molecules.

3.1. Properties of PEMs

3.1.1. Thickness

The thickness of multilayer films of PAH/PAA deposited under different pH combinations (7.5/7.5, 7.5/3.5 and 3.5/3.5 for PAH/PAA) at a polymer concentration of 0.1 g l⁻¹ in a 50 mM NaNO₃ aqueous solution was determined by ellipsometry. The used salt concentration was selected based on a previous study where optimal growth of these PEMs was achieved at 50 mM [43]. The measured average thickness for 5 bilayer thick multilayers is reported in Table 3. Clearly, the thickness of the layers is influenced by the pH of the coating solution of the polycation and the polyanion. For weak polyelectrolyte pairs such as PAH/PAA, the thickness, composition and organization of the multilayers can be systematically tuned by varying the pH of each PE solution [39,40,47]. The pH controls the charge density of the weak PEs by controlling the degree of dissociation of the basic and acidic groups on the polymer chains. PAA with pKa of 6.5 and PAH with pKa 8–9 [47], are nearly fully charged (80–90% charged groups) at a pH condition of [7.5/7.5] and thus form thin layers upon deposition, requiring just a small amount of material to compensate for all charges from a previously deposited layer, most likely with a high degree of intrinsic charge compensation inside the bulk of the layers. The thickest layers are formed when one of the PEs is only partially charged (PAA at pH 3.5) and other is fully or nearly fully charged (PAH at pH 3.5 and 7.5 respectively). The partially charged polymer segments lead to a more coiled conformation and favor diffusion of counter ions of the employed salt into the multilayer, forming more swollen layers with more mobile chains leading to more extrinsic charge compensation of the polymeric charges.

3.1.2. Adsorption of the cationic dye methylene blue (MB)

A dye test was performed on PEMs on glass surfaces to determine the excess of free carboxylic acid groups available as binding sites (for positively charged solutes) on the surface of PEMs. Fig. 3 shows the results of the MB test performed with 5 (ending with PAA) and 5.5 (ending with PAH) bilayers of PEMs deposited on glass slides. A higher absorbance of MB indicates the presence of more free carboxylic acid groups. At pH condition [7.5/7.5] for PAH/PAA, both PEs have a high charge density (fully ionized) producing polycation-polyanion contact pairs and leaving only little free carboxylic acid groups for the adsorption of positive dye. Thus, regardless whether PAH (+) or PAA (-) is the last layer, few free functional sites will be left on the surface with most of the polyions bound with an oppositely charged group. As can be seen from these results, just a small difference in MB absorbance exists for PAH (+) or PAA (-) terminated layers, and these values are always low.

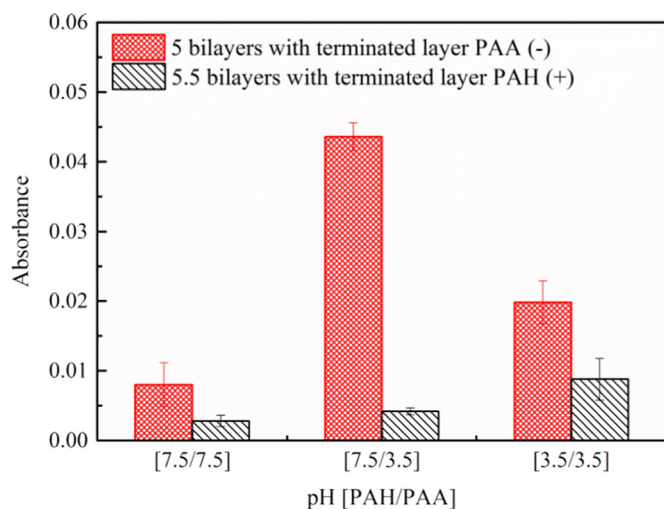However, at the pH combinations [7.5/3.5] and [3.5/3.5], an

Fig. 3. Methylene blue absorbance measured at 600 nm of 5 and 5.5 bilayers of PAH/PAA prepared at three different pH combinations with polymer concentration at 0.1 g l^{-1} and 50 mM salt.

unbalanced ionization state (PAA only partly charged during deposition at pH 3.5) results in many free acidic groups. For [7.5/3.5], this result in a very high absorbance for the PAA (-) terminated layer, indicating a highly charged layer. Still for the PAH (+) terminated [7.5/3.5] layer, the absorbance drops strongly, which indicates just a small amount of free unbound acid groups. This is an indication of the normal charge inversion leaving just a small amount of free unbound acid groups. For [3.5/3.5], absorbance is always rather high. This is an indication that this layer has many extrinsically compensated ion pairs (free NH$_2$ and COOH groups).

The results so far show at the chosen pH conditions, three entirely different PEMs are created. For [7.5/7.5], a very thin layer with a high degree of intrinsic charge compensation is found. For [7.5/3.5], the thickest layer is created that is especially highly charged when terminated with PAA (-). Finally, for [3.5/3.5] a thick layer is obtained that always has many free acid groups available, likely an indication of very high extrinsic charge compensation and thus presence of free amine and acid groups.

3.2. Characterization of support and PEMs based membranes

3.2.1. ATR-FTIR

ATR-FTIR was used to confirm the hydrolysis of the PAN support. Fig. S1 presents the ATR-FTIR spectra of a PAN and a hydrolyzed PAN membrane. The peaks at 2243 and 1451 cm^{-1} are due to stretching vibrations of the CN moiety of the PAN membrane support [48]. For hydrolyzed PAN, most of the CN groups convert to COO$^-$ groups, leading to a peak reduction at 2243 cm^{-1} and the emergence of a new peak at approximately 1674 cm^{-1}, which corresponds to the C=O bond in the COO$^-$ groups. FTIR results thus confirm the hydrolyzation of PAN into a negatively charged membrane support.

3.2.2. SEM

Surface images of the PAN-H support and PEMs based SRNF membranes [7.5/7.5], [7.5/3.5] and [3.5/3.5] showed no significant difference in the surface morphology and are given in the supporting information (Fig. S2). A cross section of the PAN-H support shows a very open pore structure with fingerlike pores (Fig. S3), while the thickness of the support layer used is in the range of 150 μm.

3.2.3. Surface morphology and surface roughness

AFM images presenting the surface morphology of the membrane support and the multilayered membranes are displayed in Fig. 4. The surface structure seems to become smooth with the deposition of polyelectrolyte multilayers. These images thus suggest that the applied polyelectrolytes form an even layer on top of the support. In images b and c, some small cracks can be observed but as they are much shallower than the thickness of the PEM films these are not believed to be true defects.

Average surface roughness values of the membranes on $1 \times 1 \mu m^2$ scans in root mean square (R$_{rms}$) and average roughness (R$_a$) are presented in Table 4. When the charge density of both PAH and PAA is high (at pH 7.5/7.5), smooth layers are formed due to a flattened conformation of the polyelectrolytes. The layers formed seem to be somewhat more rougher when one of the polymers is only partially charged [40] as at pH 7./5/3.5 and 3.5/3.5, since these thicker layers will have more coiled polymers.

3.2.4. Contact angle with water

Determining the contact angle with water is a useful method to observe changes in the hydrophilicity of the membranes. For PAN and PAN-H, contact angles of 47.0 ± 1.0 and 15.0 ± 2.0 respectively, confirm successful hydrolyzation of the PAN support. Contact angle values measured for all three types of membranes with PAH (+) and PAA (-) terminated layers are given in Fig. 5. The coating of PEMs on the hydrophilic membrane support in all cases leads to higher contact angles. Little difference in the contact angle value with the type of terminating layer is observed for [7.5/7.5] membranes, while it is substantial for the [7.5/3.5] and [3.5/3.5] membranes. Here, the PAA (-) terminated membrane is more hydrophilic as compared to the PAH (+) terminated membrane, likely because of the large excess of carboxylic groups. The [7.5/7.5] prepared layer is relatively hydrophobic, as could be expected for a PEM layer with a high degree of intrinsic charge compensation (few free –NH$_2$ and –COOH groups). On the other hand, the contact angle is considerably lower for [3.5/3.5] and a very high degree of extrinsic charge compensation can be expected. It is good to mention that also roughness influences contact angle measurements, however as the determined rough nesses were found to be very low (Table 4) this effect could be neglected.

3.3. SRNF performance of PEM based membranes

3.3.1. Pure solvent permeability

After coating the support with PEMs, the pure solvent permeability of the support and the prepared membranes was measured. The pure IPA permeance values were: 127.0 ± 7.0 l m^{-2} h^{-1} bar^{-1} for the PAN-H support, 7.0 ± 0.5 l m^{-2} h^{-1} bar^{-1} for [7.5/7.5] membranes, 4.0 ± 1.0 l m^{-2} h^{-1} bar^{-1} for [7.5/3.5] membranes, and 5.0 ± 2.0 l m^{-2} h^{-1} bar^{-1} for [3.5/3.5] membranes. The [7.5/7.5] membranes thus have a higher flux. However, when taking into account the thickness, the [7.5/7.5] membranes have much lower permeability as they are 8 times thinner (Table 3) than [7.5/3.5] and 6 times thinner than [3.5/3.5] membranes. It seems that not only is this layer quite thin, it is also quite dense, a typical behavior expected for PEM membranes with a high degree of intrinsic charge compensation [35].

3.3.2. Influence of solute size and charge

Five different dyes with double negative charges (RB, Mw 1017 Da and AF, Mw 558 Da), single negative charge (MO, Mw 327 Da), positive charge (MB, Mw 320 Da) and without charge (BTB, Mw 624 Da) were selected as solutes (Table 1). Filtrations were performed with membranes coated from 50 mM salt solutions and with different pH combinations for PAH/PAA [7.5/7.5, 7.5/3.5 and 3.5/3.5]. PAN-H support used to prepare PEMs based SRNF membranes has RB retention of 46% with a 2.2 l m^{-2} h^{-1} bar^{-1} permeance. It is important to mention that the retention of
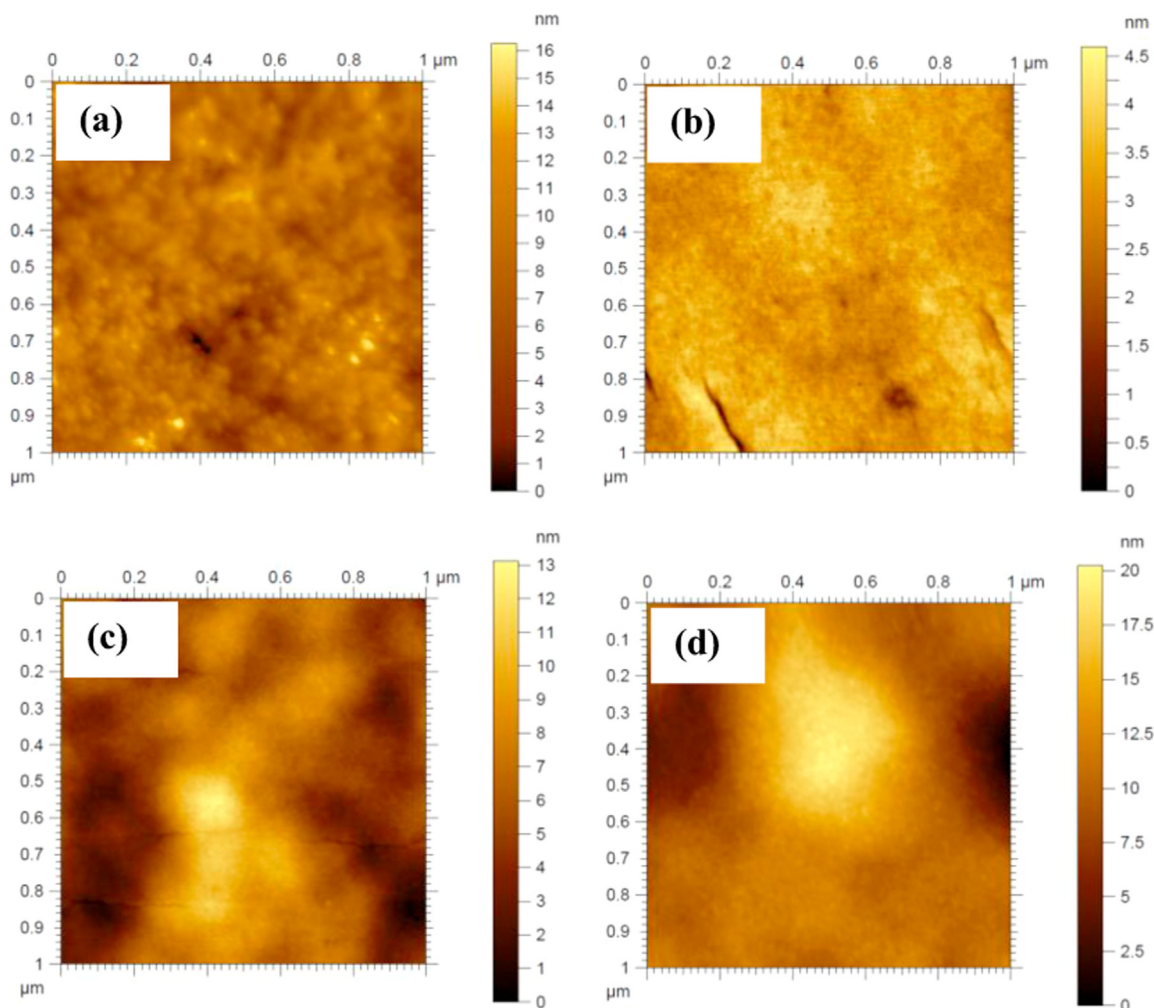
Fig. 4. AFM images of (a) support; and multilayered SRNF membranes prepared with PAH/PAA pH of (b) [7.5/7.5] (c) [7.5/3.5] (d) [3.5/3.5] with polymer concentration of 0.1 g l^{-1} and 50 mM salt.

Table 4
Calculated surface roughness of membranes with 5 bilayers of PAH/PAA (prepared at three pH combinations with 0.1 g l^{-1} polymer and 50 mM salt).

Roughness	Support	pH[PAH/PAA]		
		[7.5/7.5]	**[7.5/3.5]**	**[3.5/3.5]**
R_{rms} (nm)	2.6 ± 0.4	0.5 ± 0.1	2.1 ± 0.2	3.5 ± 0.7
R_a (nm)	2.4 ± 0.4	0.4 ± 0.1	1.4 ± 0.1	1.5 ± 0.1

organic dyes in SRNF is a complex mixture of factors including Donnan exclusion, size exclusion and the mutual affinities between the dye, the solvent and the membrane [1,49–51]. Furthermore, the dye can potentially foul the SRNF-membrane, either by adsorption on top of the PEM layer, adsorption in the PEM layer or adsorption on the charged membrane support. Such fouling will lead to lower permeance but can substantially increase the initial rejection. This is the first investigation of the SRNF performance of multilayered membranes prepared from weak PEs and because of the mentioned complexity, focus is to show the easiness of the approach in combination with its versatility and on comparing the performance of the differently prepared PEM membranes, rather than determining the exact rejection mechanism for all membrane/dye combinations.

In Fig. 6, the filtration results of multilayered membranes with 5 bilayers of PAH/PAA, prepared from polymer solutions with
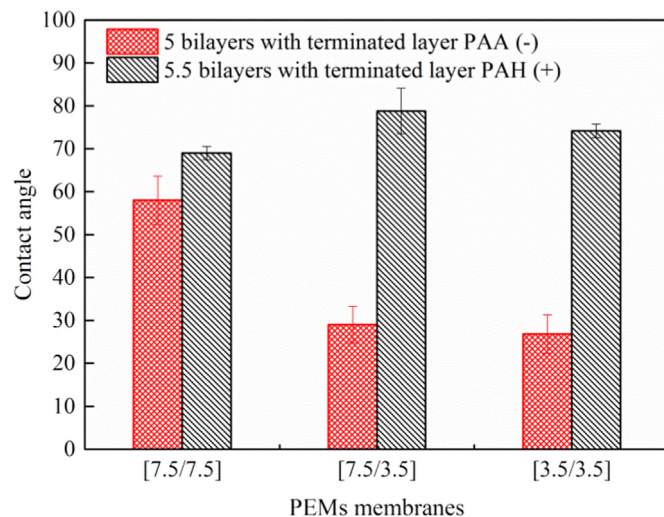

Fig. 5. Sessile droplet water contact angle of 5 and 5.5 bilayer membranes [7.5/7.5, 7.5/3.5 and 3.5/3.5] prepared at a polymer concentration 0.1 g l^{-1} and 50 mM salt. In the 5 bilayer membranes the terminating layer is of PAA and in 5.5, PAH is the terminating layer.

different pH combinations are given. The retention and permeance results are given for negatively charged solutes (RB and AF) in IPA. For all membranes, more than 90% retention for RB is observed but
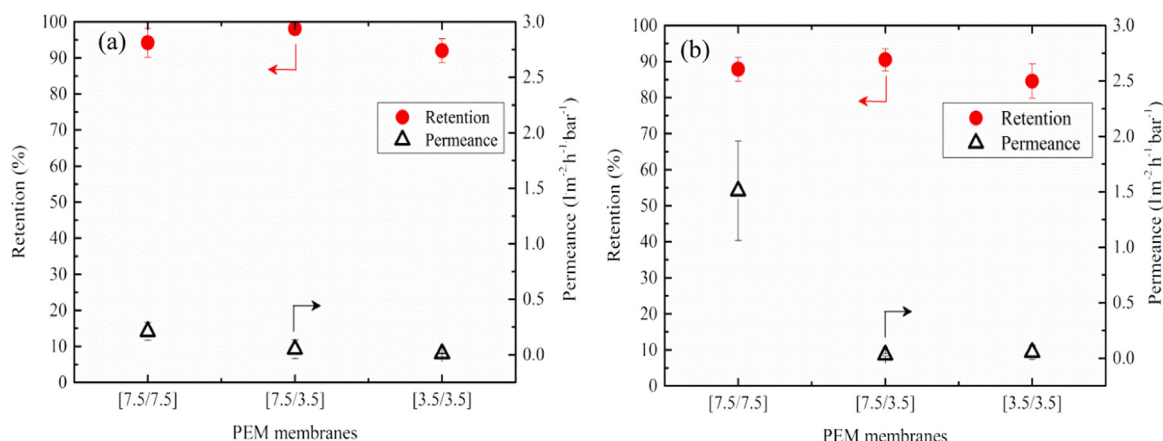
Fig. 6. SRNF performance of membranes for large sized charged solutes by 5 bilayers of PAH/PAA (prepared at three pH combinations with 0.1 g l^{-1} polymer and 50 mM salt) (a) retention and permeance of RB from IPA solution; (b) retention and permeance of AF from IPA solution.

with a sharp drop in permeability (Fig. 6(a)). Possibly, a strong solute adsorption in/on the membranes takes place which then densifies (i.e. bivalent dyes can crosslink) the membranes [30]. However, the [7.5/7.5] membrane is more permeable than the others with similar rejection. We hypothesize that the lower amount of free –NH$_2$ and –COOH groups in this layer, also leaves less adsorption sites available for the dyes. Consequently, [3.5/3.5] has the lowest permeability as compared to pure IPA filtration as it has most free –COOH and –NH$_2$ groups. AF is a smaller molecule than RB and also carries two negative charges. Membranes show slightly less rejection for AF as compared to RB (Fig. 6(b)), probably because of the smaller size. Especially membrane [7.5/7.5] (Fig. 6 (b)) shows good rejection while retaining a high operational permeability, in agreement with the RB results. It is surprising that the highly negative layer of the [7.5/3.5] membrane adsorbs so many double negatively charged molecules. It is possible that the molecules do not adsorb at the top of the layer, where the excess of charge is localized, but rather deeper inside the layers.

In Table 5, the comparison is given of the SRNF performance of membranes from the present work with previously reported PEM membranes prepared from two strong PEs or one strong and one weak PE [27,31]. The data are given for 5 bilayer thick PEM membranes for RB retention from IPA. It shows that PEM membranes prepared from both weak PEs have a RB retention comparable to that of membranes prepared from both strong PEs or from one of the weak PEs. Present work even shows the highest observed retention for RB within this comparison.

To further explore the performance of these membranes, the retention of the relatively large neutral dye molecule BTB (Mw 624 Da) was studied. For BTB, membranes [7.5/7.5] show decent
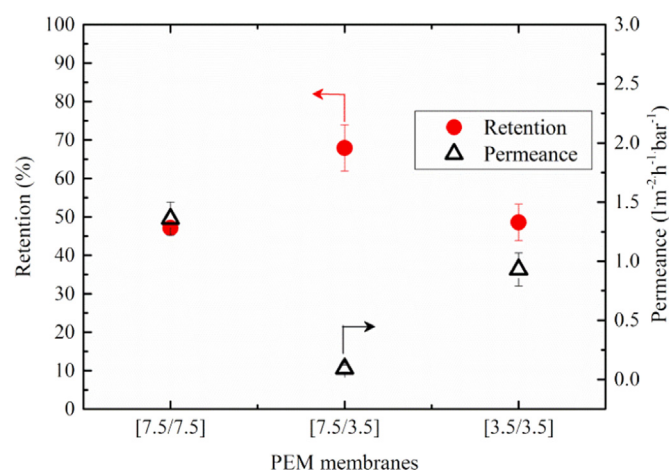
Table 5
Comparison of SRNF performance of PEMs based membranes for RB in IPA.

PEMs membrane	Permeance (l m^{-2} h^{-1} bar^{-1})	Retention (%)	References
(PAH/PAA, pH 7.5/7.5)$_5$ 50 mM	0.21 ± 0.08	95 ± 4	Present work
(PAH pH 7.5/PAA pH 3.5)$_5$ 50 mM	0.05 ± 0.09	99 ± 1	
(PDDA/PAA, pH 7/4)$_5$ 0 mM	0.03	97 ± 2	[27]
(PDDA/PAA, pH 7/4)$_5$ 100 mM	0.06	92 ± 5	
(SPEEK/PDADMAC)$_5$ 0 mM	0.40	94	[31]
(SPEEK/PDADMAC)$_5$ 100 mM	0.08	98	

Fig. 7. SRNF performance of membranes for BTB from IPA solution with 5 bilayers of PAH/PAA (prepared at three pH combinations with 0.1 g l^{-1} polymer and 50 mM salt).

performance both in terms of permeance and rejection (see Fig. 7). Here, surprisingly, the membrane [3.5/3.5] also shows reasonable performance, but the overall retention of BTB by all these three membranes is lower than for the strongly charged AF and RB. Less dye adsorption would lead to less densified films and a lower retention.

Next, MO (with a single negative charge) and MB (with a single positive charge) retentions are given as examples of smaller sized dyes (Fig. 8(a) and (b)). For MO (-), the membrane [7.5/3.5] shows good rejection and high permeance. This would be expected for such a highly negatively charged layer, having Donnan exclusion as the main separation mechanism. The other less negatively charged layers show much lower retentions, while [3.5/3.5] again suffering from very low permeabilities. For MB (+), none of the membranes show a good combination of retention and permeance. This is expected as the membranes are all negatively charged. Especially for [7.5/3.5] and [3.5/3.5], this leads to very low permeances, likely because of adsorption and densification of the layers. So by varying the pH of coating PEs, PEM membranes can be prepared with very different performances for different dyes in SRNF.

To see the role of the terminating layer charge on retention performance of membranes in terms of electrostatic repulsion, also filtrations were performed with membranes terminated with positive polyelectrolyte PAH (5.5 bilayers). RB and AF retentions for membranes with 5.5 bilayers of PAH/PAA at different pH combinations with a terminating layer of PAH (+) are given in
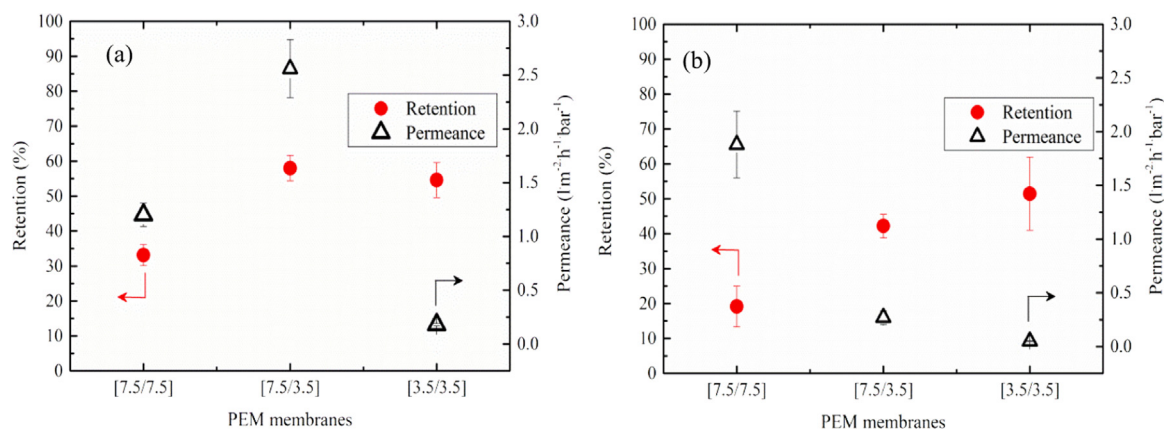
Fig. 8. SRNF performance of membranes for small sized charged solutes with 5 bilayers of PAH/PAA (prepared at three pH combinations with 0.1 g l^{-1} polymer and 50 mM salt) (a) retention and permeance of MO (-) from IPA solution; (b) retention and permeance of MB (+) from IPA solution.

Table 6
SRNF performance of PAH (+) terminating multilayered membranes with 5.5 bilayers of PAH/PAA (prepared at three pH combinations with 0.1 g l^{-1} polymer and 50 mM salt).

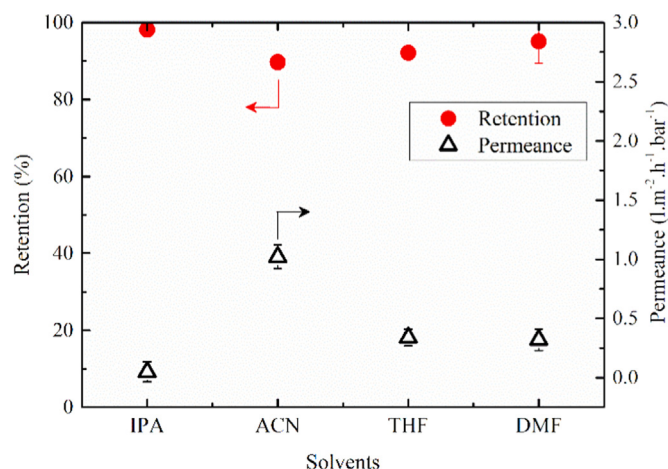| PEM membranes	Retention (%)			Permeance l m^{-2} h^{-1} bar^{-1}		
	[7.5/7.5]	[7.5/3.5]	[3.5/3.5]	[7.5/7.5]	[7.5/3.5]	[3.5/3.5]
RB	93 ± 2	96 ± 2	91 ± 2	0.22 ± 0.12	0.07 ± 0.01	0.01 ± 0.00
AF	86 ± 4	86 ± 8	96 ± 2	0.88 ± 0.22	0.45 ± 0.30	0.02 ± 0.00
MO	23 ± 1	31 ± 4	60 ± 8	1.00 ± 0.30	2.00 ± 0.22	0.10 ± 0.02
MB	28 ± 5	62 ± 3	29 ± 7	0.30 ± 0.10	0.20 ± 0.05	0.10 ± 0.02

Fig. 9. SRNF properties of weak PEM membranes for RB in different organic solvents. Tested membranes are [7.5/3.5] with 5 bilayers of PAH/PAA prepared with 0.1 g l^{-1} polymer and 50 mM salt. (a) Short term (5 h) SRNF performance for polar aprotic solvents.

Table 6. For big dyes, retentions do not significantly change with the type of terminating layer, except for RB and AF for [7.5/3.5], where it is slightly less than compared to PAA (-) terminated layers. Strong interactions of negatively charged solutes with the polycation from the membrane layers might densify the membranes [30] and make the membranes less positively charged, which in turn increases the retention and reduces permeance for these layers. The effect of the terminating layer charge is more clear in the retention of small solutes. MO (-) is more rejected by the membranes with PAA (-) terminating layer than by the PAH (+) terminating layers and vice versa for MB (+) retention with membranes prepared at pH 7.5/3.5 (Table 5). For membranes [3.5/3.5], retention of MO (-) is more for a PAH (+) terminating layer than for a PAA (-) terminating layer, but the permeance is also

lower, indicating that the higher retention is the result of more adsorption and more densification.

For all dyes, [7.5/7.5] membranes show relatively high permeances coupled with relatively good rejections compared to the other membranes (Figs. 6–8). The low degree of extrinsic charge compensation is expected to be responsible for this effect. For MO, membrane [7.5/3.5] gives the best performance, likely due to the high negative charge of this layer. Membrane [3.5/3.5] shows only decent performance for the neutral dye BTB. Ionic dyes thus seem to adsorb strongly to this layer, possibly because of a very high degree of extrinsic charge compensation. The main point however, is that by varying the pH, PEM membranes can be prepared with very different performances for different dyes in SRNF. For this system of multilayers, the pH can thus be used as a tuning parameter to optimize the performance for a specific application.

3.3.3. Influence of solvent type and long term stability

To evaluate the membrane performance over long time-scales, filtrations were performed with RB in different solvents such as THF, DMF and ACN. The membranes, coated with 5 bilayers of PAH/PAA at pH [7.5/3.5] were used as they showed the highest RB retention of all tested membranes (Fig. 6(a)). The membranes exhibited very good performance in terms of RB retention (>90%) and permeance for all of these organic solvents (Fig. 9).

The maximum retention of RB is observed in IPA and DMF with a value of 99% and 95% respectively. The permeability was found to be in the following order of ACN > THF > DMF > IPA. This variation in permeation behavior for different solvents may be attributed to solvent-membrane interactions and the physico-chemical properties of the solvents, like molar volume and viscosity. However, it is also important to consider the effect of interactions between membrane-solute, membrane-solvent, and solute-solvent [4]. A part of the viscosity effect we can see in (Fig. 9) where IPA, with the highest viscosity, shows the lowest permeance and ACN, with the lowest viscosity, is the highest. The permeability trend observed in the present study is similar to that observed in
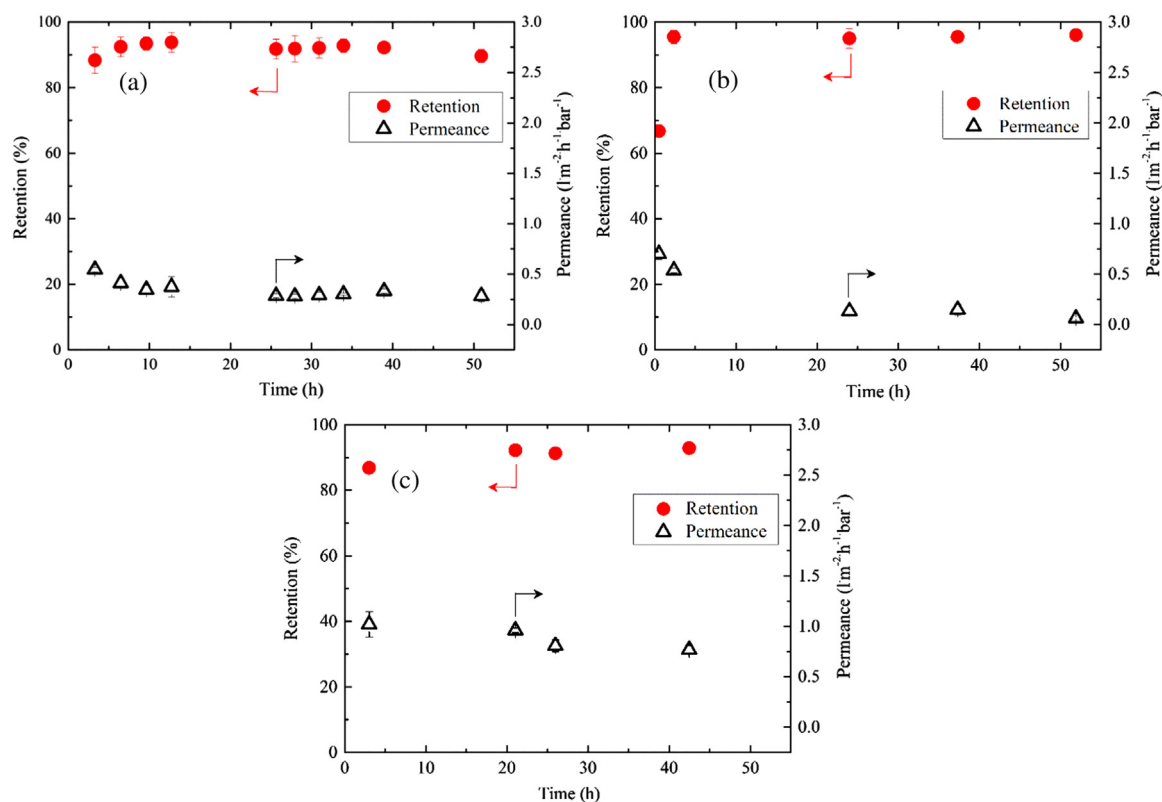
Fig. 10. Long term SRNF performance of [7.5/3.5] membranes for (a) THF and (b) DMF and (c) ACN (tested membranes are with 5 bilayers of PAH/PAA prepared with 0.1 g l^{-1} polymer and 50 mM salt).

previously reported SRNF membranes prepared with 20 bilayers of PDDA/PAA [27].

To further evaluate the long term stability of these multilayered membranes, filtrations were performed for extended periods of time (about 50 h) with RB in different solvents (Fig. 10(a)–(c)) using the membranes [7.5/3.5] prepared with 5 bilayers of PAH/PAA. The membranes show very stable performance in terms of RB retention (> 90%) and permeance as a function of time. In the case of DMF, the permeability decreased significantly in the first hour of filtration indicating strong interactions between DMF and the membrane, or RB and the membrane. The membrane seems to take up RB over time, densify and become less permeable, while the rejection shoots up (Fig. 10(b)).

In our investigation we have focused on pH as a tuning parameter. We stress that the membranes could be further improved by including the ionic strength as a variable. For example, coating at low ionic strength where intrinsic charge compensation between the layers is high and layers are thin [35,43] would lead to less free charges being available for complexation with the dye molecules, and could further reduce fouling of the PEM layers by the dye molecules.

4. Conclusions

This manuscript encompasses the first investigation into the use of weak polyelectrolyte multilayers for SRNF applications. PEM-based SRNF-membranes of the weak polyelectrolytes PAH and PAA were successfully prepared by the LbL method with varying the pH of the coating solutions to tune the charge density and structure of PEs, and thus further control the morphology and performance of the resulting membranes for specific dyes from organic media. Membranes [7.5/7.5] have high a permeance coupled with a relatively good retention performance for all the dyes

because of a low degree of extrinsic charge compensation combined with a dense structure and a thin layer. Membranes prepared under pH conditions [7.5/3.5] and [3.5/3.5] have more free acid and amine groups and were found to be much more susceptible to dye adsorption, leading to a pronounced film densification, a low permeance, but in some case excellent dye retentions. Specifically for the negative dye methyl orange, a PAA terminated [7.5/3.5] membrane was found to have good performance in terms of retention and permeance, likely due to the high negative charge of that multilayer film. The resulting membranes also showed long term (more than 50 h) stable performance for organic solvents, including troublesome aprotic solvents of industrial importance like THF, DMF and ACN. The results of this study provide a versatile and simple way of using pH to tune performance of weak PEs based multilayered SRNF-membranes for specific applications.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2016.04.073.

References

[1] P. Vandezande, L.E.M. Gevers, I.F.J. Vankelecom, Solvent resistant nanofiltration: separating on a molecular level, Chem. Soc. Rev. 37 (2008) 365–405.

[2] A.V. Volkov, D.F. Stamatialis, V.S. Khotimsky, V.V. Volkov, M. Wessling, N.A. Platé, New membrane material for SRNF applications, Desalination 199 (2006) 251–252.

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

[4] D. Bhanushali, D. Bhattacharyya, Advances in solvent-resistant nanofiltration membranes, Ann. N. Y. Acad. Sci. 984 (2003) 159–177.

[5] K. Hendrix, S. Vandoorne, G. Koeckelberghs, I.F.J. Vankelecom, SRNF membranes for edible oil purification: introducing free amines in crosslinked PEEK to increase membrane hydrophilicity, Polymer 55 (2014) 1307–1316.

[6] S. Aerts, A. Buekenhoudt, H. Weyten, L.E.M. Gevers, I.F.J. Vankelecom, P.A. Jacobs, The use of solvent resistant nanofiltration in the recycling of the Co-Jacobsen catalyst in the hydrolytic kinetic resolution (HKR) of epoxides, J. Membr. Sci. 280 (2006) 245–252.

[7] L. Peeva, Jd.S. Burgal, I. Valtcheva, A.G. Livingston, Continuous purification of active pharmaceutical ingredients using multistage organic solvent nanofiltration membrane cascade, Chem. Eng. Sci. 116 (2014) 183–194.

[8] H.J. Zwijnenberg, S.M. Dutczak, M.E. Boerrigter, M.A. Hempenius, M.W.J. Luiten-Olieman, N.E. Benes, M. Wessling, D. Stamatialis, Important factors influencing molecular weight cut-off determination of membranes in organic solvents, J. Membr. Sci. 390–391 (2012) 211–217.

[9] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review: Recent advances and future prospects, Desalination 356 (2015) 226–254.

[10] S. Hermans, H. Mariën, C. Van Goethem, I.F.J. Vankelecom, Recent developments in thin film (nano)composite membranes for solvent resistant nanofiltration, Curr. Opin. Chem. Eng. 8 (2015) 45–54.

[11] P. Silva, S. Han, A.G. Livingston, Solvent transport in organic solvent nanofiltration membranes, J. Membr. Sci. 262 (2005) 49–59.

[12] N. Joseph, P. Ahmadiannamini, R. Hoogenboom, I.F.J. Vankelecom, Layer-by-layer preparation of polyelectrolyte multilayer membranes for separation, Polym. Chem. 5 (2014) 1817–1831.

[13] L. Krasemann, B. Tieke, Selective ion transport across self-assembled alternating multilayers of cationic and anionic polyelectrolytes, langmuir: the ACS, J. Surf. Colloids 16 (1999) 287–290.

[14] W. Jin, A. Toutianoush, B. Tieke, Use of polyelectrolyte layer-by-layer assemblies as nanofiltration and reverse osmosis membranes, langmuir: the ACS, J. Surf. Colloids 19 (2003) 2550–2553.

[15] J. Park, J. Park, S.H. Kim, J. Cho, J. Bang, Desalination membranes from pH-controlled and thermally-crosslinked layer-by-layer assembled multilayers, J. Mater. Chem. 20 (2010) 2085.

[16] S.U. Hong, L. Ouyang, M.L. Bruening, Recovery of phosphate using multilayer polyelectrolyte nanofiltration membranes, J. Membr. Sci. 327 (2009) 2–5.

[17] G. Liu, D.M. Dotzauer, M.L. Bruening, Ion-exchange membranes prepared using layer-by-layer polyelectrolyte deposition, J. Memb. Sci. 354 (2010) 198–205.

[18] C. Magnenet, S. Lakard, C.C. Buron, B. Lakard, Functionalization of organic membranes by polyelectrolyte multilayer assemblies: application to the removal of copper ions from aqueous solutions, J. Colloid Interface Sci. 376 (2012) 202–208.

[19] C. Magnenet, F.E. Jurin, S. Lakard, C.C. Buron, B. Lakard, Polyelectrolyte modification of ultrafiltration membrane for removal of copper ions, Colloids Surf. A: Physicochem. Eng. Asp. 435 (2013) 170–177.

[20] B.W. Stanton, J.J. Harris, M.D. Miller, M.L. Bruening, Ultrathin, multilayered polyelectrolyte films as nanofiltration membranes, langmuir: the ACS, J. Surf. Colloids 19 (2003) 7038–7042.

[21] M.D. Miller, M.L. Bruening, Controlling the nanofiltration properties of multilayer polyelectrolyte membranes through variation of film composition, langmuir: the ACS, J. Surf. Colloids 20 (2004) 11545–11551.

[22] R. Malaisamy, M.L. Bruening, High-flux nanofiltration membranes prepared by adsorption of multilayer polyelectrolyte membranes on polymeric supports, langmuir: the ACS, J. Surf. Colloids 21 (2005) 10587–10592.

[23] X. Liu, M.L. Bruening, Size-selective transport of uncharged solutes through multilayer polyelectrolyte membranes, Chem. Mater. 16 (2003) 351–357.

[24] S.U. Hong, M.D. Miller, M.L. Bruening, Removal of dyes, sugars, and amino acids from NaCl solutions using multilayer polyelectrolyte nanofiltration membranes, Ind. Eng. Chem. Res. 45 (2006) 6284–6288.

[25] L. Ouyang, R. Malaisamy, M.L. Bruening, Multilayer polyelectrolyte films as nanofiltration membranes for separating monovalent and divalent cations, J. Membr. Sci. 310 (2008) 76–84.

[26] L.Y. Ng, A.W. Mohammad, C.Y. Ng, A review on nanofiltration membrane fabrication and modification using polyelectrolytes: effective ways to develop

[27] P. Ahmadiannamini, X. Li, W. Goyens, N. Joseph, B. Meesschaert, I.F.J. Vankelecom, Multilayered polyelectrolyte complex based solvent resistant nanofiltration membranes prepared from weak polyacids, J. Membr. Sci. 394–395 (2012) 98–106.

[28] P. Ahmadiannamini, X. Li, W. Goyens, B. Meesschaert, W. Vanderlinden, S. De Feyter, I.F.J. Vankelecom, Influence of polyanion type and cationic counter ion on the SRNF performance of polyelectrolyte membranes, J. Membr. Sci. 403–404 (2012) 216–226.

[29] P. Ahmadiannamini, X. Li, W. Goyens, B. Meesschaert, I.F.J. Vankelecom, Multilayered PEC nanofiltration membranes based on SPEEK/PDDA for anion separation, J. Membr. Sci. 360 (2010) 250–258.

[30] X. Li, S. De Feyter, D. Chen, S. Aldea, P. Vandezande, F.D. Prez, I.F.J. Vankelecom, Solvent-resistant nanofiltration membranes based on multilayered polyelectrolyte complexes, Chem. Mater. 20 (2008) 3876–3883.

[31] X. Li, W. Goyens, P. Ahmadiannamini, W. Vanderlinden, S. De Feyter, I. Vankelecom, Morphology and performance of solvent-resistant nanofiltration membranes based on multilayered polyelectrolytes: study of preparation conditions, J. Membr. Sci. 358 (2010) 150–157.

[32] N. Joseph, P. Ahmadiannamini, P.S. Jishna, A. Volodin, I.F.J. Vankelecom, 'Upscaling' potential for polyelectrolyte multilayer membranes, J. Membr. Sci. 492 (2015) 271–280.

[33] L. Krasemann, B. Tieke, Selective ion transport across self-assembled alternating multilayers of cationic and anionic polyelectrolytes, langmuir: the ACS, J. Surf. Colloids 16 (2000) 287–290.

[34] J.B. Schlenoff, H. Ly, M. Li, Charge and mass balance in polyelectrolyte multilayers, J. Am. Chem. Soc. 120 (1998) 7626–7634.

[35] J. de Groth, R. Oborný, J. Potreck, K. Nijmeijer, W.M. de Vos, The role of ionic strength and odd–even effects on the properties of polyelectrolyte multilayer nanofiltration membranes, J. Membr. Sci. 475 (2015) 311–319.

[36] S.T. Dubas, J.B. Schlenoff, Polyelectrolyte multilayers containing a weak polyacid: construction and deconstruction, Macromolecules 34 (2001) 3736–3740.

[37] D. Kovacevic, S. van der Burgh, A. de Keizer, M.A. Cohen Stuart, Kinetics of formation and dissolution of weak polyelectrolyte multilayers: role of salt and free polyions, langmuir: the ACS, J. Surf. Colloids 18 (2002) 5607–5612.

[38] S.U. Hong, R. Malaisamy, M.L. Bruening, Optimization of flux and selectivity in Cl^-/SO_4^{2-} separations with multilayer polyelectrolyte membranes, J. Membr. Sci. 283 (2006) 366–372.

[39] D. Yoo, S.S. Shiratori, M.F. Rubner, Controlling bilayer composition and surface wettability of sequentially adsorbed multilayers of weak polyelectrolytes, Macromolecules 31 (1998) 4309–4318.

[40] S.S. Shiratori, M.F. Rubner, pH-dependent thickness behavior of sequentially adsorbed layers of weak polyelectrolytes, Macromolecules 33 (2000) 4213–4219.

[41] V. Izumrudov, E. Kharlampieva, S.A. Sukhishvili, Salt-induced multilayer growth: correlation with phase separation in solution, Macromolecules 37 (2004) 8400–8406.

[42] V. Izumrudov, S.A. Sukhishvili, Ionization-controlled stability of polyelectrolyte multilayers in salt solutions, langmuir: the ACS, J. Surf. Colloids 19 (2003) 5188–5191.

[43] S. Ilyas, J. de Groot, K. Nijmeijer, W.M. de Vos, Multifunctional polyelectrolyte multilayers as nanofiltration membranes and as sacrificial layers for easy membrane cleaning, J. Colloid Interface Sci. 446 (2015) 386–393.

[44] P. Ahmadiannamini, M.L. Bruening, V.V. Tarabara, Sacrificial polyelectrolyte multilayer coatings as an approach to membrane fouling control: disassembly and regeneration mechanisms, J. Membr. Sci. 491 (2015) 149–158.

[45] ⟨http://www.biw.kuleuven.be/cok/membrane2/⟩.

[46] I.M. Smallwood, in: Handbook of Organic Solvent Properties, Butterworth-Heinemann, Oxford, 1996, pp. 73–291.

[47] J. Choi, M.F. Rubner, Influence of the degree of ionization on weak polyelectrolyte multilayer assembly, Macromolecules 38 (2004) 116–124.

[48] G. Zhang, H. Meng, S. Ji, Hydrolysis differences of polyacrylonitrile support membrane and its influences on polyacrylonitrile-based membrane performance, Desalination 242 (2009) 313–324.

[49] P. Marchetti, M.F. Jimenez Solomon, G. Szekely, A.G. Livingston, Molecular separation with organic solvent nanofiltration: a critical review, Chem. Rev. (2014).

[50] D.F. Stamatialis, N. Stafie, K. Buadu, M. Hempenius, M. Wessling, Observations on the permeation performance of solvent resistant nanofiltration membranes, J. Membr. Sci. 279 (2006) 424–433.

[51] L.E.M. Gevers, G. Meyen, K. De Smet, P. Van De Velde, F. Du Prez, I.F.J. Vankelecom, P.A. Jacobs, Physico-chemical interpretation of the SRNF transport mechanism for solutes through dense silicone membranes, J. Membr. Sci. 274 (2006) 173–182.