



# Interfacial polymerization of cyanuric chloride and monomeric amines: pH resistant thin film composite polyamine nanofiltration membranes



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## ABSTRACT

Polyamine nanofiltration membranes have a high stability at extreme pH conditions. In contrast to polyamides, polyamines do not contain the carbonyl group that is susceptible to nucleophilic attack. A previous study has shown that polyamine membranes can be prepared from the interfacial polymerization reaction of polyethylenimine and cyanuric chloride, and that indeed these membranes have a high resistance towards hydrolysis. In the present study, the potential of a variety of other multifunctional amine / cyanuric chloride combinations is screened for the formation of stable polyamine nanofiltration membranes. For several traditional amine precursors it is found that the moderate reactivity of the cyanuric chloride hampers the formation of thin selective membrane films. For two linear amine monomers, both of which are precursors to polyethylenimine, the formation of well-defined, thin, stable, and selective polyamine films is observed. In particular, diethylene triamine is identified as a suitable monomer for the interfacial reaction. The membranes derived from this amine have a higher salt rejection and water permeability as compared to the previously studied polyethylenimine based membranes, and show a comparably high stability at extreme pH conditions. Cross-flow filtration of different salts and neutral solutes at different pH indicates that both steric effects as well as Donnan exclusion effects are relevant for the rejection of solutes. The membrane skin layer is very dense at neutral pH (MWCO of about 200 Da), and becomes slightly more open at extreme alkaline conditions.

## 1. Introduction

Nanofiltration (NF) is a membrane based technique for the separation of small molecules ( $< 1000 \text{ g mol}^{-1}$ ) and multi-valent ions from a liquid [1]. The technique is widely used in wastewater treatment, water purification, water softening, food processing, and bio-separation. Conventional and widely used NF membranes are thin film composite (TFC) polyamides. These membranes offer a high flux and good selectivity, but they are inherently susceptible to hydrolysis at extreme pH conditions. For applications involving extreme pH there are a number of commercially available NF membranes, including the NF series from Microdyn-Nadir, NTR 7450 from Nitto Denko, and the MPF series from Koch Membrane Systems. These membranes have a high hydrolytic resistance, but exhibit a relatively low flux and/or limited molecular weight cut off (MWCO). This makes them less commercially attractive and limits the applicability of nanofiltration in a wide range of potential processes [2].

Recently, the authors have reported the synthesis of polyamine thin film composite membrane based on interfacial polymerization [3]. Specifically, the presented membrane formation does not involve the use of an acyl halide (i.e., trimesoyl chloride) or an isocyanate (i.e., toluene diisocyanate). Instead, cyanuric chloride (CC) has been used as the organic phase reactant to polymerize with the polymeric amine reactant polyethylenimine (PEI) from the aqueous phase. In the interfacial reaction a tight polyamine network, with triazine ring moieties, is formed on a polyethersulfone (PESf) support [3]. This polyamine membrane represents a new class of interfacial polymerization RO/NF membranes that differs from the conventional polyamide or polyurea based membranes. A major distinction is the absence of carbonyl groups that are susceptible to nucleophilic attack. This allows for a superior chemical stability of the polyamine membranes at extreme pH conditions.

In the current study, polyamine membranes with a different molecular structure are prepared, by reacting CC with monomeric

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## Nomenclature

$A_k$	membrane porosity (-)
$k$	Boltzmann constant ( $1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$ )
$K_{i,c}$	hindrance factor for convection (-)
$r_p$	pore radius (m)
$r_i$	solute radius (m)
$r_s$	Stoke radius (m)

$R_{lim}$	limiting solute rejection (-)
$T$	temperature (K)
$\lambda$	ratio of solute to pore radius (-)
$\mu_o$	bulk viscosity (Pa s)
$\mu_p$	solvent pore viscosity (Pa s)
$\Delta P$	effective transmembrane (Pa)
$\Delta x$	effective membrane thickness (m)
$\Phi$	steric partitioning coefficient (-)

amine reactants rather than with the polymeric PEI. The following aromatic or aliphatic amine monomers are included: piperazine (Pip), m-phenylene diamine (MPD), melamine (Mel), ethylene diamine (EDA), diethylene triamine (DETA), and tetraethylene pentamine (TEPA), see Scheme 1. All these amine monomers have previously been used to successfully form TFC polyamide or polyurea membranes, by interfacial polymerization with a polyacyl halide or a poly-isocyanate [4]. In comparison with polyacyl halides and isocyanates, cyanuric chloride is less reactive [5]. This potentially complicates the formation of a thin membrane film by an interfacial polymerization reaction. The film formation potential of the different amine monomers with cyanuric acid is investigated in detail by scanning electron microscopy and (cross-flow) filtration of aqueous solutions of salts or neutral solutes at neutral pH and extreme pH. The pH resistance of the polyamine membranes is examined by an ex-situ prolonged exposure treatment method [3]. Furthermore, cross-flow filtration experiments of charged or non-charged solutes were performed to obtain a deeper insight into the characteristics of mass transport across the membrane. Combined, these analyses may provide important information for prediction of fluxes and rejections [6].

## 2. Experimental section

### 2.1. Chemicals and materials

Anhydrous grade n-hexane (95%), cyanuric chloride (CC, 99% purity), diethylene triamine (DETA, 99%), m-phenylene diamine (MPD,  $\geq 99\%$ ), melamine (Mel, 99%), ethylene diamine (EDA,  $\geq 99\%$ ), piperazine (Pip, 99%), and tetraethylene pentamine (TEPA, technical grade), were acquired from Sigma Aldrich (Germany) and were used as received. Analytical grade ethylene glycol (EG), sodium azide ( $\text{NaN}_3$ ), sodium dodecyl sulfate (SDS), sodium nitrate ( $\text{NaNO}_3$ ), and synthesis quality polyethylene glycol (PEG) with mean molecular weights of 200, 600 and  $1500 \text{ g mol}^{-1}$  were acquired from Merck (Germany). Analytical grade calcium chloride ( $\text{CaCl}_2$ ), sodium chloride ( $\text{NaCl}$ ), and sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) were acquired from Acros Organics (Belgium). Analytical grade potassium chloride (KCl) was obtained from Fluka (Germany). Standard volumetric solutions of 1.0 M hydro-

chloric acid (HCl), 1.0 M nitric acid ( $\text{HNO}_3$ ), 0.25 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and 1.0 M sodium hydroxide (NaOH) were purchased from Fluka (Germany). All aqueous solutions were prepared using Deionized (DI) water.

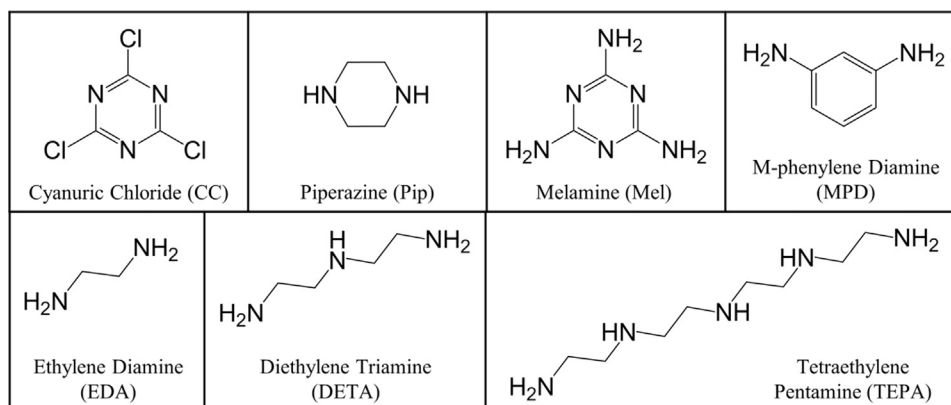
### 2.2. Membrane fabrication

The membrane fabrication method is based on interfacial polymerization and has been previously described in detail [3]. Briefly, hydrophilized polyethersulfone (PESf) ultrafiltration membranes (Microdyn-Nadir, UH 030, Germany) were pre-soaked overnight in DI water to remove contaminants/fillers, treated with a 0.05 wt% SDS solution to increase the materials wettability, impregnated with an aqueous solution containing 1–10 (w/v%) of amine reactant and 1 wt% of NaOH as acid receptor [4], and finally contacted with either 1 or 5 (w/v%) cyanuric chloride (CC) in n-hexane for 120 s. After draining, and rinsing with n-hexane, the membrane was stored in DI water for at least 24 h prior to testing. More information about the membrane fabrication can be found in the Supporting Information. In our prior work [3], the PESf support membrane has been demonstrated to be stable between pH=0–14.

### 2.3. Membrane characterization

#### 2.3.1. Materials characterization

Field emission scanning electron microscope (SEM) micrographs (LEO-1550 Schottky field emission scanning electron microscope, Carl-Zeiss, Germany) were made of virgin membrane samples, without any sputtering. A low accelerating voltage (0.5–1.0 kV) was used to avoid excessive charging. Streaming currents (SurPASS, Anton Paar, Graz, Austria) were measured with 5 mM KCl solution at 25 °C, in duplo. The pH was adjusted with  $\text{HNO}_3$  or NaOH. All membranes were dried before the measurements. Fourier Transform Infrared Spectroscopy (FTIR) analyses were performed (ALPHA FTIR Spectrometer, Bruker Optics Inc, Germany) on dry and clean membranes in Attenuated Total Reflectance (ATR) mode.



Scheme 1. Molecular structures of the reactants used for interfacial polymerization.

**Table 1**  
Diffusivities and stokes radii of the neutral molecules investigated.

	EG	PEG 200	PEG 600	PEG 1500
MW (g mol <sup>-1</sup> )	62	200	600	1500
D <sub>∞</sub> (×10 <sup>-9</sup> m <sup>2</sup> s <sup>-1</sup> )	1.09	0.64	0.38	0.25
r <sub>s</sub> (nm)	0.24	0.37	0.58	0.83

#### 2.4. Dead-end permeation experiments and long term pH stability test

Dead-end permeation experiments at trans-membrane pressures ranging from 5 to 30 bar were performed ambient conditions, in dedicated equipment, using a protocol described in previous work [3]. Salt rejection was measured using aqueous solutions of 2 or 10 g L<sup>-1</sup> of NaCl, Na<sub>2</sub>SO<sub>4</sub>, or CaCl<sub>2</sub>. The salt concentrations of the feed, the permeate, and the retentate were derived from the conductivity (340i conductivity meter, WTW, Germany). Long-term pH stability was assessed from comparing the permeance, the salt rejection, and the MWCO, measured at 10 bar and neutral pH (6.8), before and after ex-situ exposure to 0.1 M HNO<sub>3</sub> or NaOH solutions. After exposure, the samples were rinsed with DI water. Additional information on the dead-end permeation experiments can be found in the Supporting information.

#### 2.5. Cross-flow permeation and in-situ extreme pH filtration experiments

Cross-flow (400 L h<sup>-1</sup>, ≈1.25 m s<sup>-1</sup> superficial velocity) nanofiltration was conducted in three-in-series-membrane cell setup (Supporting Information, Fig. S2). The change in feed concentration during an experiment was always less than 5%. Flux and rejection data were recorded in steady-state operation, which in all cases was achieved within 2 h.

For salt solutions filtration was done in the acidic range (pH=3–4), non-adjusted range (pH=6–7) and the alkaline range (pH=10–11). The pH (measured with an Omega PHB 600 R) was adjusted with an acid with the same anion (e.g. H<sub>2</sub>SO<sub>4</sub> for Na<sub>2</sub>SO<sub>4</sub>), or NaOH as base. The cation concentration was measured with a flame photometer (BWB-XP). The anion concentration was measured by Capillary Zone Electrophoresis (CE Instrument, Hewlett Packard 3DCE 1600, equipped with a diode array detector).

The molecular weight cut off (MWCO) of uncharged solutes was evaluated with an aqueous mixture of ethylene glycol (EG) and polyethylene glycols (PEGs, mean molecular weights 200, 600 and 1,500 g mol<sup>-1</sup>; each fraction 1 g L<sup>-1</sup>). Experiments were performed at five different pH ranges (pH=1 ± 0.05, 4 ± 0.2, 7 ± 0.5, 10 ± 0.2, and 13 ± 0.05), adjusted using H<sub>2</sub>SO<sub>4</sub> or NaOH. Compositions were analyzed by gel permeation chromatography (GPC, Agilent Technologies 1200 series), using a previously developed protocol [7]. To prevent bio-fouling, sodium azide (NaN<sub>3</sub>, 0.05 g L<sup>-1</sup>) was added to the eluent and the samples. The Supporting Information contains more details about the cross flow permeation experiments.

#### 2.6. Donnan Steric Partitioning Model (DSPM)

A number of models are available to describe mass transfer through an NF membrane [8]. Among them, modelling of solute transport based on the extended Nernst-Planck equation, accounting for diffusion, convection and electromigration, is widely applied [9]. Bowen and Mohammad further developed the Nernst-Planck equation into the Donnan Steric Pore Model (DSPM) [10]. The details of the model derivation are included in the Supporting Information. Briefly, the DSPM assumes a fully developed flow velocity inside the pores in which Hagen-Poiseuille flow behavior can be applicable. Hence, the flow

velocity in the membrane pores is defined by:

$$v = \frac{r_p^2 \Delta P}{8\mu_p (\Delta x/A_k)} \quad (1)$$

where  $r_p$  is the pore radius,  $\mu_p$  is the solvent pore viscosity,  $\Delta x/A_k$  is the ratio of effective membrane thickness to membrane porosity,  $\Delta P$  is the effective transmembrane pressure. For a system in which convection dominates the mass transfer of solute, the rejection of solute can be obtained by:

$$R_{lim} = 1 - K_{i,c} \Phi \quad (2)$$

where  $R_{lim}$  is the limiting solute rejection,  $K_{i,c}$  is the hindrance factor for convection and  $\Phi$  is the steric partitioning coefficient.  $K_{i,c}$  and  $\Phi$  are functions of  $\lambda$ , i.e., the ratio of solute to pore radius:

$$\lambda = \frac{r_i}{r_p} \quad (3)$$

$$K_{i,c} = (2 - \Phi)(1 + 0.054\lambda - 0.988\lambda^2 + 0.441\lambda^3) \quad (4)$$

$$\Phi = (1 - \lambda)^2 \quad (5)$$

#### 2.7. Stokes radius

Several empirical correlations are available to estimate the molecular size of small solutes. Despite the differences of the coefficients in the equations, these empirical logarithmic correlations are in similar form and the differences in estimation are negligible. The Stokes radius,  $r_s$ , which is derived from the hydrodynamic volume of a molecule, is the most widely used. For neutral molecules, the Stokes radius  $r_s$  (in nm) is estimated by Eq. (6), which was previously used by Bowen and Mohammad for nanofiltration transport modelling based on steric-hindrance [10]. The empirical relation based on the molecular weight ( $MW$ , in g mol<sup>-1</sup>) is as follows [10]:

$$\log(r_s) = -1.3363 + 0.395 \log(MW) \quad (6)$$

The diffusivity can be calculated with the Stokes-Einstein equation:

$$D_\infty = \frac{kT}{6r_s \pi \mu_0} \quad (7)$$

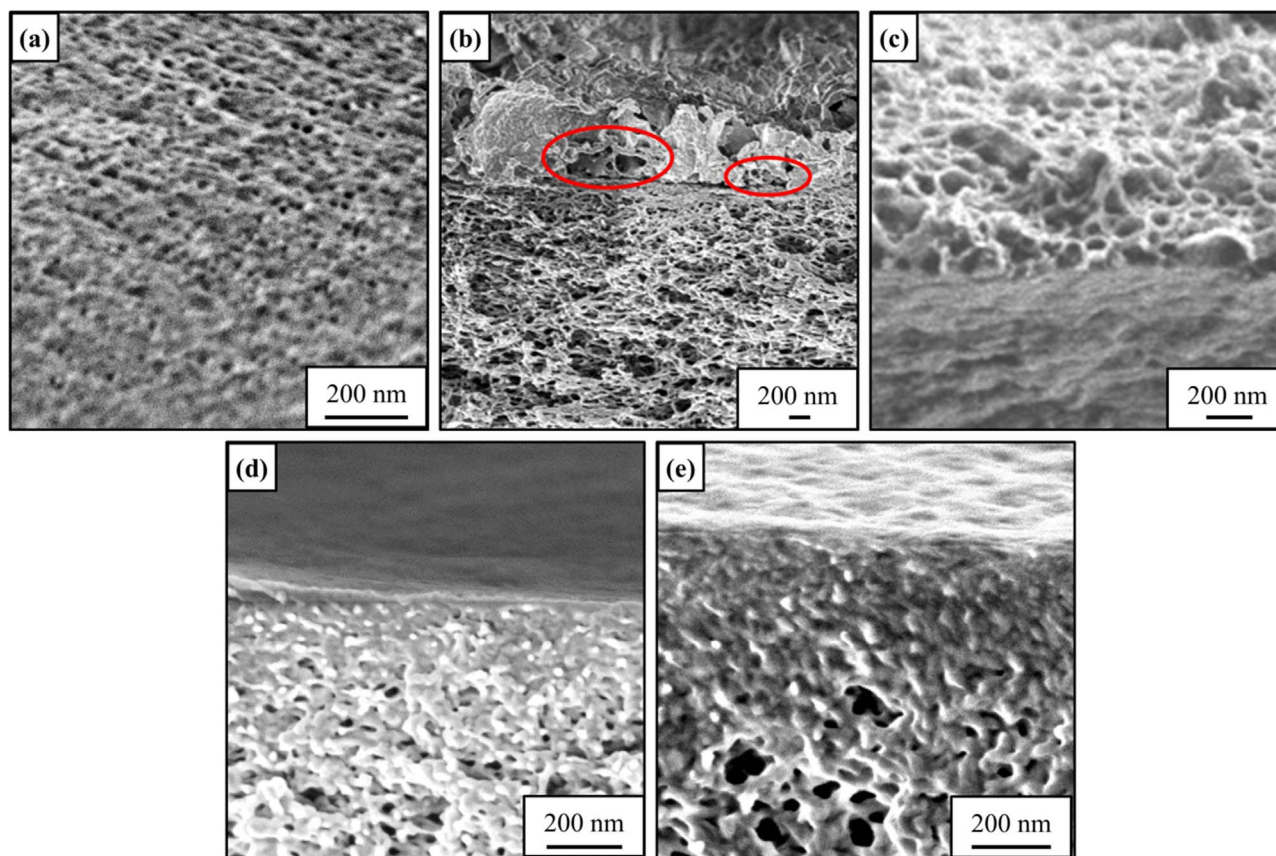
where  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $\mu_0$  is the bulk viscosity.

For DSPM fitting, the diffusivity and Stokes radii of the EG and PEG molecules are determined using correlations based on Eqs. 6 and 7 (see Table 1). Due to the low concentration of the PEG solutions, the difference of bulk viscosity from water is negligible, i.e., 1.002 mPa s at 20 °C.

**Table 2**

Dead-end permeances and NaCl rejections (2.0 g L<sup>-1</sup> NaCl, 10 bar) of the PESf support and membranes made by the interfacial polymerization of several different amines with CC. Two membrane samples for each combination of reactant were prepared and each sample was measured twice. The values below are the average of four measurements with standard deviation.

Membrane	Permeance (L m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	NaCl rejection (%)
PESf support	32.4 ± 1.6	0.9 ± 1.0
PEI / CC <sup>3</sup>	0.9 ± 0.1	62.0 ± 3.5
TEPA / CC	1.0 ± 0.1	61.5 ± 2.4
DETA / CC	1.5 ± 0.1	85.2 ± 3.0
DETA / CC (without NaOH)	0.4 ± 0.1	57.4 ± 6.2
EDA / CC	13.2 ± 1.1	8.9 ± 1.1
MeI / CC	20.3 ± 0.9	1.4 ± 0.8
MPD / CC	11.3 ± 0.9	13.5 ± 2.3
Pip / CC	20.5 ± 2.0	2.1 ± 1.3



**Fig. 1.** In (b), the circled area indicates the formed EDA/CC structure that is not totally dense or continuous. SEM micrographs showing the topography of the bare PESf support top surface (a), and the cross-sectional morphology of the membranes formed with EDA/CC (b), DETA/CC (c), TEPA/CC (d) and PEI/CC (e, reprinted with permission from previous work [3]).

### 3. Results and discussion

#### 3.1. Interfacial polymerization of cyanuric chloride and several amine monomers

The formation of a thin polymer layer by the interfacial reaction between CC and different monomeric amines is strongly affected by the physico-chemical characteristics of the amine monomers. This is evident from the large differences in permeance and salt rejection of the membranes presented in Table 2.

Table 2 shows that the membranes formed from the reaction between CC and Pip, MPD, EDA, and Mel, exhibit very low salt rejections, and permeances that are only slightly lower than those of the bare PESf support. Also for very high concentrations (10%) of Pip, MPD, and EDA, low salt rejections are observed. The low solubility of Mel prevented such a check. In contrast, the membranes formed from reactions with DETA, TEPA, or PEI show NaCl rejections > 55%, and permeances that are over 20 times lower than those of the bare PESf support. These results can be explained by the different morphologies of the membranes (Fig. 1). The reaction between EDA and CC results in a very rough, open, and discontinuous layer on top of the porous support (Fig. 1b). The formed layer is not sufficiently tight to restrict the transport of reactant, allowing the polymerization reaction to proceed. This resulted in the formation of a EDA/CC layer that is ~800 nm thick. The reactions between CC and Pip, MPD, or Mel yield similar non-continuous layers, with different degrees of surface roughness. In contrast, by reacting CC with PEI; a large polymeric molecule that has many functional amine groups (Fig. 1e), the formed membrane has a continuous dense film with very low degree of roughness. This skin layer dominates the salt rejection. The reaction between the biggest monomeric polyamine reactant, TEPA, and CC yield a layer

with a morphology that is similar to that of the PEI/CC layer (Fig. 1d). The membrane formed by DETA/CC (Fig. 1c) combines the morphological features of the previous examples. This DETA/CC layer is continuous and fully covers the PESf support. The rough structure complicates estimating the thickness of DETA/CC layer. It is estimated to be ~200 nm, which is thinner than the EDA/CC layer. It exhibits a distinctive rough surface and discrete cavities. This structure is different from, for example, the ridge-and-valley surface of the common MPD/TMC membranes [11].

The surface structure of the skin layer is strongly dependent on the kinetics and mechanisms of the interfacial reaction [12]. TMC is an aromatic polyfunctional acyl halide that is very reactive; all three functional groups can be coupled to an amine under aqueous conditions (Schotten-Baumann reaction conditions). This enables the formation of tight skin layers via the interfacial polymerizations of TMC with many amine reactants. The high reactivity of the chloride functional groups of TMC is due to presence of the strongly electronegative chloride and oxygen that make the carbon in the carbonyl group very susceptible to nucleophilic attack. In comparison, the chloride groups in CC are directly connected to the triazine ring, resulting in less fast nucleophilic substitution reactions with amines. The nucleophilic substitution becomes progressively slower for the second and third chlorine [13]. The distinct reactivity differences for TMC and CC are also evident from their hydrolysis in water at ambient conditions, where all three functional groups of TMC are hydrolyzed while only mono-nucleophilic substitution occurs in CC [5,14].

The low reactivities of the second and third functional groups of CC explain that its polymerization reaction with bifunctional amines does not yield well-defined thin macromolecular films that are sufficiently tight and continuous to effectively hinder the transport of salts. EDA is a small ( $M_w=60$  Da) linear nucleophilicity aliphatic diamine that is

expected to have relatively high reactivity diffusivity, but with CC it forms a skin layer is not sufficiently tight for salt rejection. The formation of a thin film that can reject salts apparently requires that CC reacts with an amine that is at least tri-functional; in this study we therefore focus on Mel, DETA, TEPA, and PEI. Of these amines, melamine gives the worst results. Compared to DETA and TEPA, melamine is less reactive and has a much lower solubility in water at room temperature ( $< 1 \text{ g L}^{-1}$ ) [15]. In the case of PEI, and its precursors DETA and TEPA, membranes are formed that exhibit NF properties (permeance  $\sim 1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ , NaCl rejection  $> 60\%$ ). The best results, in terms of permeance and selectivity, are obtained with DETA ( $1.5 \pm 0.1 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$  and  $85.2 \pm 3.0\%$ , respectively). In comparison to TEPA and PEI, DETA is the shortest molecule and has the highest ratio of primary over secondary amine groups (2:1). As a consequence, the highest amount of reacted CC is expected in the polymer formed with DETA.

The data in Table 2 confirm the importance of the presence of acid acceptor for the formation of a dense and selective film [4]. When no sodium hydroxide is added to the aqueous phase the membrane has lower permeance and selectivity. This is because the reaction between the amine functional groups with cyanuric chloride can yield protons and chloride ions. The protons can protonate the amine groups and reduce their reactivity with cyanuric chloride. The reduced reactivity causes the formed polyamine layer to be less tight / dense. In addition, due to the rather loose structure formed, further film thickening is possible since the reactants can transport through the formed membrane relatively easily. Adding an acid acceptor can prevent the protonation of the reactive amine groups, facilitating a fast reaction that results in a tighter and thinner polyamine layer. Consequently, addition of an acid acceptor can simultaneously result in a higher salt rejection as well as a higher permeance.

Because of the superior performance of the DETA/CC membranes, a more elaborate characterization is conducted with membranes derived from this reaction pair, with emphasis on stability and separation performance in extreme pH conditions.

### 3.2. Surface properties of DETA/CC membranes

Although most of the aqueous phase reactants with at least three amine groups can instantaneously react with CC to form a salt separating skin layer, their morphology can differ significantly. For example, our previous study has shown that the use of PEI macromolecules will form a rather smooth skin layer, and the growth of the skin layer appears to be directed inwards into the support layer [3]. This is because the diffusion of bulky PEI molecules is hindered by the already formed PEI/CC skin layer, whereas the smaller CC molecules can more readily diffuse through the skin layer.

In contrast, the membrane formed by an interfacial reaction involving smaller monomeric amines, for example DETA (Fig. 1c), has a rather rough surface. This is in line with the generally accepted hypothesis that under regular conditions the polymerization reaction proceeds in the organic phase and is amine-reactant-diffusion controlled in the formed IP film layer [16]. The rough surface texture has been attributed to swelling phenomena that occur during polymerization [17,18]. Swelling of the film causes the film to rise and fold, while the polymerization continues. In addition, for the resulting irregular film the growth rate will spatially vary, due to fluctuations of the local variables such as the reactant concentration and the local pH. Eventually, the rough surface texture becomes permanent. Recently, it has been suggested that the surface roughness of IP films can be a result of heat effects arising from the exothermic polymerization reaction, inducing instabilities through buoyancy driven by Rayleigh-Bénard convection [19]. However, such effects are not expected at the very low Rayleigh numbers associated with interfacial polymerization reactions. Moreover, the surface features of supported films made via interfacial polymerization are generally insensitive to a horizontal or

vertical alignment of the support during the reaction, and hence insensitive to buoyancy effects.

The ATR FTIR data confirm the formation of the DETA/CC polyamine layer on the PESf support (Fig. 2). The IR spectrum of DETA/CC membrane is very similar to the previously studied PEI/CC membrane [3]. This is expected since PEI is a polymeric arrangement of DETA monomers. The formed DETA/CC layer is essentially a crosslinked polyamine network that consists of amine, alkyl, and triazine ring moieties. It does not exhibit the distinctive peak for carbonyl groups that are typical for the conventional polyamide NF/RO membranes. The spectrum of the DETA/CC TFC membrane is only slightly different from that of the PESf support. The separating layer has peaks that correspond to the amine groups and triazine rings, Particularly, the peak  $1418 \text{ cm}^{-1}$  corresponds to the C=N in the triazine ring, and is absent in the spectrum of PESf support.

The surface charge of NF and RO membranes can induce electrostatic attraction/repulsion of charged species, and thus has an influential role on the selective mass transport of charged species. As shown in Fig. 3, the pristine PESf support membrane is negatively charged in the full pH range investigated. This is due to the high density of sulfonic groups [3]. After interfacial polymerization, the DETA/CC dense layer exhibits a positive zeta potential at acidic conditions and a negative zeta potential at alkaline conditions. The isoelectric point falls between  $\text{pH}=7.0$  to  $8.0$ . Conventional TFC NF membranes, for example poly-piperazin-amide [20], generally have a lower isoelectric point, in the range  $\text{pH}=3-4$ . This low IEP is the results of the hydrolysis of unreacted acyl halide groups into hydroxyl or carboxylic groups on the membrane surface. In contrast, the DETA/CC and PEI/CC membranes contain large amounts of secondary and tertiary amines, and triazine rings with nitrogen atoms, that can be protonated and form positive groups. Therefore, the DETA/CC membrane has a positive charge in the acidic range. In the alkaline range, the negative charges can be attributed to the unreacted chloride groups from the CC. The unreacted chloride groups can hydrolyse at higher pH [5] and thus become negatively charged.

### 3.3. Dead-end filtration test of the DETA/CC membranes

#### 3.3.1. Filtration with different salt types

The separation characteristics of DETA/CC membranes were determined in dead-end stirred cells with a variety of salts at different concentrations. The pH of the solutions was not adjusted, in the range

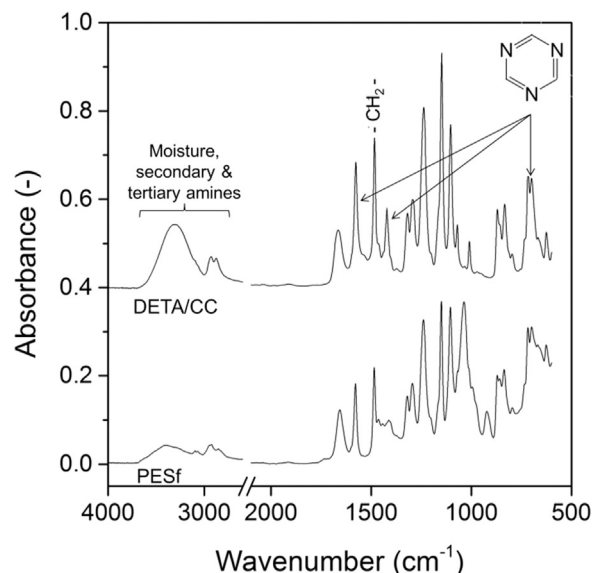
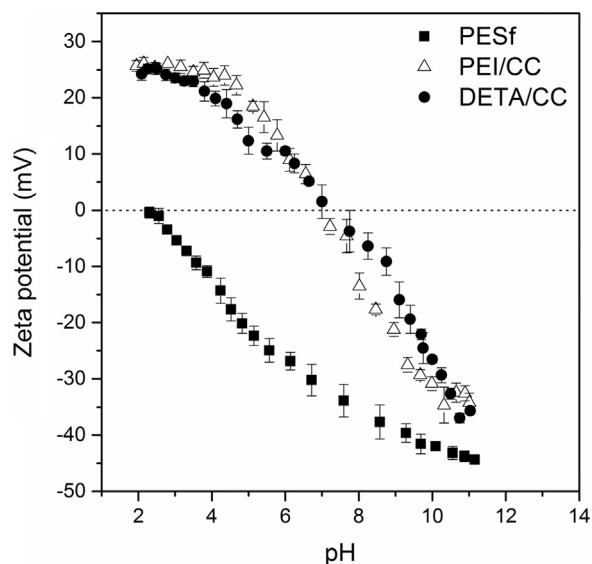
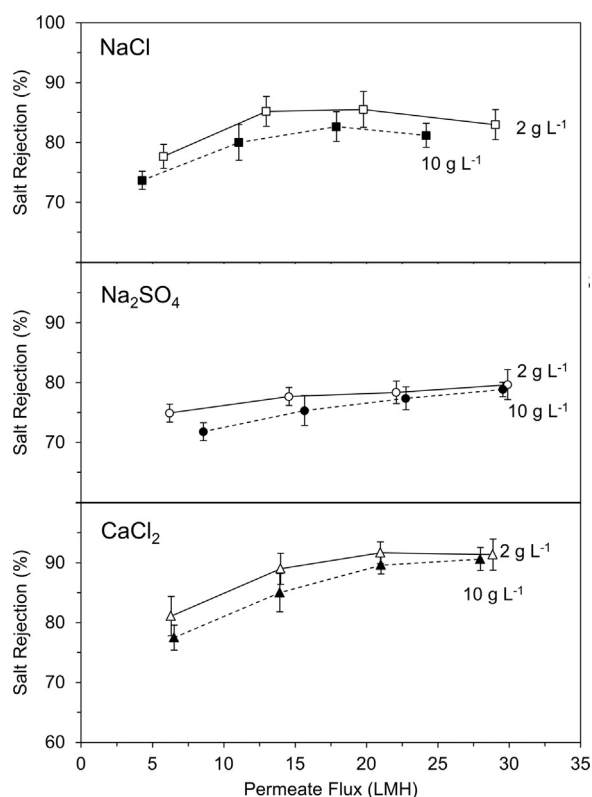


Fig. 2. Fourier transform infrared spectroscopy (FTIR) of the bare PESf support and DETA/CC membrane.



**Fig. 3.** Zeta potential profiles of PESf support and DETA/CC membranes. Data for PESf and PEI/CC are reproduced with permission from previous work [3].



**Fig. 4.** The permeate flux and rejection of various salts for the DETA/CC membranes. The dead-end filtration was performed using stirred cells at 6, 10, 15 and 20 bar for 2 g L<sup>-1</sup> solution; and 13, 20, 25, 30 bar for 10 g L<sup>-1</sup> solutions.

between pH=6.0 and 7.0. The tests were performed at four different values of the feed pressure (for 2 g L<sup>-1</sup>:  $p_{feed}$ =6, 10, 15, and 20 bar, for 10 g L<sup>-1</sup> and 13, 20, 25 and 30 bar). For the higher concentration a higher feed pressure is required to overcome the higher osmotic pressure difference.

In Fig. 4 the salt rejection is depicted a function of the permeate flux, for different salts. In general a positive correlation between rejection and flux is observed in the lower flux regime. This positive correlation is attributed to the increase in water transport with increasing pressure gradient (driving force). This increasing driving

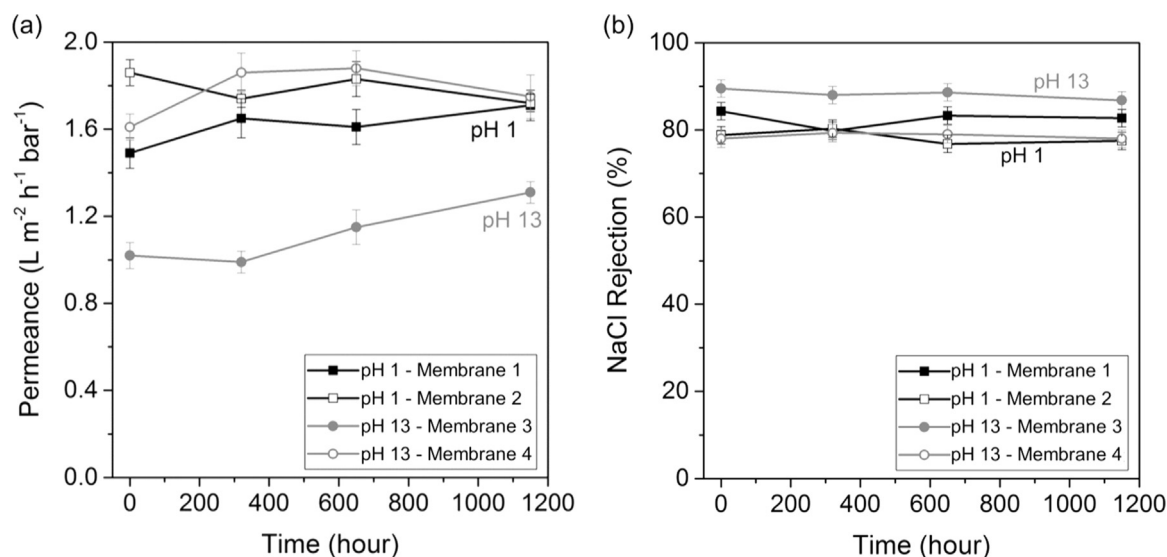
force increases the relative contribution of convection over diffusion for water and salt transport. When comparing the different salts, the retentions are of similar order of magnitude at neutral pH and show the following order  $R_{CaCl_2} > R_{NaCl} > R_{Na_2SO_4}$ . This implies the contribution of charge effects to the separation is relatively small at near to neutral pH and the membrane is expected to be slightly positively charged. This is in agreement with the zeta-potential data in Fig. 3, where the IEP of the DETA/CC membrane is observed in the pH range of the retention measurements. Relatively low charge density of the membrane at near to neutral pH can be confirmed from the relatively small change in NaCl retention when the ionic strength is significantly changed, i.e., when comparing the 2 g L<sup>-1</sup> with the 10 g L<sup>-1</sup> data. A stronger reduction in NaCl rejection is to be expected when Donnan exclusion has a very strong impact on retention behavior as is seen for polyamide based interfacial polymerization membranes such as Desal DK and NF [21]. The presumption that size exclusion also plays a role in the separation is further verified by the MWCO measurements and DSPM modelling in Section 3.4.2.

### 3.3.2. Long term pH stability test

In our previous work [3], thin film composite PEI/CC membranes have demonstrated high pH stability, as compared to the conventional and commercially available TMC based polyamide NF/RO membranes. The performance of those membranes persists after exposure to pH=1 or pH=13 solutions for more than 5 weeks. The high pH stability is attributed to the absence of the carbonyl group in the PEI/CC membranes. This carbonyl group is also absent in the DETA/CC membranes, fabricated in the current work. Fig. 5 illustrates the permeance and NaCl rejection of DETA/CC membranes, after several exposures to acidic (pH=1) and alkaline (pH=13) conditions. At each pH, two separately prepared DETA/CC membrane samples were tested (four membranes in total). Similar to what has been observed for PEI/CC membranes, the exposure to extreme pH has limited effect on the permeance and salt rejection. All membranes have similar permeance even after multiple long term exposure to acidic or alkaline solutions. After treatment at pH=13 both membranes show a slight overall increase in permeance. In particular, the membrane with the lowest starting permeance (membrane 3), has a permeance increase of about 25% (relative) after more than six weeks of treatment without NaCl rejection loss. This increase in permeance after exposure to the alkaline solution is most likely due to the hydrolysis of the unreacted chloride groups from CC during interfacial polymerization. This will increase the hydrophilicity of the membrane and subsequently the permeance. The salt rejection of all four membranes stayed nearly constant after each treatment interval. Despite the small fluctuations observed in the measurements, it is reasonable to conclude that exposure of the DETA/CC polyamine membranes to extreme pH treatment has negligible effects on the membrane.

### 3.4. In-situ extreme pH filtration using DETA/CC membranes

Section 3.3.2 demonstrates that the DETA/CC membranes keep their integrity after harsh pH treatments and do not undergo irreversible chemical degradation in the time period investigated. However, at the extreme pH values reversible changes in membrane properties can be anticipated. The most obvious example of such properties is the surface charge, as is apparent from Fig. 3, but in association with the increasing electrostatic effects the morphology of the free volume in the polymer can also be affected [21,22]. For membrane processes involving extreme pH it is imperative to investigate the separation performance of the membranes at the relevant pH. The pseudo-steady-state achieved by stirred dead-end filtration is not suitable for this in-situ investigation due to the build-up of rejected solutes on the feed side over time. Therefore, these experiments were performed in cross-flow configuration to ensure a good steady-state in continuous mode.



**Fig. 5.** Long term pH stability of DETA/TMC membranes after prolonged ex-situ exposure to 0.1 M HNO<sub>3</sub> or 0.1 M NaOH solutions. Feed: 2 g L<sup>-1</sup> NaCl, pH is not adjusted (pH=6.8). Transmembrane pressure 10 bar. (a) water permeance and (b) NaCl rejection.

### 3.4.1. Salt rejection

Three types of salt, i.e., NaCl, Na<sub>2</sub>SO<sub>4</sub> and CaCl<sub>2</sub>, were studied individually by cross-flow filtration. Two different feed concentrations, i.e. 2 and 10 g L<sup>-1</sup> were tested for each salt type. To adjust the pH of each solution, bases or acids with corresponding ion types were used to prevent mixing ions. For example, the acidity of NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions were achieved by addition of hydrochloric acid and sulfuric acid, respectively. By testing the conductivity and pH of permeate every 15 min, all experiments were found to reach steady-state within an hour. Samples were collected at the second, third and fourth hour.

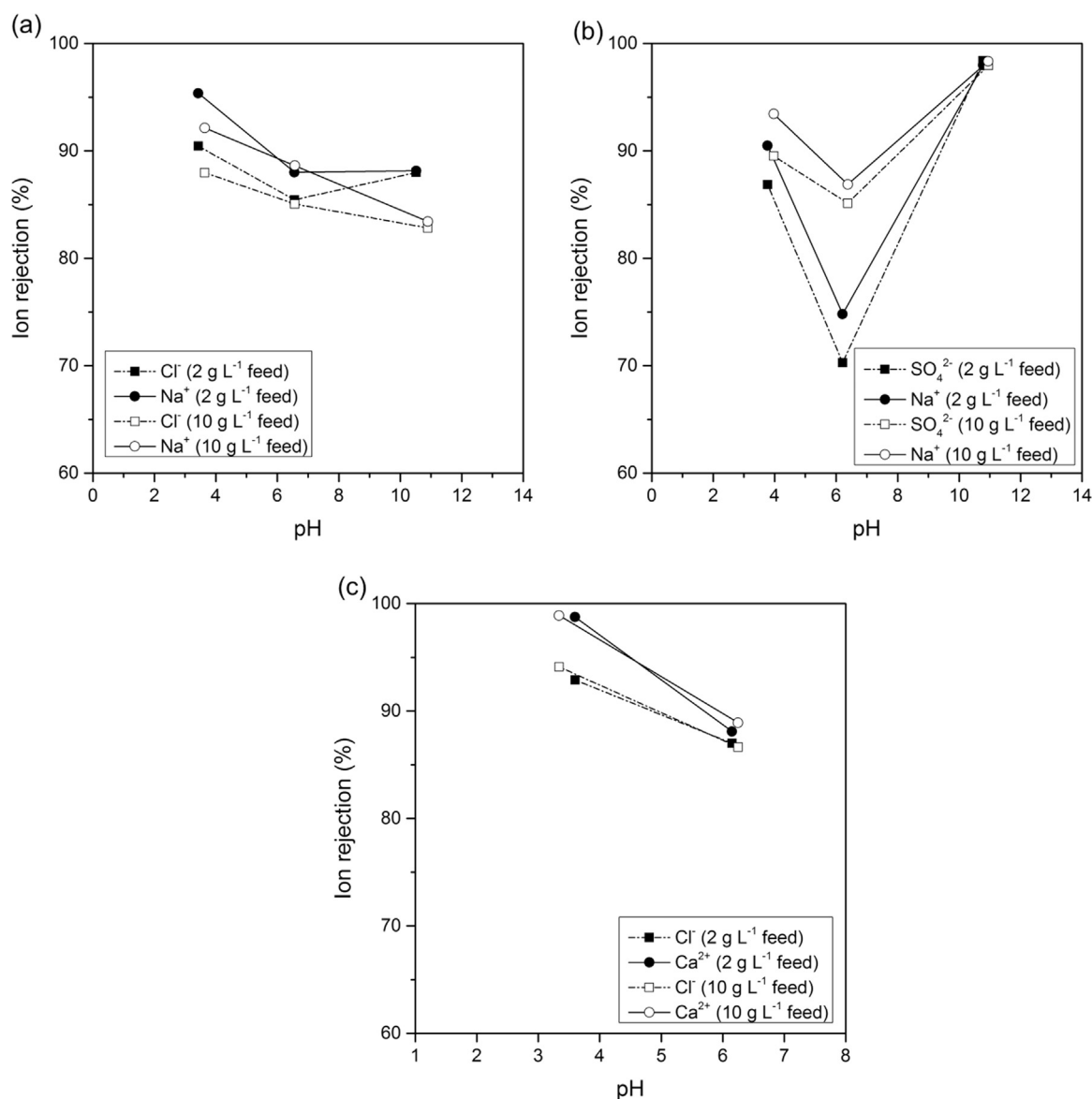
Fig. 6 depicts the ion rejection in each experiment, at different pH conditions, namely the acidic condition (pH=3–4), non-adjusted range (pH=6–7) and the alkaline range (pH=10–11). For CaCl<sub>2</sub> solutions nanofiltration at high pH was not possible due to the low solubility of Ca(OH)<sub>2</sub>.

For the experiments in the acidic or non-adjusted pH range, the pH of the permeate samples were significantly lower than for the feed. This was observed for all different salt types. For example, when 10 g L<sup>-1</sup> NaCl was filtered at pH=3.13, the pH of the permeate was 2.95. This can be attributed to a negative rejection of protons [23], a common behavior for a more mobile co-ion in a mixture of electrolytes. For instance, the 10 g L<sup>-1</sup> NaCl solution at pH=3.13 consists of Na<sup>+</sup>, H<sup>+</sup>, Cl<sup>-</sup> and OH<sup>-</sup> ions. The small protons have a higher mobility than the Na<sup>+</sup> ion. When the concentration ratio of the more permeable ion (H<sup>+</sup>) to the less permeable ion (Na<sup>+</sup>) is low, negative rejection of the more permeable ion is possible. In our study, the concentration ratio of the proton to the sodium ion (taking all NaCl solutions used into account) is between 10<sup>-5</sup> and 0.20, enabling a negative rejection of protons. The zero current condition requires that the difference between the total transport of negative - and positive charges is zero. The combined transport of Na<sup>+</sup> and H<sup>+</sup> implies that the retention of the Cl<sup>-</sup> will be lower than that of Na<sup>+</sup>, which is indeed observed in the low pH range. These effects are much less pronounced for Cl<sup>-</sup> and OH<sup>-</sup>, because the difference in their mobility is smaller. These anions have, for instance, a similar hydrated radius in the range 0.30–0.33 nm [23].

Increasing the pH from practically neutral (6) to 11 results in a change in zeta potential of the membranes from just in excess of zero (slightly positive) to negative, implying a more significant contribution of charge effects (Donnan exclusion) to the retention of salts at high pH. A higher Donnan exclusion at high pH is caused by the more negatively charged membrane surface leading to repulsion of the anion and thus lower entrance rates of the anions into the membrane, and the higher (negative) charge density within the membrane pores, leading to

more friction between the anions and the (negatively charged) membrane pore surface [24]. Yet, for nanofiltration of the 2 g L<sup>-1</sup> NaCl solution, the NaCl retentions at neutral and high pH appear to be similar. This means that the expected higher Donnan exclusion effect at high pH (as a consequence of the higher zeta potential of the membrane) should be counteracted by a lower size exclusion effect for instance due to electrostatically enhanced swelling of the material. This explanation is in agreement with reduced EG and PEG retentions at higher pH and pore radius calculations as reported in Section 3.4.2. For nanofiltration of the 10 g L<sup>-1</sup> NaCl solution, the NaCl retention at high pH is even slightly lower than at neutral conditions. This means that the change in size exclusion more than off-sets the increased overall Donnan exclusion effect at higher pH. An explanation for this observation is that at higher NaCl concentrations the overall Donnan exclusion effects usually plays a less important role as explained earlier. Furthermore, for negatively charged membranes the charge density inside the separating layer of the membrane (the membrane pores) increases with increasing mole fraction of the chloride ions in the pores as has for instance been shown by Straatsma et al. [25]. For negatively charged nanofiltration membranes several authors describe the charge concentration  $Q_m$  in the membrane by a Freundlich type adsorption  $Q_m = Q_0 (x_{Cl^-})^{K_s}$  (where  $Q_0$  is the charge concentration per pore volume model constant and  $x_{Cl^-}$  is the mole fraction of chloride ions in the membrane pores) with reported values of  $K_s$  between 0.16 and 1 [21,24]. Thus, despite the fact that the charge density of the membrane increases when higher chloride concentrations are present inside the membrane pore, the Donnan exclusion is still smaller than that for lower chloride concentrations in the pore, since the increase in ionic strength of the solution is higher than the increase in charge concentration of the membrane as a consequence of the  $K_s$  value being 1 or lower. For the (at high pH) negatively charged DETA/CC membrane similar effects can be expected. This means that due to the adsorption of ions onto the membrane surface the charge density for a 10 g L<sup>-1</sup> NaCl solution is most likely higher than for a 2 g L<sup>-1</sup> solution. This implies that due to electrostatic effects the membrane will most likely be more swollen for the 10 g L<sup>-1</sup> solution, leading to reduced size exclusion effects and thus lower chloride retention.

For Na<sub>2</sub>SO<sub>4</sub> a higher rejection is observed at high pH. This change in rejection for the divalent anion is ascribed to the change in membrane charge from slightly positively at pH=6 to negative membrane charge at pH=11. This leads to a shift from attraction of the divalent anion at pH=6 to (strong) repulsion of the di-valent anion by the negatively charged membrane surface at pH=11, preventing the sulfate



**Fig. 6.** Ion rejections of DETA/CC membranes as a function of pH. The experiments were carried out with (a) NaCl, (b) Na<sub>2</sub>SO<sub>4</sub> and (c) CaCl<sub>2</sub> single salt solutions, respectively. The operating pressure was maintained at 10 and 14 bar for 2 and 10 g L<sup>-1</sup> salt concentrations, respectively.

ions from entering the separating layer. This effect is more important for di-valent anions (sulfate) than for monovalent anions (chloride). Thus, there will be a higher sulfate mole fraction in the membrane pores at (almost) neutral pH than at high pH. This will affect both Donnan exclusion as well as size exclusion in such a way that the sulfate retention will be higher at high pH. Further explanation of these phenomena is outside of the scope of this study, but it is recommended to perform ellipsometry measurements to further elucidate the observed phenomena.

In Fig. 6b, an outlying case was observed for Na<sub>2</sub>SO<sub>4</sub> filtration at neutral pH. For the high concentration salt solution (10 g L<sup>-1</sup>) a higher rejection is observed, as compared to the lower concentration (2 g L<sup>-1</sup>) and the dead-end experiments in Fig. 4. Previously, higher rejection of MgCl<sub>2</sub> or CaCl<sub>2</sub> by a negatively charged polyamide membrane at increased ionic strength have been reported [25]. Such behavior can be due to complex interactions between multivalent ions and the membrane surface, in particular at high salt concentration. In our case of Na<sub>2</sub>SO<sub>4</sub> filtration, the binding/adsorption of SO<sub>4</sub><sup>2-</sup> to the membrane surface may have induced a switch from a positive surface charge to a negative one. Interestingly, this higher rejection at higher concentration is not observed in Fig. 4 for dead-end filtration. In the dead-end

filtration, the increase in salt concentration of the feed in time complicates an accurate calculation in retention.

### 3.4.2. Membrane MWCO and Donnan Steric Pore Model (DSPM) modelling

The filtration of non-charged solutes at different pH was investigated by using ethylene glycol EG and polyethylene glycol PEGs solutes. For non-charged solutes, the separation mechanism is solely size exclusion. The aim is to relate the pH-induced changes in membrane performance to pH-induced changes in the structural properties of the membranes.

**Table 3**

MWCO of one of the tested DETA/CC membranes operated in series during the cross-flow filtration. The error presented was associated error MWCO reading from sieving curves. Cross-flow filtration was performed at 10 bar with a cross-flow velocity 1.25 m s<sup>-1</sup>. Samples were collected every hour to confirm steady-state.

pH	1.3 ± 0.2	4.1 ± 0.1	6.8 ± 0.3	10.2 ± 0.2	13.1 ± 0.1
MWCO (Da)	220 ± 30	220 ± 20	200 ± 10	240 ± 10	330 ± 20

The cross-flow filtration of non-charged solutes was performed at different pH values. The sieving curve of the membrane at each pH was plotted to determine the MWCO. Table 3 demonstrates the change in MWCO at different pH for one of the membranes tested (the others showed similar trends). When the pH is approximately neutral, the DETA/CC membrane is rather tight with a MWCO of 200 Da. This is much tighter than the previously reported PEI/CC polyamine membrane, which has a MWCO of about 500 Da [3]. This explains the higher salt rejection at neutral pH by DETA/CC membranes compared to the PEI/CC membranes. Reducing the pH to the lower range does not appear to affect the MWCO substantially. At a pH of 1.3 only a slight increase of 20 Da in MWCO is found as compared to the MWCO at neutral pH, but given the error in the absolute values, this change cannot be considered significant. However, in the high pH range a higher value of the MWCO is observed (330 Da, still a rather tight NF membrane). It has been previously reported by other researchers that the rejection of neutral solutes, i.e., glucose and PEGs, decreases as the pH increases to 12 [20]. A well-recognized explanation for this is that the membrane pore size increases as a result of membrane swelling at alkaline conditions [1].

The Donnan-Steric Partitioning Model can be used to quantify the changes in the structural properties of the membranes, based on the rejection of solutes in a range of operating conditions (in particular the trans membrane pressure difference). Here, DSPM fitting is performed for EG and PEG 200. For larger solute molecules the retention was more or less constant (> 95%) over the entire pressure range. The rejection of EG and PEG 200 as a function of pressure, at different pH, is depicted in Fig. 7. The dots are experimental data, while the lines represent the best fits obtained with the DSPM theory. Two parameters are fitted: the membrane pore radius, and the ratio of membrane thickness to porosity. The results are listed in Table 4. For EG and PEG 200 similar trends are observed, the differences can reasonable be attributed to for instance the errors from the fitting and the estimation of solute size by empirical correlations.

As can be seen in Fig. 7a and b, both EG and PEG 200 rejections are the highest at neutral conditions and the lowest at high pH. The DSPM translates this into a pore radius increase following the order of pH=7 > 1 > 13. The increase in pore size when comparing neutral and acidic conditions is small. In contrast, a more apparent increase in the pore size is observed at alkaline conditions. The more pronounced swelling at alkaline conditions, as compared to acidic condition, can be explained by the streaming potential data as illustrated in Fig. 3. In the pH range below pH=4, the zeta potential is approximately constant

**Table 4**

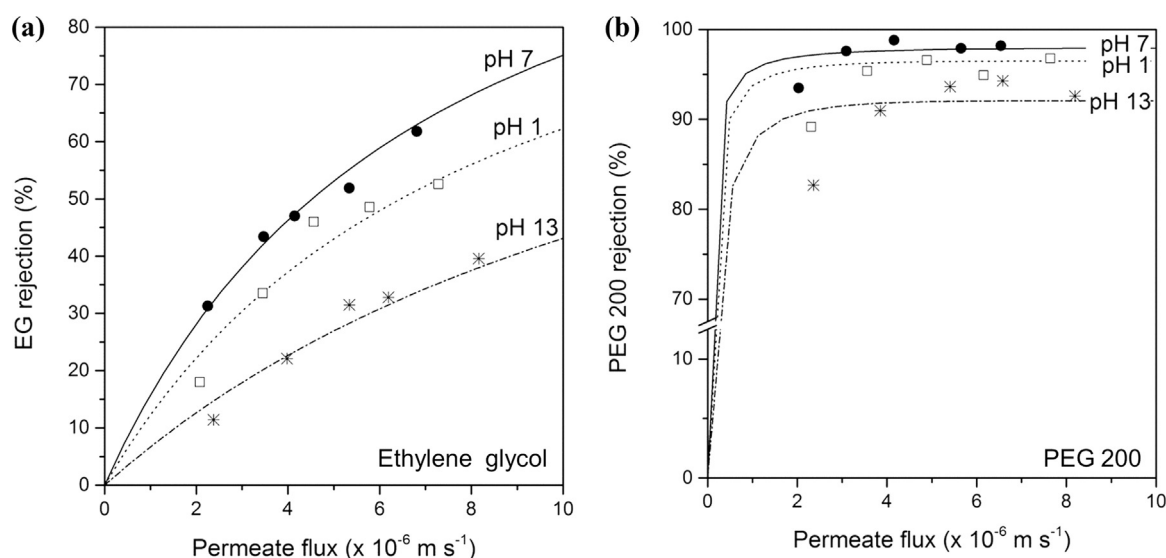
The structural properties, namely the pore radius and the ratio of membrane thickness to porosity, estimated based on DSPM fitting of experimental results from filtration of EG and PEG 200 at different pH conditions. All of the fits have a squared regression factor above 0.90.

pH	EG filtration		PEG 200 filtration	
	$r_p$ (nm)	$\Delta x/A_k$ ( $\mu\text{m}$ )	$r_p$ (nm)	$\Delta x/A_k$ ( $\mu\text{m}$ )
pH = 1	0.46	6.39	0.44	6.13
pH = 7	0.43	5.97	0.42	5.88
pH = 13	0.54	7.34	0.51	7.05

at around 25 mV. At pH=11, the zeta potential already reached -35 mV, and further extrapolation of the curve to pH=13 will lead to an even more negative zeta potential. This substantial difference in absolute zeta potential at alkaline and acidic condition can explain the difference in swelling behavior, and thus observed differences in the MWCO and the modelled pore radius (see Table 4). A similar phenomenon was observed by Dalwani et al. [20]. These pH induced changes in the morphology of the free volume of the polymer, and hence the membrane performance, are entirely reversible and cannot be predicted from solute retention at a single pH value.

#### 4. Conclusion

The formation of polyamine thin film composite membranes by interfacial polymerization between monomeric amines and cyanuric chloride is investigated. Among the tested monomeric amines only those with at least three functional groups can form a tight salt-rejecting skin layer in the interfacial polymerization reaction with cyanuric chloride. The membranes formed by the reaction between diethylene triamine and cyanuric chloride (DETA/CC) show the best combination of flux and rejection. These membranes have a high surface roughness and have very limited charge at neutral pH. This is due to the relatively high value of the IEP, resulting from the high concentration of amine groups that can be protonated. Similar to the previous study of polyethylenimine/CC (PEI/CC) membranes, the DETA/CC membranes also exhibit superior resistance towards nucleophilic attack induced by extreme pH conditions. The superior stability is verified by the stable permeance and salt rejection after an extended period of exposure to pH =1 or pH =13 environments. The DETA/CC membranes are relatively dense, with an approximate MWCO =200 Da



**Fig. 7.** The effect of pH on filtration performance of (a) ethylene glycol and (b) PEG 200. The filtration was performed from 5 to 15 bar. The data points are the experimental measurements whereas the lines represent the fitting from the DSPM model.

at neutral and acidic conditions. At neutral pH the rejection of salts is predominately due to size exclusion effects. At high and low pH a contribution of electrostatic effects to the rejection of salt becomes apparent. In particular at high pH, electrostatically induced swelling of the membranes results in an increase in pore size, evidenced by an increase in the MWCO and a decrease in rejection of small neutral solutes. The pH-induced changes are reversible, but relevant for process design.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.memsci.2016.10.012](https://doi.org/10.1016/j.memsci.2016.10.012).

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