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Heterogeneous anion exchange membranes with nitrate selectivity and low electrical resistance

T. Mubita [a,b], S. Porada [b,c], P. Aerts [d], A. van der Wal [a,e,*]

[a] Department of Environmental Technology, Wageningen University, Bornse Weilanden 9, 6708WG, Wageningen, the Netherlands
[b] Wetsus, European Centre of Excellence for Sustainable Water Technology, Oostergoweg 9, 8911MA, Leeuwarden, the Netherlands
[c] Soft Matter, Fluidics and Interfaces Group, Faculty of Science and Technology, University of Twente, Meander ME 314, 7500, AE Enschede, the Netherlands
[d] Dow Water & Process Solutions R&D, The Dow Chemical Company, Herbert H. Dowweg 5, 4542 NM Hoek, Terneuzen, the Netherlands
[e] Evides Water Company, Schaardijk 150, 3063, NH Rotterdam, the Netherlands

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ABSTRACT

Selective transport of specific ions across ion-exchange membranes can be enhanced by controlling membrane properties such as hydrophobicity. Previous studies have shown that hydrophobic membranes enhance transport of ions with low hydration energy, although such membranes often have increased electrical resistance. In the present work, we study the separation of monovalent ions, specifically nitrate and chloride, using newly-designed heterogeneous anion-exchange membranes. These membranes show high selectivity for nitrate over chloride and have low electrical resistance. We use a functionalized polymeric binder (ionomer) and three ion-exchange resins with different hydrophobic groups, i.e., resins with quaternary ammonium groups and methyl, ethyl, and propyl substituents, respectively. We find that in electrolyte solutions with nitrate and chloride, nitrate over chloride selectivity in our membranes increases with increasing length of the alkyl groups. The membrane with propyl groups, i.e., which has the highest selectivity for nitrate, was further tested in electrolyte solutions containing nitrate, chloride, sulfate, and nitrate, chloride, iodate. The transport of sulfate and iodate ions across the membrane with propyl groups was 6% and 2% of the total counterions transport, respectively. For monovalent ions with similar hydrated size it is possible to report selectivity trends based on the ion hydration energy. We find that the chemical structure of the membrane can either promote or hinder the transport of ionic species.

1. Introduction

Ion-exchange membranes (IEM) act as selective barriers that enable the separation of anions from cations [1–6]. With recent advances in IEMs, specific membranes can further enable the separation between the mono- and divalent ions [7,8], but there are limitations associated with the selective separation of ions with the same charge and valence e.g., nitrate and chloride or sodium and potassium. The selective separation of ions is particularly challenging because most of water sources contain higher concentrations of other competing ions with similar physico-chemical properties.

Technologies that use IEM for water desalination, such as electrodialysis (ED) and membrane capacitive deionization (MCDI), can benefit from the use of ion selective membranes, e.g., because of the possibility of removing ions that are toxic to humans and/or ecosystems, or by recovering ions with high economic value from various water streams without using harsh chemicals [9–11]. A wide range of processes require selective ion separation, e.g., i) recovery of lithium from seawater or brine solutions; ii) recovery of rare earth elements from wastewater streams [12,13]; and iii) removal of sodium ions from irrigation water [14] or nitrate ions from groundwater. Nitrate is ubiquitous in most natural waters. However, its concentration in several water sources, especially in groundwater, has increased due to the use of fertilizers [15,16]. The potentially harmful effects of nitrate on human health have prompted research to selectively remove it [17–24].

The increasing number of potential applications for selective IEMs has led to research on modifying the electrostatic interactions between counterions (ions with opposite charge to the charged functional groups in the membrane) and ion-exchange sites in the membrane as well as the membrane matrix [1,25–28]. The ion-exchange sites in IEMs determine most of the membrane properties such as water uptake, electrical resistance, and selectivity [29]. There are two main classes of IEMs:

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* Corresponding author. Department of Environmental Technology, Wageningen University, Bornse Weilanden 9, 6708WG, Wageningen, the Netherlands.
E-mail address: bert.vanderwal@wur.nl (A. van der Wal).

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Table 1
Physicochemical properties of the IERs and polymeric binder used to fabricate CB-hAEMs.

	PWA15	PWA5	Ionac SR7	Fumion FAS
Matrix	Crosslinked copolymer	Crosslinked copolymer	Crosslinked polystyrene	Polyaromatic polymer
Structure	Gel	Macroporous	Macroporous	–
Amine	$(C1)_3N$	$(C2)_3N$	$(C3)_3N$	Quaternary ammonium
IEC	≥1.3 eq/L	≥1.0 eq/L	0.8 eq/L	1.7–1.9 meq/g
Counterion	Chloride	Chloride	Chloride	Bromide

C1, C2, and C3 refer to methyl, ethyl, and propyl substituents, respectively.

homogeneous and heterogeneous [30,31]. In homogeneous membranes, the ion-exchange sites are chemically bound to the membrane matrix [2], whereas in heterogeneous membranes particles that contain ion-exchange sites are dispersed in a polymer matrix [32]. These particles can be organic such as ion-exchange resins (IER) [33,34], inorganic with ion-exchange sites such as silicates and zirconium phosphates [35,36], or a combination of the two [37]. The binder in heterogeneous membranes is often an uncharged binder such as polyethylene [38], polystyrene [39], polyvinyl chloride [40], polycarbonate [41]. The main drawback of heterogeneous membranes is that the ion-exchange sites are not uniformly distributed. Hence, for the same membrane thickness, heterogeneous membranes have higher electrical resistance than homogeneous membranes [42–44]. A large variety of heterogeneous IEM can be modified by using blends of polymeric binders [32], varying the concentration of IER [45], applying an electric field to arrange the distribution of the IER particles [46], using binders with charged functional groups [47].

To increase the selectivity of IEM towards monovalent ions, one possible route is to apply a charged layer on top of the membrane surface, which repels those counterions with higher valence [48–50]. Another approach is to decrease the mobility of large ions inside the membrane by increasing the degree of crosslinking [51] or by changing the hydrophobicity. Previous work has shown that hydrophobic membranes are more selective to the transport of ions with low hydration energy [18,52,53]. Membrane hydrophobicity has been used to achieve the separation of nitrate from chloride. For example, by varying the length of the alkylated quaternary ammonium groups [52,54] or by incorporating hydrophobic additives, i.e., activated carbon particles (AC) [55]. Results show that the increase in alkyl length leads to more selectivity for nitrate, but also to an increase of electrical resistance [52]. On the other hand, it has been shown that the addition of AC particles increases membrane hydrophobicity, but this addition did not result in an increase in nitrate selectivity [55].

The present study focuses on the separation of different monovalent ions using new conductive binder heterogeneous anion-exchange membranes (CB-hAEMs). CB-hAEMs are made of ion-exchange resin particles with different hydrophobicity and a polymeric binder with charged functional groups in order to decrease the electrical resistance. We characterize and quantify the effect of hydrophobicity of ion exchange groups on selective ion transport. Our results show that selective transport of nitrate over chloride and low electrical resistance can be achieved with CB-hAMEs. In addition, we also show that the hydrophobic membrane effectively rejects bulky ions such as iodate and sulfate.

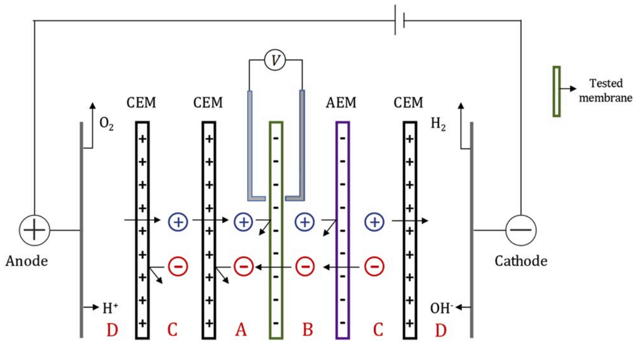

Fig. 1. Schematic of the six-compartment electrochemical cell used to measure electrical resistance and ion selectivity.

2. Materials and methods

2.1. Membrane fabrication

Three heterogeneous anion exchange membranes, which we refer to as conductive binder heterogeneous anion-exchange membranes (CB-hAEM) were prepared using different commercial IER with quaternary ammonium groups: Amberlite PWA15, PWA5, and Ionac SR7. These IER are specially designed for the removal of nitrate from water streams. To bind the IER particles together an ionomer solution (fumion FAS solution, FumaTech GmbH, Germany) was used as a polymeric binder. Relevant physicochemical properties and specifications for the IER and polymeric binder as reported by suppliers are given in Table 1.

For comparison, two commercial AEM were used, a homogeneous membrane (Neosepta AMX, ASTOM Corporation, Tokyo, Japan), and a heterogeneous membrane (Ralex AMH-PES, Mega a.s., Czech Republic).

First, ion-exchange resins were dried in a vacuum oven at 40 °C for 24 h and then ground in a ball mill. The resulting powder was sieved using a mesh size of 40 µm. Then, a suspension was prepared by mixing the IER powder with the ionomer solution containing N-methyl-2-pyrrolidone as solvent. The weight ratio of polymeric binder to IER was 60:40. To obtain a homogenous distribution of the IER particles in the membranes, the suspension was stirred for 1 h and then sonicated for 6 min. The resulting mixture was cast using a doctor blade knife onto a glass plate heated at 50 °C. The cast solution was exposed to the environment until complete evaporation of the solvent. In the final synthesis step, all membranes were immersed in deionized water for 12 h and stored in a 0.5 M NaCl solution. Four different AEM were fabricated: three membranes containing IER (CB-hAEMs) and one membrane consisting only of the polymeric binder (PB-membrane).

2.2. Membrane characterization

2.2.1. Morphological analysis of membranes

Morphology of the membranes was visualized by scanning electron microscopy (SEM) using a JEOL, JSM-6480LV scanning electron microscope at an accelerating voltage of 10 kV. Before analysis, membranes were coated with gold using a sputter coater (JFC-1200 Fine Coater, JEOL, Tokyo, Japan).

2.2.2. Water uptake

Water uptake was determined as the weight difference between the wet and dry membrane. First, membrane pieces of 12 cm^2 were immersed in deionized water for 24 h, and the wet weight was measured after removing excess water from the membrane surface. Thereafter, the membranes were dried at 55 °C for 24 h and the dry weight was measured. Water uptake was calculated as follows:

$$\text{Water uptake} = \left(\frac{W_{wet} - W_{dry}}{W_{dry}}\right) \cdot 100\%, \tag{1}$$

where W_{wet} and W_{dry} are the wet and dry mass of the membrane, respectively.

2.2.3. Ion-exchange capacity

Ion-exchange capacity (IEC) was calculated by measuring the number of equivalents of Cl^- exchanged with NO_3^-. First, the membranes were immersed in 0.5 M NaCl solution for 48 h and then excessive Cl^- was removed from the membrane surface by washing in deionized water. Subsequently, the membranes were immersed in 0.5 M $NaNO_3$ solution for 24 h and the concentration of Cl^- in solution was measured by ion chromatography (IC) using a Metrohm Compact IC 761 with conductivity detector and chemical suppression. IEC was related to the equivalent of exchanged ions (a) according to:

$$\mathrm{IEC} = \frac{\mathrm{a}}{\mathrm{W_{dry}}}. \tag{2}$$

2.2.4. Electrical resistance

The membrane area resistance (ER) was measured using a six-compartment electrochemical cell (Fig. 1) following the procedure described by Galama et al. [56]. The six-compartment electrochemical cell consisted of four-electrodes: i) two Haber-Luggin capillaries, on either side of the tested membrane; and ii) the cathode and anode. The capillaries were filled with 3 M potassium chloride solution and connected to a reservoir with Ag/AgCl electrodes. The effective membrane area was 7.0 cm^2. Four compartments of the cell were filled with 0.5 M NaCl solution (compartments A, B, and C in Fig. 1). Electrode compartments (compartments D in Fig. 1) were filled with 0.5 M Na_2SO_4 solution. All solutions were circulated through the compartments at 170 mL/min. The potential across reference electrodes was measured at different current densities (mA/cm^2) in the cell with and without tested membrane. Electrical resistance is obtained from the slope of voltage (mV) versus current density. The membrane area resistance ($\Omega \cdot cm^2$) was calculated by subtracting the resistance obtained without the membrane from the value obtained with the membrane. In this work, we report the specific membrane resistance, ρ in Ω·cm [57], which is the ER normalized by the membrane thickness in wet form (l_{wet}) [58]. Therefore, ρ is given by

$$\rho = \frac{\mathrm{ER}}{\mathrm{l_{wet}}}. \tag{3}$$

2.2.5. Ion selectivity in ion-exchange membranes

Ion selectivity was investigated under equilibrium conditions, i.e., adsorption experiments to measure the number of adsorbed counterions inside the membranes, and dynamic conditions to measure ion transport through the membranes under electrical potential driving force.

a) Equilibrium conditions

Membranes of 12 cm^2 were placed for 24 h in a stirred solution containing 0.05 M NaCl and 0.05 M $NaNO_3$. Thereafter, the membranes were transferred to 200 mL of a 0.05 M K_2SO_4 solution for 48 h to exchange NO_3^- and Cl^- for SO_4^{2-}. Aliquots of the solutions were taken and analyzed with IC to determine NO_3^- and Cl^- concentration. To ensure the complete exchange of NO_3^- and Cl^-, the membranes were immersed once more in a smaller volume of SO_4^{2-} solution for 24 h. The NO_3^- and Cl^- concentration in the second SO_4^{2-} exchange solution was below detection limit. We calculate the nitrate to chloride selectivity inside the membranes (SE) by

$$\mathrm{SE}_{NO_3^-/Cl^-} = \left(\frac{c_{NO_3^-}}{c_{Cl^-}}\right)_{\text{exchanged in } SO_4^{2-} \text{ solution}}. \tag{4}$$

b) Dynamic conditions

To study the preferential transport of ions across the AEMs, selectivity tests were conducted in the six-compartment cell (Fig. 1). Before each experiment, all membranes were equilibrated in the test solution for 24 h. At the beginning of each experiment, compartments A, B, and C were filled with the same solution, whereas compartment D was filled with a 0.1 M K_2SO_4 solution. In compartments C and D, solutions were recirculated at a flow rate of 170 mL min^{-1} using a peristaltic pump. A fixed volume of 130 mL of a multicomponent solution (0.1 M ionic strength, Table 2) was continuously stirred in compartments A and B, and after applying certain current density samples were taken from these compartments at different time intervals to measure ion concentration by IC.

Table 2
Composition of electrolyte solutions and current densities applied in the electrochemical cell to measure ion selectivity.

Solution	Composition compartments A, B, and C	Current density ($A \cdot m^{-2}$)	Tested membrane
I	50 mM KCl + 50 mM KNO_3	20; 50	CB-hAEMs and commercial
II	20 mM KCl + 20 mM KNO_3 + 20 mM K_2SO_4	20	CB-hAEM with propyl groups and commercial
III	33 mM KCl + 33 mM KNO_3 + 33 mM KIO_3	20	CB-hAEM with propyl groups

Two sets of experiments were conducted to study the effect of competing ions on nitrate selectivity. In the first set, ion selectivity of all AEMs, i.e., CB-hAEMs and commercial membranes, was tested in a solution containing anions with similar size and valence, i.e. Cl^- and NO_3^- (Solution I, Table 2). Ion selectivity was measured at two current densities, i.e., 20 A m^{-2} for 5 h and 50 A m^{-2} for 2 h. In the second set of experiments, the effect of competing ions with different size and valence on ion selectivity was further study. To that end, the CB-hAMs with the highest selectivity towards NO_3^- was tested in two multicomponent solutions containing: i) Cl^-, NO_3^-, and SO_4^{2-} (Solution II, Table 2), and ii) Cl^-, NO_3^-, and IO_3^- (Solution III, Table 2). The applied current density for these experiments was 20 A m^{-2} for 5 h.

Ion selectivity under dynamic conditions (SD) is defined as

$$\mathrm{SD}_{i/j} = \left(\frac{\Delta c_i}{\Delta c_j}\right)_A \cdot \left(\frac{c_j}{c_i}\right)_B \tag{5}$$

$$\Delta c_i = c_{i,t} - c_{i,\mathrm{initial}} \tag{6}$$

where subscript i indicates nitrate ions and j another anion present in the solution. c_{initial} and c_t are the initial concentration and the concentration at time t; subscripts A and B refer to compartment A (receiving solution) and compartment B, respectively. In compartment B, the concentration of both anions i and j was the same at the beginning of each experiment and remain constant throughout the experiment. This implies that $\left(\frac{c_j}{c_i}\right)_B = 1$ in Eq. (5).

The current efficiency (η) was calculated based on the measured change of the amount of counterions (Δn in mol) in the receiving compartment (compartment A) at the beginning and at the end of the experiment

$$\eta = \frac{(\Delta n_i + \Delta n_j) \cdot F}{I \cdot t} \cdot 100\% \tag{7}$$

where F is the Faraday's constant, I is the applied current in A, and t is the total experiment time in s. We note here that Eq. (7) does not consider water transport across the membrane by osmosis and electro-osmosis.

3. Results and discussion

3.1. Membrane characterization

3.1.1. Membrane morphology

SEM images of heterogeneous AEMs with conductive binder (CB-hAEMs) with propyl groups show the polymeric matrix as well as the dispersed resins. Irregularities on the membrane surface (Fig. 2a) are the result of agglomerates of IER particles. We also observed that IERs

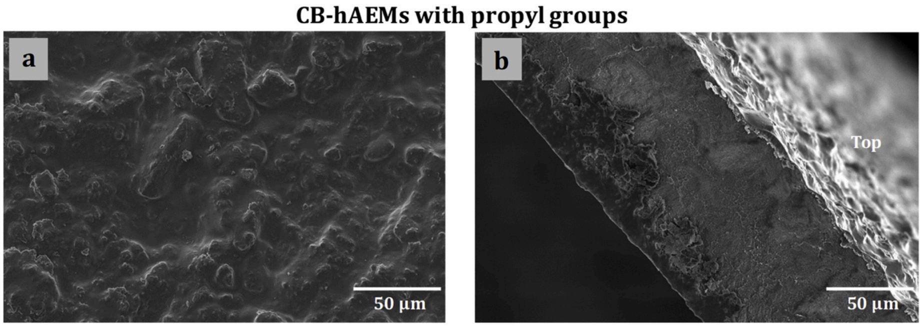

Fig. 2. SEM micrographs of a) the surface and b) the cross-section of CB-hAEM with propyl groups. Differences in light intensity in panel (b) are related to height difference across the cross-section area of the membrane as a result of sample preparation.

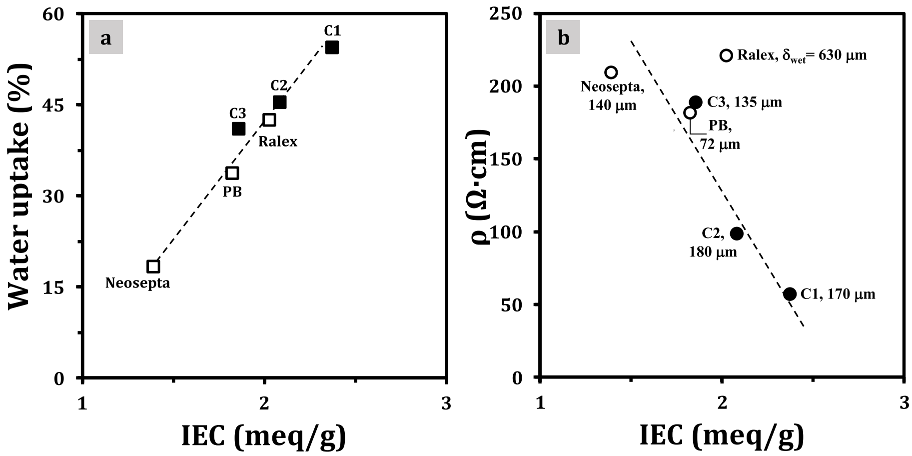

Fig. 3. a) Water uptake and b) specific membrane resistance (ρ) of CB-hAEMs and commercial homogeneous (Neosepta) and heterogeneous (Ralex) membranes as a function of the ion-exchange capacity. C1, C2, and C3 refer to methyl, ethyl, and propyl groups in the IER, respectively. PB refers to the polymeric binder membrane without IER. Dashed lines are to guide the eye. Numbers in panel (b) indicate the thickness of wet membranes (δ_{wet}) to help the reader with the conversion to the membrane area resistance (in Ω·cm^2).

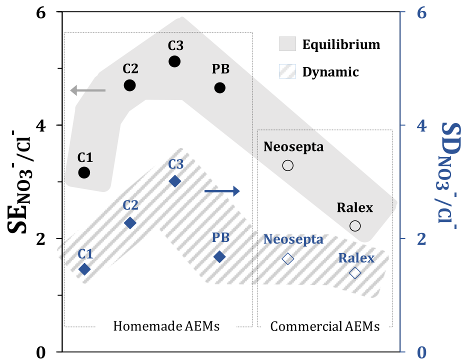

Fig. 4. Nitrate selectivity of CB-hAEMs, polymeric binder (PB) and commercial anion exchange membranes at equilibrium (SE) and under dynamic conditions (SD). Selectivity in dynamic conditions was measured in solution I (50 mM KCl + 50 mM KNO_3) at 20 A m^{-2}.

particles are covered by the polymeric binder and are uniformly distributed throughout the membrane matrix. The cross-section micrograph (Fig. 2b) show dense structure and the absence of empty spaces.

3.1.2. Ion-exchange capacity, water uptake, and electrical resistance

Figure 3 shows the effect of IEC on water uptake and ER (shown as specific membrane resistance, ρ) in CB-hAEMs and commercial membranes, which are used as a reference. Overall, we observe an increase in water uptake (Fig. 3a) and a decrease in ρ (Fig. 3b) as IEC increases. This result is in line with results measured for other IEMs [32,58]. For CB-hAEMs, Fig. 3 shows that water uptake and ρ are influenced by the chemical structure of the membranes, i.e., structure of functional groups with methyl (C1), ethyl (C2), and propyl (C3) substituents. The effect of the length of alkyl chain on water uptake (Fig. 3a) can be explained by the increase in hydrophobicity of the ion-exchange sites with the addition of methylene groups ($-CH_2-$) to the alkyl chain [59].

Table 3
Physicochemical parameters of the anions studied in this work.

Ion	Ionic radii (Å) [64]	Hydrated radii (Å) [64]	Hydration energy (kJ/mol) [65]	Diffusion coefficient[a] (10^{-9} m^2/s) [66]
Cl^-	1.81	3.32	−381	2.03
NO_3^-	2.64	3.35	−314	1.90
IO_3^-	3.30	3.74	−326	–
SO_4^{-2}	2.90	3.79	−1059	1.06

[a] In water at 25 °C.

Importantly, the ρ in CB-hAEMs is lower in comparison with commercial membranes. The use of conductive binder creates an extra pathway for ion transport, in addition to the ones via IER and the liquid film between resin particles and the polymeric binder [60].

3.1.3. Selectivity between nitrate and chloride

3.1.3.1. Equilibrium conditions. Figure 4 shows the preferential adsorption of NO_3^- over Cl^-—i.e., $SE_{NO3^-/Cl^-} > 1$ (Eq. (4)), in CB-hAEMs and commercial membranes. In CB-hAEMs, NO_3^- selectivity increases with increasing the length of alkyl group, and the highest value of $S_{NO3/}$

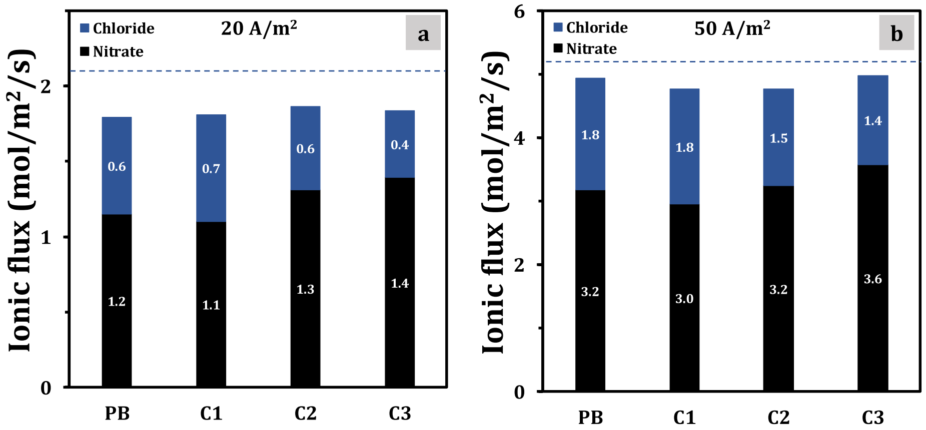

Fig. 5. Nitrate and chloride flux through fabricated membranes at a) 20 A m^{-2}, and b) 50 A m^{-2}. Membranes were tested in solution I (Table 2), whereby the ionic flux is the average over a period of 5 h. Dashed lines indicate the expected total ionic flux through the membranes.

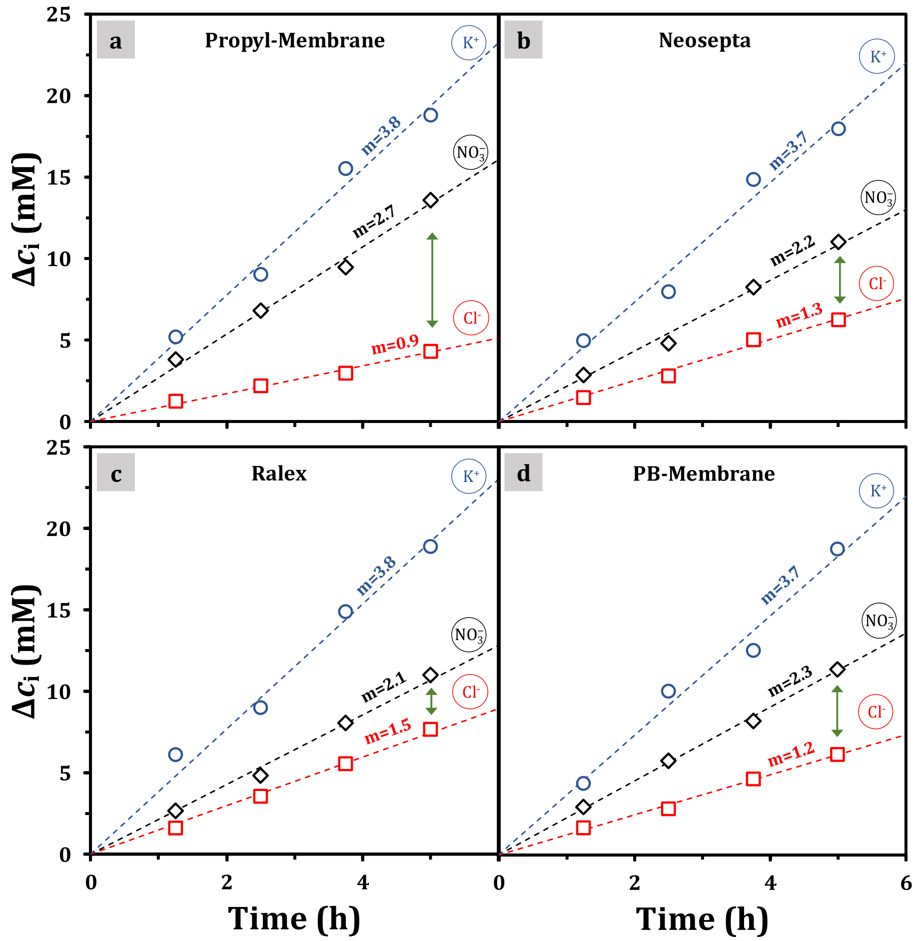

Fig. 6. Experimental data (symbols) of the bulk ion concentration change at 20 A m^{-2} as a function of time with a) propyl-membrane; b) Neosepta membrane; c) Ralex membrane; and d) PB-membrane. Dashed lines are the linear regression of experimental data. The value of m indicates the slope of dashed lines. Membranes were tested in solution I (Table 2).

$_{Cl^-} = 5.3$ is obtained for the membrane with propyl groups. Ion selectivity at equilibrium is influenced by specific electrostatic interactions between the ion-exchange sites in the membranes and the counterions. The strength of these interactions depends on ion hydrated size and hydration energy [52,53]. Our results suggest that NO_3^-, with lower hydration energy (Table 3), can establish stronger electrostatic interactions with the ion-exchange sites in AEMs, owing to the presence of fewer water molecules around this ion. We believe that the strength of these interactions is what leads to the preferential adsorption of NO_3^- over Cl^- ions. In addition, in CB-hAEMs, the increase in hydrophobicity and size of the ion-exchange sites with increasing alkyl chain can induce partial loss of water molecules in the hydration shells of the counterions [61–63]. It has been pointed out that the required energy to rearrange hydration shells is compensated by stronger interactions between ions and ion exchange sites in the membranes [53].

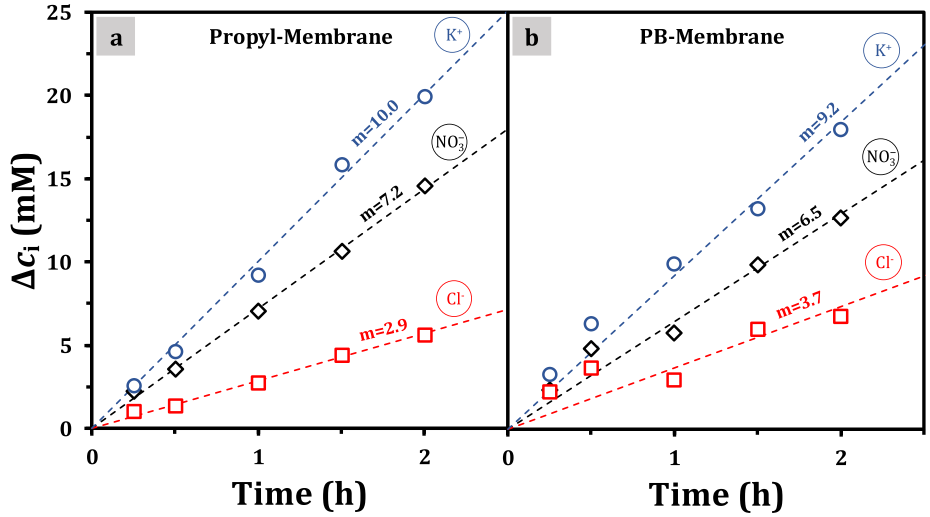

Fig. 7. Experimental data (symbols) of the bulk ion concentration change at 50 A/m^2 as a function of time with a) propyl-membrane; and b) PB membrane. Dashed lines are the linear regression of experimental data. The value of m indicates the slope of dashed lines. Membranes were tested in solution I (Table 2).

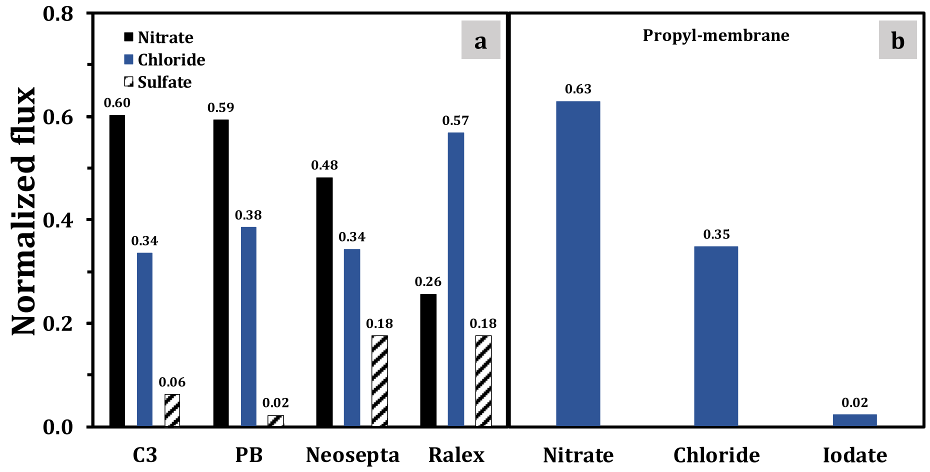

Fig. 8. a) Normalized flux of ions, i.e., the ratio of the flux of one anion to the total flux of anions, through propyl-and PB-membrane as well as commercial membranes in solution II, b) normalized flux through propyl-membrane in solution III. Experiments conducted at 20 A m^{-2}.

3.1.3.2. Dynamic conditions. Under dynamic conditions, when ions are transported through the membranes due to the electric field, NO_3^- selectivity (SD) significantly decreases compared to selectivity at equilibrium conditions (Fig. 4). Despite this decrease, we observe the same selectivity trend in CB-hAEMs: propyl-membrane > ethyl-membrane > methyl-membrane, which is related to a higher transport of NO_3^- across the membranes compared to that of Cl^- (Fig. 5**).** Both PB- and methyl-membranes show the same flux of NO_3^- and Cl^- (Fig. 5a), and therefore same selectivity towards nitrate (Fig. 4, SD). The difference between selectivity values obtained at equilibrium and under dynamic conditions may be seen as the result of different mechanisms occurring during ion adsorption in and transport across the membrane. As we mentioned before, at equilibrium conditions ion selectivity is associated with differences in affinity, related to chemical/physical interactions, between the charged functional groups in the membranes and the counterions. However, under dynamic conditions ion selectivity also depends on kinetic effects related to the differences in ion diffusion coefficients in water (Table 3) and in the membrane. At current densities of 20 and 50 A m^{-2}, the current efficiency was on average 90% and 95%, respectively. The lower current efficiency measured at 20 A m^{-2} is the result of undesirable transport of co-ions (potassium ions) and concentration changes caused by water transport across the membrane due to the longer experimental time (5 h compared to 2 h at 50 A m^{-2}).

Figure 6 shows ion concentration change with time at 20 A m^{-2} in compartment A. The slope 'm' of the fitted lines in Figs. 6 and 7 represents the rate of ion concentration change. In Fig. 6, the ion concentration change rate of NO_3^- is higher for CB-hAEMs with propyl groups ($m = 2.7$) in comparison to the PB ($m = 2.3$) and commercial Neosepta ($m = 2.2$) and Ralex ($m= 2.1$) membranes. In compartment B, the ion concentration change is negligible (data not shown). Additionally, in Fig. 7, we further show the effect of the IER particles on NO_3^- selectivity at 50 A m^{-2}.

3.1.4. Selectivity between anions with different valence and size

In the previous section, we showed that for monovalent ions with similar hydrated size it is possible to report selectivity trends based on hydration energy. In this section, we show that when ions have different valence or size, hydration energy is not sufficient to predict ion selectivity. Figure. 8a shows that overall AEMs are more selective to monovalent (NO_3^- and Cl^-) than to divalent ions (SO_4^{2-}). The low transport of SO_4^{2-} can be explained by i) hydrophobic effects, the membranes allow the preferential transport of ions with low hydration energy, i.e., NO_3^- and Cl^-, and limit the transport of ions with high hydration energy, i.e., SO_4^{2-}, (Table 3), ii) steric hindrance, related to the large size of SO_4^{2-}

(Table 3), and iii) stronger electrostatic interactions between SO_4^{2-} and the ion-exchange sites [67]. In CB-hAEMs with propyl groups and PB-membrane, the flux of monovalent ions is similar, with significantly lower transport of SO_4^{2-} compared to Neosepta and Ralex membranes. The difference in SO_4^{2-} transport between commercial membranes and CB-hAEMs with propyl groups and PB-membranes may be related to variations in the distance between ion-exchange sites, i.e., the transport of SO_4^{2-} requires the presence of two closely-spaced ion-exchange sites [68,69]. Results in Fig. 8b show that in mixtures of monovalent ions with different hydrated size, the decrease in hydration energy, i.e., $NO_3^- < IO_3^- < Cl^-$ (Table 3), cannot account for the observed preferential ion transport, which follows the sequence $NO_3^- > Cl^- > IO_3^-$. In this case, the difference in size between IO_3^- and the other anions seems to play a more important role. In addition to the large size of IO_3^-, some studies have reported that this ion behaves as a cation in aqueous solutions [70,71], which can lead to electrostatic repulsion with the ion-exchange sites. The low selectivity of the AEMs towards IO_3^- was also measured at equilibrium (data not shown) in which on average for CB-hAEMs with propyl groups and PB membranes IO_3^- concentration represents ~ 3% compared to 15% for Cl^- and 82% for NO_3^-, whereas for Neosepta membrane the IO_3^-, Cl^-, and NO_3^- concentrations are 4%, 20%, and 76%, respectively. Our results show low adsorption and transport of IO_3^-, but they do not allow to make conclusions about whether the observations are related to the large size of these ions or their cation-like behavior.

4. Conclusions and outlook

Heterogeneous anion-exchange membranes were fabricated with ion-exchange resins with different alkyl groups and a polymeric binder with charged functional groups (CB-hAEMs). We showed that nitrate selectivity in CB-hAEMs correlates with the hydrophobicity of the alkyl groups in the membrane. CB-hAEM with the longest alkyl group (propyl-membrane) showed high nitrate selectivity under dynamic conditions, about two times higher than commercial AEM.

Selectivity is the consequence of the interplay between different factors among whereby the hydration energy is a dominant factor. We observed that for monovalent ions with the same size such as nitrate and chloride, the selectivity is linked to the difference in hydration energy. In solutions containing ions with different size and valence, it is not possible to relate ion selectivity to one single parameter. Ion selectivity is the combination of electrostatic interactions between ions and ion-exchange sites, and steric hindrance due to the size of the ions and structure of the ion-exchange sites.

The use of a charged polymeric binder enables the fabrication of selective membranes with low electrical resistance, comparable to commercially available non-selective membranes. These membranes can potentially be used in electrochemical desalination technologies such as electrodialysis and membrane capacitive deionization to obtain selective removal of ions.

Author statement

T.M. Mubita: Conceptualization, Methodology, Investigation, Writing - original draft.

S. Porada: Conceptualization, Supervision, Writing - review & editing.

P. Aerts: Conceptualization, Resources. A. van der Wal: Conceptualization, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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