

A comparative study on Donnan dialysis separation using homogeneous and heterogeneous anion-exchange membranes

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ABSTRACT

Donnan dialysis separations of nitrate, bicarbonate and sulfate ions at different concentrations were studied; aiming to test the anions transport in membrane diffusion-controlled regime, boundary layer diffusion-controlled regime, and the transition region. Differences in the transport rates were correlated to differences between the properties of a homogeneous (Selemion AMV) and a heterogeneous (Ralex AM(H)-PES) anion-exchange membranes. As expected, under boundary layer diffusion control conditions, the separation of the three anions was similar with both membrane types, supporting the potential applicability of heterogeneous membranes for water treatment by Donnan dialysis. The transition region was obtained at a lower concentrations range with the heterogeneous membrane. Under membrane diffusion-controlled conditions, superior transport of all three anions were observed with the homogeneous ion-exchange membrane, suggesting that this membrane type is better for Donnan dialysis separation at higher concentrations.

Keywords: Anion exchange; Membrane properties; Separation mechanism; Nitrate; Bicarbonate; Sulfate

1. Introduction

Ion-exchange membranes (IEMs) are finding increasing use in applications including water treatment, electro-dialysis, fuel cells, redox flow batteries, and diffusion dialysis [1,2]. The growing applications are expected to promote the development of more affordable ion-exchange membranes [3,4]. Ion-exchange membranes are of two types: homogeneous and heterogeneous. Homogeneous membranes are obtained by co-polymerization of monomers which incorporate the functional groups onto the polymer chain in a nearly uniform distribution. Heterogeneous membranes consist of macro-particles of ion-exchange resin blended with inert polymeric binders and display discontinuities and uneven distribution of the ion-exchange functional groups [5,6].

The homogeneous Selemion AMV membrane is prepared by the paste method from a blend of polyvinyl chloride and a copolymer synthesized from styrene, chloromethylstyrene, and divinylbenzene. The copolymer is then functionalized by the introduction of an ammonium strongly basic ion-exchange group. Aside from quaternary amine groups, the membrane also contains some weak base pyridine groups because 4-vinylpyridine and 2-methyl-5-vinylpyridine are normally used as the co-monomers during the membrane preparation [7]. Ralex AMH heterogeneous ion-exchange membrane is a strongly basic anion-exchange membrane with quaternized ammonium functional groups. The matrix of the membrane is a polystyrol cross-linked with Lewatit M500 divinylbenzole ion-exchange resin (washed, dried, and milled). The membrane is produced by

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rolling a thermoplastic mixture consisting of a fine powder of the ion-exchange resin and low-density polyethylene, at a weight ratio of 60/40 (resin/PE). A reinforcing mesh (Ulester 32S) is rolled into both sides of the membrane during its production while the membrane was still hot [8,9].

The major advantages of heterogeneous membranes over homogeneous membranes are excellent mechanical properties, high chemical stability, and lower cost [3,4,6,10]. Additionally, heterogeneous IEMs are more easily modified than homogeneous membranes as their characteristics can be changed by adjusting the properties of the ion-exchange resin, polymer binders, additives, reinforcing fabric, and/or the manufacturing method [11]. Generally, the electrochemical properties of heterogeneous IEMs are weaker than those of homogeneous membranes [4,12,13].

Donnan dialysis utilizes ion-exchange membranes that allow a selective transport of target ions to a concentrated receiver solution [5]. The total mass transfer resistance in Donnan dialysis is equal to the sum of the resistances of the diffusion boundary layer and the resistance of the membrane itself. At low feed concentration, the resistance of the diffusion boundary layer, in the feed, controls the mass transfer process. Transport through the diffusion boundary layer is proportional to the concentration difference between the solution bulk and the membrane interface. An increase in the concentration difference increases the boundary layer diffusion rate thus decreasing the mass transfer resistance relative to the membrane diffusional resistance. Under boundary layer diffusion dominant conditions, the membrane properties have little effect on the transport of the target ions [14]. At high concentrations, the transfer is controlled by the resistance of the membrane, that is, the transport is membrane diffusion-controlled [14,15].

Literature results report superior performance of homogeneous membranes over heterogeneous membranes in Donnan dialysis applications. For example, aluminum recovery using a homogeneous membrane (Nafion 117) was three times higher than with the IONAC 3470 heterogeneous membrane [16]. Cyanide transport rate and separation efficiency of homogeneous membranes (Neosepta AFN and AM3) were higher than that of the heterogeneous IONAC MA3475XL membrane. This was attributed to the heterogeneous membrane thickness, its low water content, and unfavorable structure to diffusion [17]. Similarly, the homogeneous membrane Neosepta AXE01 yielded better pre-concentration of phosphate from industrial wastewater compared to Ralex AMH-PES membrane [18]. Cobalt and nickel ionic fluxes, through cation exchange membranes, were higher for a homogeneous membrane than those of a heterogeneous membrane, as the transport rate of the metal ions was governed by the flux of hydrogen ions [19].

The objective of the present work was to study the effect of target ions concentration (nitrate, bicarbonate and sulfate) on Donnan dialysis separation characteristics using a homogeneous (Selemion AMV) and a heterogeneous (Ralex AM(H)-PES) anion-exchange membranes. Results are used to confirm the controlling mechanism of anion-transport by the membrane or/and the diffusion layers as a function of concentration as well as to examine the relation between membrane properties and Donnan dialysis separation efficiency.

2. Experimental

2.1. Membranes characterization

The main properties of the homogeneous (Selemion AMV; AGC, Japan) and the heterogeneous (Ralex AM(H)-PES; Mega, Czech Republic) membranes were characterized and are listed in Table 1.

2.1.1. Morphology

The cross-section and surface of the membranes were visualized with a Zeiss Ultra Plus high-resolution scanning electron microscope (SEM). Analysis was conducted with a Schottky field-emission gun operated at a low acceleration voltage of 1 kV and working distances of 3.5–5.0 mm. The Everhart-Thornley (SE2) was used as a secondary electron imaging detector. Low-dose imaging was applied to all specimens to minimize radiation damages. Cross-section specimens were prepared by plunging a piece of the membrane into liquid nitrogen and fracturing it under cryogenic conditions to create a cross-section that represents the bulk of the membrane. Following the fracture, specimens were dried and mounted on a dedicated cross-section stub for SEM imaging.

2.1.2. Water uptake and porosity [20]

Water uptake [Eq. (1)] was measured using the dry-wet weight method. Membrane pieces, of 1 cm², were immersed in double-deionized (DI) water for 24 h, wiped and weighted. Then the samples were dried, at 75°C for 3 h, and weighted.

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

where W_{dry} and W_{wet} are the weight of the dry and the wet membrane, respectively. The porosity was calculated based on the water uptake of the membrane [Eq. (2)].

Table 1
Membranes properties

Parameter	Selemion AMV	Ralex AM(H)-PES
Fixed ion ^a	-NR ₃ ⁺	R-(CH ₃) ₃ N ⁺
Ion-exchange capacity ^a (meq/g)	1.85	1.80
Permselectivity ^a (%)	≥0.98	>0.90
Density (g/cm ³)	1.09	0.91
Thickness (mm)	0.12	0.49
Wet thickness (mm)	0.12	0.65
Water content (%)	14.6	49.7
Porosity (%)	15.4	38.0
Total pore volume (cm ³ /g)	0.045	0.225
Contact angle (°)	69	103

^aData from manufacturers.

$$\text{Porosity}(\%) = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{\rho_w A \delta} \right) \cdot 100\% \quad (2)$$

where ρ_w is the density of the pure water, A is the membrane area (cm^2) and δ is the wet membrane thickness (cm).

2.1.3. Contact angle

The contact angle was measured using a drop shape analyzer DSA100 (Krüss, Germany). The image of a sessile drop at the points of intersection between the drop contour and the projection of the surface was analyzed. A water droplet of 5 μL was positioned on the membrane top surface. For each membrane, five measurements were conducted, and the average value is reported.

2.1.4. Membrane selectivity

The selectivity coefficients (K_c), under equilibrium conditions, were determined according to the method described by Vyas et al. [21]. Membrane samples ($4 \text{ cm}^2 \times 4 \text{ cm}^2$) were conditioned for 48 h in 100 mL of 1 M HCl. Then, each membrane cut-off was soaked for 48 h in 100 mL 0.1 M NaCl to exchange any anions with chloride. Excess electrolytes were wiped off the membrane surfaces using filter paper. Next, the membranes were immersed in 1 mM of the target anion mixed with 15 mM of NaCl solution (100 mL). The samples were placed in a water bath (100 rpm), at 25°C, until equilibrium was achieved. The K_c value was calculated according to Eq. (3). No ionic activity corrections were applied. The average K_c value based on seven samples is reported.

$$K_{\text{Cl}}^x = \left(\frac{[\text{Cl}]_b}{[\text{Cl}]_m} \right)^z \left(\frac{[x]_m}{[x]_b} \right) \quad (3)$$

where K_{Cl}^x is the selectivity coefficient between chloride (Cl^-) and the target anion x^{z-} ; the indices b and m refer to

the concentration at the bulk solution and the concentration inside the membrane, respectively; z is the target anions charge.

2.2. Experimental system

The transport of nitrate, bicarbonate, and sulfate by Donnan dialysis was tested in batch dialysis experiments. The experimental system is described in detail elsewhere [22]. In brief, the system consisted of a rectangular dialysis cell ($400 \text{ mm} \times 50 \text{ mm} \times 20 \text{ mm}$) and two solutions vessels-recycling feed and stripping (receiver) solutions. The dialysis cell contains two rectangular flow chambers ($400 \text{ mm} \times 50 \text{ mm} \times 8 \text{ mm}$) separated by the anion exchange membrane (0.02 m^2). Initial concentrations of the feed solution ranged from 0.5 to 223.0 mM nitrate, sulfate and bicarbonate, as a sole component, in DI water. The concentration of the NaCl receiver solution was 100 mM for the experiments carried out under diffusion boundary layer and combined controlled conditions. For experiments conducted under membrane diffusion-controlled mechanism, a receiver concentration of 1,000 mM NaCl was used. Reynolds number (Re) was controlled by adjusting the flow rates of the recycle pumps to 1.0 L/min ($Re = 575$) or 4 L/h min ($Re = 2,155$). The flow velocities of 0.04 and 0.17 m/s, respectively were maintained constant throughout the experiment.

2.3. Analytical methods

Nitrate was measured by absorbance at a wavelength of 220 nm (Evolution 201 UV-Vis spectrophotometer, Thermo Scientific, China). Sulfate was determined using HACH DR2800 spectrophotometer (Germany) method 8051. Bicarbonate was analyzed using Standard Methods 2320B [23].

3. Results

As explained in the introduction, the overall rate of Donnan dialysis mass transfer is governed by boundary layer diffusion and diffusion within the ion-exchange membrane

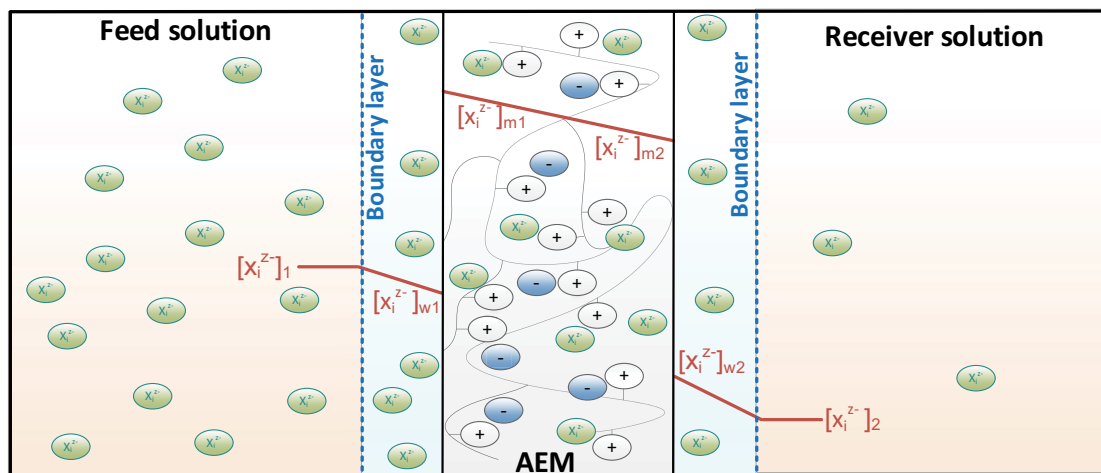


Fig. 1. Transport of target ion X_i^{z-} from the feed to the receiver solution through the boundary layer and through the anion exchange membrane along with its concentration profile. (Subscript 1 and 2 are for the feed and receiver, respectively, w is for boundary layer-membrane interface, and m is for membrane).

(Fig. 1). Generally, it is established that boundary layer diffusion prevails for dilute solutions, thinner membrane, lower diffusion coefficient in solution, and higher selectivity of the membrane [24]. Nonetheless, the criteria for the controlling mechanism are only approximated. Therefore, determination of the Donnan dialysis transport regimes was based on the following guidelines: (i) under boundary layer diffusion-controlled conditions, the target anion concentration, in the feed solution, does not affect the transport rate; (ii) slower rate with increased target anion concentration, in the feed solution, points to combined boundary layer and

membrane diffusion-controlled mechanisms; (iii) under membrane diffusion-controlled regime, variation of the flow conditions, that is, change of the Reynolds number has no impact on the target anion transport. Accordingly, the results are divided into the transport regimes.

3.1. Boundary layer diffusion-controlled mechanism

The concentrations in which boundary layer diffusion-controlled mechanism predominated are presented in Figs. 2–4. The boundary layer diffusion mechanism

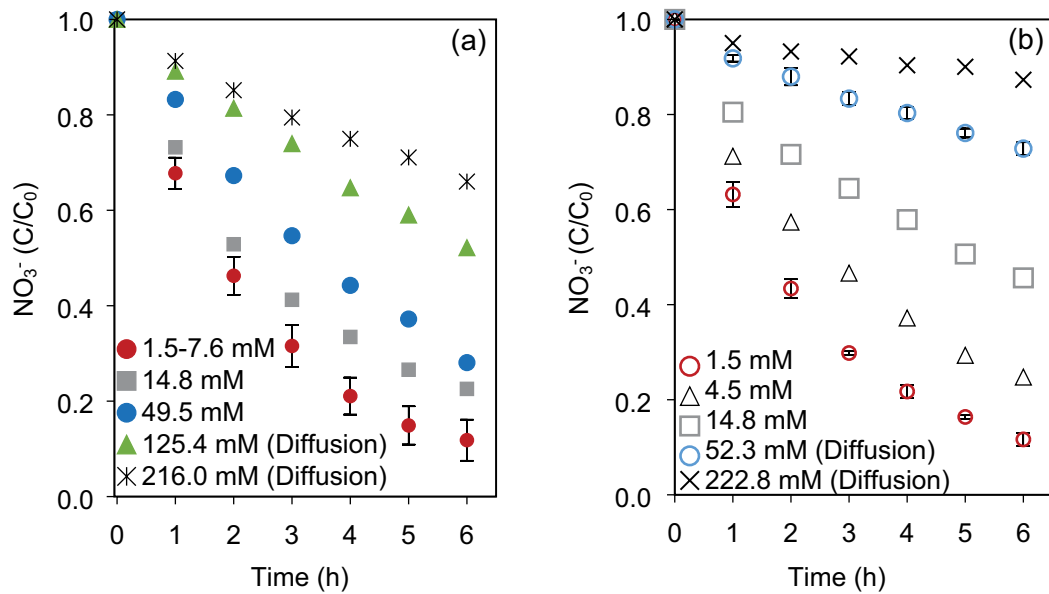


Fig. 2. Removal of nitrate from the feed solution at concentrations ranging from 1.5 to 222.8 mM using the (a) homogeneous Seleminion AMV and (b) heterogeneous Ralex AM(H)-PES membranes.

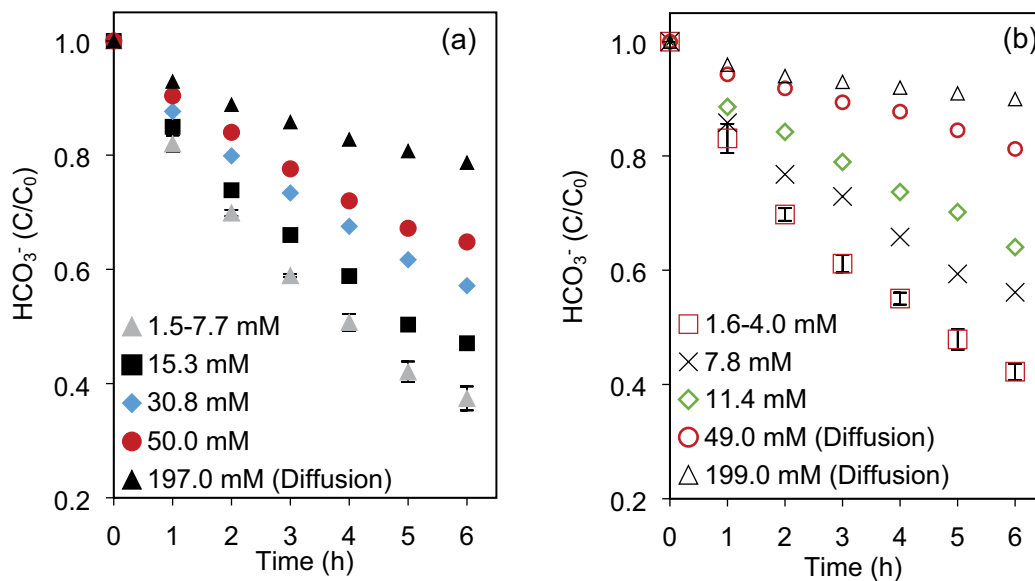


Fig. 3. Removal of bicarbonate from the feed solution at concentrations ranging from 1.5 to 199.0 mM using the (a) homogeneous Seleminion AMV and (b) heterogeneous Ralex AM(H)-PES membranes.

controlled the nitrate transport, in the AMV membrane, at concentrations ranging from 1.5 to 7.6 mM (Fig. 2a) while for the Ralex membrane it dominated at a concentration of 1.5 mM (Fig. 2b). Boundary layer diffusion-controlled the bicarbonate transport, in the AMV membrane, at concentrations ranging from 1.5 to 7.7 mM (Fig. 3a) while for the Ralex membrane it dominated at concentrations of 1.6–4.0 mM (Fig. 3b). Sulfate transport was controlled by boundary layer diffusion, in the AMV membrane, at concentrations ranging from 0.5 to 3.8 mM (Fig. 4a) while for the Ralex membrane it dominated at concentrations of 1.0 mM (Fig. 4b).

Under boundary layer diffusion-controlled conditions similar transport of all the tested anions was obtained with

both the homogeneous and heterogeneous membranes (Fig. 5). This is expected since the resistance of the anion exchange membrane is negligible under these conditions, that is, the rate depends on the transport behavior of the anions in the aqueous solution. These results are of practical importance, as at concentrations relevant to water treatment, boundary layer diffusion-controlled conditions prevail.

3.2. Transition region

The transition from boundary layer diffusion control to combined boundary layer and membrane diffusion-controlled mechanisms is indicated by a reduction in the level

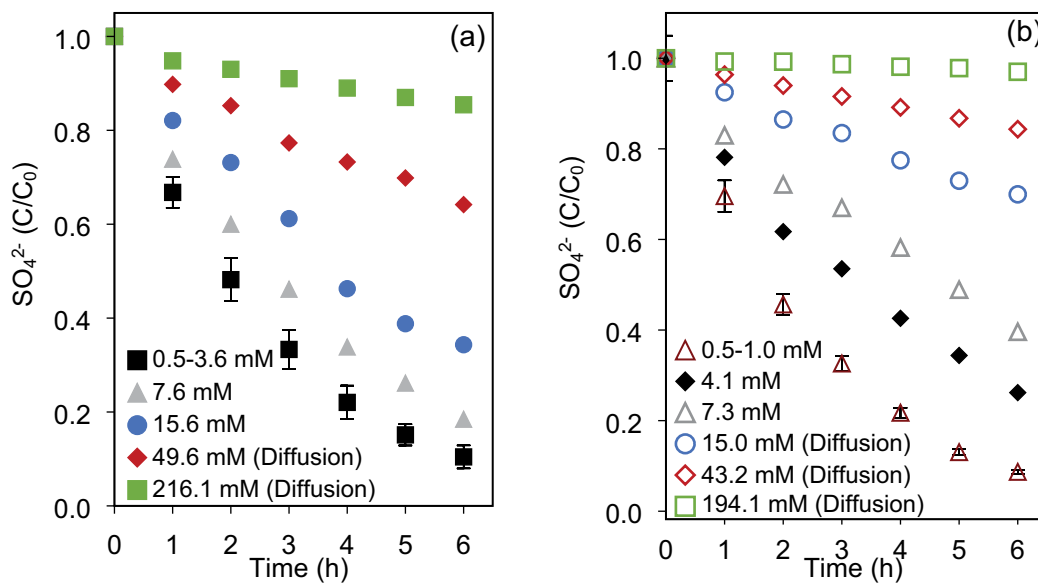


Fig. 4. Removal of sulfate from the feed solution at concentrations ranging from 0.5 to 216 mM using the (a) homogeneous Selemin AMV and (b) heterogeneous Ralex AM(H)-PES membranes.

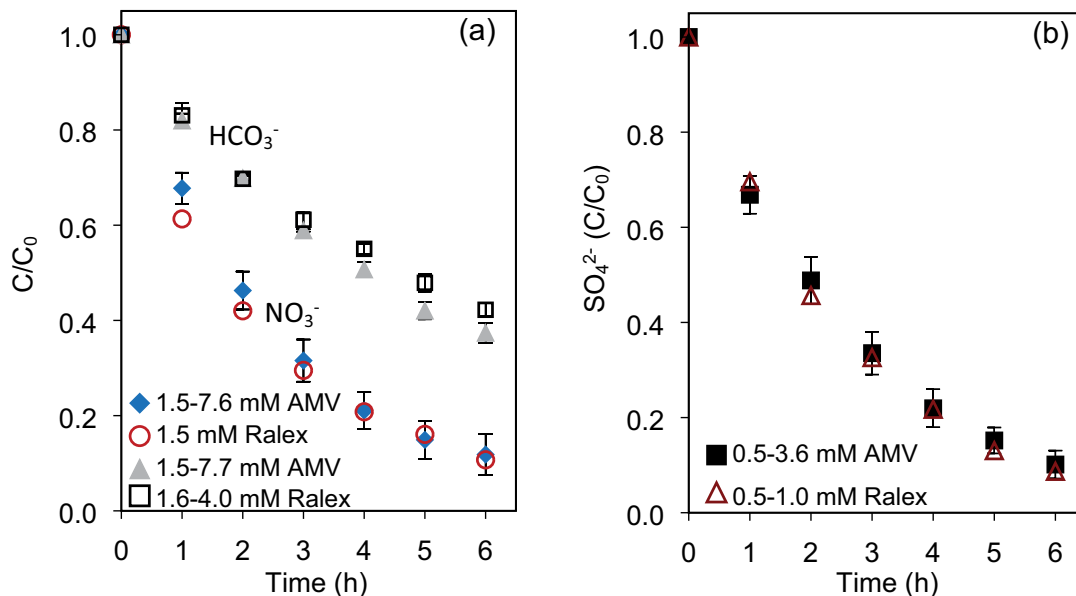


Fig. 5. Removal of (a) nitrate and bicarbonate; and (b) sulfate under boundary layer diffusion controlled regime.

of the target anion transport rate. Approximately the same transfer rate was obtained, at the transition regime, with nitrate concentrations of 4.3 and 14.8 mM for the AMV and Ralex membranes, respectively (Fig. 6a); with bicarbonate concentrations of 7.8 and 30.8 mM for the AMV and the Ralex membrane, respectively (Fig. 6a); and with sulfate concentrations of 4.1 and 7.6 mM for the AMV and the Ralex membrane, respectively (Fig. 6b). These results indicate that combined control conditions were obtained at lower concentrations (by a factor of 2–4) of the tested target anions in the Ralex membrane as compared to the AMV membrane. It is also evident that the concentration range of the combined control mechanism, for all tested anions, is narrower with the heterogeneous membrane, as seen in Figs. 2–4. These results correspond well with the thickness of the membranes. The heterogeneous membrane is four times thicker than the homogeneous membrane (Table 1). It is established that the thinner the membrane, the higher the ion concentration required to shift the rate-control from boundary layer to membrane diffusion [14]. With increased membrane thickness, the length of the transport pathway increases, and the membrane resistance rises, hence at a thinner membrane the diffusion-controlled conditions are achieved at higher concentrations.

The contact angle obtained for Ralex membrane (103°) indicates a hydrophobic surface area [25] while the surface of the AMV membrane (69°) is hydrophilic (Table 1). It was reported that hydrophilicity of the membrane facilitates the transport of ions between the solution and membrane interface [26,27], thus allowing a wider range for the combined mechanism in the AMV membrane. The hydrophobic surface of the Ralex membrane hinders the co-existence of a combined control mechanism hence, facilitating the transition to membrane diffusion.

In the heterogeneous membrane, the pores are non-uniformly distributed and cavities on the surface of the membrane between the ion-exchange particles and the polymer (Fig. 7a and c) allow the flow of the ionic solutions into

the membrane [28], resulting in a transition regime at lower concentrations. Whereas, the dense and uniform dispersed pores (Fig. 7b and d) arrangement of the homogeneous membrane enables uniform transport of ions through the surface of the membrane.

3.3. Membrane diffusion-controlled mechanism

At high anions concentrations, the transport is completely controlled by membrane diffusion. Therefore, the transport rate of anions is closely related to the microstructure of the membrane [14]. Fig. 8 displays the effect of the Reynolds number on nitrate, bicarbonate and sulfate transport. The experiments were conducted at Re numbers 575 and 2,155. Under diffusion boundary layer controlled conditions, an increase in the Reynolds number augments the ions transport while membrane diffusion control is identified by conditions at which change in the Reynolds number has no impact on the ions transport [29]. Membrane diffusion-controlled conditions were obtained at 50 mM of nitrate and bicarbonate with the Ralex membrane while the transition regime was observed at this concentration with the AMV membrane (Figs. 8a and b). Membrane diffusion-controlled transport of the sulfate ions was observed in the Ralex membrane at a lower concentration of 15 mM while a transition regime was obtained at this concentration by the AMV membrane (Fig. 8c).

Prolonged experiments (30 h), performed under membrane diffusion-controlled conditions, at a feed concentration of 200 mM of each individual target anion and a receiver solution of 1,000 mM of NaCl, indicated better transport with the homogenous membrane (Fig. 9). While the homogeneous membrane provides a relatively uniform distribution of functional groups, the heterogeneous membrane is typically considered to be a system of two or more phases. As discussed in Section 3.2, the heterogeneous membrane contains discontinuities and non-conducting regions. This membrane structure imposes resistance to

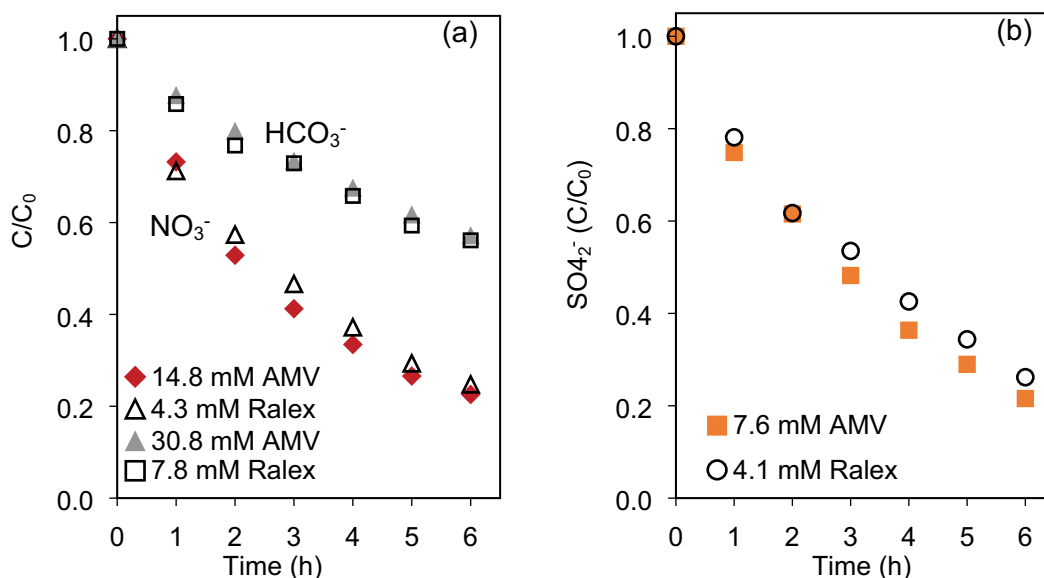


Fig. 6. Removal of (a) nitrate and bicarbonate and (b) sulfate in the transition region.

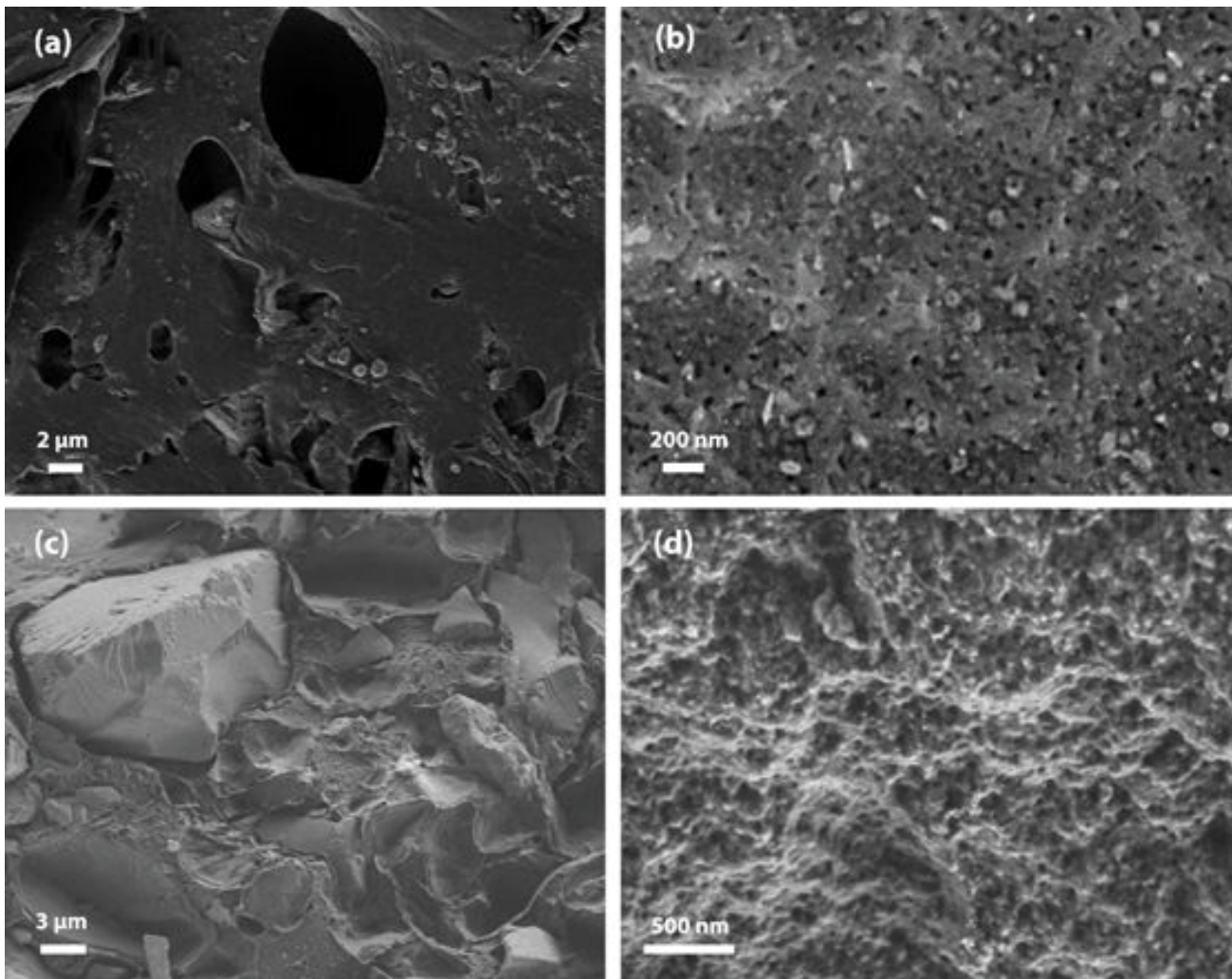


Fig. 7. SEM images of the membranes surface of (a) Ralex AM(H)-PES heterogeneous membrane and (b) Selemion AMV homogeneous membrane; images of cross-sections of (c) Ralex and (d) AMV.

the transport of ions [16]. On the other hand, the interfacial regions of the heterogeneous membrane (i.e., meso-, macro-pores and cavities), are filled with free water that forms hydrophilic channels in which the ionic transfer mechanism is similar to that in aqueous solutions [30,31]. As seen in Table 1, the water content of the Ralex heterogeneous membrane is about 50%. The combined effect of the heterogeneous membrane structure that imposes resistance to the anions transport on one hand and that facilitates transport due to high water content on the other hand controls the overall rate of Donnan dialysis diffusion through the AEM.

Under membrane diffusion-controlled conditions in both membranes, the anions transfer followed the decreasing order of $\text{NO}_3^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. These results correspond with the selectivity of the membranes toward the three anions, as shown in Table 2. It is reported that the selectivity sequence of the AMV membrane reflects the hydrophobicity of the aqueous anion with sulfate being the most hydrophobic followed by bicarbonate and nitrate. It may therefore be concluded that the preference of both membranes toward hydrophobic anions is relatively low [32].

The sequence at which the anions are transported is related to their structure and charge. It is well established that the resistance of the membrane toward di-valent ions, such as sulfate, is higher than toward monovalent ions due to the fact that ions in the membrane are transferred from one fixed ion to another while maintaining electro-neutrality. A mono-valent ion moves from one fixed charge group to another, while a divalent ion can only transfer from two fixed ions to another two fixed charge groups [33]. Additionally, a monovalent ion can move easier than a divalent ion within the membrane since its radius is smaller. A smaller radius means less resistance due to contact with the wall of pores in the membrane [33]. In terms of the anions characteristics, a higher number of water molecules are hydrogen-bonded to sulfate and bicarbonate ions as compared to nitrate ions [34,35], hindering transport through the membrane.

It is established that at equilibrium conditions the ion selectivity is related to differences in affinity between the charged functional groups in the membranes and the counter-ions. Under dynamic conditions, ion selectivity

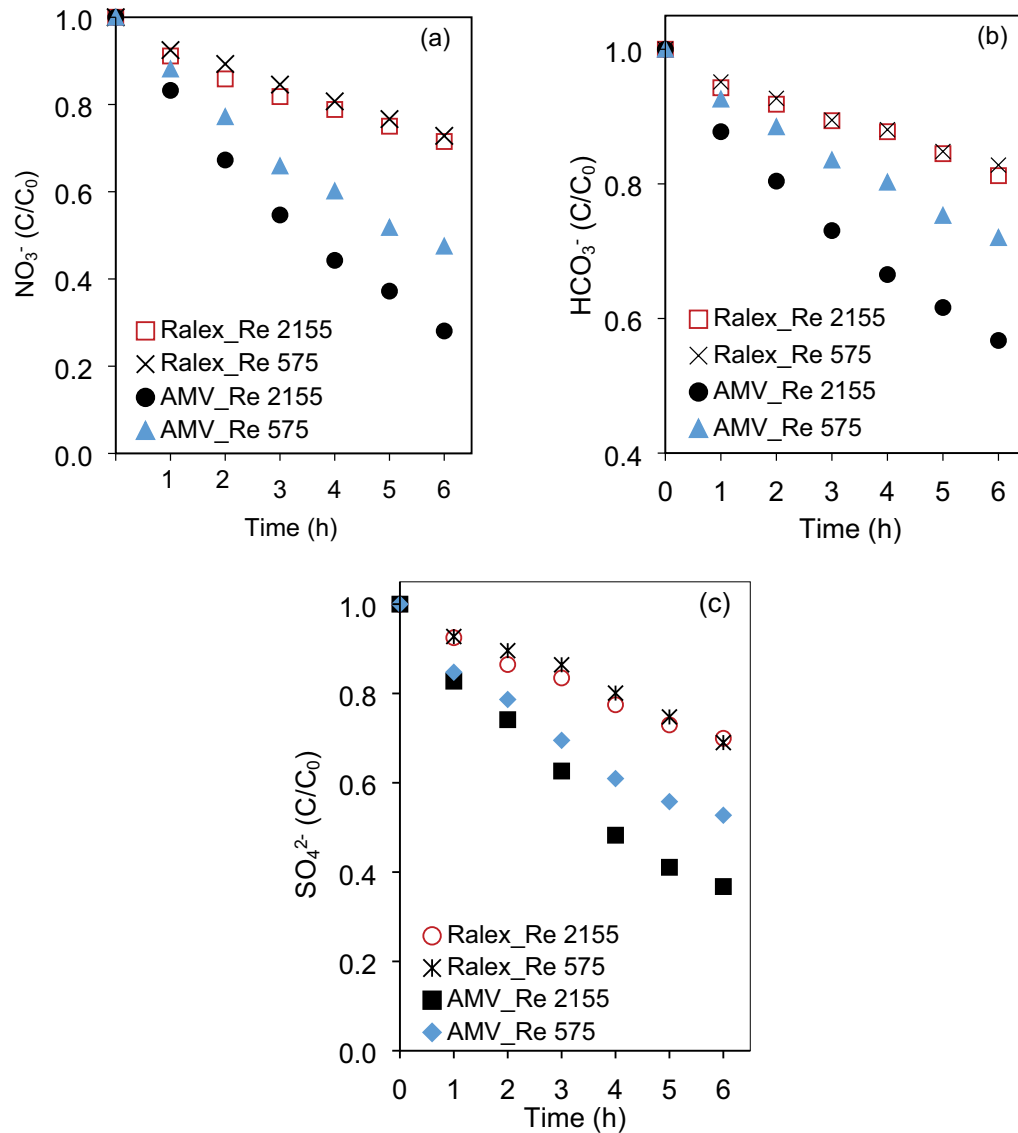


Fig. 8. Ion transfer from the feed solution at Reynolds numbers of 575 and 2,155 (a) nitrate at 50 mM, (b) bicarbonate at 50 mM, and (c) sulfate at 15 mM.

also depends on kinetics effects related to the differences between the ion diffusion coefficient in water (bulk solution) and in the membrane. Therefore, lower selectivity is obtained under dynamic conditions. Nonetheless, the same selectivity trend is observed under equilibrium and dynamic conditions [36]. At equilibrium, the selectivity coefficients of the Ralex membrane appear to be higher than those of the AMV membrane (Table 2). This is unexpected as the wider ionic channels/pores and looser structure of the heterogeneous membrane exhibit decreased selectivity [13,37,38]. It is postulated that the higher K_c values of the heterogeneous membrane result from lower concentrations of chloride inside the homogeneous membrane.

The permeability (P_m) and ion diffusion coefficients (D_m) of the membranes, were calculated using Eqs. (4)–(7). A detailed description of Donnan dialysis membrane diffusion control kinetic, including Eqs. (4)–(7) is shown elsewhere [29]. The experimental data presented in Fig. 9 was

used to calculate the permeability and diffusion coefficients, displayed in Table 2. Permeability of a diffusing species in the membrane governs the transport flux across the membrane. As seen in Table 2, the heterogeneous membrane exhibits lower permeability as compared to the homogeneous membrane most likely due to its greater thickness.

$$[X_i^{Z-}]_{m1/0} = [X_i^{Z-}]_{1/0} \left\{ \frac{[X^+]_m / Z[X_i^{Z-}]_0 - [X_i^{Z-}]_{m1/0}}{1 - [X_i^{Z-}]_{1/0}} \right\}^Z \quad (4)$$

$$[X_i^{Z-}]_{m2/0} = (1 - [X_i^{Z-}]_{1/0}) \left\{ \frac{[X^+]_m / Z[X_i^{Z-}]_0 - [X_i^{Z-}]_{m2/0}}{[Cl^-]_0 / Z[X_i^{Z-}]_0 - (1 - [X_i^{Z-}]_{1/0})} \right\}^Z \quad (5)$$

Table 2

Selectivity coefficients membrane permeabilities, and diffusion coefficients determined under diffusion controlled conditions (200 mM of each anion as a sole component in the feed and 1,000 mM of NaCl in the receiver)

Parameter	NO ₃ ⁻		HCO ₃ ⁻		SO ₄ ²⁻	
	AMV	Ralex	AMV	Ralex	AMV	Ralex
K_c	5.51 ± 0.79 ^a	7.01 ± 0.50	0.37 ± 0.04 ^a	0.65 ± 0.07	0.08 ± 0.03 ^a	0.42 ± 0.01
$P_m \times 10^{-4}$ (m/h)	12.3	3.6	4.7	2.2	5.3	2.4
$D_{mv} \times 10^{-7}$ (cm ² /s)	4.1	4.9	1.6	3.1	1.8	3.2

^aShemer et al. [41].

$$t \cdot \frac{S \cdot P_m}{V_F} = \int_{[X_i^{Z-}]_{i/0}}^1 \frac{d[X_i^{Z-}]_{1/0}}{[X_i^{Z-}]_{m1/0} - [X_i^{Z-}]_{m2/0}} \quad (6)$$

$$P_m = \frac{D_m}{\delta} \quad (7)$$

where X_i^{Z-} is the target ion, $[X_i^{Z-}]_0$ is the initial concentration of the target ion, $[X_i^{Z-}]_{1/0}$ the normalized concentration of the target ion in the feed; $[X_i^{Z-}]_{m1/0}$ and $[X_i^{Z-}]_{m2/0}$ are the normalized concentrations on the feed and receiver sides of the membrane, respectively; $[X^+]_m$ is the membrane ion-exchange capacity; V_F is the feed solution volume; S is the membrane surface area; δ is the thickness of the membrane.

Higher diffusivity coefficients were obtained for the heterogeneous membrane as compared to the homogeneous one (Table 2). It is not uncommon for a heterogeneous membrane to have a higher or similar diffusion coefficient as a homogeneous membrane [26,31,39,40]. This is attributed to free spaces in the heterogeneous membrane that facilitate the diffusion through the membrane. Inside the free spaces, the diffusion coefficients are higher by one to two orders of magnitudes compared to their diffusivity in the membrane [33]. Yet, due to its thickness, the transport through the heterogeneous membrane is lower than through the homogeneous membrane regardless of the higher diffusion coefficients [31]. The diffusion coefficients, listed in Table 2, are not to be confused with diffusion coefficients measured in the presence of an external driving force such as an electric field.

It is important to note that despite the structural differences between the membranes no electrolyte leakage and/or water osmosis transport was evident in both membrane types

4. Conclusions

Donnan dialysis separations of nitrate, bicarbonate, and sulfate, using homogeneous and heterogeneous membranes, were compared and correlated to the transport mechanism and to the properties of the anion exchange membranes. As expected, under boundary layer diffusion-controlled conditions a similar transport of each of the tested anions was observed with both the homogeneous and the heterogeneous membranes. Differences in the membrane's surface properties yielded a transition regime (i.e., combined boundary layer and membrane diffusion-controlled mechanisms) at a

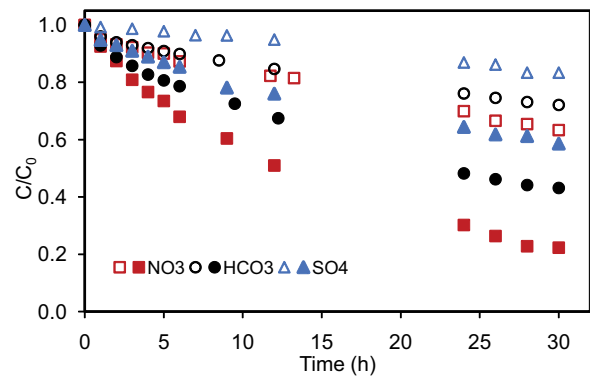


Fig. 9. Transfer of nitrate, bicarbonate and sulfate under membrane diffusion controlled conditions. Filled symbol for AMV and hollow symbols for Ralex ($[X^-]_0 = 200$ mM; $[NaCl] = 1,000$ mM).

lower concentration in the heterogeneous membrane. The range of concentrations at which both boundary layer and membrane diffusion prevail was found to be higher in the homogeneous membrane. The heterogeneous membrane showed lower separation efficiency under membrane diffusion-controlled conditions due to its inner structure and a greater thickness. The use of heterogeneous IEM for nitrate removal, from contaminated groundwater, by Donnan dialysis may be advantageous given the lower price of heterogeneous membranes and the fact that nitrate concentration in contaminated groundwater falls in the boundary layer diffusion-controlled regime; at which similar anions removal efficiencies are obtained using both membrane types.

Acknowledgments

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