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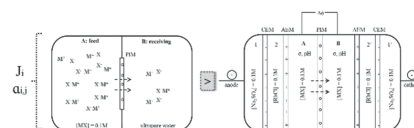
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Effect of Diffusion and Migration on the Selectivity of a Polymer Inclusion Membrane Containing Dicyclohexano-18-crown-6

Anna Casadellà, Anne Haye Galama, Olivier Schaetzle, Katja Loos*

Ion transport and selectivity are compared across a polymer inclusion membrane (PIM) containing dicyclohexano-18-crown-6 (DCH18C6, K^+ selective) under two driving forces: concentration gradient (diffusion) and electrical potential gradient (migration). The K^+ flux is much larger under diffusion ($140 \text{ mmol cm}^{-2} \text{ h}^{-1}$) than under migration ($\approx 4 \text{ mmol cm}^{-2} \text{ h}^{-1}$). The selectivity of NH_4^+ over K^+ is 86.0 for diffusion and 1.0 for migration. The selectivity of Na^+ over K^+ is 21.4 for diffusion and 1.16 for migration. Migration transport might induce a change in the orientation of DCH18C6 and reduce selectivity. Therefore, it is more favorable to apply diffusion rather than migration.



1. Introduction

Selective ion transport of cations and anions is possible with ion-exchange membranes (IEMs), as is for instance carried out in electrodialysis (ED).^[1,2] Also separation of monovalent and divalent ions is shown to be possible until a certain extent in ED processes.^[3,4] However, ions of equal charge, ion valence, size and mobility cannot be separated with IEMs. For that reason supported liquid membranes (SLMs) and polymer inclusion membranes (PIMs) are developed.^[5–9] It is recognized that PIMs have several advantages over SLMs, such as higher stability and higher fluxes.^[10,11] PIMs consist of a polymeric base that provides mechanical strength, a plasticizer that provides greater ion mobility, and a carrier that provides selectivity. In this

work, potassium selective PIMs are used which were previously developed and tested in diffusion experiments.^[10,12] The main drawback of diffusion-driven experiments and applications is that the transport and the recovery rate are limited by the chemical potential difference ($\Delta\mu$) generated by the two solutions adjacent to the membrane. When an additional driving force, for instance an electric potential difference ($\Delta\phi$) is added to the system, the ion transport rate can be enhanced and the process can be continued after the chemical equilibrium is reached.^[13] The application of an electric potential difference to extract and separate analytes from samples started in the late 19th century and its application across membranes, in the early beginning of the 20th century.^[14–17] It was not until 2006 that a $\Delta\phi$ was applied in a system containing a SLM inspiring the concept of electrokinetic membrane extraction (EME).^[18] In 2011 its application on PIMs was carried out by See et al. to extract lipophilic anions. However, their system required high potentials (1500 V) and the coulombic efficiency (CE) was limited by water splitting and gas bubble formation.^[19–21] The ion transport resistance of PIMs is much larger than that of commercially available IEMs, which leads to development of a high voltage drop over the membrane at relative low applied current densities. At these high voltage differences across the membrane water splitting will take place resulting in the formation of for instance oxygen gas and hydrogen gas bubbles. These gas bubbles have an

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insulating effect on the electrode and membrane surface, which leads to a further increase of transport resistance. In the event of water splitting additional charge carriers (protons and hydroxyl ions) are formed, when these ions move through the membrane (ineffective transport, not contributing to the intended ion separation) and a lower CE is observed. CE can be defined as the amount of charge transported by ions that need to be separated (effective transport) divided by the total amount of charge that is applied to the system.^[4] When an ED like setup is used, in which the electrodes are not directly located in the compartments adjacent the PIM, the CE of the process is likely to be increased as bubbles generated in the electrodes are not affecting the effective membrane surface area.

In this article, we evaluated the effect of two different applied driving forces: a concentration gradient and an electric field, on the transport of potassium and its competitive ions that have equal charge (+1), size and mobility across a PIM containing a carrier selective for K^+ (dicyclo-18-crown-6, DCH18C6).^[22,23] To prevent gas bubble formation in the compartments adjacent to the membrane, we used an ED setup. The selectivity of K^+ over Na^+ and NH_4^+ of both systems and the membrane resistance and the CE of the ED system were evaluated as well.

2. Experimental Section

2.1. Chemicals

Potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$), ammonium nitrate (NH_4NO_3), rubidium chloride ($RbCl$), sodium sulfate (Na_2SO_4), cellulose triacetate (CTA), 2-nitrophenyl octyl ether (2-NPOE), tris-(2-butoxyethyl)-phosphate (TBEP), dichloromethane (DCM), and dicyclohexano-18-crown-6 (DCH18C6) were purchased from Sigma Aldrich (The Netherlands). All chemicals (highest purity grade) were used without further purification. Aqueous solutions were prepared using ultrapure water obtained by a Millipore purification unit.

2.2. Membrane Preparation

Membranes were prepared following the procedure reported by Schow et al. and Sugiura et al.^[10,24] The composition of the membrane was 4 mL of 25.0 g L^{-1} of CTA in DCM, 3 mL of 74.5 g L^{-1} (200×10^{-3} M) of DCH18C6 in DCM and 0.05 g of TBEP and 0.15 g of 2-NPOE without dilution. The mixture was placed in a 9 cm diameter flat bottom glass Petri-dish. The dish was put in a flat box under nitrogen atmosphere overnight to allow the solvent to evaporate slowly and have little contact with air humidity, thus to avoid formation of pores (phase inversion). Then, membranes were peeled off the dish by adding a few droplets of ultrapure water. The resulting membranes had a thickness of 108 ± 13.6 μm , which was measured with a thickness gauge.

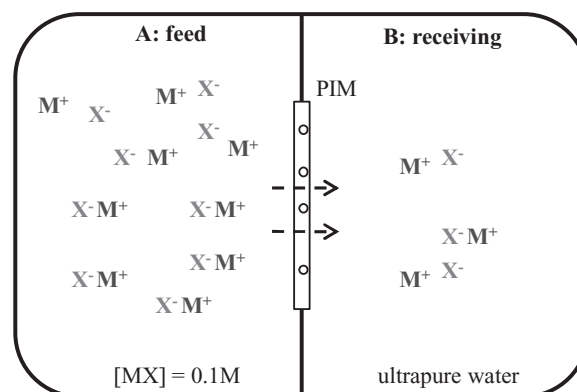


Figure 1. Schematic representation of the two-compartment system for diffusion assessment of cations (M^+) and anions (X^-).

Membranes were conditioned for 24 h in the nitrate solutions related to each test.

2.3. Transport Characterization

The evaluation of the ion transport across the PIM induced by an electric field (migration) was compared to the diffusion transport across the PIM. The capacity to transport 50% of the starting solution was evaluated as well as the ionic flux.

2.3.1. Diffusion

The diffusion of potassium, sodium, and ammonium across the synthesized PIM was investigated using a two-compartment system (Figure 1). The system was made of poly(methyl) methacrylate (PMMA) and consisted of two compartments between which the PIMs were clamped on a Teflon ring-shaped support. The PIM had a working area of 7.07 cm^2 . For reference the side of the membrane exposed to the nitrogen atmosphere during its synthesis was placed facing the receiving compartment. Each of the compartments had a volume of 150 mL and was continuously stirred at a speed of 500 rpm with magnetic stirring bars. The feed compartment was filled with 0.1 M aqueous solutions containing the nitrate salts, and the receiving compartment was filled with ultrapure water. All measurements were carried out at room temperature.

Samples of 1 mL were taken from each compartment at different time intervals. The volume difference was compensated by adding 1 mL of ultrapure water in the corresponding compartment after every sample. Because of the addition of ultrapure water, a dilution is induced in the phases so it was taken into account during calculations considering the added volume.

The flux J_i ($mmol\ cm^{-2}\ h^{-1}$) across the membranes for each of the ions was calculated as Equation (1):

$$J_i = \frac{V}{A} \frac{dC_i}{dt} \quad (1)$$

where V (L) is the volume of the compartment, A (cm^2) is the membrane working area and $\frac{dC_i}{dt}$ ($mmol\ L^{-1}\ h^{-1}$) is the concentration change in time.

The selectivity between two different ions ($\alpha_{i,j}$) (–) was calculated as Equation (2):

$$\alpha_{i,j} = \frac{J_i \Delta C_j}{J_j \Delta C_i} \quad (2)$$

where ΔC_i and ΔC_j are the concentration difference of each of the ions (i and j) at the end of the measurement.

2.3.2. Migration

To assess the migration of ions under influence of an applied electric field, the synthesized PIM with an active area of 7.07 cm^2 was tested in a six-compartment electro dialysis (ED) cell (Figure 2) equipped with a platinum electrode (7.07 cm^2) at each extreme. This ED system made of PMMA had a total volume capacity of 150 mL for compartments A and B and 75 mL for the other compartments (SST, The Netherlands). The compartments 1 and 1' located at both ends of the cell contained $0.1 \text{ M Na}_2\text{SO}_4$ (electrode rinse fluid). Solutions in 1 and 1' were connected and recycled by a double-head gear pump (Cole-Parmer Instrument Co., Digital Gear Pump, USA) (30 mL min^{-1}) to avoid the influence of the pH changes due to water splitting at the electrodes. Compartments 1 and 2 and 1' and 2' were in both cases separated by a cation-exchange membrane (CEM) (CMX, Neosepta, Tokuyama Co., Japan). Compartments 2 and 2' contained 0.1 M of RbCl. This solution was used to assess the permeability for Rb^+ of the anion-exchange membrane (AEM) (AMX, Neosepta, Tokuyama Co., Japan) that separated 2 and 2' from compartments A and B correspondingly. The RbCl solution was also used to receive anions from compartment A and provide anions to compartment B. RbCl solutions were recycled individually by a double-head gear pump (Cole-Parmer Instrument Co., Digital Gear Pump, USA) (30 mL min^{-1}). Taking into account the compartment volume and the recycling solution, each of the compartments 1, 1', 2 and 2' had a solution volume of 1 L.

All recycled solutions temperatures were controlled at $25 \pm 1.0 \text{ }^\circ\text{C}$ with a temperature-controlled water bath. The synthesized PIM was clamped in-between compartments A and

B located in the inner part of the setup and were continuously stirred at 500 rpm to reduce concentration polarization. Compartments A and B, adjacent to the PIM, were not recycled to simplify the determination of the transport of the ions.

For each of the experiments, both compartments contained 0.1 M of the solution. Samples of 1 mL were taken from each compartment to determine the concentration of cations (Rb^+ , Na^+ , K^+ , and NH_4^+) and anions (NO_3^- and Cl^-) in time. After sampling, 1 mL of ultrapure water was added back in both compartments to preserve the volume. The dilution effect was taken into account for the calculations considering the added volume.

A potentiostat/galvanostat (Autolab, Metrohm, The Netherlands) was used to apply a fixed current density and simultaneously measure the potential drop across the entire system. We used GPES as software. In the compartments A and B pH meters (CPS11D-7AA21, Endress Hauser), conductivity meters (σ) (QC205X, Quality in Sensing) and Ag/AgCl reference electrodes ($\Delta\phi$) (QM711X/gel, Quality in Sensing) were placed and connected to a data logger (RSG30, Endress Hauser).

In order to have a fair comparison with diffusion, compartments A and B should contain the same solutions as feed and receiving so 0.1 M KNO_3 and ultrapure water. However, the low conductivity of ultrapure water resulted in an internal resistance too high for the galvanostat/potentiostat. Therefore, compartments A and B contained the same solutions.

The CE (%) of the system was calculated as Equation (3):

$$\text{CE} = \frac{z_i F \Delta n_i}{Q} \times 100 \quad (3)$$

where $z_i(-)$ is the valence of the ion i, F (C mol^{-1}) is the Faraday constant, Δn_i (mol) is the measured amount of i transported and Q (C) is the charge that is applied to the system.

2.3.3. Ion Transport Resistance

The resistance of the membrane was studied by electrochemical impedance spectroscopy (EIS). We used a two-compartment system (as for diffusion) equipped with four platinum electrodes:

two working electrodes in solution of 0.1 M KNO_3 at 2 cm of the PIM and two reference at both extremes, which were long enough to be in contact with the PIM (Figure 3). The electrodes at both extremes crossed the system and only had contact with the solution and the PIM at their end point, the end of each of the membrane Teflon supports (same as the diffusion set-up). Therefore, the distance between the PIM and the extreme electrodes was negligible. The four electrodes were connected to a potentiostat/galvanostat (Autolab, Metrohm) and NOVA (Autolab, Metrohm) was the software used. Current densities from 0.0 to 10.0 A m^{-2} were applied with an amplitude of 10 mA and the frequency of the perturbation signal was from 1 Hz to 100 MHz.

The equivalent circuit model used for the simulation of the electrochemical impedance

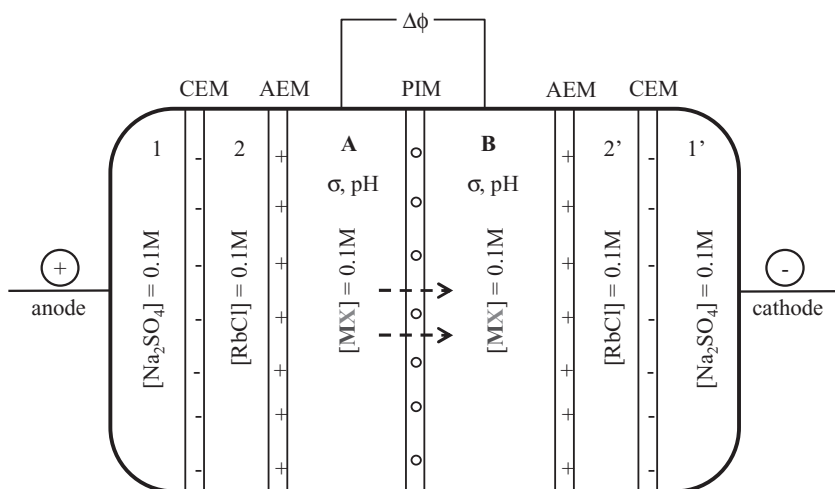


Figure 2. Schematic representation of the six-compartment system used for migration experiments.

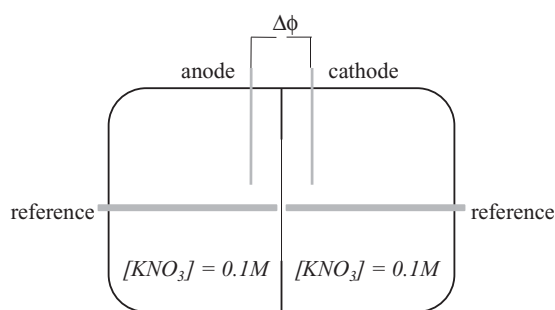


Figure 3. Schematic representation of the system used to measure EIS.

of the PIM is shown in Figure 4. The model has a resistance corresponding to the solution (R_{solution}), which is connected in series to the part corresponding to the bulk of the membrane. This part consists of a constant phase element ($\text{CPE}_{\text{membrane}}$) in parallel with a resistance (R_{membrane}). The equivalent impedance ($Z(\omega)$) of a parallel R-CPE circuit is calculated as Equation (4):

$$Z(\omega) = \frac{R}{1 + RQ(i\omega)^n} \quad (4)$$

where R is resistance, Q is the CPE admittance coefficient, $i = (-1)^{0.5}$, ω is the angular frequency of the perturbation signal and n ($0 < n < 1$) is a parameter that gives an indication of the capacitance of the system, where $n = 1$ would be a perfect capacitor.

A more complex R(R-CPE)(R-CPE) model taking into account the interface between the membrane and the solution was discarded since the Chi-square tests (χ^2) resulted in higher values.^[25]

The resistance of the six-compartment cell was measured prior to the start of the experiments using a milliohm meter (4338B, Agilent Technologies Inc., Santa Clara, USA).

2.4. Analyses

To determine the mass balance in both compartments, the concentration of K^+ , Na^+ , NH_4^+ , Rb^+ , Cl^- , and NO_3^- was determined by ion-chromatography (IC, Metrohm Compact, for cations IC 761 and for anions IC Pro 881). All required dilutions were carried out with ultrapure water (Millipore purification unit). DCH18C6 released into the aqueous phases was determined by LC-MS (Agilent 1200 series, column: G1316B – 6410 Triple Quad) using as mobile phase a solution (25:75) of formic acid-ammonia buffer at pH 8.75 and acetonitrile with 0.1 v/v% formic acid.

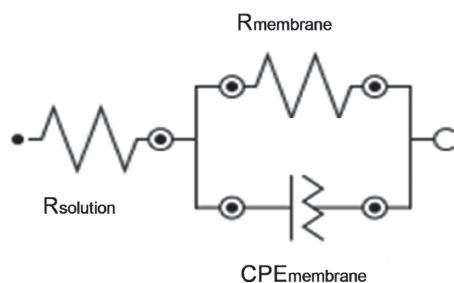


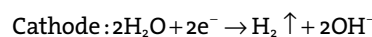
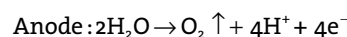
Figure 4. Equivalent circuit model for simulation of the membrane impedance.

3. Results and Discussion

The advantages of using a six-compartment cell in experiments requiring a potential difference were evaluated in terms of pH difference and bubble formation. The difference in flux and selectivity for ion transport driven by diffusion and a potential difference was assessed as well as the ion transport resistance.

3.1. Assessment of Buffer Compartments 2 and 2'

In our migration system (ED), the electrodes were placed at both ends of the system in compartments 1 and 1'. Due to the application of the potential difference, reactions occur at the electrodes and to prevent the products to reach the PIM, compartments 2 and 2' were used as buffer. These reactions at the electrodes are:



The electrode reactions, therefore, involve a pH change in the electrolyte and gas formation since H^+ and OH^- and O_2 and H_2 are produced. pH changes are highly unwanted when using a CTA-based PIM as already studied for example by Gherrou et al. and Gardner et al.^[26,27] Acidic conditions lead to the loss of the methyl groups of the CTA due to hydrolysis and therefore the CTA-based PIM becomes less hydrophobic and degrades into the aqueous phase. In addition, the change of pH alters the rinsing solutions leading to an acidic one in the anode and an alkaline one in the cathode increasing the resistance of the system as they saturate in time. Another possible drawback is related to NH_4^+ which pK_a is 9.25 and alkaline pH above the pK_a forwards the reaction to the release of $\text{NH}_3(\text{g})$ therefore the studying solutions in A and B are altered as well.^[23] To avoid these drawbacks, besides the incorporation of 2 and 2' as buffers, compartments, 1 and 1' were mixed and recycled together so that the pH of the incoming electrolyte remains constant. Table 1 presents the difference between the initial and final pH in compartments A and B for the three current densities (j) applied. We considered that a difference up to 5% was attributed to the sensor intrinsic error. Due to a difference in every case within 5%, the strategy to connect compartments 1 and 1' and the presence of the buffer compartments 2 and 2' guarantee a negligible effect of the pH changes in 1 and 2' in A and B and no modification of the chemical structure of the PIM due to pH.

■ Table 1. Difference between the initial and final pH in compartments A and B regarding the j applied.

j [Am ⁻²]	A		B	
	pH _{initial}	pH _{final}	pH _{initial}	pH _{final}
5	4.83	4.61	5.06	5.15
10	4.91	4.67	5.90	6.08
15	4.98	5.02	5.63	5.91

In compartments A and B no gas bubbles were visibly detected so the ion transport was not affected by O₂ and H₂—the gas products at the electrodes.

3.2. Transport of K⁺

The transport of K⁺ was characterized and compared between diffusion (transport induced by a concentration difference) and migration (transport induced by an applied electric field) to evaluate the effect of an applied current on the performance of the PIM. Tests regarding solely diffusion in the two-compartment system were carried out until equilibrium was reached, which was when half the amount of K⁺ (7.5 mmol) was transported from the feed to the receiving side. To evaluate whether the application of an electric field enhanced the transport regarding flux, the experiments regarding migration were carried out for as long as the theoretically required (100% CE) time required to transport 7.5 mmol of K⁺.

As mentioned in the experimental section, compartments A and B should contain the same solutions as feed and receiving so 0.1 M KNO₃ and ultrapure water. However, the low conductivity of ultrapure water resulted in a big resistance of the system that the used galvanostat/potentiostat could not overcome. Therefore, compartments A and B contained the same solutions. The aim here is to evaluate if ion-exchange enhanced the ion transport for the PIM under study.

Analysis showed no transport of Rb⁺, Na⁺, and SO₄²⁻ into the compartments A or B, therefore, unwanted transport of undesired ions was not occurring.

Table 2 is an overview of the effect of the applied driving force (concentration or potential difference) on the transport of 7.5 mmol of K⁺ regarding the time, the current efficiency (CE) and the amount of mmoles in the PIM. The higher the applied current density (j), the lower is the theoretical time (regarding charge transport) required to transport 7.5 mmol. However, the measured amount of transported mmoles is substantially lower as shown by the mass balance in Table 2 of the feed and receiving compartments, leading to a reduced calculated CE. The amount of transported K⁺ increases as the applied current density increases, but does not reach the established transport of 7.5 mmol. Because undesired ions were not transported, our hypothesis is that this transported amount is not reached mainly due to the participation of electrons or ions in side steps for instance back diffusion of ions from compartment B to A or water splitting (electrolysis) at the electrodes. Moreover, the low concentration difference between compartments A and B could be another reason for the low CE.^[28] The mechanism of such PIM is usually co-transport (cation and anion are transported in the same direction to maintain electroneutrality) and in the ED system ion-exchange is forced (cation and anion are transported in opposite directions due to the electric field) and results show it is not favorable for the system.^[8,12]

3.3. Selectivity

The application of an electric field across the PIM decreased the selectivity of the membrane considerably as shown in Table 3. When the ion transport was driven by diffusion,

■ Table 2. Comparison of K⁺ transport by diffusion and at different applied current densities.

j [A m ⁻²]	Time [h]	CE [%]	$J_i \times 10^{-3}$ [mmol cm ⁻² h ⁻¹]	K ⁺ transported [mmol]		K ⁺ in PIM [mmol]
				A	B	
Diffusion ^{a)}	50.5 ^{b)}	n/a	140	10.7 ± 0.51	7.42 ± 0.37	3.28
0.0	∞	n/a	n/a	n/a	n/a	n/a
5.0	56.9 ^{c)}	33.3	11.2	3.98 ± 0.64	2.25 ± 0.11	1.73
10	28.4 ^{c)}	37.1	14.3	4.20 ± 0.53	2.85 ± 0.64	1.35
15	18.9 ^{c)}	44.0	24.4	4.17 ± 0.24	3.30 ± 0.25	0.87

^{a)}Two-compartment system; ^{b)}Experimental time for the transport of 7.5 mmol; ^{c)}Theoretical time for the transport of 7.5 mmol.

Table 3. Selectivity of K^+ over Na^+ and NH_4^+ regarding the driving force.

	Diffusion	Migration
$\alpha_{K,NH_4} [-]$	86.0	1.00
$\alpha_{K,Na} [-]$	21.4	1.16

the membrane reached a selectivity of 86.0 for K^+ over NH_4^+ and 21.4 over Na^+ . However, when the ion transport was driven by an electric field, the selectivity was negligible (1.0) for K^+ over NH_4^+ and very low (1.16) over Na^+ . The selectivity reached by the electric field is lower than the mobility ratios between K^+ and the NH_4^+ (1.05) and K^+ and Na^+ (1.47).^[23] This suggests that the selectivity is mainly based on the electric field, not the mobility of the ions. Our main hypothesis is that the reduction of the selectivity might be due to the application of a higher potential than the one DCH18C6 applies to complex the cations and give selectivity. Therefore, cations are not retained by the crown ether and the selectivity provided is canceled. The effect of the electric field could rely on the alteration of the orientation of the DCH18C6 as only 0.01 wt% of DCH18C6 was determined by LC-MS when measuring its release in compartments A and B. This ionophore (Figure 5) contains 6 ethers (C—O—C) that provide a negative charge density to the molecule and allows its complexation with cations and also determine the size of the ionophore together with the two cyclohexans. These two facts combined and the proper activation energy for the complex grant the selectivity of DCH18C6.^[29,30] However, the application of an electric field could lead to a change in the orientation of the crown because the ethers (negative charge density) could rearrange to the field. This fact was already studied by Bezrukov et al. who saw that a crown ether in the presence of a potential difference changed its conformation in the *cis* or *trans* form regarding the direction of the field.^[31] This changes lead to an effect on the transport across the membrane.

3.4. Ion Transport Resistance

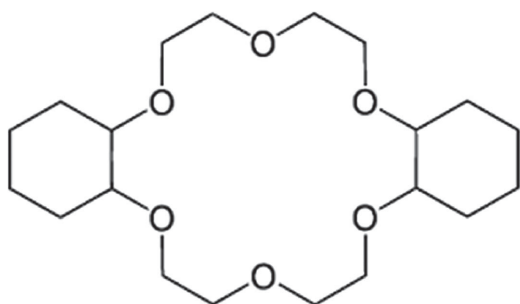


Figure 5. Chemical structure of DCH18C6.

The reorientation of the DCH18C6 in the electric field therefore provides an ion transport resistance. The large difference in ion flux between the diffusion and migration experiment could be associated with the resistance of the PIM. When a current was applied, a large potential drop was measured over the membrane stack, which was caused by the PIM as the IEMs separating the other compartments have only small resistance at the given ion concentrations.^[32] Electrochemical impedance spectroscopy (EIS) was used to estimate the resistance of the PIM in a solution of 0.1 M KNO_3 . Employing the equivalent circuit described in the experimental section, a simulation of the resistance of the PIM was carried out for the range of the studied current densities. The fitting and simulation gave for the Chi-square test (χ^2) values between 0.974 and 0.998, an n parameter between 0.89 and 0.99 and, a PIM resistance of $7258 \pm 177.2 \Omega \text{ cm}^2$. Commercial IEM with comparable thickness ($\approx 100 \mu\text{m}$) either CEM or AEM have in general a resistance below $10 \Omega \text{ cm}^2$.^[32] Thus our PIM based on CTA, DCH18C6, TBEP and NPOE has an ion transport resistance around 725 times higher than the commercial IEMs. Moreover, taking into account the resistance of the six-compartment cell is $10\,605 \Omega \text{ cm}^2$, the resistance of PIM corresponds to 68.44% of the total resistance. The contribution of both resistances explains the slow ion fluxes.

4. Conclusions

The enhancement of the selective ion transport across a PIM by applying an electric potential gradient as well as by the setup used was investigated. To evaluate if an enhanced process could be obtained, results of experiments with a fixed applied electrical current were compared with the results obtained from diffusion experiments.

The transported K^+ had a higher flux for diffusion ($140 \text{ mmol cm}^{-2} \text{ h}^{-1}$) than for migration ($\approx 4 \text{ mmol cm}^{-2} \text{ h}^{-1}$). This was due to side reactions at the electrodes such as water splitting, a high resistance of the PIM ($7258 \pm 177.2 \Omega \text{ cm}^2$) and a favorable transport mechanism of co-transport rather than ion exchange. Due to high resistance only small applied current densities can be applied and water splitting occurs even at the small applied current densities what resulted in a relative low coulombic efficiency of 33%–44%.

Besides a flux that is about 35 times lower, also the selectivity of a PIM in an electro dialysis like system appears to be much smaller than in the diffusion system. The selectivity of NH_4^+ over K^+ is 86.0 for diffusion while it is 1.0 for migration. The selectivity of Na^+ over K^+ is 21.4 for diffusion while it is 1.16 for migration. The application of an electric field could alter the orientation of the crown as the ethers (negative charge density) could rearrange to the field and therefore the selectivity is reduced. Further

investigation on the effect of an applied electric field on the PIMs is required. This study shows that in terms of selectivity, and ion flux it is more advantageous to use a diffusion based system compared to a migration based system for the selective removal of K^+ from an aqueous K^+ , Na^+ , and NH_4^+ solution.

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