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Influence of anion hydration status on selective properties of a commercial anion exchange membrane electrochemically impregnated with polyaniline deposits

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There is currently great interest in the use of polyaniline (PAni) to impart particular properties to anion exchange membranes, employed in several fields. This special polymeric material can be obtained both chemically and electrochemically; however, the latter affords better control of morphology, which could be used to promote some properties of PAni-based membranes, such as their selectivity or hydrophobic/hydrophilic balance. In this work, commercially available membranes were electrochemically modified with PAni to improve their hydrophobic/hydrophilic balance, and this was achieved by cyclic voltammetry in acidic solutions. The performance of the modified membranes in the electrodialysis process of a nitrate–chloride mixture in neutral solutions was then evaluated. The impregnation imparts specific selective properties to the commercial membrane that lead to a greater retention of chloride ions. This property derives from the higher hydrophobicity of the PAni deposited on the membrane, which leads to a more effective exclusion of the more hydrated chloride anions.

1. Introduction

The selectivity of an ion exchange membrane (IEM) is influenced by the interactions between the species passing through it and each of the components of the membrane.[1–4] These interactions are controlled by different factors, such as the hydrophobic/hydrophilic balance of the membrane, or the intensity of the electrostatic interactions.[5,6] For example, the selectivity of the membrane increases when the concentration of fixed charged groups in the membrane is high; however, an excess of charge results in poor mechanical properties. Furthermore, an increase in the number of fixed charges produces accumulation of solvating water, which in turn results in a higher electrical resistance of the membranes, increasing the costs of the processes in which they are employed. The nature of the species passing through the membrane also plays an important role: it has been shown that the ion exchange membranes exhibit greater selectivity towards higher-charge and more hydrated ions.[6]

Several studies reported in the literature describe attempts to improve the selectivity of a membrane by exploiting the effects discussed above.[7–13] For example, polyaniline (PAni) has been used to impart specific properties to the membranes because – besides its flexibility and unique electrical conductivity – this material has the special capacity to generate charges in its bulk under certain conditions (such as chemical or electrochemical doping).[11–17] Furthermore, its different chemical forms exhibit not only specific structural characteristics, but also particular hydrophobic/hydrophilic properties. For example, the non-protonated form of PAni, named leucoemeraldine base, is more hydrophobic due to the polar C–N, C═N, and N–H bonds in its structure; moreover, due to its ability to form hydrogen bonds, leucoemeraldine base presents the most compact and rough structure among the different PAni forms. On the other hand, protonated emeraldine (doped) is the oxidized form of PAni and has a lower hydrophobicity, due positive charges present in its structure; moreover, the repulsive interactions associated to these charges produce a more homogeneous and porous material. The last form of PAni, called pernigraniline, is the most oxidized one and contains single C–N and double C═N bonds, which cause it to be highly hydrophobic.[14,18–20]

According to the literature, PAni could be obtained in any of these chemical forms by varying the potential applied to it, using either a voltammetric potential scan or a potential pulse. For example, at potential values lower than +0.2 V *vs.* SCE, PAni is found in the leucoemeraldine form, whereas pernigraniline is formed at potentials higher than +0.55 V *vs.* SCE. Between these two limits, PAni is found in the protonated emeraldine form. These data suggest that a specific chemical form of PAni can be selected by adjusting the imposed potential.[19]

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These characteristics of PAni have generated expectations that the selectivity properties of membranes can be modified. Despite this, however, efforts have concentrated mainly on their use as cation-exchange membranes,[11–13,21–24] while there is very little information on anion exchange membrane modifications using different chemical forms of polyaniline.[21]

Cation-exchange membranes modified with PAni have been used to establish the influence of ion hydration and the hydrophobic balance of the membrane on selectivity. For example, van der Bruggen *et al.*[22] and Farrokhzad *et al.*[23] established that small, hydrated, cations can penetrate and diffuse through a hydrophilic surface and the modified membrane consequently has a high cation-removing capability.

A similar result was obtained by Sata when using anion exchange membranes chemically modified with polypyrrole.[24] The author suggests that the affinities of less-hydrated anions for these membranes increase with decreasing membrane hydrophilicity, irrespective of the charge.

This work investigates the selectivity of commercially available anion exchange membranes modified with PAni; in particular, we investigate the effect of applying a specific potential in order to promote the formation of a chemical form of PAni, which impart a different hydrophobic/hydrophilic character to the membrane. The properties of membranes modified with PAni were fully characterized, in order to rationalize their selectivity in the electrodialysis (ED) of a nitrate–chloride mixture with neutral pH. The selected ionic species in the mixture have similar size and charge but a significantly different hydration number.

2. Experimental

2.1 Materials and methods

2.1.1 Properties of NO_3^- and Cl^- ions. Table 1 shows some of the physicochemical characteristics of the nitrate and chloride ions investigated in this work.[24,25]

The data in the table show that the two anions have similar characteristics such as charge, ionic radius, and conductivity at infinite dilution, whereas other properties such as molar mass and hydration number differ. In particular, the table shows that the chloride ion is more hydrated, with six water molecules in its hydration shell, compared to only four molecules for the nitrate ion.

2.2.2 Commercial membrane. PAni was deposited on a Neosepta anion exchange membrane (ASTOM Co., Japan) denoted AFN by the manufacturer. This is a homogenous membrane with $-NR_3^+$ groups as fixed charges. Some of the main properties of this membrane are shown in Table 2.[26,27]

Table 1 Properties of NO_3^- and Cl^- ions.[24,25]

Property	NO_3^-	Cl^-
Molecular weight (g mol^{-1})	62.01	35.50
Ionic radius (nm)	0.3	0.3
Charge	−1	−1
Hydration number	4	6
Gibbs hydration energy (kJ mol^{-1})	−270	−317

Table 2 Selected properties of the AFN membrane.[26,27]

Parameter	Value
Electrical resistance (Ω cm^2)	0.4–1.5
Transport number of NO_3^- in $NaNO_3$ 0.1 M	0.93
Transport number of Cl^- in NaCl 0.1 M	0.92
Thickness (μm)	130–180
Ion exchange capacity (meq g^{-1})	2.0–3.5

Circular cuts of the membrane with an area of 4.9 cm^2 were used for the different experiments carried out in this work. In addition, a pretreatment was used to remove any possible contaminants introduced during the transportation of the membrane to the laboratory. The pretreatment consisted in placing the membrane in a 1 M nitric acid bath for 24 h with moderate agitation, followed by rinsing several times with deionized water in order to eliminate any trace of HNO_3. Finally, the membranes where kept in H_2SO_4 1 M for 24 h before the modification treatment.[28–30]

2.2 Modification of the commercial membrane with polyaniline

The amount of PAni deposited on the membrane was controlled by cyclic voltammetry (CV) in acidic solution following the methodology described below.

2.2.1 Working electrode. A carbon paste electrode was used for the membrane modification.[28] The electrode was prepared by intimately mixing 1.0 g of finely ground graphite powder (<50 μm, Merck) with 1.0 g of Nujol (Alfa Aesar) as a binder. The resulting paste was placed in a plastic tube for easier manipulation and a piece of copper wire was wound to produce electrical contact with the potentiostat. Before each experiment the surface of electrode was smoothed using weight paper. Subsequently the membrane was adhered to the surface of paste electrode. This procedure resulted in a work surface on the carbon paste electrode of 3.8 cm^2, which also corresponds to the modified surface of the membrane.

2.2.2 Aniline working solution. The solutions used to modify the membranes were prepared from reactive grade aniline obtained from Sigma-Aldrich, H_2SO_4 (Fermont, 97%), and deionized ultrapure water with a resistivity of 18 MΩ cm, obtained from a Millipore Milli-Q water purification system. The aniline was distilled and kept under refrigeration before use, whereas the other reagents were used as received. The concentration of the aniline working solution was 0.1 M in H_2SO_4 1 M. All experiments were carried out at room temperature.

2.2.3 Experimental setup. A 3-electrode cell was employed in the experiments. The working electrode was a tube filled with carbon paste, over which the membrane was attached. An Ag|AgCl|NaCl (3 M) cell was used as reference electrode, which was placed inside a glass extension filled only with the supporting electrolyte. Finally, a 25 cm-long Pt wire was used as auxiliary electrode, also placed inside a glass extension filled only with the supporting electrolyte.

All electrodes were connected to an Autolab PGSTAT 302 N potentiostat/galvanostat, which was used to modify the membrane by carrying out potential scans from −100 to +1000 mV for 40 cycles at a scan rate of 100 mV s^{-1}. It should be noted that the initial and final potential during this process was −100 mV. Following the formation of the PAni deposits, the membrane was separated from the carbon paste electrode and washed using chloroform and an ultrasonic bath until every trace of paste was eliminated. After this procedure, the membrane was rinsed several times with deionized water and finally stored in a 1 M NaCl solution.[29,30] This procedure was repeated as many times as needed to produce sufficiently modified membranes, suitable for the subsequent experiments.

2.2.4 Use of the modified membrane. Before using the modified membrane in each experiment, a clean carbon paste electrode was used to attach the modified side of the membrane to the working electrode and a potentiostat was used to apply a potential of −100 mV *vs.* Ag|AgCl|NaCl (3 M) for 20 min. After this procedure, the membrane was cleaned of any residual paste and stored in a 1 M $NaNO_3$ or 1 M NaCl solution for later use in the characterization or electrodialysis experiments.

Each experiment was performed in triplicate on a newly modified membrane, obtained through the sequence of steps described above.

In the case of electrodialysis experiments only the recently modified membranes were used.

2.3 Characterization of the modified membranes

The modified membranes were characterized by analyzing their counterion transport number (t_a), ion exchange capacity (IEC), water content (% H_2O), contact angle as well as their *I–E* curves and infrared spectra. The methodology used to obtain each set of data is described in the following sections.

2.3.1 Determination of the counterion transport number. The counterion transport number was measured using the concentration cell method introduced by Ltief *et al.*,[31] which consists in using reference electrodes to measure the membrane potential generated when the membrane separates two solutions with different chemical activity.

The corresponding experimental setup involved placing the membrane (of exposed area 0.7853 cm^2) between two symmetric glass beakers with a tube of 1 cm length and 1 cm internal diameter. Two Ag|AgCl|NaCl (3 M) reference electrodes were used to measure the membrane potential. Each electrode was placed inside a glass extension filled with NaCl 3 M. The top of the glass extension was blocked with an agar plug (3% w/w), which prevented loss of NaCl solution and established the ionic contact. The membrane potential was measured every 10 s for 15 min with a UNI-T UT70C multimeter, which was connected to a computer by a R232 port and was controlled through the UT70C software. The experiments were performed under constant agitation and the initial and final temperatures were recorded in each experiment.

For the determination of the transport number at a concentration of 0.01 M, we employed a set of four solutions of different concentrations (namely, two higher and two lower concentrations); t_a was determined from the measured membrane potential, E_m, according to the following equation:

$$E_{\mathrm{m}} = (2t_a - 1)\frac{RT}{zF}\ln\frac{a_1}{a_2} \tag{1}$$

where a_1 and a_2 are the chemical activities of a solution whose concentration is kept constant and a solution of variable concentration, respectively. *R* represents the gas constant, *T* the temperature, while *z* and *F* are the charge and the Faraday constant, respectively.

When working with the modified membranes, special care was taken to ensure that the modified side of the membrane was in contact with the solution of higher concentration.

2.3.2 Determination of the ion exchange capacity. The ion exchange capacity of a selective membrane is directly related to the concentration of fixed groups in the membrane itself. The methodology employed for its determination exploits the acid-base properties of the fixed groups. For the specific case of an anion exchange membrane, it is necessary to transform the membrane to its basic form first, after which the OH− ions are exchanged by another anion, for example NO_3^-. The OH− ions are quantified by titration using a normalized acidic solution. The equivalence point can be tracked by using an indicator or by following the changes in pH as a function of the volume of acid used.[27,32,33]

The membranes examined in this study were equilibrated in a normalized NaOH solution (0.1 N, Hycel) for 24 h. After this step, the membrane was rinsed with deionized water and equilibrated for 24 h in 50 mL of a 0.1 M solution of $NaNO_3$. The increase in basicity of the $NaNO_3$ solution was monitored by acid-base titrations using a normalized HCl solution (0.1 N, CTR Scientific) and a Metrohm 827 pH Lab pH meter. Finally, the IEC was calculated as:

$$\mathrm{IEC} = \frac{VC}{w_{\mathrm{s}}} \tag{2}$$

where *V* represents the volume of acid employed, *C* its concentration, and w_s the dry weight of the membrane.

2.3.3 Determination of the water content in the membrane. The water content in the membrane depends of several factors, such as the chemical nature of the polymer, the type and concentration of fixed groups, the counterions, the crosslinking degree, and the homogeneity of the membrane. Some water molecules present in the membrane are free, whereas others are bonded to the polymeric structure, and the remaining ones form the solvation sphere of the fixed charges and counterions. The fraction of the latter molecules depends on the concentration and chemical nature of the ions, for example the size of the hydrated ion.[27]

The methodology employed for determining the water content consists in evaporating the water molecules inside the membrane by drying at constant temperature. For this purpose, the membrane was kept in deionized water for 24 h, after which it was superficially dried with a paper towel and weighed (W_0). Then, the membrane was dried at 55 °C for 2 h or until a constant weight (W_f) was reached. The water content in the membrane was then calculated using the following expression:

$$\%\,\mathrm{H_2O} = \frac{W_0 - W_{\mathrm{f}}}{W_{\mathrm{f}}} \times 100 \tag{3}$$

2.3.4 Contact angle measurements. The contact angle of water on the modified membranes was measured with a Ramé-hart instrument Models 250. Prior to measurement, the membranes were dried for 1 h in a DHG-9145A Hinotek oven.

2.3.5 Infrared spectroscopy measurements. Infrared spectra were obtained by Fourier transform infrared spectroscopy (FTIR) using a Thermo Nicolet 470 FTIR spectrophotometer.

2.3.6 *I–E* curves. The experimental setup used for obtaining the *I–E* curves consists of three membranes; the membrane under study was placed between a Neosepta AFX membrane used to isolate the anode and a Neosepta CMX membrane used to isolate the cathode. The effective area of all membranes was 0.7854 cm^2. The membranes were placed for 24 h in a 1 M solution of $NaNO_3$ in order to replace the counterions with NO_3^-, and then equilibrated for at least 1 h in the working solution before each experiment. Two identical Pt wires were used as anode and cathode, and two Ag/AgCl/NaCl (3 M) reference electrodes were employed to measure the membrane potential developed during the experiments. $NaNO_3$ 0.01 M was used as working solution.[29,30]

The *I–E* curves were obtained by performing linear current scans with a scan rate of 1×10^{-5} A s^{-1}. An Autolab PGSTAT 302 N potentiostat/galvanostat was employed to control the applied current and measure the potentials. The working solution was renewed after every experiment and all experiments were performed in triplicate.

2.4 Electrodialysis

The use of the modified membranes for the separation of nitrates in a nitrate–chloride mixture was assessed by electrodialysis under a constant electric current density, as detailed in the following sections.

2.4.1 Solutions. The solutions used in this part of the work were prepared from $NaNO_3$ and NaCl salts (Fermont), along with deionized water (of resistivity 18 MΩ cm) obtained from a Millipore system. The concentration of each ion in the mixture was 0.1 M. A 0.3 M solution of Na_2SO_4 (Fermont) was used for rinsing the electrodes.

2.4.2 Complementary membranes. The electrodialysis experiments were performed using two cationic exchange membranes denoted CMX (Tokuyama Soda Ltd.) as auxiliary membrane. These membranes were used to prevent Cl_2 production ($2Cl^- \rightarrow Cl_2 + 2e$) at the anode, and pH increases resulting from the migration of OH– from the cathode.

2.4.3 Electrodes. Two platinum plates of 99% purity obtained from Heraeus Vectra were used as electrodes for controlling the applied current during the experiments. These electrodes were rinsed during ED by a 0.1 M solution of Na_2SO_4.

2.4.4 Experimental setup of the electrodialysis tests. The ED stack used in this work was fabricated in our laboratory; it was made of acrylic material and consisted of two compartments of 3 cm (length) × 5 cm (width) dimensions. This design allowed using three ion exchange membranes with an exposed area of 1 cm^2. Special attention was paid to ensure that the modified side of the membrane always faced the cathode, in order for the PAni deposit to be the first barrier encountered during the migration of the anions.

According to the design of the ED stack, three separated circuits for the diluate, concentrate, and electrode rinsing solutions were obtained. Each solution was 50 mL in volume, and was recirculated by a separate peristaltic pump (Mityflex). The initial concentrations in the diluate and concentrate compartments were 0.1 M NaCl + 0.1 M $NaNO_3$. The membrane stack was connected to a homemade DC power supply operated under constant current during a 2 h experiment.

In addition, two multimeters (UNI-T UT70C) and a pH meter (Oaklon) were used to complement the experimental setup (Fig. 1).

2.4.5 Sampling. The efficiency of the unmodified and PAni-modified membrane used in the separation of a nitrate–chloride mixture was assessed by periodically taking an aliquot of 5 mL from the solutions (diluate and concentrate) on both sides of the membrane under study, in order to avoid significant variations in the solution volumes passing through the electrodialyzer. Only the aliquot taken from the diluted compartment was analyzed for extracting the concentration of nitrates and chlorides. The nitrate concentration was determined by UV-vis spectrophotometry using a wavelength of 302 nm, whereas the chloride concentration was determined with a silver nitrate standard.

2.4.6 Membrane selectivity and Cl^- and NO_3^- fluxes. After the ED experiment had been running for 180 min, the fluxes (J_{anion}) of Cl^- and NO_3^- through each membrane was evaluated using eqn (4):

$$J_{\text{anion}} = \frac{V}{A_{\text{m}}} \times \left(\frac{\mathrm{d}C_{\text{anion}}}{\mathrm{d}t}\right) \tag{4}$$

where V is the volume of the circulated solution and A_{m} is the membrane area. The concentration changes with time ($\mathrm{d}C_{\text{anion}}/\mathrm{d}t$) in the diluate compartment was calculated using the plot of Canion *vs.* ED performance time.

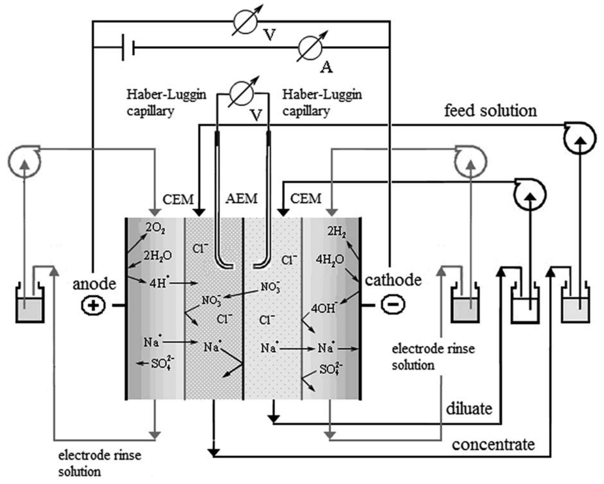

Fig. 1 Schematic representation of the experimental setup: CEM and AEM denote cationic exchange and anionic exchange membranes, respectively.

The ion selectivity of each membrane was calculated at the end of the treatment using eqn (5):[24]

$$P_{\mathrm{Cl}^-}^{\mathrm{NO_3}^-} = \frac{t_{\mathrm{NO_3}^-} \big/ t_{\mathrm{Cl}^-}}{C_{\mathrm{NO_3}^-} \big/ C_{\mathrm{Cl}^-}} \qquad (5)$$

where $t_{\mathrm{NO_3}^-}$ and t_{Cl^-} are the transport numbers of the nitrate and chloride ions in each membrane and $C_{\mathrm{NO_3}^-}$ and C_{Cl^-} are the average concentrations of the two anions during electrodialysis using each membrane.

3. Results and discussion

3.1 Optimization of the number of cyclic voltammetry cycles for the electrosynthesis of polyaniline

Cyclic voltammetry (CV) is a versatile technique that has proven its relevance in the electrosynthesis of conductive polymers.[34] Among the main characteristics of CV, is the possibility to control both the morphology of the conductive polymer and the amount deposited onto a surface by means of the number of potential scanning cycles, at a certain potential scan rate and between the appropriate potential limits.

To optimize our procedure, we determined the appropriate number of potential scanning cycles needed to modify the commercial membrane used in this work. To achieve this, different membranes were modified with PAni deposits, which were obtained using 20–70 sweep cycles. Based on previous studies, the potential range was fixed between −100 and 1000 mV and the sweep velocity was fixed at 100 mV s^{-1}.[29,30]

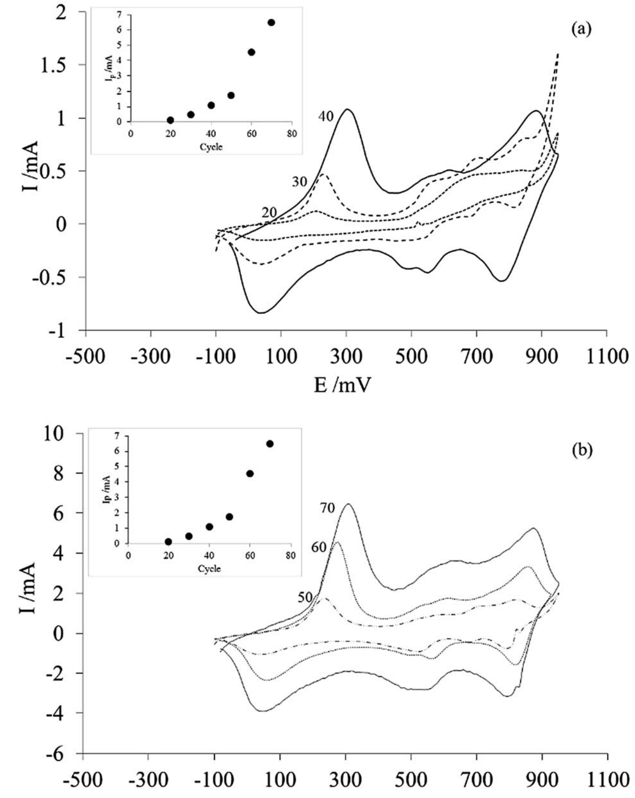

Fig. 2 Cyclic voltammograms of PAni deposited on membranes using (a) 20 to 40 and (b) 50 to 70 potential scanning cycles, obtained in a solution of 0.5 M sulfuric acid at 100 mV s^{-1}. The peak current (I_p) of the anode peak located between −100 mV and 500 mV, as a function of the number of scan cycles, is shown in the inset.

Fig. 2 shows the voltammograms of each of the PAni deposits obtained by varying the number of cycles in a 0.5 M sulfuric acid solution.

From the voltammograms, it can be seen that the order of magnitude of the current for each of the responses obtained is directly proportional to the number of sweep cycles. This is clearer in the inset with the peak current (I_p) of the anodic peak located between −100 mV and 500 mV. Assuming that the area under the curve corresponds to the charge and that the charge is proportional to the amount of material deposited, the amount of PAni deposited on the membrane increases with increasing number of sweep cycles. In addition, another characteristic of these curves is that the obtained voltammograms (Fig. 1) correspond to the typical response of PAni only if the number of sweep cycles is greater than 40.[20]

This confirms that the number of potential scanning cycles determines the amount of PAni deposited onto the commercial membrane; thus, membrane modification can be controlled using cyclic voltammetry.

Finally, considering this, we decided to use the modified membrane, prepared using 40 scanning cycles, to ascertain how small amounts of PAni could affect membrane selectivity during electrodialysis.

3.2 Electrochemical modification of the membranes *via* PAni deposition

Fig. 3 shows the last 17 scan cycles recorded during the electropolymerization process of PAni on the membrane (Fig. 2a), along with the voltammetric response of the electrode/modified membrane assembly obtained in an acidic solution free of aniline monomer (Fig. 3b). The main feature of the *I–E* curves in Fig. 2a is that the current recorded during the electropolymerization of PAni increases with each scan cycle, which is a behavior typical of the growth of an electroactive film on the electrode (paste/membrane assembly). Additionally, all voltammograms exhibit the characteristic features (number and shape of peaks) of PAni.[20,34] These same features are also present in the voltammetric response obtained after moving the post-modification electrode assembly to a solution free of aniline monomer (Fig. 3b). The characteristics of both responses confirm the progressive growth of polyaniline on the paste/membrane assembly.

3.3 Electrochemical characterization of the membrane modification

The electrochemical modification of the membrane by PAni deposition *via* cyclic voltammetry implies a better control of the characteristics of the polymeric material; however, due to the modification procedure, which involves attaching the membrane to the surface of the carbon paste, it is necessary to determine if both sides of the membrane were successfully

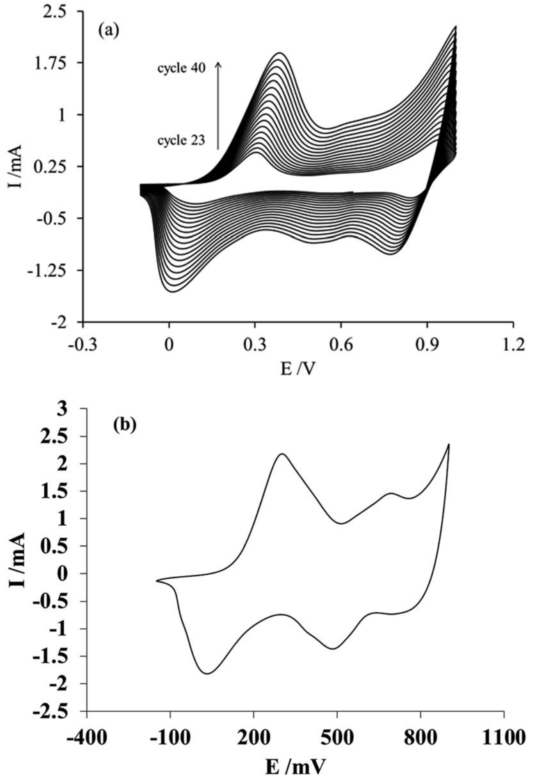

Fig. 3 (a) Voltammetric response corresponding to the last scan cycles during aniline polymerization on the membrane; (b) voltammogram obtained after the membrane modification process in a solution free of aniline monomer. A scan rate of 100 mV s^{-1} was employed.

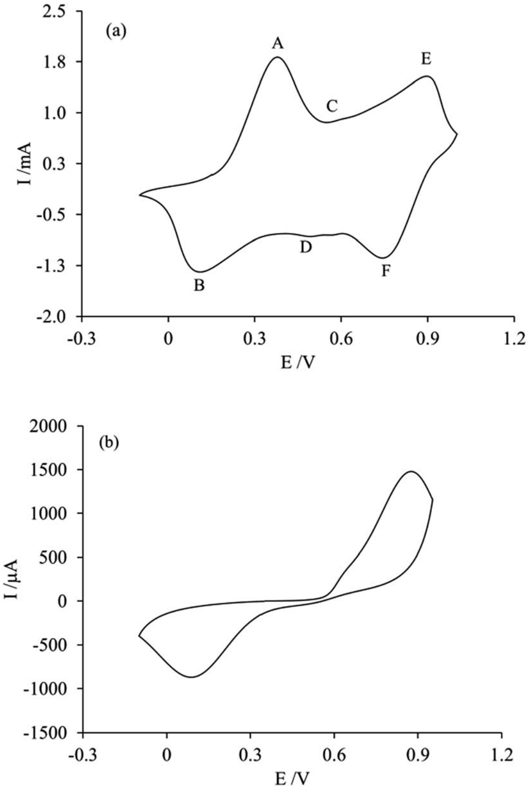

Fig. 4 Voltammetric responses of the membrane in 1 M H_2SO_4 at a scan rate of 100 mV s^{-1}. Panels (a) and (b) show the response of the side of the membrane in contact with the carbon paste electrode and with the solution, respectively, during the electropolymerization of aniline.

modified with PAni. For this purpose, the voltammetric responses of both sides of the membrane were obtained in a 1 M H_2SO_4 electrolytic solution free of aniline monomer.

Fig. 4 shows the voltammetric responses of the membrane side in contact with the carbon paste (Fig. 3a) and with the solution (Fig. 3b), obtained after attaching the membrane over a renewed surface of carbon paste electrode, during the modification procedure.

As can be seen in the figure, only one side of the membrane shows the characteristic response of PAni (Fig. 4a), whereas the other side shows the response of an unmodified membrane, which will be discussed later. This indicates that the membrane modification only occurs on the side of the membrane in contact with the carbon paste electrode during the electropolymerization process. The voltammetric response presents the typical features of PAni,[20] which consist of three peaks (A, C, E) on the anodic side and their cathodic counterparts (B, D, F) representing the redox reactions occurring in the polymer. The A/B pair of peaks, between 0 and +300 mV, correspond to the PAni transformation from its reduced form leucoemeraldine to the partially oxidized state emeraldine. The peaks E/F, located approximately at +800 and +950 mV, are related to the transition from leucoemeraldine to pernigraniline. While the peaks C/D at +500 and +600 mV correspond to the redox reaction of *p*-benzoquinone, they are generally less intense than the previous ones, and their intensity provides insight into the over-oxidation of the polymer.[35,36] As will be discussed later, an applied potential could be used to favor the occurrence of a specific chemical form of PAni, in order to impart particular separation characteristics to the membrane.[19,20]

Since the voltammetric response of PAni (shown in Fig. 4a) was obtained after moving the paste/membrane/PAni assembly to an acidic solution free of aniline monomer, it can be inferred that the deposited PAni is located at the interface between the carbon paste and the membrane.

In practice, since the membrane is not an electronic conductor (whereas a conductor would be required for the electropolymerization of aniline to proceed) the polymerization process begins at the carbon paste surface not blocked by the membrane, following which the deposit grows towards the solution, reaching the channels of the membrane nearest to the carbon paste and impregnating its walls. However, the number of potential scans performed is not sufficient for the polymerization process to reach the other side of the membrane, which explains why the deposits are located only at the side of the membrane in contact with the carbon paste electrode.

One possible way to assess how the impregnation with PAni affects the membrane involves determining the capacitance of the electrochemical double layer (C_{dl}) of the system formed by the paste/PAni/membrane electrode and the electrolyte, using cyclic voltammetry.[37]

Fig. 5 shows the voltammetric response between 420 and 440 mV (Fig. 4a) and the plot of $|I_a - I_c|$ (where I_a and I_c are the anodic current and cathodic current respectively) as a function of the scan rate (v) used to determine C_{dl} at $E = 425$ mV.

All curves in Fig. 5 exhibit a rectangular shape regardless of the scan rate used, without current peaks associated to faradaic processes. The absence of faradaic processes implies that the current flowing through the electrode/PAni/membrane system is used exclusively for the charge and discharge of the electrochemical double layer; this behavior is characteristic of a parallel plate capacitor.[38,39] However, this characteristic is observed only at low scan rates, whereas at scan rates higher than 100 mV s^{-1} the rectangular shape tends to tilt slightly to the right. While in the case of the carbon paste the processes taking place correspond only to the arrangement of the double layer, in the case of the paste/PAni/membrane system the relevant processes involve the insertion–deinsertion of the doping anions in the PAni deposit from or to the electrolyte. In other words, at low scan rates the ions diffusing from the electrolyte can access all sites (pores) available in the PAni deposit; therefore, the observed behavior resembles that of an ideal capacitor. On the other hand, at high scan rates, the insertion process is incomplete. The electrode thus behaves as an ideal parallel plate capacitor at low scan rates, through the whole potential range explored; however, if the scan rate is higher than 100 mV s^{-1}, the electrode assembly deviates from this ideal behavior.

The capacitance of the electrochemical double layer determined from the slope of the curve in inset of Fig. 5 was 1.736 μF cm^{-2} for the paste/PAni/membrane/electrolyte assembly, whereas the value measured for the paste/electrolyte system was only 2.5 nF cm^{-2}. This result can be explained considering that the capacitance of the electrochemical double layer is given by the equation:

$$C_{dl} = \frac{\varepsilon\ \varepsilon_o}{d} \times A \tag{6}$$

in which d represents the distance between the electrodes, ε_o is the vacuum permittivity (8.854×10^{-12} C^2 J^{-1} m^{-1}), ε is the dielectric constant of the medium separating the two electrodes, and A is their respective area. Therefore, if the concentration of the electrolytic solution, the dielectric constant, and the distance between electrodes are maintained constant, then the increase in capacitance is due to an increase in electroactive area caused by the PAni modification.

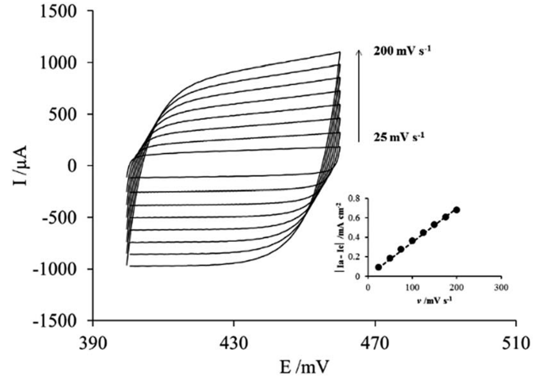

Fig. 5 Voltammetric responses in H_2SO_4 1 M of the paste/PAni/membrane/electrolyte system; (inset) plot of $|I_a - I_c|$ *vs.* scan rate at $E = 425$ mV, where I_a and I_c are the anodic current and cathodic current respectively.

3.4 Reproducibility and homogeneity of the PAni deposits

Another aspect investigated in this work was the reproducibility and the homogeneity of the modification procedure. For this purpose, the voltammetric responses of three modified membranes are shown in Fig. 6A.

As the figure shows, the voltammetric responses of the modified membranes show essentially the same form and intensity: this indirectly proves that the deposits on each membrane contain the same amount of PAni material, which indicates that the modification procedure is reproducible.

In addition, the homogeneity of the membranes was also investigated. For this purpose, a modified membrane was cut into pieces, and each piece was attached, from the modified side, to the carbon paste electrode, in order to obtain the corresponding voltammetric response in sulfuric acid without monomer, shown in Fig. 6B.

The obtained *I–E* curves display similar shape and intensity, which again reflects the presence of similar amounts of deposited PAni in different regions of the membrane, thus proving that PAni is homogeneously distributed over the membrane surface. Moreover, the curves obtained, Fig. 5B, show lower current values compared with Fig. 6A, which is

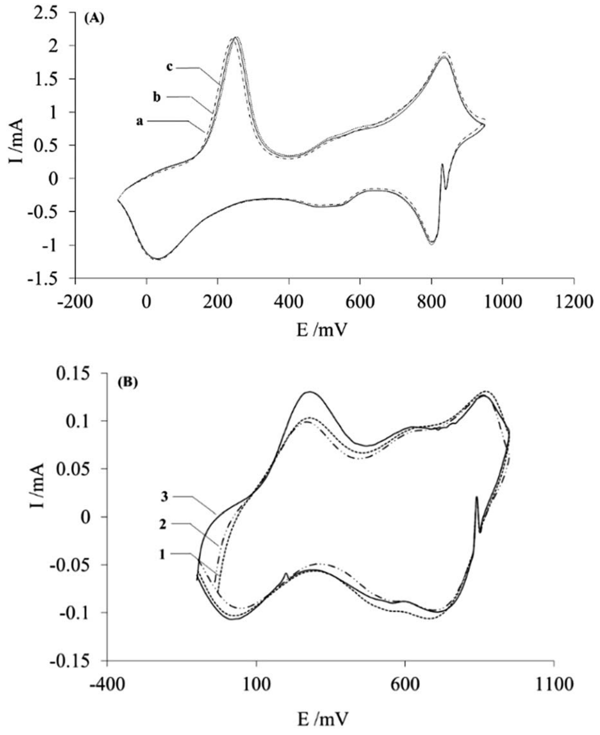

Fig. 6 (A) Voltammetric responses of three (a, b and c) membranes modified with PAni, obtained at a scan rate of 100 mV s^{-1} in H_2SO_4 1 M. (B) *I–E* curves of three (1, 2 and 3) sections cut from a modified membrane, obtained in 0.5 M sulphuric acid at a scan rate of 100 mV s^{-1}.

attributed to the use of a smaller membrane area in this experiment, and therefore a lower quantity of PAni.

3.5 Characterization by Fourier transform infrared spectroscopy of the modified membranes after the application of a potential pulse

The application of a potential pulse to the PAni deposits produces a change in their chemical forms, as reported before by several authors.[40–42] A potential value was thus applied for 20 min to the PAni deposits on the membrane, in order to promote a chemical form in the modification. The potential value selected was −100 mV, to promote the formation of the partially oxidized emeraldine structure. In order to confirm the presence of this form of PAni, analyses of the Fourier Transform Infrared (FTIR) spectra of the PAni deposited on the membranes can provide information on this matter. Fig. 7 depicts the FTIR spectra of unmodified (AFN) and modified (AFN-PAni) membranes.

The spectrum of the modified membrane (AFN-PAni) exhibits a broad band between 2200 and 3700 cm^{-1}, which is associated with N–H bond stretching and is characteristic of PAni deposits.[23] Additionally, the FTIR spectrum shows other characteristics peaks associated with PAni deposited on ion exchange membranes. For example, the band at 1149 cm^{-1} is related to in-plane C–H bending of an aromatic ring, while the band at 1581 cm^{-1} is attributed to the C═N stretching vibration of the quinoid unit, and the band at 1502 cm^{-1} is due to the C═C stretching vibration of the benzenoid unit.[23,43,44] In fact, these peaks confirm that the emeraldine structure of PAni is the predominant form on the membrane surface, as mentioned above.

3.6 Characterization of the surface of the modified membrane

Fig. 8 shows the surface morphologies obtained by Scanning Electronic Microscopy (SEM) of a membrane before (Fig. 8a) and after (Fig. 8b) electrochemical modification with PAni. Membrane tissue reinforcement and morphological changes to the surface after modification with PAni are evident in these images. Indeed, before modification (Fig. 8a), the surface membrane is completely smooth, while after modification with PAni (Fig. 8b) the modified side of the membrane is rougher due to the homogeneous distribution of small clusters (see arrows).

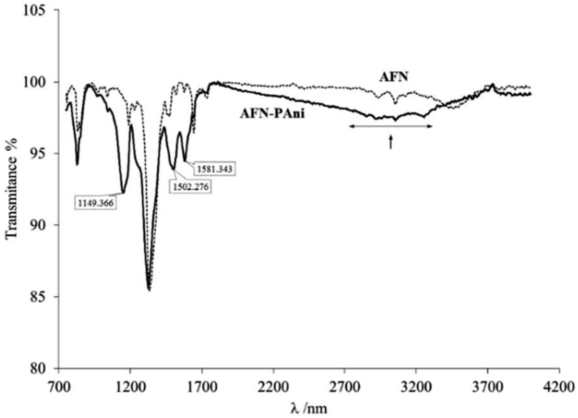

Fig. 7 FTIR spectra of unmodified (AFN) and modified (AFN-PAni) membranes.

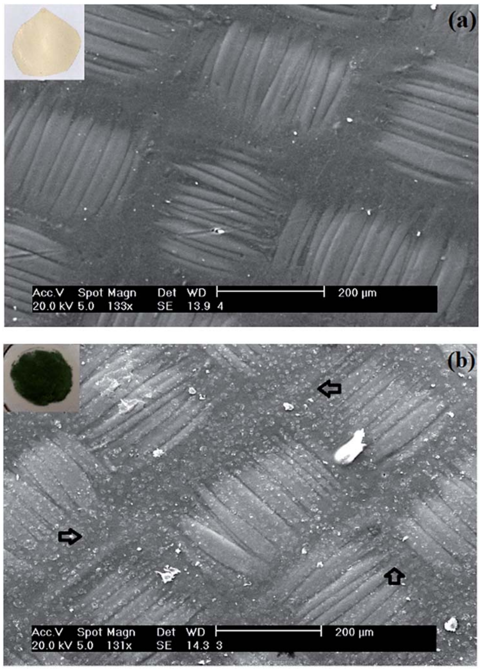

Fig. 8 SEM micrographs of the membrane surface before (a) and after (b) electrochemical modification with PAni in acidic solution.

This rough character of the modified-membrane surface affects the ionic transport properties of the membrane, as can be deduced by analysis of the *I–E* curves shown in Fig. 9.

The *I–E* curves in Fig. 9 exhibit the typical shapes of homogeneous ion exchange membranes, with three well-defined zones,[45–47] implying that modification with PAni does not affect the overall structure of the commercial membrane. The first zones of these polarization curves, which begin at the origin and end at the potential value ($E(I_{\text{lim}})$), where the current becomes constant (I_{lim}), are referred to as "ohmic regions" because of the linear relationship between current and voltage displayed in these zones. These zones are of particular interest because, according to some

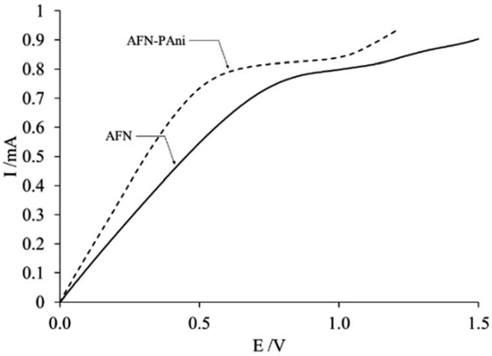

Fig. 9 *I–E* curves of the modified (AFN-PAni) and unmodified (AFN) membranes in a 10^{-2} M solution of $NaNO_3$.

Table 3 Transport resistance (R_t), limiting current (I_{lim}), and corresponding potential ($E(I_{lim})$) obtained for the two membranes in this study in a 10^{-2} M solution of $NaNO_3$. The resistance of the membrane (R_m) was obtained by electrochemical impedance spectroscopy (EIS) using a 0.5 M solution of $NaNO_3$

Membrane	R_t/kΩ	I_{lim}/mA	$E(I_{lim})/V$	R_m/Ω cm^2
AFN	0.93	0.791	0.83	0.767
AFN-PAni	0.60	0.826	0.50	0.687

authors,[45,47] the corresponding potential and current values provide insight into the transport of counterions through the membrane, with no diffusion limitations. Since the linear segments of both *I–E* curves in Fig. 8 end at the same current value, but different values of $E(I_{lim})$, the only possible source of this observed difference counterion transport is the membrane modification. The parameters that quantify this effect are listed in Table 3.

According to the data in the table, the R_t and $E(I_{lim})$ values of the modified membrane are less than those of the unmodified membrane. This behavior can be understood if we consider that R_t is composed of different components:

$$R_t = R_m + R_{sol} + R_{dif} + R_{dl} \quad (7)$$

where R_m is the membrane resistance and R_{sol}, R_{dif}, and R_{dl} represent the resistances of the solution, diffusion layer, and double layer, respectively. The expression for the resistance of the modified membrane includes an additional term, R(PAni), which represents the resistance of the PAni deposit. Taking into account that the R_t values for the different membranes in this study were determined under the same experimental conditions, all the terms that contribute to R_t in eqn (7) can be considered constant, with the only exception being R_m, which now also depends on R(PAni). Consequently, the unmodified membrane exhibits a higher R_t compared to the modified membrane due to the chemical nature of PAni; in other words, the anion crosses the modified membrane more easily than the unmodified membrane, implying that the membrane–ion interaction is less strong when the membrane is modified with PAni. This result is very interesting because it proves that the conductive properties of emeraldine, which were imparted to the membrane through the application of a potential pulse in an acidic medium, are retained in the neutral aqueous solution, *i.e.*, they are not lost under these conditions as might be expected. This is confirmed by the R_m obtained by Electrochemical Impedance Spectroscopy (EIS). Indeed, R_m is lower for the modified membrane (0.687 Ω cm^2) than for the unmodified membrane (0.767 Ω cm^2).

With respect to the limiting potentials of the two studied membranes, $E(I_{lim})$ for the modified membrane was observed to be less than that of the unmodified membrane, which is in agreement with previous reports,[48] and implies that the limiting current is reached more easily for the modified membrane that for the unmodified analog. On the other hand, the current limit is slightly higher for modified membrane than for the unmodified membrane, which implies that a greater amount of counterion exists in the diffusion layer next to the surface of the modified membrane. Both parameters are related to the surface roughness of this membrane. In agreement with different authors,[49] in the case of the modified membrane, its surface roughness (Fig. 6) promotes depletion of the counterion in the diffusion layer near the membrane more easily than the smooth surface of the unmodified membrane. Additionally, this roughness also promotes a mixture of counterion concentration gradients, in this case of the nitrate ions, in the diffusion layer and therefore an additional supply of nitrate ions, which leads to an increase in the value of the limit current associated to the modified membrane.

Despite these results, it is possible that the changes in the values of the parameters associated with the modified membrane are caused by the membrane itself, since, as mentioned above, it exhibits moderate electroactivity (Fig. 3b). In order to evaluate this possibility, a potential pulse of −100 mV (AFN red) was applied to unmodified membranes, and values of R_m and $t(NO_3^-)$ were determined for these samples (Table 4).

Taking as a reference the R_m value of a pristine membrane (0.767 Ω cm^2), the application of a potential pulse causes an increase in R_m, which means that the pristine membrane opposes less resistance to the passage of ions; however, the value of $t(NO_3^-)$ obtained after the pulse is the same regardless of the value of the potential applied. These results demonstrate that the electroactive component of the membrane does not affect its selectivity properties.

Moreover, because the R_m value for the membrane with potential pulse, shown in Table 4, is higher than those of the modified membranes (see Table 3), the effect of the PAni modification on R_m is consistent with the previous discussion, that is, the lower R_m of the membrane modified by a negative potential pulse is due to the greater conductivity of the emeraldine form of PAni deposit.

Based on the previous observations, it is possible that the electroactive properties of the membrane affect other aspects of the modified membranes, for example the polymerization process of PAni or different parameters relevant for its characterization and use in electrodialysis. This prompted us to investigate the origin of the electrochemical activity of the membrane, along with possible ways to minimize it.

The voltammetric response of the membrane in Fig. 3b shows a pair of current peaks separated by 0.5 V, which denotes an irreversible process. This irreversibility is also indicated by the lack of symmetry in the peaks, where the anodic peak reaches a higher current value, whereas the value reached by the cathodic peak is very small. It is important to note that the peaks observed

Table 4 Membrane resistance (R_m), obtained by electrochemical impedance spectroscopy (EIS) using a 0.5 M solution of $NaNO_3$, and transport number values ($t(NO_3^-)$) obtained upon application of a potential pulse to unmodified membranes

Membrane	R_m/Ω cm^2	$t(NO_3^-)$
AFN	0.767 ± 0.069	0.947 ± 0.012
AFN red	0.838 ± 0.054	0.949 ± 0.004

are related to the fabrication process of the membrane. Copolymers such as 4-vinylpyridine and 2-methyl-5-vinylpyridine are used in the fabrication of the AFN membrane.[50] According to some authors,[51] these copolymers show a moderate electroactivity associated to the pyridine group, which is indicated by a marked irreversibility in their voltammetric responses. Due to the latter effect, the peaks observed in the voltammetric response of the membrane are most likely caused by the electroactivity of the copolymer residues.

In order to reduce the impact of the membrane electroactivity on the process of electropolymerization and on the other properties of the modified membranes, the unmodified membrane was scanned in the range where the peaks were detected, for example from −100 to +1200 mV, for several cycles. The intensity of the peaks decreased with each successive scan, until they disappeared. This trend suggests that the peaks, and their possible effect on the properties of the modified membrane, will disappear during the electropolymerization process of aniline.

3.7 Electrodialysis

Based on the results shown elsewhere,[52] a current of 40 mA and a flow rate of 4.4 mL min^{-1} were selected. These parameters were used when removing aliquots from both solutions in order to assess the efficiency of the process.

3.7.1 Nitrate removal. Fig. 10 shows the time evolution of nitrate removal by electrodialysis with the modified membranes. This figure shows that the membrane modified with PAni in its reduced form has practically the same nitrate removal capacity as the unmodified membrane.

Nitrate anion transport numbers, $t(NO_3^-)$, and anion fluxes through the membrane, listed in Table 5, show a certain degree of correlation with the corresponding nitrate removal capacity.

Firstly, according to these data, the selectivity of the modified membrane is slightly greater than that of the unmodified membrane; however, this difference is not the decisive factor since it is not reflected in the removal curves shown in Fig. 10. Secondly, the nitrate fluxes obtained for both membranes are practically identical, implying that PAni modification does not affect the transport of this ion.

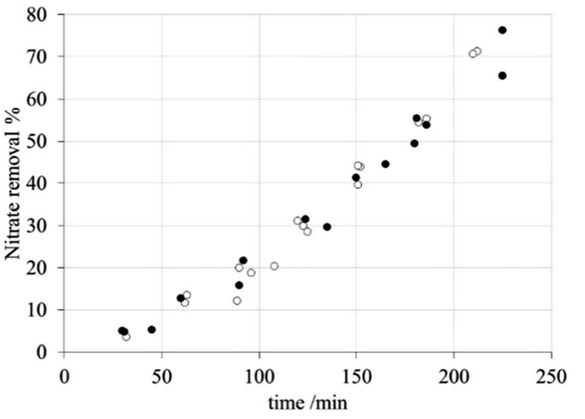

Fig. 10 Nitrate removal percentage during electrodialysis with the modified membranes: (●) AFN and (○) AFN-PAni.

Table 5 Transport number of nitrate ions, $t(NO_3^-)$, and the nitrate fluxes ($J_{NO_3^-}$) obtained for unmodified (AFN) and modified (AFN-PAni) membranes

Membrane	$t(NO_3^-)$	$J_{NO_3^-}/10^7$ mol cm^{-2} s^{-1}
AFN	0.915 ± 0.012	147
AFN-PAni	0.947 ± 0.012	146

Accordingly, there appears to be another factor that impairs the selectivity of the modified membrane, which is not based purely on electrostatic effects.

3.7.2 Chloride removal. Fig. 11 shows the removal percentage of chloride ions achieved using the modified membrane with PAni (AFN-PAni) and the unmodified membrane (AFN).

The experimental data shown in Fig. 11 clearly indicate that higher chloride removal capacities are achieved using the unmodified membrane, compared to the AFN-PAni-modified membranes, during treatment. In other words, a higher retention of chloride is achieved by the modified membrane, and the difference with respect to the unmodified membrane further increases with increasing treatment time. The modification with a PAni deposit thus increases the chloride exclusion by the membrane, which already presents a slightly rather low intrinsic selectivity towards this ion (see Table 2). For example, at the end of the treatment (180 min) the increases in chloride retention by the modified membrane compared to the unmodified one reach almost 22%.

The chloride separation capacity exhibited by the modified membrane is harder to interpret than their nitrate separation capacity, due to the different parameters, shown in Table 6. These parameters, can be used to understand the behaviour of the modified membrane. For example, the corresponding chloride transport numbers highlight a clear difference in the selectivity of the modified membranes. In particular, the AFN-

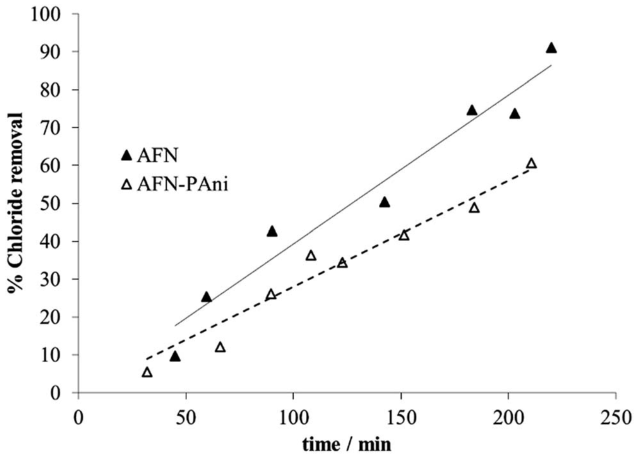

Fig. 11 Chloride removal percentage during electrodialysis performed with PAni-modified membrane, compared to the unmodified (AFN) membrane.

Table 6 Chloride transport number, $t(\mathrm{Cl}^-)$, ion exchange capacity, IEC, anion selectivities, $P_{\mathrm{Cl}^-}^{\mathrm{NO_3}^-}$, chloride fluxes, J_{Cl^-}, water content (% H_2O) and water contact angle for the unmodified (AFN) and modified (AFN-PAni) membranes

Membrane	AFN	AFN-PAni
$t(\mathrm{Cl}^-)$	0.87 ± 0.06	0.83 ± 0.01
IEC/meq g^{-1}	0.829 ± 0.059	0.771 ± 0.038
$P_{\mathrm{Cl}^-}^{\mathrm{NO_3}^-}$	1.719	1.333
$J_{\mathrm{Cl}^-}/10^7$ mol cm^{-2} s^{-1}	230	195
% H_2O	44.6 ± 0.02	43.9 ± 0.01
Contact angle/°	85.4 ± 3.3	91.3 ± 2.2

PAni-modified membrane has a slight low selectivity than the unmodified membrane (low transport number), which explains the higher chloride removal obtained with the latter.

This result can be understood by considering the IEC values, which show that, due to its higher IEC, the unmodified membrane exhibits a higher relative selectivity (higher transport number) compared to that of the modified membrane. In this case, the observed decrease in IEC may be due to the blocking of fixed charges by the deposited polymer; however, the difference between the IEC values of the two membranes is not statistically significant and does not decisively explain the different selectivity properties of the two studied membranes.

Several similar examples are found in literature that can help to understand these results, with the exception that cation-exchange membranes modified with PAni were used with cations of different degrees of hydration.[22–24] For example, Farrokhzad *et al.* consider that the PAni deposited on the membrane confers a greater hydrophobicity to its surface, and that because of this, the more-hydrated ions are more strongly repelled.

This behavior is due to the chemical nature of the PAni deposit; that is, the PAni deposit creates a more hydrophobic surface compared to that of the unmodified membrane, owing to the nonpolar N–H and C–N bonds present in the reduced form of polyaniline. In this form, if a hydrated ion, in our case an anion, intends to penetrate the membrane, the energy barrier associated with the partial dehydration of the ion needs to be overcome. The parameter relating to this barrier is the hydration energy of the anion. Hence, an anion with a high hydration energy will have more difficulty in overcoming this barrier and therefore will be more easily rejected by a hydrophobic surface. In our case, the chloride ion has a higher energy of hydration than the nitrate, see Table 1, so the chloride ion will be more strongly rejected by the modified membrane.

This is confirmed by the membrane selectivities ($P_{\mathrm{Cl}^-}^{\mathrm{NO_3}^-}$) and the chloride fluxes (J_{Cl^-}) listed in Table 6.

As shown in Table 6, the selectivity of $\mathrm{NO_3}^-$ over Cl^- is lower for the modified membrane compared to that of the unmodified counterpart. In addition, the chloride ion flux is higher for the unmodified membrane than for modified membrane, which implies that the chloride ions (more hydrated) are more strongly rejected by the modified membrane (higher hydrophobicity) that by the unmodified membrane. In addition, these data show that the nitrate ions are not only more weakly rejected by the modified membrane due to the decrease of the IEC in the membrane, but also because of weak interactions between the hydrophobic surface and the weakly hydrated ions. Therefore, the affinities of anions with different degrees of hydration, with the anion-exchange membranes in this study are thought to increase with decreasing membrane hydrophilicity.

This hypothesis is further supported by the measured water content (% H_2O) of the studied anion-exchange membranes and their contact angles, as shown in Table 6.

Both membranes have a water content (% H_2O) in the range of 40–45%; nevertheless, the AFN-PAni-modified membrane has a slightly lower water content (43.9%) compared to the unmodified membrane, which contains around 45% water. In addition, the high value of the contact angle obtained for the modified membrane (91.3°), also listed in Table 6, implies a water repelling surface.

This is not surprising behavior since the PAni in the membrane is in the emeraldine form and in this form PAni possesses functional groups of differing polarity that give rise to a highly hydrophobic surface.

This hydrophobicity of the membrane is expressed through low water content and high contact angles.

4. Conclusions

We investigated the selectivity of an anion exchange membrane that had been electrochemically modified with PAni deposits through the application of a negative potential pulse. The information obtained by voltammetry and infrared spectroscopy established that the PAni in the membrane is mainly in its emeraldine form. This modification not only imparted greater hydrophobic character to the membrane, but also greater roughness to its surface, resulting in different selectivities, depending on the anion being studied. For example, the modified membrane exhibited almost identical selectivity towards the nitrate ion when compared to the unmodified membrane, which is attributed to decreases in repulsions between the PAni and the anion, because the anion is weakly hydrated.

On the contrary, when the anion is more hydrated, as is the case with chloride, the anion is more strongly rejected by the more hydrophobic membrane and it is more highly retained.

Finally, the high hydrophobic character of the modified membrane was confirmed by high contact angles and low water content.

Acknowledgements

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