

Article

Characterization of a Commercial Anion-Exchange Membrane Modified with Electrosynthesized Polyaniline Deposits at Different Temperatures

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Abstract

Phenomena associated with an ion-exchange membrane (IEM) in contact with an ionic solution, such as its selectivity and ionic transport, commonly occur when an ion approaches the membrane surface. Because of this, if a change occurs in the IEM/Solution interfacial region, then it is expected that these processes will be affected. For example, if the IEM surface is modified with an electronic conducting polymer (ECP), then its selectivity and the phenomena associated with ionic transport will change. These changes can be quantified by parameters such as the permselectivity, the contact angle, and others, and are associated with the hydrophilic/hydrophobic balance of its surface. This work reports the characterization of commercial anion-exchange membrane samples modified voltammetrically with polyaniline (PAni) obtained at different temperatures (10, 15, and 20 °C). Among the main results obtained, it was found that with an increase in synthesis temperature of the PAni, the membrane's permselectivity will increase from 0.757 to 0.782 to 0.808. While contrary behavior is observed in the case of the contact angle, since an increase in the synthesis temperature will cause a greater hydrophilic character when going from 67° to 53° to 50°. According to this work, these trends in the properties of the modified membranes are related to the morphological characteristics of PAni deposits conferred by the variation in the synthesis temperature.

Keywords: anion-exchange membrane; polyaniline; cyclic voltammetry; chronopotentiometry; current–potential curve; contact angle



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1. Introduction

Ion-exchange membranes (IEMs) are thin synthetic materials of polymeric nature that have found application in various technical domains, such as obtaining drinking water (electrodialysis) [1], energy (concentration gradients, lithium cells) [2], hydrogen (water electrolysis) [3], concentrated compounds of interest [4,5], and the reuse of effluents generated in industry [6]. This versatility of IEMs is possible because they possess within them, among other components, ionizable chemical species covalently fixed to a polymeric matrix, which when brought into contact with an ionic solution, act as a barrier that obstructs the passage of ions of the same charge sign, while ions of the opposite charge sign pass through without facing any opposition. Thus, according to this, in some of the various technical domains in which they are used, one of the properties required of IEMs is to allow the passage of only certain species with well-defined characteristics of charge and size (a

property sometimes referred to as selectivity or permselectivity) [7] from among all the ionic species found in the solution. It should be noted that the selectivity process consists of different stages, among which are some that have a purely interfacial nature. For example, when an ion passes from the solution phase, in which it is initially found, to the solid phase of the membrane, this process is affected by the properties of the membrane and by the composition of the solution with which it is in contact. In the case of membrane properties that can influence selectivity, there are the type and quantity of ionizable groups as well as the interweaving of the polymeric network that provides mechanical support, called the degree of crosslinking. Regarding the solution that is in contact with the membrane, it is important to consider as influential factors in its selectivity the quantity, charge, degree of solvation, and size of the species that are authorized to cross it. Thus, if any of the mentioned properties of the membrane or the solution are changed, then the selectivity process will be impacted. In this sense, there are various works that show the varied approaches existing to improve the selectivity of an ion-exchange membrane by playing precisely with the factors indicated above. An example of the proposal is the surface modification of the membrane by using electronic conducting polymers (ECPs) by virtue of various properties of these materials such as their characteristic hydrophobic/hydrophilic balance or their degree of crosslinking that can favorably impact the selectivity phenomenon [8–10]. This interest has remained valid since the pioneering work published by the group of T. Sata et al. in the nineties of the last century; until this moment, the reports of various groups that have proposed to clarify the role played by ECPs in the new properties of modified membranes [11,12]. One of the members of this family of materials that has attracted attention for modifying the general properties of IEMs is polyaniline (PAni), so various research groups such as the aforementioned one led by Sata [8–10], that of R.K. Nagarale [11], and more recently the group headed by N. D. Pismenskaya [12] and other groups have contributed to the understanding of this type of modification in the transport properties of commercial ion-exchange membranes. According to these research groups, the interest in the use of PAni does not lie in the property of electrical conductivity, which distinguishes these materials, but in their ability to develop charges within them, as well as their simplicity and inexpensive preparation by chemical or electrochemical oxidation [13]. Additionally, PAni possesses other properties that can impact the selectivity process of an IEM such as the hydrophilic/hydrophobic balance or the degree of crosslinking, characteristics mainly dependent on the three main redox forms in which it can be found (emeraldine, pernigraniline, or leucoemeraldine), which have well differentiated morphologies, structures, and chemical properties [13–16]. Thus, among the main results obtained from these studies, the prevalence of the hydrophobic/hydrophilic balance and the degree of crosslinking associated with the surface modification of PAni stand out as the new properties of the modified membranes, which are a function of the preparation method and the synthesis conditions [16]. Despite these results, the modified membranes have been prepared, without taking into account the methodological differences, by using an oxidizing chemical agent to produce the polymerization of the monomer in multiple stages, which makes it difficult to rigorously modulate the aforementioned properties of the polymer. This situation opens up the possibility of using other types of methodologies that allow for easier modulation of the polymer properties that impact the selectivity of the IEM. In this regard, there is sufficient information highlighting the advantages of electrochemical methods for controlling polymer properties in a single step. Among them, cyclic voltammetry (CV) is a versatile and relatively easy-to-implement technique that has been used to prepare PAni deposits on a metal electrode. Currently, a large amount of information is available, allowing control not only of the amount of polymer formed in a single step through the number of potential sweep cycles, but also the identity of the predominant chemical species and the

water affinity properties and morphology of the prepared deposit through the potential value at the end of the potential sweep. Furthermore, if the temperature of the synthesis solution is varied, the synthesized polymeric material can be given specific morphological and structural properties. According to various works, if the temperature is maintained between 0 and 20 °C, the electrical conductivity remains practically invariant, and only the morphology of the PANi deposits acquires diverse granular compositions associated with a combination of different molecular weight and crystallinity values [14–16]. Thus, as the synthesis temperature increases, both the molecular weight and crystallinity decrease, which generates a low degree of crosslinking and a predominantly granular composition of the deposits. Similarly, it has been demonstrated that each chemical structure possesses well-defined properties of the hydrophobic/hydrophilic balance of its surface [16–20]. However, it is in this situation that some questions arise, which this work proposes to clarify. For example, more rigorous control of the PANi properties synthesized at different temperatures can be extended to deposits present in ion-exchange membranes to determine whether these properties impact the different parameters that express their selectivity. To answer these and other questions, our research team has implemented a methodology based on the use of a carbon paste electrode to adhere the membrane samples. In this methodology, the paste/membrane assembly acts as the working electrode, allowing for the use of any electrochemical technique and the corresponding variation of synthesis conditions in a simple manner [16]. Therefore, in this work, we present the results obtained by studying samples of a commercial anion-exchange membrane modified with polyaniline deposits obtained voltammetrically at temperatures of 10, 15, and 20 °C. These samples were characterized by obtaining various parameters related to the selectivity to evaluate the effect of the synthesis temperature on the PANi deposits.

2. Materials and Methods

2.1. Study Membrane Samples

The ion-exchange membrane used in this study was an anion-exchange membrane designated by the manufacturer as AFX. Table 1 shows some properties of this anion-exchange membrane [21–23].

Table 1. Some characteristic properties of the study membrane [21–23].

Parameter	AFX
Fixed charge	$-N(R_3)^+$
Electrical resistance/ $\Omega\text{ m}^2$	10^{-4} – 1.5×10^{-4}
Thickness (mm)	0.14–0.30
Transport number (NO_3^-)	0.947
Water content (%)	25–35
g H_2O /g dry membrane ^a	0.202
Ion-exchange capacity/meq g^{-1}	1.5–2.0

(^a) Our values [24].

It is important to note that the membrane provided by the supplier consists of a 1 m sheet per side, so for this work, circular cuts of approximately 1.5 cm in diameter ($A_m = 1.77\text{ cm}^2$) were used, with a mark to identify each of their faces.

2.2. Electrochemical Modification of Membrane Samples

2.2.1. Working Solutions and Carbon Paste Electrode

All working solutions used in this part of the work were prepared from reagent-grade substances. In the case of the aniline solution (SIGMA, Mexico city, México), it was prepared from a previously distilled reagent to have a concentration of 0.1 M in 1 M

H₂SO₄ (Fermont, Monterrey, México). Regarding the preparation of the carbon paste mixture to form the electrode, graphite powder (<50 µm, Merck, Mexico city, México) and mineral oil (Sigma-Aldrich, Mexico city, México) were used as a binder in a mass ratio of 60:40, respectively.

2.2.2. Experimental Setup and Membrane Sample Modification Technique

The experimental setup used for the preparation of polyaniline-modified membrane samples required a three-electrode cell specially designed to allow water to pass through it in order to control the temperature of the working solution. Regarding the electrodes used, a plastic tube filled with carbon paste was used as the working electrode, in which one of its ends served as a support to adhere the study membrane sample. As a reference, a Ag | AgCl | KCl (3 M) electrode was used, and a Pt rod served as the auxiliary electrode. In both cases, they were housed inside a glass extension filled only with a supporting electrolyte based on 1 M H₂SO₄.

The cell described above was connected to an AUTOLAB PGSTAT 302N potentiostat/galvanostat (Metrohm AG, St. Gallen, Switzerland) to proceed with the modification of the study membrane samples. The synthesis temperature values used in this work were selected considering the findings of Yilmaz et al. [16]. According to this, between 0 and 20 °C PANi can acquire properties that influence its structural characteristics, so the values of 10, 15, and 20 °C were chosen. To identify the membrane samples, they were named according to the temperature of interest as M-10, M-15, and M-20 when modified at 10, 15, and 20 °C, respectively, while the unmodified membrane was named non-M. It should be noted that the temperature control of the working solution used for the polyaniline synthesis was possible thanks to a LAUDA Alpha RA 8 thermoregulation equipment (Lauda-Koenigshofen, Germany), which can set the temperature between −25 °C and 100 °C.

The modification of the commercial membrane samples was carried out by means of cyclic voltammetry using the number of sweep cycles to control the amount of synthesized material. To this end, the magnitude of the peak anodic current in the voltammograms, associated with the leucoemeraldine/emeraldine transition [25–27], characteristic between potentials of 200 and 400 mV vs. Ag | AgCl(s) | Cl[−] (3M), was monitored during polymer synthesis to ensure it was approximately equal for the different replicates of the modified membrane samples at the study temperatures, with the intention of obtaining the same amount of polymer. This was verified after modification by obtaining the voltammograms of the PANi deposits in the samples and calculating the charge under the peak current curve. Regarding the potential range used to perform the different sweep cycles, these were performed between −200 mV and 900 mV vs. Ag | AgCl(s) | Cl[−] (3M), with a scan rate of 100 mV/s. Finally, it is worth noting that, according to previously published results, this method leads to the surface modification of the membrane face directly adhered to the carbon paste [11,28].

It should be noted that at least three replicates of the modified membrane samples were obtained, so some of them were used for more than one characterization test in which there was no risk of altering it.

2.2.3. Storage of Modified Membrane Samples

After the modification of the study membrane samples, they were rinsed with ethanol and/or deionized water with the aid of a BRANSON 1510 ultrasound (New Carlisle, IN, USA). The samples were immediately stored in a 0.1 M NaCl solution until their subsequent characterization.

2.3. Characterization of Modified Membrane Properties

2.3.1. Voltammetric Characterization of Modified Membrane Samples

The modified membranes were electrochemically characterized using cyclic voltammetry in an acidic medium. For this, the experimental conditions described below were implemented.

Working Solutions

The solutions used for the voltammetric characterization of the study membrane samples were prepared from reagent-grade substances as received from the supplier. Thus, the solution used in this case was prepared from H₂SO₄ (Fermont, Monterrey, México), with a concentration of 1 M, and deionized water obtained from a Millipore system (Merck KGaA, Darmstadt, Germany) with a resistivity of 18 MΩ cm.

Electrochemical Cell

The electrochemical cell was a glass container with a Teflon lid with three holes that served to house three electrodes. These were the same as those used in the electrochemical modification of the commercial membrane, which has been previously described. The temperature was not controlled and corresponded to the ambient temperature value.

Technique and Parameters

The voltammetric characterization of the modified membrane samples was carried out in a potential range limited between −200 mV and 900 mV. The potential sweep rate was set at 100 mV s^{−1}.

2.3.2. Permselectivity

The permselectivity *P* of an ion-exchange membrane is defined using the counterion transport number in the two components of the membrane/solution interface, as shown in Equation (1) [29]:

$$P = \frac{t_i^m - t_i^{sol}}{1 - t_i^{sol}} \quad (1)$$

where t_i^m and t_i^{sol} are the transport numbers of the *i*-th species (counterion or co-ion) in the membrane and in the solution, respectively. t_i^{sol} was determined by the equivalent conductivities under infinite dilution conditions of the ions through the equation:

$$t_i^{sol} = \frac{\lambda_i^\infty}{\lambda_i^\infty + \lambda_j^\infty},$$

with *i* as the counterion and *j* as the co-ion, whose values were $50.08 \times 10^{-4} \text{ m}^2 \text{ S mol}^{-1}$ and $71.42 \times 10^{-4} \text{ m}^2 \text{ S mol}^{-1}$ for the Na⁺ and NO₃[−] ions, respectively [30].

In the case of the counterion transport number in the ion-exchange membrane t_i^m , this was determined by the concentration cell or EMF method [31].

Next, the experimental considerations that led to obtaining t_i^m will be briefly described.

Solutions and Working Device

The working solutions used were prepared with reagent-grade NaNO₃ (Fermont brand, Monterrey, México) to have a concentration of 1 M and 0.1 M. Regarding the working device, it was built in the laboratory and consisted of two compartments separated by the membrane under study. Each compartment was filled with nitrate solutions of different concentrations (1 M and 0.1 M) and a helix (Caframo LTD, El Crisol S.A. de C.V., San Luis Potosí, México, model BDC250) was placed to ensure the necessary continuous stirring during the experiment. The modified face of the membrane was oriented in the

device to have contact with the concentrated solution. Similarly, at the beginning and end of the experiment, the temperature value was determined in both solutions, and the membrane potential difference E_m was measured with two Ag|AgCl|KCl (3 M) electrodes placed on each side of the membrane [31].

Calculation of the Transport Number

The obtaining of the counterion transport number in the different prepared membrane samples, by means of the membrane potential E_m , was carried out through the expression:

$$E_m = (2t_{ct}^m - 1) \frac{RT}{z_{ct}F} \ln \frac{a_1}{a_2} \quad (2)$$

where a_1 and a_2 correspond to the activities of the solutions in contact with the membrane with $a_1 > a_2$, whose values corresponded to those suggested by Cha et al. to obtain a value of t_{ct}^m as independently as possible of them (with $a_2 = 0.1$ M and $a_1 = 1.0$ M [32]). R is the gas constant, T is the temperature of the solutions in Kelvin, z_{ct} represents the absolute value of the counterion charge (in this case the NO_3^- ion) and F is the Faraday constant. To calculate the activities of the solutions in the working cell, the extended Debye–Huckel equation was used to determine the activity coefficient $f_{\pm}$, which consists of:

$$-\log f_{\pm} = \frac{A|z_+z_-| \cdot \sqrt{\mu}}{1 + B \cdot a \cdot \sqrt{\mu}} \quad (3)$$

where $f_{\pm}$ is the mean coefficient of the electrolyte that gives rise to the counterion and represents the ionic strength of the solution, is the minimum approach distance (3 Angstroms for NaNO_3 [33]), z_i is the charge of the cation or anion, and A and B are the Debye–Huckel constants, which have a value of 0.512 and 0.328 at 25 °C on the molar scale.

2.3.3. Ionic Resistance of Modified Membrane Samples Solutions and Working Cell

The working solution used in this determination was based on reagent-grade Fermont-brand sodium chloride at a concentration of 0.1 M. The water used was obtained from a MilliPore device (Merck KGaA, Darmstadt, Germany) with an electrical resistivity equal to 18 MΩ cm. The experimental device used in this determination was made in the laboratory and consisted of two compartments to house an electrode in each of them. These electrodes were two symmetrical Pt plates (area exposed to the solution was 1 cm²) separated by a distance of 6 mm, between which the study membrane was placed. Both compartments were filled with the same working solution.

Calculation of Ionic Resistance

The resistance value was obtained from the Nyquist diagrams, which result from plotting the real component of impedance (Z') that is in phase and the imaginary component (Z'') that is out of phase [34]. Both components were determined by imposing a sinusoidal potential perturbation in the frequency range of 10^3 to 10^{-2} Hz and an amplitude of 10 mV, thanks to the use of an AUTOLAB PGSTAT 302N potentiostat/galvanostat equipped with an FRA2 impedance module (Metrohm AG, St. Gallen, Switzerland).

From the intersection of the line with the real component axis, at high frequencies, the resistance in the Nyquist diagram is determined. In this way, the measurement is made with the membrane, and subsequently, it is removed from the compartment, and the measurement is made without it.

The membrane resistance was converted to specific resistivity, r_m , through the following equation:

$$r_m = \rho_{m+s}(d_m + d) - \rho_s d \quad (4)$$

where ρ_{m+s} represents the resistivity of the membrane and solution, d_m is the thickness of the membrane, d is the distance between electrodes, and ρ_s is the resistivity of the solution.

2.3.4. Ion-Exchange Capacity

Procedure

The ion-exchange capacity, IEC, was determined by the UV absorption spectroscopy of nitrate solutions [35]. First, the sodium nitrate solutions used both to equilibrate the membrane and to make the calibration curve were prepared using reagent-grade sodium nitrate (Fermont brand, Monterrey, México) and deionized water with a resistivity of 18 MΩ cm. For the first, the concentration was 1 M, while for the calibration curve, it was prepared between 1 mM and 0.1 M sodium nitrate. Regarding the sodium chloride solution, which was exchanged with the nitrate ions present in the membrane, it was prepared with a reagent-grade substance of the same brand, and its concentration was 0.1 M. Secondly, for the spectrophotometric determination of the nitrate ions exchanged by the membrane, a Genesys 10S UV–Vis spectrophotometer from Thermo Fisher Scientific (Thermo Fisher Scientific, Mexico city, México) was used. Finally, the number of ions exchanged by the membrane (meq NO_3^-), present in the sodium chloride solution, is related to the weight of the dry membrane (W_f) to determine the exchange capacity according to the following formula:

$$\text{IEC} = \frac{\text{meq NO}_3^-}{W_f} \quad (5)$$

2.3.5. Determination of Water Content

Water can be part of an ion-exchange membrane mainly due to two causes: solution absorption or solvation of fixed charges. To determine which, the membrane is subjected to heating for a certain time, and the wet and dry weights are recorded.

Procedure

The membrane was previously stored in water and then introduced into a HINOTEK DHG-9145A oven (HINOTEK Group Limited, Ningbo, China) with an integrated temperature homogenizer at a temperature of 60 °C until constant weight. The calculation of the water content, %H₂O, was done using the following equation:

$$\% \text{H}_2\text{O} = \frac{W_o - W_f}{W_f} \times 100 \quad (6)$$

where W_o is the initial weight of the membrane, and W_f is the final weight of the membrane when its weight is constant.

2.3.6. Determination of Pure Water Permeation Flux

Weight Difference Procedure

The determination of pure water permeation flux through the membrane by weight difference used a clean and dry CPVC cylindrical mini-container, homemade, in which 5 mL of deionized water was placed. The container was closed with an adjustable threaded cap of the same material, but with a design that allows the membrane of interest to be placed. This threaded cap had a hole in the center with a diameter of 1.0 cm, through which 0.7854 cm² of the membrane of interest was exposed to water vapor. The use of modified membranes involved placing the face with the deposit towards the inside of the container.

Finally, the assembled device was placed in an oven at 60 °C for 6 h to evaporate the water and allow the vapor to pass through the membrane. The weight of the entire device was recorded at intervals of 20 min for the first three measurements and then at intervals of 30 min. Using these data, the variation in the number of moles of water was plotted as a function of time, and the slope (dw/dt) was obtained. With this data, the water vapor flux was calculated using the equation [36]:

$$J = \frac{dw/dt}{A_m} \quad (7)$$

where J is the pure water permeation flux through the membrane of interest ($\text{mol cm}^{-2} \text{s}^{-1}$), and A_m is the effective exposed area of the membrane (cm^2).

2.3.7. Characterization of Surface Properties of Modified Membrane Samples

Contact Angle and Static Friction Force (SFF)

The method used to determine the contact angle was the sessile drop method using perfluorooctane [37], which consisted of dropping a drop of known volume onto the surface to be analyzed and then determining the angle using specialized software and a professional camera (Ramé-hart Instrument Co., Succasunna, NJ, USA). On the other hand, the static friction force, SFF, was determined using the advancing and receding angles of a drop that moves across the membrane surface. The SFF (mN/m) calculation was obtained using the equation [38]:

$$\text{SFF} = (\cos \theta_{\text{Re}} - \cos \theta_{\text{Av}}) \times 54.35 \quad (8)$$

where the factor 54.35 mN/m corresponds to using perfluorooctane in the angle measurement. The advancing angle is θ_{Av} , and the receding angle is θ_{Re} .

X-Ray Diffraction Spectroscopy (XRD)

The acquisition of X-ray diffraction spectra, XRD, allowed for evaluating the degree of crystallinity of the PANi deposits obtained under different synthesis conditions using the Panalytical X'Pert PRO equipment (Malvern Panalytical Ltd, Worcestershire, UK). Previously, the modified membrane samples were dried at 60 °C until constant weight.

FT-IR Spectroscopy

The infrared spectra of the modified membrane samples were obtained using a Thermo Scientific Nicolet iS10FT-IR Fourier transform spectrophotometer (Thermo Fisher Scientific, Mexico city, México) equipped with a diamond ATR module. The membranes were previously dried at 60 °C using the same equipment as in the %H₂O determination.

SEM Microscopy

The acquisition of micrographs of the surfaces of the PANi-modified membranes by scanning electron microscopy was performed with a Quanta 250 (scanning electron microscope, Thermo Fisher Scientific, Mexico city, México) at 5000× and 20,000× magnification. The conditions used in the equipment were a high vacuum, 100 Pa chamber pressure, and a power of 18 kV.

2.3.8. Chronopotentiometric Study

Chronopotentiometry (CP) is an electrochemical technique that is based on imposing an electric current to the membrane/solution system and recording its potential as a function of time, which is known as a chronopotentiogram [39]. As has been demonstrated in various publications, this technique allows for obtaining both quantitative and qualitative

information about membranes. Among the former are the counterion transport number and the ionic conducting fraction of its surface, and the analysis of chronopotentiograms allows for highlighting various processes that occur in the ion-exchange membrane depending on its surface properties.

Electrochemical Cell

In the experimental setup, a four-compartment cell was used to house 1 cm³ of solution in each compartment. Two symmetrical platinum plates of 99.997% purity from Alfa Aesar, one square centimeter each, were placed at the ends of the device to impose constant currents for a certain time. Between them, in the center of the device, the membrane sample under study ($A_m = 1 \text{ cm}^2$) was placed using CMX auxiliary cation-exchange membranes to avoid the influence of the electrode compartments. In addition, two Ag | AgCl, 3 M NaCl reference electrodes were placed, one on each side of the membrane sample under study, with the help of plastic extensions filled with a 3 M NaCl solution and a freshly prepared Agar-Agar plug. Finally, the modified face of the membrane sample was placed towards the cathode.

Working Solutions

A 0.3 M sodium sulfate solution was used to fill the electrode compartments to avoid gas production with the pH variations inherent in water electrolysis. In the intermediate compartments, a 0.01 M sodium nitrate solution was used. Both solutions were prepared from Fermont reagent-grade substances and deionized water.

Basic Equation

The basic equation in this methodology applicable to ion-exchange membranes is the so-called Sand expression [39]:

$$j\tau^{1/2} = \epsilon \frac{z_i F \pi^{0.5} D_s^{0.5}}{2(\bar{t}_i - t_i)} C_0 \quad (9)$$

where j represents the current density, τ is the transition time (the time it takes for the concentration of the counterion near the membrane to deplete at a certain current), ϵ is the conductive fraction of the membrane surface, C_0 the initial concentration of the solution, z is the (counter)ion charge, F is the Faraday constant, $\bar{t}_i$ and t_i are the transport numbers of the counterion in the membrane and in solution, respectively, and D is the diffusion coefficient of the solution. In this work, the transport number of the NO_3^- ion in solution was 0.586. The diffusion coefficient of the solution was calculated from the diffusion coefficients of each species ($D(\text{Na}^+) = 1.33 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$, $D(\text{NO}_3^-) = 1.90 \times 10^{-5} \text{ cm}^2\text{s}^{-1}$) with the formula:

$$D_s = \frac{2D^+D^-}{(D^+ + D^-)} \quad (10)$$

where D^+ and D^- represent the diffusion coefficient of the cation and anion, respectively.

It is important to note that equation 9 is valid only if the counterion moves through a narrow portion of the solution adjacent to the surface under conditions of infinite diffusion, in the absence of convection, which implies that the curves $j\tau^{0.5}$ vs. j and j vs. $\tau^{-0.5}$ are verified.

It is important to note that the characterization was performed with at least three replicas according to each methodology. In some cases, the same membrane sample was used to obtain different parameters where the methodologies did not pose a risk of altering it.

3. Results and Discussion

3.1. Voltammetric Polymerization of Polyaniline onto Membrane Samples

The polymerization of aniline using the samples of the study membrane at different temperatures presented very similar general voltammetric characteristics. This is described below in the analysis of the polymer electrosynthesis process obtained at a temperature of 10 °C. Figure 1 presents the voltammetric responses of scan cycles numbers 14, 28, and 42, obtained during the polymerization of aniline at this temperature.

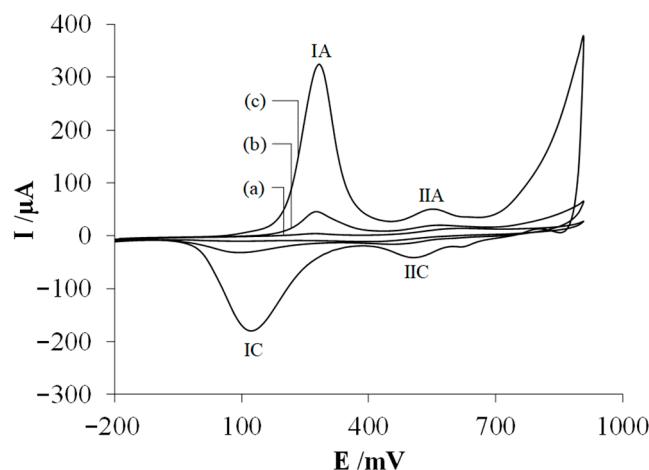


Figure 1. Voltammetric responses during aniline polymerization process in the electrode/membrane assembly obtained at 10 °C and 100 mV/s at the (a) 14th, (b) 28th, and (c) 42nd potential sweep cycles. The aniline concentration in solution is 0.1 M with 1.0 M H₂SO₄.

A first aspect to highlight is that these curves, especially the responses of cycles 28 and 42, have the typical shape of the voltammograms of the growth of polyaniline deposits in an acid medium on a solid electrode [40]. According to this, in the selected potential range, the presence of two pairs of well-defined current peaks can be detected, of which the first pair appears in the potential range from 0 to 400 mV, IA and IC, and the second pair is located between 450 and 700 mV.

According to existing reports [40,41], peaks IA and IC correspond to the oxidation and reduction, respectively, of the chemical forms of polyaniline emeraldine and leucoemeraldine, previously formed in the immediately preceding cycle, while peaks IIA and IIC are attributed to the overoxidation of emeraldine and to the polymerization by products. It is important to note that a particular characteristic of these peaks is that as successive potential sweep cycles are performed, their current magnitude increases proportionally. For example, peak IA goes from a nearly zero magnitude in the first cycles to 50 and 350 μA when moving from cycle 28 to 42, while peak IC goes from almost zero to −25 and −190 μA, in the same order. This tendency of the current of peaks I and II to increase with the increase in the number of sweep cycles is related to the corresponding progressive increase in the amount of polyaniline deposited in the paste/membrane assembly. This polymer growth process is possible when the electrode, in this case the paste/membrane assembly, reaches potential values greater than 700 mV, leading to an almost exponential increase in the anodic current, which is characteristic of aniline polymerization. As previously mentioned, similar behavior is observed in the voltammetric responses obtained during membrane modification at 15 and 20 °C.

It is important to specify that it was decided that the modified membranes prepared by this method and used in this work would have the same amount of polyaniline, so the magnitude of the current of the pair of peaks IA and IC was used to control it, although this led to varying the number of total sweep cycles for each temperature.

3.2. Characterization of Modified Membrane Samples

3.2.1. Voltammetric Characterization

Once modified with polyaniline at different temperatures, the membrane samples were rinsed and re-adhered to a clean carbon paste surface for voltammetric characterization using an aniline-free sulfuric acid solution. The voltammetric responses obtained from the modified membrane samples at the different temperatures of interest are presented in Figure 2.

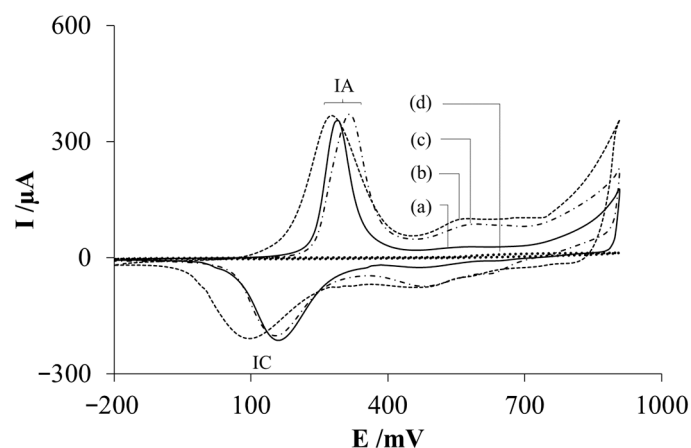


Figure 2. Voltammetric responses of the electro-synthesized polyaniline deposits at different temperatures present in the commercial membrane samples obtained at 100 mV/s with 1.0 M H₂SO₄ solution. Synthesis temperature: (a) 10 °C, (b) 15 °C, (c) 20 °C, and (d) non-M.

According to these curves, the typical response of the electroactivity of polyaniline in a sulfuric acid medium on a solid electrode is observed in the potential range explored, with minimal differences [42]. Thus, according to different authors, the voltammetric responses of the polymer deposits, obtained in this work at the three synthesis temperatures, show the characteristic peaks of the leucoemeraldine $\rightleftharpoons$ emeraldine transition located between 0 and 400 mV [43]. These curves also reveal the existence in the polymeric material obtained of small quantities of compounds from the overoxidation of the polymer, generated during the synthesis, associated with voltammetric waves located between 400 and 700 mV. Additionally, these responses also show that the peak current intensity and the area under the curve of the anodic peak of the leucoemeraldine $\rightarrow$ emeraldine transition (peak IA) are almost identical; see the data in Table 2. That is, the maximum current of the anodic peak is close to 346.4 μ A, and the charge under the peak is around 371 μ C, for the three cases (Table 2). Thus, according to these data, after washing the modified membrane samples, obtaining the typical voltammetric response of the PANi at the three synthesis temperatures confirms the presence of the polymer in the membrane samples. Furthermore, it is confirmed that from the constancy in the intensity of the anodic peak IA and its charge, the synthesis method used in this work allows for controlling the amount of polymeric material obtained in the commercial membrane samples.

Table 2. Data of the maximum currents (I_p) of the IA peak, leucoemeraldine $\rightarrow$ emeraldine transition, and of the charge under the peak (Q_p) of the voltammograms of the polyaniline deposits obtained at the different synthesis temperatures on the membrane samples (see Figure 2).

T/°C	I_p/μ A	Q_p/μ C
10	346.4 ± 13.5	371.0 ± 24.5
15	342.8 ± 22.5	372.5 ± 2.5
20	350.0 ± 2.4	371.0 ± 0.5

A complementary analysis of the voltammograms of the PANi deposits prepared at different temperatures was performed based on the responses obtained at different scan rates. Figure 3 shows the logarithmic curves of the maximum current of the anodic peak, associated with the leucoemeraldine $\rightarrow$ emeraldine transition (peak IA), where the insertion/disinsertion of counterions into the polyaniline deposits occurs as a function of the scan rate.

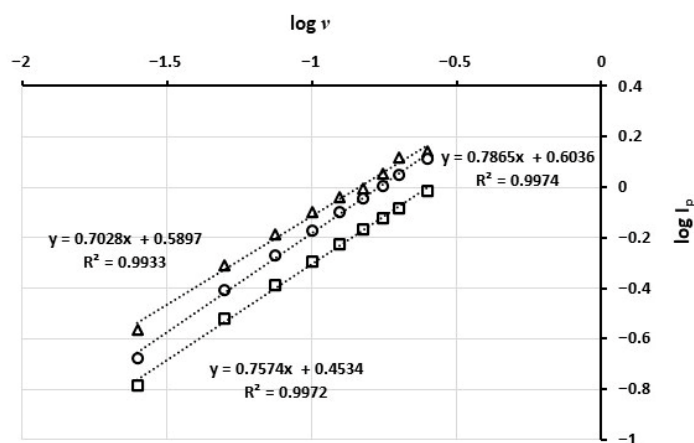


Figure 3. Logarithmic curves of the anodic peak current of the leucoemeraldine $\rightarrow$ emeraldine transition (peak IA) and the scan rate for the PANi deposits in the membrane obtained at different synthesis temperatures: (Δ) 20 °C, ($\square$) 15 °C, and ($\circ$) 10 °C.

According to this figure, the slopes of the curves are between 0.5 and 1.0 units, which implies that in the immobilized material (the polyaniline deposited on the membrane), on the carbon paste electrode, the mass transfer process that controls the reaction of peak IA is not pure diffusion, as in cases where the deposit is thick [44,45]. For example, the slope changes from 0.7028 to 0.7574 to 0.7865 when the synthesis temperature of PANi in the membrane samples varies from 20 °C to 15 °C to 10 °C respectively. This slope behavior reveals that the insertion/disinsertion process in the polymer present in the membrane moves away from being diffusion-controlled when the synthesis temperature decreases, which in turn indicates that the deposits have a structure that facilitates the diffusion of counterions as the synthesis temperature increases [43,46]. Additionally, the plot of these curves indicates that the PANi deposits in the membrane samples correspond to a thin (not thick) material with marked effects due to the degree of crosslinking [47–49]. Of course, this characteristic of the degree of crosslinking in the polymeric material is dependent on the synthesis temperature.

Another aspect to highlight is that this method of electrochemical preparation of the modified commercial membrane samples leads to the deposition of the polymer on only one of the faces of the membrane samples. According to previous reports, the modified side of the membrane corresponds to the face that remains adhered to the carbon paste during the synthesis of PANi [11,28]. This is because the polymer forms (is born) in the sections of the carbon paste in contact with the aniline solution, not blocked by the adhered membrane, and its growth is directed towards the solution; on its way, it intertwines in the channels of the membrane and therefore impregnates it. If the amount of polymeric material formed is controlled, then the polymer is located on the face adhered to the carbon paste, but if the amount of polymer is not controlled, then the polymer could pass through the membrane and distribute throughout its volume. In the first case, the voltammetric response of both faces would only show the presence of PANi on one of them, while in the second case, the voltammetric responses would reveal the presence of the polymer on both

faces. Figure 4 presents the voltammograms of one of the membrane samples obtained in this work, corresponding to a synthesis temperature of 10 °C.

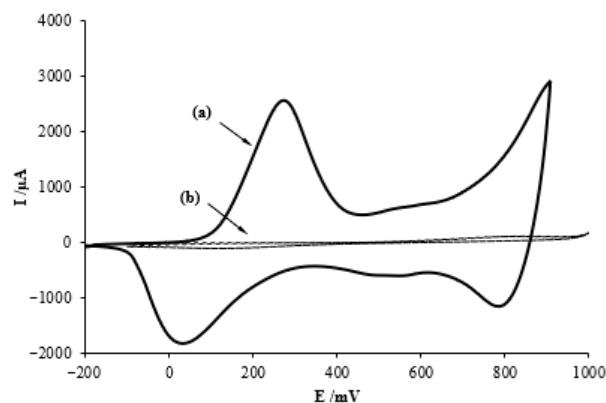


Figure 4. Voltammetric curves (a) of the modified side and (b) of the unmodified side of the membrane sample, obtained in 1 M H₂SO₄ at 100 mV s^{−1}. Synthesis temperature of PANi 10 °C.

According to these voltammetric responses, the characteristic response of PANi effectively appears on the side of the membrane that was adhered to the carbon paste during the formation of the polymer, so the PANi is located on the face of the membrane adhered to the carbon paste.

3.2.2. Analysis of the Permselectivity of Membrane Samples

Figure 5 shows the data obtained from the permselectivity *P* (using the NO₃[−] counterion) of all the samples of the study membrane modified with PANi electrosynthesized at different temperatures.

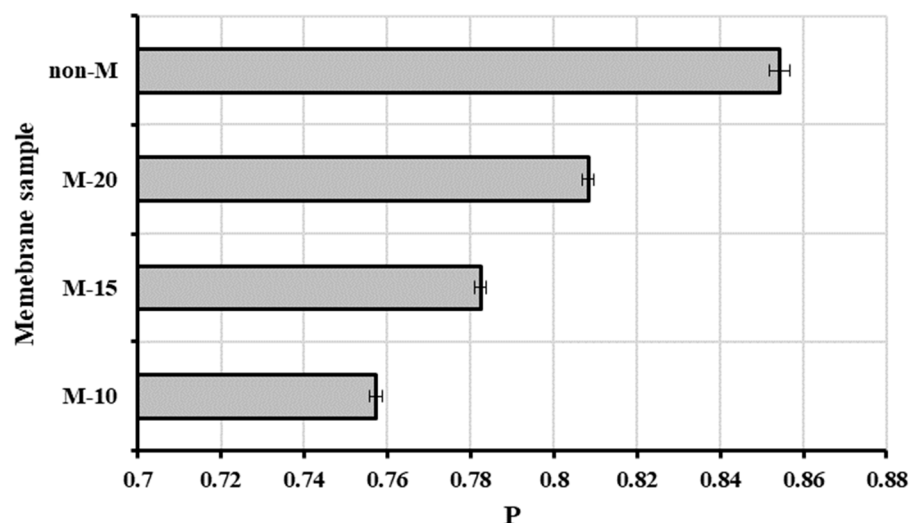


Figure 5. Permselectivity values, *P*, obtained with the PANi-modified membrane samples electroprepared at 10, 15, and 20 °C.

According to this figure, it is first noteworthy that all the permselectivity values *P* obtained with the modified membrane samples are lower than the permselectivity obtained using the unmodified membrane (non-M). Furthermore, when comparing this parameter obtained for the modified membrane samples, it is clearly observed that increasing the synthesis temperature also increases the permselectivity value. These two characteristics of the modified membrane samples clearly indicate that their selectivity is affected by the

presence of the polymer and by the characteristics acquired by it due to the variation in the synthesis temperature during its preparation.

There are enough reports in the literature [7,50,51] indicating that two types of effects come into play in the selectivity of a membrane: (a) electrostatic effects, related to the interaction between the ionic species that try to cross the membrane and the fixed charges (Donnan potential) present in it, and (b) steric effects brought into play when, for example, the dimensions of the channels within it are comparable with the dimensions of the particles that cross the membrane, or when the surface is given some property that influences the affinity between the ions and the membrane. Regarding the first, it is generally known that if the amount of ionizable fixed groups, equivalent to the ion-exchange capacity (IEC), increases, then the intensity of the electrostatic interactions between all the species that try to cross it (ions of the same and different charge to that of the fixed groups) and the fixed charges in the membrane increase, and therefore, the selectivity towards one type of ion must increase (Donnan exclusion) [2,52]. As for the second effect, if the microchannels in the membrane are wide, then the amount of solution that it can accommodate is high, and consequently, the proportion of ions of the same sign as the fixed charges (co-ions) will increase. This means that the ions present within the membrane will also contribute to current transport, and therefore the membrane's selectivity will decrease as the amount of solution in the channels increases. The opposite effect is also important to consider.

With the above in mind, the lower selectivity of the modified membrane samples could be due to the blocking of fixed charges on the membrane caused by the deposition of the conducting polymer on it. To determine whether this is the reason for the loss of selectivity in the modified membranes, Figure 6 presents the values obtained from the ion-exchange capacity (IEC), equivalent to the number of fixed charges in the membrane, for the different membrane samples prepared.

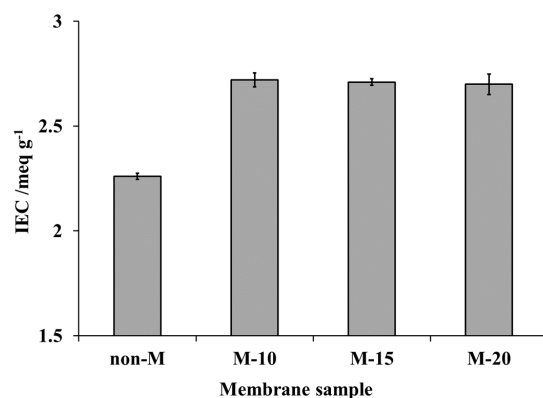


Figure 6. Ion-exchange capacity (IEC) values obtained with the different PANi-modified membrane samples electrosynthesized at 10, 15, and 20 °C.

According to this figure, the modified membrane samples have practically the same IEC value; in addition, their IEC values are higher in all cases than those of the pristine membrane. These results can be understood if we consider that the ion-exchange capacity of the IEC-modified membrane samples is composed of two terms:

$$\text{IEC} = \text{IEC}_m + \text{IEC}_{\text{PANi}} \quad (11)$$

where IEC_m corresponds to the number of fixed charges originally in the membrane sample due to the $-\text{N}(\text{R}_3)^+$ groups, and IEC_{PANi} is associated with the number of fixed charges added by its modification with the conducting polymer due to its doped state [41]. Thus, if we consider, as indicated in the previous paragraph, that the amount of polyaniline

deposited in all the membrane samples studied is practically the same, this results in the contribution of fixed charges in the modified membranes due to the polymer being the same for all of them. This results in the IEC_{PAni} value being also equal, that is, approximately 20% higher than the loading amount of the unmodified membrane sample, for all prepared membrane samples.

It should be noted that this behavior is not surprising given that Nagarale et al. reported similar results when studying the chemical modification, at constant temperature, of selective membranes with PANi [11]. Thus, according to this report, the imino/amino groups present in the chemical structure of the conductive polymer can develop a positive charge thanks to the chemical doping process in acid solution and, therefore, contribute to increasing the IEC of the modified membrane samples. According to these authors, this is possible because the PANi deposit in anion-exchange membranes is located mainly on the surface of the membrane without penetrating into the bulk of the membrane, so the fixed charges of the membrane are not blocked by the PANi deposits, and therefore, their quantity remains constant. However, the IEC values of the modified membrane samples obtained in our work are not associated with higher selectivities, as would be expected, compared to the unmodified membrane sample, since as shown in Figure 3, the highest selectivity corresponds to the unmodified membrane, which in turn has the lowest IEC value. Thus, as it appears, the permselectivity values obtained are dependent on some of the properties conferred to the membrane samples by the polymer deposits, so the IEC is not the only factor that should be considered to understand the selectivity of the modified membrane samples in this work.

In this sense, another effect that can influence the selectivity of ion-exchange membranes is the dimensions of the microchannels through which the ions pass through (crosslinking) [51,53]. One parameter that can provide information about the reticular or crosslinking characteristics of the PANi-modified membrane samples is the electrical resistance (or specific resistivity). Figure 7 presents the specific electrical resistance as a function of the counterion transport number obtained for each of the modified membrane samples.

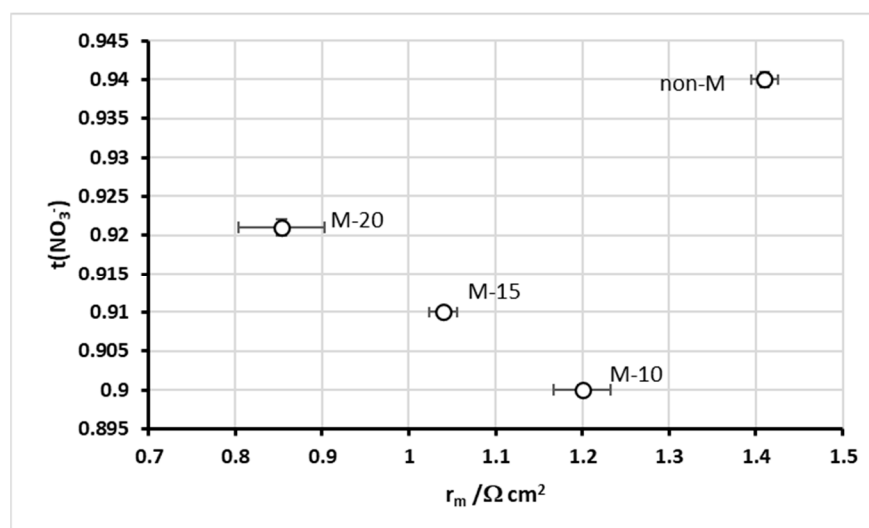


Figure 7. Values of the counterion transport number, $t(\text{NO}_3^-)$, in the commercial membrane samples modified with electrochemically prepared PANi deposits at different synthesis temperatures as a function of their specific resistance, r_m .

The first thing that draws attention to these values is that the electrical resistance obtained for all samples of the modified commercial membrane are lower than the value of

the same parameter of the unmodified membrane (non-M). Furthermore, all these samples of the modified membrane present lower values of the transport number with respect to the pristine membrane. When comparing the values of these parameters between the modified membrane samples, it is seen that the specific resistance r_m decreases with increasing PANi synthesis temperature, while the transport number follows the opposite behavior, since it increases proportionally with the increase in temperature. This behavior can be understood if we consider that the incorporation of the polymer into the membrane occurs on the walls of the microchannels, which leads to their widening and therefore to less opposition to the ionic transit of both counterions and co-ions through them, which translates into lower specific resistance values. However, this process of ionic transport across the membrane appears to be affected by the affinity between the ions crossing the membrane and the PANi present in the microchannels. That is, specifically the physicochemical characteristics of the counterions (hydration or size) and the chemical form of the PANi and its morphology, the latter obtained at different synthesis temperatures, affect the selectivity of the modified membrane samples (transport number). According to the literature [53,54], it has generally been found that if crosslinking in exchange membranes increases, keeping the IEC constant, then the selectivity will decrease, probably through the decrease of hydrophilic moieties, which in turn restrict ionic mobility. As will be seen later, in the case of this work, this characteristic is linked to the synthesis conditions used to prepare the PANi hosted in the commercial membrane samples.

3.2.3. Characterization of Hydrophilic Properties

Water Content and Pure Water Permeation Flux

One way to know if the decrease of hydrophilic portions in PANi deposits and their degree of crosslinking are the causes of the selectivity behavior of the membrane samples, as established at the end of the previous paragraph, is through the analysis of the water content (%H₂O) in the modified membrane samples and the pure water permeation flux, $J(\text{H}_2\text{O})$, through them. The results obtained from both parameters are presented in Figure 8.

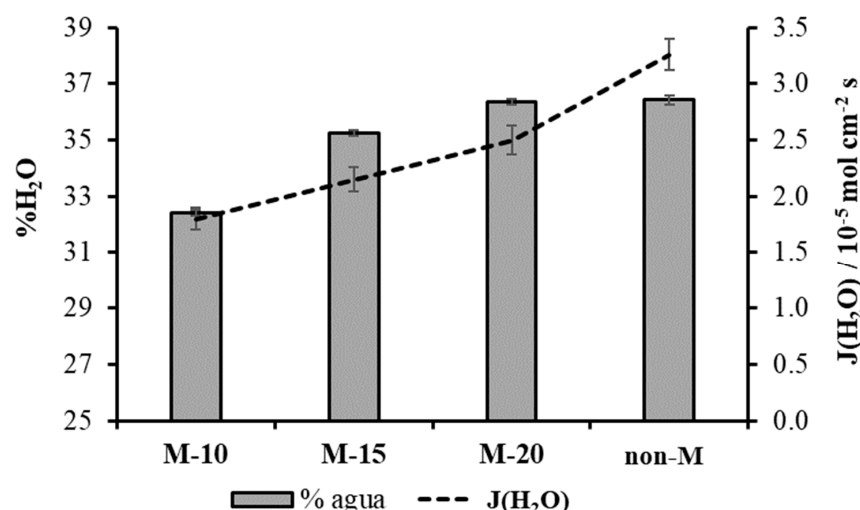


Figure 8. Relationship between polymerization temperature, water content (%H₂O), and pure water permeation flux, $J(\text{H}_2\text{O})$, using the modified and pristine membrane samples.

According to this figure, it can be observed that the water content (%H₂O) in the membrane samples studied follows the decreasing order:

$$\text{non-M} \approx \text{M-20} > \text{M-15} > \text{M-10}$$

Therefore, the membrane sample modified at 20 °C has a similar affinity to the unmodified membrane and is the most affine to water compared to the rest of the modified membrane samples, while the least affine to water is the membrane sample modified at 10 °C.

Regarding the pure water vapor permeation flux, this parameter is defined as the amount of water vapor that passes through the ion-exchange membrane per unit of time and unit of area of exposed membrane. Thus, this parameter can indirectly provide information on the hydro/oleophobicity of the membrane in terms of the properties of the commercial membrane and the morphological characteristics of the PANi deposited on it [55]. Considering the above, in the data obtained, a proportional decrease in the pure water permeation flux was observed in the modified membrane samples proportionally with the decrease in the PANi electrosynthesis temperature, while the unmodified membrane sample presented the highest value of this parameter of all of them.

Thus, according to the data obtained, both from the water content and the pure water permeation flux, they show that the PANi deposits in the modified membrane samples hinder the passage of water vapor through the membrane samples to different degrees depending on their affinity for water. For example, the membrane sample that was modified with PANi electrosynthesized at the lowest temperature, M-10, had the lowest water content and presented the lowest pure water permeation flux, while the sample modified at the highest temperature presented the highest water content and the highest pure water permeation flux. In essence, these data show that as the synthesis temperature of the PANi present in the membrane samples decreases, blocking becomes more important. This means that the PANi deposits exert a hydrophobic barrier effect in the microchannels of the different membrane samples of interest, and this effect becomes more important as the synthesis temperature decreases. According to this, the porosity level of the membrane samples must be affected by the PANi present in them. Therefore, the following expression was used to determine the porosity level of the membrane samples (π) under study [56]:

$$\pi = \frac{w_w - w_d}{\rho_w \times V} \quad (12)$$

where ρ_w is the density of water (g/cm^3), V is the volume of the membrane sample (cm^3), and w_w and w_d correspond, respectively, to the wet and dry weight of the membrane sample (g). Therefore, the data obtained are shown in Table 3.

Table 3. Porosity level values of the membrane samples (π) under study as a function of the electrosynthesis temperature.

Membrane	non-M	M-20	M-15	M-10
π^a	0.0314 C	0.0309 C	0.0294 C	0.0170 C

Note. $(^a) C = \frac{1}{\rho_w \times V}$, where ρ_w is the water density (g/cm^3) and V is the volume of the membrane samples (cm^3).

Considering that the modified membrane samples, as mentioned above, have the same amount of PANi and that they only differ in their morphology, depending on the temperature, the volume of the membrane samples can be considered constant, assuming that the values of the thickness and area of the samples are the same. Then the “C” quantity is the same for all membrane samples, and therefore, the porosity level values π can be explained as being dependent only on the structural characteristics of the PANi deposits conferred by the temperature. Thus, according to the data presented in Table 3, the porosity level of M-10, modified at 10 °C, is the one with the lowest value. On the other hand, the M-20 membrane sample, modified at 20 °C, and the unmodified membrane present very similar π values, which is reflected in their similar porosity levels. Finally, among them is the M-15 membrane, modified at 15 °C, with an intermediate porosity level.

According to the behavior of these data, it is inferred that the blockage of the micro channels by the deposited PANi is consequently reflected in the pure water permeation flux, since the lower the porosity (size of the micro channels, π), the lower the pure water permeation flux. Thus, as the synthesis temperature of PANi increases, the size of the microchannels (porosity) also increases, and therefore, the pure water permeation flux increases.

Furthermore, these porosity data also allow us to understand the behavior of the amount of water in the membrane samples, since as the dimensions of the microchannels (porosity) increase, the amount of water they contain also increases.

Additionally, these porosity results allow us to explain the behavior of the values obtained from the transport number and the ionic strength of the modified membrane samples, presented in Figure 7. That is, the decrease in the diameter of the channels of the membrane samples, caused by the PANi deposits, not only hinders the passage of counterions, which leads to a decrease in the transport number, but also of co-ions, which increases the resistance, since this parameter is affected by what happens to the two types of species in their transit through the membrane, counterions and co-ions (see Figure 7). Regarding the values of these parameters, for the unmodified membrane sample, it seems that they are affected by another type of interaction that does not occur when PANi is deposited on the membrane, such as the affinity of the surface of the commercial membrane with water and the interactions of the fixed charges with a single type of species that crosses the highly selective membrane (counterion).

3.2.4. Morphological Characterization of Polyaniline Deposits in Membrane Samples

As mentioned in previous paragraphs, the morphological characteristics of the polymer deposits on the surface of the membrane samples play a key role in their new selective properties. In this regard, some additional properties of the surface of the membrane samples are addressed below, which will allow for a better understanding of the selective properties of the membranes discussed up to this point.

Contact Angle (SCA—Static Contact Angle)

Figure 9 presents the contact angle values of the different membrane samples prepared in this paper.

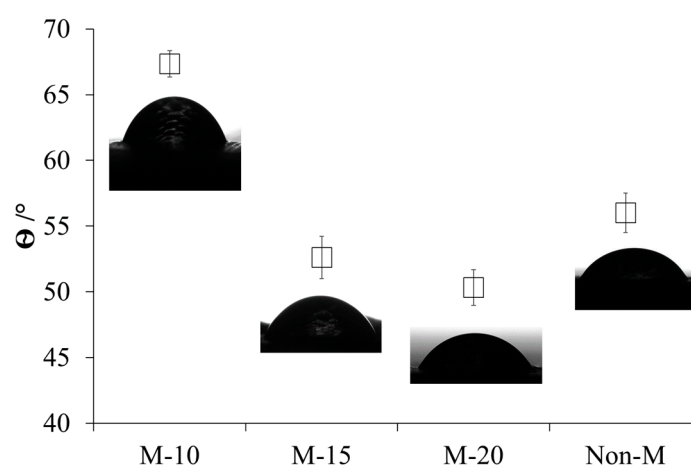


Figure 9. Values obtained from the contact angles (θ) using the different samples of the study membrane modified with polyaniline deposits.

According to these results, the contact angle decreases with increasing temperature used to modify the membrane samples with polyaniline. For example, at a PANi synthesis

temperature of 10 °C, the modified membrane sample has a contact angle of 60°, while at 20 °C, the angle is 43°. The unmodified membrane has a contact angle of 50°, which is between the two limits mentioned above. This contact angle behavior reflects a change in the affinity of water for the membrane surface when modified with polyaniline at different temperatures. That is, by increasing the synthesis temperature, a decrease in the hydrophobic character of the surface of the modified membrane samples is observed, compared to the unmodified membrane, which leads to an increase in the affinity for water. In contrast, if the synthesis temperature decreases, then the surface of the membrane sample becomes more hydrophobic, which implies a lower affinity for water. This behavior allows us to understand, for example, the results of the determination of water content, %H₂O, in Figure 8 for the different membrane samples. According to this figure, the %H₂O values increase proportionally with increasing PANi synthesis temperature, which is consistent with the increasing in the surface's affinity for water, reflected by the decreased contact angle.

These results support the assumption that there is a close relationship between the water affinity of the modified membrane samples, and consequently the transport properties, and the PANi deposits present in them prepared at different temperature conditions. Thus, according to the existing literature, it should be considered that the chemical composition and topography of the surface can affect this affinity to water [57,58]. Figure 10 shows the X-ray diffraction patterns of the different membrane samples studied.

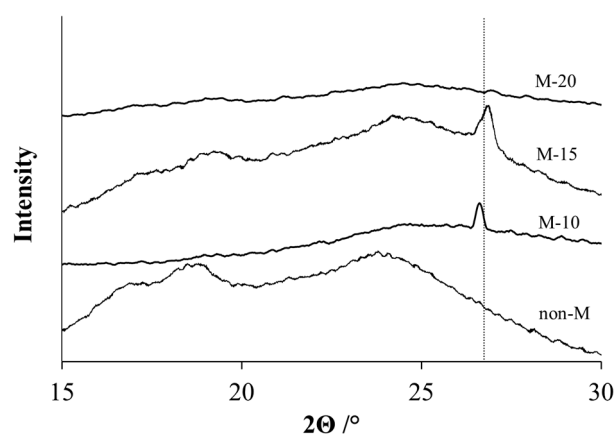


Figure 10. X-ray diffraction patterns of the polyaniline-modified membrane samples prepared at different temperatures.

As has been widely documented, all diffraction patterns obtained with the study samples present the characteristic shape of materials that have an amorphous/semi-crystalline condition, in this case, depending on the preparation temperature of the PANi deposit [59,60]. Specifically, the diffraction patterns of the membrane samples modified at 10 °C, M-10, and at 15 °C, M-15, show a peak around 26°, characteristic of a certain degree of crystallinity in the PANi deposit. According to the existing literature, this peak is associated with the ordering of the planes of the benzoid and quinoid groups present in the PANi chains, so the preparation temperature of the polymeric deposits determines the ordering of these chemical entities [61]. Furthermore, the diffraction pattern peak of the membrane sample modified at 10 °C is sharper, presenting a full width at half maximum (FWHM) of 0.25°, compared to the value of 0.5° in the case of the membrane sample modified at 15 °C, indicating that PANi has a higher regularity in its crystalline structure at the low synthesis temperature of the conducting polymer [59,60]. The opposite is observed in the diffraction patterns of the membrane sample prepared at 20 °C, M-20, and in the unmodified membrane, non-M, due to the absence of diffraction maxima. Thus,

these characteristics of the set of diffraction patterns of the different membrane samples indicate that decreasing the PANi deposit preparation temperature increases their ordering. According to existing literature on the subject, this could be due to its intrinsic effect on the kinetics of the polymer formation process [16,62–64]. This means that the chains of polymer prepared at low temperatures arrange themselves more regularly than at high temperatures. Furthermore, at low temperatures, the possibility of dimers, trimers, etc. diffusing into the solution and away from the electrode surface is reduced, which impacts various properties of the polymer. This allows for a high molar mass of the conducting polymer, which in turn influences the material's morphology and various properties, such as a high degree of crosslinking and high conductivity, due to the high crystallinity of the PANi obtained under these conditions. All of this gives the PANi deposition on the membrane's lower roughness and narrower pores.

According to microphotographs obtained at two magnifications of the surface of the modified membranes prepared in this work, Figure 11, different topographic features of the polyaniline deposits can be effectively appreciated depending on the preparation temperature. Indeed, at a low preparation temperature (M-10 membrane), microphotographs obtained at different magnifications show that the surface of the conducting polymer in the membrane sample is mainly composed of small sheets or flakes. Conversely, at a high synthesis temperature (M-20 membrane), and also in the unmodified membrane sample (non-M membrane), the surface is composed mainly of small grains, in accordance with what has been reported by different authors, see references [10,11], according to which it is the result of the decrease in molecular weight and the low crystallinity of the PANi. Finally, at an intermediate polymer synthesis temperature (M-15 membrane), the surface displays a topology dictated by the presence of both flakes and small grains.

The information obtained from both microphotographs, the X-ray diffraction patterns, and contact angles (Figures 10 and 11) supports the idea that the morphological properties of the PANi deposits obtained are closely related to the temperature at which they were obtained. Thus, it can be noted that by decreasing the synthesis temperature, the polyaniline deposits in the membrane are less rough, leading to a more hydrophobic surface, while by increasing the polymer preparation temperature, its surface is rougher and therefore less hydrophobic. This means that as the polyaniline synthesis temperature increases, the modified membrane sample accumulates more solution in the cavities of the polyaniline reservoir and therefore presents a higher %H₂O value.

Additionally, these characteristics of the surface of the modified membranes express their influence on different parameters as shown in Figure 12, which presents the values of the static surface force, SSF, for each membrane sample.

According to this figure, the membrane sample surfaces can be grouped into two categories based on SSF values. On the one hand, there are unmodified membrane samples and those modified at 20 °C, and on the other, the samples modified at 10 and 15 °C. In the first category, SSF values were around 35 units, while in the second group, SSF values were around 5 units. The difference between the SSF values indicates a marked difference in roughness because of temperature. On the one hand, a very rough surface is obtained when using a PANi synthesis temperature of 20 °C, which leads to a high SSF value, and on the other hand, less rough surfaces are obtained when using a synthesis temperature between 10 and 15 °C, which leads to obtaining low SSF values.

Further results will be presented below to better understand the results obtained regarding the effects of the topographical aspects of the polyaniline deposits on the new properties of the selective membrane samples studied.

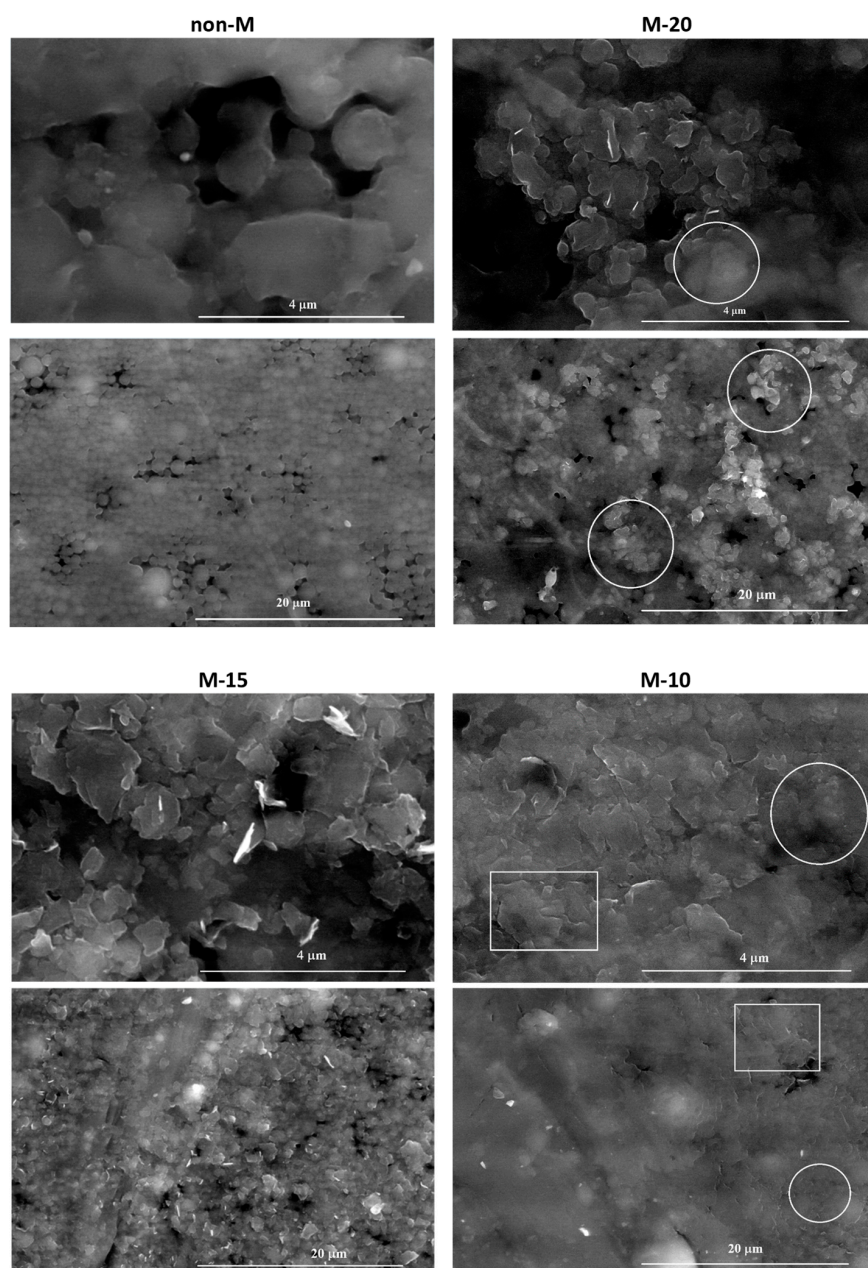


Figure 11. Micrographs of the modified membrane samples at 20, 15, and 10 °C and unmodified non-M. □ sheets and ○ small grains.

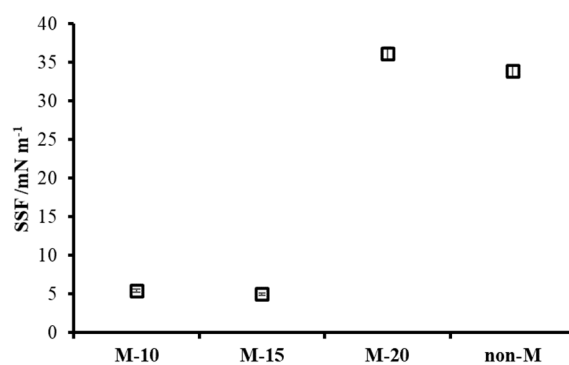


Figure 12. Behavior of the surface static force, SSF, as a function of the synthesis temperature of the polyaniline present in the commercial membrane samples.

3.2.5. Analysis of the Chronopotentiometric Responses of Modified Membrane Samples

Chronopotentiometry is a fundamental technique for obtaining information on the selectivity of an ion-exchange membrane, in which various effects intervene, such as the quantity or type of counterion, or properties of the membrane such as its surface characteristics [39,65,66]. In this technique, the membrane under study is placed between two solutions of equal concentration, each containing an electrode. When a current is applied, a potential is generated, known as the membrane potential (E_m), which is measured using two reference electrodes due to the processes taking place near the membrane. If the obtained potential is plotted against the duration of the applied current, a chronopotentiometric curve (CC) is obtained, which reveals different processes that depend on the applied current and the topographical characteristics of the membrane. Thus, Figure 13a shows a typical example of the chronopotentiometric curves obtained with the different modified samples of the commercial membrane of interest, in this case modified at 10 °C, using a 0.01 M NaNO₃ solution and a current of 1.4 mA.

Before analyzing the results obtained from the membrane samples produced in this work, it is necessary to mention different aspects of the chronopotentiometric curves.

According to various authors [39,65,66], the behavior of the membrane potential as a function of time in these curves makes it possible to identify different sections in which specific phenomena are associated, allowing important information to be generated when an electric current is applied to the membrane. For example, at low times in section I of the CC curve (Figure 13a), the potential suddenly goes from a zero value, when the current has not yet been applied, to a certain value, when the imposition of current begins, dependent on the magnitude of the applied current. With this segment of the curve, it is possible to obtain the resistance of the membrane/solution assembly through the slope of the curve of the maximum potential value as a function of the applied current. In this same section, the potential evolves slowly, passing through an inflection point, which generates a value called the transition time on the current application time axis. This parameter represents the moment at which the counterion concentration in the solution near the membrane reaches a minimum. Since this parameter is important for the quantitative analysis of the modifications of the membrane samples studied, the t vs. dE_m/dt curve used to obtain it is presented in Figure 13b. As for section II, the evolution of the potential stops when it reaches a certain value, higher than that of section I, which remains constant for the remaining time of the current application if the topography of the membrane surface is regular and if the applied current is not very high. This behavior of E_m is because as the pulse time increases, the thickness of the area where the counterion is depleted increases, so for the counterion to continue passing through the membrane, this area must be supplied with a counterion from far away from the membrane. Finally, in section III, the potential drops abruptly due to the cessation of application of the current, which only in some cases occurs slowly over a certain time until reaching the initial value before the application of the current. This is because the dissipation of the concentration gradients created by the imposition of the current on the membrane linked to ionic transport in the membrane occurs, and these processes are closely linked to the topographic characteristics of the membrane surface. It is worth mentioning that, from this section, the last potential value can be used, just before the current interruption, for each applied current to thus obtain the current–potential curve, I-E, which allows for obtaining various parameters, among which are the limit current, I_{lim} (see next paragraph), the counterion transport number, or the thickness of the diffusion layer. It is important not to lose sight of the fact that chronopotentiometric curves such as the one presented in Figure 13 are only obtained if the applied current has a value greater than I_{lim} ; see for example ref. [65].

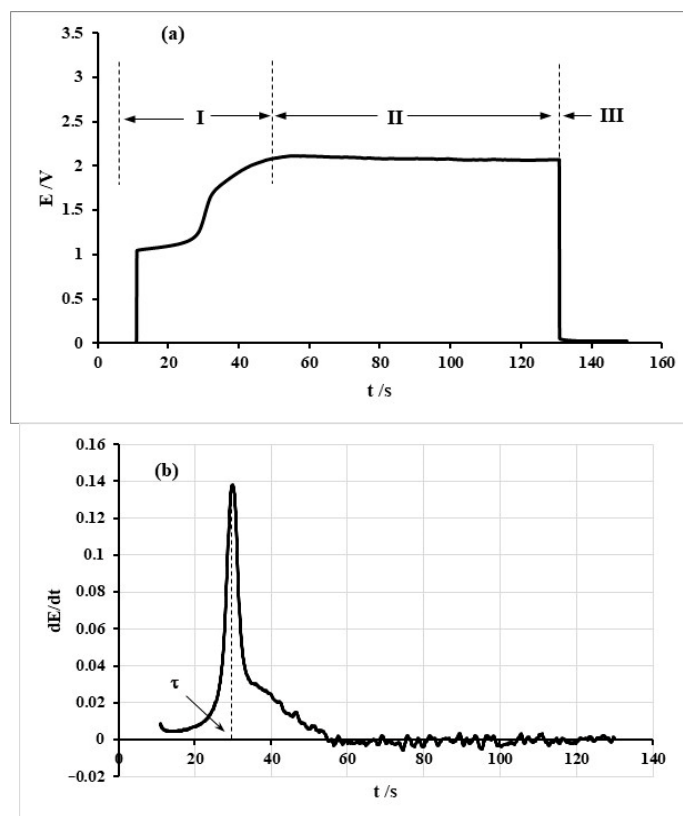


Figure 13. (a) Chronopotentiometric (CC) curve obtained with the modified membrane sample at 10 °C in contact with a 0.01 M NaNO₃ solution and an applied current of 1.4 mA and (b) t vs. (dE_m/dt) curve. In section I of the CC curve, the potential suddenly goes from a zero value, when the current has not yet been applied, to a certain value, when the imposition of current begins. This potential dependent on the magnitude of the applied current. Thus, the relationship between the maximum potential value and the applied current is dependent on the ohmic resistance of the membrane assembly and the adjacent solution on each of its sides. In this same section, the potential evolves slowly, passing through an inflection point, which generates a value called the transition time on the current application time axis. This parameter represents the moment at which the counterion concentration in the solution near the membrane reaches a minimum. As for section II, the evolution of the potential stops when it reaches a certain value, higher than that of section I, which remains constant for the remaining time of the current application if the topography of the membrane surface is regular and if the applied current is not very high. This behavior of E_m is because as the pulse time increases, the thickness of the area where the counterion is depleted increases, so for the counterion to continue passing through the membrane, this area must be supplied with a counterion from far away from the membrane. Finally, in section III, the potential drops abruptly due to the cessation of application of the current, which only in some cases occurs slowly over a certain time until reaching the initial value before the application of the current.

Table 4 presents the values obtained for the transition time, τ , for the various modified membrane samples as well as other parameters used in their quantitative analysis at the same applied current (in the form of current per unit area of membrane, j_{apl}).

As can be noticed, in all cases, the experimental values of τ obtained with the different samples of the modified commercial membrane are lower than the values obtained with the unmodified non-M membrane. Furthermore, when comparing the transition times obtained between the modified membrane samples, a regular behavior of this parameter can be detected in which the PANi-modified membrane at 10 °C (M-10) has the lowest transition time values, while the modified membrane sample at 20 °C (M-20) has the largest values of this parameter; see for example the values given in the last row of the table.

Table 4. Transition time (τ) values for the study membrane samples as a function of the applied current density (j_{apl}).

$j_{\text{apl}} \times 10^6/\text{A cm}^{-2}$	τ/s			
	M-10	M-15	M-20	non-M
1.44	40.31 $\pm$ 0.12	40.57 $\pm$ 0.13	40.21 $\pm$ 0.13	57.68 $\pm$ 0.13
1.69	37.14 $\pm$ 0.53	35.94 $\pm$ 0.53	36.95 $\pm$ 0.53	49.15 $\pm$ 0.53
1.96	32.39 $\pm$ 0.47	33.01 $\pm$ 0.47	32.73 $\pm$ 0.47	42.38 $\pm$ 0.47
2.25	29.45 $\pm$ 0.14	29.55 $\pm$ 0.14	29.77 $\pm$ 0.14	36.92 $\pm$ 0.14

According to the existing literature on the subject, the transition time can be affected by two factors: (a) the membrane selectivity and (b) the proportion of non-conductive portions of the membrane surface. Since the selectivity, based on the permselectivity or counterion transport number obtained in this work, has been analyzed to be different for each membrane sample, the discussion of the non-conductive portions of the surface of the PANi-modified samples will be addressed below.

This analysis starts with the determination of the conductive fraction, defined by ϵ , for all membrane samples from the slope of the curves $(C_0/j)^2$ vs. τ . This slope presents the expression given by Sand's equation for a membrane in the form [65,67]

$$m = \frac{\tau}{\left(\frac{C_0}{j}\right)^2} = \frac{\epsilon^2 \pi D}{4} \left(\frac{|z_{\text{ct}}| F}{t_{\text{ct}}^{\text{m}} - t_{\text{ct}}^{\text{sol}}} \right)^2 \quad (13)$$

where m is the slope of the $(C_0/j)^2$ vs. τ curve, with C_0 in mol cm^{-3} and τ in seconds; in addition, D ($= \frac{2D^+D^-}{D^+ + D^-}$, with D^k for the cation or the anion) is the average diffusion coefficient of the electrolyte solution in contact with the membrane, F is the Faraday constant ($96,500 \text{ C mol}^{-1}$), π ($3.1416 \dots$), and t_{ct}^{m} and $t_{\text{ct}}^{\text{sol}}$ are the transport numbers of the counterion in the membrane and in the solution, respectively. It should be noted that the parameters D and $t_{\text{ct}}^{\text{sol}}$ were calculated from the values of $u^\infty(\text{NO}_3^-) = 6.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ and $u^\infty(\text{Na}^+) = 4.6 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ [68].

Table 5 presents the values obtained from the slope m and the conductive fraction ϵ of the modified membrane samples in addition to the values of the counterion transport number obtained and analyzed in the paragraphs above.

Table 5. Values of the parameters involved in the determination of the conductive fraction of the modified membrane samples ϵ . t_{ct}^{m} and $t_{\text{ct}}^{\text{sol}}$ are the transport numbers of the counterion in the membrane and in the solution, respectively.

Membrane	t_{ct}^{m}	$t_{\text{ct}}^{\text{sol}}$	$m/\text{mol}^2 \text{ A}^{-2} \text{ cm}^{-2}$	ϵ
non-M	0.940 $\pm$ 0.001	0.586	676,763 $\pm$ 106,040.6	0.916 $\pm$ 0.013
M-20	0.921 $\pm$ 0.001	0.586	617,896 $\pm$ 11,481.8	0.829 $\pm$ 0.004
M-15	0.910 $\pm$ 0.001	0.586	615,559 $\pm$ 29,240.0	0.800 $\pm$ 0.004
M-10	0.900 $\pm$ 0.001	0.586	616,797 $\pm$ 63,544.4	0.776 $\pm$ 0.005

It is necessary to clarify that the calculation of the conducting fraction of the membrane samples depends on knowing the transport number of the counterion, called real, through the study membranes using the concentration of 0.1 M of counterion [32,69–71]. Therefore, two things must be specified: (i) It is considered that t_{m} , obtained by the concentration cell method, called apparent, using the conditions of the Experimental Section, is typical of the concentration 0.1 M, as concluded by Cha et al. using the same methodology, since when using different combinations of counterion concentrations, they found that in the

case of high values of counterion concentration, such as the one used in this work, the transport number of the counterion varies very little and can be considered independent of the concentration [32]. (ii) According to Petrovick et al. [72], the water transport number can be considered low and constant for the membrane samples prepared in this work given that they have low water contents of less than 30%. This implies that the counterion transport number, obtained by means of the concentration cells, is equal to the actual transport number obtained, for example, by the Hittorf method or by chronopotentiometry, as indicated by different authors [73,74].

The analysis of the values of the conductive fraction of the modified membrane samples, reported in the last column of Table 5, reveals that the unmodified membrane of interest presents the highest value of this parameter (0.916 ± 0.013), while when comparing the behavior of the ϵ values between modified membranes, it is observed that they follow a regular behavior depending on the PANi synthesis temperature. Thus, the conductive fraction of the unmodified membrane coincides with that reported by Santana Barros et al., consistent with a homogeneous membrane [65]. Regarding the values obtained with the modified membrane samples, it must be considered on the one hand that the amount of PANi used to modify them is practically the same, so the changes in the conductive fraction must be associated with the morphological characteristics of the PANi deposits, as has been pointed out in this work. Thus, we recall that, according to Figure 11, the surface of the membrane sample modified with PANi at 10 °C is mainly composed of small, evenly distributed flakes. Furthermore, Figure 8 indicates that if the membrane sample has narrow channels, thus hindering ionic transit, then the deposition of PANi produces a blockage of the membrane surface, which is reflected in a low value of the conductive fraction. This effect is expressed in other properties such as a high ionic resistance associated with a low conductive fraction (Figure 7).

In contrast, according to Figure 11, the surface of the membrane sample modified at 20 °C is composed of small, evenly distributed grains. Furthermore, Figure 8 shows that the membrane has wide channels that hinder ionic transit to a lesser degree, so these characteristics of the sample surface are expressed with a high ϵ value.

Finally, the membrane sample modified at 15 °C, which has a surface consisting of a mixture of both small flakes and small grains, exhibits intermediate behavior, and this is reflected in a value of the conductive fraction that lies between the two mentioned above.

To complement this information mentioned above, by interrupting the current applied to the membrane samples in chronopotentiometric experiments (section III of the CC), it is possible to determine the current–potential curve I-E or j-E, from which important information about the surface characteristics of the membrane can be obtained [65]. Since all the curves obtained present the characteristic shape when using a homogeneous membrane, only one of them is presented in Figure 14.

According to Figure 14, the curves obtained using the membrane samples show the three characteristic sections of an I-E curve typical of a homogeneous membrane [75]; that is, in sections I and III, the potential and current follow a linear pattern. Between these two sections, the current varies very little (section II). A careful analysis of these curves yields various parameters, which are grouped in Table 6 for all the membrane samples considered in this work.

This table shows parameters such as the resistance of the segment in section I, R_I , which gives information about the opposition that the membrane presents to ionic flow, the limit current, I_{lim} . This indicates the beginning of the concentration polarization of the membrane, the amplitude of the plateau, in section II. This indicates the homogeneous character of the membrane surface and finally the resistance of the curve in section III, R_{III} , which allows us to know the resistance of the membrane in electroconvection conditions [75].

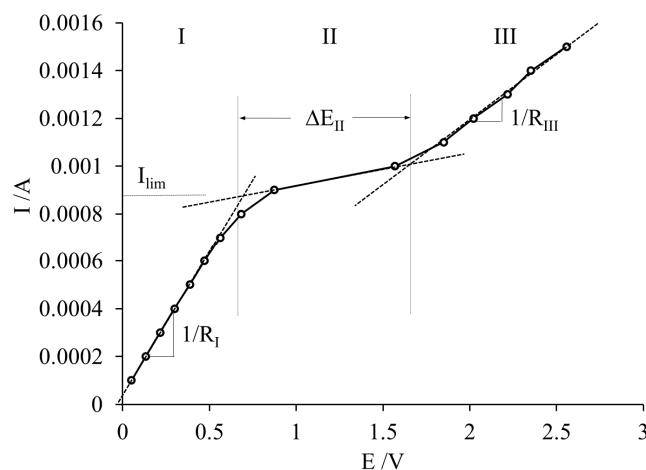


Figure 14. Current–potential I-E curve obtained from the chronopotentiometric responses using the PAni-modified membrane sample at 20 °C. $A_m = 1 \text{ cm}^2$. In section I, the potential and current follow a linear relationship. The slope of this relationship is associated with the opposition that the membrane presents to ionic flow. Segment I is limited by the limit current, I_{lim} , which indicates the beginning of concentration polarization of the membrane. As the potential increases, the current varies very little, defining a plateau, section II, which provides information about the homogeneous character of the membrane surface. Finally, the current and potential resume their linear relationship, and their slope provides information about the resistance of the membrane under electroconvection conditions.

Table 6. Parameters obtained from the polarization curves of the commercial membrane samples modified with polyaniline at different temperatures: limiting current density (j_{lim}), resistance of section I (R_I), amplitude of section II (ΔE_{II}), resistance of section III (R_{III}), and the thickness of the solution close to the membrane (δ). $A_m = 1 \text{ cm}^2$.

Membrane	non-M	M-20	M-15	M-10
$R_I/k\Omega$	1.588 ± 0.002	0.769 ± 0.002	0.775 ± 0.001	0.909 ± 0.013
$j_{lim}/\text{mA cm}^{-2}$	0.78 ± 0.06	0.90 ± 0.03	0.87 ± 0.01	0.78 ± 0.05
$\Delta E_{II}/\text{mV}$	600 ± 10	1015 ± 33	734 ± 2	719 ± 8
$R_{III}/k\Omega$	0.49 ± 0.03	2.00 ± 0.02	1.84 ± 0.01	1.21 ± 0.03
$\delta/\mu\text{m}$	482.9	442.3	476.6	544.5

According to the analysis of this data, the R_I resistance is lower in all cases when the membrane samples are modified with PAni, associated with the fact that PAni deposits decrease membrane resistance, while among modified membrane samples, the tendency is that as the preparation temperature of the modification decreases, the resistance increases. If we consider that R_I depends on both the resistance of the membrane samples (membrane and PAni reservoir) as well as the resistance associated with effects that cause the diffusion of the counterion in the solution close to its surface [65], then the R_I behavior must be understood by first considering topographical characteristics of the PAni deposits located on the membrane surface. Taking into account what has been mentioned in the paragraphs above, the R_I decreases when the PAni synthesis temperature increases since the PAni deposits are less compact and smoother. Furthermore, these surface characteristics of the modified membrane samples indirectly impact the extent of the diffusion layer, δ , in which ionic flux occurs close to the membrane surface, which influences the values of R_I [76].

$$j_{lim} = \frac{|z_{ct}|FCD}{\delta(t_{ct}^m - t_{ct}^{sol})} \quad (14)$$

where the diffusion coefficient of the counterion D ($1.382 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) remains invariant with the concentration and the transport numbers of the counterion in the membrane samples t_{ct}^{m} correspond to the values reported in Table 5.

According to the values of δ found in the last line of values in Table 6, it is observed first that the thickness of the diffusion layer is of the order of magnitude found in other studies for similar concentrations [77]; furthermore, its value increases in the opposite direction with the increase in the PANi synthesis temperature. For example, for the modified membrane sample at 10°C , M-10, the diffusion layer thickness is $544.5 \mu\text{m}$, while when using a temperature of 20°C δ , it is equal to $442.3 \mu\text{m}$. This implies that by using a low synthesis temperature, the resistance of the portion of the solution close to the membrane surface will increase, since δ is large, and therefore R_{I} will be high. On the other hand, if the synthesis temperature is high, the resistance of the portion will be low, given that the parameter δ is low, and consequently, R_{I} will be small. Thus, according to the behavior of the R_{I} values, these are more closely related to the thickness of the solution adjacent to the membrane surface, which is a consequence of the surface characteristics of the membrane samples. As will be seen below, the topographical characteristics of the surface of the modified membrane samples influence other parameters obtained from the current–potential curves.

Table 6 also presents the limiting current density (j_{lim}) values for all the membrane samples studied, which show regular behavior associated with the synthesis conditions of the PANi deposits. This means that the unmodified membrane shows the lowest j_{lim} value compared to the values obtained using the modified membrane samples. Furthermore, among modified membrane samples, it is observed that j_{lim} tends to decrease as the synthesis temperature decreases. For example, when using a temperature of 20°C , M-20, the limit current has a value of 0.90 mA/cm^2 , while when using 10°C , M-10, the j_{lim} now has a value of 0.78 mA/cm^2 . This behavior can be explained if one takes into account that j_{lim} depends on various effects, among which is the conductive area of the membrane; thus, if the data in Table 5 are reviewed, the modified membrane samples have different conductive portions on their surface, which explains the j_{lim} values obtained. Indeed, the membrane sample obtained at 10°C has a conductive fraction of 0.776 and therefore presents a low j_{lim} , while the membrane sample modified at 20°C has a conductive fraction equal to 0.829, which leads to a high j_{lim} value. It should be noted that in the case of the unmodified membrane, the j_{lim} value obtained does not seem to be directly related to the conductive fraction, since this membrane sample has the highest value, equal to 0.916. Considering what was reported by Choi et al. [67], this parameter is also affected by the topographic properties of the surface, for example the roughness, and it is striking that this membrane has a j_{lim} value close to that of the modified membrane sample that has been given a high roughness by the deposition of PANi (M-10).

Related to this, the ΔE_{II} values obtained, reported in the third line of Table 6, show a similar trend to that detected with the j_{lim} values, that is, the ΔE_{II} values obtained are higher for all modified membrane samples compared to the value obtained with the unmodified membrane sample. Furthermore, when comparing the ΔE_{II} values between modified membrane samples, a decrease in this parameter is observed as the PANi synthesis temperature decreases. These results can be described with the help of what was reported by Balster et al. [78], considering that the extension of this parameter is directly related to the degree of heterogeneity of the membrane surface, in this case of the polymer deposits. Indeed, for a homogeneous and regular (smooth) surface, the value of ΔE_{II} is more important than for a heterogeneous, wavy, and rough surface. The basis for this statement is that the plateau of the voltage–current curve acts as a transition zone between two different moments in which, in one, the contribution of counterion to the vicinity of the membrane occurs in the absence of convection, and in the other, this contribution is favored by what

some authors call electroconvection [79]. In the latter case, the counterion input near the membrane is affected by the irregularities inherent or induced in the membrane surface. Thus, in a homogeneous, smooth membrane, this area extends several tens of millivolts, since the transition is not affected by the topographical characteristics of the membrane surface. Whereas, in a heterogeneous, rough, and irregular surface membrane, the zone extends only a few tens of millivolts because the topography of the membrane favors the mixing of the different concentration gradients that form. According to this, it is found that PANi deposits appear to decrease the pre-existing roughness in the unmodified membrane samples, and therefore, the ΔE_{II} values of these membrane samples are higher than those of the unmodified membrane sample. If we consider that the surface of the unmodified membrane is made up of valleys and plateaus [80], then the surface decoration by PANi deposition occurs mainly in the valleys and therefore tends to smooth the surface. Of course, the decoration of the valleys with PANi deposits is affected by temperature, which confers different characteristics to the PANi. Thus, according to the results obtained, the PANi deposits present in the membrane samples at different temperatures confer a less rough character to the surface when a high temperature is used to synthesize the polymer. Furthermore, at a low synthesis temperature, the roughness conferred by the PANi is high but closer to that of the unmodified membrane sample than to the other modified membrane samples. This behavior can be understood considering that the conductive fraction of the membrane samples (ϵ) follows a similar trend (see Table 5), so the topographical characteristics of the PANi deposits, conferred by the synthesis temperature, dictate the trend of the ΔE_{II} values. Indeed, a lower conductive fraction of the modified membrane sample is characteristic of a smaller transition zone.

Finally, the resistance values of the third segment of the current–potential curves of all membrane samples, R_{III} , are presented in the fourth line of Table 6. According to the values obtained from R_{III} , the same behavior as the values of ΔE_{II} , discussed in previous paragraphs, is detected. That is, the R_{III} values for the modified membrane samples are higher than those obtained with the unmodified sample; furthermore, when comparing R_{III} values between modified membrane samples, it is observed that this parameter decreases as the synthesis temperature decreases. If we consider that segment III of the current–voltage curve reflects the effect of counterion replenishment in the vicinity of the membrane, due to electroconvection originated by the heterogeneities of its surface, then the slope of the segment reflects the resistance of this phenomenon and of the concurrent effects. For example, among the latter is the increase in the diffusion layer caused by the creation of vortices near the conductive areas of its surface. Considering this, the resistance is higher in segment III with respect to the resistance of segment I. Several reports confirm this description [75]. In relation to the results obtained in this work, the R_{III} values are higher than the R_I values only when the modified membrane samples are used. It is to be considered that the study membrane has a high value of conductive fraction, and therefore the formation of vortices does not seem to affect the R_{III} value so that its value is lower than the value obtained from R_I . Regarding the modified membrane samples, it is observed that R_{III} decreases as the synthesis temperature decreases. This behavior can be understood if two parameters are taken into account; on the one hand, the conductive fraction (ϵ) decreases in the same direction as R_{III} , that is, as the temperature decreases. On the other hand, the thickness of the layer adjacent to the membrane surface (δ) increases as the synthesis temperature decreases. It should not be overlooked that under overpotential conditions, such as potentials at which segment III of the current–voltage curve takes place, the thickness of the portion of solution adjacent to the membrane tends to increase from a certain value given by δ [81]. This behavior of both ϵ and δ indicates that on a surface with a high degree of non-conductive portions and an adjacent solution thickness that tends

to increase, vortices are formed that contribute to a more effective mixing of the different gradients generated, leading to a low resistance.

4. Conclusions

This work reports the characterization of commercial anion-exchange membrane samples modified with equivalent amounts of polyaniline electrosynthesized by cyclic voltammetry at 10, 15, and 20 °C. Among the most important results obtained is that as the modification temperature decreases, the selectivity of the membrane samples decreases proportionally. This result reveals that the characteristics of the polyaniline deposits, conferred by the synthesis conditions, play a determining role in different properties of the prepared membrane samples. For example, the hydrophobic nature of the polyaniline deposits on the membrane increased with decreasing temperature, which was reflected in a lower amount of water in the modified samples of the commercial membrane at a temperature of 10 °C. According to the results found in this work, temperature plays a determining role in the topographic properties of the polyaniline present in the membrane samples, since a lower synthesis temperature generates more compact and rough deposits. These properties significantly influence parameters such as the proportion of conductive sections on the membrane surface, since the membrane sample modified with polyaniline prepared at 10 °C has the lowest conductive fraction, while the high roughness of this membrane sample causes, in the current-potential curve *j*-*E*, a lower amplitude of the plateau, and consequently, a rapid transition to the overlimiting current zone with respect to the membrane with lower roughness synthesized at 20 °C.

It is important to note that these results stem from the influence of synthesis temperature on polymer growth kinetics; that is, as synthesis temperature decreases, the polymer's structural order increases, resulting in a more compact and rough material. Conversely, at high temperatures, the material will be less ordered, and therefore its morphology will be less compact and have a smoother surface.

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