Novel proton-conducting polymer inclusion membranes

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ABSTRACT

The preparation and characterization of new polymer inclusion membranes (PIMs) for proton transport is described. PIMs were prepared with different polymeric cellulose-based compounds and PVC as supports, tris(2-butoxyethyl)phosphate (TBEP) and 2-nitrophenyl octyl ether (NPOE) as plasticizers and dinonyl-naphthalenesulfonic acid (DNSA) and dinonylnaphthalenedisulfonic acid (DNDSA) as carriers. The effects of the nature and content of the supports, plasticizers and carriers on membrane proton conductivity was studied using electrochemical impedance spectroscopy (EIS). This technique was also used to evaluate the chemical stability of a CTA–NPOE–DNDSA membrane while its selectivity was monitored with respect to sodium and calcium ions through counter-transport experiments. DSC and TGA techniques were used to determine the thermal stability of these membranes. A PIM based on CTA–DNDSA–NPOE showed the highest proton conductivity (3.5 mS/cm) with no variation of its behavior during 2 months of evaluation. FTIR characterization did not show structural changes of the membrane in this period of time. Thermal analysis indicates that it is stable up to 180 °C. An empirical functional relationship between PIM resistance and composition indicates that increasing plasticizer and carrier concentrations enhances the conductivity of the membranes, while increasing CTA content tends to decrease this property. Transport experiments showed a good selectivity of the CTA–DNDSA–NPOE membrane for protons over calcium or sodium ions.

1. Introduction

In the past few years there has been an increasing interest in the synthesis and characterization of polymeric membranes. These materials are of great scientific and technological importance due to the numerous fields in which they find applications. Nowadays, it is possible to find a great variety of membranes with different chemical and physical properties on which the final use depends. Among polymeric membranes, polymer inclusion membranes (PIMs), which consist of a polymeric support (such as cellulose triacetate, CTA, or polyvinyl chloride, PVC), a plasticizer and an extracting agent (carrier), have recently been the subject of an interesting review by Nghiem et al. [1]. The main applications of PIMs have been directed to improve extraction and separation processes of metal ions. In this sense, most of the published work reports on the facilitated extraction and transport (from a feed phase to a stripping phase) of metal ions such as: Au(III) [2,3], Ag(I) [3,4], Cd(II) [5,6], ^{60}Co(II) [7], Cu(II) [3,5,8] Cr(VI) [9,10], Pb(II) [6,11],

^{90}Sr(II) [7,12], Zn(II) [13,14], As(V) [15], Na$^+$ [16], K$^+$ [17] and ^{137}Cs$^+$ [7,12,18]. Another important application of PIMs is in ion selective membrane electrodes for potentiometric measurements. In this case, the carrier can be an ionophore, an ion exchanger or a mixture of both; the support is usually PVC and it has been reported that the plasticizer has an important effect in the electrode selectivity. Some examples are sensors developed for Hg(II) [19], Yb(III) [20], F$^-$ [21], and H$^+$ [22] ions.

Furthermore, nowadays the technology of ion-conducting membranes is widely used not only in separation and purification processes, but also has been extended to energy conversion devices, batteries and sensors [23,24]. One of the main properties of ion conducting polymeric membranes (ICPM) is that they can substitute the liquid solutions which are conventionally used as electrolytes in several electrochemical devices [25]. The use of ion conducting membranes can actually improve the operating conditions of systems such as lithium batteries and fuel cells and of large-scale processes such as electrodialysis and chloro-alkali cells [25,26]. In several of these applications the membrane must allow proton transport.

In spite of the widespread applications of ICPMs, the need to improve their performance characteristics is well recognized.

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Thus, the interest of several research groups in the development of new inexpensive ICPMs, particularly with improved mechanical and thermal stability, together with high ionic conductivity values. Cation selective membranes having fixed negatively charged groups like R-SO$_3^-$, R-COO$^-$, R-PO$_3$H$^-$, etc., facilitate the selective transport of cations with a generally reduced transport of anions. In the case of some persulfonated ion-exchangers the proton conduction is explained on the basis that protons can be transferred from one sulfonic group to the next, along the polymeric chain, due to the presence of water molecules included in transport channels [27,28]. This transport process has been identified to occur in Nafion® membranes although it has not been thoroughly explained.

In this work we report the preparation and characterization of polymer inclusion membranes containing dinonylnaphthalenesulfonic acid (DNSA) and dinonylnaphthalenedisulfonic acid (DNDSA) as carriers for proton transport. DNSA has been used before as ion carrier for transport of some radioisotopes [7,29] and for Pd(II) extraction [30]. The effects of the nature and content of several supports and plasticizers on membrane proton conductivity was studied using electrochemical impedance spectroscopy (EIS). Since Nafion® (Du Pont) membranes are some of the materials most frequently used for proton transport in electrochemical devices, a Nafion 115 membrane was pretreated as described in the literature [31] and used as a reference material in order to compare the conductivity values obtained with the PIMs prepared in this work. EIS was also used to evaluate the chemical stability of a cellulose triacetate–2-nitrophenyl octyl ether–dinonylnaphthalenedisulfonic acid (CTA–NPOE–DNDSA) membrane while its selectivity was monitored with respect to sodium and calcium ions through transport experiments. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to determine the thermal stability of the membranes.

2. Experimental

2.1. Reagents

For the preparation of the proton transport polymer inclusion membranes, different supports were used: cellulose triacetate (CTA), cellulose acetate butyrate (CAB), cellulose acetate propionate (CAP), cellulose acetate hydrogen phthalate (CAH) and polyvinyl chloride (PVC). Two compounds containing sulfonic groups, dinonylnaphthalenesulfonic acid and dinonylnaphthalenedisulfonic acid were tested as carriers and tris(2-butoxyethyl)phosphate (TBEP, 94%) and 2-nitrophenyl octyl ether (NPOE, 99%) were used as plasticizers. All these reagents were Aldrich AR. The solvents employed, dichloromethane (CH$_2$Cl$_2$) and tetrahydrofuran (THF), were used as received.

2.2. Membrane preparation

For membrane preparation weighted amounts of the polymeric support were dissolved together with the appropriate amounts of carrier and plasticizer in 10 mL of solvent using a magnetic stirrer until an homogenous solution was obtained [8]. For the membranes containing CTA, CAB and CAP the solvent used was CH$_2$Cl$_2$, while with PVC and CAH, THF was used. The solution was poured into a glass dish (5 cm diameter), the solvent was allowed to evaporate overnight and the membrane formed was peeled off after adding cold water. Membrane thickness was measured with a digital micrometer (Fowler IP54).

2.3. Membrane characterization

2.3.1. Proton conductivity

Membrane proton conductivity was determined by EIS [32–34] using a computer controlled Solartron 1287 potentiostat coupled to a Solartron 1260 impedance analyzer. The experimental data were acquired and analyzed using the Zplot and Zview software suite. Impedance measurements were carried out for membranes previously equilibrated with 0.5 mol/dm^3 HCl using an electrochemical cell with two stainless steel mesh electrodes. The electrodes were separated by two polyethylene rings that allow the exposure of 1 cm^2 (geometric area) of the membrane. The electrochemical impedance spectra were obtained from 0.1 Hz to 1 MHz frequencies with a logarithmic collection of the data of 7 steps per decade. The perturbation amplitude was of 10 mV at the applied potential. The electrochemical impedance measurements were performed at a bias potential of 0 mV. The electrical conductivity of the membranes was calculated using the measured membrane resistance through equation (1):

$$\sigma = \frac{L}{RA} \tag{1}$$

where σ is the electrical conductivity (S/cm) of the material, L the membrane thickness (cm), R the measured membrane resistance (Ω) and A is the geometric membrane area (cm^2).

2.3.2. Selectivity

The corresponding transport experiments were carried out using a 80 mL two-compartment cell as described elsewhere [8] at 20 ± 2 °C and a stirring rate of 650 rpm. One compartment contained 0.50 mol/dm^3 HCl or 0.50 mol/dm^3 NaCl while the other one was filled with distilled water as the receiving phase. Conductivity values were measured at several time intervals using a SevenMulti potentiometer-conductimeter and a conductivity cell InLab 730, both from Mettler Toledo. Additionally counter-transport experiments were carried out using the same two-compartment cell. The metal ion (sodium or calcium) concentration in the strip phase at several time intervals was determined by FAAS using a PerkinElmer 3100 spectrometer. Instrumental conditions were used as recommended by the manufacturer. For sodium counter-transport experiments a feed phase consisting of 0.127 mol/dm^3 sodium acetate solution +0.073 mol/dm^3 acetic acid (pH 5.0) and a 0.50 mol/dm^3 HCl strip solution were used. For calcium counter-transport the same strip solution was used and the feed phase was 0.125 mol/dm^3 CaCO$_3$ (pH 7.3).

2.3.3. Thermal stability

Thermograms were obtained with a Mettler-Toledo Star Thermal Analysis System (DSC 821 differential scanning calorimeter and TGA/SDTA 851e thermogravimetric analyzer) with STAR 8.10 software at a heating speed of 10 °C/min under air within the temperature interval of 25–600 °C.

2.3.4. FTIR characterization

Some structural features and the chemical stability of the membranes prepared were characterized using a PerkinElmer Spectrum GX infrared spectrophotometer coupled to a diamond ATR sampling accessory (DuraSampl IR II from SensIR Technologies). The spectra were obtained in the 4000–580 cm^{-1} interval using Spectrum software.

Table 1
Effect of polymeric support in membrane preparation.

Support	DNSA	DNDSA
CTA	+	+
CAP	−	Fragile
CAB	−	Fragile
CAH	−	Fragile
PVC	+	+ (Inhomogeneous)

+, homogeneous, durable membranes were formed.
−, no membranes could be obtained.

3. Results and discussion

3.1. PIM preparation

Membranes containing different polymeric supports (CTA, CAB, CAP, CAH or PVC) and either DNSA or DNDSA as ion carrier reagents were prepared. In each case, blank membranes containing only the polymeric support were also obtained. In particular, the preparation of membranes with CAP and CAB was tested since it has been reported that these compounds increase the membrane durability and its resistance to hydrolysis in similar PIM systems [35]. With DNSA, no film was obtained when CAP, CAB and CAH were used, while DNDSA containing membranes were fragile. These observations indicate that acetate substitution by propionate, butyrate and phatalate groups affects the compatibility of the supports with the ion carrier, i.e., changes in the flexibility of the macromolecules and in the structure of the polymer, resulting in the alteration of the regularity and decrease in intermolecular interactions, depend on the amount and type of polymer substitution [36]. When CTA was used as the polymeric matrix, well formed membranes were obtained disregarding the carrier added, while with PVC the membranes containing DNDSA showed a very inhomogeneous composition. The results just described are summarized in Table 1.

Based on these results, preliminary studies were carried out keeping constant the amounts of CTA (0.1 g) and varying the carrier content (0.1–0.3 for DNSA and 0.03–0.27 for DNDSA). The best film formation and adequate conductivity values were obtained when 0.25 g (DNSA) and 0.044 g (DNDSA) were used. The same amounts of carrier were used in the preparation of membranes of which conductivities are reported in Table 2.

3.2. Membrane characterization

3.2.1. Proton conductivity
3.2.1.1. Influence of plasticizer.
The nature of the plasticizer exerts a considerable influence on the performance of PIM systems [13,37]. The different intermolecular forces acting between the membrane components are responsible for the properties of the membrane system, such as permeability, mechanical and thermal stability and electric conductivity [8]. In the case of the membranes prepared using PVC (or CTA), NPOE (or TBEP) and DNSA, it was observed that when the solid support is PVC, the use of NPOE as the plasticizer enhances proton conductivity by an order of magnitude when com-
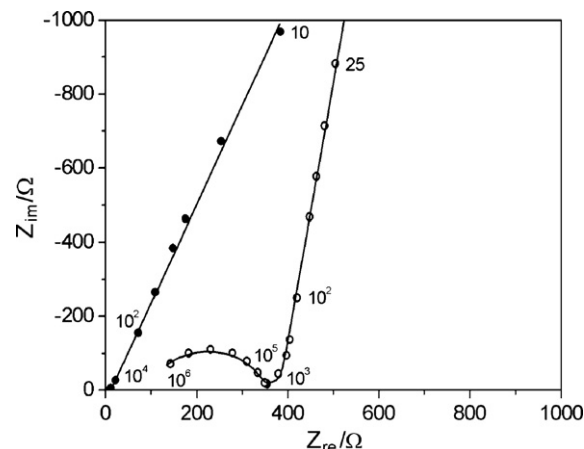

Fig. 1. Nyquist plots for blank membrane (CTA), ○, and CTA (0.1 g)–NPOE (0.03 g)–DNSA (0.25 g) membrane, ●. Symbols represent some experimental data (numbers are frequencies in Hz corresponding to those particular points) while solid lines are fitting results obtained using the equivalent circuits of Fig. 2(a) and (b), respectively.
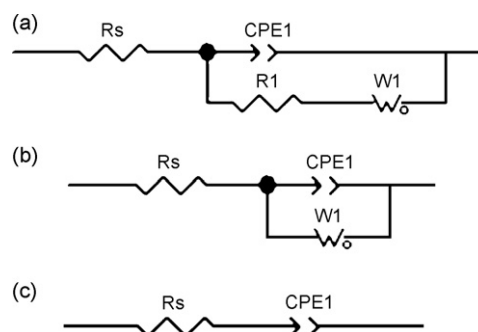

Fig. 2. Equivalent circuits used in this work to fit and simulate the electrochemical impedance behavior of the membranes prepared. (a) Blank membranes; (b) CTA–NPOE–DNSA membranes; (c) CTA–NPOE–DNDSA and Nafion® 115 membranes. R_s is the resistance of the electrolyte, CPE1 corresponds to a constant phase element related to the membrane capacitance; R_1 is the bulk resistance, and W_1 represents a Warburg impedance.

pared to membranes prepared using TBEP. This fact is partly due to the different permittivities of the plasticizers (Table 2), since NPOE has a much higher dipolar character than TBEP [37]. CTA membranes generally display higher conductivities than their PVC analogs since CTA is slightly less hydrophobic than PVC.

Regarding the chemical stabilities of the membranes prepared, CTA membranes containing TBEP or NPOE and DNSA showed severe degradation after a few days of use, even if their electric conductivities were relatively high (Table 2). Blank (pure CTA) membranes showed a high resistance (~250 Ω), since ion conduction across these membranes can only take place when a certain amount of an aqueous solution is contained by sorption within the polymeric matrix, creating a number of restricted transport pathways. This
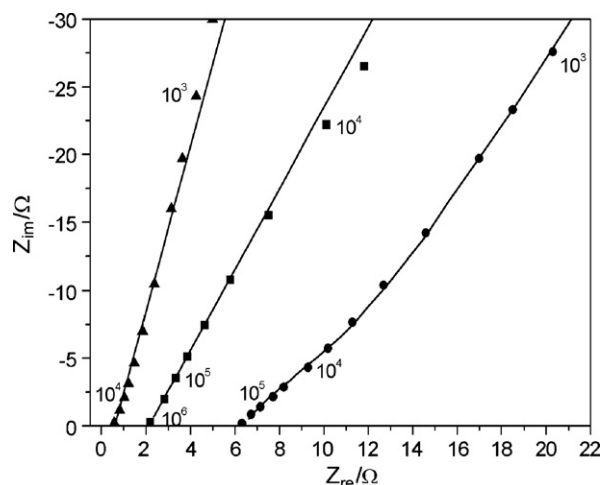
Table 2
Conductivity values for Nafion® 115 and for PIMs prepared using CTA or PVC as support, TBEP or NPOE as plasticizer and DNSA or DNDSA as ion carrier.

Plasticizer	Conductivity (mS/cm)				
	DNSA			DNDSA	
	CTA	PVC		CTA	PVC
TBEP ($\varepsilon_r = 8.7$)	3.50 (205 ± 5 μm)	0.09 (190 ± 10 μm)		1.10 (75 ± 5 μm)	0.10 (65 ± 5 μm)
NPOE ($\varepsilon_r = 23.1$)	3.20 (195 ± 5 μm)	0.90 (165 ± 5 μm)		3.50 (70 ± 5 μm)	0.15 (88 ± 5 μm)
Nafion® 115			26.00		

Values between parentheses are the average thickness of the different prepared membranes.

Fig. 3. Nyquist plots for CTA–NPOE–carrier (DNSA, ●, or DNDSA, ■) membranes. The impedance response of a Nafion® 115 membrane, ▲, is displayed for comparison. Symbols represent some experimental data (numbers are frequencies in Hz corresponding to those particular points) while solid lines are fitting results obtained using the equivalent circuits of Fig. 2(b) (for DNSA membrane) and (c) (for DNDSA and Nafion® 115 membranes).

Table 3
Fractional compositions of the PIMs in the ternary CTA–DNDSA–NPOE system studied by EIS.

CTA	DNDSA	NPOE
0.56	0.16	0.28
0.64	0.04	0.32
0.86	0.05	0.09
0.73	0.20	0.07
0.49	0.03	0.48
0.68	0.13	0.19

rier from DNSA to DNDSA. The weight of ion-exchanger used for CTA–NPOE–DNSA membrane preparation is about 6 times higher than the one used in the preparation of the CTA–NPOE–DNDSA membranes. Since the molecule of DNDSA contains two sulfonic acid groups instead of the single one present in DNSA, the amount of DNSA (in mole) needed to prepare a membrane with an electrical conductivity comparable to that found with DNDSA membranes would have to be about 10 times greater. Therefore, it is possible that the relative solubilities of DNSA and DNDSA in the membrane matrix be in part responsible for these observations. This premise is sustained by the fact that when evaluating theoretically the fractional solubility parameters for the dispersion (fd); polar (fp) and hydrogen-bonding (fh) forces of DNDSA (fd = 61.8, fp = 17.5, fh = 20.7) and DNSA (fd = 68.2, fp = 14.5, fh = 17.3) and comparing it with the CTA solubility window as explained in Ref. [8], a higher solubility interaction between the carrier and the polymer is expected for DNDSA than for DNSA. Based on these results further experiments were performed using DNDSA as carrier.

3.2.1.3. Composition–resistance relationship. On the basis of the results discussed in Sections 3.2.1.1 and 3.2.1.2, several membranes were prepared varying the weight fractions of the components (w_i, where i stands for CTA, DNDSA or NPOE) within the following intervals: $0.49 < w_{CTA} < 0.87$, $0.03 < w_{DNDSA} < 0.20$, and $0.07 < w_{NPOE} < 0.49$ (Table 3). The resistance values of these PIMs determined from EIS experiments were fitted by least square minimization to a linear three-component model. The equation denoting the functional relationship between the parameters and the response is:

$$R = 303w_{CTA} - 773w_{DNDSA} - 204w_{NPOE} \quad (r^2 = 0.9449) \qquad (2)$$

which indicates that, within the composition interval studied, the increase in plasticizer and carrier concentrations tend to reduce the resistance value, i.e., increase the conductivity, while the increase in CTA content tends to increase the resistance. It was also observed that for $w_{CTA} > 0.5$ and $w_{DNDSA} > 0.1$, lower resistances independent of the plasticizer content were obtained.

3.2.2. Water sorption

Water sorption was determined by weighing dried disks of CTA (0.1 g)–NPOE (0.03 g)–DNDSA (0.044 g) membranes (~6 mm of diameter), and after immersion in distilled water for 24 h. The wet membranes were carefully wiped with absorbent paper and weighed again. The water sorption (in weight percent) of membranes was determined from equation (3):

$$\text{water sorption}\,(\%) = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100 \qquad (3)$$

where W_{wet} and W_{dry} are the weights of wet and dried membranes, respectively.

Five samples of these membranes were measured giving a water sorption average of 13.5% (±2%). The same procedure was followed for blank and Nafion® 115 disks giving a water sorption average (for 3 samples) of 16 ± 0.7% and 17 ± 1.5%, respectively.

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fact is revealed by the appearance of a semicircle at high frequencies (>10^4 Hz) in the Nyquist plot of these membranes after 24 h of equilibration with a 0.5 mol/dm³ aqueous HCl solution (Fig. 1).

The impedance characteristics of the membranes studied in this work can be simulated for frequencies within the 10 Hz < frequency < 1 MHz region, using the equivalent circuits (EC) shown in Fig. 2.

Plasticized CTA membranes show the same behavior but with lower resistances (~50 Ω) when no ion carrier is present in the membrane (data not illustrated), while membranes containing both the plasticizer and DNSA or DNDSA (Fig. 3) behave in quite a different way. For membranes with DNSA, the impedance responses comply with the EC presented in Fig. 2(b) for frequencies higher than >10 Hz, where the bulk resistance term (R1 in Fig. 2(a)) practically vanished. The open finite-length Warburg impedance W1 used in the circuits (Fig. 2(a) and (b)) contributes to the appearance of the low frequency feature shown in Fig. 1 for the blank plasticized membrane and in Fig. 3 for the CTA–NPOE–DNSA membrane. The slow but effective diffusion of the ions across the dielectric thin membrane towards the blocking electrodes is mainly responsible for this behavior. This circuit element practically disappears when fitting the impedance response of the more conductive membranes [38]. Therefore, in more resistive membranes, where the charge carrying species cannot traverse the membrane thickness even at low frequencies (in the order of 0.1 Hz) [37], this diffusion related circuit element is not necessary to describe the corresponding impedance response. However, for the Nafion® 115 and DNDSA-containing membranes, where the membrane acts almost as a pure ionic conductor at very high frequencies, the equivalent circuit in Fig. 2(c) fits reasonably well the impedance data, implying that the charge is being transported across ion-transport channels present in these membranes.

3.2.1.2. Influence of ion-carrier. The electrical conductivity of CTA–NPOE membranes substantially improved, as well as their chemical stability, when they were prepared using DNDSA as the ion carrier (Fig. 3, Table 2). In Fig. 3, the Nyquist plot of the impedance of CTA–NPOE–DNSA and CTA–NPOE–DNDSA membranes shows the differences in membrane resistance (high frequency intercept with the x-axis) when changing the ion car-
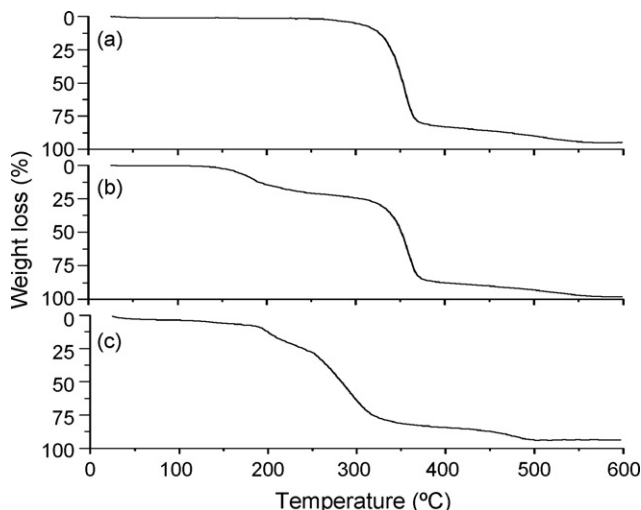
Fig. 4. Thermograms of (a) CTA (0.1 g), (b) CTA (0.1 g)–NPOE (0.03 g) and (c) CTA (0.1 g)–NPOE (0.03 g)–DNDSA (0.044 g). Obtained under air atmosphere at a heating speed of 10 °C/min.

Fig. 5. H+ and Na+ conductivity values measured in the water stripping solution as a function of time for the CTA (0.1 g)–NPOE (0.03 g)–DNDSA (0.044 g) membrane and a blank membrane (only H+).

3.2.3. Thermal analysis

Fig. 4 shows the percent weight loss *vs.* temperature thermograms (TGA) for some components present in non-equilibrated membranes. The most important weight loss takes place at 350 °C due to the thermal degradation of CTA. In the presence of a plasticizer (NPOE), membrane thermal degradation starts at a lower temperature (180 °C), while the loss of CTA continues to appear at the same temperature of 350 °C. For a membrane containing CTA–NPOE–DNDSA, the thermogram presents a weight loss at 138 °C which corresponds to the solvent (isobutanol) present in the DNDSA reagent, a weight loss at 200 °C which corresponds to NPOE and finally a slow degradation of the support as the temperature increases. In this case it is possible to establish that the membrane is thus reasonably stable up to 180 °C. The slow degradation of CTA observed in the latter case confirms that a strong integration of the membrane components takes place for a PIM prepared with DNDSA (Section 3.2.1.2). Also, the TGA results show that the thermal decomposition of CTA shifts to a lower temperature in the presence of the ion carrier–plasticizer mixture. This phenomenon has been observed in PIMs before [39], and may be due to acceleration effects on the decomposition of specific parts of the polymeric chains enhanced by interactions among the components [40].

3.3. Selectivity

Conductivity values measured in the water strip solution using a CTA (0.1 g)–NPOE (0.03 g)–DNDSA (0.044 g) membrane are shown in Fig. 5. As observed the conductivity of the HCl solution ($J_{H^+} = 7.5 \times 10^{-4}$ mol/m^{2}s, $P_{H^+} = 1.5 \times 10^{-6}$ m/s, where J_i and P_i stand for flux and permeability, respectively, and were calculated according to Ref. [37]) is about 6 times higher than that of the NaCl solution ($J_{Na^+} = 5.6 \times 10^{-4}$ mol/m^{2}s, $P_{Na^+} = 1.1 \times 10^{-6}$ m/s). Null conductivity is obtained with a blank membrane containing CTA (0.1 g)–NPOE (0.03 g). Counter-transport experiments for monoelemental sodium or calcium chloride solutions indicated that after 8 h 15% of Na+ ($J_{Na^+} = 1.1 \times 10^{-4}$ mol/m^{2}s, $P_{Na^+} = 9 \times 10^{-7}$ m/s) and less than 7% of Ca2+ ($J_{Ca^{2+}} = 0.5 \times 10^{-4}$ mol/m^{2}s, $P_{Ca^{2+}} = 4 \times 10^{-7}$ m/s) were transported. The selectivity coefficient between these two ions defined as $\alpha_{Na^+/Ca^{2+}} = P_{Na^+}/P_{Ca^{2+}}$ at pH 7.0 was 2.8.
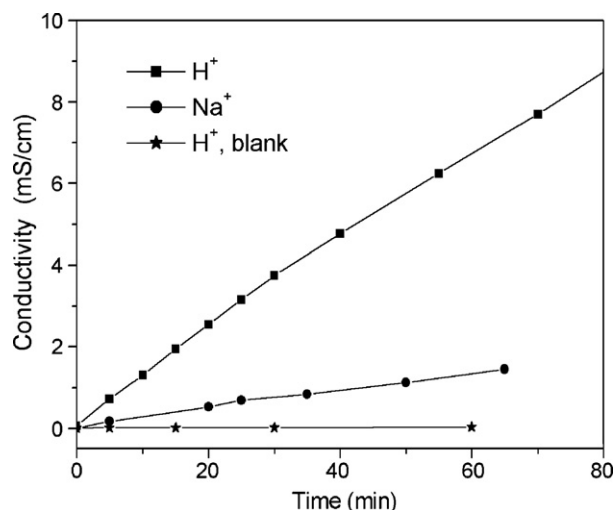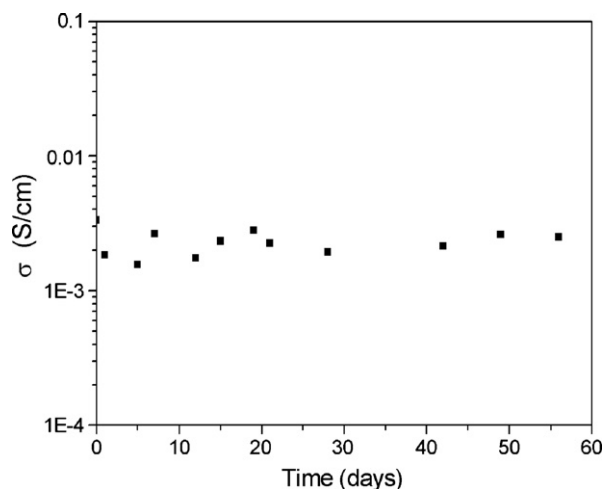

Fig. 6. Conductivity of the CTA (0.1 g)–NPOE (0.03 g)–DNDSA (0.044 g) membrane equilibrated in HCl 0.5 mol/dm^3 aqueous solution during 24 h and stored in distilled water.

3.4. Stability

After 24 h of equilibration with a 0.5 mol/dm^3 aqueous HCl solution the electrical conductivity of a TAC–NPOE–DNDSA PIM was measured on a daily basis. After each measurement, the membrane was kept in water to be used the next day. Results of such experiments are shown in Fig. 6. As observed the PIM maintained its conductivity during the tested period, denoting adequate stability for its continuous use.

FTIR characterization of the membrane used for conductivity stability indicates that no structural changes were produced in that period of time.

4. Conclusions

Cellulose derivatives and PVC-based PIMs with dinonylnaphthalenesulfonic acid or dinonylnaphthalenedisulfonic acid as carriers and tris(2-butoxyethyl)phosphate or 2-nitrophenyl octyl ether as plasticizers were developed and tested for proton conduction using electrochemical impedance spectroscopy. Results showed that the nature of the different carriers and plasticizers

exerts great influence in membrane conductivity, while the nature of the polymeric support additionally modifies film formation. Conductivity values for these PIMs range between 0.09 and 3.50 mS/cm. The best membranes in terms of good conductivity, mechanical resistance, and chemical stability were those prepared using cellulose triacetate, DNDSA, and NPOE. The influences of the nature of the plasticizer and carrier in PIM conductivity were conceptualized considering differences in the structural forms of the molecules that lead to different permittivities, hydrophobic character (plasticizers), and relative solubilities in the polymeric matrix (carriers), which modify the chemical interactions among the membrane components. An empirical functional relationship between PIM resistance and composition for the CTA–DNDSA–NPOE membrane was thus obtained. This relationship indicates that, within the composition range studied, the increase in plasticizer and carrier concentrations tend to increase the conductivity, while the increase in CTA content tends to decrease this parameter. The amount of water present in this membrane (13.5%) was estimated through water sorption analyses, while thermal analyses and ATR-FTIR characterization confirmed chemical interactions and membrane integrity. The optimized PIM was thermally stable up to 180 °C and was successfully reused for a 2-month period without modification in its conductivity. Transport experiments using monoelemental solutions revealed good selectivity between proton and sodium or calcium ions.

Acknowledgements

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