Evaluation of the influence of method preparation in properties of heterogeneous ion exchange membranes

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Abstract

In order to produce membranes with good features, this study aimed to evaluate the influence of the method of preparation of heterogeneous anion exchange membranes (AEMs). Membranes were prepared by spread coating and casting methods. In the latter method, different solvents were used: tetrahydrofuran (THF) and dimethylformamide (DMF). Membranes with different quantities of anion exchange resin (AER), 50% and 35%, were prepared. The characterization of the AEMs was performed by means of conductivity, ion exchange capacity (IEC) and swelling. Membranes prepared by coating showed lower conductivity, possibly due to the degradation of some functional groups of the AER during processing because of high temperatures. Evaluating the solvent influence, the membrane obtained in DMF had the highest conductivity. The IEC of membranes prepared by casting method was very similar, showing that this is not a parameter influenced by solvent exchange. It was noted that coated membranes had lower IEC, reinforcing the hypothesis of losing functional groups during processing. Finally, membranes prepared using THF as solvent showed higher swelling than those using DMF because THF evaporates quickly leading to the formation of small voids where water accumulation is favored. The coated membranes had the lowest swelling since these membranes do not use solvent in their preparation. Lastly, it can be inferred that the choice of the methods and/or the solvents can modify AEMs properties. Among the methods, the most satisfactory was casting due to the possibility of functional group loss by thermal degradation during the coating process. Concerning the solvents, DMF has been demonstrated the best one for casting process since it does not provide large voids which increase the swelling

and reduce the conductivity. Ultimately, the best membrane was obtained by casting method with 50% of AER with conductivity, IEC and swelling of $2.17.10^{-3}$ S.cm^{-1}, 1.58 meq.g^{-1} and 59.8%, respectively.

1 Introduction

For many years, electrodialysis (ED) has been used on a large industrial scale for water desalination, wastewater treatment and a large number of applications in biotechnology as well as food and beverage industry [1]. Ion exchange membranes play a leading part in an electrodialyzer, and the ED performance strongly depends on the characteristics of ion exchange membranes [2].

Heterogeneous Ion Exchange Membranes (IEMs) consist of fine ion exchange particles embedded in an inert binder polymer such as polyethylene, phenol resins, or polyvinylchloride. Heterogeneous IEMs are characterized by the discontinuous phase of the ion exchange material. These membranes can easily be prepared by mixing an ion exchange powder with a dry binder polymer and extrusion of sheets under the appropriate conditions of pressure and temperature or by dispersion of ion-exchange particles in a solution containing a dissolved film forming binder polymer, casting the mixture into a film and then evaporating the solvent [3].

The research on heterogeneous IEMs has grown because they are less expensive to produce, easily manufactured and have better mechanical strengths and good dimensional stability when comparing with the homogeneous ones [4]. Another advantage of heterogeneous IEMs is that during their preparation it is not used hazardous chemicals as, for example, fuming H_2SO_4 or chlorosulfonic acid to prepare Cation Exchange Membranes (CEMs) or chloromethyl ether and trimethylamine to prepare Anion Exchange Membranes (AEMs). Although heterogeneous IEM are easily prepared and have great mechanical strength, their electrochemical properties are slightly inferior to homogeneous membranes. Heterogeneous type membranes, however, are essential in industries due to their high mechanical strength and ease of handling [5].

The properties of IEMs are substantially determined by two parameters that are the basic material they are made from and the type and concentration of the fixed ionic moiety (ion exchange resin). The basic material determines to a large extent the mechanical, chemical, and thermal stability of the membrane. The type and the concentration of the fixed ionic charges determine the permselectivity and the electrical resistance of the membrane, but they also have a significant effect on the mechanical properties of the membrane and their swelling in solution [3]. Hosseini *et al.* [6] showed that the solvent type can also modify the IEMs properties; besides, Vyas *et al.* [7] observed that ion exchange resin particle size can also modify IEMs properties.

In this paper, anion exchange membranes using the same base polymer were prepared using the same type and particle size of anion exchange resin, but from two different methods of processing: laminating spread coating and solvent evaporation (casting). The objective was to determine the differences in

membranes properties with the same composition originated by changing the method of production. In addition, in the casting method, membranes were prepared using two different solvents, tetrahydrofuran (THF) and dimethylformamide (DMF), in order to assess its influence on the properties of the membranes.

The main difference between the preparation methods lies in the fact that as the coating method requires application of high temperatures for the membrane formation, on the other hand, the casting method produce membranes by simple solvent evaporation at room temperature. With respect to the solvents, they have very different boiling temperatures, 66°C for THF and 153°C for DMF, requiring special care during handling the mixture until the beginning of the solvent evaporation and stabilization of the membrane film. The main advantage of using THF is that it solubilizes the polymer and the plasticizers easily even at room temperature while for solubilization in DMF is necessary heating to about 60°C. In contrast, the main advantage of DMF in relation to the other solvent is that it is considerably cheaper, costing half value.

2   Materials and methods

2.1 Membrane preparation

The base polymer for all prepared membranes was polyvinyl chloride (PVC) obtained from Braskem®: Norvic® P55LM. The anion exchange resin (AER) was A400 supplied by Purolite®. Prior to membrane formulation, AER was dried in oven at 40°C for 24 hours, milled in a ball mill during 1.5 hour, sieved at 200 mesh, and then dried again at 40°C for 24 hours.

Membranes were prepared by spread coating lamination (coating) and solvent evaporation (casting) methods, in the latter method, the membranes were prepared using two different solvents: THF and DMF. In the composition, membranes contain, in addition to PVC and anion exchange resin, plasticizer to make the membrane flexible. In total, five membranes were prepared, three of them containing 50% of anion exchange resin: one by the coating method, another by casting with THF and the last one by casting with DMF, named CO50, CA50T, and CA50D respectively. Once the membrane prepared by coating was not stable, two other membranes have been prepared, in this time with 35% resin, one by coating and other by casting with DMF, named CO35 and CA35D, respectively. Table 1 presents a summary of the compositions and methods of obtaining the membranes.

The anion exchange membranes (AEMs) preparation by coating method started mixing the PVC with plasticizers and AER. It was also used 1.5% of a dispersant. After physical mixture of all components, formulation was coated in an oven at 190°C during 5 min and resulting on a membrane.

The AEM prepared by solvent casting method, using THF as solvent proceeded by dissolving polymer and plasticizers into solvent at room temperature for 1 hour. This was followed by the addition of AER. The blend was then mixed at room temperature for 30 minutes to obtain uniform particle distribution in the polymeric

Table 1:   Specifications of prepared membranes.

Membrane	AER* amount (%)	Preparation method	Solvent
CO50	50	Coating	-
CA50T	50	Casting	THF
CA50D	50	Casting	DMF
CO35	35	Coating	-
CA35D	35	Casting	DMF

*AER: anion exchange resin.

solution. Then, the mixture was cast onto a clean and dry glass. The membrane was obtained after solvent evaporation at room temperature. Using DMF as the solvent, the AEM obtainment process was very similar to the previous one, employing THF as solvent. Indeed, the difference was related to the temperature concerning the polymer and plasticizers dissolution into the THF that occurred at 60°C in contrast to room temperature for DMF.

All membranes were storage in deionized water prior to characterization. Besides, a reinforcing fabric was used to increase mechanical properties of all prepared AEM in this research.

2.2 Membrane characterization

The prepared membranes were characterized and their performance evaluated by the tests described below. The measurements were done in three samples of each membrane and the average results will be presented in results and discussion item.

2.2.1 Morphology study

A scanning electron microscopy (SEM) was used to investigate the cross section morphology of the membranes. SEM micrographs were obtained in equipment JEOL JSM-6510LV using 10 kV of energy. Previous to analysis, membranes were dried, underwent cryogenic fracture and then were coated with gold.

2.2.2 Conductivity by impedance spectroscopy

The conductivity of the membranes was measured by AC impedance spectroscopy using a Solartron 1260 analyzer with software Zplot®. AC impedance spectroscopy consisted in measuring the changes in electrical impedance of a sample of membrane upon a variation in frequency from 1 to 10^7 Hz and bias voltage of 1000 mV. The data was reported in the complex plane (Z', Z'') [8, 9]. Samples, with 18 mm length and 5 mm width, where hydrated by soaking in deionized water during 24 hours and then clamped between two stainless steel electrodes. During the measurements, the environment was kept at 20°C and 100% of relative humidity. The conductivity σ of samples was calculated from the impedance data, using the relation:

$$\sigma = \frac{d}{R.S} \tag{1}$$

where d is the thickness, S is the face area of sample (length multiplied by width) and R is the resistance derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis [10].

2.2.3 Ion exchange capacity (IEC)

IEC indicates the number of milli-mol of exchangeable charge in 1.0 g of dry membrane. Firstly, samples were dried in oven at 40°C for 24 hours and then weighed, after cooling in desiccator under room temperature until constant mass. In the sequence, the membranes were equilibrated in deionized water for 72 hours; then, they were immersed for two days in 1M KOH aqueous solution to convert the membrane into OH⁻ form. The membranes were then washed with deionized water to remove excess of alkali. In the next step, samples were equilibrated in 0.02 M HCl aqueous solution for 48 hours and the anion exchange capacity determined by back titration with 0.005M NaOH aqueous solution [11]. The ion exchange capacity of the AEM was calculated by:

$$IEC = \left(\frac{a}{W_{dry}} \right) \tag{2}$$

where a is the milli-mol of ion exchange group in membrane and W_{dry} is the weight of dry sample of membrane (g) [6].

2.2.4 Water content

The water content was measured as the weight difference between the swollen (W_{wet}) and the dried (W_{dry}) membranes. The membranes were equilibrated on deionized water, at room temperature for 72 hours, weighed and then dried at 40°C in oven until the constant weight was obtained [12]. The following equation was used to calculate de water content:

$$Water\ content\ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \ x\ 100\ . \tag{3}$$

3   Results and discussion

3.1 Morphology study

Analyzing the SEM images for the membranes cross section, shown in fig. 1 2,000 times increased, it can be seen that membranes prepared using solvent exhibit little voids. In CA50T membrane, prepared with THF, the gaps are larger due to rapid solvent evaporation without time to polymer accommodation. For CA50D membrane, prepared with DMF, these spaces are also observed; however, they are fewer in amount and smaller in sizes.

It can also be seen, in fig. 1, that in membranes prepared by casting the polymer is not completely surrounding the AER particles. On the other hand, in coated membranes, resin particles are completely encased in the polymer matrix. In addition, in membranes obtained by casting the polymer phase is continuous, while CO35 and CO50 matrix phase membranes present surface irregularities that possibly will lead to lower mechanical properties.
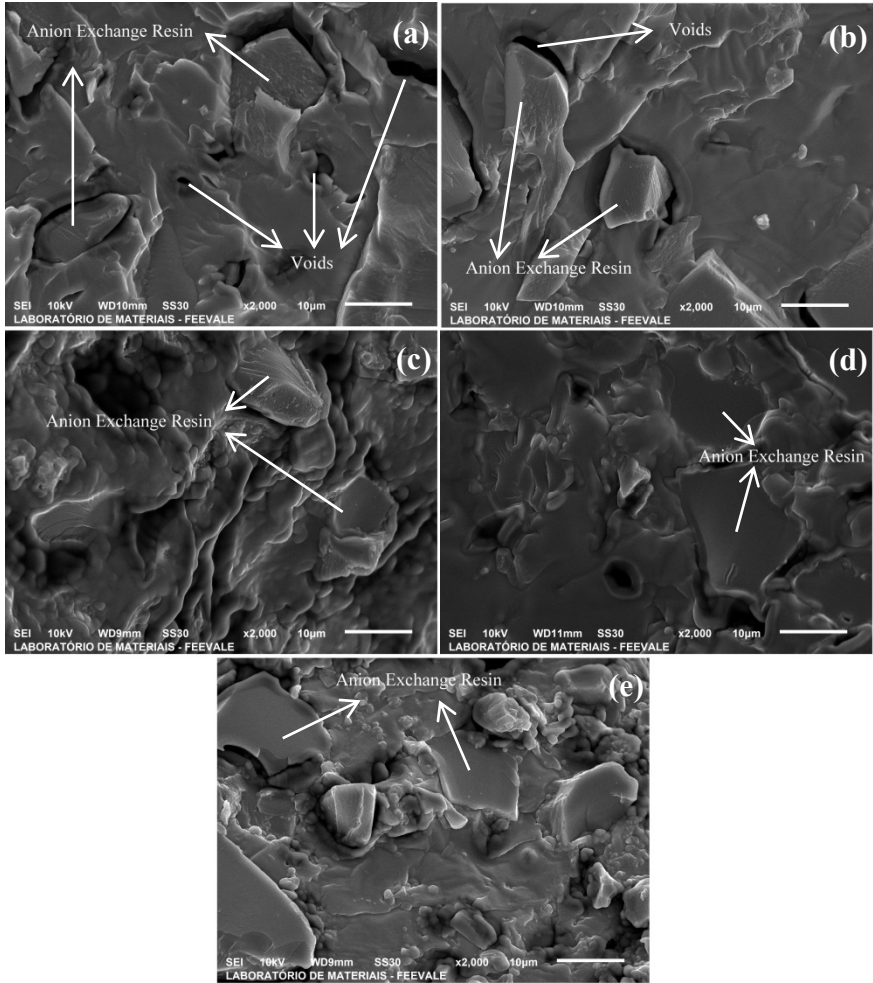
Figure 1:   SEM images of CA50T (a), CA50D (b), CO50 (c), CA35D (d) and CO35 (e) membranes with an increase of 2,000x.

Membranes' conductivity, IEC and swelling, measured as described before, are presented in table 2 and will be discussed below.

Table 2:   Membranes properties.

Membrane	Conductivity (S.cm^{-1})	Ion Exchange Capacity (mmol.g^{-1})	Swelling (%)
CO50	6.15×10^{-4}	1.38	56.5
CA50T	7.93×10^{-4}	1.56	67.4
CA50D	2.17×10^{-3}	1.58	59.8
CO35	1.84×10^{-4}	1.23	44.1
CA35D	1.60×10^{-3}	1.16	46.6

3.2 Conductivity by impedance spectroscopy

As it was already presented, conductivity was calculated from resistance measurements. For each membrane, measurements were performed on three samples and, illustratively, fig. 2 shows representative curves of only a sample of each membrane for visual comparative purpose.

From fig. 2, it can be observed that CA50T and CA50D membrane samples showed similar resistance, about 33 kΩ each one. However, when the conductivity is calculated, one should take into account that the dimensions of the sample have to be considered in the calculation. As the referred dimensions may slightly vary from one sample to another, different sample conductivities for the same measured resistance may be obtained. The CO50 membrane, despite containing the same amount of AER, showed greater resistance: 65 kΩ. Finally, membranes with 35% of AER, CO35 and CA35D, presented resistances of 103 kΩ and 266 kΩ, respectively. These differences among the membranes will be discussed concerning only the calculated conductivity and not the minimum differences in size of the samples.
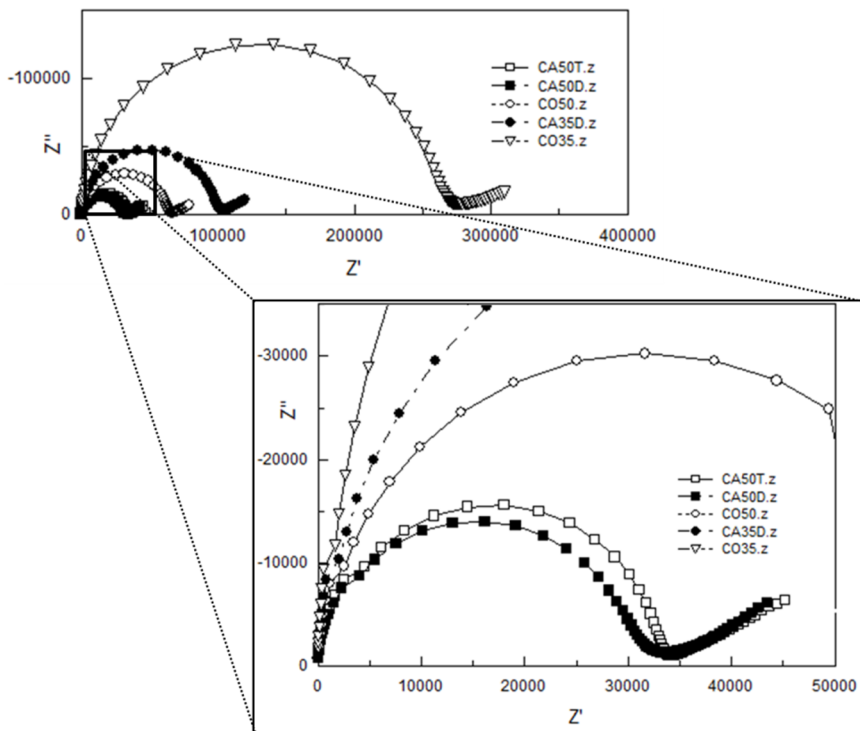

Figure 2:   Representative complex impedance responses of membranes.

Thus, from the resistances and the exactly dimension of each sample the conductivity was calculated. As it can be seen in table 2, the membranes prepared by coating, CO50 showed lower conductivity than CA50T and CA50D membranes. Since membranes with equal amount of ion exchange resin with the same particle size should present similar conductivities [7], the difference found may be due to the fact that some functional groups of the ion exchange resin have been degraded as a result of high temperatures during processing, or because the AER particles were partially encapsulated [13, 14]. In fact, the hypothesis of encapsulation can be seen in the SEM images.

Evaluating the solvent influence, the membranes prepared using THF, that rapidly evaporates even at room temperature, had the lowest conductivity comparing with those prepared using DMF. The rapid solvent evaporation might have caused the existence of small voids in the membrane morphology, which led to fewer functional groups per membrane area and, consequently, to a lower conductivity. The SEM images presented earlier show these gaps, corroborating this hypothesis.

The conductivity in heterogeneous membranes is due to the presence of ion exchange resin in the polymer matrix [7]. However, it is well known that PVC is an excellent insulator, employed, for example, in the insulation of electrical cables [15]. Thus, by comparing these membranes conductivity with membranes reported in the literature prepared from other base polymers, certainly it will be found different conductivities.

3.3 Ion exchange capacity (IEC)

Regarding the ion exchange capacity (IEC), it is known that this property is due to the amount and size of ion exchange resin particle in the membranes [4, 7]. Besides, the IEC of heterogeneous membranes is in the range of 1–2 mmol.g^{-1} dry membrane [3]. In this research, it was noticed that membranes prepared by the casting method, CA50T and CA50D, presented very similar values, showing that for this polymer and for these solvents, IEC is not a property influenced by solvent exchange in this research. Since this parameter is assessed in terms of membrane unit mass, the existence of voids does not affect the results. Contrary to the conductivity that is measured according to a specific area, the IEC is evaluated by mass.

It was also noted that CO50 membrane had a lower IEC than the ones prepared by casting with the same amount of AER, reinforcing the hypothesis of functional group loss or AER encapsulation. For CO35 and CA35D membranes, the IEC values were quite similar, 1.23 mmol.g^{-1} and 1.16 mmol.g^{-1}, respectively.

3.4 Water content

According to the literature and in consonance with IEC results, the swelling occurs due to the AER amount once the base polymer is hydrophobic [16]; the PVC water absorption at 25°C in 24 hours varies from 0.05% to 0.10% by weight [17]. In this research, the membranes CA50T and CA50D presented water absorption of 67.4% and 59.8% by mass, respectively. This difference is due to the fact that the THF

evaporates quickly, leading to the formation of small voids, in which the accumulation of water is favored.

Comparatively, CO50 membrane, which does not use solvent during preparation, not allows water accumulation in small voids. Additionally, this lower water absorption also occurs because of reduction of active sites which may have been degraded during processing or may have been encapsulated (shown in conductivity analysis).

In turn, CO35 and CA35D membranes showed, as expected, lower swelling values in comparison to other membranes with higher AER proportion. In addition, the fact that the membrane prepared by coating presents lower swelling than casting was noticed once more.

4   Conclusions

It is noticed that both method of obtaining membranes, spread coating lamination or solvent evaporating (casting), and the solvent used in the casting process, can modify the membranes properties. When preparing heterogeneous anion exchange membranes using PVC as matrix, it was found that, among the methods, casting presented to be the most satisfactory one due to the possibility of the loss of functional groups by thermal degradation during processing via coating or due to AER encapsulation. Concerning the tested solvents, the best suited for casting process was DMF which does not provide large voids with subsequent decrease of the conductivity and increasing swelling over to required values. Finally, the membrane with better properties obtained was CA50D. This membrane was prepared by casting method using DMF as solvent and presented conductivity, IEC and swelling of $2.17.10^{-3}$ S.cm^{-1}, 1.58 mmol.g^{-1} and 59.8%, respectively. This membrane possibly will present the best performance in the ED process among the synthesized and evaluated membranes, providing a better quality in the effluent treated by this technique.

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