



POTENTIOMETRIC TITRATION OF POLYMERIC ELECTROLYTES USED AS MEMBRANES IN FUELL CELLS

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ABSTRACT

In order to improve generation of energy from fuel cells, alternative ion exchange polymeric membranes were prepared from copolymers of sulfonated poly {styrene-co-acrylic acid} at comonomer ratios of 92:8 and 94:6 %mol. Equilibrium studies by means of potentiometric titration allowed determination of the average protonation constants of these copolymers. The materials suffered protonation and deprotonation reactions in the sulfonate and carboxylic groups and the log of equilibrium ratio values found are: for carboxylate group $[HPOLI]/[POLI] [H] = 3.65$ (for 92:8) and 3.64 (for 94:6), and for sulfonated group $[H_2POLI] / [HPOLI] [H] = 2.12$ (for 92:8) and 2.23 (for 94:6). The protonation sites are partly a result of the sulfonation procedure of these copolymers.

Key words: Potentiometric Titration, copolymers, electrolytes, fuel cells.



1. INTRODUCTION

The requisite to generate energy with minimal impact to the environment became a challenge for current and future generations. Fuel cells have been studied for generating clean energy from renewable sources. In this context, the fuel cell membrane ion exchange (PEMFC – proton exchange membrane fuel cell), where the electrolyte is a polymer membrane, is a viable alternative technology.¹ A vital component for the performance of these cells is the membrane ion exchange polymeric membrane, such as the well known Nafion® membrane does. Such material is a fluorinated polymer that contains sulfonic acid groups fixed on the polymer chain which has been widely used as a chemically inert structure in oxidizing or reducing agents. It has also associated high charge conductivity necessary for the transport of protons. It displays conductivity in the order of 2.0×10^{-2} S/cm and water absorption of 38% by weight at 25°C.^{2,3}

The limitations for their use conditions and dependence on hydration restrict their applications. The high cost of this membrane is also a limiting factor for the use of fuel cells as alternative sources of energy. Such disadvantages have stimulated the development of other membranes economically more attractive.⁴⁻⁷ In order to get materials with wider range of operational parameters, our research group has been working to develop new polymer electrolytes for this purpose. Thus, the copolymers used in this study were prepared by bulk polymerization, with ratios of styrene:acrylic acid of 92:8 and 94:6 %. Membranes were prepared by casting method and the acid copolymers of poly-(styrene-acrylic) characterized and described elsewhere in literature.⁸ In a recent study, it was also reported the preparation and characterization of similar sulfonated poly (styrene-acrylic) to be used as humidity and pH sensors for quality control in the food industry.⁹

The potentiometric titration is a useful tool to help understanding the chemical equilibrium of such ionic materials especially the acid-base balance. It can also observe and differentiate the equilibrium involving different substances at different concentrations.¹⁰ The technique is applied in this work to determine the equilibrium of protonation and deprotonation

of the sulfonated copolymer. The protonation constants of the copolymer obtained, are defined by Equation 1.



The HPOLI is the specie with carboxylate group and the H₂POLI is the sulfonated specie. The copolymer solution in water/acetone (50/50% v/v) behaves as a diprotic acid, involving carboxylic and sulfonic acid units. The protonation of these groups were determined.

2. EXPERIMENTAL

The titrations were performed in the automatic titrator Metrohm 84811 Titrino Plus, using burette Metrohm 806 and stirrer Metrohm 801. The cell was thermally controlled at $25.0 \pm 0.1^\circ\text{C}$ using a circulating bath (Microchimica Ind. Com.). For the analysis of polymers it was used the MET mode (monotonic) and a fixed reagent addition during the entire range of pH considered between 2 to 12. For measurement of pH values a combined electrode type Ag/AgCl was used. As supporting electrolyte, KCl was used to maintain ionic strength constant at 0.10 mol L^{-1} . The inert atmosphere was maintained through the flow of purified argon and a solution of KOH 0.10 mol L^{-1} used to remove traces of carbon dioxide.

The electrode calibration was adjusted by several titrations with dilute solutions of aqueous HCl and water/acetone (50/50 % v/v)^{12,13}, in order to obtain direct readings of $-\log[H^+]$. Each experiment was performed using about 0.05 mmols of the copolymer sample (relative to monomeric units), with volumes of 30.0 mL (with 10.0 and 20 mL of solvent water/acetone (50/50 % v/v) and 10^{-2} mol/L HCl) and the support electrolyte of KCl. Each potentiometric titration was carried out at least three times. There were usually some 40–50 points obtained per p[H] (H^+ ions potential) profile providing in general at least 20 pairs of data (volume of base and p[H]) per neutralization equivalent. The constant values represent the average value of each titration. The water containing 0.10 mol L^{-1} KCl used for the calculations had a $pK_w = 13.78$ ¹⁴ (potential of the constant for water dissociation) and for the solution containing water/acetone

(50/50%v/v) KCl with 0.10 mol L^{-1} was of 15.17.¹³ The constants were determined with the aid of the BEST7 program^{14,15} and the diagrams of distribution of species in solution as a function of pH, were obtained with the SPECIES program.¹⁶

3. RESULTS AND DISCUSSIONS

The studies of chemical equilibrium of the acid-base species involved in the copolymer used as membranes for fuel cells were carried out for the specific chemical structure observed in Figure 1.

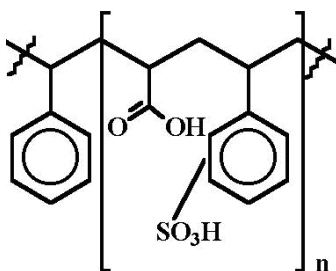
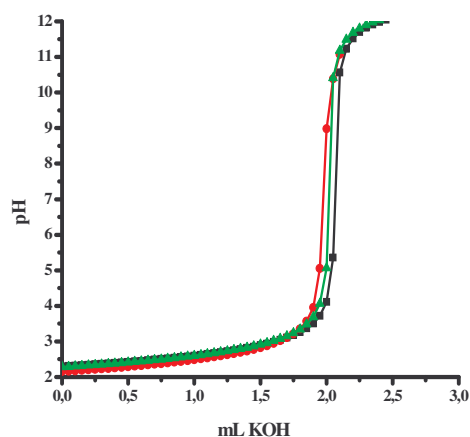


Figure 1. Sulfonated copolymer poly {styrene-co-acrylic acid }.

The potentiometric titration curves corresponding to the evaluated copolymers are shown in Figure 2. The inflections in the curves provide quantitative information regarding the stoichiometry of the solution, suggesting the possible chemical species present in the system under study. Considering the samples show similar curves, only one of each is displayed. One for samples in the monomer proportion of 92:8 (% of styrene:acrylic acid) (Figure 2 A) and another for samples of 94:6 (Figure 2 B).



(A)

(B)

Figure 2. Potentiometric titration curves for the sulfonated copolymer, A= 92:8, B= 94:6 (% of styrene:acrylic acid).
0.05 mmol of sample, $T = 25.0 \pm 0.1$ °C and $\mu = 0.10$ molL⁻¹.

The species distribution curves followed by this method are shown in Figure 3, showing the percentage of every specific specie as a function of pH during titration. The SO_3^- and SO_3H are the non and the protonated species respectively of the sulfonated group attached to the copolymer, while the $-\text{COO}^-$ and the $-\text{COOH}$ are the corresponding non protonated and protonated ones of the carboxylate group from the acrylic acid in the copolymer.



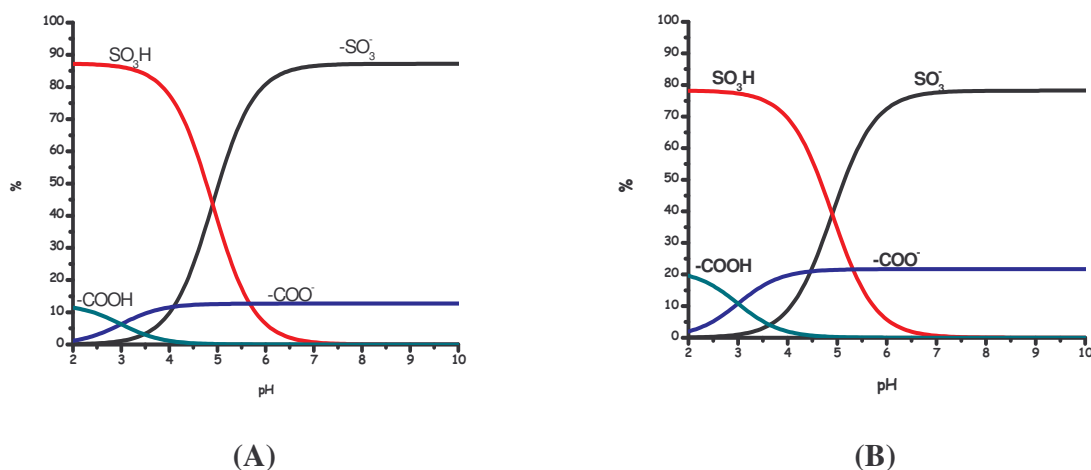


Figure 3. Species distribution curves of sulfonated copolymers as a function of pH. 0.05 mmoles of sample (in monomeric units) and $\mu = 0.10 \text{ mol L}^{-1}$ (KCl). (A) (92:8) and (B) (94:6).

Taking quantitative values for the different species from the curves observed in Figure 3, some similarity between materials can be observed as follows, but with different values:

For 92:8 sample (A) at $\text{pH} = 7.4$ an amount of 86.9% of deprotonated sulfonic acid groups and 13.1% from carboxylate groups (deprotonated carboxylic acid). While at $\text{pH} = 2.0$, it has 87.2% of protonated sulfonic acid group, SO_3H , 11.45% of $-\text{COOH}$ (the protonated carboxylate group) and only 1.15% of $-\text{COO}^-$ (the deprotonated carboxylate).

For 94:6 sample (B) at $\text{pH} 7.4$ an amount of 77.96% of deprotonated sulfonic group and 21.71% of $-\text{COO}^-$ is observed. While it was observed at $\text{pH} 2.0$ a 78.19% of SO_3H (the protonated of sulfonic group), 19.61% $-\text{COOH}$ (the protonated carboxylate) and 1.96% of $-\text{COO}^-$.

Using the data obtained from the potentiometric titration and taking into account the concentration (mmol) of material involved in the evaluation, the following percentage of

sulfonation values were calculated for the samples: 12% for the samples (92:8 – styrene:acrylic acid) and 13% for the 94:6 samples. Table 1 shows the equilibrium ratios for the samples.

Table 1 - Logarithms of protonation constants of the sample of sulfonated copolymers, $T = (25.0 \pm 0.1)^\circ\text{C}$ and $\mu = 0.1 \text{ mol L}^{-1}$ (KCl).

Samples	Equilibrium Ratio	
	$[\text{HPOLI}]/[\text{POLI}][\text{H}]$	$[\text{H}_2\text{POLI}]/[\text{HPOLI}][\text{H}]$
A	3.65(3)	2.12(5)
B	3.64(2)	2.23(4)

From Table 1 it can be seen that the values obtained for the logarithm of the protonation constants corresponding to the carboxylate group ($[\text{HPOLI}]/[\text{POLI}][\text{H}]$), for both samples A and B, are basically the same; small differences are also observed for the sulfonated groups ($[\text{H}_2\text{POLI}]/[\text{HPOLI}][\text{H}]$). They are also lower than the pK_a of acetic acid (4.5), which is expected considering its solvation ability with respect to a monomer unit of polymer having steric effects and intra and intermolecular interactions. This may be the reason for the lower value observed in the protonation of the polymer.

3. CONCLUSIONS

The chemical equilibrium studies indicate that the sulfonation reaction effectively occurred in the copolymer samples. On the other hand, as the materials are intended to be used as membranes in fuel cells, where the presence of H^+ ions is responsible for the reaction in the interior of the cell, the existence of deprotonation and protonation reactions of sulfonate and carboxylate groups makes these samples with possibilities to be used for such purpose.

4. ACKNOWLEDGEMENT

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