

Electron Spin Resonance Measurements of Cu^{++} Distribution in Cation Exchange Membranes

R. VÁSQUEZ and J. ÁVALOS, *Departamento de Física, Universidad Nacional de Ingeniería, Casilla 1301, Lima, Perú*, F. VOLINO* and M. PINERI, *DRF/PHS, Equipe Physico-Chimie Moléculaire, Centre d'Etudes Nucléaires de Grenoble, 85 X F-38041 Grenoble Cédex, France*, and D. GALLAND, *DRF/R.M., Centre d'Etudes Nucléaires de Grenoble, 85 X F-38041 Grenoble Cédex, France*

Synopsis

Electron spin measurement of the local Cu^{++} concentrations have been performed in different cation exchange membranes by comparison with reference frozen aqueous solutions of Cu^{++} salts. Comparison of the obtained values with the average chemical concentrations has therefore permitted direct evidence of microphase separation in these systems. Local concentrations approximately four times larger than average chemical concentrations have been found. Information about composition of this ion-containing phase has also been obtained from changes in local Cu^{++} concentrations versus water content.

INTRODUCTION

We are interested in the microstructure of ion-containing polymers, especially in this paper of polymeric cation exchange membranes. Ion associations will generally depend on both ion concentration and the dielectric constant of the matrix. Small ionic associations called multiplets, involving a few ion pairs and larger aggregates, have to be considered when the dielectric constant of the matrix is small.¹ In polymeric membranes, the situation is complicated because the ions of one sign are fixed on the chain leading to an excluded volume effect. Larger ionic associations are possible which give specific mechanical and physical properties to these materials. Knowledge of the microstructures of these membranes is therefore very important to explain membrane characteristics such as permselectivity, ionic conductivity, water diffusion, etc. Different experiments can be performed involving bulk properties measurements up to very local investigation of specific nuclei.

The knowledge of the local ionic concentration and its comparison with the overall chemical concentration will be an efficient way to define a possible ionic phase segregation and to give information about its composition. The aim of this paper is to estimate the local Cu^{++} concentrations by electron spin resonance (ESR) measurements of different Cu^{++} neutralized cationic membranes. Small-angle neutron scattering experiments have shown that no drastic change

* CNRS.

occurs in the microstructure of these membranes upon neutralization.^{2,3} General information about the microstructure of these membranes can therefore be obtained by introduction of cationic probes. A different situation exists in other ion-containing polymers where a complete reorganization of the microstructure occurs upon neutralization of the acidic groups.^{4,5}

Local Cu^{++} concentrations in the membranes have been obtained by comparison of the corresponding ESR spectra with the spectra obtained with reference Cu^{++} solutions. Frozen reference solutions—at liquid nitrogen temperature—permit us to get rid of the molecular motions. Prior to the experiment the samples have therefore been quenched from room temperature down to 77 K in the finger dewar of the ESR spectrometer. The reference solutions are aqueous solutions in which we have added a cryoprotector. It has been shown^{6,7} that such an addition prevents crystallization of water during cooling and therefore a possible change in the local Cu^{++} concentrations. The Cu^{++} concentration range of the reference solutions (0.02–0.2 g $\text{Cu}^{++}/\text{cm}^3$) has been chosen in order to match the possible concentrations found in the membranes. It turns out that in this concentration range there are dramatic changes in the shape of the ESR spectra, these changes being due to relatively important changes in the dipole–dipole and exchange interactions between the electronic spins. For low concentrations, the spectrum is very similar to that of isolated Cu^{++} ions where the four lines due to hyperfine interactions with the Cu^{++} nuclear spins are clearly seen. For large concentrations one observes only a broad line. A continuous

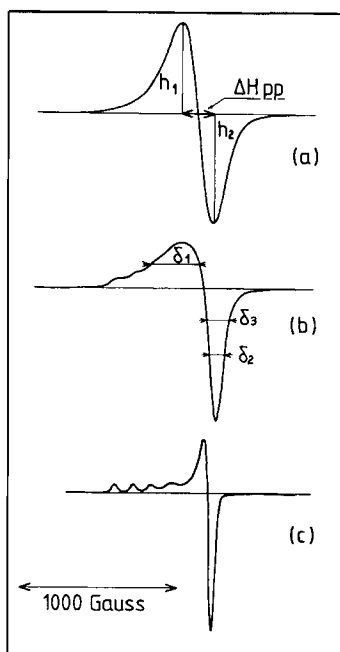


Fig. 1. ESR spectra of reference solutions at 77 K with different Cu^{++} concentration (g $\text{Cu}^{++}/\text{cm}^3$): (a) 0.19; (b) 0.105; (c) 0.042; and definition of the different parameters used to characterize the spectra.

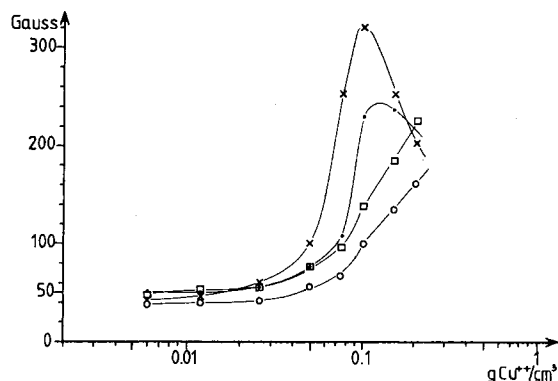


Fig. 2. Changes in the width spectral parameters vs. Cu^{++} concentration of the reference solutions: (X) δ_1 ; (O) δ_2 ; (\square) δ_3 ; (\bullet) Δ , H_{pp} .

change in the spectra is observed when varying the concentration (Fig. 1). A few empirical parameters such as the widths at half and quarter of maximum and relative heights of various components have been used to characterize the spectra, and their change vs. Cu^{++} concentrations have been plotted in Figures 2 and 3.

The various reference solutions obtained by changing both the nature of the salt (sulfate, nitrate, and bromure) and the cryoprotector (dimethylsulfoxide, glycerol, ethyleneglycol) have given essentially the same results for the same Cu^{++} concentration. The changes observed from one spectrum to another are small compared to the changes observed with a small modification of the Cu^{++} concentration. We can therefore assume in first approximation that an ESR spectrum is characteristic of the Cu^{++} concentration. Because the dipole-dipole and exchange interactions are short range, the measured concentrations are local concentrations—on a few tens of Å scale. Use of cryoprotectors permits us to have homogeneous solutions so that the local and average concentrations are the same in the reference solutions. On the contrary, in the membranes where we expect ionic segregations, the local concentrations as measured by ESR should

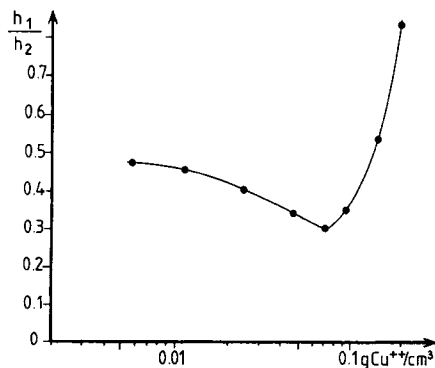


Fig. 3. Changes in the h_1/h_2 parameter vs. Cu^{++} concentration of the reference solutions.

be different from the average one as defined from chemical analysis.

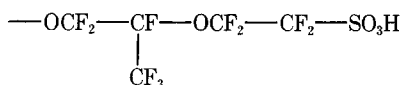
Evidence of water reorganization has been given in some of these membranes when cooling the membrane equilibrated at 100% relative humidity at room temperature. Proton NMR indeed show a change in the proportion of mobile water molecules involving some migration followed by a freezing of this water.⁶ We will also report here measurements at 77 K of the local concentrations obtained after isothermal annealing below room temperature followed by a quenching at liquid nitrogen temperature.

EXPERIMENTAL

Samples

We have studied the following membranes: "Nafion 120," and two different acrylic acid irradiation-grafted polytetrafluoroethylenes, a "Raipore 4010," and sulfonated polysulfones.

(a) Nafion 120—a polymer developed by the DuPont Co.—consists of a perfluoroethylene backbone with side chain of the form

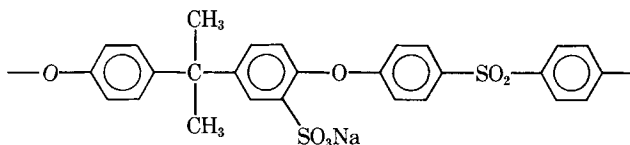


The sample used in this study contains 0.8 meq/g. All information about the chemistry and physical structure can be found in a very recent book.⁸

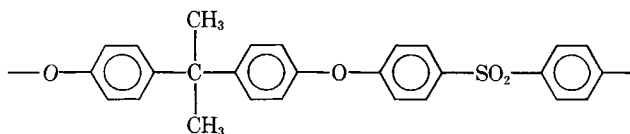
(b) Acrylic acid has been grafted on PTFE by γ irradiation by Chapiro and Jendrychowska-Bonamour.⁹ Formation of long side chains containing the acid groups depends on the γ intensity. We will check here two specimens corresponding to a similar ion exchange capacity (IEC) but obtained with γ intensity of 2300 rad/mn (short pendant chains and IEC = 3.33 meq/g) and 50 rad/mn (long pendant chains and IEC = 3.2 meq/g).

(c) Raipore 4010 is a sulfonated-styrene-grafted membrane of a fluorinated ethylene propylene copolymer. These membranes have been synthesized by RAI Research Corp. By radiation, styrene monomer are grafted as pendant chains to the linear starting polymer. Sulfonation of the styrene groups is then realized.

(d) The sulfonated polysulfone can be considered as a copolymer of the sulfonated



and nonsulfonated units



Different degrees of sulfonated and ion exchange capacity have been obtained.

We will use the following nomenclature to define the samples: x AAA y z in which x is the ion exchange capacity (meq/g), AAA is the name of the membrane—SPS for sulphonated polysulfone, NAF for Nafion 120, RAI for the Raipore 4010, PTFE for the acrylic acid grafted polytetrafluorinated— y is the overall Cu^{++} concentration (g/cm^3), and z is the water content (g) water/g dried sample.

Different degrees of neutralization have been obtained by immersion of the membranes in a water solution of $0.2M$ Cu SO_4 during different times. After neutralization the samples have been washed in water. Sample drying has been done at room temperature.

ESR Results

(a) Nafions. In Figure 4 are shown the ESR spectra obtained after quenching three different 0.8 NAF samples at 77 K. These spectra are very similar to the spectra obtained from the quenched reference solutions with no evidence of distributions in concentrations. The local concentration of Cu^{++} inside these three membranes can therefore be obtained from Figure 2, and are given in Table I.

The most important result is the factor of ~ 4 which is obtained between the local and average concentrations. This is a direct evidence for a nonrandom distribution of ions in the Nafion. In the low water content samples it would mean that the ionic phase represents only $\sim 25\%$ of the polymer. Such a large ionic concentration cannot be explained only by a phase segregation of the ether comonomer, which would give a factor smaller than 2. The ionic phase has therefore to contain Cu^{++} ions, water, and only part of the side chain. Another

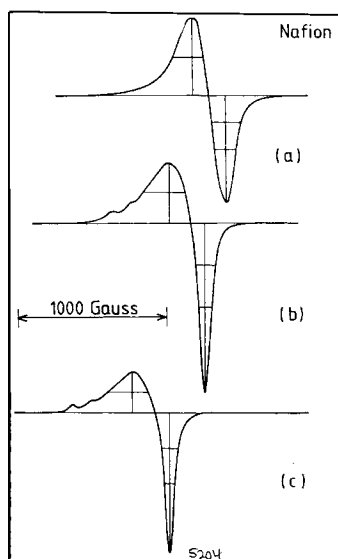


Fig. 4. ESR spectra of the quenched NAF samples at 77 K: (a) 0.8 NAF 0.047 0.045; (b) 0.8 NAF 0.039 0.15; (c) 0.8 NAF 0.018 0.03.

TABLE I

Specimen				Local [Cu ⁺⁺] (g/cm ³)	Concentration ratio
0.8	NAF	0.047	0.045	0.21	4.46
0.8	NAF	0.039	0.15	0.115	2.96
0.8	NAF	0.018	0.03	0.082	4.53
3.33	PTFE	0.049	0.061	0.088	1.8
3.33	PTFE	0.016	0.095	0.065	4.06
3.2	PTFE	0.055	0.047	0.045	2.65
3.2	PTFE	0.01	0.148	0.048	5.03
1.2	RAI	0.0524	0.03	0.208	3.97
1.2	RAI	0.0518	0.03	0.21	4.05
1.2	RAI	0.0652	0.03	0.21	3.22
1.2	RAI	0.0422	0.15	0.094	2.24
1.2	RAI	0.0417	0.15	0.0987	2.36
1.2	RAI	0.0525	0.15	0.105	2
1.0	SPS	0.027	0.015	0.096	3.55
1.0	SPS	0.022	0.23	0.077	3.5
0.75	SPS	0.0063	0.03	0.042	6.6
0.75	SPS	0.0125	0.03	0.046	3.68
0.99	SPS	0.0227	0.04	0.0924	4.07
0.99	SPS	0.0272	0.04	0.113	4.15

interesting point is the change in local concentration when changing the water content. If the local Cu⁺⁺ concentration in the sample containing 4.5% water by weight is 0.21 g/cm³, we can calculate the new Cu⁺⁺ concentration if we suppose that when changing the water content from 4.5% to 15% all the new absorbed water molecules are absorbed in the Cu⁺⁺ ions containing phase. With such an hypothesis we would have to observe a change in the local concentration from 0.21 g/cm³ to 0.107 g/cm³. This number is pretty close to the experimental value of 0.115 g/cm³ and is consistent with the hypothesis that most of the water molecules are absorbed in this ionic phase.

We have also to compare the local Cu⁺⁺ concentration with the concentration, which is obtained by supposing that we have a ionic phase in this hydrated sample containing only water and Cu⁺⁺ ions. The 15% water content sample contains 20.5 water per Cu⁺⁺ and the corresponding solution would therefore have a concentration of $63/(63 + 20.5 \times 18) = 0.145$ g Cu⁺⁺/g and will give a larger concentration in g/cm³ because the density is larger than 1. This value is definitely larger than the local concentration found in this sample (0.115 g/cm³).

The absolute values of the local concentration are given within 20% accuracy. The relative values corresponding to changes in water contents are obtained with an accuracy better than 5%.

All this shows that we have a phase segregation of the Cu⁺⁺ ions in this membrane. The local Cu⁺⁺ concentration is three times larger than the average concentration in the fully hydrated specimen, and this ratio is still larger (~4.5) for the low water contents specimens. The changes which are observed in the local concentrations when changing the water contents are consistent with the hypothesis that most of the water molecules are going inside this ionic phase. Since the local Cu⁺⁺ concentration has been shown to be smaller than the Cu⁺⁺ concentration obtained from a ionic phase containing only water and Cu⁺⁺ ions,

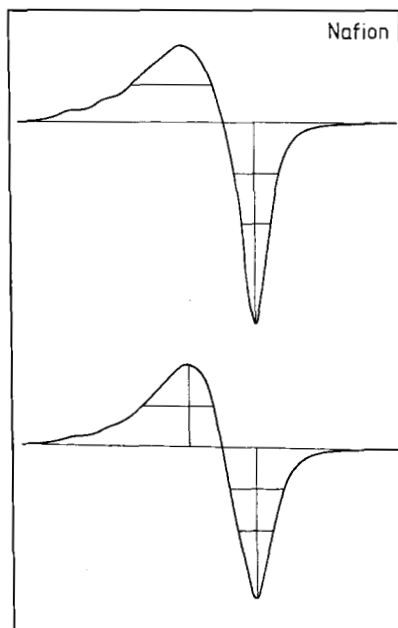


Fig. 5. ESR spectra of the 0.8 NAF 0.039 0.15 sample at liquid nitrogen temperature after quenching from room temperature (top) or from -40°C following a 24-h isothermal annealing at this temperature (bottom).

this means that some other organic groups have therefore to be included in this phase.

Evidence of water desorption during cooling is obtained from Figure 5. Isothermal annealings of 0.8 NAF 0.039 0.15 have been realized at temperatures between ambient and -40°C . Measurements of the local Cu^{++} concentrations have been done at liquid nitrogen temperature after a rapid transfer (Fig. 6). The changes in Cu^{++} concentration observed are consistent with the previous measurements of NMR¹⁰ and involve a desorption of water out of the ionic phase.

The largest changes in local Cu^{++} concentrations have been obtained during annealings between -10°C and -30°C . Two different factors have to be involved in this desorption process. The difference between the annealing temperature and room temperature defines the total amount of water which can be

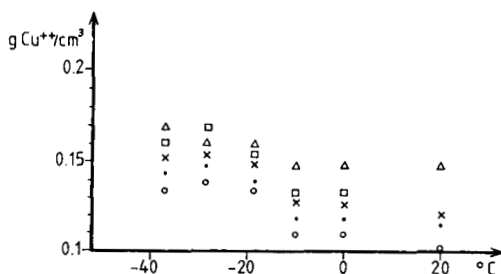


Fig. 6. Local concentrations of the 0.8 NAF 0.039 0.15 sample at liquid nitrogen temperature after isothermal annealing at different temperatures. The local concentrations have been obtained from the δ_1 (Δ), δ_2 (\circ), δ_3 (\square), h_1/h_2 (\times) and ΔH_{pp} (\bullet) values.

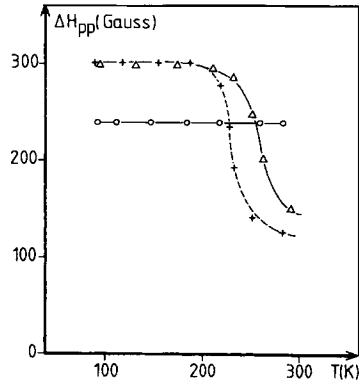


Fig. 7. Line width changes vs. temperature for a 0.8 NAF 0.047 specimen with different water contents: (+) 15%; (Δ) 9%; (O) 4%.

desorbed. The kinetics of desorption will depend only on this annealing temperature and therefore will be very small at low temperatures.

Another evidence of the importance of temperature on the local motions is given in Figure 7. We have plotted the changes in the line width vs. temperature for a 0.8 NAF containing $34 \text{ mg Cu}^{++}/\text{cm}^3$ in the dry state and different water contents. The drastic changes observed in ΔH_{pp} between 210 K and 280 K for the high water content samples can be explained by a motional narrowing due to large amplitude and fast motion of the Cu^{++} ions (time scale shorter than $2 \times 10^{-10} \text{ s}$).

(b) PTFE ESR measurements on irradiation-grafted polytetrafluoroethylene (PTFE reference) are more difficult to interpret because most of the observed spectra give evidence of superposition of at least two different local concentrations (Fig. 8). Only qualitative results which are summarized in Table I can be obtained.

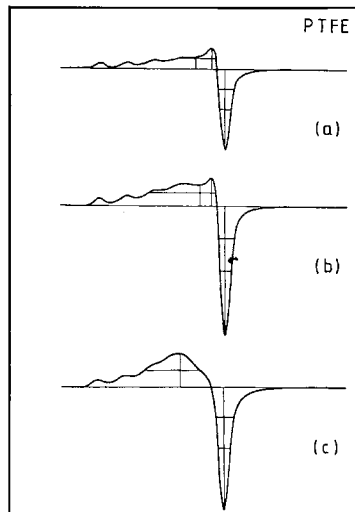


Fig. 8. ESR spectra at 77 K of three different irradiation-grafted PTFE: (a) 3.2 PTFE 0.01 0.148; (b) 3.33 PTFE 0.016 0.095; (c) 3.33 PTFE 0.049 0.061.

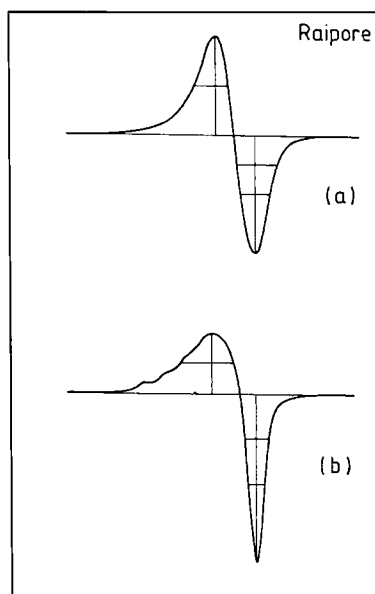


Fig. 9. ESR spectra at 77 K of Raipore membranes: (a) 1.2 RAI 0.0524 0.03; (b) 1.2 RAI 0.0422 0.15.

A value between 2 and 5 has been found for the ratio between the mean local and macroscopic concentrations. These local concentrations are poorly defined and, for example, in the 3.2 PTFE 0.055 0.047 we have after dehydration a mixture of two local concentrations corresponding, respectively, to $0.115 \pm 0.01 \text{ g/cm}^3$ and $0.16 \pm 0.01 \text{ g/cm}^3$. Changes in local concentration have also been evidenced during isothermal annealing below room temperature. In specimen 3.2 PTFE

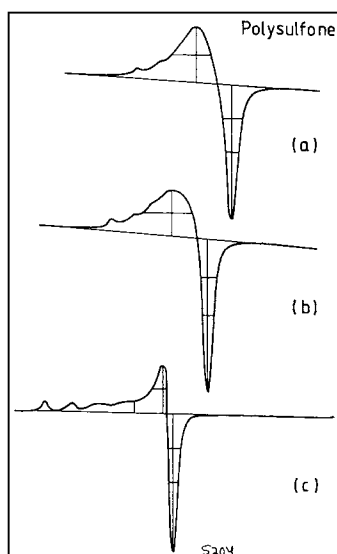


Fig. 10. ESR spectra at 77 K of polysulfone membranes: (a) 1.0 SPS 0.027 0.05; (b) 1.0 SPS 0.022 0.23; (c) 0.75 SPS 0.0065 0.03.

0.01 0.148 the local concentration increases from 0.048 g/cm³ up to 0.067 g/cm³ after an isothermal annealing at -30°C during 24 h. The water desorption is usually observed from the most diluted ionic phase.

(c) Raipore. Similar results have been obtained with the irradiation grafted perfluoroethylene Raipore membranes (Fig. 9). Local concentrations are larger than average concentrations by a factor of 3-4. The situation here is similar to the Nafion situation because we only have a single value for the local concentration rather than a mixture as for the PTFE samples. Different samples with similar average concentrations (0.0524 and 0.0518 g/cm³) have been obtained by changing the exchange conditions (pH and Cu⁺⁺ concentration of the external solution). Concentrations have been obtained for these two specimens with a ratio of 4 between the local and average concentrations. The changes in local Cu⁺⁺ concentration by hydration are consistent with a dilution of the ionic phase. The factor of 4 involves concentration of ions in 0.25 cm³ for a 1 cm³ sample. Changes of water content between 3% and 15% roughly gives an additional 0.24 cm³/cm³ starting material. If water molecules are located inside the ionic phase, the local concentration will be divided by a factor of about 2, which has been found experimentally.

Water desorption has been evidenced in all three samples. After isothermal annealing at -30°C for 24 h the local concentrations have been respectively increased from 0.094 to 0.144 g/cm³, 0.0487 to 0.122 g/cm³, 0.105 to 0.155 g/cm³.

(d) In polysulfone samples we also have a poor definition of the local concentration because of superposition of two different species. These different local concentration are more or less evident depending on the sample and on the water concentrations. For example, after hydration of the 0.75 SPS 0.063 0.03 specimen the two different concentrations are better seen. Absence of water desorption is a characteristic feature of these membranes compared to the others.

DISCUSSION

These electron spin resonance studies have therefore definitely shown that we have a phase segregation in the ion exchange membranes which have been studied here. The local cation concentrations are larger than the average macroscopic concentration by a factor between 2 and 5. It has to be noted that such a study has been possible because in the range of local Cu⁺⁺ concentrations observed in these membranes there is a drastic change in the parameters which characterize the ESR spectrum. Other ESR experiments have been performed on different acid copolymers neutralized with copper salts and have shown the existence of both isolated Cu⁺⁺ ions and Cu⁺⁺-Cu⁺⁺ pairs.^{11,12} Such structures have been evidenced in neutralized butadiene carboxylic telechelics, butadiene-methacrylic acid, and styrene-methacrylic acid copolymers. Many differences exist between these materials and the membranes which have been described in this article: the acid concentration of the starting materials is lower; they contain carboxylic groups, and they do not absorb much water. No study of the local concentrations of isolated Cu⁺⁺ ions and Cu⁺⁺-Cu⁺⁺ pairs has been done in these systems.

Further studies along this line can be performed and give more information on the structure of the membranes. Analytical decompositions of the complex

spectra obtained in the PTFE irradiation-grafted membranes and in the polysulfone would give the different local concentrations. Changes of these local concentrations versus different parameters (total cation content, water contents, irradiation dose, IEC, etc.) would give a better understanding of the properties of the membranes in connection with their microstructure. The extent of ionic hydrophilic and hydrophobic phase separation can be achieved by comparison of the local concentrations versus water contents.

Such experiments have also to be done in other ion-containing polymers because they constitute a very simple way to show ionic clustering and to measure the cation concentration inside the ionic phase.

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