Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Structure and dynamics of water in molecular models of hydrated polyvinylamine membranes
Supplementary materials (ESI)

Pierre Fayon* and Lev Sarkisov

School of Engineering, Institute for Materials and Processes,
The University of Edinburgh, Edinburgh, UK

Contents

1 Systems

1.1 Details of partial charge distribution and force field parameters

We use a polymer chain of 20 monomers, and perform an *ab initio* optimization with GAUSSIAN09 package [1]. The charge distribution is calculated using the 12 central monomers to obtain an average charge for each atom type. For the protonated system we use the charges calculated by Kondinskaia *et al* [2]. To be consistent, we compared the impact of the charges employed on the structure for the P00 at all water contents. There is little difference between the two set of charges for the P00 monomer which resulted in no significant differences in the structure and the diffusion properties. All the charges employed are summarized in table S1. The corresponding atoms within the monomer and their types can be found in Figure S1.

P00		P20 & P50 [2]			
Neutral monomer		Neutral monomer		Charged monomer	
Atom type	Charge	Atom type	Charge	Atom type	Charge
c3c	-0.35497	c3c	-0.3	c3c	-0.31
c3n	0.47841	c3n	0.2	c3n	0.62
n3	-0.99836	n3	-1.0	n4	-0.47
hn	0.36157	hn	0.4	hn	0.33
hc	0.08202	hc	0.1	hc	0.11
h1	-0.01226	h1	0.1	hx	-0.05

Table S1: Atom types and the associated partial charges of PVAm monomers employed in this work.

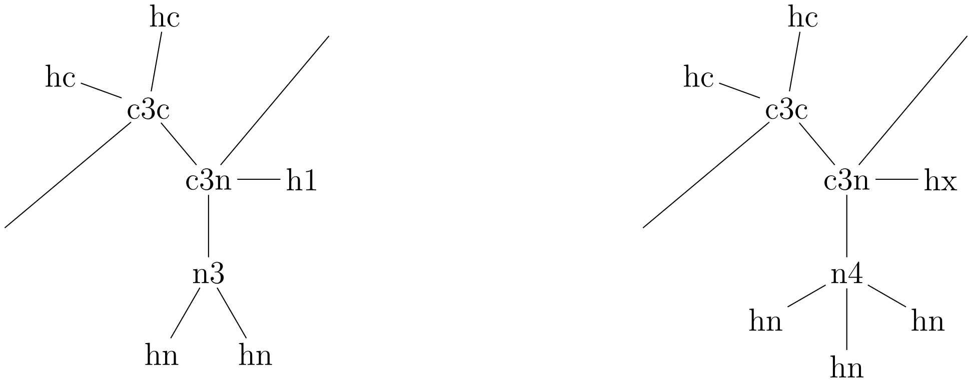

Figure S1: Atom types within a single PVAm monomer. The neutral monomer is shown on the left, the charged monomer is shown on the right.

1.2 Position of the neutral and charged monomers in the model polymer chain

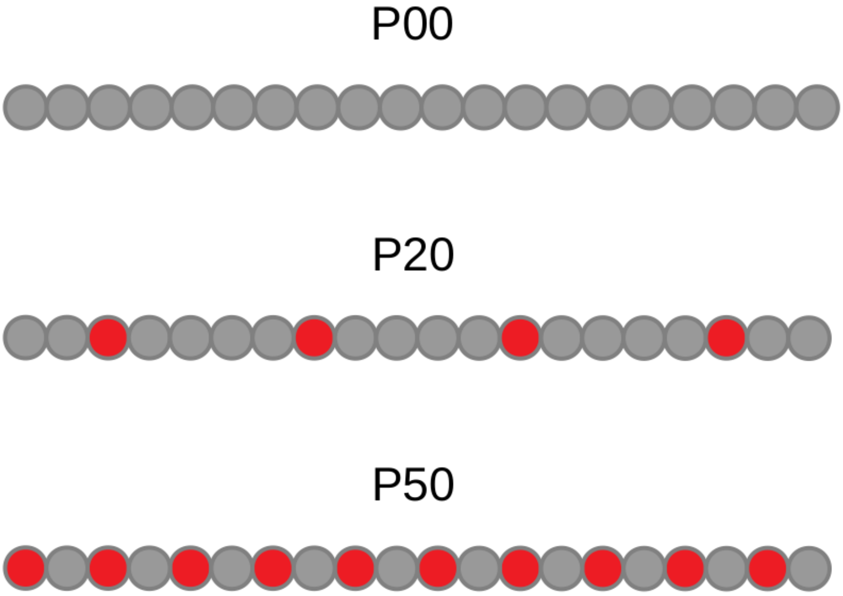

Figure S2: Position of the neutral monomer NH_2 (grey) and the charged monomer NH_3^+ (red) in the P00, P20 and P50 systems.

1.3 Summary of compositions of the systems

Pxx	Wxx	Total number of water molecules	Number of PVAm chains	Number of NH_2 monomers per chain	Number of NH_3^+ monomers per chain	Total number of Cl^- ions
00	00	00	25	20	0	0
	05	60				
	10	120				
	15	180				
	20	240				
	30	360				
	40	480				
	50	600				
	60	720				
	70	840				
	80	960				
	90	1080				
20	00	00	25	16	4	100
	05	60				
	10	120				
	15	180				
	20	240				
	30	360				
	40	480				
	50	600				
	60	720				
	70	840				
	80	960				
	90	1080				
50	00	00	25	10	10	250
	05	60				
	10	120				
	15	180				
	20	240				
	30	360				
	40	480				
	50	600				
	60	720				
	70	840				
	80	960				
	90	1080				

Table S2: Composition of the P00, P20 and P50 systems at all levels of hydration. The polymer chain length in all case is 20 monomers.

2 Sensitivity analysis to the system size

2.1 Structural characterization

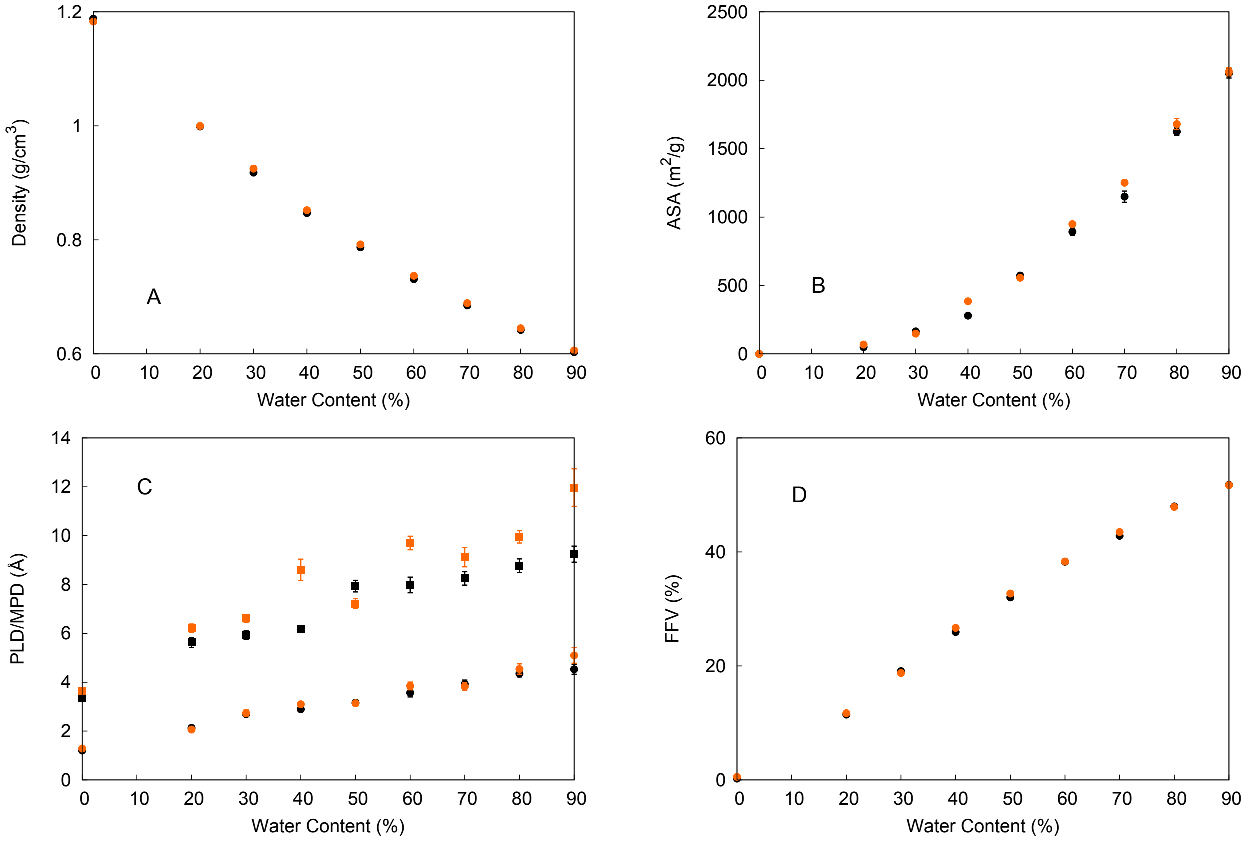

Figure S3: Structural characteristics of the P00 system at different water content for two different chain lengths, 20 (black symbols) and 50 (orange symbols) monomers at 300 K. (A) density of the polymer (g/cm^3); (B) accessible surface area (ASA) (m^2/g); (C) pore limiting diameter (circle) and maximum pore diameter (square) in Å; (D) fractional free volume (FFV) (%).

2.2 Diffusion data

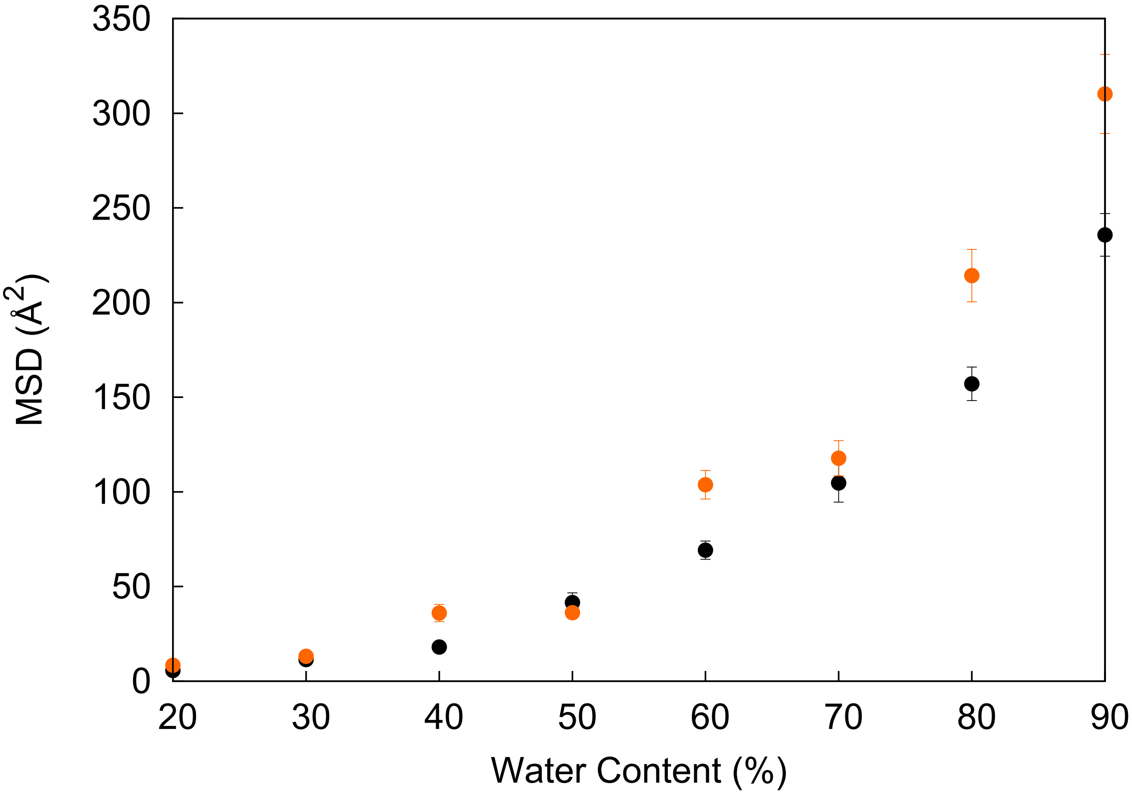

Figure S4: MSD of water at the end of 5 ns run for the P00 system at different water content for two different chain lengths, 20 (black symbols) and 50 (orange symbols) monomers at 300 K.

Here we notice that there are some differences between the two system sizes for the hight water content W60, W80 and W90. We attribute these divergence to the MPD difference (Figure S3(C)), resulting in larger pores of bulk like water increasing the average self-diffusion. It is possible that this difference are associates with some structural differences between the two systems. Specifically, the maximum pore diameter (Figure S3(C)) is bigger in systems with longer polymer chains, resulting in larger pores. These large pores may bring dynamic behavior of water closer to the bulk behaviour and faster diffusion.

3 Sensitivity analysis to matrix realization

3.1 Structural characterization

Figure S5 shows variation of structural properties from six different independent matrix realizations.

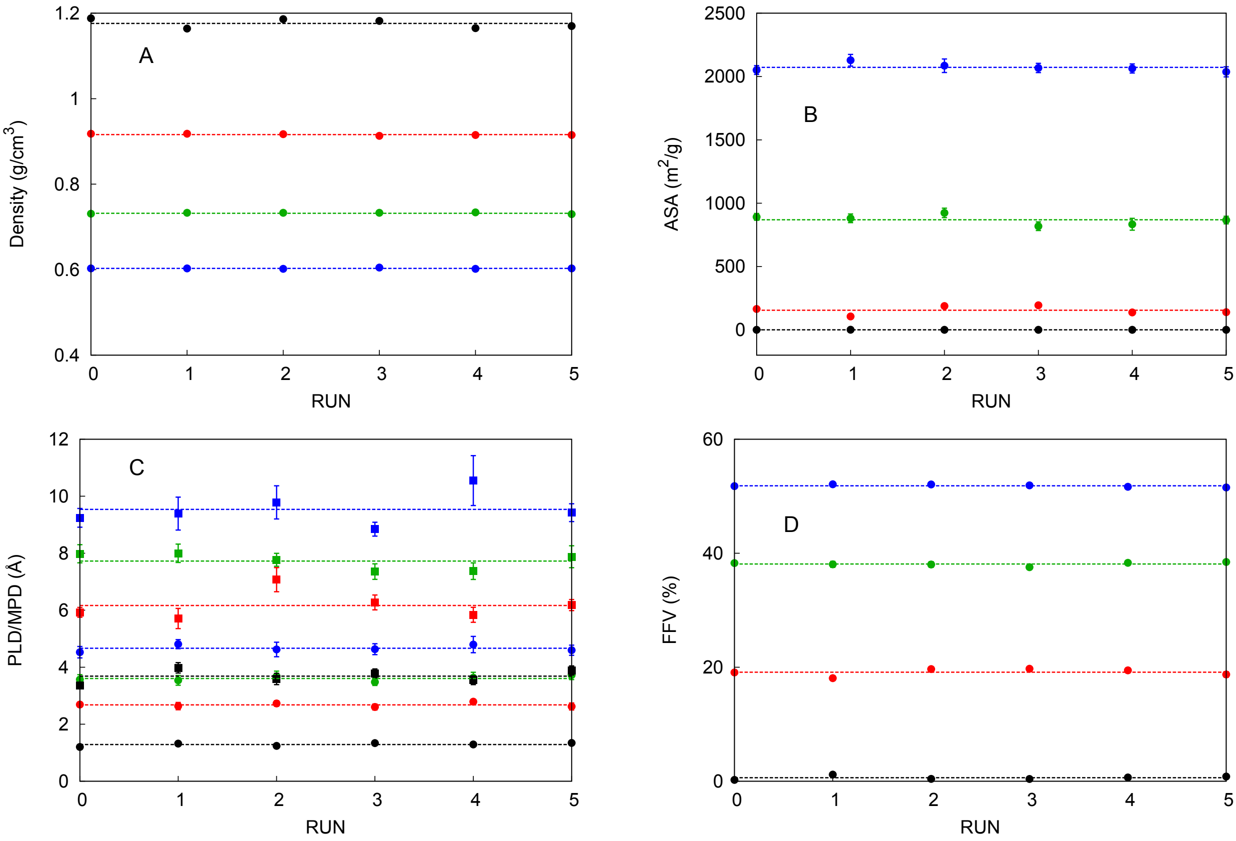

Figure S5: Structural characteristics of the P00 system at different water content at 300 K. In this graphs, black symbols correspond to P00W00; red symbols to P00W30; green symbols to P00W60; and blue symbols to P00W90. (A) density of the polymer (g/cm^3); (B) accessible surface area (ASA) (m^2/g); (C) pore limiting diameter (circle) and maximum pore diameter (square) in Å; (D) fractional free volume (FFV) (%). The dash lines are the average value of the property over six matrix realizations.

3.2 Diffusion data

Here we present the sensitivity analysis of dynamic properties to matrix realization. We use MSD (mean-squared displacement) for comparison between the runs only.

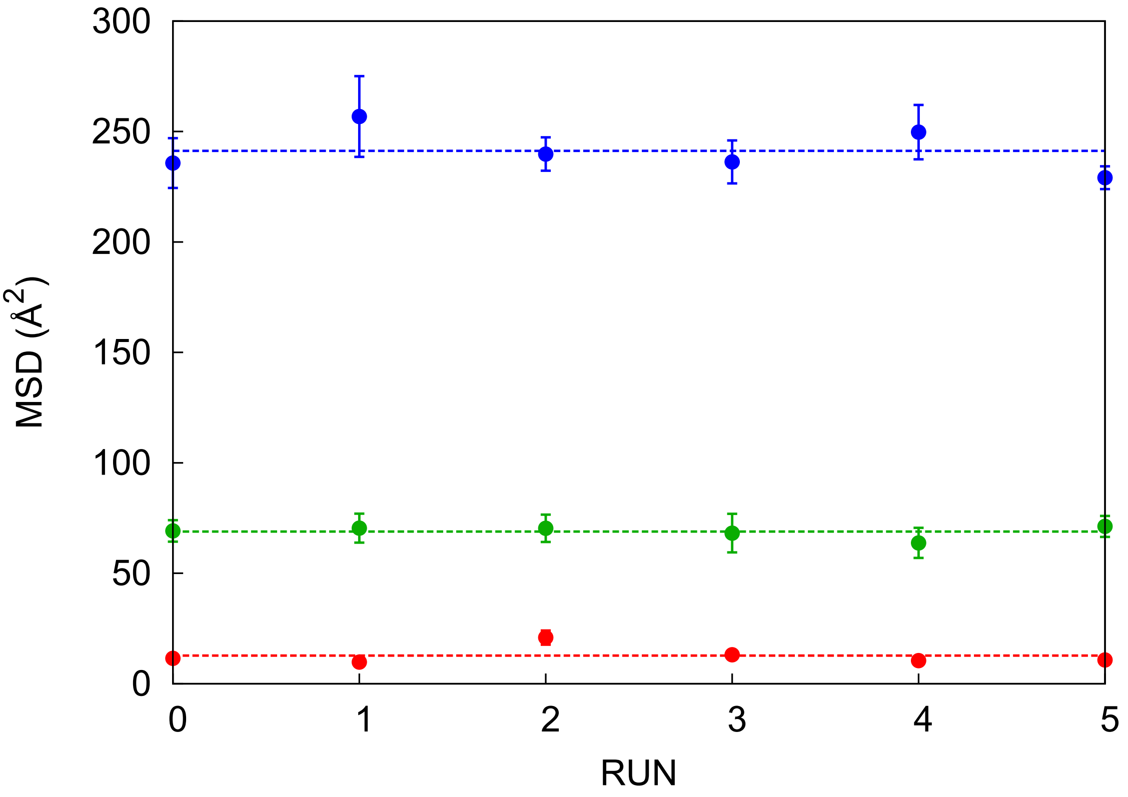

Figure S6: MSD of water at the end of 5 ns run for the P00 system at different water content at 300 K. In this graphs, red symbols correspond to P00W30; green symbols to P00W60; and blue symbols to P00W90. The dash lines are the average values from the six matrix realizations.

4 Additional analysis

4.1 Radius of gyration of PVAm chains in model systems

We present here the radius of gyration of the PVAm chains for all water contents and the three protonation states. For each water content, we calculate the radius of gyration of each chain and average it over 20 chains. The radius of gyration is used to describe whether the polymer chain tends to be in a folded or elongated state as a function of hydration and degree of protonation. This property is calculated using the following equation:

$$Rg = \sqrt{\sum \left(\frac{x_i^2 + y_i^2 + z_i^2}{N} \right)} \tag{1}$$

where N is the number of atoms and x, y, and z are the atomic coordinates relative to the center of mass.

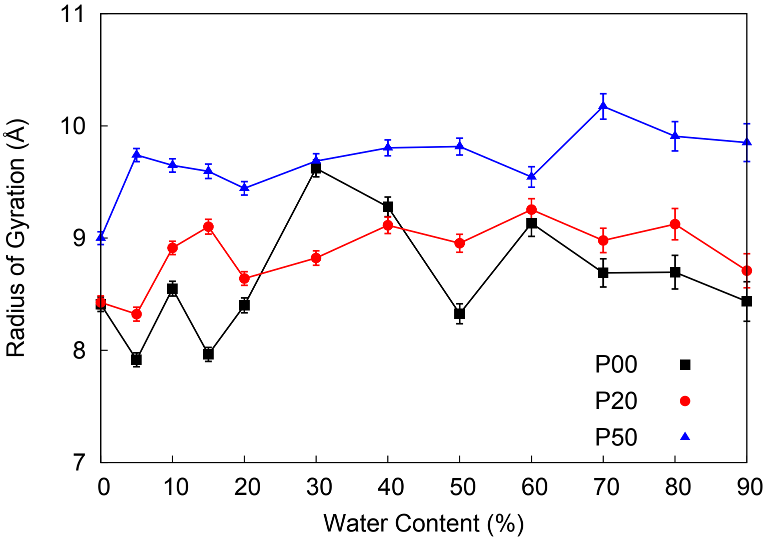

Figure S7: Average radius of gyration of the polymer chain as a function of water content and protonation at 300 K. In this graph, black lines and symbols correspond to the uncharged system P00; red and blue lines and symbols to P20 and P50 systems, respectively (lines are for eye guidance only).

We can see in Figure S7 that the water content does not have a significant impact on the radius of gyration of the chain. Indeed, the maximum difference is 1.5 Å between the P00W15 and the P00W30 system. However, the degree of protonation have a stronger effect onto the radius of gyration, we can see that for the P50 systems, the radius of gyration is systematically larger than for P00 and P20. This is likely to be associated with the electrostatic repulsion effect in the chains with high charge density.

4.2 Polymer density

We present here the polymer density ρ_P for all water contents and the three protonations states, we calculated the density in two different way. First we calculated the density only taking into account the polymer chain, this density, ρ_P is calculated using the following equation:

$$\rho_P = \frac{M_{pol}}{V_{sys}} \tag{2}$$

where M_{pol} is the polymer mass and V_{sys} the volume of the system.

An other approach is to consider the chloride ions as part of the polymer matrix ρ_{PCl^-}, defined as:

$$\rho_{PCl^-} = \frac{M_{pol} + M_{Cl^-}}{V_{sys}} \tag{3}$$

with M_{pol} and V_{sys} same as before and M_{Cl^-} the mass of chloride ion.

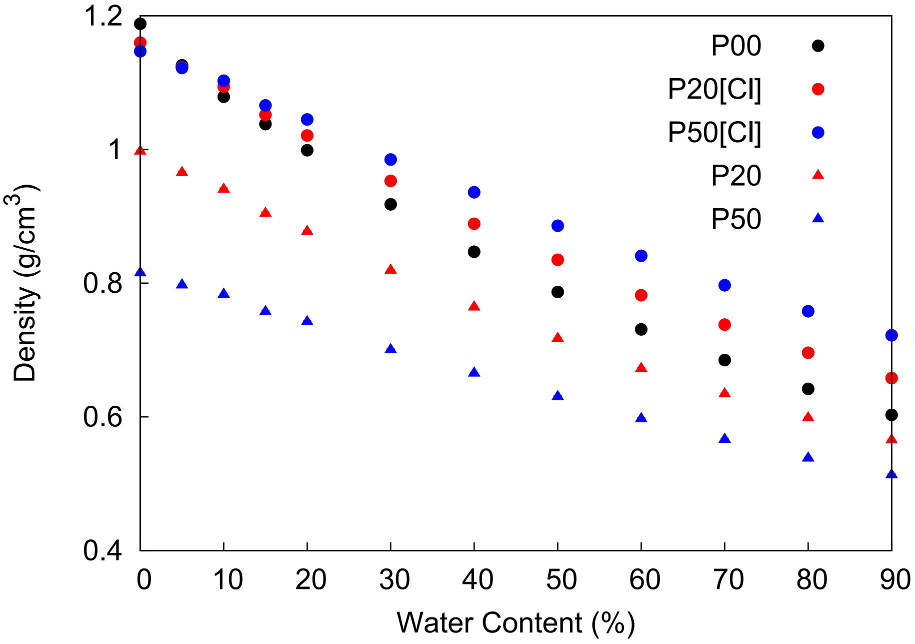

Figure S8: Polymer density of the systems (water has been removed for this analysis) as a function of water content and protonation. In this graph black symbols correspond to the system P00; red and blue symbols correspond to P20 and P50 systems, respectively. The triangle symbols represent density in the protonated systems, where only polymer is considered as the membrane structure, but not chloride ions.

4.3 Accessible Surface Area

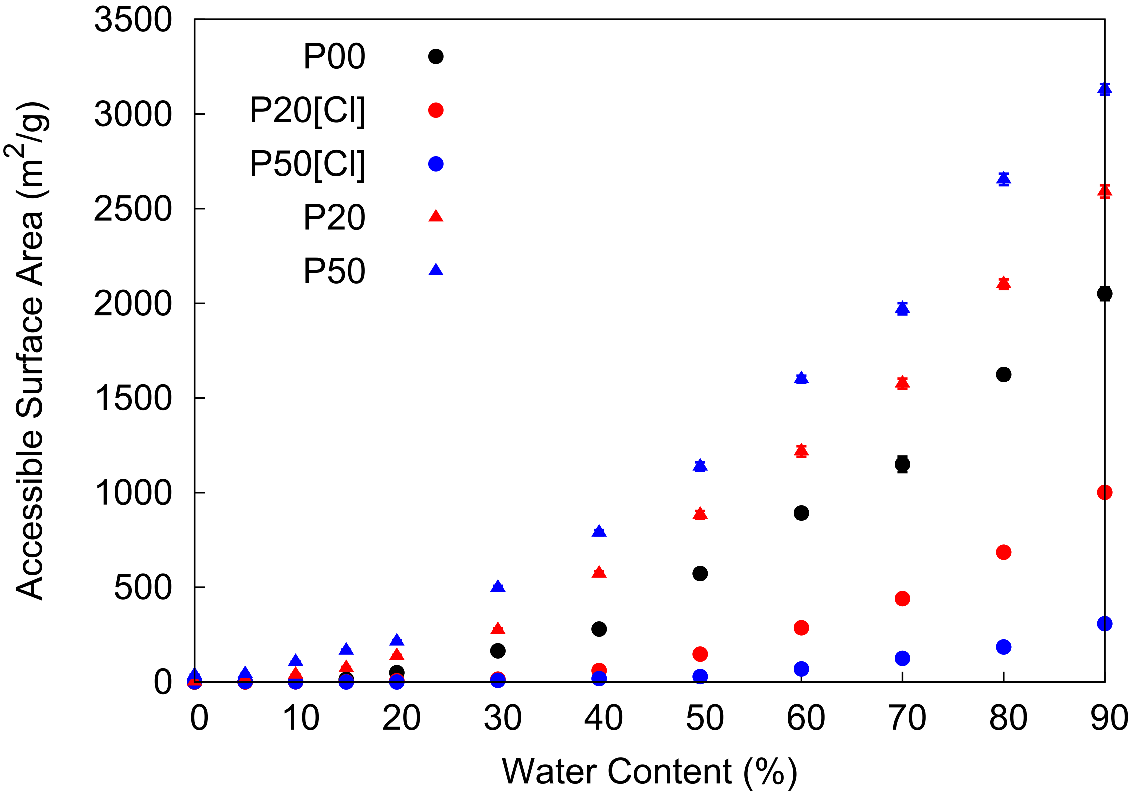

Figure S9: Accessible Surface Area (ASA) as a function of water content and protonation. In this graph, black symbols correspond to the P00 system; red and blue symbols to P20 and P50 systems, respectively. The triangle symbols represent the ASA in the protonated systems, where only polymer is considered as the membrane structure, but not the chloride ions.

4.4 Pore size distribution in model systems

In this section we provide a brief analysis of the evolution of the pore size distribution (PSD) for the three protonation states at different degrees of water content. The PSD presented here are calculated considering the chloride ions as part of the polymer matrix at 300 K.

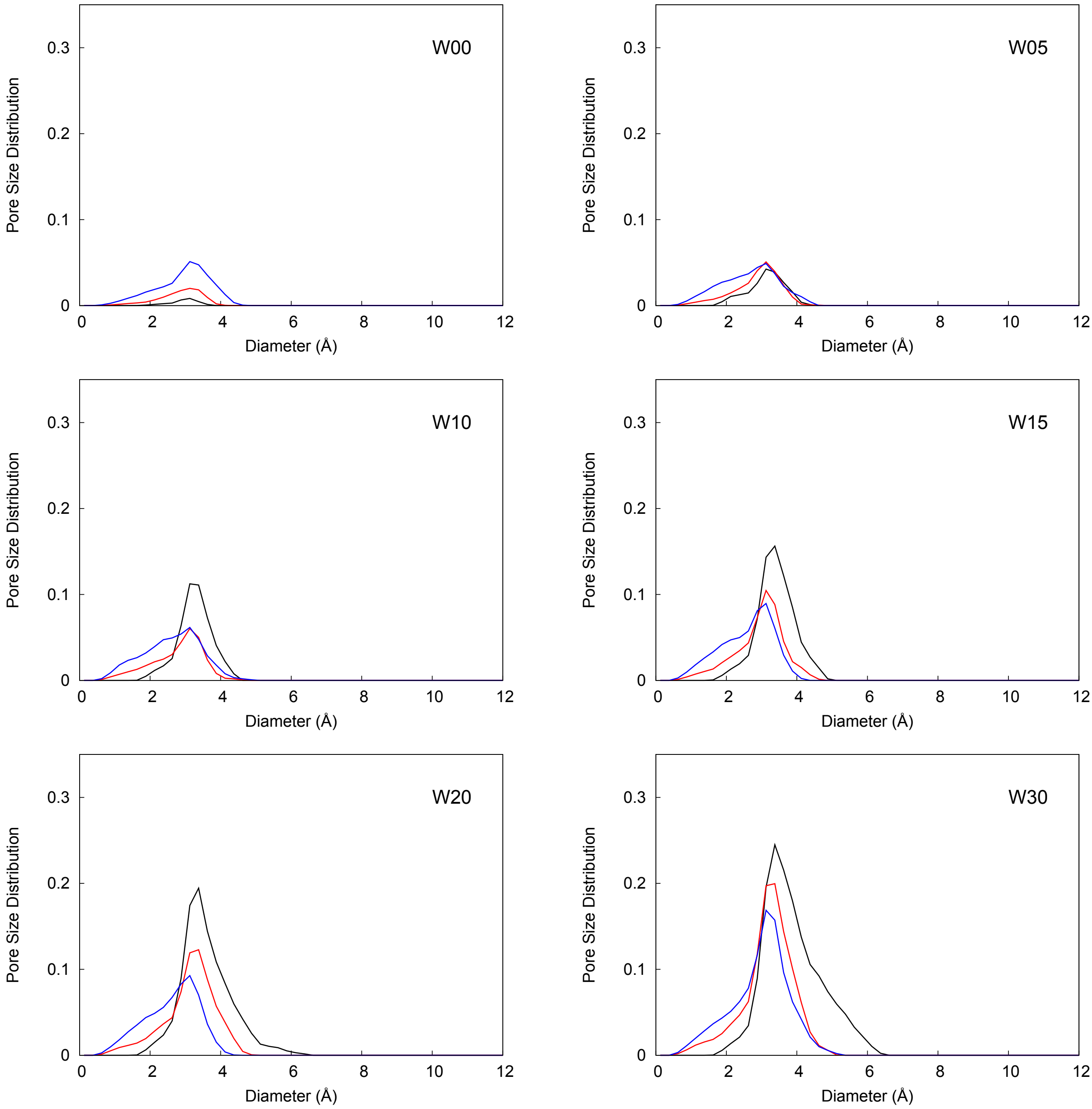

Figure S10: Pore Size Distribution (PSD) for P00 (black), P20 (red), and P50 (blue) systems at W00, W05, W10, W15 and W30 water contents at 300 K. Chloride ions are considered as part of the polymer structure.

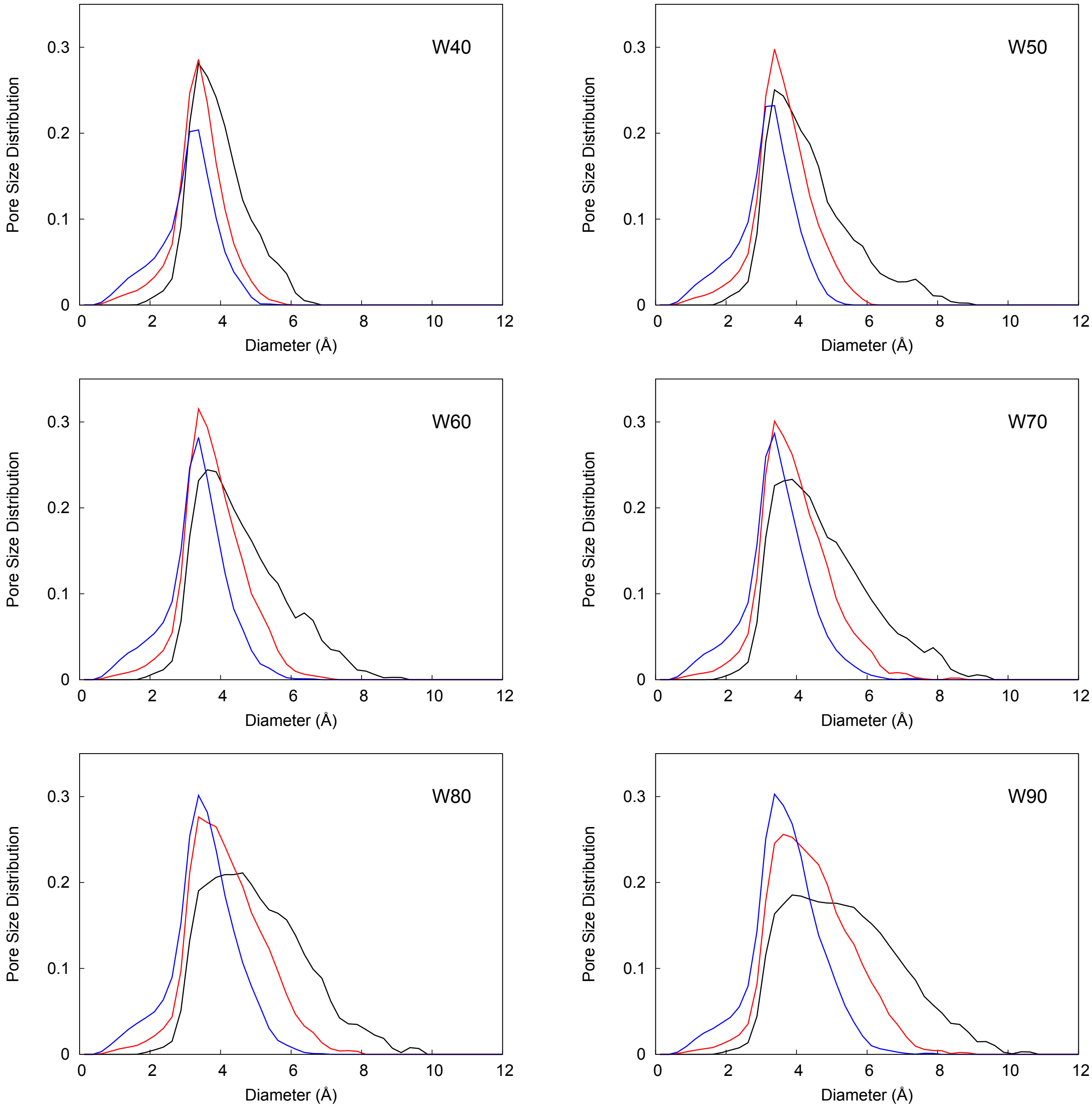

Figure S11: Pore Size Distribution (PSD) for P00 (black), P20 (red), and P50 (blue) systems at W40, W50, W60, W70, W80 and W90 water contents at 300 K. Chloride ions are considered as part of the system.

4.5 Summary of structural characteristics of model membrane systems from the Poreblazer analysis

Pxx (%)	Wxx (%)	Density (g/cm^3)	ASA (m^2/g)	PLD (Å)	MPD (Å)	FFV (%)
P00	00	1.188 (0.003)	0.0 (0.0)	1.203 (0.040)	3.352 (0.082)	0.2 (0.1)
	05	1.126 (0.002)	0.5 (0.2)	1.486 (0.075)	3.997 (0.114)	1.8 (0.1)
	10	1.079 (0.002)	4.2 (1.1)	1.532 (0.048)	4.272 (0.061)	4.8 (0.2)
	15	1.038 (0.002)	13.5 (1.4)	1.910 (0.082)	4.692 (0.051)	7.6 (0.2)
	20	0.999 (0.002)	49.3 (4.5)	2.130 (0.096)	5.630 (0.203)	11.4 (0.3)
	30	0.918 (0.002)	164.5 (10.6)	2.690 (0.083)	5.927 (0.173)	19.0 (0.3)
	40	0.847 (0.001)	279.3 (8.6)	2.892 (0.065)	6.188 (0.128)	25.9 (0.2)
	50	0.787 (0.001)	572.1 (17.8)	3.160 (0.068)	7.933 (0.238)	32.0 (0.2)
	60	0.731 (0.001)	892.1 (27.1)	3.569 (0.171)	7.982 (0.319)	38.2 (0.2)
	70	0.685 (0.001)	1149.3 (41.1)	3.925 (0.162)	8.250 (0.275)	42.8 (0.1)
	80	0.642 (0.001)	1624.2 (27.9)	4.348 (0.133)	8.769 (0.278)	47.9 (0.2)
	90	0.603 (0.001)	2051.3 (34.8)	4.528 (0.201)	9.242 (0.328)	51.7 (0.2)
P20	00	1.160 (0.002)	0.0 (0.0)	1.302 (0.031)	3.667 (0.091)	0.9 (0.1)
	05	1.123 (0.002)	0.2 (0.2)	1.405 (0.060)	3.952 (0.113)	2.2 (0.1)
	10	1.094 (0.002)	0.4 (0.5)	1.482 (0.071)	3.990 (0.121)	2.9 (0.1)
	15	1.052 (0.002)	2.0 (0.5)	1.542 (0.069)	4.338 (0.099)	5.0 (0.1)
	20	1.021 (0.002)	6.5 (1.0)	1.713 (0.058)	4.514 (0.085)	6.9 (0.2)
	30	0.953 (0.001)	14.3 (1.4)	2.005 (0.077)	4.792 (0.098)	12.0 (0.2)
	40	0.889 (0.001)	60.0 (6.1)	2.395 (0.067)	5.355 (0.159)	18.8 (0.2)
	50	0.835 (0.001)	147.2 (8.8)	2.736 (0.076)	5.764 (0.089)	24.0 (0.2)
	60	0.782 (0.001)	286.3 (10.2)	2.966 (0.071)	6.323 (0.217)	30.0 (0.3)
	70	0.738 (0.001)	440.4 (20.5)	3.068 (0.078)	6.888 (0.343)	34.0 (0.2)
	80	0.696 (0.001)	685.4 (16.8)	3.395 (0.070)	7.195 (0.221)	38.9 (0.2)
	90	0.658 (0.001)	1001.0 (22.3)	3.602 (0.114)	7.576 (0.311)	43.2 (0.1)
P50	00	1.147 (0.002)	0.9 (0.48)	1.395 (0.061)	4.202 (0.085)	2.5 (0.1)
	05	1.122 (0.001)	1.4 (0.38)	1.315 (0.023)	4.251 (0.072)	3.0 (0.1)
	10	1.103 (0.001)	0.8 (0.44)	1.442 (0.045)	4.293 (0.138)	3.9 (0.1)
	15	1.066 (0.002)	0.1 (0.12)	1.586 (0.058)	3.960 (0.090)	5.0 (0.1)
	20	1.045 (0.002)	0.2 (0.13)	1.600 (0.063)	4.028 (0.077)	5.6 (0.2)
	30	0.985 (0.001)	8.8 (1.48)	1.838 (0.049)	4.843 (0.106)	10.2 (0.2)
	40	0.936 (0.001)	18.4 (2.87)	1.935 (0.049)	4.914 (0.132)	13.9 (0.1)
	50	0.886 (0.001)	28.0 (2.44)	2.162 (0.051)	5.069 (0.098)	17.1 (0.2)
	60	0.841 (0.001)	68.9 (6.50)	2.375 (0.079)	5.592 (0.218)	21.8 (0.1)
	70	0.797 (0.001)	124.3 (11.8)	2.575 (0.074)	6.122 (0.281)	25.2 (0.2)
	80	0.758 (0.001)	184.5 (11.5)	2.652 (0.053)	6.019 (0.189)	29.4 (0.2)
	90	0.722 (0.000)	307.9 (15.9)	2.913 (0.079)	6.472 (0.322)	33.8 (0.3)

Table S3: Results from Poreblazer structural analysis; all systems are at 300 K. ASA: Accessible Surface Area; PLD: Pore Limiting Diameter; MPD: Maximum Pore Diameter; FFV: Fractional Free Volume. Values in the brackets are estimates of the uncertainty. The chloride ions are consider as part of the polymer matrix.

5 Analysis of Radial Distribution Functions

Several radial distribution functions (RDFs) between different atoms in the model membrane are calculated. We employ this analysis to understand the interaction between different atoms of each component of the system. Since our main focus in this study is the behaviour of water inside a confined system, the major part of the RDFs analysis is focused on the oxygen atom (OW) of the water molecule interacting with other atoms in the system. All RDFs presented here are at 300 K.

5.1 RDFs of the oxygen atom of water

We start with the RDFs between the oxygen atoms of water molecule. Figure S12 shows the RDFs(OW-OW) for different levels of protonation and water content.

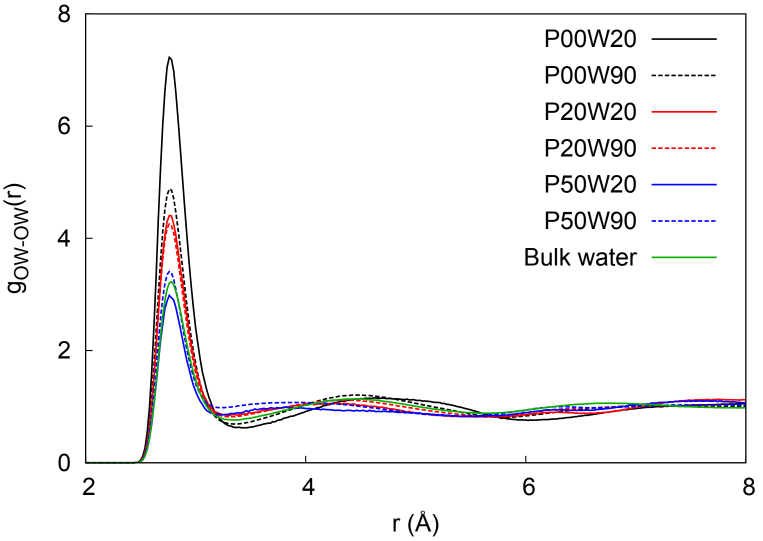

Figure S12: Radial distribution functions between oxygen atoms of water molecules (OW-OW). Black, red and blue colors correspond to P00, P20, and P50 protonation states, respectively. Solid lines correspond to W20 water content and dashed lines to W90 water content, respectively. Green line corresponds to the bulk water RDF.

The position of the first peak in all systems is independent of water content or protonation. This position is also the same as for the bulk water. At low water content W20, the height of the first peak decreases when the protonation level increases, implying that the electrostatic interactions favour the spread of water into the system. For the P00 and P20 systems, the first peak is higher than for bulk water. For the P50W20 system, the first peak is lower than the one of bulk water.

When water content is W90, the height of the first peak for P00 and P20 systems decreases, whereas for P50W90 it increases. When water content increases the height of

	Pure Water		P00W20		P00W90		P20W20		P20W90		P50W20		P50W90	
r(A)	3.34	5.64	3.46	6.06	3.38	5.80	3.30	5.74	3.3	5.70	3.24	5.58	3.26	5.52
CN	4.48	24.11	1.74	6.61	3.34	15.22	0.96	4.43	2.7	12.98	0.56	3.16	2.04	10.24

Table S4: OW-OW CN

the first peak tends to get closer to the one of bulk water (green line), as expected.

5.2 RDFs of the oxygen atom of water and the nitrogen atom of the PVAm chain

The second RDFs of interest is the one between the oxygen atoms of water molecule and the nitrogen atoms of the amine group of the PVAm chain. In the case of the charged systems (P20 and P50), there are two different types of nitrogen, describing two kinds of amine groups present in the polymer chain. There is a distinction between the nitrogen of a neutral monomer group, NH_2, labelled n3 and the nitrogen of a charged monomer group, NH_3^+, labelled n4. For a better understanding, the reader is referred to Figure S1 and Table S1 describing the nomenclature of the force field employed. We present the two RDFs (RDFs(OW-n3) and RDFs(OW-n4)) in Figure S13.

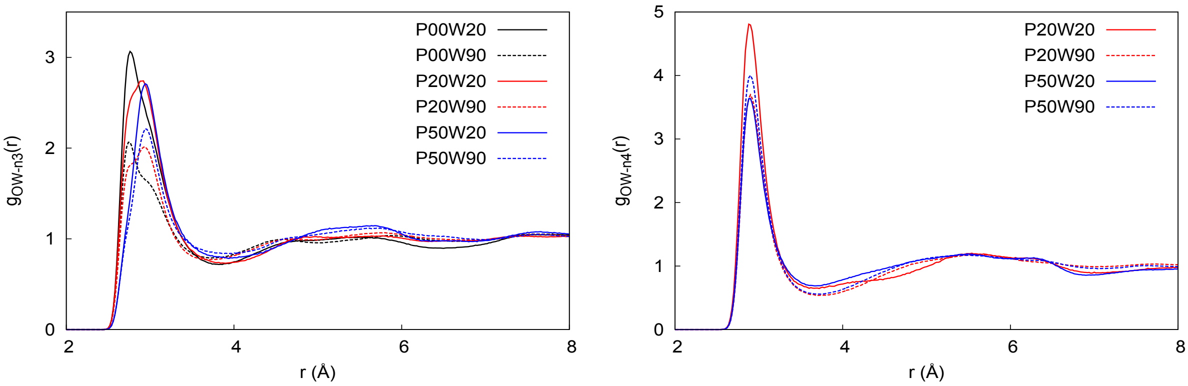

Figure S13: Left: Radial distribution functions between the oxygen of water (OW) and the nitrogen of the neutral amine group (n3), for the three protonation states P00 (black), P20 (red) and P50 (blue) at two water contents W20 full line and W90 dash line. Right: Radial distribution functions between the oxygen of water (OW) and the nitrogen of the charged amine group (n4), for two protonation states P20 (red) and P50 (blue), at two water contents, W20 (full line) and W90 (dash line).

First, let us focus on the RDFs(OW-n3) at W20 water content. The P00 system presents the highest first peak. When the protonation increases the height of the first peak decreases and its position is shifted to the right. This is due to the presence of chloride ions between the amine group and the water molecules. For W90 system, the

	OW-n3					
	P00W20	P00W90	P20W20	P20W90	P50W20	P50W90
r(A)	3.82	3.78	3.90	3.72	3.98	3.98
CN	3.24	1.53	2.36	1.11	1.22	0.78
	OW-n4					
	P00W20	P00W90	P20W20	P20W90	P50W20	P50W90
r(A)			3.70	3.76	3.68	3.74
CN			1.34	3.27	0.95	3.10

Table S5: OW-n3 OW-n4 CN

first peak remains in the same position, and the height decreases.

For the RDFs(OW-n4) at W20 the first peaks are in the same position for both protonation levels. The height of the peak decreases when the protonation increases. When water content increases, the behaviour of P20 and P50 systems has opposite trend. The height of the first peak decreases for the P20 system, whereas the height of the first peak increases for the P50 system.

If we now compare the RDFs(OW-n3) and RDFs(OW-n4) for the two protonation states and the two water contents, the maximum of each peak is at the same position. The height of the peaks for the RDFs(OW-n4) is bigger than the equivalent one for the RDFs(OW-n3) meaning that the electrostatic interaction favours the water molecules being next to the charged amine group.

5.3 RDFs of the hydrogen atom of water and the nitrogen atom of the PVAm chain

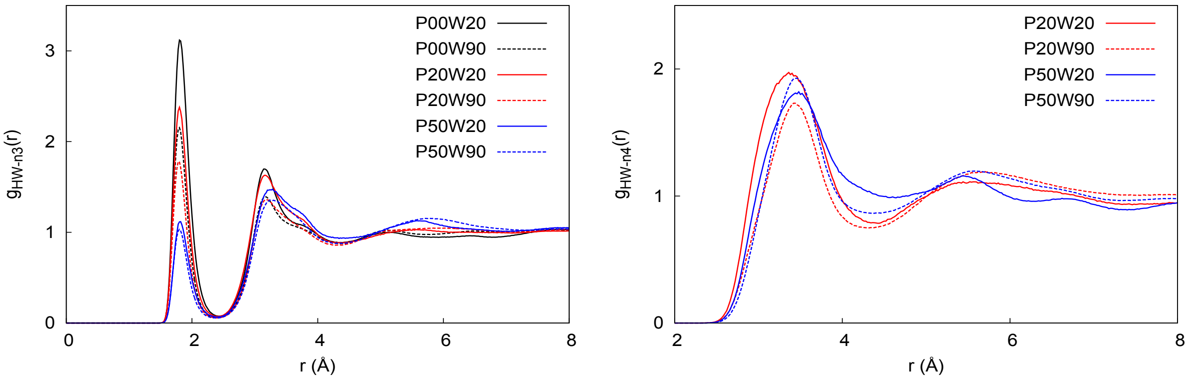

Figure S14: Left: Radial distribution functions between the hydrogen of water (HW) and the nitrogen of the neutral amine group (n3), for the three protonation states P00 (black), P20 (red) and P50 (blue) at two water contents W20 full line and W90 dash line. Right: Radial distribution functions between the hydrogen of water (HW) and the nitrogen of the charged amine group (n4), for two protonation states P20 (red) and P50 (blue), at two water contents, W20 (full line) and W90 (dash line).

HW-n3

	P00W20		P00W90		P20W20		P20W90		P50W20		P50W90	
r(A)	2.44	4.34	2.38	4.34	2.42	4.30	2.38	4.28	2.40	4.38	2.38	4.34
CN	0.58	4.54	0.23	2.43	0.30	3.06	0.14	1.70	0.08	1.61	0.05	1.00

HW-n4

	P00W20		P00W90		P20W20		P20W90		P50W20		P50W90	
r(A)					4.42	7.34	4.30	7.40	4.64	6.26	4.36	7.30
CN					4.14	19.55	9.20	58.18	4.08	10.39	9.54	51.08

5.4 RDFs of the oxygen and the hydrogen atom of water and the hydrogen atom of the amine group of the PVAm chain

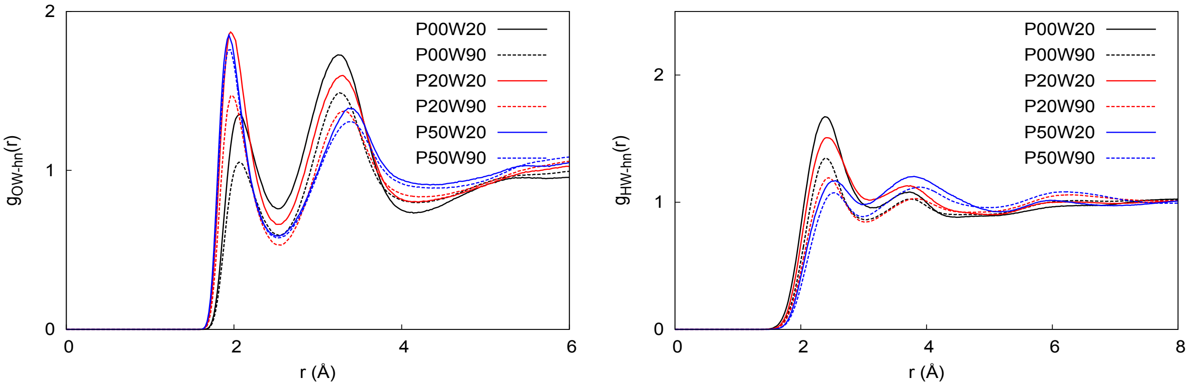

Figure S15: Left: Radial distribution functions between the oxygen of water (OW) and the hydrogen atom of the amine group, for the three protonation states P00 (black), P20 (red) and P50 (blue) at two water contents W20 full line and W90 dash line. Right: Radial distribution functions between the hydrogen of water (HW) and the hydrogen of amine group, for the three protonation states P00 (black), P20 (red) and P50 (blue) at two water contents W20 full line and W90 dash line.

OW-hn

	P00W20		P00W90		P20W20		P20W90		P50W20		P50W90	
r(A)	2.52	4.14	2.54	4.14	2.52	4.20	2.52	4.20	2.50	4.40	2.52	4.36
CN	1.18	8.56	0.57	4.55	1.36	8.50	0.70	4.88	1.17	8.82	0.80	5.74

HW-hn

	P00W20		P00W90		P20W20		P20W90		P50W20		P50W90	
r(A)	3.16	4.48	3.04	4.52	3.10	5.10	3.02	4.58	3.00	5.24	2.98	5.04
CN	3.58	10.29	1.53	5.83	3.10	14.51	1.42	6.18	2.12	15.23	1.28	8.94

5.5 RDFs of the oxygen and hydrogen atom of water and the chloride ion

We present in Figure S16 the RDFs between the oxygen and hydrogen atoms of water molecule and the chloride ion in P20 and P50 systems at two water contents, W20 and W90.

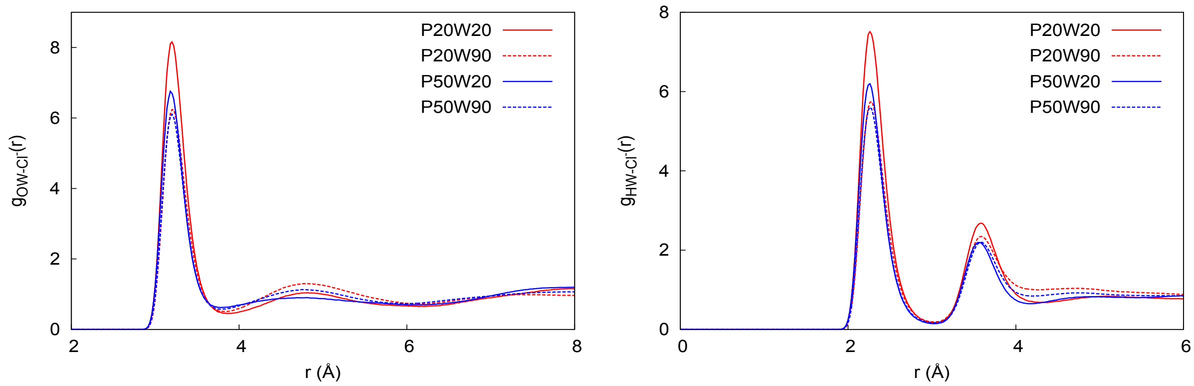

Figure S16: Left: Radial distribution functions between oxygen atoms of water (OW) and the chloride ion (Cl^-) for two protonation states, P20 (red) and P50 (blue), at two water contents, W20 (full line) and W90 (dash line). Right: Radial distribution functions between hydrogen atoms of water (HW) and the chloride ion (Cl^-) for two protonation states, P20 (red) and P50 (blue), at two water contents, W20 (full line) and W90 (dash line).

The RDFs (OW-Cl^-) for all cases have the same position of the first peak. The height of the peak decreases when water content increases. This result indicates that increasing water content improves the solvent effect of the water, the chloride ions are moving to the bulk water phase when the water content increases. This observation is confirmed, because in all cases the second peak increases when the water content increases, meaning that the chloride ion is gaining a second solvation shell.

OW-Cl

	P20W20		P20W90		P50W20		P50W90	
r(A)	3.88	6.14	3.84	6.14	3.78	6.18	3.78	5.98
CN	2.27	5.63	5.29	17.3	1.56	4.51	4.5	13.7

HW-Cl

	P20W20		P20W90		P50W20		P50W90	
r(A)	3.02	4.28	3.04	4.22	3.02	4.18	3.04	4.18
CN	2.20	5.35	5.14	14.1	1.50	3.55	4.38	11.26

5.6 RDFs of the chloride ion and the nitrogen atom of the PVAm chain

Finally, the RDFs between the chloride ion and the nitrogen of the amine group of the polymer chain is consider. As mentioned earlier in section 5.2, we are making a distinction between the two types of nitrogen atoms employed.

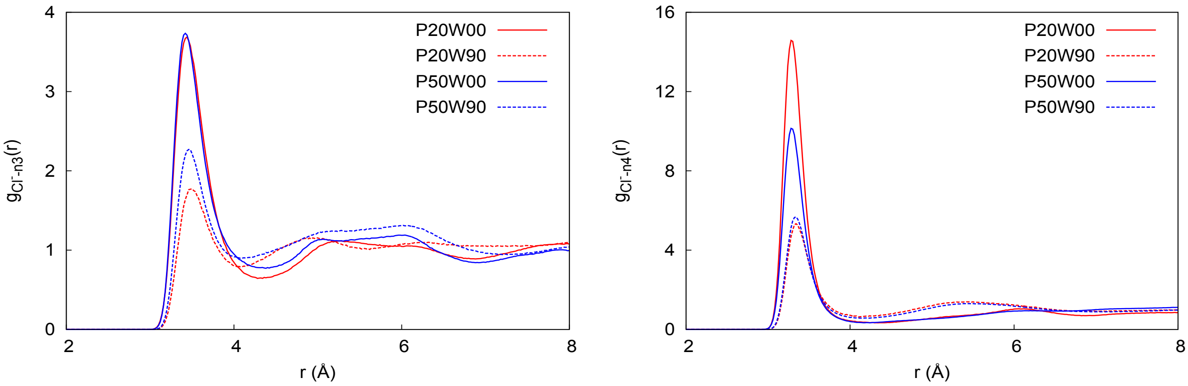

Figure S17: Left: Radial distribution functions between the chloride ion (Cl^-) and the nitrogen atoms of the neutral amine group (n3), for the two protonation states P20 (red) and P50 (blue), at two water contents W20 (full line) and W90 (dash line). Right: Radial distribution functions between the chloride ion (Cl^-) and the nitrogen atoms of the charged amine group (n4), for two protonation states P20 (red) and P50 (blue), at two water contents, W20 (full line) and W90 (dash line).

First, we consider the RDFs(Cl^--n3), i.e chloride ion and nitrogen of the neutral amine group. The first peak decreases when the water content increases and has its maximum in the same position. The distance of the chloride ion towards the neutral nitrogen (n3) is the same in both P20 and P50 systems.

Looking now at the RDFs(Cl^--n4), the first peak has the same behaviour as the first peak of the RDFs(Cl^--n3), it decreases when water content increases.

If we now compare the two sets of RDFs provided, the first thing we notice is that the intensity of the first peak is higher for the RDFs(Cl^--n4) for both water contents and protonation states meaning the electrostatic interactions are stronger with the charged nitrogen (n4) and have an ordering effect on the position of the ions.

When water content increases, the intensity of the second peak increases in all cases, the chloride ions are moving into the water phase. It is a confirmation of the analysis made in section 5.5 for the RDFs(OW-Cl^-).

Cl-n3

	P20W00		P20W90		P50W00		P50W90	
r(A)	4.28	6.82	4.08	5.62	4.38	6.92	4.08	7.26
CN	3.59	14.50	1.05	4.06	1.96	8.00	0.72	6.01

Cl-n4

	P20W00		P20W90		P50W00		P50W90	
r(A)	4.30	6.82	4.12	6.84	4.18		4.16	7.10
CN	1.88	3.96	0.53	2.36	2.82		1.24	5.60

6 Summary of mean-square displacement values for polymer, water and ion

In the Figure S18 we present some results from the long runs (200 ns) simulation, characterized in terms of mean-squared displacement (MSD) for PVAm, water and chloride ions.

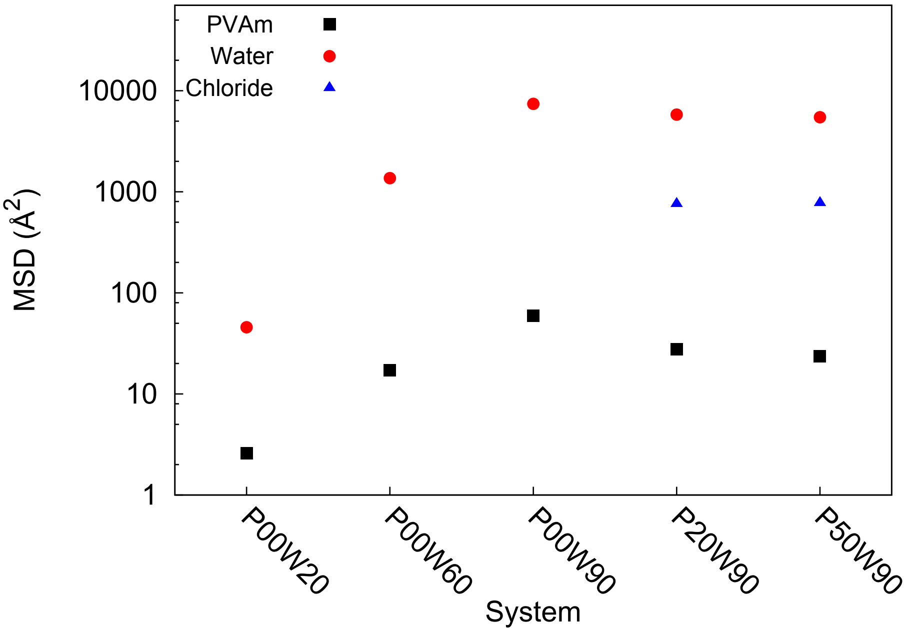

Figure S18: MSD value at the end of the 200 ns trajectory for water (circle), PVAm (square) and chloride ions (triangle), at 300 K for the P00W20, P00W60, P00W90, P20W90 and P50W90 system.

References

[1] MJ Frisch, GW Trucks, HB Schlegel, GE Scuseria, MA Robb, JR Cheeseman, G Scalmani, V Barone, B Mennucci, GA Petersson, et al. Gaussian 09, revision d. 01, 2009.

[2] Diana A Kondinskaia, Andrei Yu Kostritskii, Alexey M Nesterenko, Alexandra Yu Antipina, and Andrey A Gurtovenko. Atomic-scale molecular dynamics simulations of DNA-polycation complexes: two distinct binding patterns. *The Journal of Physical Chemistry B*, 120(27):6546–6554, 2016.