

Molecular simulation of a hydrated cation exchange membrane system used in reverse electro dialysis

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I. INTRODUCTION

Ion exchange membranes have a fundamental role in reverse electro dialysis (RED) technology [1]. In RED, membranes separate solutions with high and low salinity and allowing the extraction of energy due to salinity gradients. However, there are important drawbacks associated with membranes used in RED devices. Firstly, the cost of membranes represents a significant portion of the total investment (up to 80%) in RED technology [1], [2]. Also, most of them were originally designed for electro dialysis processes, due to the low state of development of polymers specifically fabricated for RED applications [1], [3], [4]. [4]. In consequence, efforts have been made to synthesize and explore alternative low-cost polyelectrolytes. These new membranes need to exhibit high selectivity for the transport of monovalent ions (typically Na⁺ and Cl⁻) [5], [6], and have both good performance and low cost to enhance the commercial competitiveness of this technology compared to other renewable energy sources [1], [2], [5].

The efficiency and power output of the RED system are directly influenced by the ionic transport properties of the membranes [4], [3]. The key properties of membranes used in RED include electrical resistance, permselectivity, mechanical strength, and chemical stability [1], [4]. The presence of multivalent ions in natural water can affect the permselectivity and electrical resistance of membranes [7], [8]. Particularly, divalent ions, such as Mg²⁺, Ca²⁺ and SO₄²⁻, could have a significant impact on voltage generation and decrease the efficiency and power density of RED system [5].

In general, the presence of multivalent ions has a more significant influence on cation exchange membranes [3], [9]. Mg²⁺ ions have a lower diffusion coefficient and exhibit stronger binding to the fixed charge groups of the membrane compared to monovalent ions like Na⁺ and K⁺

[9], [6]. This leads to a decrease in the fixed charge density of the membrane and simultaneous permeation of co-ions, reducing the membrane's permselectivity [6], [9], [10].

Improving membrane properties requires understanding the molecular structure and macroscopic properties relationship [4], [10]. Experimental and theoretical studies have been conducted to investigate the transport mechanisms of water and ions through membranes [11], [12], [13]. Theoretical studies, although scarce in this field, offer a higher level of detail on the phenomenological nature of the process concerning experimental observations [1], [11], [14]. In this sense, simulation and modeling tools facilitate the analysis and interpretation of experimental data and the generation of new experiments [4], [10]. In particular, a full atomic multiscale procedure is needed to deepen in the understanding of the ions' diffusion through ion exchange membranes and to investigate the relationship between their molecular structure and macroscopic properties to improve membrane properties [10], [11].

This study focuses on researching the structural characteristics of a segment of sulfonated polyether ether ketone (SPEEK) polymer at two different hydration levels using density functional theory (DFT) and molecular dynamics (MD) simulation techniques. We examine the role of hydrogen bonds and specific electrostatic interactions between the polymer's fixed-charged groups and the cations Na⁺ and Mg²⁺, given their practical importance in applications involving electro dialysis and reverse electro dialysis for transporting ions with multiple charges. Furthermore, molecular dynamics simulations are performed to explore counter-ion diffusion within a cation exchange membrane, considering variations in membrane hydration levels. This study provides valuable insights into the fundamental factors that govern ion transport and membrane performance in reverse electro dialysis applications.

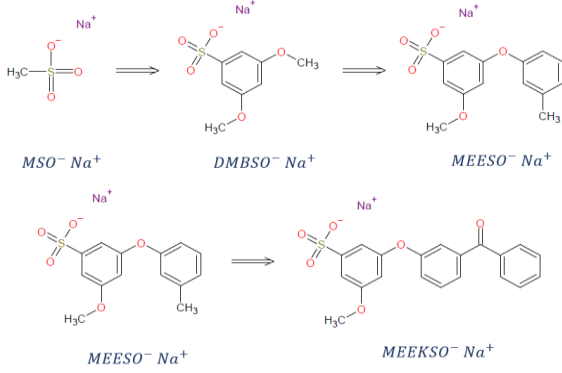


Fig. 1. Simulation strategy implemented to represent the monomer subunit of the SPEEK polymer ($MEEKSO^- Na^+$).

2. THEORETICAL METHODS

A. Membrane models

The basic repeating unit of the polymer was constructed in stages, as shown in Fig. 1., based on the simulation of four simpler structures: a) $MSO^- Na^+$; b) $DMBSO^- Na^+$; c) $MEESO^- Na^+$; and d) $MEEKSO^- Na^+$. Each structure was optimized using Density Functional Theory (DFT) formalisms. Additionally, a representative fragment of the SPEEK monomer, $MEEKSO^- Na^+$, was simulated with 11 and 16 water molecules.

The structure optimizations were performed using the Quantum Espresso package. The total energy was calculated using the generalized gradient approximation (GGA) and the revised Perdew-Burke-Ernzerhof functional for solids (PBEsol). Furthermore, the ionic nuclei were described using ultrasoft pseudopotentials, and the valence states of a Kohn-Sham electron were computed with plane waves. For all simulations, a cutoff radius for the kinetic energy of $E_{cut} = 822$ eV and an automatic k-point scheme based on the Monkhorst-Pack grid were employed, ensuring convergence and consistency of the final energy and bond distances between atoms.

To investigate ion transport within the membrane, we considered molecular dynamics techniques. The transport properties of ions Na^+ , Mg^{2+} , and Ca^{2+} have been investigated in the hydrated SPEEK polymer matrix under an external concentration of NaCl similar to that of seawater (0.5 mol/kg of water).

Initially, the results from the DFT simulations were utilized to construct a polymeric chain consisting of three monomeric subunits. This chain was then employed in the LAMMPS package for studying ion transport within the membrane. The final structure obtained from the DFT simulations was replicated to generate a model of the membrane composed of 216 subunits, considering hydration levels $\lambda = 11$ and 16.

The following simulation details were considered to

carry out the molecular dynamics simulations: (i) Molecular dynamics simulations have been conducted under temperature and pressure conditions of 298 K and 1 atm, respectively. (ii) Periodic boundary conditions were considered in all three spatial dimensions. (iii) Cutoff radius of 16 Å for short-range interactions. (iv) we are using the Particle-Particle-Particle-Mesh method (PPPM) to compute long-range interactions. (v) Integration of the equations of motion has been done using the Verlet algorithm with a time step of 1.0 fs.

B. Ions concentration in the membrane

The concentrations of Na^+ and the co-ion Cl^- within the membrane will be determined by applying the Donnan equilibrium model (Equation 1) and the Manning model, specifically developed for binary salts:

$$(\gamma_+^s \gamma_-^s)(C_+^s C_-^s) = (\gamma_+^m \gamma_-^m)(C_+^m C_-^m) \quad (1)$$

where γ_+^s and γ_-^s correspond to the activity coefficients of the cation γ_-^s in the solution and the membrane, respectively; and γ_-^m represent the activity coefficients for the anion in the solution and the membrane, respectively; C_+^s and C_+^m are the concentrations of the cation in the solution and the membrane; and C_-^s and C_-^m denote the concentrations of the anion in the solution and the membrane, respectively.

The Donnan equilibrium model enables us to estimate the distribution of ions based on the external concentration of NaCl solution. Additionally, the Manning model will be utilized to calculate the ion activity coefficients in polyelectrolyte solutions, providing further insights into the transport properties of the hydrated SPEEK polymer.

C. Calculation of diffusion coefficients

The self-diffusion coefficients were computed by calculating the mean square displacement (Equation 2):

$$\frac{1}{2d_\alpha} \lim_{t \rightarrow \infty} \frac{d}{dt} \left\langle \frac{1}{N} \sum_{i=1}^N |r_{\alpha,i}(t) - r_{\alpha,i}(0)|^2 \right\rangle \quad (2)$$

where α represents the Cartesian coordinates (x, y, or z); d_α is the dimensionality (1, 2, or 3); r is the position at time t ; N is the number of atoms or molecules.

Considering that system size effects can be significant and impact the diffusion coefficient calculation, the diffusion coefficient for the 'infinite' box size was determined using the correlation presented in Equation 3 [15]:

$$D_\infty = D(L) + \frac{k_B T \epsilon}{6\pi\mu L} \quad (3)$$

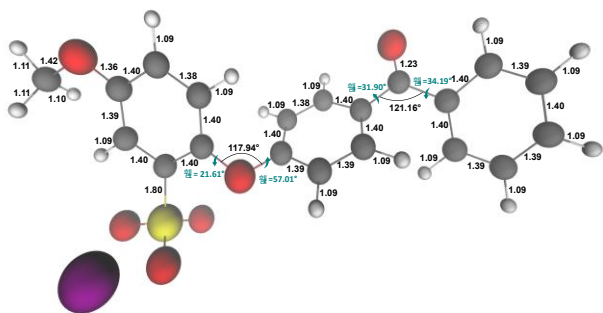


Fig. 2. Final configuration of MEEKSO- Na^+ segment (monomer subunit of the SPEEK polymer). Here, oxygen is in red, sulfur atom is in yellow, sodium is in purple, carbon is in gray and hydrogen atoms are in white.

where D_∞ is the self-diffusion coefficient for the infinite box size; $D(L)$ is the self-diffusion coefficient calculated for a cubic box with length L ; k_B is the Boltzmann constant, T is the absolute temperature, μ is the viscosity, and $\varepsilon = 2.83729$ is a dimensionless constant for an Ewald-type summation.

II. RESULTS

A. Final structure of MEEKSO- Na^+ segment

The final structure of the MEEKSO segment is shown in Fig. 2. The covalent bond distances, torsional angles θ_1 , θ_2 , θ_3 , and θ_4 , as well as the angles between the central C-O-C atoms of the ether group and the C-C-C atoms of the ketone, are also presented in Fig. 2. To validate the consistency of the final MEEKSO configuration, the bond distances of the structure were compared to experimental values reported in the literature. In most cases, the percentage of error was below 2.0%, with a maximum error percentage of 3.5%, demonstrating good consistency with experimental data [16].

In the hydrated structures of MEEKSO- Na^+ , it was observed that the water molecules are positioned near the functional group and the cation. The oxygen atoms tend to be in closer proximity to the cation, while the hydrogen atoms are closer to the functional group atoms. The presence of water facilitates the establishment of donor-acceptor type bonds between the cation and adjacent water molecules, as well as between the cation and the functional group of the polymer. Additionally, the formation of hydrogen bonds between water molecules and dative-type bonds between water molecules and the functional group can be observed. On average, it was determined that water molecules form an average of 2.36 dative bonds with other water molecules or charged groups.

B. Electron localization function and electronic charge density results

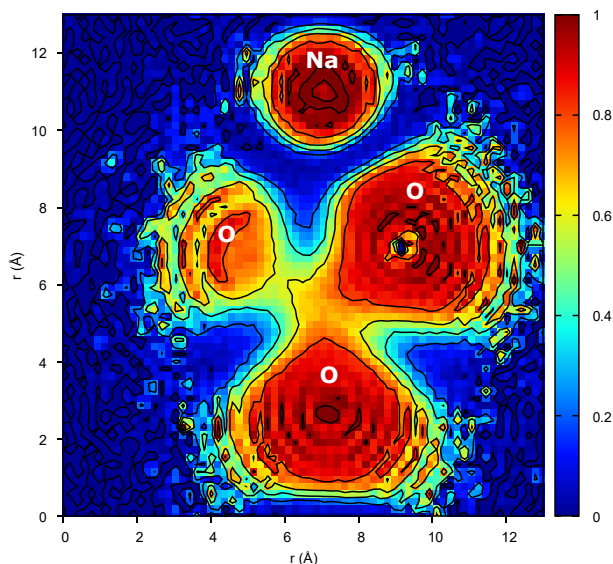


Fig. 3. Electron localization function

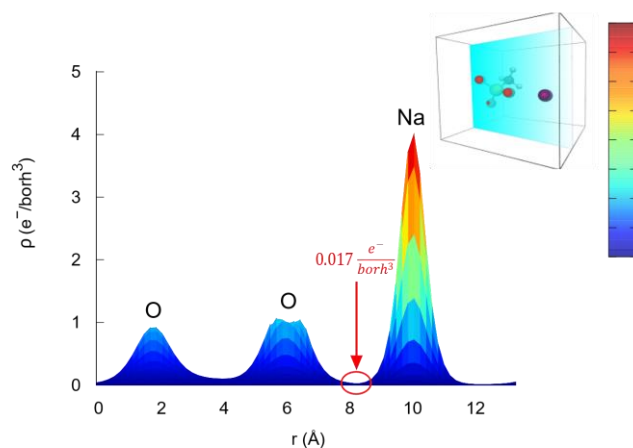


Fig. 4. Electronic density charge

Electron localization function (ELF) (see Fig. 3.) and electronic charge density results (Fig. 4.) were calculated for the final structure of MSO- Na^+ . Both analyses were performed on the plane that intersects two of the oxygen atoms of the anionic group and the cation. ELF results provide an estimation of the electron probability distribution in space, depicting the bonding and non-bonding regions between the atoms graphically. Fig. 3. illustrates a non-zero electron charge density region between the sodium ion and the hydrophilic sulfonic acid group, indicating the presence of interactions between them.

The electronic charge density profile (Fig. 4.) displayed three peaks: two corresponding to the oxygen atoms close to the cation and one associated with the sodium atom, which had the highest concentration of electronic charge density. A minimum electronic charge density ($\rho = 0.017 e^-/\text{bohr}^3$) was observed between the sodium ion and the nearest oxygen atom, suggesting a weak interaction. This magnitude can be considered low compared to values reported for covalent and ionic

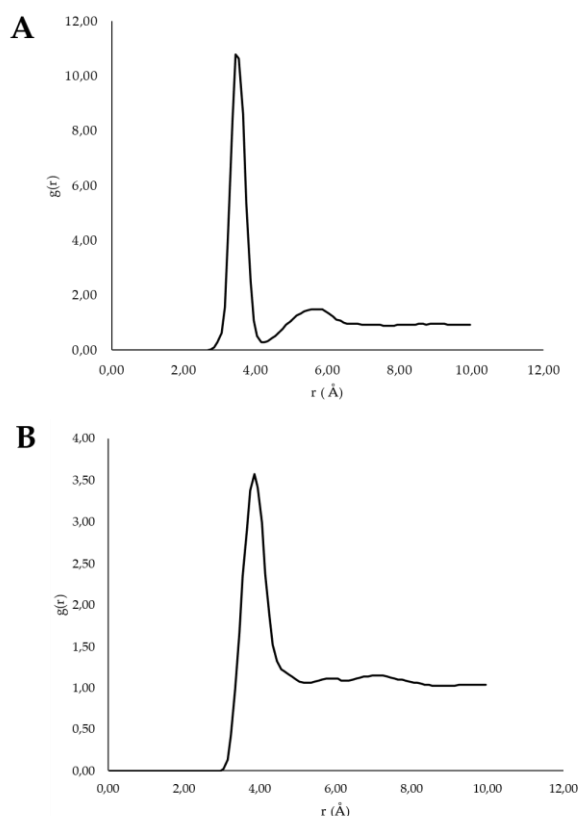


Fig. 3. Electron localization function

interactions ($\rho > 1 e^-/borh^3$ and $\rho > 0.1 e^-/borh^3$, respectively).

C. Molecular dynamic simulations

The initial molecular dynamic simulations were performed using 216 monomer subunits with sodium counter ions and the corresponding concentrations of sodium and chloride ions. These simulations utilized the pre-equilibrated cell obtained from the preceding DFT simulations. To validate the accuracy of the computational procedure, radial distribution functions (RDFs) were calculated for sulfur-sodium and sulfur-water oxygen atom pairs. The sulfur-sodium RDF exhibited a prominent peak at approximately 10.8 Å, indicating a strong interaction between sulfur and sodium ions. In the sulfur-water oxygen RDF, a less intense peak was observed, reaching its maximum at approximately 3.6 Å, suggesting a weaker interaction between sulfur and water oxygen atoms.

III. DISCUSSION & CONCLUSION

A. Final structure of MEEKSO segment

SPEEK is a semi-crystalline polymer that prefers conformations of lower energy, resulting from intramolecular and intermolecular interactions. Therefore,

the conformational energy of the molecule depends on steric interactions between non-covalently bonded atoms or groups and torsional angles.

The torsional angles and central angles obtained in this study were compared with conformational analysis studies of diphenyl ether and diphenyl ketone molecules in their minimum energy configurations. The torsional angles θ_1 and θ_2 in our work were measured as 21.6° and 57.0°, respectively, which are lower than the values reported in the literature for diphenyl ether (29° and 70° for θ_1 and θ_2 , respectively) [17]. Additionally, the calculated central angle C–O–C based on our simulation results was determined to be 117.94°, slightly deviating from the experimentally reported value for diphenyl ether (116° ± 5°) by approximately 1.7% [17]. Furthermore, the torsional angles θ_3 and θ_4 around the carbon of the ketone were found to be 31.90° and 34.19°, respectively, matching the values reported in the literature for diphenyl ketone (both 30°) [18].

The reduced rotation of the molecule around the ether functional group in comparison to diphenyl ether can be attributed to the presence of the sulfonic acid group (SO₃) in the SPEEK monomer, which restricts the internal rotation of the molecule around the oxygen atom and introduces greater steric hindrance. Considering the distances between covalently bonded atoms and the torsion angles of the final MEEKSO molecule structure, along with the relatively low error percentages compared to experimental values, it can be concluded that the DFT simulation results are consistent and that the obtained structure is in a minimum-energy configuration, in agreement with previously reported experimental data.

B. Chemical interaction between the sodium atom and the sulfonic acid functional group

According to the classification by Macchi et al. [18] and the results of the electron charge density analysis, the following criteria were considered to determine the nature of the interaction between the sodium atom and the nearest oxygen atom of the anionic groups in the monomer: (i) the magnitude of the charge density is greater than zero and less than 0.1 $e^-/borh^3$; (ii) the critical point is located near a nodal surface; and (iii) the Laplacian at that point is positive ($\nabla^2\rho > 0$). Based on these criteria and the classification, it can be concluded that the interaction between the sodium and oxygen atoms of MSO is of the dative type. In this type of interaction, the oxygen atom acts as a donor, while the sodium atom acts as an electron acceptor, resulting in the formation of a coordination bond between the two atoms

The previous results are also consistent with the distance between the sodium atom and the closest oxygen atom, which averages 2.46 ± 0.20. This distance is greater than the average distance observed for atoms that are covalently bonded, for example, the bond distance between oxygen and sulfur (1.49 ± 0.01) and sulfur and

carbon atoms (1.78 ± 0.01). Furthermore, this distance is in line with the distances reported for dative bonds and is lower than that of the ionic bond.

C. Molecular dynamic simulations

The analysis of the radial distribution function (RDF) provides valuable insights into the interactions and spatial arrangement of particles within a system. The RDF analysis, as shown in Figure 5, confirmed the reliability of the computational approach as the results were found to agree with previous findings [20], [21], [22]. It was observed that variations in the intensity and displacement of the RDF peaks were influenced by the degree of hydration and the degree of sulfonation of the polymer. Specifically, higher degrees of hydration led to greater displacements in the intensity of the first peak. Additionally, differences in the sulfonation level of the polymer also contributed to variations in the RDF peaks. These observations highlight the significance of hydration and sulfonation in shaping the spatial organization and interactions within the system.

The determination of ion diffusion coefficients is a crucial objective in the proposed model. This analysis aims to provide significant insights into the impact of multivalent ions on the system, specifically focusing on their specific interactions with the hydrophilic sulfonic acid groups. Additionally, the investigation seeks to assess the influence of co-ions within the system. Furthermore, this study offers valuable insights into the role of water in facilitating ion transport across the membrane. By examining these factors, a comprehensive understanding of the ion dynamics and the role of water in the transport process can be achieved.

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