



Structural properties of cation exchange membranes: Characterization, electrolyte effect and solute transfer



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ABSTRACT

Experimental investigations have shown that the presence of electrolytes has a strong influence on the transfer of neutral organic solutes through ion exchange membranes used in electro dialysis. It was further demonstrated that this influence is due to the impact of the membrane counter-ions on the noncovalent interactions existing between the hydrated and charged polymer chains in the membrane.

The aim of this work is to investigate the structural properties of hydrated CMX membranes equilibrated with different counter-ions. Different methods, such as Infrared spectra (IR), contact angle and Differential Scanning Calorimetry (DSC) measurements, were used to characterize the membrane samples soaked in different electrolytes. In addition, IR spectra were calculated using a quantum mechanics approach and compared with the experimental ones. Shifts of characteristic IR peaks as function of membrane ionic form were observed in both experimental and computed spectra. Both spectra present shifts to lower wavenumber in presence of cations with higher hydration number. The contact angle of CMX membranes also increases in presence of more hydrated ions revealing a decrease of the hydrophilicity of the membrane. Concerning DSC, the freezing temperature of the water entrapped in the membrane polymeric network soaked with different electrolytes was measured. A shift at lower temperature was found for more hydrated trapped ions. The computational and experimental membrane structural properties were correlated with the corresponding transfer properties (sugar fluxes) and a good agreement was obtained.

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1. Introduction

The increasing demand of natural resources as raw materials is difficult to face, especially in the view of sustainable development. However, nowadays, considering the balance between Earth capabilities and human demand, it is not more possible to postpone the introduction of sustainable development constrains [1]. A possible way to contrast the increasing human demand is the process intensification that means improvement in plant efficiency, minimization of energy consumption and waste production, thus reducing costs and environmental impact.

Membrane technologies can play a primary role considering their lower energy consumption (in comparison with traditional methods), their capability to transport in an efficient and selective

way specific compounds (recycling of water, chemicals and/or raw material), while their potential to boost the reaction processes and scale up can decrease the plants size [2–4].

In the frame of process intensification for complex fluids, the electro dialysis has found a second life. In the past decades, electro dialysis was widely applied in brackish water desalination, but nowadays, its potentialities are investigated to improve the process performances in chemical, food and pharmaceutical industries such as: wine productions (cold stabilization), deacidifications of fruit juice, whey demineralization, treatment of brines or lixiviates, production of green chemicals building blocks (organic acids), purification of saccharides, textile industry waste treatment [5–9].

However, the bottleneck for the spreading of membrane applications is in their high sensitivity to the composition of the feed solution, which makes the prediction of system performance difficult. A strong impact of the ions on the membrane transport properties was discovered in nanofiltration (NF) and electro dialysis (ED) processes. Most of the results, found in literature,

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concern the case of NF and only few of them the case of ion exchange membranes used in ED. For instance, the influence of the ionic composition on the transfer of a neutral solute through nanofiltration membranes was first reported by Wang et al. [10] in the case of sugar (glucose or sucrose)/NaCl solutions. It was shown that the transfer of sucrose is weakly affected by the presence of the electrolyte. On the contrary, the transfer of glucose was found to increase for increasing NaCl concentrations. In 2005, Bouchoux et al. [11] have established a relationship between the hydration of the ions and the mass transfer increase of glucose in presence of salt. Boy et al. [12] made a step forward, pointing out that the diffusion flux of sugars (xylose, glucose and sucrose) through a NF membrane, in presence of various electrolytes (NaCl, Na₂SO₄, CaCl₂, MgCl₂), is mainly fixed according to the influence of the electrolyte on the solute properties. Other evidences of the salts effect on the transfer of organic molecules through NF membranes have been also observed with PEG (poly ethylene glycol). The transfer of this molecule was investigated by Bouranene et al. [13] for inorganic NF membrane, as well as by Escoda et al. [14] with an organic NF membrane. Both works have demonstrated that the presence of salts (KCl, LiCl, MgCl₂) increases the transfer of PEG through the membrane and that the salt effect depends on its concentration as well as on its hydration. Electrodialysis can be applied in the separation of small organic ions from salts [15,16], but only few work are focused on the electrolyte effect on the transport properties of the membrane. In particular, in a recent work dealing with the transfer of neutral organic solutes through cation-exchange membrane in diffusion condition, Galier and Co-workers [17] found that the fluxes of three sugars, through a CMX membrane (Neosepta) equilibrated with Na⁺ are more than twice with respect to the fluxes through the same membrane but equilibrated with Mg²⁺. Moreover, using a specific procedure, able to discern whether the effect of ions is caused by their presence in the solution or in the membrane (as counter-ions), they pointed out that the ions inside the polymer matrix are the principal cause for the observed trend. A successive quantum and molecular mechanics modeling work showed that the noncovalent interaction energy per water molecule or water wire between hydrated polymer chains and equilibrated with different cations correlates with the sugar fluxes values and depends on the counter-ion. A water wire is defined as the shortest path of water molecules connecting two oxygen atoms of SO₃⁻ groups located in two different chain fragments of the membrane [18].

The analysis of the effects of various electrolytes on some key characteristics of CMX membrane is the aim of this work. To achieve this objective, experimental characterizations and calculation of infrared peaks are carried out. Hence, this work provides useful information to understand, at the molecular level, the mechanisms at the basis of the performance of these membranes in similar conditions. Moreover, this work aim to be a nice starting point for future fundamental works concerned with the mechanisms of organic and inorganic solute transfer through membranes for electrodialysis, taking into account the effect of applied current density and other process parameters.

The infrared spectra of a CMX membrane soaked in various electrolytes, are calculated in the framework of Density Functional Theory and compared with measured experimental spectra. In fact, molecular vibrations are very sensitive to changes in the environmental conditions. A relationship between the presence of different cations and the shift of characteristic infrared peaks was demonstrated by Falk [19] with Nafion based membranes. In particular, he has pointed out that, in Nafion membrane, the effect of the cation is highly identifiable in the water and SO₃⁻ vibrational modes properties, influencing the energy of these vibrations, thus their position in the IR spectra.

Both contact angle and differential scanning calorimetry (DSC)

methods are also used in this work. The first was chosen for its simplicity and because it is known that changes in contact angle are related to modifications in the membrane surface properties. Thus, this is a way to characterize the feed-membrane interface according to the environmental conditions. DSC is also used as it gives information on the sample bulk allowing investigation of the state of the water molecules in the membrane as function of the different cations [20,21].

2. Materials and methods

2.1. Infrared frequencies computational details

The IR spectra were computed in the framework of the Density Functional Theory (DFT) by using the hybrid functional X3LYP [22]. Structural models, formed by one cation, one or two functionalized monomers and one water molecule, were used to describe the noncovalent interactions between the cation functional groups and water molecule. In order to take into account different water arrangements in the models containing divalent cations, two initial configurations were considered for Mg²⁺ and Ca²⁺ cations: the first, with one water molecule in a central position with respect to the two SO₃⁻ groups and the other more external. More information on the construction of the molecular models used in the computational IR analysis can be found elsewhere [23]. The model geometries were fully optimized to a minimum of energy after which the vibrational analysis was performed.

Since the aim of this work is a qualitative comparison between theoretical and experimental vibrational frequencies in order to elucidate the counter-ions effect, these simple models can be considered appropriate for this purpose. A starting geometry with the same high theory level was not available for NH₄⁺, thus the vibrational modes of this cation were not computed here.

All the calculations were performed by NWChem 6.1 [24], an ab initio computational chemistry software package with extensive capabilities for large scale simulations of chemical systems. Triple- ζ basis sets were used for the geometry optimization and the vibrational analysis. On C, H, S and O atoms a "6-311G**" basis set was applied while the "6-311+G**" set was used on the cations. The reliability of the used basis sets and functional was tested in previous works [25,26]. The convergence criteria for the optimization of the model geometries, based on Cartesian displacement and gradient thresholds were set as tight [27], while the energy convergence threshold, for the self-consistent field procedure, was imposed to 10⁻⁸ a.u. and the root-mean-square of the electron density to 10⁻⁶ a.u.

2.2. Membrane and membrane conditioning

The membranes used in this work are CMX membranes (Neosepta), cation exchange membranes of sulfonated polystyrene-divinylbenzene. Before the characterizations, the membrane samples were conditioned following the NF X 45-2000 standard procedure [17]. This treatment consists of a washing cycle with acid (HCl), base (NaOH) and electrolyte solutions to clean the membrane from eventual impurities due to the manufacturing process and to equilibrate the membrane with the different cations. The complete procedure is reported in previous work [17,23]. The differently equilibrated membranes were stored in their own electrolyte solutions. Before performing the analysis such as IR and DSC, the membrane was washed in ultrapure water to remove the excess of salt. The ultrapure water in the washing bath was exchanged until no more increase of its conductivity was measured. For all the electrolyte solutions, only salts containing chloride as anion were used in order to avoid any secondary effects that could

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