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### Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci



## Correlation between macroscopic sugar transfer and nanoscale interactions in cation exchange membranes



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#### ARTICLE INFO

# Article history: Received 10 April 2015 Received in revised form 19 June 2015 Accepted 21 June 2015 Available online 29 June 2015

Keywords: QM/MM modeling Cation exchange membrane Counter-ion effect Chain – chain interactions Sugar transfer

#### ABSTRACT

Previous experimental work has shown that the transfer of organic solutes through ion-exchange membranes depends on the membrane counter-ion and that this dependence is probably linked to the interactions taking place at the nanoscale inside the membrane matrix. In this paper, a computational approach is carried out, combining quantum mechanics and molecular mechanics to determine the interactions occurring at the nanoscale, taking a cation exchange membrane as example. Building blocks are first accurately studied at high level of quantum theory, before being merged in macromolecular models. The computed interactions are then compared to the experimental values of the solute flux in order to point out the nanoscale mechanisms governing the solute transfer. The computed glucose – polymer fragment interactions, related to the sugar solubility inside the membrane, are found to be almost independent from the membrane counter ion. On the contrary, significant variations of the chain - chain interaction, i.e. the interaction energies per trapped water molecule or hydrogen bonding wire connecting the polymer fragments, were observed according to the cation. Moreover, a correlation was pointed out with the experimental sugar fluxes obtained with 3 different sugars. Increasing chain – chain interactions inside the membrane was found to give decreasing sugar flux. Then this work shows that the cohesion energy between the polymer fragments fixes the dependence of the sugar flux versus the membrane counter-ion. The crucial role of the water molecules coordinating the cations is also highlighted.

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#### 1. Introduction

In agreement with the Global Footprint Network, human demand exceeds the regenerative capacity of our natural ecosystem [1] thus process intensifications are highly required.

Process intensification is a concept introduced in the chemical industry in the beginning of our century to minimize the environmental impact, reducing energy and raw material consumption, increase the safety and reduce the plants size. Membrane processes meet these preliminary conditions due to 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), their potential to boost the reaction processes and their peculiarity to be built in modules can decrease the plants

size [2-4].

An example of process intensification by membrane processes is the desalination of water. The request of fresh water is increasing while its sources are decreasing, thus desalination systems are more and more growing [5]. In this context, membrane processes can play an important role. For example the energy required to desalinate seawater by evaporation is approximately 18–37 kW h m<sup>-3</sup>, while the energy required using membrane technology is lesser than 4 kW h m<sup>-3</sup>. This difference in energy consumption explains why, membrane technology is used to produce more than 50% of desalinated seawater [6,7].

In addition, many other applications can be addressed by membrane technology to improve the process performances such as: wine productions (cold stabilization), deacidifications of fruit juice, whey demineralization, treatment of brines, lixiviates, production of green chemicals building blocks (organic acids), purification of saccharides, textile industry waste treatment etc.

Nevertheless, the expansion of membrane processes still suffers from the fact that it is hardly possible to predict their performances when new applications or stronger constraints are

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considered. In fact, these processes are very sensitive to the composition of the feed solutions and to the environmental conditions in general.

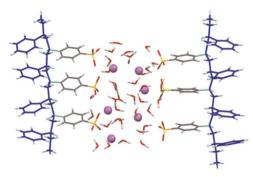
In the process intensification framework, Electrodialysis (ED), a mature membrane process, can take a significant place. ED is applied from more than 50 years in the brackish water desalination or in the desalination of sea water to produce drinking water. But in the last decades other membrane processes, like nanofiltration or reverse osmosis, became predominant in such applications. However, nowadays, electrodialysis is investigated and applied in a large number of projects dealing with process intensification in environmental, chemical, food and drugs industry [8].

Recent experimental studies have demonstrated that the ionic composition of the solution, i.e. the nature and concentration of the ions, has a significant impact on the transport of neutral organic matter through ion exchange membranes like those used in electrodialysis [9]. Solvent (water) and organic matter (saccharides of different molecular weights) transfer were measured, in a diffusion regime, through a CMX cation exchange membrane (sulfonated polystyrene-divinylbenzene, Neosepta Tokuyama corp. Japan) soaked in different electrolyte solutions: NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub> and NH<sub>4</sub>Cl. It was found that the sugar fluxes are influenced by the membrane counter ion. For xylose, glucose and sucrose, decreasing flux was observed when the membrane is equilibrated with cations of increasing hydration. It was concluded that the solute transfer modification was mainly due to a modification of the membrane properties. But no variations of the membrane macroscopic characteristics were observed indicating that membrane modifications at the nanoscale are involved. The understanding of the mechanisms, at the molecular level, and interactions governing such trends is thus crucial to optimize the Electrodialysis process.

Thus, in this work, the correlation between nanoscale interactions occurring in a CMX membrane on one hand and the sugar transfer on the other hand is investigated by means of a combined molecular modeling free from adjustable parameters. Previous abinitio (quantum) studies have highlighted the crucial role of noncovalent interactions, and in particular hydrogen bonding, on the polymeric membrane properties, such as the ion exchange capacity, molecular affinity and the non-linear increase of the water sorption as function of additive content in polymer [10-13]. In particular, the present work is focused on the noncovalent interactions and molecular mechanism by which the counter-ions, used to soak a cation-exchange membrane, affect the fluxes of sugars. Building blocks, such as the hydrated polystyrene monomers neutralized with the different cations, Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup>, and the hydrated glucose were assembled in supramolecular structures i.e.: glucose - polymer complexes and double polymer chain fragments, representing different parts of the macroscopic system. Hence, these building blocks were first studied with a high level of quantum theory, before being assembled in supramolecular models. In their turn, these larger models were studied by means of a Quantum and Molecular Mechanics approaches (OM/MM). Then polymer – sugar interactions as well as chain – chain interactions are computed and compared to the sugar flux obtained experimentally.

#### 2. Computational approaches

An accurate assessment of noncovalent interactions requires quantum chemical approaches; however, quantum calculations need also long computational times. When noncovalent interactions at the nanoscale have to be investigated in large systems, as in this work, Quantum Mechanics and Molecular Mechanics (QM/MM) approaches have to be applied. QM/MM methods have



**Fig. 1.** Model used in QM/MM calculations. MM region in blue color, boundary in green color, other colors indicating the QM region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

proven to be reliable and helpful in investigating such large systems [14–16]. Thus, here, building blocks were first studied at quantum level and then for larger systems (more than 100–150 atoms) a QM/MM method was adopted.

In the QM/MM approaches, a large system is divided in two regions: a classical part (less computational expensive) treated at MM level and a quantum zone. In general, the non-interacting atoms of the macromolecular system define the classical region, whereas the atoms involved in short range interactions, such as hydrogen bonds and electrostatic interactions, delineate the quantum region. In Fig 1, an example of quantum and classical regions are shown.

The total energy of the large model (Fig. 1) is calculated as the sum of the energies of classical and quantum parts. As regards, instead, the geometries optimizations carried out by the used QM/MM method, a step by step energy minimization of the two separated regions is carried out. In the first step, the QM region is optimized fixing the MM atoms. Afterwards a MM step is run for the optimization of the classical region with QM atoms characterized by a quantum potential; the cycle is repeated until the convergence criteria are reached.

A conformational research of the sulfonated styrene fragments was also carried out in this work. This task was performed at Molecular Mechanics level by using the Avogadro code [17] and the Universal Force Field [18]. A weighted rotor search of the more probable conformers and subsequently MM optimizations (500 steps and convergence energy criterion at  $10^{-8}$  a.u.) was carried out. The energy of each conformer was then calculated at quantum mechanics level to select the most stable among them.

Both pure QM and QM/MM calculations were performed using NWChem 6.1 [19,20] code in the frame of Density Functional Theory and using the X3LYP [21] hybrid functional due to its reliability in the modeling of noncovalent interactions in polymer-solute – water systems [10-12]. Basis sets and convergence criteria were set depending on the size of the quantum models or quantum parts in the investigated macromolecules such as the hydrated counter-ions, glucose and large models as shown in Fig. 1.

The hydration of counter-ions attached to the sulfonated monomers was computed by adding water molecules to cations one by one and then optimizing at QM level the structures of the complexes, obtained after each  $\rm H_2O$  insertion. The QM optimizations allow the relaxation of the entire water cluster around each cation finding new water arrangements at each insertion steps. The criteria, used for the QM geometry optimizations, were the maximum and root-mean-square of total energy gradients equal to  $4.5 \times 10^{-4}$  and  $3.0 \times 10^{-4}$  a.u., respectively, and the maximum and root-mean-square of the Cartesian displacement vectors equal to  $1.8 \times 10^{-3}$  and  $1.2 \times 10^{-3}$  a.u., respectively. The energy convergence threshold for the quantum self-consistent field

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