Modelling facilitated transport in Polyvinyl amine membranes for CO2 capture: insights from Molecular Dynamics and PC-SAFT EoS.

Modelling facilitated transport in Polyvinyl amine membranes for CO_2 capture: insights from Molecular Dynamics and PC-SAFT EoS.

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Introduction

The removal of CO_2 from flue gas in power plants or energy-intensive industries is one of the main ways to reduce the increasing CO_2 atmospheric levels, that cause global warming. Among the various technologies identified for this aim, such as solvent absorption and adsorption, membrane separation is considered as the most flexible and environmentally friendly option. For this reason the project NANOMEMC^2 (www.nanomemc2.eu) aims at developing innovative membranes with improved CO_2 capture ability, which can make the capture less costly. The project focuses on *Facilitated Transport* (FT) membranes, that are endowed with higher selectivity values with respect to conventional ones. Such materials bear amine groups that, in presence of humidity, promote reactions that boost the transport of CO_2 while not affecting the other gases. A possible reaction route is shown in Figure 1.

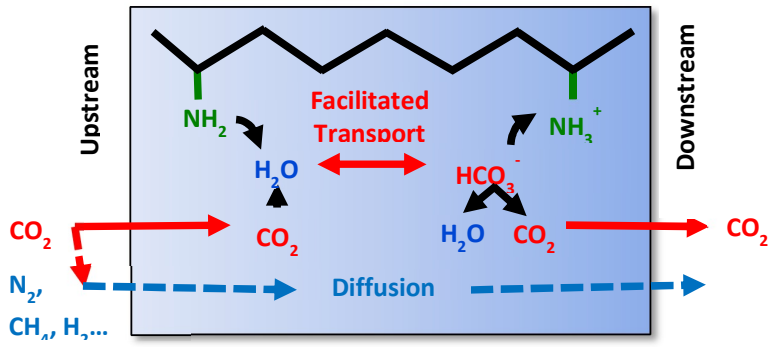

Figure 1: Facilitated transport of CO_2 across a facilitated transport polymeric membrane bearing amine groups

Such process has selectivities comparable to chemical absorption, but it is less energy intensive. However, contrary to what happens for amine absorption, very few modelling studies are present in the literature concerning FT membranes. In the present work therefore we aim to partially fill this lack by a thermodynamic and kinetic analysis of CO_2/H_2O/polyamine systems. In particular, we consider polyvinyl amine (PVAm) for which we built molecular and macroscopic models of the humidified membrane and estimated the sorption and diffusion coefficients of CO_2, which enable to predict the FT membrane performance. Molecular Dynamics (MD) and PC-SAFT EoS were used to represent the process of sorption of CO_2 in such a complex, strongly polar environment.

PC-SAFT EoS modelling. First, the binary system formed by H_2O and PVAm was studied. Different sets of associating sites can be identified, as depicted in Figure 2. In particular, self associating and induced association were assumed for water and PVAm,

respectively. The comparison with experimental data of water vapor solubility in PVAm allowed to choose the best associating scheme. Then, the ternary system formed by CO_2, water and PVAm was considered. In this case, we compared the results obtained by considering CO_2 as an associating and non associating species. Such approach allowed to precisely identify the effect of relative humidity on the CO_2 sorption in the membrane, in a completely predictive way, and ultimately evaluate the capture performance of the membrane (Figure 3).

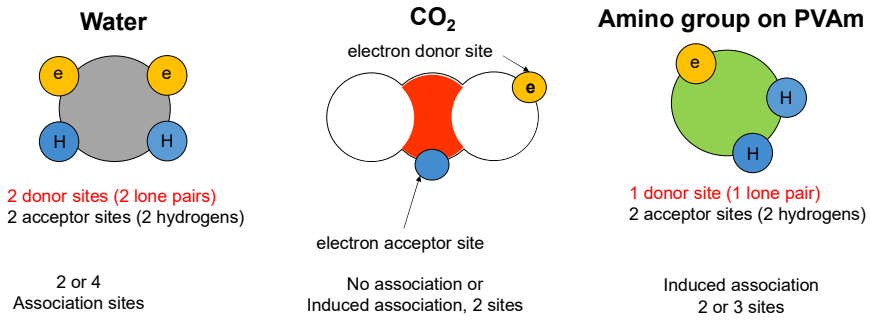

Figure 2: Possible association sites for PC-SAFT EoS in water, CO_2 and PVAm molecules

MD simulations. Molecular models of solvated PVAm membranes were constructed by explicitly considering a binary mixture of short chains (20 monomers) of PVAm and water. Structural characteristics of these systems, such as pore size distribution and pore limiting diameter were obtained at different levels of hydration and correlated to self-diffusion of water in these structures. Results for diffusion of water from molecular dynamics, experiments and scaling model of Phillies (1989) are compared in Figure 3.

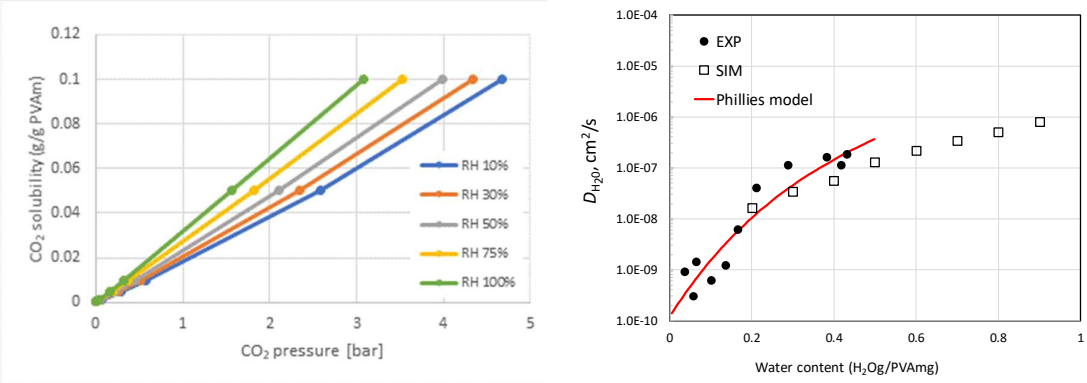

Figure 3. Left: CO_2 solubility in PVAm from PC-SAFT as a function of hydration. Right: self-diffusion of water in model PVAm membranes as a function of water content from MD (SIM), model by Phillies and experiments (EXP).

Conclusions. Sorption and transport of CO_2 in humidified PVAm membranes were calculated via macroscopic and microscopic models, to predict the CO_2 capture performance of FT membranes. The two approaches show good mutual agreement, and are in line with the available experimental data. To our knowledge, this is the first successful attempt to rigorously simulate the process of facilitated transport in membranes for CO_2 capture.

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