# *Mathematical description of water vapor influence on gas separation performance in hydrophobic polyimides*

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Water vapor is frequently present in membrane-based gas separation applications[1,2] and its influence must be taken into account for a reliable characterization of the separation process. In case of hydrophobic polymers, such as aromatic polyimides, the low water uptake observed in sorption experiments[3,4] does not correspond to a negligible effect on the membrane gas transport properties, which can be severely affected[5,6]. Although a small literature is dedicated to the description of the physical mechanisms of gas permeation in the presence of water, the implementation of a theoretical model in membrane processes simulations represents a great opportunity to improve the separation process design.

In the present study, the influence of the water vapor on the gas transport properties of several hydrophobic polyimides, characterized in our lab (6FDA-6FpDA, Matrimid, 6FDA-mHAB and 6FDA-pHAB), or obtained from literature (CARDO-ODA and NTDA-BAPHF) has been analyzed, in different experimental conditions and for several penetrants ($CH_4$, $N_2$, $CO_2$, $H_2$ and He).

Interestingly, very similar trends have been observed at increasing the relative humidity (R.H.) of the feed stream: the gas permeability decreased at increasing the water vapor concentration in the membrane, with different extent of variation for the considered polymers.

The monotonic decrease of permeability coefficient is explained in terms of competitive sorption; indeed, due to its higher condensability, $H_2O$ is absorbed preferentially in the polymer matrix, reducing the amount of free volume available to the other gas to permeate across the membrane. The physical phenomenon can be explain from the mathematical point of view, with a simple but effective model based on the free volume theory[7]. Indeed, starting from the solubility of water vapor in the polymer, retrieve from sorption isotherms, the relative humidity of the feed stream is correlated with the water concentration in the membrane. The residual fraction free volume available for the less condensable penetrants to diffuse across the selective layer is then evaluated accounting for the presence of water molecules within the polymer. Finally, the gas permeability calculation is obtained by means of a simple approach based on the free volume theory[7], using only two adjustable parameters.

In addition, for those materials whose pressure-volume-temperature data are available, a more accurate degree of description could be achieved, considering the effect of the presence of water on solubility and diffusivity, separately. Solubility of different gases and water vapor in the polymer matrix can be predicted by means of the non-equilibrium thermodynamic model[8] (NELF, non equilibrium lattice fluid), whereas the free volume theory could be used in its original formulation to describe the variation of the diffusion coefficient at different water vapor concentration in the membrane.

In spite of its extraordinary theoretical simplicity, the model proposed is able to describe consistently and accurately the experimental data, providing a physical sound representation of the mechanism of gas transport in the presence of water, at all the temperatures and activities values inspected.

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