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**Molecular modeling of thermodynamical properties of the poly (vinyl alcohol) active layer used in ethanol pervaporation dehydration processes**

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**Introduction**

Using ethanol as alternative fuel requires to separate ethanol/water azeotropic mixtures (ca. 4 wt% water). Such a separation can be performed via azeotropic distillation, molecular sieves or pervaporation. As pervaporation separation is almost a passive separation process based on the higher permeability of hydrophilic membranes for water than for ethanol, it is considered as less energy-consuming and more environment-friendly process. For maximizing fluxes at industrial scale, a significant gradient in partial vapor pressure is applied on both sides of the membrane [1]. Although inorganic membranes based on ceramics or zeolites attracted more research attention in recent years, most of industrial pervaporation membranes rely on hydrophilic polymers as reviewed by [2]. Poly(vinyl alcohol) (PVA) is one of the preferred water-soluble polymers as PVA films exhibit high selectivity, tensile strength, elongation and flexibility [3]. PVA is produced from polyvinyl acetate after hydrolysis of acetate groups by saponification. Along with polymerization degree, the hydrolysis ratio enables to modulate the properties of the polymer either before or after processing. Chemical cross-linking and annealing can additionally reduce free-volumes available for transport and therefore increase PVA selectivity. We argue that the effective membrane selectivity in process conditions arises more particularly from the asymmetric swelling (*i.e.* free volumes) of the active PVA layer when a strong vapor pressure gradient is applied. As a result, the membrane should not be considered as a homogeneous material with equivalent properties but as a material with property gradients. Retro-engineering should therefore seek optimal membrane asymmetry by adapting molecular mass distributions, local hydrolysis and cross-linking ratios to specific needs.

The final goal of this study is to build atomistic models of PVA membranes with various molecular masses, cross-linking rates and hydrolysis rates that can be used to study both thermodynamical and transport properties in arbitrary ternary mixtures water-ethanol-PVA in presence or not of impurities (e.g. methanol). The presented paper reports the feasibility of such an approach on binary mixtures: water-PVA and ethanol-PVA with respect to typical composition of permeate and retentate sides. The predominance of electrostatic interactions including hydrogen bonds in swollen PVA dramatically slows down the convergence rate of molecular dynamics (MD) simulations to macroscopic quantities. Early MD studies of water swollen PVA [4-5], based on a forcefield initially modified from poly(ethylene oxide), showed in particular that the gauche-trans transitions of backbone dihedral are at least one magnitude order slower than the renewal of intramolecular hydrogen bonds along the polymer chains [6]. Convergence acceleration was gained by back-mapping detailed simulation results onto a coarse-grain model that was subsequently used to study the chain-folding process of PVA [7]. More recently, estimation of water sorption properties has been addressed in frozen polymer structures, below the glass transition temperature (T<sub>g</sub>) of dry PVA (ca. 349 K after [8]) [9-10]. To meet industrial conditions up to 373 K in ceramic-supported cross-linked PVA [11], our methodology was tested systematically to estimate partial molar volume of water and ethanol above PVA glass transition temperature.

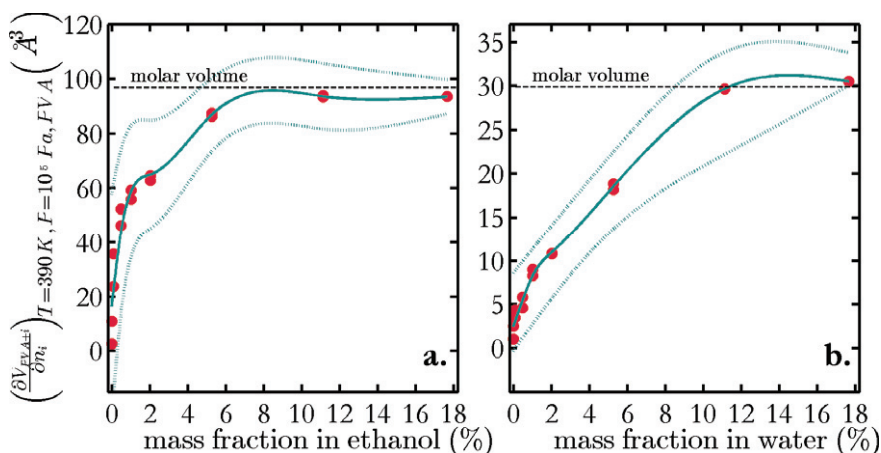
**Simulation details**

The binary systems consisting in 20 chains of 128 monomers and a proper number of water or ethanol molecules to reach mass fractions of 0.1%, 0.5%, 1%, 2%, 5%, 10% and 15% were

prepared using a compression box technique [12] until to reach an intermediate density of  $900 \text{ kg.m}^{-3}$ . Local close contacts and overlapping were relieved successively by a combination of minimization steps and short 50 ps NVT molecular dynamics at 600 K. Long-term isobaric equilibration molecular dynamics up to 8 ns were finally performed to reach the equilibrium density at 390 K (50 K above its  $T_g$ ) and a pressure of  $10^5 \text{ Pa}$ , chosen as the barycentric pressure on both sides of the membrane. Temperature was kept constant using a Nose-Hoover thermostat and a fictitious mass of  $4 \text{ kJ.mol}^{-1}.\text{s}^{-1}$ . Volume was allowed to change via an Andersen barostat and a cell mass prefactor of  $3.32 \cdot 10^{-26} \text{ kg}$ . To enable a stable creation of hydrogen bonds, barostat corrections were switched off every 90 ps during 10 ps. A detailed type II forcefield Compass (Accelrys, San Diego, USA), optimized on ab-initio calculations, was used for covalent interactions. The three-site geometric T13P model was specifically used for water molecules. Van-der-Waals interactions were calculated using a non-bond cutoff distance of 1.55 nm with a spline width of 0.5 nm and a buffer width of 0.2 nm. Long-range Coulombic interactions were summed using a Ewald method with relative accuracy of  $10^{-4}$  and an update of 0.5 nm.

## Main results

Partial molar volumes were inferred by differentiating the volumes of 32 equilibrated boxes with the number of solute molecules (either water or ethanol) as reported in Fig. 1. Continuous estimates with membrane composition were derived by using regularized spline approximants.



**Fig. 1** Partial molar volumes calculated from independent long-term NPT dynamics.

## Conclusions and outlook

Proposed simulations enabled the first direct calculations of partial molar volumes in PVA above its  $T_g$ . They confirmed the non-ideal behavior of binary mixtures and the presence of clusters of ethanol and water above 4 wt% and 8 wt% respectively. Current work aims at studying the dynamics of hydrogen bonding. Studies of ternary mixtures will follow.

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