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Water, salt, and ethanol diffusion through membranes for water recovery by forward (direct) osmosis processes

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ABSTRACT

Measurements of the diffusive permeances of water, NaCl, and ethanol through several, *unoptimized* membranes are presented. Such data can facilitate analysis and development of water recovery from highly impaired sources using hybrid processes based on forward (direct) osmosis (FO) with aqueous ethanol solutions as the "osmotic" agent. The membranes we have studied include anion and cation exchange materials and cross-linked poly(vinylalcohol) (PVA) gels, the latter being a membrane chemistry commercially used for ethanol dehydration via pervaporation. The measured transport properties are reported and suitability of these materials for an FO-based water recovery process is discussed in the context of process simulations.

A major economic consideration for most FO processes is the cost of the lost "osmotic" agent. Thus, we focus our evaluations around the relative selectivity of the membranes for water versus ethanol, $\alpha_{w/E}$. We made measurements using initial NaCl concentrations of 3.5–9.5 mass% with constant ethanol mole fraction ($x_{EtOH} = 0.2$) in the draw solution. We also varied ethanol mole fraction with a constant initial salt concentration (3.5 mass%). The water/ethanol selectivity of all the membranes showed variability with these changing solution conditions. The average $\alpha_{w/E}$ in PVA, and Selemion AMV and CMV (anion and cation exchange membranes, respectively), over the range of salt concentrations, were ~7, 11, and 34, respectively. However, all the membranes exhibited a high degree of variability with respect to the changing boundary conditions (interfacial compositions) over the course of these measurements, likely due to differential swelling. We concluded that selectivities reported for pervaporation-based separations do not necessarily translate to dialysis-based ones, and that significantly higher selectivities than we obtained are likely required for commercially viable processes.

1. Introduction

In this work, we have measured membrane transport figures-of-merit to identify material properties suitable for using ethanol–water solutions as the receiving (osmotic agent) phase in forward (aka direct) osmosis (FO) processes for recovery of water from highly impaired sources. FO as a separation process is the transport of a liquid solute across a permselective membrane driven by its chemical potential gradient across it. In general, the basic FO water recovery process consists of the diffusion of water through the membrane into a well-defined solution (the "draw"), where water has a lower activity. The draw solution is chosen to be more amenable (than the starting feed water source) for the ultimate potable water recovery via some separation process—usually thermal. For aqueous systems, the water's gradient is generally referred to as the osmotic pressure (Π) gradient and can be readily determined from the solution's vapor–liquid equilibrium (VLE) data [1]. The osmotic pressure gradients that can be obtained by FO far exceed pressure gradients easily generated by industrial mechanical pumps, thus, providing a broader range of possible recoveries than with conventional pressure-driven processes. The rationale for FO (as a separation process) has recently been extensively reviewed by Cath et al. [2], including much discussion of its niches in the water recovery milieu that support the premise that FO is a potentially useful process scenario. Our focus in this work is simply to expand on the options with respect to possible osmotic agents, thus, we will just provide a very general FO process description in the following.

Water selectively permeates across the membrane from an impaired water source (feed) rich in dissolved solids (lower water osmotic pressure) to a draw solution where water has significantly higher osmotic pressure. The resulting water + osmotic solution is

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then separated into a potable water stream and the draw solution is recycled back into the FO process. The main energy demand for an FO process is the water/draw solution separation which ideally utilizes energy sources that includes, *but is not limited to*, the use of lower quality fuels—creating a potential for lower operating cost. Thus, since the separability of the draw solution from the product water is the primary energy input, it is the first critical design parameter when selecting a suitable osmotic agent.

Osmotic agents such as ammonium bicarbonate, sulfur dioxide, potassium nitrate with sulfur dioxide, aluminum sulfate, glucose, glucose and fructose solutions and even mixtures of water and aliphatic alcohols have been investigated or proposed for use with water-selective membranes [3–9]. The selection of the osmotic agent dictates the membrane material that may be employed in an FO unit process based on the membrane's stability and transport figures-of-merit relative to *both* the feed and draw solutions. The most efficient FO membrane will minimize the loss of osmotic agent. Osmotic agent lost through the membrane reduces the water recovery and represents an added cost, as it must be replaced to maintain a continuous process. Thus, membrane characteristics that allow the selective transport of water and retard the transport of the osmotic agent becomes the second critical design parameter for an FO water recovery process.

Many of the chemistries and structures of commercial FO membranes are confidential. However, they are considered dense (non-porous) and performance is macroscopically described by the percentage of water recovery and the loss of the osmotic agent into the feed. In FO processes, mass transfer resistance arises from both external (bulk phase) and, if an asymmetric structure is used, internal concentration polarization (CP) [10]. External CP is strictly dependent on the balance between the hydrodynamics of the FO module and the fluxes through the membrane, and is therefore assumed to similarly affect the mass transfer of any FO process. Internal CP mass transfer resistance however arises from the physicochemical structure of the composite membrane and can therefore be reduced by utilizing different membrane structures (and chemistries). Since membrane selection is dependent upon the osmotic agent, it is useful to consider osmotic agents that facilitate optimal FO membrane structures, as well as, efficient water/osmotic agent separation processes.

Assuming one has an appropriate permselective membrane, an ideal draw solution should have a high available osmotic pressure gradient over a wide range of compositions, as well as, being readily removed and re-concentrated from the product water stream for reuse and recycle in the FO process—without having to distill the water as an overhead product. For this study, ethanol was investigated as a model ideal osmotic agent because of its low molar mass, and high solubility in water which translates into high water osmotic pressures (see Fig. 1).

Currently, very little exists in the literature to describe the diffusive transport in membranes for systems containing aqueous ethanol and electrolyte solutions on opposite sides of the membrane. Besides the water's permeation, there is also a chemical potential gradient in the opposite direction for the draw solution's ethanol to diffuse into the electrolyte feed. Thus, an effective water–ethanol FO membrane must have a high selectivity of water to ethanol to minimize this loss. As a starting point for selection of a water/ethanol selective membrane we evaluated some membrane materials previously studied for pervaporation (PV) processes.

PV is a common membrane-based process used commercially for dehydration of aqueous ethanol solutions [12]. But there are potentially significant differences in transport between FO and PV. PV involves a phase change, since the feed is a liquid and the permeate is a vapor, and the transport mechanism is conceived as evaporation on the feed side, followed by solution-diffusion through the membrane into the permeate stream [11–14]. On the other hand, FO also involves a solution-diffusion (aka dialysis) transport mechanism, but does not incorporate a phase change. In addition, during PV both the ethanol and water are diffusing in the same direction, but during FO, their transport is in opposite directions. These differences in operating conditions can affect the component permeances as a result of the differential swelling at the membrane interfaces; the mass transfer velocities being in different directions; and the presence of salts in the feed solution. Thus, there are immediate rationales for measurements to better predict the multicomponent diffusive transport figures-of-merit even when using familiar ethanol-dehydration PV materials in a dialysis (FO) configuration.

2. Background and theory

2.1. Ethanol as an osmotic agent

There exists a great deal of VLE data in the literature, for example [15–20], to easily calculate the chemical potential (and osmotic pressure) of aqueous ethanol solutions [1] (see Fig. 1), and to facilitate accurate process design calculations for thermal separations processes, such as, distillation. In terms of the separability of the ethanol/product water stream, ethanol has both a lower enthalpy of vaporization (ΔH_{vap}) 42.32 kJ/mol, compared to H_2O (43.99 kJ/mol at 298.15 K), as well as a lower boiling point 351.65 K (at atmospheric pressure) compared to 373.15 K for H_2O [21]. Both properties should provide a greater ease-of-separation between the two compounds when using existing aqueous-ethanol dehydration technologies such as distillation, adsorption, or pervaporation to re-concentrate the ethanol draw solution.

2.2. Ethanol dehydration membranes

An extensive literature exists for hydrophilic pervaporation membranes designed for the dehydration of ethanol solutions because it is a commercial technology [12]. Polyelectrolytes, including ion exchange (IEX) membranes, and poly(vinyl alcohol) (PVA) represent successful and often-used classes of material that have been studied and developed further. In addition to creating membranes useful for dehydration, the transport of water and alcohol in IEX membranes has been of interest for direct methanol fuel cell (DMFC) systems.

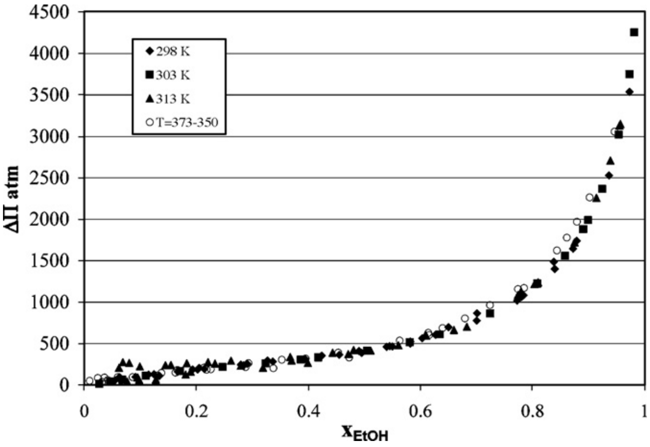

Fig. 1. Water osmotic pressure in ethanol solutions at a variety of temperatures, as calculated from vapor–liquid equilibrium data.