Journal of Membrane Science 461 (2014) 114–122

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Temperature-variation study of neutral solute and electrolyte fractionation through cellulose acetate and polyamide membranes

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ARTICLE INFO

Article history:
Received 23 January 2014
Received in revised form
1 March 2014
Accepted 9 March 2014
Available online 15 March 2014

Keywords:
Membrane fractionation
Temperature variation
Biobutanol

ABSTRACT

To help elucidate the mechanisms for solute transport in polyamide (PA) and cellulose acetate (CA) reverse-osmosis membranes, we have conducted temperature-variation permeation experiments with aqueous solutions containing NaCl and 3- and 4-carbon solutes that possess different numbers of hydroxyl groups. Mass transport metrics were calculated using the solution–diffusion model and the Eyring equation. The molar volume of the neutral (organic) solute is less important than the number of hydroxyl groups in determining solute permeance. For both membrane materials, the neutral solutes with higher permeance also have higher activation enthalpies for permeation, and higher predicted solubilities in the polymer based on Hansen solubility parameters. The higher activation enthalpies may be associated with lower mobility due to more favorable polymer–penetrant interactions. The solution–diffusion permeance coefficients provide a reasonable estimate of permeate composition at different pressures with a new set of membranes. At elevated temperatures of ~320 K, we found negative rejections of n-propanol and n-butanol in the CA membrane, while maintaining relatively high electrolyte and glycerol rejections. Using these results, we suggest a strategy to efficiently harvest n-butanol produced by *Clostridium pasteurianum* while retaining its glycerol carbon source and nutrient electrolytes.

1. Introduction

Many microorganisms are useful bio-catalysts that can upgrade waste streams into higher-value products such as biofuels. For example, the bacterium *Clostridium pasteurianum* can metabolize glycerol into butanol, a more energy-dense and less-volatile liquid fuel than ethanol [1]. However, efficient separation techniques must be developed to harvest these products, which are often toxic to the microbes producing them [2]. In addition to harvesting the product, it is also desirable to minimize the loss of nutrient electrolytes, as nutrient inputs can be a major life-cycle burden to the overall production cycle [3–5]. Thus, the challenge is to fractionate electrolytes from small, neutral organic molecules produced by the microbes.

Pressure-driven membrane fractionation has been investigated as a way to separate neutral solutes from aqueous electrolytes [6–17], but separation factors are often insufficient [18]. A more detailed review of past studies is contained in [19]. Dense-layer polymer membranes have been used commercially for reverse osmosis (RO) for decades. While novel materials continue to be developed, there are still fundamental questions regarding the mass-transport mechanisms of small, neutral organics. Although it is generally accepted that solutes permeate via a solution–diffusion mechanism, the relative importance of solubility (i.e., the solute dissolving in the polymer) versus diffusion (i.e., the mobility of the solute once it has dissolved) is not unambiguous for any specific mixture of solutes. Improved understanding of mass transport in existing, broadly applied materials would help guide selection of materials and operating conditions, and also guide the systematic development of new materials.

Herein, we performed temperature-varying transport measurements and a thermodynamics-based analysis of the mass transport of small, neutral organics in an aqueous electrolyte through dense polymer membranes. Two types of reverse osmosis (RO) membranes are studied, which belong to different polymer classes: one fully-aromatic polyamide (PA), and one cellulose acetate (CA). The neutral organics are 3- and 4-carbon (*referred to as 3C and 4C reduced carbons heretofore, as microbes may reduce a carbon source such as CO_2 or sugar to make these products*) "-ols", with varying numbers of hydroxyl groups. The solution–diffusion model is used

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http://dx.doi.org/10.1016/j.memsci.2014.03.023
0376-7388/

to determine permeance coefficients for water, NaCl, and the reduced carbons as a function of temperature. These permeance coefficients are in turn used to determine thermodynamic parameters for the free energy of permeation, following the Eyring equation [20,21]. Finally, we test the validity of our transport parameters at different pressures, and use the results to inform biofuel production scenarios.

2. Materials and methods

2.1. Membrane filtration (apparatus, membranes, protocol)

Experiments were conducted using the same 3-cell membrane apparatus and experimental methods described in our previous work [19], using a BR1 CA membrane (U.S. Bureau of Reclamation) and an ESPA1 PA membrane (Hydranautics), with the following protocol modifications. First, the membranes were conditioned with deionized (DI) water at 1.4 MPa until the permeance changed less than 4% over the previous 24 h. Next, the pure water permeance was measured at three feed temperatures in the range of 290–320 K. The feed temperature was controlled by submersion of the feed reservoir (a 4 L glass Erlenmeyer flask) in a temperature-controlled bath. The feed temperature was monitored with a digital thermometer. After the pure water permeance was measured at three different temperatures, the feed was exchanged for an aqueous solution of 0.14 M NaCl and 0.014 M of one of the four, (randomly-selected over the course of our measurements) reduced carbons (glycerol, 1,2-propanediol, n-propanol, or n-butanol). The water, reduced carbon, and NaCl permeances were then measured at 14 bar at four different temperatures in the same temperature range, after allowing at least 3 h to equilibrate at each temperature. After measurements were complete with the first reduced carbon/NaCl/water solution, the feed was switched to DI water and the pure water permeance was again measured at 298 K. Then, the feed was replaced with the next reduced carbon/NaCl/water solution, and the temperature-variation procedure was repeated. After this procedure was repeated for each of the four reduced carbon/NaCl/water combinations, the final DI water permeance was again measured at 298 K.

Sample compositions were later analyzed using HPLC with refractive index detection (Agilent 1100 Series). 50 μL samples were injected into a hydrogen column (Phenomenex Rezex RHA), which was maintained at 60 °C. The mobile phase was degassed DI water with a flow rate of 0.6 mL/min. Calibration standards were used to create calibration curves, ensuring that measurements were taken within the linear response range between concentration and refractive index.

2.2. Analysis

2.2.1. Boundary-layer mass transfer

Film theory was used to describe mass transfer in the boundary layer, on the feed side of the membrane:

$$J_v = k_i \ln\left[\frac{(C_{i,f} - C_{i,p})}{(C_{i,b} - C_{i,p})}\right], \tag{1}$$

where J_v is the total volumetric flux, k_i is the mass-transfer coefficient, $C_{i,f}$ is the concentration in solution at the feed–membrane interface, $C_{i,p}$ is the permeate concentration, and $C_{i,b}$ is the bulk concentration. Next, the mass-transfer coefficient was calculated using the Sherwood correlation for laminar flow in a slit:

$$Sh = \frac{k_i d_h}{D_i} = 1.86 Re^{0.33} Sc_i^{0.33} \left(\frac{d_h}{L}\right)^{0.33}, \tag{2}$$

where d_h is the hydraulic diameter, Re is the Reynolds number, and Sc is the Schmidt number. Combining (1) and (2) allows the concentration at the feed–membrane interface, $C_{i,f}$, to be determined for a given bulk concentration in the feed, $C_{i,b}$. The precise geometry of our cross-flow apparatus used to calculate k_i was described previously [19]. This previous manuscript also includes a detailed discussion of how uncertainty in the calculated mass-transfer coefficient propagates into the calculated separation factors. In short, unless our estimates for the hydrodynamic mass-transfer coefficients (using Eq. (2)) are off several fold, the effect of their uncertainty on the calculated solute permeances is within the variance of those permeance determined from replicate measurements.

2.2.2. Solution–diffusion model

The solution–diffusion model was used to determine solute and solvent permeance coefficients, with a slight modification. To better describe non-idealities of the solutions, we used the activity difference across the membrane as the driving force instead of the concentration difference. Briefly, the transport of solute i is described by

$$J_i = \frac{P_i}{l}\left[\gamma_{i,f} C_{i,f} - \gamma_{i,p} C_{i,p} \exp\left(\frac{-\nu_i \Delta p}{RT}\right)\right], \tag{3}$$

where $P_i = D_i K_i$ is the permeability coefficient of solute i, K_i is the liquid-phase/membrane-phase sorption coefficient, l is the membrane thickness, γ_i is the activity coefficient, C_i is the concentration, ν_i is the permeant's partial molar volume (assumed here to be the same in the liquid and membrane phases), Δp is the transmembrane pressure, R is the gas constant, T is the absolute temperature, and subscripts f and p refer to the liquid phases of the feed and permeate at the membrane interfaces, respectively [22]. The transport of water (subscript w) is described by the same equation, which can be rearranged to include the osmotic pressure difference $\Delta\pi$:

$$J_w = \frac{P_w \gamma_{w,f} C_{w,f}}{l}\left[1 - \exp\left(\frac{-\nu_w(\Delta p - \Delta\pi)}{RT}\right)\right]. \tag{4}$$

The solute activity coefficients, water molarity, osmotic pressure, solution density, and solution viscosity were calculated using OLI Analyzer Studio 9.0. To describe the fractionation properties of each membrane, the separation factor $\alpha_{i/j}$ is calculated as the ratio between permeance coefficients for species i and j, i.e., $\alpha_{i/j} = P_i/P_j$. Given the same chemical potential gradient for solutes i and j, if $\alpha_{i/j} > 1$, then solute i has a greater overall molar permeation velocity than solute j; if $\alpha_{i/j} < 1$, the converse is true.

The molar volumes as a function of temperature were compiled from the literature [23–26], and our model inputs are summarized in Table 1. Permeant molar volumes were assumed to be independent of pressure for the range of pressures we tested [26]. Reduced carbon molar volumes were assumed to be independent of electrolyte concentration, because the molar volumes of small sugars in 1.0 M electrolyte (7 times higher than our electrolyte concentration) are less than 1% higher than the molar volumes in pure water [27].

Table 1
Molar volume [cm^3/mol] of each species as a function of temperature.

T [K]	290	298	313	320
Glycerol	70	71	72	72
1,2-Propanediol	70	71	72	72
n-Propanol	70	71	71	72
n-Butanol	86	86	88	89
Water	17	17	17	17
NaCl	16	17	17	18