On negative rejection of uncharged organic solutes in forward osmosis

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ABSTRACT

Negative rejection of 7 alcohols in Forward Osmosis (FO) is reported. The alcohols used in this study are uncharged, hydrophilic organic solutes. It is shown that current membrane transport models are not capable of reproducing the rejection pattern presented here, and consequently, a new model is developed. The model relies on adsorption of the solutes to the membrane followed by coupled transport. Adsorption is caused by salting out of the solutes, while coupled transport is caused by their small size and hydrophilicity, yielding comparatively strong water-solute interactions. It is calculated that the solutes are enriched 4–5 times in the membrane compared to the feed solution. Coupled transport is also demonstrated using the same membrane and solutes in RO mode. The novel model yields an excellent fit, and model parameters are discussed.

1. Introduction

Negative rejection of feed solutes by membranes, i.e. enrichment of a feed solute in permeate, is a relatively rare phenomenon. In this study, negative rejection of organic, uncharged solutes during forward osmosis (FO) is described and modeled, with the solutes being 7 alcohols. Negative rejection in aqueous solutions is rarely encountered because of some properties of water. Compared to organic solutes, water has a small molar volume, high diffusivity, is strongly polar and has a high surface tension. High diffusivity and high surface tension of water both contribute to high feed solute rejection: water diffusion across a membrane active layer is relatively fast compared to feed solutes, and the high surface tension causes strong solute-water and water-membrane interactions, diminishing the importance of solute-membrane interactions [1,2]. The contribution of a low molar volume to rejection is more ambiguous. Small molecules are less sterically hindered during membrane permeation, but on the other hand, the chemical activity of a solute in a pressurized incompressible fluid increases exponentially with molar volume [3,4,2], the latter causing increasing diffusivity at increasing pressure, coined pressure-induced diffusion.

Much of the research into negative rejection has focused on organic solvent nanofiltration (OSN), as negative rejection is encountered more frequently in non-aqueous solutions [1,2,5–7]. In OSN, solvent surface tension is much lower compared to water, allowing for stronger solute-membrane interactions. Negative rejection is reported for solutes having a high solute-membrane affinity [1,6,7], and stronger negative

rejection for solutes of increasing size has been reported as well. For instance, the latter has been observed by Postel et al. [6] for homologue series of alkanes, styrene and ethylene glycol oligomers. This seemingly contradictory result can be explained by the exponential increase of solute chemical activity due to increased molar volume and thus increased flux [3,2], and can be modeled using a generalized solution-diffusion model [2,7].

In aqueous solutions, negative rejection has been observed mainly for ionic solutes. In nanofiltration, negative rejection of ions has been studied in depth by Yaroshchuk [8] who defined different mechanisms which can cause negative rejection. Such mechanisms are Donnan potential decreasing the rejection of mobile counterions, enrichment of ions in the membrane phase of charged membranes (particularly charge-mosaic membranes), or the acceleration of ions in the membrane phase. Perry and Linder [9] presented a modified Spiegler-Kedem model including a Donnan exclusion correction which could describe negative ion rejection. Negative rejection of uncharged organic solutes in aqueous solutions has been observed, a well-described case being phenolic compounds permeating through cellulose acetate (CA) RO membranes [10–12]. It was noted that rejection became more negative with increasing pressure, and negative rejection was explained as a combination of strong adsorption of phenolic compounds on CA and an increase of their chemical potential due to the exerted pressure, similar to the generalized solution-diffusion model. Mandale and Jones [13] observed negative rejection of 5 uncharged, non-dissociable organic compounds in the presence of Na_2HPO_4 during NF. The results were

interpreted using the model presented by Perry and Linder; assuming that the organic compounds were in fact partially charged. This assumption appears questionable: the organics, 3 sugars, an alcohol and caffeine, were required to substitute for Na^+ ions according to the Donnan model, even though all of those compounds are Lewis bases [14] and hold no permanent charges.

In this study, negative rejection of uncharged organic solutes during FO is reported, in the absence of a transmembrane hydraulic pressure difference. The rejection pattern presented in this study shows strong negative rejection at low water flux, and rejection increases and becomes positive as the water flux increases. As is shown below, commonly used transport models are however unable to reproduce this rejection pattern, or are unable to predict negative rejection altogether. Therefore, in order to describe this phenomenon, a new transport model is needed. Compared to the above described cases, the driving forces and feed solute chemical activity in FO are different. Given the absence of a transmembrane pressure difference, feed solute flux is not subject to pressure-induced diffusion, and feed solute activity is only modulated by feed solute-draw solute interactions. The latter interactions can lead to salting-in or salting-out, in which the solute chemical activity is reduced or increased respectively [15]. Salting effects are explored by comparing solute rejection during both FO and RO, using the same membrane and at similar water fluxes, yielding contrasting rejection patterns. A new mechanistic model is developed, based on sequential adsorption followed by washing out of the adsorbed solutes by the water flux; the latter process assumes flux coupling between water and the feed solutes. Differences between FO and RO results are discussed, and flux coupling as well as salting effects are explored.

2. Materials and methods

2.1. Chemicals and analysis

The non-ionic organics used in this study were 7 alcohols (Sigma-Aldrich), the properties of which are given in Table 1. N_aCl was used as a draw solute, draw solution concentrations ranged from 0.15 to 5.3 M. The alcohols were used at a concentration of 100 mg/L each, and were used as a mixture. As the alcohols dissolved in the feed and draw solutions were quantified by headspace-GC-MS, the influence of salting effects by N_aCl on alcohol volatility cannot be neglected. To this end, isobutanol was added to all samples as an internal standard. In order to
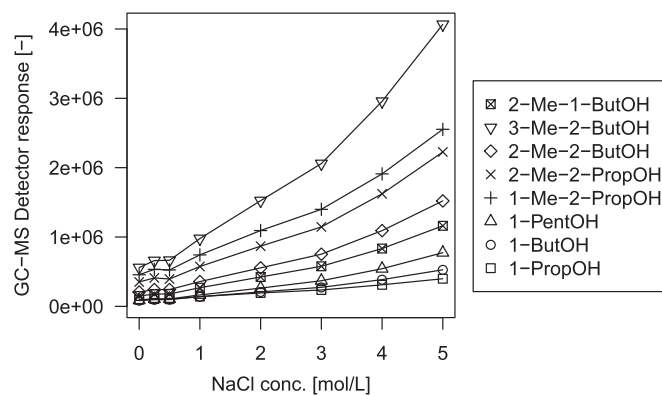

Fig. 1. GC-MS detector response for each alcohol as a function of NaCl concentration, showing salting out of the alcohols. Alcohol concentration was equal in all samples.

account for quantitatively different salting effects for the different alcohols, volatility of each alcohol relative to isobutanol as a function of N_aCl concentration was quantified in a N_aCl dilution series. The dilution series consisted of 8 alcohol standards in N_aCl solutions spanning 0–5 M N_aCl; the relative deviation compared to the isobutanol response was measured. Salting out of alcohols was observed, which is qualitatively illustrated in Fig. 1, in which the GC-MS detector response for the N_aCl dilution series is plotted for each alcohol Table 2. It should be noted that the alcohol concentration was the same in each sample of the dilution series; the trend in GC-MS response is due to increased alcohol volatility. Also, at 5 M N_aCl, volatiliy of the analytes relative to isobutanol was in the range of 75–135% compared to pure water, clearly showing that volatility deviations could not be ignored.

Samples were analyzed using Headspace GC-MS, using an Agilent 6890 GC equiped with a Gerstel MPS headspace injection system. The sample vials were incubated at 80 °C during 5 min while shaking prior to sampling. The syringe temperature was maintained at 90 °C. The injection volume was 2500 µl. The inlet temperature was set at 230 °C. A split ratio of 50:1 was used; using helium as carrier gas. The GC was equiped with an Alltech Hiliflex 15,881 column of 30 m length and 0.25 µm film thickness. The GC oven temperature was ramped from 35 °C to 200 °C, using an initial ramp rate of 3°/min for 10 min followed by 20°/min for the remaining 6.75 min runtime. The MS detector was an Agilent 5973 mass selective detector.

Table 1
Properties of the feed solutes used in this study. References for diffusivity: [a] Hoa and Leaist [16], [b] Funazukuri [17]; density: vendor MSDS, Pubchem, ChemSpider.

Name	Molecular str.	Density (kg/m³)	Diffusivity (10⁻⁹ m²/s)	Abbreviation
1-propanol		803	1.06[a]	1-PropOH
1-butanol		810	0.96[a]	1-ButOH
2-methyl-2-propanol		781	0.88[a]	2-Me-2-PropOH
1-pentanol		811	0.89[a]	1-PentOH
2-methyl-1-butanol		815	0.92[b]	2-Me-1-ButOH
2-methyl-2-butanol		815	0.87[b]	2-Me-2-ButOH
3-methyl-2-butanol		818	0.90[b]	3-Me-2-ButOH