Osmotically Driven Membrane Processes:
Characterization of Water Transport Phenomena through Asymmetric Polymeric Membranes

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ABSTRACT

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Jeffrey R. McCutcheon

2008

Freshwater availability is one of the most critical issues facing humanity today. With our available freshwater resources continuing to dwindle, mankind must turn to the ocean and brackish groundwater as sources of freshwater. Desalination technologies like reverse osmosis (RO), while capable of producing high quality potable water, are, however, expensive, energy intensive, and environmentally unsustainable due to a high volume of concentrated brine discharge. Forward osmosis (FO) might be a sustainable alternative to reverse osmosis and thermal desalination technologies. The major obstacle to the further development of FO and other osmotically driven membrane processes is the poor water flux performance of the membrane. The primary culprit of this poor water flux performance is concentration polarization, a membrane boundary layer phenomenon which afflicts forward osmosis processes to a much greater extent than their RO counterparts.

In this dissertation, the influence of asymmetric membrane support layer structure and chemistry on water transport in osmotically driven membrane processes is elucidated and discussed. Using a custom designed benchtop forward osmosis system, asymmetric membranes used for pressure driven RO separation were found to perform very poorly
under osmotically driven flow conditions with several draw solutions (or osmotic agents). The poor water flux performance of these membranes was attributed to the prevalence of internal concentration polarization (ICP), a phenomenon contained within the porous support structure of asymmetric membranes. A commercially available forward osmosis membrane was found to perform far better. Higher water fluxes coupled with higher salt rejections and feedwater recoveries were obtained using this membrane tailored for forward osmosis. The superior performance of this membrane was attributed to a thinner, more porous support layer, which resulted in a less severe ICP. Even so, the membrane was itself asymmetric and ICP was found to have a profound effect on water flux considering the very large osmotic pressure driving forces utilized in these experiments.

Subsequent investigations presented in this dissertation examined the severity of ICP using various solutes and characterize the severity of ICP within the membrane structure. The culmination of this aspect of the work resulted in the successful development of a predictive water flux model, which incorporated both internal and external CP effects. This model was tested against experimental data and was used to predict improved flux behavior based on reduced ICP effects due to hypothetical improvements in membrane structural design. Furthermore, a new finding presented as part of this dissertation showed that support layer hydrophobicity may critically hinder water flux for all osmotically driven membranes processes and, therefore, must be considered when explaining poorer than expected flux performance. While not affecting water transport in pressure driven separation processes, the degree of water saturation of these various support layers was found to play a critical role in water transport through the membrane during osmosis. It was concluded that improving membranes by designing asymmetric membrane support layers with thinner, more porous, and more hydrophilic
support structures will be essential to the further development of osmotically driven membrane processes. The implications for improved membrane design based on the findings in this dissertation are discussed.
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Chapter 1:

Introduction
1.1. Motivation

1.1.1. The problem

There is a finite amount of freshwater readily available for human consumption and use. This supply is currently strained due to competing utilization demands for farming, industrial, commercial, and domestic uses. Increasing populations, especially in water starved regions of the world, place excessive strain on already dwindling or otherwise impaired water sources. With the world population expected to break ten billion by 2040, the expected draw on these resources will be even less sustainable with many of these 4 billion new humans being required to find their water from alternative sources [1].

One of these alternatives is the vast quantities of saline water in the oceans and large brackish groundwater reserves often found in arid regions. These sources represent over 97% of the world’s water, and hence if tapped economically would yield a virtually unlimited supply of water. The costs associated with desalinating these types of water, though, is high. Until a few years ago, the most utilized technologies for desalination were thermal technologies, primarily multi-stage flash (MSF) distillation and multi-effect distillation (MED). MSF and MED are popular in parts of the world where thermal energy is readily available and inexpensive. The drawbacks of these technologies are the large thermal energy inputs required to vaporize water, process brine discharges, relatively low water recoveries, and significant electrical requirements [2].

Due to the expense and enormous energy costs associate with MSF and MED, reverse osmosis has become far more popular. Reverse osmosis (RO), which provides just over half of the world’s current desalination capacity, is an electrically driven process which uses a semi-permeable membrane to separate salt from water. This process is
capable of somewhat higher recoveries than its thermal counterparts while no thermal energy. Electricity use is still high, however, and its cost comprises the largest portion of the RO cost structure (for seawater desalination) as shown in Fig. 1.1 [3]. Energy costs are less for lower salinity feedwaters, such as brackish groundwater. In addition to the high energy costs, brine discharge is a critical drawback of all desalination processes and requires the locating of a plant near an ocean where the discharge of brine has less, albeit still a non-negligible, environmental impact. These technologies, therefore, cannot be used to desalinate inland brackish groundwater sources since the brine cannot be disposed of in a sustainable manner. With high energy use and extensive brine disposal problems, the overall sustainability of these technologies is called into question. Recent reports by Sandia National Laboratories and the U.S. Bureau of Reclamation have in fact claimed that [4] “We cannot realistically increase the volume of water available in the future while relying solely on the evolution of current-generation desalination technologies”.
With the issues of energy use and water recovery at the forefront of the desalination debate, this dissertation will describe an alternative to these current generation technologies. Forward osmosis (FO) is a membrane based separation process, like RO, which relies on the semipermeable character of a membrane to remove salt. However, unlike RO, the driving force for separation is osmotic pressure, not hydraulic pressure. By using a concentrated solution of high osmotic pressure, called the draw solution, water can be induced to flow from saline water across the membrane, rejecting the salt, and into the concentrated draw solution [5]. The now diluted draw solution must be reconcentrated, liberating potable water and recycling the draw solute. Fig. 1.2 shows the general process diagram.
1.1.2. The history of forward osmosis

The idea of using osmotic pressure to drive separation is not new. In fact, the concept of using FO for desalination was considered back in the 1970’s [7-9]. These early FO designs used concentrated sugar solutions and various membrane configurations, resulting in diluted sugar solutions intended for drinking. After these early investigations, FO use for separation processes disappeared in the peer reviews journals until recently when FO was reintroduced as a means for concentrating food products (direct osmotic concentration, DOC) [10,11] and as a means for desalination [12,13] and wastewater treatment [14]. During this 30 year gap a new osmosis based technology emerged called pressure retarded osmosis (PRO) [15-18]. PRO is an osmotic energy conversion processes utilizing naturally occurring osmotic pressure gradients such as those that exist where any freshwater river or stream meet a saline water body. This work began in the 1970’s and continues today. Combined, the work of forward osmosis, direct osmotic concentration, and pressure retarded osmosis form the new field of osmotically driven...