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Forward osmosis using draw solutions manifesting liquid-liquid phase separation

Siavash Darvishmanesh, Brian A. Pethica, Sankaran Sundaresan*

Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, USA

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ABSTRACT

Desalination via forward osmosis using draw agents whose regeneration is aided via liquid-liquid phase separation has gained much attention in recent years. In the present study, mixtures of two different glycol ethers, tripropylene glycol methyl ether and tripropylene glycol n-butyl ether, have been studied as potential draw agents. Water activity, viscosity and diffusion coefficient of draw solutions have been measured at different mixture compositions, concentrations and temperatures. Osmotic pressures of these draw solutions decreases strongly with increasing temperature. Forward osmosis experiments performed with these draw solutions reveal appreciable initial loss of trans-membrane water flux, reverse solute flux and severe concentration polarization.

1. Introduction

In forward (or direct) osmosis (FO), water from an aqueous solution selectively passes through a membrane to a second solution (referred to as the draw solution) at the same pressure based solely on the difference in the water activity (osmotic pressure) of the two solutions [1]. A number of studies have explored the feasibility and benefits of FO as an alternative to reverse osmosis (RO) for seawater desalination [2–6]. The overall cost of producing desalinated water from seawater via FO process is affected by the type of draw solution employed and its regeneration. Regeneration processes using waste heat or geothermal sources are being explored as routes to cost-effective desalination [7–9]. For example, a recyclable salt solution (a mixture of ammonium bicarbonate and ammonium hydroxide dissolved in water) has been employed as a draw agent in FO, in which low-grade heat can be employed to remove this thermolytic salt from diluted draw solution [10]. In another proposed process, FO is coupled with membrane distillation (MD) [11], where FO is applied to reduce membrane fouling and scaling which is detected in pressure-driven membrane processes such as RO and nanofiltration (NF); MD process separates the water and regenerates the draw solution for FO using waste heat or geothermal sources. Aqueous solutions of thermo-responsive organics (chemicals or polymers) showing lower critical solution temperature (LCST) have also been explored as draw solutes [12–17]; in this case, draw solution diluted via water extraction in an FO process step is heated to a temperature above LCST to induce spontaneous phase separation into organic-rich and water-rich phases. The water-rich phase is then further upgraded through second-stage RO or NF. The use of thermo-responsive organics as draw solutions for FO was first patented in 1968 [18]; however lack of suitable FO membranes thwarted its application. Recently, modifications of this concept for a draw solution manifesting LCST have been patented for integrated FO-NF systems [12,13].

Two types of FO processes using thermo-responsive materials, whose aqueous solutions manifest LCST, have been reported in the literature: (i) Direct use of the thermoresponsive material as a draw agent [14,17]; (ii) Indirect use by formation of aqueous two-phase system with an inorganic draw agent [19]. Thermo-responsive draw agents include block copolymers of polyethylene oxides and polypropylene oxides [12] and fatty acid or fatty alcohol polyethylene glycols polymers [13]. Concentrated aqueous solutions of these molecules are much more viscous than aqueous solutions of inorganic salts (such as $MgSO_4$), leading to severe internal concentration polarization (ICP) in the membrane's support layer (in the so-called FO mode where the support layer faces the draw solution) as well as external concentration polarization (ECP) in the flowing draw solution (in both FO mode of operation and the so-called Pressure Reduced Osmosis (PRO) mode). Furthermore, these organic molecules tend to foul the membrane [20].

Indirect use of thermo-responsive inorganics for desalination was introduced by Rajagopalan et al. [19] as the Aquapod© desalination process. In this method, an aqueous solution of an inorganic salt (specifically $MgSO_4$) is employed as draw agent in the FO step. The diluted draw solution is sent to an aqueous two-phase contactor, where it is concentrated by extracting water using a concentrated aqueous solution of UCON660©, which is a polyethylene oxide-polypropylene oxide block copolymer. The polymer-rich phase is then separated and heated

* Corresponding author.
E-mail address: sundar@princeton.edu (S. Sundaresan).

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to a temperature above its cloud point temperature (T_{cl}) to form two phases; a polymer-rich phase which is cooled and returned to the aqueous two-phase contactor, and a water-rich phase which is sent to a further upgrading step.

Potential application of low molecular weight polymers and non-ionic surfactants as FO draw agents has been examined by several other researchers. Polypropylene glycol (PPG425) as a draw agent for FO was assessed by Jørgensen [17]. The largest osmotic pressure recorded in this study was ~50 atm at 288 K, well below the magnitudes cited by patents [12,13] for their draw agents.

Polyethylenimine (PEI) derivatives and glycol ethers (GEs), whose aqueous solutions manifest LCST and have lower viscosities (than aqueous solutions of polymers mentioned above), have been patented recently [21]. It appears that these draw solutions have rather low osmotic pressures and can barely draw water from synthetic seawater feed solution (3.5 wt% NaCl). Nakayama et al. [14] recently demonstrated extraction of water from seawater via FO using a draw solution consisting of an aqueous solution of diethylene glycol n-hexyl ether (DEH; 146.23 *Da*; LCST ~10 °C). It is likely that reverse solute diffusion would be more pronounced for this solute because of its low molecular weight, but reverse solute flux was not reported. These authors have also suggested an integrated FO-FO process [14,15].

Strong temperature (T) and composition dependencies of the osmotic pressure of aqueous solutions of thermo-responsive draw agents play central roles in the success of FO process. To the best of our knowledge, there is only one published study on the temperature dependence of osmotic pressure of aqueous solutions of thermoresponsive draw agents at conditions relevant to desalination via FO [17]. In this study, Jørgensen [17] found that the osmotic pressure of aqueous solutions of PPG425 increases with concentration at constant T. Furthermore, the osmotic pressure at fixed concentration increases appreciably with decreasing T, without any sign of reaching a plateau (in the temperature range studied). In other words, one could increase the driving force significantly by lowering the operating T; however, lowering T increases the viscosity of the draw solution and decreases the diffusivity appreciably, thereby lowering FO-based desalination process efficiency. Higher viscosity implies higher pumping cost and lower diffusivities increase the severity of concentration polarization (CP). On the other hand, lowering T could decrease reverse solute flux of the draw agent (as a result of lower diffusivity). Thus, experimental data and a good understanding of the concentration and temperature dependencies of osmotic pressure, viscosity and diffusivity would be valuable for FO process optimization. This consideration motivated the present study, where we have studied the temperature and concentration dependence of the phase behavior, osmotic pressure, kinematic viscosity and self-diffusivities of a model thermo-responsive material as potential draw agent. Specifically, we have studied mixtures of two GEs: Tripropylene glycol methyl ether (TPM) (206.27 *Da*) and Tripropylene glycol mono-n-butyl ether (TPnB) (248.35 *Da*). Aqueous solutions of each of these GEs manifest a LCST, but they are widely separated; by mixing them, one can tune the LCST. FO experiments were also performed at three different temperatures with a draw solution at one particular composition in order to identify achievable water flux, fouling and reverse flux characteristics.

2. Materials and methods

DOWANOL™ TPM Glycol Ether, DOWANOL™ TPnB Glycol Ether and Deuterium oxide (D_2O) were purchased from Sigma-Aldrich (USA). The two GEs were mixed at various weight ratios to prepare composite draw agents. The composite draw agent was then mixed with deionized water (DI) to make draw solutions. Each draw solution was thus characterized by wt% of GE and TPM-TPnB composition ratio.

A test tube containing the draw solution was immersed and heated in a jacketed beaker connected to a water bath (Fisher Scientific Model 3013S Heating-Cooling Recirculator, USA) to identify the temperature at which the draw agent turned cloudy (to the eye). This experiment was repeated several times, after allowing the sample to cool down yielding a transparent single-phase. For a given composite draw agent, T_{cl} changed with wt% GE, and the minimum was recorded as its LCST.

Two instruments were tested for the osmotic pressure measurement: Knauer K-7000 Vapor Pressure Osmometer (VPO) [22] and the AquaLab Tunable Diode Laser (TDL) infrared vapor pressure meter [23]. The VPO measures the difference in temperature between a drop of the test solution on a thermistor and a reference solution (which is pure water) in a closely thermostatted cell (± 0.001 °C) which results from condensation of water vapor on the test drop [22]. The TDL instrument measures water vapor concentration from the absorption of an infrared laser beam passing through (an equilibrated) vapor phase in contact with the test liquid in a sealed thermostatted cell. The temperature in the chamber is accurate to ± 0.2 °C [23]. The water activity can be estimated with an accuracy of ± 0.005. Both methods were calibrated using as reference standard solutions of NaCl [24] or pure water (unit activity). Measurements with the VPO instrument manifested slow long-term drift with GE solutions, particularly at higher concentrations (but not with solutions of inorganic salts). In contrast, the TDL instrument consistently yielded reproducible measurements.

A key test of the reliability of an instrument was made as follows. By heating a draw solution to a chosen temperature above its cloud point the solution was allowed to separate into two phases. After allowing ample time for the two phases to equilibrate (typically overnight), the two phases were separated and the water activities of the two phases were measured at the chosen phase separation temperature. The TDL instrument yielded nearly identical water activities for both phases, which is what one would expect for phases in equilibrium; in contrast, the VPO yielded very different results. (See Table 1 summarizing results from TDL meter.) Therefore, in what follows, we present only the data obtained from the TDL instrument.

The relationship between the osmotic pressure and water activity of sodium chloride solutions at various temperature can be found in the literature [24]. The water activities of various draw solutions measured in our study are converted to *equivalent osmotic pressures* of sodium chloride solution possessing the same water activity as the draw solution at the temperature of interest. This equivalent osmotic pressure (or more directly the water activity) is the most relevant metric to assess the driving force afforded by a draw solution for water extraction from seawater (which is mostly a sodium chloride solution) in an FO process.

Viscosities were measured using an SI-Analytics Ubbelohde viscometer, where the temperature was controlled to within ± 1 °C.

Self-diffusion coefficient measurements were made on ^1H NMR using a Bruker Avance III 500 MHz NMR spectrometer. The 1D diffusion ordered spectroscopy (DOSY) experiments were run with 50 G/cm magnetic field gradient, and the data were analyzed using advanced Bayesian DOSY transformation method. Samples were mixtures of the two glycol ethers in D_2O.

The performance of GE mixtures as draw solutes in the FO system was tested on a lab-scale circulating filtration unit, as described by Cath et al. [25]. Cellulose acetate FO membrane was purchased from Fluid Technology Solutions, Inc. (USA). DI water and NaCl solution were employed as a feed solution. The Sepa CF042 solvent-stable cross-flow permeation cell was purchased from Sterlitech™ (USA); it has an active

Table 1
Water activities of two phases obtained through phase separation of 50 wt% aqueous solution of a composite glycol ether mixture (50%TPM-50%TPnB). Measurements were made using TDL water activity meter (with accuracy ± 0.005).

Temperature (K)	Water-rich phase water activity	Organic-rich phase water activity
293	0.971	0.974
303	0.974	0.973
313	0.977	0.981

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