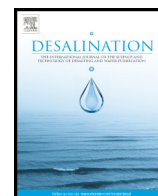




Contents lists available at ScienceDirect

Desalination

journal homepage: [www.elsevier.com/locate/desal](http://www.elsevier.com/locate/desal)

## Finding better draw solutes for osmotic heat engines: Understanding transport of ions during pressure retarded osmosis

Hui Gong<sup>a</sup>, Daniel D. Anastasio<sup>b</sup>, Kaijun Wang<sup>a</sup>, Jeffrey R. McCutcheon<sup>c,\*</sup>

<sup>a</sup> State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, PR China

<sup>b</sup> Department of Chemical Engineering, Rose Hulman Institute of Technology, Terre Haute, IN 47803, United States

<sup>c</sup> Department of Chemical and Biomolecular Engineering, Center for Environmental Sciences and Engineering, University of Connecticut, 191 Auditorium Drive, Room 204, Storrs, CT 06269-3222, United States

### HIGHLIGHTS

- The osmotic heat engine (OHE) can convert thermal energy into electrical energy.
- The choice of osmotic agent determines the production and storage capacity of the OHE.
- Two membranes were tested with three draw solutes for potential OHE performance.
- Hydrated ion size impacts ion transport and boundary layer formation inside membranes.

### ARTICLE INFO

#### Article history:

Received 4 January 2017

Received in revised form 22 March 2017

Accepted 23 March 2017

Available online xxx

#### Keywords:

Pressure retarded osmosis

Forward osmosis

Cellulose-acetate

Thin-film composite

Engineered osmosis

### ABSTRACT

The osmotic heat engine (OHE) is a process by which engineered salinity gradients can be utilized as source of energy generation and storage. The OHE collects low grade thermal energy to concentrate a salt solution and then releases that chemical potential energy via pressure retarded osmosis (PRO). The closed loop feature of the OHE allows the user to select any number of solutes for the draw solution so long as they can be thermally regenerated. The potential to generate energy from a particular solute is dependent on the concentration and chemistry of the solute since both diffusivity of the solute and selectivity of the membrane for that solute determine transport. In this work we evaluated three inorganic draw solutes (sodium chloride (NaCl), magnesium chloride (MgCl<sub>2</sub>) and magnesium sulfate (MgSO<sub>4</sub>)) on their potentials to be used in OHE. Power densities over 13 W/m<sup>2</sup> and 14 W/m<sup>2</sup> were achieved with MgCl<sub>2</sub> and NaCl respectively. However, NaCl generated much larger salt flux than MgCl<sub>2</sub>. Substantially lower power densities were achieved by MgSO<sub>4</sub>. Differences in power density could be partly attributed to differences in hydrated ion radius which had substantial impacts on reverse solute flux and the subsequent development of internal concentration polarization.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

Salinity gradients have been recently considered as a source of renewable and emission-free energy [1–4]. Natural salinity gradients have been of particular interest due to their “renewable” feature of harnessing the salinity gradient from continuously flowing river water with an “infinite” amount of seawater. However, while global estimates have put the power generating potential of naturally occurring salinity gradients as high as  $2 \times 10^{12}$  W (~13% of the current world energy consumption [5]), the reality is far different. The limited osmotic pressure differential coupled with extensive pretreatment requirements for

natural waters will likely prevent use of natural waters for salinity gradient energy [6].

However, there is a way to harness the energy of salinity gradients in an *engineered system* rather than a natural one. Solutions can be created with various solutes and diluted with freshwater to harness energy created from mixing. Energy harvesting can be accomplished with either pressure retarded osmosis (PRO) or reverse electrodialysis (RED). PRO captures the energy of mixing as water moves and creates a hydraulic head [7–10] while RED captures the current generated as ions move across ion exchange membranes [11–13].

The primary requirement in these engineered systems is that the salty solution must be regenerated after dilution and energy harvesting takes place. Thermal evaporation or stripping is a common means of concentrating salty solutions. If a thermal concentration process is coupled with a salinity gradient power process, an engine cycle is

\* Corresponding author.

E-mail address: [jeff@engr.uconn.edu](mailto:jeff@engr.uconn.edu) (J.R. McCutcheon).

created with pure water acting as the working fluid. This has been described specifically for the PRO process and is referred to in the literature as an osmotic heat engine (OHE) [14–16].

Choosing the right draw solute is essential to maximize power production of an OHE system. Previous work was carried out on assessing alternative draw solutions in forward osmosis, including organic ionic salts [17] and mixed draw solutions [18], along with a techno-economic analysis [19], but few have been investigated for PRO for OHE applications. This is largely a result of most PRO studies in the literature being focused on solutes common in naturally occurring gradients. The OHE offers a PRO option for any regenerable draw solute.

Given the wide availability of regenerable draw solutes that have been tested for FO, numerous options exist for OHEs. While we could test many of these in a large study, we have instead have chosen to select specific, inorganic solutes that represent various aspects of draw solutes that are available. We have limited our solutes to sodium chloride (NaCl), magnesium chloride (MgCl<sub>2</sub>) and magnesium sulfate (MgSO<sub>4</sub>) since these are all highly soluble, easily measurable, and representative of ionic draw solutes (ionic draw solutes are commonly used because of their higher osmotic pressures relative to non-ionic solutes). Choosing these solutes also allows us to examine how the cation (NaCl vs. MgCl<sub>2</sub>) and anion (MgCl<sub>2</sub> vs. MgSO<sub>4</sub>) size and valence impact performance. It is noteworthy to mention that while these inorganic, non-volatile salts can be regenerated by evaporative methods (i.e. membrane distillation), it is not the intent of this paper to demonstrate or provide a techno-economic assessment of such a process. We are seeking only to understand how various transport phenomenon of different ions will impact PRO performance for a potential OHE application. We add further dimension to this study through the comparison of two types of forward osmosis membranes.

## 2. Materials and methods

### 2.1. Draw solutions

Certified ACS-grade salts (Fisher Scientific, Pittsburg, PA) were used to prepare draw solutions of sodium chloride (NaCl), magnesium chloride (MgCl<sub>2</sub>) and magnesium sulfate (MgSO<sub>4</sub>). DI water was used as the feed solution in all experiments. For each draw solution, five operation pressures (0, 3, 6.5, 9.5, 13, 16.5 bar) and two temperatures (20 ± 1 °C and 40 ± 1 °C) were evaluated. Osmotic pressures ( $\pi$ ) of draw solutions could be calculated using van't Hoff's Eq. (1) [20]:

$$\pi = \varphi i CRT \quad (1)$$

where  $\varphi$  is osmotic coefficient,  $i$  is the dissociation constant (assumed complete dissociation for salts in this study),  $C$  is concentration of all solutes (moles/L),  $R$  is universal gas constant ( $R = 0.083145 \text{ L} \cdot \text{bar}/\text{mol K}$ ),

and  $T$  is absolute temperature (K). Solutions of 1 M NaCl, 0.67MgCl<sub>2</sub>, and 1 M MgSO<sub>4</sub> were prepared respectively so that all draw solutions had the same osmolarity of 2 M. We recognize that osmotic pressures may still differ somewhat (especially at higher concentrations), but this was decided to be the least problematic approach to comparing draw solutions since we wanted to maintain the same effective ion concentration on both sides of the membrane. We report osmotic pressures in Table 1 to compare various fluid properties to allow for more relevant comparisons between the data below. While the tests described here use lower concentration draw solutions, these comparisons between fundamental solution properties are relevant to higher concentration solutions (which are generally preferred with OHE designs to maximize power densities). A sometimes neglected benefit for using low concentrations is that it enables us to capture more of the power density curve and, in some cases, measure performance at peak power density.

Benefits for choosing these often studied solutes is that that are inexpensive, safe to use, highly soluble, and form solutions that are well characterized. Viscosity and diffusion coefficients of these solutes are also readily available from literature [20–23] and are listed in Table 1. The properties of saturated draw solutions, including molality and osmotic pressure at saturation, are also listed in Table 1. The molality at saturation for MgSO<sub>4</sub> is much lower than NaCl and MgCl<sub>2</sub>, indicating an inherent disadvantage of its use in an OHE. Osmotic coefficients ( $\varphi$ ) were used at these concentrations [20] to calculate the corresponding osmotic pressures. The low osmotic coefficient of MgSO<sub>4</sub> (0.922) at saturation compared to NaCl (1.277) and MgCl<sub>2</sub> (3.048) also suggest a poorer performing draw solute for OHE applications.

### 2.2. Characteristic of membrane parameters

Both the CA and TFC membranes used in this study were provided by Hydration Technologies, Inc. (HTI, Albany, OR), though this company no longer exists. The TFC membrane used in this study was considered by HTI as an early generation membrane. A bench-scale cross-flow RO testing unit was used to determine the intrinsic pure water permeance ( $A$ ), observed salt rejection ( $R$ ) and solute permeability coefficient ( $B$ ) for all solutes with both the CA and TFC membranes. Permeance was measured at pressures ranging from 6.9 bar to 17.2 bar. The pure water flux ( $J_w$ ), was calculated by dividing the volumetric permeate rate by the membrane area. Permeance was calculated by dividing the water flux by the applied pressure and averaging over all pressures tested.

$$A = J_w / \Delta P \quad (2)$$

Observed salt rejection ( $R$ ) was measured using a 50 mM NaCl feed solution at a transmembrane pressure of 13.8 bar [27]. Observed salt

**Table 1**  
Properties of draw solutions.

	Unit	NaCl	MgCl <sub>2</sub>	MgSO <sub>4</sub>
Molecular weight	g/mol	58.44	95.21	120.37
Concentration	mol/L	1	0.67	1
Temperature	°C	20	40	20
Viscosity	mPa·s	1.090[24]	0.719[24]	1.298[23]
Diffusion coefficient	$\times 10^{-9} \text{ m}^2/\text{s}$	1.300 <sup>b</sup>	2.296 <sup>b</sup>	0.952 <sup>b</sup>
Osmotic pressure	bar	45.04[26]	48.50[26]	48.50[20]
Molality at saturation	mol/kg	6.143	6.228	5.735
Osmotic pressure at saturation	bar	382 <sup>c</sup>	416 <sup>c</sup>	1278 <sup>c</sup>

<sup>a</sup> Values are calculated based on empirical equation at 35 °C according to [22].

<sup>b</sup> Diffusion coefficients of 1 M NaCl, 0.67 M MgCl<sub>2</sub> and MgSO<sub>4</sub> at 20 °C and 40 °C are calculated based on data at 25 °C according to  $D_{T1}/D_{T2} = (T1 \cdot \mu_{T1}) / (T2 \cdot \mu_{T2})$ , where  $T1$  and  $T2$  denote temperatures 1 and 2 respectively,  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $T$  is the absolute temperature (K),  $\mu$  is the viscosity of the solvent (Pa·s). Diffusion coefficients of 1 M NaCl, 0.67 M MgCl<sub>2</sub> and MgSO<sub>4</sub> at 25 °C are  $1.483 \times 10^{-9} \text{ m}^2/\text{s}$ ,  $1.075 \times 10^{-9} \text{ m}^2/\text{s}$  and  $0.389 \times 10^{-9} \text{ m}^2/\text{s}$ .

<sup>c</sup> Osmotic pressures at saturation was calculated using Eq. (1)  $\pi = \varphi i CRT$ . Osmotic coefficient ( $\varphi$ ) of NaCl saturated solutions at 20 and 40 °C was 1.277 and 1.284 respectively [26]. Osmotic coefficient ( $\varphi$ ) of MgCl<sub>2</sub> and MgSO<sub>4</sub> saturated solutions was estimated as 3.048 and 0.922, respectively [20].

Download English Version:

<https://daneshyari.com/en/article/4987565>

Download Persian Version:

<https://daneshyari.com/article/4987565>

[Daneshyari.com](https://daneshyari.com)