CHEMICAL ENGINEERING TRANSACTIONS

VOL. 81, 2020

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Petar S. Varbanov, Qiuwang Wang, Min Zeng, Panos Seferlis, Ting Ma, Jiří J. Klemeš
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ISBN 978-88-95608-79-2; **ISSN** 2283-9216

DOI: 10.3303/CET2081227

Analysis of Energy Production by Pressure Retarded Osmosis

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The mass transfer rate and the power density are presented here using a pressure retarded osmosis membrane process. This process was researched for more than two decades as an energy production process, mixing seawater and river water through a selective membrane layer. According to this process, the osmotic pressure difference, due the difference in ion-concentrations across the membrane, can provide a portion of liquid with relatively high pressure, which can then produce energy by means of a turbine. However, according to the present state of art of this process, applying seawater and river water pair, it is not enough economic yet due to the limited performance of the membrane as well as the relatively low osmotic pressure of the seawater. That is why alternate process might be the realization of the energy production in a closed-loop with regeneration of the solutes, which then makes possible to use much higher draw solute concentration and due to it, with much higher energy density. The usage of ionic liquids is thought to be a possible solution because they can be regenerated and can be using for more cycles. The study discusses, partly here, and partly in the presentation, the possible application of a home-prepared ionic liquid for energy generation.

1. Introduction

Osmotically driven membrane processes as forward osmosis (FO) and the pressure retarded osmosis processes (PRO) play very important roles in several industrial processes as producing fresh water from seawater (Coday et al., 2015), capturing clean energy (Altaee et al., 2015), water and waste water treatment (Linares et al., 2014), foodstuff processing (Jiao et al., 2004). These promising membrane processes are intensively researched throughout the word, proving by the rapidly increasing number of research papers for both the FO and PRO processes (Cath et al., 2016). The PRO is a promising process for the so-called blue energy generation without essential emission of CO_2. These osmotic processes operate on the principle of osmotic transport of water across a semi-permeable membrane from a low salinity feed solution (e.g. fresh water, river water) into a high salinity brine/draw solution (e.g. seawater, brine water (Cath et al., 2006). The draw solution side is pressurized to obtain power by depressurizing the portion of water permeated through the membrane from the low salinity solution in case of PRO process. The performance of these processes strongly depends on the salt- and water transport rates. The mixing of seawater (with about 35 g/L solute concentration) and river water (with about 3.5 g/L salt concentration) pair has theoretically 0.721 kWh/m^3 (O'Toole et al., 2016), Most of the theoretical Gibbs free energy is lost during the present technology processes (theoretical loss of energy is 0.3 kWh/m^3, parasitic loads predicted to be 0.418 kWh/m^3) and the extractable net specific energy is practically less than 0.124 kWh/m^3. This about 17 % of the free energy is not enough for an economic energy production. That is why an essential improvement of the membrane properties and even the more accurate description and analysis of the effect on the different operating conditions should be made to find a real economic solution of this problem.

On the other hand, an alternate process solution is also recommended to be looked for (Klaysom et al., 2013). A promising and perhaps more simply removable solute might be the switchable polarity compound, which is soluble in its ionic form in aqueous solution and it separates in its non-ionic form, forming a water insoluble organic phase.

Paper Received: 03/05/2020; Revised: 27/07/2020; Accepted: 28/07/2020
Please cite this article as: Nagy E., Hegedüs I., Fehér C., Skoda-Földes R., 2020, Analysis of Energy Production by Pressure Retarded Osmosis, Chemical Engineering Transactions, 81, 1357-1362 DOI:10.3303/CET2081227

Question arises whether the energy generation with the regeneration process could make the energy extraction more economic or not. It has been prepared different ionic liquid components by authors and measured their performance. The novelty of this work is to apply aqueous solution of a switchable polarity ionic solute for energy generation, with relatively high molecular weight, which can easily be separated from the aqueous solution with changing its polarity. The aim of this study is to show whether this switchable polarity component, which can easily be removed by precipitation, can offer an economic alternate process, for energy production, to the seawater-river water pair.

2. Transport theory

In this sub-section the basic expressions are listed here to better understanding of the solute transport across the asymmetric, selective membrane layer. This model was developed by Nagy (2014) and then extended to take into account of the fouling layer (Nagy, 2019). The physical model of the PRO and FO processes is discussed in the literature (see e.g. Chae et al., 2019).

$$J_s = \beta_d \left(C_d e^{-J_w/k_d} - C_m \right) \tag{1}$$

$$J_s = -B\left(C_m - C_s\right) = -B\Delta C_m \tag{2}$$

$$J_s = \beta_{sp} \left(C_s e^{-J_w S/D} - C_{sp} \right) \tag{3}$$

$$J_s = \beta_f \left(C_{sp} e^{-J_w/k_f} - C_f \right) \tag{4}$$

where

$$\beta_d = \frac{J_w}{e^{-J_w/k_d} - 1}; \qquad \beta_{sp} = \frac{J_w}{e^{-J_w S/D} - 1}; \qquad \beta_f = \frac{J_w}{e^{-J_w/k_f} - 1}; \tag{5}$$

Note D denotes here the solute diffusion coefficient in the draw solution, while S expresses the real diffusion path, namely $S=\delta\tau/\varepsilon$, where δ means the thickness of the support layer, τ is the tortuosity factor, ε is the hold-up of the support layer, B is the solute permeability, β_i (i=d,f,sp,m) are the convective mass transfer coefficients, J_i (i=w, s) water and salt fluxes, C_i is concentration (i=d, m, s, sp, f, draw solution, surface of the selective layer, support layer surface, feed layer surface of membrane, feed solution) . Literature often uses K parameter where $K=S/D\equiv\delta\tau/(\varepsilon D)$.

Applying any traditional method using the above equations, the overall salt transfer rate, which involve the effect of every transport layer, can be expressed as:

$$J_s = \beta_{ov} \left(C_d - C_f e^{J_w\left(1/k_d + 1/k_f + S/D\right)} \right) \tag{6}$$

where

$$\frac{1}{\beta_{ov}} = \frac{1}{J_w} - \frac{e^{J_w/k_d}}{B} - \frac{e^{J_w\left(1/k_d + 1/k_f + S/D\right)}}{J_w} \tag{7}$$

The solute transfer rate expressing by means of the concentration difference of the selective layer be expressed as (Nagy, 2019)

$$J_s = B\left(C_m - C_s\right) = \frac{B\left(C_d e^{-J_w/k_d} - C_f e^{J_w\left(1/k_f + S/D\right)} \right)}{1 + \frac{B}{J_w}\left(e^{J_w\left(1/k_f + S/D\right)} - e^{-J_w/k_d} \right)} \tag{8}$$

The water flux can then be expressed as (the osmotic pressure, $\pi = iMCR_gT$ where i is van' t Hoff dissociation factor (it is 2 for NaCl), C salt concentration, M molecular weight, R_g gas constant, T temperature) (Cath et al., 2006):

$$J_w = A(\Delta\pi_m - \Delta P) \tag{9}$$

where ($\Delta\pi_m$ is the effective osmotic pressure difference across the selective layer, $\Delta\pi_m = \pi_m - \pi_f$.

$$\pi_m - \pi_s \equiv \Delta\pi_m = \frac{\left(\pi_d e^{-J_w/k_d} - \pi_f e^{J_w\left(1/k_f + S/D\right)}\right)}{1 + \frac{B}{J_w}\left(e^{J_w\left(1/k_f + S/D\right)} - e^{-J_w/k_d}\right)} \tag{10}$$

3. Materials and methods

Shortly some information is given here on the switchable ionic component prepared and used for the experiments and also on the experimental device, as well

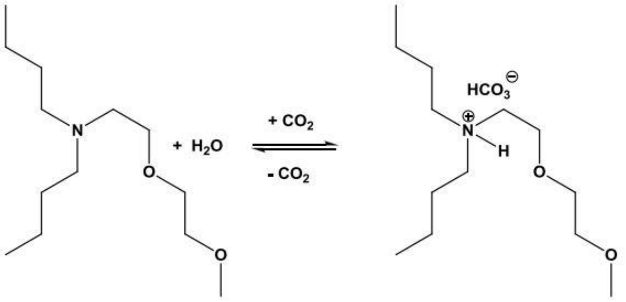

Figure 1: The above scheme illustrates how the organic amine can be reacted to dissociable ionic liquid. The boiling point of the dibutil-(2-2-metoxietoxi)-etil-amine is 161 °C, while its specific density is 0.91 g/mL and its molecular weight is 293 g/mol

3.1 Switchable ionic component

As a switchable polarity ionic liquid, dibutil-(2-2-metoxietoxi)-etil-amine, was prepared by the authors by reaction of dibutil-amine (≥ 99.5 %, Merck) and 2-(2-metoxietoxi)etilenclorid (≥ 98.0 %, Merck) at 130 °C, until the full reaction of the amine (Samori et al., 2014). Tertiary-amine obtained was purified by vacuum distillation. The purity of it was 99 % according to chromatography analyzes. Its ionic form was then used, after reaction according to Figure1, as ionic solute in PRO process. The ionic liquid was produced bubbling CO_2 through the liquid organic amine compound, while its decomposition can be carried out by Argon or N_2 atmosphere at elevated temperature for its removal from the diluted draw solution and from the used feed solution. The creation of the water-soluble ionic component takes place as follows: the in water not soluble, home-made, organic component [dibutil-(2-2-metoxietoxi)-etil-amine] was bubbled by gaseous CO_2, and after a certain bubbling time, the organic amine was practically completely transformed into water soluble ionic form. This ionic form of organic component produces ions in water, which will then create osmotic pressure difference between the two layers of the selective membrane and forces water to be transported through the membrane into the high salinity draw solution.

Production of the ionic liquid: for its production, an aliquot portion of dibutil-(2-2-metoxietoxi)-etil-amine is mixed and stirred at room temperature under CO_2 atmosphere for 12 h. At the end of the reaction, the originally biphasic mixture turned into a homogeneous one and its conductivity increased from 0.68 mS to 12.5 mS that is consistent with the total formation of the ionic species.

Due to the water transport into the draw solution against hydrodynamic pressure difference, which is lower than the osmotic pressure difference, dilutes the draw solution lowering, with it, the driving force of the water convective transport. On the other hand, the selectivity of the membrane does not generally work with 100% rejection; this phenomenon also decreases the ion concentration of the high salinity solution. That is why the exchange or regeneration of this solution is important after certain time period of operation. After the energy production, the amine content of the transported water (it can be about 10-30 wt% of the draw solution), applied for energy production, as well as that in the feed solution, should be removed. It can be done either by membrane distillation or by means of its back-transform into organic amine. The harvestable energy is 0.13 MJ, calculating for 3 M starting draw concentration with volume of 1 m^3 and using commercially available membrane properties. The energy demand of the distillation of the 0.13 m^3 transported liquid is 0.3 MJ. The reaction heat of CO_2 and the organic amine reaction is about 15 kJ/mol CO_2. The energy demand of the removal of amine from the transported portion of liquid is 3.9 MJ (2 M x 0.13 m^3 x 15 kJ). This energy will be formed and consumed in every cycle, resulting in its balance, with suitable operation, might be close to zero. Only the energy loss of process should be added. Similarly, the distillation heat also recoverable during condensation and repeatedly can it be used. The repeated application of the consumed and the recovered energy can make this closed-cycle process economic.

The decomposition of the ionic liquid: The ionic solution is heated up to 85 °C or 90 °C with gently stirring and then argon was slowly bubbled through it for a short time period (about 5-10 min is enough). The remaining part can also be removed by NaOH solution. The forming CO_2 can be absorbed in dibutil-(2-2-metoxietoxi)-etil-amine solution to later application, replacing the lost of ionic solute. It can be 1-2 % of the applied amine solution. During this process the organic amine will be separated from the water in a water insoluble organic phase (two immiscible liquid phases are formed). During this process the 95-97 % of the amine is removed from the aqueous solution.

3.2 Experimental device

The water flux was measured using Porifera pressure retarded osmosis, flat sheet membrane (Porifera Inc., San Leandro, CA). Distilled water was used as a feed solution and 2 to 50 g/L (0.007-0.5 17 M) aqueous ionic liquid as draw solution for determination of the water flux without using hydraulic pressure. A home-made membrane cell with 90 cm^2 active membrane interface was used with recirculation of both the feed and draw solutions, separately, in closed system, at room temperature. Both solutions were separately fed from a reservoir and back into this reservoir. In these experiments, the water and solute flux were measured with continuous measurement of the weight increase of the draw and feed side reservoirs. The concentration was measured by conductivity.

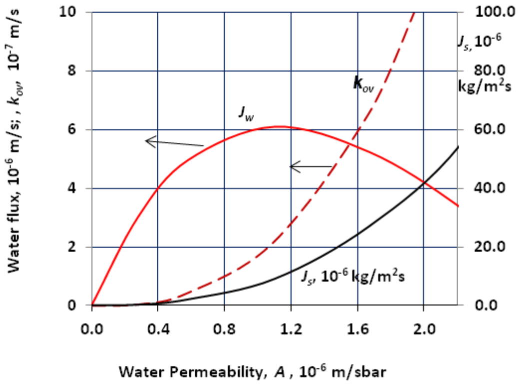

Figure 2: Water and solute flux as a function of the water permeability. Values of parameters are: C_d*=0.6 M;* C_f*=0.015 M;* k_d*=3.85 x* 10^{-5} *m/s; D=1.5 x* 10^{-9} m^2*/s; A=1.1 x* 10^{-6} *m/sbar (=3.96 L/*m^2*hbar);* k_f*=*k_d*;* ΔP*=12 bar; B=*γA^3*; γ=0.1724 x* 10^{-6} s^2bar^3/m^2*)*

4. Results and discussion

Three sub-sections discussed the PRO process, using typical transport parameters for prediction of the water flux and power density, then experimental data as well as the regeneration process will briefly be discussed.

4.1 Water flux and power density

Several studies discuss the harvestable energy by PRO process. Typical curves have been plotted using Eq(1) – Eq(10) (Figure 2). The plots illustrate the water flux and the ion flux as a function of the water permeability, applying the presented equations for calculation. The applied parameters are characteristic ones of the available industrial membrane.

The water permeability is the other crucially important parameter which can decisively determine the efficiency of a PRO process as its effect is illustrated in the Figure 2. As a result, the water flux has maximum value as a function of the water permeability, i.e. the value of J_w starts to decrease after a certain value of A. The hydraulic pressure difference is 12 bar, thus 10 x 10^{-6} m/s water corresponds to about 1 W/m^2 power density (more exactly 10 bar of ΔP gives 1 W/m^2 power density at this water flux). This fact clearly shows the importance of the water permeability of the available membranes. Its right value can give the maximal energy.

4.2 Experimental results

The main aim of this investigation to find an economic technology of closed cycle PRO process. The separation of the switchable ionic solute compound can offer such a methodology, which makes possible the removal of the solute from the thin feed solution and the diluted draw solution used for energy generation by means of a turbine. The essence of our idea is that the organic dibutil-(2-2-metoxietoxi)-etil-amine can reversibly be formed to ionic liquid by its reaction with carbon dioxide. After its usage in a PRO process, this ionic compound can be separated as organic phase, by its deconstruction at higher temperature using inert gas flow through its containing aqueous phase.

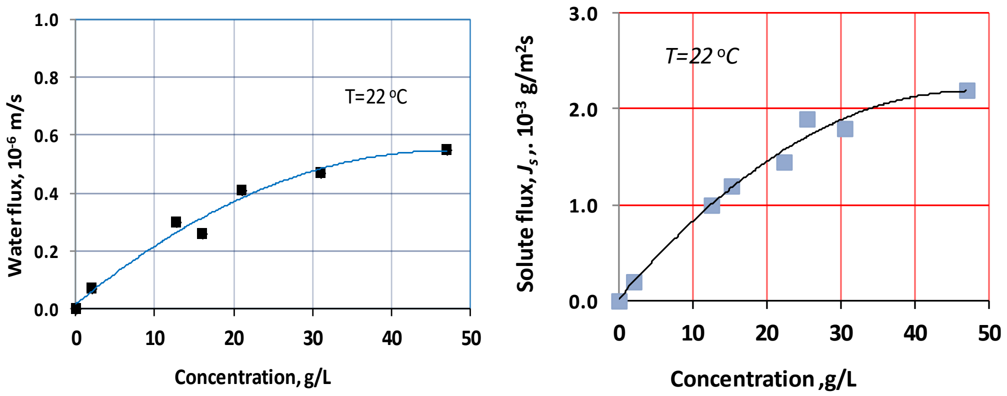

Figure 3: Water flux and the solute flux as a function of ionic liquid concentration

Figure 3 illustrates the change of the water and solute transport across the membrane as a function of the solute concentration in the draw solution. Both functions increase gradually, though with lowering intensity, with the increase of the ion concentration. This tendency is caused by the internal and external mass transfer resistances. This water flux data are similar to that obtained by NaCl solution at this concentration range given in M.

The water permeability, A (m/sbar), coefficient and the solute permeability coefficient, B (m/s), were measured by known methods in separate experiments (not shown here). Value of A was determined by measuring the water flux as a function of hydrostatic pressure, while the solute permeability by RO process using 2 g/L solute concentration. Their values obtained are: A = 1.7 x 10^{-7} m/sbar; B = 4.5 x 10^{-8} m/s. Knowing these values as well as the external diffusive mass transfer coefficients, k_d and k_f, the value of the structural parameter can be predicted. All necessary parameters are known to predict the power density using these switchable polarity ionic solute components. This will then be discussed in detail in the presentation.

The regeneration of the ionic component is taking place in two steps: at 90 °C for 30 min, bubbling by inert gas, and then the rest of the ions is removed by NaOH, which form inorganic salt with the organic amine bound CO_2. This reaction is an instantaneous one. In the first step 93 mol% of the organic amine, while in the second step it increases up to 98 mol%. The rest should probably be considered as lost to the process.

5. Conclusion

The application of the switchable polarity ionic component is an alternate possibility to PRO process, which enables the user to realize this process in closed cycles due to it easy regeneration. This makes it possible to use high salinity draw solution, which can provide high value of power density. This can be potentially applied economically in systems with opposite seawater-river water pair.

Acknowledgement

The National Development Agency grant OTKA 116727 and NKFIH-1158-6/2019 greatly acknowledged for the financial support.

Nomenclature

A	Water permeability coefficient, m/(s atm), (m^3/m^2s atm)
B	Salt permeability of the sponge layer, m/s
C	Salt concentration, kg/m^3, g/L
D	Fluid diffusion coefficient, m^2/s
J_s	Solute transport rate, kg/m^2s
J_w	Water flux, m^3/m^2s, m/s
K	Diffusive mass transfer coefficient, m/s
K	Salt resistivity, s/m
R	Rejection coefficient
S	Structural parameter, m
W	Maximum energy density, W/m^2

Subscripts

f	*Feed solution*
d	*Draw solution*
m	*Surface of the membrane selective layer faces the draw solution*
s	*Interface between the active and support layer*
sp	*Interface between the support and the feed solution*
w	*Water*

Greek

β	Mass transfer coefficient, m/s
π	Osmotic pressure, atm
δ	Thickness of the fluid boundary layer, m
ε	Porosity
τ	Tortuosity
ΔP	Hydraulic pressure difference, atm
ΔC_m	Concentration difference of the selective layer, kg/m^3
$\Delta\pi_m$	Osmotic pressure difference of the selective layer, atm

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