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The Effect of Solute Leakage on the Thermodynamical Performance of an Osmotic Membrane

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Abstract

We derive an equation for the Second Law efficiency of an osmotic membrane. This expression of efficiency depends on the ratio between the solvent and solute flux, but remains independent of the actual values of the fluxes and of any transport model. The equation can be used to find the magnitude of solute leakage that can be accepted for optimally performing osmotic membranes. Special emphasis is given to osmotic power generation systems. We additionally compare the fraction of total power destruction that occurs inside the selective layer of the membrane, and the fraction that occurs inside the support material of the membrane.

1. Introduction

The power produced by an osmotic membrane (P_{membrane}) can be expressed as

$$P_{\mathrm{membrane}} = v\,\Delta p, \tag{1}$$

where v is the volume flow through the membrane per membrane surface area, i.e., the osmotic flux, and Δp is the pressure difference over the membrane. For an ideal, completely semi-permeable membrane, the optimum pressure difference that maximises the power of the membrane is half the osmotic potential difference ($\Delta \pi$) [1]

$$\Delta p = \frac{\Delta \pi}{2}. \tag{2}$$

This result is based on substitution of the following osmotic flux equation

$$v = A(\Phi\,\Delta\pi - \Delta p) \tag{3}$$

into Eq. (1), setting the coefficient Φ to unity, and setting the derivative of power with respect to Δp to zero. The maximum power design of Eq. (2) is also recognised in fluids engineering [2]. For real, solute leaking membranes $\Phi < 1$, and furthermore the coefficient A may depend on the concentration [3]. However, this dependence of A on the osmotic pressure has no effect on the optimal pressure difference. In osmotic power generation systems with non-ideal membranes, turbines and pumps, the optimal pressure difference will be somewhat lower than stated in Eq. (2), [4]. Different kinds of osmotic energy conversion systems have been compared in [4–6].

Although Eq. (1) approximately maximises the power of the system, it does not provide details of the effect of solute leakage on the membrane (except briefly through the coefficient Φ in Eq. (3)). Therefore, to obtain a deeper understanding of the effect of solute leakage, we have formed a thermodynamic second law efficiency equation that depends on the ratio

$$r = \frac{J_w}{J_s} \tag{4}$$

between the molar flux of solvent (J_w) and solute (J_s), but does not depend on the actual values of the fluxes. The value of r is negative in osmosis because solvent and solute move in opposite directions. Furthermore, we will analyse the fraction of lost power inside the support structure of the membrane.

2. The System

The system under study, the osmotic membrane, is illustrated in Figure 1. It is composed of a very thin selective layer (skin) and a considerably thicker porous support structure. The osmotic phenomenon occurs inside the skin. The purpose of the support structure is to give mechanical support for the skin to sustain pressure differences. On the other hand, the disadvantage of the support layer is that it causes an additional resistance to the transport through the membrane.

3. Second Law Equations

3.1. Second Law efficiency equation of the membrane

The power lost (P_{lost}) during a process at constant temperature can be expressed via the Gouy-Stodola theorem as a product of absolute temperature (T) and rate of entropy generation (σ):

$$P_{\text{lost}} = T\sigma. \tag{5}$$

From the fundamentals of classical thermodynamics, we can derive the following equation for an isothermal steady state process:

$$\sigma = \sum_{\text{out}} Js - \sum_{\text{in}} Js - \frac{\dot{Q}}{T}, \tag{6}$$

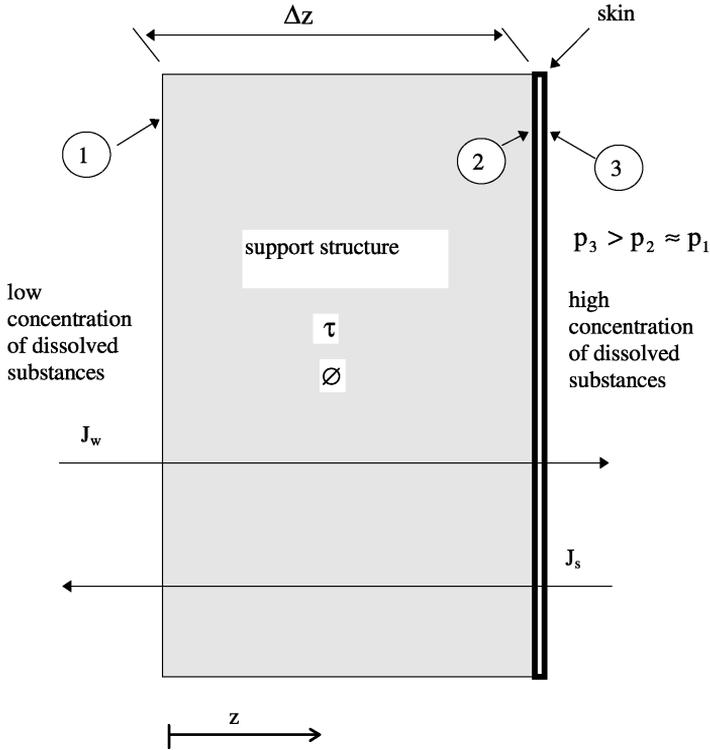where $\dot{Q}$ is the net heat flux into the membrane and s the molar specific entropy.

Fig. 1. Membrane structure and the positions of indexes 1, 2, and 3. J_s and J_w are the molar flux of solute and solvent, respectively. ϕ, τ, and Δz are the porosity, tortuosity and thickness, respectively, of the support structure.

For constant partial molar volume (v_i) and constant isobaric coefficient of volume expansion (γ_i), the partial specific entropy of the component i can be expressed as

$$s_i(T, p, a_i) = s_i^0(T) - \Re \ln a_i - v_i \gamma_i (p - p_0), \tag{7}$$

where $\Re$ is the universal gas constant, a = activity and $s_i^0(T)$ the reference entropy at temperature of T. The energy balance for the isothermal steady-state process, corresponding to Figure 1, yields

$$\dot{Q} = -\Delta \dot{H} = -Jv\,\Delta p, \tag{8}$$

where $\dot{H}$ is the enthalpy flux of the mixture. In Eq. (8), the enthalpy of mixing is assumed to be small. The pressure difference inside the support is so small that it can be ignored, i.e., $p_1 \approx p_2$. Combining Eqs. (6–8), we get the entropy generation rate

$$\sigma_{1(2)-3} = J_s \Re \ln\left(\frac{a_{s,1(2)}}{a_{s,3}}\right) + J_w \Re \ln\left(\frac{a_{w,1(2)}}{a_{w3}}\right) + \frac{v(p_1 - p_3)}{T}. \tag{9}$$

The subscript notation 1(2) in Eq. (9) and in all subsequent equations is used for two possible interpretations of the equations: the same equations can be interpreted either to cover the complete membrane (see Fig. 1., from point 1 to point 3) or to cover only the skin (from point 2 to point 3). Because we consider osmosis, where $v = Jv \approx J_w v_w$, we can express Eq. (9) additionally applying the definition of Eq. (4) to result in

$$\sigma_{1(2)-3} = J_w \left[\frac{\Re}{r} \ln\left(\frac{a_{s,1(2)}}{a_{s,3}}\right) + \Re \ln\left(\frac{a_{w1(2)}}{a_{w3}}\right) + \frac{v(p_1 - p_3)}{T} \right]. \tag{10}$$

Note that the term $\dfrac{v(p_1 - p_3)}{T} \leq 0$ in Eq. (9) is negative (because in osmosis $p_1 \leq p_3$), and thus the pressure term acts to diminish the rate of entropy generation. One can show (compare the pressure term to the power generation rate Eq. (1), and use the same model Eq. (3) for v) that this term has a minimum value (the value is negative, i.e., maximum reduction of entropy production rate) at the same point as the maximum power occurs.

The theoretical available maximum power is $P_{\text{membrane}} + P_{\text{lost}}$, so we can define a Second Law efficiency (η) equation of the membrane

$$\eta = \frac{P_{\text{membrane}}}{P_{\text{membrane}} + P_{\text{lost}}}. \tag{11}$$

If one also takes into account that in osmosis $|J_w| >> |J_s|$, from Eqs. (1), (5) and (10), one gets for the efficiency

$$\eta = \frac{\Delta p}{\Delta \pi - \dfrac{\Re T \Delta \ln(a_s)}{v_w r}}, \tag{12}$$

where the osmotic potential (osmotic pressure) is denoted as

$$\pi = -\frac{\Re T \ln(a_w)}{v_w}. \tag{13}$$

Here v_w is the molar specific volume of water and Δ is the difference between the high and low concentration solution. This efficiency can be interpreted, as denoted previously, either as the efficiency of the selective layer or as the efficiency of the complete membrane. In the first case, Δ is taken over the selective layer and in the latter case, over total membrane thickness. Note that this efficiency does not depend on the actual magnitude of fluxes, but only on the ratio between them. The maximum second law efficiency is achieved when r approaches (minus) infinity. The result is

$$\eta_{\text{max}} = \frac{\Delta p}{\Delta \pi}. \tag{14}$$

3.2. *Power lost inside the support structure*

The pressure drop through the support structure can be approximated to be zero. Then, we get from Eq. (10) the entropy generation rate for the support structure

$$\sigma_{1-2} = J_w \Re \left[\frac{1}{r} \ln \left(\frac{a_{s,1}}{a_{s,2}} \right) + \ln \left(\frac{a_{w1}}{a_{w2}} \right) \right]. \tag{15}$$

The fraction (f) of power destroyed inside the support structure compared to the total destruction is then found from

$$f = \frac{\sigma_{1-2}}{\sigma_{1-3}}. \tag{16}$$

Substituting Eq. (10) and Eq. (15) into Eq. (16), we get

$$f = \frac{\ln \left(\dfrac{a_{s1}}{a_{s2}} \right) + r \ln \left(\dfrac{a_{w1}}{a_{w2}} \right)}{\ln \left(\dfrac{a_{s1}}{a_{s3}} \right) + r \ln \left(\dfrac{a_{w1}}{a_{w3}} \right) + \dfrac{rv(p_1 - p_3)}{\Re T}}. \tag{17}$$

Furthermore, this equation is explicitly independent of the actual values of the fluxes. However, we shall study the effect of the support structure, and therefore need to estimate the values of activity at position 2 in the function of activity at position 1. For this task, we need the product of the osmotic flux (v) and the diffusion resistance (R_{diff}) of the support structure. The estimation of the concentrations, and thus the activities, at the boundary of the skin and support structure is based on a well known solution of a 1-dimensional differential balance of solute inside the porous support:

$$c_{s2} = \frac{J_s}{v} + \left(c_{s1} - \frac{J_s}{v} \right) e^{vR_{\text{diff}}} = \frac{1}{v_w r} + \left(c_{s1} - \frac{1}{v_w r} \right) e^{vR_{\text{diff}}}, \tag{18}$$

where we have denoted the diffusion resistance of the support structure as

$$R_{\text{diff}} = \frac{\Delta z \cdot \tau}{\phi D}. \tag{19}$$

The last equality of Eq. (18) results from approximation $v = Jv \approx J_w v_w$ and from Eq. (4).

4. Results

We calculated examples of particular interest in the field of osmotic power generation systems, where ocean water is used on the high concentration side and river water on

the low concentration side. The activity of water can be expressed as $a_w = \dfrac{\varphi_w c_w}{c_{tot}}$, where φ_w is the activity coefficient of water, and for symmetrical strong electrolytes $a_s = \left(\dfrac{\varphi_{s\pm} m_s}{m_0} \right)^2$, where m_s is the molality of the solute and $m_0 = 1$ mol/kg. The activity coefficient of NaCl ($\varphi_{NaCl\pm}$) in water solution is taken from data of [7], and in positions 1 and 2 (see Fig. 1) we can approximate $\varphi_w \approx 1$. We shall consider a case of known constant total concentration, and therefore achieve the concentration of water from $c_w = c_{tot} - c_s$, where $c_{tot} = 55\,555$ mol/m^3.

4.1. The efficiency of the membrane

In Figure 2, we have plotted some efficiency curves according to Eq. (12). To determine the pressure difference, we have used $\Delta p = 10$ bar. For other values of Δp, note that Eq. (12) and Eq. (14) have such a linear response to Δp that the shape of the curves and the relative distance of a certain point of the curve from the maximum value of the same curve do not change if the pressure value is changed. We can see
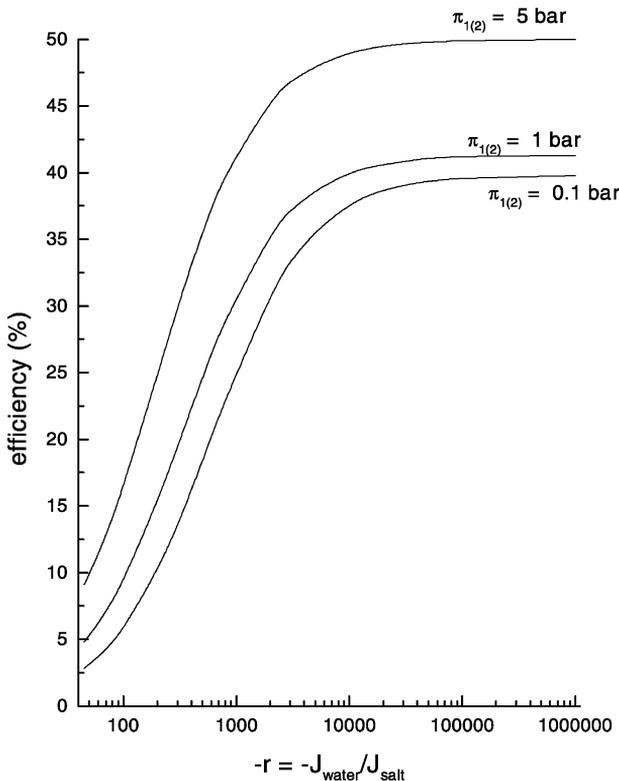

Fig. 2. Efficiency of the membrane as a function of the water flux – solute flux ratio (r). The following parameter values were used: $p_3 - p_1 = 10$ bar, $\pi_3 = \pi_{ocean} = 24$ bar, $T = 298$ K.

that, to obtain high efficiency of the membrane, the ratio $|r|$ should be high. However, no additional advantage is gained if the ratio $|r|$ approaches infinity. Therefore, the membrane had to be highly selective, but for high efficiency there is no need to obtain a completely semi-permeable membrane. For example, in Figure 2 we see that there is a considerable difference in efficiency between value $|r| = 100$ and $|r| = 1000$. But for value $|r| > 10\,000$, the efficiency does not, increase further in practice.

4.2. Power destruction inside the support structure

The purpose of the support structure is to give mechanical support to the selective layer; it is not involved in the actual energy transformation process. Therefore, we want to avoid entropy generation inside the support as far as possible. In Figure 3a–c, we have plotted some curves corresponding to Eq. (17). We have used Eq. (18) to obtain the concentrations (and activities) at position 2. All solutions in Figure 3a–c that result in more than 100% power destruction will violate the Second Law of thermodynamics. In such cases, Eq. (18) produces at position 2 such a low concentration of water and high concentration of salt that the entropy generation rate inside the membrane becomes negative.

An example

If we set a target, with the goal to economically produce power from an osmotic power plant, of for example $P_{\text{membrane}} = 6$ W/m^2, and set $\Delta p = 10$ bar, then we get from Eq. (1) that $v = 6 \times 10^{-3}$ mm/s. Furthermore, if $R_{\text{diff}} = 670$ s/mm (which is a typical value, e.g., for cellulose acetate membranes measured in [3], that can be achieved, e.g., when $\Delta x = 167$ μm, $\phi = 0.3$, $\tau = 2$, $D = 1.5 \times 10^{-9}$ m^2/s), then we get $v R_{\text{diff}} \approx 4$. From Figure 3a–c, we can see that the thermodynamical losses inside the support will always be considerable compared to those inside the membrane unless $|r|$ is extremely high and π_1 is extremely low. In membranes measured in [3, 8, 9], $|r|$ varies typically between 30 and 2000 (the value depends principally on the membrane type, the concentration and the pressure differences applied in tests). If we are able to reduce the diffusion resistance for example to a numerical value $R_{\text{diff}} = 335$ s/mm, keeping v as 6×10^{-3} mm/s, then $vR \approx 2$. Low power destruction inside the support becomes now more accessible, but only when $|r|$ is very high.

5. Conclusions

We have analysed the effect of solute leakage of the membrane on its thermodynamic performance. The derived Second Law efficiency equation shows that, in order to obtain high performance, the membrane should be highly reflective to the solute. On the other hand, the membrane does not need to be completely semi-permeable. In the example calculations presented in this paper, efficiency did not increase in practise when the ratio of solvent to solute flux $|r|$ was more than $10\,000$. We have also examined the ratio between the destruction activity inside the support structure of the membrane and the complete membrane. The example calculation showed that the amount of power lost inside the support structure is sensitive to the
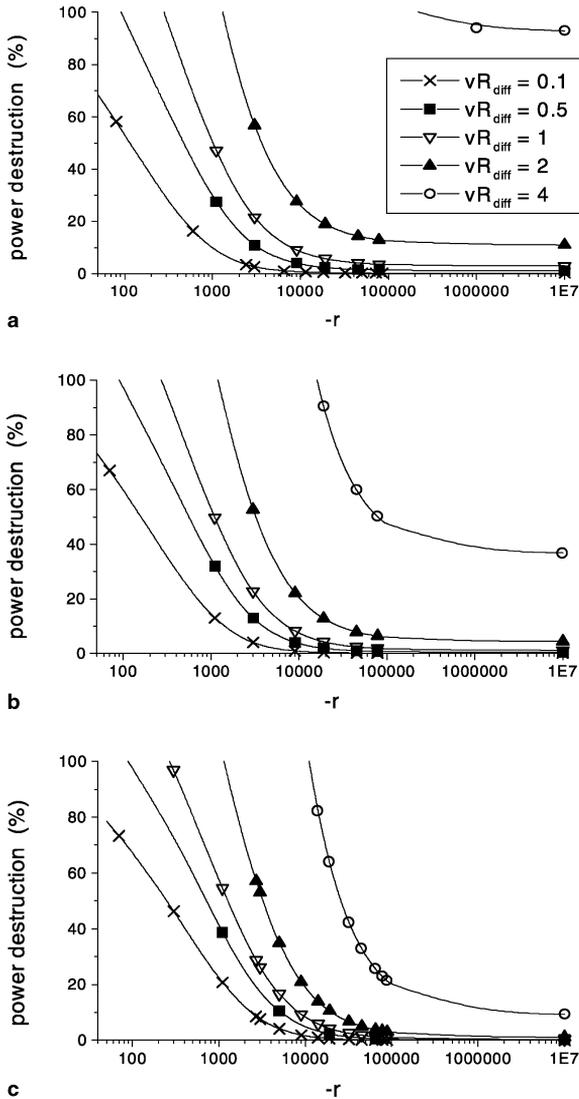
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Fig. 3. Proportion of the power lost inside the porous support structure for NaCl-water solution corresponding to $\pi_3 = \pi_{ocean} = 24$ bar. In Fig. 3a) $\pi_1 = 0.5$ bar ($c_{NaCl} = 10$ mol/m^3), 3b) $\pi_1 = 0.1$ bar ($c_{NaCl} = 2$ mol/m^3) and 3c) $\pi_1 = 0.025$ bar ($c_{NaCl} = 0.5$ mol/m^3).

product of the osmotic flux (v) and the diffusion resistance (R_{diff}) of the support structure.

Acknowledgement

Nomenclature

A	transport coefficient for the membrane, m/sPa
a	activity, dimensionless
c	concentration, mol/m^3
D	diffusion coefficient, m^2/s
f	the fraction of lost power inside the support structure, dimensionless
$\dot{H}$	enthalpy flux, W/m^2
J	molar flux, mol/m^{2}s
m	molality, mol/kg
p	hydrostatic pressure, bar or Pa in equations
P	power, W/m^2
r	ratio between solvent and solute flux, dimensionless
R_{diff}	diffusion resistance, s/m
$\dot{Q}$	heat flux, W/m^2
s	molar specific entropy, J/molK
$\Re$	universal gas constant, J/molK
T	absolute temperature, K
υ	volume flow per surface area of the membrane, m/s
γ	isobaric coefficient of volume expansion, 1/K
Δz	thickness of the support layer, m
η	efficiency, dimensionless
π	osmotic potential (osmotic pressure), bar or Pa
σ	rate of entropy generation per surface area of the membrane, W/Km^2
τ	tortuosity, dimensionless
υ	partial molar volume, m^3/mol
ϕ	porosity, dimensionless
φ	activity coefficient, dimensionless

Subscripts

1, 2, 3	different locations of the membrane (see Fig. 1)
s	solute
tot	total
w	solvent

References

[1] Lee, K.L., Baker, R.W., Lonsdale, H.K., Membranes for power generation by pressure-retarded osmosis, J. Membrane Sci., 8 (1981), 141.
[2] Bejan, A., Maximum power from fluid flow, Int. J. Heat Mass Transfer, 39 (1996), 1175–1181.
[3] Seppälä, A., Lampinen M.J., On the non-linearity of osmotic flow, submitted for publication in Experimental Thermal and Fluid Science (2003).
[4] Seppälä, A., Lampinen, M.J., Thermodynamic optimizing of pressure-retarded osmosis power generation systems, J. Membrane Sci., 161 (1999), 115–138.
[5] Loeb, S., Honda, T., Reali, M., Comparative mechanical efficiency of several plant configurations using a pressure-retarded osmosis energy converter, J. Membrane Sci., 51 (1990), 323–335.

[6] Seppälä, A., Lampinen, M. J., Kotiaho, W., A new concept for an osmotic energy converter, Int. J. Energy Res., 25 (2001), 1359.

[7] Ensor, D. D., Anderson, H. L., Heats of dilution of NaCl: Temperature dependence, J. Chem. Eng. Data, 18 (1973), 205.

[8] Loeb, S., Mehta, G.D., A two-coefficient water transport equation for pressure-retarded osmosis, J. Membrane Sci., 4 (1979), 351.

[9] Ludwig, W., Seppälä, A., Lampinen, M.J., Experimental study of the osmotic behaviour of reverse osmosis membranes for different NaCl solutions and hydrostatic pressure differences, Experimental Thermal and Fluid Sci., 26 (2002), 963.

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