

Supporting Information

Derivation of the Theoretical Minimum Energy of Separation of Desalination Processes

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Effect of Solution Activity on the Equilibrium Driving Force for Desalination

In our analysis, we assumed an ideal salt (NaCl) solution with the activity coefficient being unity. However, for the robustness of the analysis, it is necessary to check the validity of this assumption. In this section, we consider a non-ideal solution and determine the equilibrium hydraulic pressure and the equilibrium cell voltage which are used to calculate the theoretical minimum energy of separation for desalination by reverse osmosis (RO) and electrodialysis (ED), respectively.

The equilibrium hydraulic pressure in batch RO is equal to the osmotic pressure of the brine, π , which is a function of the molar fraction of water (x_w):

$$\pi = - \frac{RT \ln(\gamma_w x_w)}{\hat{V}_w} \quad (S1)$$

We note that eq S1 is similar to eq 15 in the main text, but includes the activity coefficient of water, γ_w . The later depends on the molar fraction of water, x_w , and can be calculated by^{1, 2}

$$\gamma_w = -1.9407(\ln x_w)^2 - 0.1605(\ln x_w) + 1 \quad (S2)$$

For an ideal solution (as assumed in the main text), we calculated the osmotic pressure of the NaCl solution using the van't Hoff equation:

$$\pi = 2RTc \quad (S3)$$

where the molar fraction of water is related to the molar salt concentration by

$$x_w = 1 - x_s = 1 - 2c\hat{V}_w \quad (S4)$$

Similarly, the equilibrium voltage in ED for non-ideal solution can be calculated by modifying the eq 34 in the main text:

$$\Delta E_{eq} = 2 \frac{RT}{F} \ln \frac{\gamma_{s,b} x_{s,b}}{\gamma_{s,p} x_{s,p}} \quad (S5)$$

where $\gamma_{s,b}$ and $\gamma_{s,p}$ are the salt activity coefficients of the brine and the permeate streams, respectively, and $x_{s,b}$ and $x_{s,p}$ are the salt molar fractions of the brine and the permeate streams, respectively. We use the following equation to estimate the salt activity coefficient:^{1, 2}

$$\gamma_s = -0.06602(\ln(x_s - 0.0001217)) + 9.563(x_s)^2 + 0.5551(x_s) + 0.4049 \quad (S6)$$

The osmotic pressure and cell voltage calculated for an ideal solution (i.e., using salt concentration) and a non-ideal solution (i.e., using activity coefficients) are shown in Figure S1. Within the investigated conditions and salt concentrations, the osmotic pressures calculated with the two methods are very close to each other. Similarly, the cell voltages obtained from the two methods are in remarkable agreement over a wide range of salt removal (up to 99%). Hence, the assumption of an ideal solution (i.e., unity activity coefficients) does not compromise the accuracy of the calculations presented in the main text.

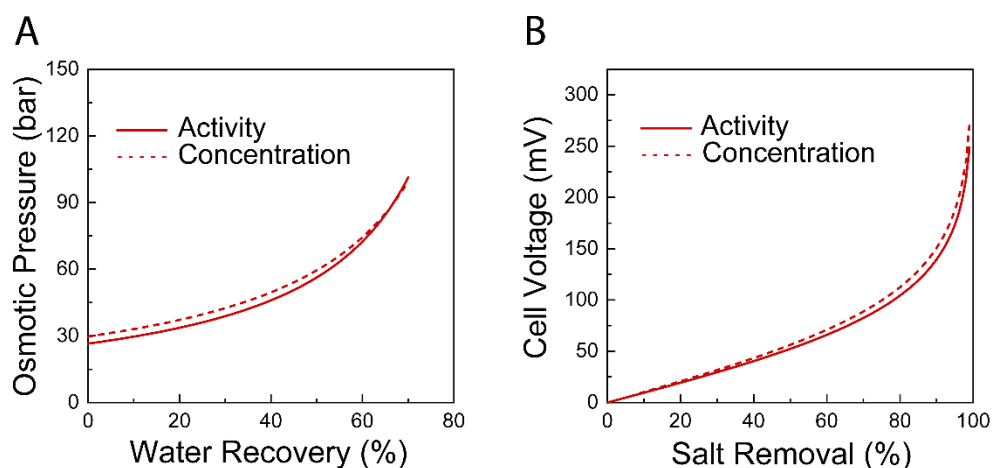


Figure S1. Impact of non-ideal solution on calculating the (A) osmotic pressure and (B) cell voltage as a function of water recovery (in RO) and salt removal (in ED), respectively. In both cases, the feed solution (NaCl concentration is 0.6 M. The salt rejection for RO is fixed at 100%, while the water recovery for ED is fixed at 50%.

Nomenclature for Equations in the Article

Symbols	Description
c	Concentration
c'	Concentration during the process of electrodialysis
E	Electrical voltage
F	Faraday constant
n	Total moles of solution
n_s	Moles of salt transported from the feed
n_T	Ultimate moles of salt removed from the feed

P	Hydraulic pressure
Q	Transferred electrical charge
R	Gas constant
r	Cumulative water recovery
R_w	Final water recovery
T	Absolute temperature
V	Solution volume
\hat{V}	Molar volume
W	Work
x	Mole fraction
N	Total number of stages
$\bar{\mu}$	Electrochemical potential
π	Osmotic pressure
$\Delta_{\text{mix}}G$	Gibbs free energy of the mixture
$\Delta_{\text{mix}}\hat{G}$	Molar Gibbs free energy of the mixture
$\Delta_{\text{sep}}\hat{G}$	Molar Gibbs free energy of separation
Acronyms	
AEM	Anion exchange membrane
CEM	Cation exchange membrane
ED	Electrodialysis
IEM	Ion exchange membrane
RO	Reverse osmosis
SEC	Specific energy consumption
Subscripts	
1	Single stage
b	Brine
c	Cation
eq	Equilibrium
f	Feed
i	Species i
min	Minimum
p	Permeate
rev	Reversible
w	Water
Superscripts	
0	Reference state

References

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2. Yip, N. Y.; Elimelech, M., Comparison of Energy Efficiency and Power Density in Pressure Retarded Osmosis and Reverse Electrodialysis. *Environ Sci Technol* **2014**, *48*, (18), 11002-11012.