Supporting Information

Thermodynamic and Energy Efficiency Analysis of Power Generation from Natural Salinity Gradients by Pressure Retarded Osmosis

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ENERGY OF MIXING

When two solutions of different composition are mixed, the Gibbs free energy of mixing is released. Here, we draw upon established thermodynamic concepts[1-5] to present the theoretical background on the energy change of mixing, and subsequently focus the discussion on a binary system of aqueous strong electrolyte solutions pertinent to this study.

Gibbs Energy of Solutions. In a solution containing two or more species, the partial molar Gibbs energy of species i, $\bar{G}_i$, describes the free energy per mole of the individual species in solution.[1]

$$\bar{G}_i = G_i(T,P) + RT \ln(\gamma_i x_i) \tag{S1}$$

where $G_i(T,P)$ is the molar Gibbs energy of pure species i at temperature T and pressure P, R is the gas constant, and x_i is the mole fraction of species i in solution. The activity coefficient, γ_i, is incorporated to account for the behavior of non-ideal solutions, and is a function of the temperature, pressure, and solution composition.[2] The total molar Gibbs free energy of the solution, G, is a measure of the thermodynamic potential of one mole of the solution and is the sum of the weighted contribution of the individual species (eq S1):[1]

$$G = \sum x_i \bar{G}_i = \sum x_i G_i + RT \sum x_i \ln(\gamma_i x_i) \tag{S2}$$

Mixing Releases Free Energy. Mixing two solutions, A and B, of different composition yields a resultant mixture, M. The difference in the Gibbs free energy between the final mixture (G_M) and initial (G_A and G_B) solutions gives the change in free energy of mixing. The Gibbs free energy of mixing per mole of the system, ΔG_{mix}, is therefore[2]

$$-\Delta G_{mix} = G_M - (\phi_A G_A + \phi_B G_B) \tag{S3}$$

where ϕ_A and ϕ_B are the ratios of the total moles in solutions A or B, respectively, to the total moles in the system (i.e., $\phi_A + \phi_B = 1$). Here, we adopt the negative convention for the energy of mixing to reflect that energy is released; that is, $G_M - (\phi_A G_A + \phi_B G_B) < 0$.

As all species are conserved in the mixing process (i.e., no chemical reaction), the composition of the resultant mixture, $x_{i,M}$, is determined by the proportion and composition of the

initial solutions (ϕ_A, ϕ_B, $x_{i,A}$, and $x_{i,B}$). Species conservation also dictates that the sum of the Gibbs energy of the pure species in solution A and B is equal to the sum of G_i in the resultant mixture:[2] $\left(\sum x_i G_i\right)_A + \left(\sum x_i G_i\right)_B = \left(\sum x_i G_i\right)_M$. Substituting this and eq S2 into eq S3 reduces the energy change of mixing to

$$-\Delta G_{mix} = RT\left\{\left[\sum x_i \ln\left(\gamma_i x_i\right)\right]_M - \phi_A\left[\sum x_i \ln\left(\gamma_i x_i\right)\right]_A - \phi_B\left[\sum x_i \ln\left(\gamma_i x_i\right)\right]_B\right\} \qquad (1)$$

Note that this equation is eq 1 of the main manuscript. An inspection of eq 1 reveals that ΔG_{mix} is dependent on the relative proportion of the initial solutions (ϕ_A and ϕ_B) and the composition of the solutions (x_i and, implicitly, γ_i) for a mixing process at constant temperature and pressure. The Gibbs free energy of mixing described in eq 1 is applicable for all general mixing processes,[1] and it is equal and opposite in sign to the minimum energy required to separate the mixture M into products A and B.[4]

Energy Change of Mixing for Strong Electrolyte Solutions. For a two-component system of aqueous strong electrolyte solutions, species $i = 1$ is water and $i = 2$ is a salt that dissociates completely in solution (denoted by subscripts w and s, respectively). For relatively low salt concentration solutions, both the mole fraction of water, x_w, and the activity coefficient, γ_w, can be approximated to unity.[3] Therefore, $\ln(\gamma_w x_w)$ for the initial solutions and final mixture approaches zero. In this case, the contribution of the salt species to ΔG_{mix} overwhelms the contribution of the water species. To account for the multiple ionic species contribution of the strong electrolyte salt, ν is introduced into eq 1 as the exponent of the $\gamma_s x_s$ terms.[2] The molar Gibbs free energy of mixing thus becomes

$$-\frac{\Delta G_{mix}}{RT} \approx \left[x_s \ln\left(\gamma_s x_s\right)^\nu\right]_M - \phi\left[x_s \ln\left(\gamma_s x_s\right)^\nu\right]_A - (1-\phi)\left[x_s \ln\left(\gamma_s x_s\right)^\nu\right]_B \qquad (S4)$$

where ϕ is the ratio of the total moles in solution A to the total moles in the system (i.e., $\phi = \phi_A$ and $1-\phi = \phi_B$) and ν is the number of ions each electrolyte molecule dissociates into. That is, $\nu = 2$ for sodium chloride as the salt dissociates in water to form a cation-anion pair of Na^+ and Cl^-. Note that this equation is equivalent to eq 2 of the main manuscript.

For practicality and ease of application, here we will convert the mole fraction and molar mixing energy in eq S4 to molar salt concentration and Gibbs free energy of mixing per unit

volume, respectively. Dividing the molar energy of mixing by the molar volume of the resultant mixture (i.e., V_M/N_M) yields the specific Gibbs free energy of mixing, $\Delta G_{mix,V_M}$, defined as the energy per unit volume of resultant mixture:

$$\Delta G_{mix,V_M} = \Delta G_{mix,N_M} \frac{N_M}{V_M} \qquad (S5)$$

where V_M is the volume of the resultant mixture. Substituting eq S4 into eq S5 yields:

$$-\frac{\Delta G_{mix,V_M}}{\nu RT} = \frac{x_{s,M} N_M}{V_M} \ln\left(\gamma_{s,M} x_{s,M}\right) - \phi \frac{x_{s,A} N_M}{V_M} \ln\left(\gamma_{s,A} x_{s,A}\right) - \left(1-\phi\right) \frac{x_{s,B} N_M}{V_M} \ln\left(\gamma_{s,B} x_{s,B}\right) \quad (S6)$$

For relatively dilute solutions, the volumetric and mole contribution of salt to the solution is negligible compared to water. Thus, the solution volume and the total number of moles in solution are approximately the volume of water and the moles of water, respectively. By further assuming that the volume of the system does not change in the mixing process ($V_A+V_B = V_M$), i.e., the solutions exhibit ideal behavior, the mole fractions can be approximated to the volumetric fractions:

$$\frac{N_A}{N_M} = \phi \approx \frac{V_A}{V_M} \qquad (S7)$$

$$\frac{N_B}{N_M} = 1-\phi \approx \frac{V_B}{V_M} \qquad (S8)$$

The molar salt concentration of the solution, c, is the product of the salt mole fraction, x_s, and the total number of moles in solution, N, divided by the solution volume, V. Hence, the molar salt concentration of the resultant mixture is:

$$c_M = \frac{x_{s,M} N_M}{V_M} \qquad (S9)$$

Applying eqs S7 and S8 to the molar salt concentration of solutions A and B, we arrive at following expressions:

$$c_A = \frac{x_{s,A} N_A}{V_A} = \frac{x_{s,A} \phi N_M}{V_A} \approx \frac{x_{s,A} N_M}{V_M} \qquad (S10)$$

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$$c_B = \frac{x_{s,B} N_B}{V_B} = \frac{x_{s,B}(1-\phi) N_M}{V_B} \approx \frac{x_{s,B} N_M}{V_M} \qquad (S11)$$

Substituting eqs S9, S10, and S11 into eq S6 yields

$$-\frac{\Delta G_{mix,V_M}}{\nu RT} \approx c_M \ln\left(\gamma_{s,M} x_{s,M}\right) - \phi c_A \ln\left(\gamma_{s,A} x_{s,A}\right) - (1-\phi) c_B \ln\left(\gamma_{s,B} x_{s,B}\right) \qquad (S12)$$

Since the volumetric contribution of salt is negligible compared to water, the mole fraction of salt in solution $x \approx c\bar{V}$, where $\bar{V}$ is the molar volume of pure water. Substituting this into eq S12 and rearranging the terms:

$$-\frac{\Delta G_{mix,V_M}}{\nu RT} \approx c_M \ln\left(\gamma_{s,M} c_M\right) - \phi c_A \ln\left(\gamma_{s,A} c_A\right) - (1-\phi) c_B \ln\left(\gamma_{s,B} c_B\right)$$

$$+ \left[c_M - \phi c_A - (1-\phi) c_B \right] \ln \bar{V} \qquad (S13)$$

Applying salt mass balance on the initial and final solutions yields $c_M = \phi c_A + (1-\phi) c_B$. That is, $c_M - \phi c_A - (1-\phi) c_B = 0$. Thus, the last term in eq S13 vanishes and the specific Gibbs free energy of mixing simplifies to

$$-\frac{\Delta G_{mix,V_M}}{\nu RT} \approx c_M \ln\left(\gamma_{s,M} c_M\right) - \phi c_A \ln\left(\gamma_{s,A} c_A\right) - (1-\phi) c_B \ln\left(\gamma_{s,B} c_B\right) \qquad (3)$$

The specific Gibbs free energy of mixing, $\Delta G_{mix,V_M}$, is expressed in terms of the molar salt concentration of the initial solutions and resultant mixture, c, the salt activity coefficients, γ_s, and mole fraction (or volume fraction) of solution A to the whole system, ϕ — parameters that are more practical and easier to apply. Note that this equation is eq 3 of the main manuscript.

Multiplying eq 3 by V_M/V_A ($\approx 1/\phi$) yields the Gibbs free energy of mixing per unit volume of A (the more dilute solution):

$$-\frac{\Delta G_{mix,V_A}}{\nu RT} \approx \frac{c_M}{\phi} \ln\left(\gamma_{s,M} c_M\right) - c_A \ln\left(\gamma_{s,A} c_A\right) - \frac{(1-\phi)}{\phi} c_B \ln\left(\gamma_{s,B} c_B\right) \qquad (4)$$

This equation is eq 4 of the main manuscript.

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Using eq 4, $\Delta G_{mix,V_A}$ is determined in 0.1 increments of ϕ for dilute solutions (A) of river water and brackish water, represented by 1.5 and 17 mM (88 and 1,000 mg/L) NaCl, respectively. The concentrated solution, B, is seawater, taken to be 600 mM (35 g/L) NaCl and the temperature is 298 K. The calculated values are presented in Table S1 of the Supporting Information and plotted in Figure 1 of the main manuscript (indicated by the blue square symbols for river water and red circle symbols for brackish water). The activity coefficients of the initial solutions (A and B) and resultant mixture (M) were approximated by linear interpolation from the data in Table S2 of the Supporting Information.

Table S1. The Gibbs free energy of mixing per unit volume of the dilute solution (A). Seawater is employed as the concentrated solution and the temperature is 298 K. Values determined using eq 4 incorporates the activity coefficients, while calculations using eq 5 assumes $\gamma = 1$ (i.e., ideal behavior).

	$\Delta G_{mix,V_A}$ (kWh/m^3)			
Dilute Solution	**River Water**		**Brackish Water**	
ϕ	**Eq 4**	**Eq 5 (difference)**	**Eq 4**	**Eq 5 (difference)**
0.0	0.768	0.811 (5.7%)	0.682	0.719 (5.4%)
0.1	0.721	0.769 (6.7%)	0.637	0.679 (6.5%)
0.2	0.678	0.723 (6.6%)	0.597	0.636 (6.4%)
0.3	0.627	0.674 (7.4%)	0.549	0.589 (7.3%)
0.4	0.574	0.619 (7.8%)	0.500	0.538 (7.7%)
0.5	0.517	0.559 (8.1%)	0.446	0.482 (8.1%)
0.6	0.455	0.492 (8.2%)	0.387	0.419 (8.1%)
0.7	0.381	0.414 (8.7%)	0.319	0.347 (8.6%)
0.8	0.295	0.321 (9.1%)	0.240	0.262 (9.3%)
0.9	0.185	0.202 (8.9%)	0.143	0.156 (9.0%)
1.0	0	0 (-)	0	0 (-)

Table S2 of the Supporting Information presents a summary of the NaCl activity coefficients for the range of salt concentrations relevant to this study.[3,5] The molar concentrations, c, presented were converted from molal concentrations using salt solution density data.[5] For c between 1.5–17 mM (representative of river water and brackish water, respectively) and 600 mM (representative of seawater) NaCl, the activity coefficient, γ, varies from 0.957–0.879 to 0.672.

Table S2. Summary of the sodium chloride activity coefficients at different molar concentrations.[3,5]

Molar Concentration, c (mM)	0	1.51	6.03	13.6	24.1	37.7	54.4	74.1
Activity Coefficient, γ (-)	1	0.957	0.920	0.888	0.860	0.835	0.813	0.794

Molar Concentration, c (mM)	94.6	190	238	286	383	480	579	678
Activity Coefficient, γ (-)	0.778	0.735	0.720	0.710	0.693	0.681	0.673	0.667

ΔG_{mix} for Ideal Solutions. For the relatively low salt concentrations investigated in this study, the mole fraction of salt (or molar salt concentration) dominates over the salt activity coefficient in the logarithmic term in eq 4, i.e., $\ln(\gamma_s x_s) = \ln(\gamma_s) + \ln(x_s) \approx \ln(x_s)$. For example, for a 600 mM NaCl solution which is representative of seawater, $\ln(x_s) = \ln(0.0107) = -4.54$ is much greater in magnitude than $\ln(\gamma_s) = \ln(0.672) = -0.40$. To further simplify the analysis, we can neglect the effects of the activity coefficient and eq 4 further reduces to

$$-\frac{\Delta G_{mix,V_A}}{\nu RT} \approx \frac{c_M}{\phi}\ln c_M - c_A \ln c_A - \frac{(1-\phi)}{\phi}c_B \ln c_B \tag{5}$$

Note that this equation is eq 5 of the main manuscript.

Figure 1 of the manuscript shows $\Delta G_{mix,V_A}$ as a function of ϕ assuming negligible effect from γ. The dilute solutions (A) of river water and brackish water (indicated by the solid blue line and dashed red line) are paired with seawater (concentrated solution B). Table S1 of the Supporting Information shows $\Delta G_{mix,V_A}$ calculated using eq 5 for 0.1 increments in ϕ. The difference between the Gibbs free energy of mixing determined using eq 4 and 5 signifies the imprecision that arises from neglecting the influence of γ.

NOMENCLATURE

Symbols

c	molar concentration
G	molar Gibbs free energy of solution
$\bar{G}_i$	partial molar Gibbs energy of species i
G_i	molar Gibbs energy of pure species i
ΔG_{mix}	molar Gibbs free energy of mixing
$\Delta G_{\text{mix},V_A}$	specific Gibbs free energy of mixing
$\Delta G_{\text{mix},V_M}$	Gibbs free energy of mixing per unit volume of the resultant mixture
N	number of moles in solution
P	pressure
R	gas constant
T	absolute temperature
V	volume of solution
x_i	mole fraction of species i in solution

Greek Symbols

γ_i	activity coefficient of species i
ν	number of ions each electrolyte molecule dissociates into
ϕ	ratio of total moles (or volume) of the solution to total moles (or volume) of the system

Subscripts

A	solution A
B	solution B
M	resultant mixture
s	salt species
w	water species

References

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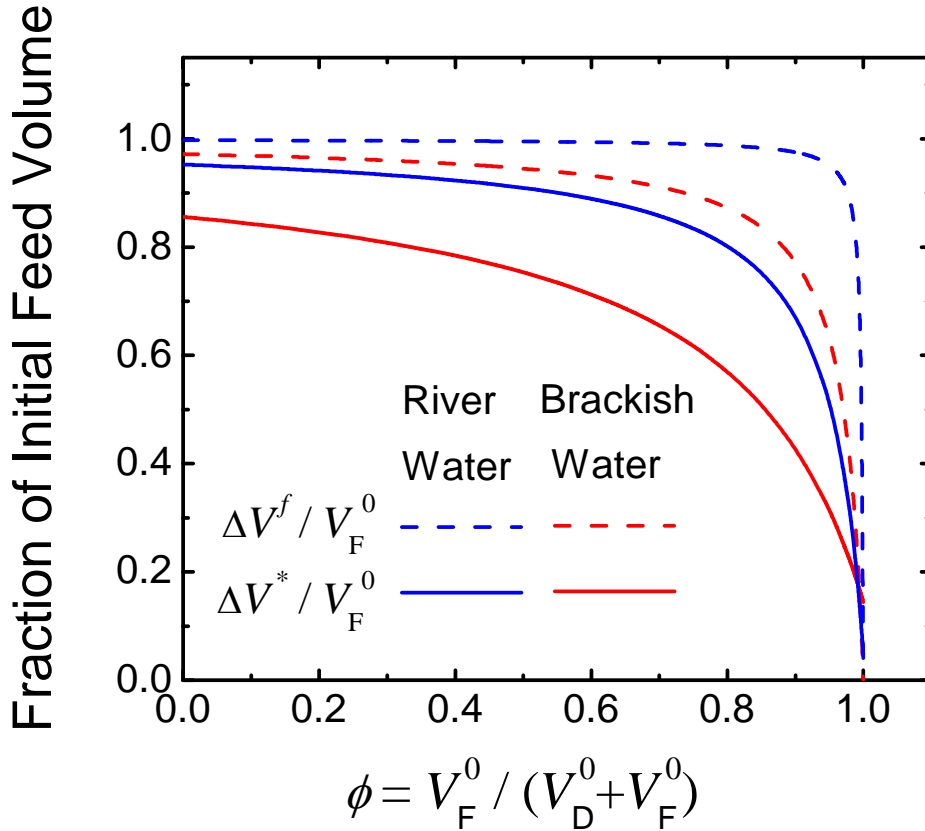
FIGURE S1. Fraction of initial feed solution volume that permeates into the draw solution, as a function of the volumetric fraction of the feed solution (river water or brackish water as indicated by the blue or red lines, respectively) to both the draw (seawater) and feed solutions, ϕ. Dashed blue and red lines represent the fraction of feed solution that permeates into the draw solution in a reversible thermodynamic PRO process (i.e., eq 7). Solid blue and red lines represent the fraction of feed solution that permeates into the draw solution in a constant-pressure PRO process that maximizes extractable work (i.e., eq 13). The salt concentrations of the river water, brackish water and seawater are 1.5, 17, and 600 mM (88 mg/L, 1000 mg/L, 35 g/L) NaCl respectively.
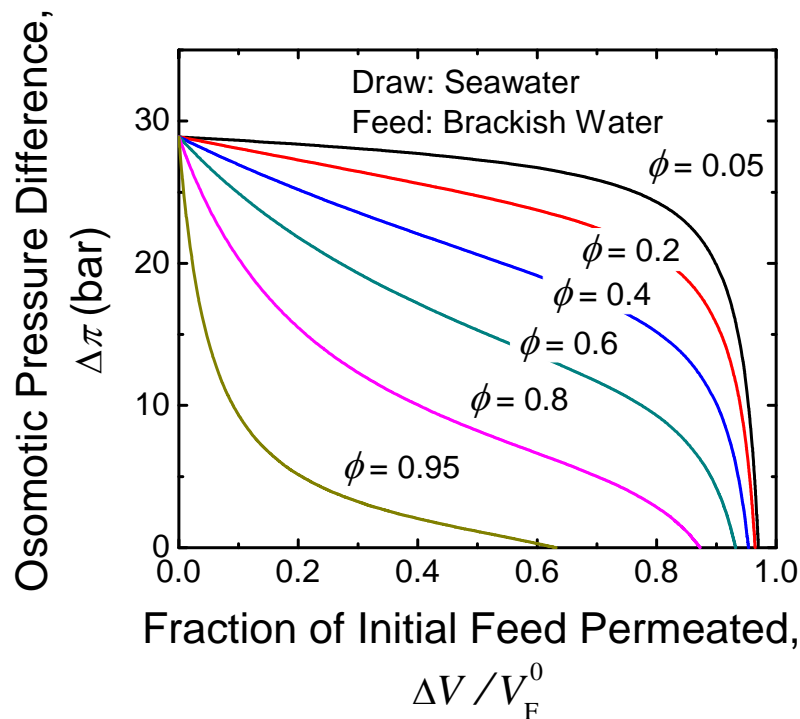
FIGURE S2. Osmotic pressure difference between the draw and feed solutions, $\Delta\pi$, as a function of the volumetric fraction of initial feed solution permeated, $\Delta V/V_F^0$ (i.e., eq 9). The plots for a range of ϕ (volumetric ratio of the feed solution to both the draw and feed solutions) is presented. The seawater draw solution (600 mM or 35 g/L NaCl) and brackish water feed solution (17 mM or 1000 mg/L NaCl) have initial osmotic pressures of 29.7 and 0.84 bar, respectively. The temperature is taken to be 298 K. The horizontal axis intercepts signify the fraction of initial feed solution volume that will ultimately permeate across the membrane (eq 7 and Figure S1 of Supporting Information). The convex shape of the plots for low volumetric fractions of initial feed solution volume, e.g., $\phi = 0.05$, is attributed to the increase in salt concentration of the feed solution as pure water permeates across to the draw side. Conversely, for large ϕ, the permeate dilutes the relatively small V_D^0 rapidly to produce the concave shape curve. The area under each pressure-volume curve represents the specific ideal work (extractable energy per unit volume of the initial feed solution) for a reversible thermodynamic PRO process.
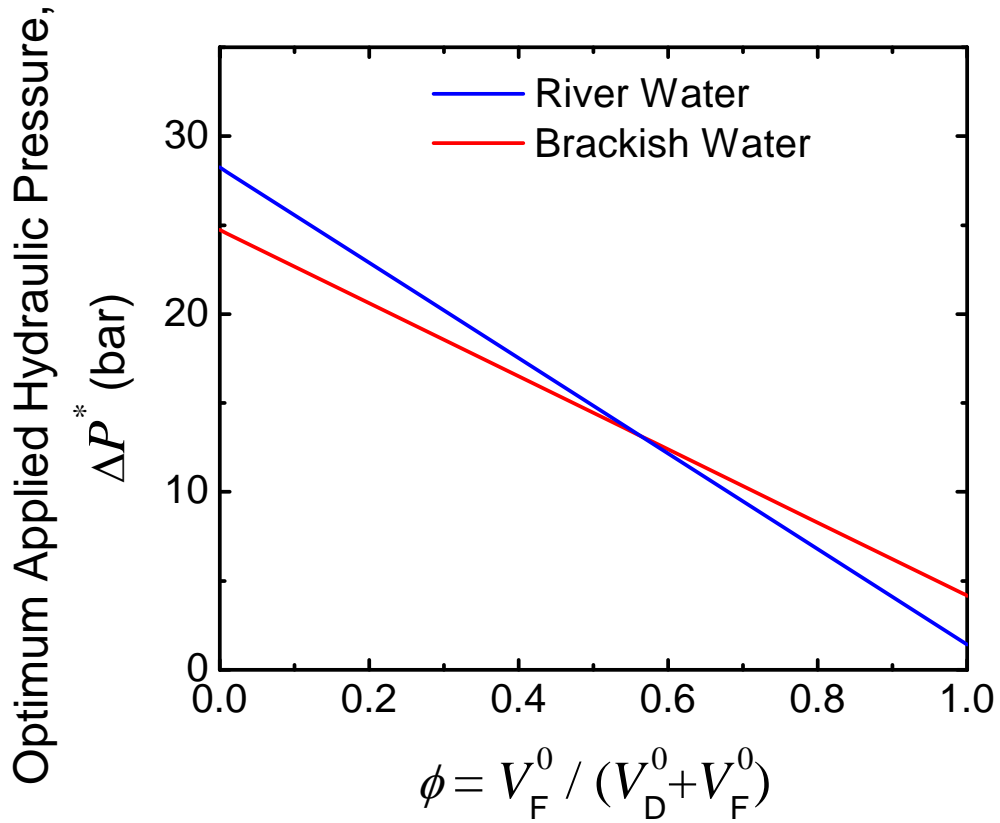
FIGURE S3. Applied hydraulic pressure difference in order to maximize the work that can be extracted in a constant pressure PRO process, ΔP^*, as a function of the volumetric fraction of the feed solution (river or brackish water) to both the draw and feed solution, ϕ (eq 14). The concentration of the seawater draw solution was assumed to be 600 mM NaCl, while the concentration of river water (blue line) and brackish water (red line) feed solutions were taken to be 1.5 and 17 mM NaCl, respectively. Temperature $T = 298$ K.