

Supporting Information

Salinity Gradients for Sustainable Energy: Primer, Progress, and Prospects

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Energy of Mixing. The Gibbs free energy of mixing, ΔG_{mix} , represents the energy that can potentially be harnessed for useful work production when two solutions of different composition are combined. For aqueous solutions of a strong electrolyte (i.e., the solute completely dissociates in water), the Gibbs free energy of mixing per mole of the system, $\Delta G_{\text{mix},N_T}$, is expressed in eq 1 of the main manuscript:

$$-\frac{\Delta G_{\text{mix},N_T}}{R_g T} = \left[\sum x_i \ln(\gamma_i x_i) \right]_{\text{M}} - \phi \left[\sum x_i \ln(\gamma_i x_i) \right]_{\text{LC}} - (1-\phi) \left[\sum x_i \ln(\gamma_i x_i) \right]_{\text{HC}} \quad (1)$$

where R_g is the gas constant, T is the absolute temperature, and x_i is the mole fraction of species i in the resultant mixture, low concentration solution, and high concentration solution (denoted by subscripts M, LC, and HC, respectively). The ratio of the total moles in the LC solution to the total moles in the system is denoted by ϕ . For single electrolyte solutions, $\sum x_i \ln(\gamma_i x_i) = x_w \ln(\gamma_w x_w) + x_s \ln(\gamma_s x_s)$ as the two species are water and dissociated ions of the salt (designated by subscripts w and s, respectively). Because the activity coefficients used in eq 1, γ_w and γ_s , are not readily available in literature, the Pitzer equations are adopted in this analysis to determine the free energy of mixing.¹⁻³

Pitzer Equations for Nonideal Electrolytes. The excess Gibbs free energy G^{EX} of a system is the difference between the Gibbs energy of the real system, G , and that of an ideal system under the same conditions.³

$$G^{\text{EX}} = G - N_1 G_1^\circ - N_2 \bar{G}_2^\circ + R_g T \nu N_2 (1 - \ln m) = R_g T \nu N_2 (\ln \gamma_{\pm} + 1 - \phi) \quad (\text{S1})$$

where N_1 and N_2 are the moles of solvent and solute, G_1° and \bar{G}_2° are the Gibbs energies of solvent and solute in their standard states, respectively, ν is the number of ionic species each electrolyte molecule dissociates into (e.g., $\nu = 2$ for NaCl), and m is molal concentration. For the electrolytes considered here, the standard states are defined as pure liquid water and hypothetical 1 m ideal NaCl solution. The average salt activity coefficient, $\gamma_{\pm} = (\gamma_+ \gamma_-)^{1/\nu}$, accounts for nonideal behavior of the ions, while the osmotic coefficient, ϕ , factors in both the concentration and nonideal effects on activity. Note that γ_{\pm} and ϕ used in the Pitzer equations are based on

molal concentrations and are defined fundamentally differently from the activity coefficients in eq 1 of the main manuscript, which are based on mole fraction concentrations.

Rearranging eq S1 and normalizing by the total moles of the system, N_T , yields the Gibbs free energy per mole for an aqueous solution of a single strong electrolyte (such as, NaCl):

$$G_{N_T} = x_1 G_1^\circ + x_2 \bar{G}_2^\circ + R_g T \nu x_2 (\ln m + \ln \gamma_\pm - \varphi) \quad (S2)$$

$$= x_w G_1^\circ + x_2 \bar{G}_2^\circ + R_g T [x_s \ln(\gamma_\pm m) - x_s \varphi] \quad (S3)$$

where x_1 is the mole fraction of water (i.e., equivalent to x_w), x_s is the mole fraction of the dissociated salt, while x_2 is the mole fraction of the undissociated salt. That is, $x_w + x_s = 1$. It is informative to note that the $\ln(m)$ term represents the Gibbs free energy due to salt concentration and the $\ln(\gamma_\pm)$ term accounts for the non-idealities of the ions, while the contribution of concentration and non-idealities of water to G is treated in a fundamentally different manner, being grouped together into the product of x_s and φ .

The Gibbs free energy of mixing a low concentration, LC, and a high concentration, HC, solution is the difference in G of the mixture and the initial solutions:

$$-\Delta G_{\text{mix}, N_T} = G_{M, N_T} - \phi G_{\text{LC}, N_T} - (1 - \phi) G_{\text{HC}, N_T} \quad (S4)$$

where ϕ is the ratio of the total moles in LC solution to the total moles in the system (i.e., $\phi = N_{\text{LC}}/N_T$). Substituting eq S3 into eq S4 gives:

$$\begin{aligned} -\Delta G_{\text{mix}, N_T} = & \left\{ x_w G_1^\circ + x_2 \bar{G}_2^\circ + R_g T [x_s \ln(\gamma_\pm m) - x_s \varphi] \right\}_M \\ & - \phi \left\{ x_w G_1^\circ + x_2 \bar{G}_2^\circ + R_g T [x_s \ln(\gamma_\pm m) - x_s \varphi] \right\}_{\text{LC}} \\ & - (1 - \phi) \left\{ x_w G_1^\circ + x_2 \bar{G}_2^\circ + R_g T [x_s \ln(\gamma_\pm m) - x_s \varphi] \right\}_{\text{HC}} \end{aligned} \quad (S5)$$

Because the moles of water and solute are conserved before and after mixing, $x_M = \phi x_{\text{LC}} + (1 - \phi) x_{\text{HC}}$ and $\Delta G_{\text{mix}, N_T}$, thus, reduces to:

$$-\frac{\Delta G_{\text{mix}, N_T}}{R_g T} = [x_s \ln(\gamma_\pm m) - x_s \varphi]_M - \phi [x_s \ln(\gamma_\pm m) - x_s \varphi]_{\text{LC}} - (1 - \phi) [x_s \ln(\gamma_\pm m) - x_s \varphi]_{\text{HC}} \quad (S6)$$

For small x_s , $-x_s \approx \ln(1-x_s) = \ln(x_w)$. Comparing the terms within the square brackets of eq 1 in the main manuscript, $x_s \ln(\gamma_s x_s) + x_w \ln(\gamma_w x_w)$, and eq S6 above, $x_s \ln(\gamma_{\pm} m) - x_s \varphi \approx x_s \ln(\gamma_{\pm} m) + \varphi \ln(x_w)$, reveals the similarity in general form and also the distinct differences in definition of the coefficients.

Determination of Pitzer Coefficients. The salt activity coefficient and osmotic coefficient can be calculated using the Pitzer equations:²⁻⁴

$$\ln \gamma_{\pm} = -A_{\phi} \left[\frac{\sqrt{\mu}}{1+b\sqrt{\mu}} + \frac{2}{b} \ln(1+b\sqrt{\mu}) \right] + mB_{\gamma} + m^2 C_{\gamma} \quad (\text{S7})$$

$$\varphi = 1 - \frac{A_{\phi} \sqrt{\mu}}{1+b\sqrt{\mu}} + mB_{\phi} + m^2 C_{\phi} \quad (\text{S8})$$

where A_{ϕ} is the Debye–Hückel slope for osmotic coefficient (0.3915 at 25 °C and 1 bar), μ is the ionic strength, constant $b = 1.2$, and m is molal concentration. Parameters B_{γ} , B_{ϕ} , C_{γ} , and C_{ϕ} are further determined by

$$B_{\gamma} = \beta_0 + \frac{2\beta_1}{\alpha^2 \mu} \left[1 - (1 + \alpha\sqrt{\mu}) e^{-\alpha\sqrt{\mu}} \right] + B_{\phi} \quad (\text{S9})$$

$$B_{\phi} = \beta_0 + \beta_1 e^{-\alpha\sqrt{\mu}} \quad (\text{S10})$$

$$C_{\gamma} = 3C_{\phi} \quad (\text{S11})$$

$$C_{\phi} = 2C_{\phi} \quad (\text{S12})$$

where constant $\alpha = 2 \text{ (kg/mol)}^{-1/2}$, and the Pitzer parameters β_0 , β_1 , and C_{ϕ} are 0.0754 kg/mol, 0.2770 kg/mol, and $0.70 \times 10^3 \text{ (kg/mol)}^2$, respectively, for aqueous sodium chloride solutions at 25 °C and 1 bar.³

Because both molal and mole fraction concentrations are utilized in eq S6 and the Pitzer equations, the following conversion is required:

$$x_s = \frac{\nu m}{\nu m + \text{MW}_w^{-1}} \quad (\text{S13})$$

where molecular weight of the water, MW_w , is 18.01528×10^{-3} kg/mol. With solution density, ρ , and molecular weight of the salt, MW_s (0.05844 kg/mol for NaCl), molal concentrations, m , can be converted to molar concentrations, c :

$$c = \rho \left(\frac{m}{1 + mMW_s} \right) \quad (S14)$$

The solution density is the ratio of the molar mass to molar volume of aqueous NaCl solution, \bar{M} and \bar{V} , respectively.

$$\rho = \frac{\bar{M}}{\bar{V}} \quad (S15)$$

Because mass is conserved whereas the aqueous solution volume is not simply equal to the volumetric addition of solid salt and pure water, \bar{M} can be determined from molecular weights and moles of water and salt, N_w and N_s , respectively, while Pitzer equations are used to determine \bar{V} :^{3, 5}

$$\bar{M} = \frac{N_w MW_w + N_s MW_s}{N_w + N_s} \quad (S16)$$

$$\bar{V} = \frac{N_w \bar{V}_w^0 + N_s \phi_{V,s}}{N_w + N_s} \quad (S17)$$

$$\phi_{V,s} = \bar{V}_s^0 + 2A_v h + 2R_g T (mB_v + m^2 C_v) \quad (S18)$$

$$h = \frac{\ln(1 + \alpha\sqrt{\mu})}{2b} \quad (S19)$$

where \bar{V}_w^0 is the molar volume of pure water (18.068 cm³/mol), $\phi_{V,s}$ is the apparent molar volume of the salt, \bar{V}_s^0 is the partial molar volume of the salt at infinite dilution (16.68 cm³/mol for NaCl), A_v is the Debye–Hückel slope for volume, and B_v and C_v are the Pitzer parameters (1.875 cm³kg^{0.5} mol^{-1.5}, 1.234×10^{-5} kg mol⁻¹bar⁻¹, and -6.450×10^{-7} , kg² mol⁻²bar⁻¹, respectively, for aqueous sodium chloride solutions at 25 °C and 1 bar).

The activity coefficient of NaCl, γ_{\pm} , and osmotic coefficient, ϕ , (left and right vertical axes, respectively), as a function of molal concentration are shown in Figure S1. The corresponding

salt mole fraction, x_s , and molar concentrations, c , are indicated on the secondary and tertiary horizontal axes label (note that the scales are not directly proportional to the primary axis of m). The calculated γ_{\pm} and ϕ are then input into eq S6 to determine the Gibbs free energy of mixing, as presented in Figure 1 of the main manuscript.

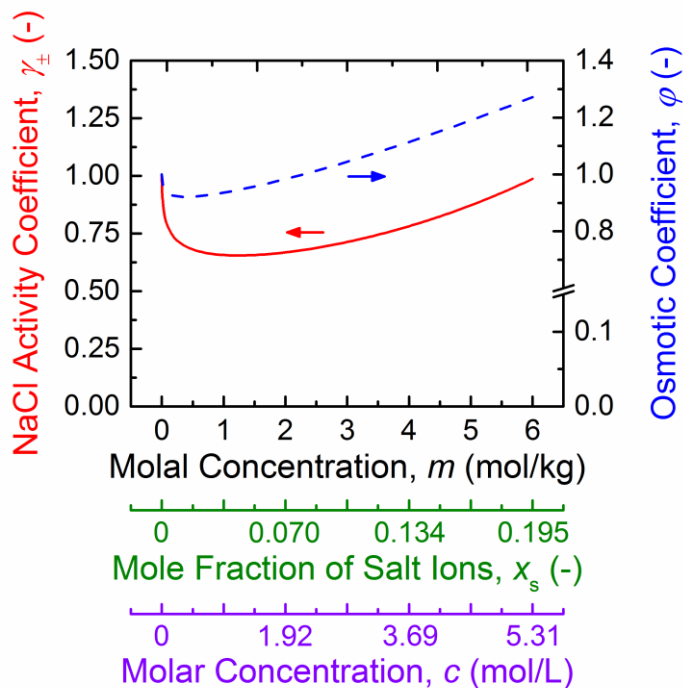


Figure S1. NaCl activity coefficient and osmotic coefficient (solid red and dashed blue lines, respectively) as a function of the molal concentration. Activity coefficient and osmotic coefficient for NaCl electrolyte solutions are determined using the Pitzer equations (eqs S7-12). Eqs S13-14 are employed for conversions between mole fraction, molal, and molar concentrations, while density of the aqueous NaCl solutions is calculated using eqs S15-19.

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