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Effect of composition and nonideal solution behavior on desalination calculations for mixed electrolyte solutions with comparison to seawater

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Abstract

Proper evaluation of physical properties of aqueous solutions is essential in the analysis of desalination systems. While standard seawater property data are readily accessible, they are generally not accurate for aqueous solutions requiring desalination that have significantly different composition than seawater. Since experimental data for a given solution may be unavailable under the conditions of interest, thermodynamic models are needed for relevant physical properties, particularly, activity and fugacity coefficients. Effects of composition and nonidealities in mixed electrolyte solutions are considered through a parametric study of the least work of separation. Conditions under which existing single electrolyte solution models, including ideal solution approximation, Debye-Hückel theory (Davies equation), and Pitzer's ionic interaction model, are valid when analyzing mixed electrolyte solutions are examined by comparing them to the Pitzer-Kim mixed electrolyte model. It is found that single electrolyte models often result in greater error than the ideal solution approximation when studying all but the most dilute mixed electrolyte solutions. Additionally, an effective molality can be used with the Pitzer model to increase the accuracy of the single electrolyte model as applied to mixed electrolytes. Finally, composition is a significant variable in the

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overall work of separation requirements.

1. Introduction

Growing water demand resulting from rising population, increasing standards of living, and the contamination of existing water sources is motivating substantial research on desalination. Accurate evaluation of physical properties of various water sources is essential to the reliable calculation of the energy requirements and performance characteristics of desalination systems.

Despite the fact that seawater has been studied in depth and physical properties are well documented [1–4], these properties are only appropriate for water sources that have an ionic composition similar to standard seawater [5]. Unfortunately, many natural and produced waters, including river water, ground water, flowback from hydraulic fracturing, and industrial waste waters, have ionic compositions that are substantially different from that of seawater [6]. Therefore, it is essential to evaluate physical properties for individual ionic compositions for many desalination-related calculations.

Mistry and Lienhard [7] discussed the role of nonidealities in single electrolyte solutions and illustrated the importance of accurately evaluating the activity and fugacity coefficients. Electrolyte solution models considered included the ideal solution approximation, Debye-Hückel theory, and empirical data. As discussed, the ideal solution approximation is commonly used in order to avoid the problem of evaluating activity coefficients entirely [8–12]. Unfortunately, for complex electrolyte solutions such as natural waters, it is unclear for what finite concentrations of arbitrary mixtures this approximation is justifiable.

This paper builds on the work of Mistry and Lienhard [7] which dealt with sodium

chloride solutions only, to consider the validity of the ideal solution approximation as applied to mixed electrolytes of complex composition. The approximation is studied through calculation of the least work of separation. Gibbs free energy for electrolyte solutions is evaluated using several common property models including the ideal solution approximation, Debye-Hückel theory (specifically, Davies equation), Pitzer's ion interaction model, and the Pitzer-Kim model for mixed electrolytes. A parametric study is conducted in which the least work of separation is evaluated as a function of feed salinity and recovery ratio using each of these models. The Pitzer-Kim model for mixed electrolytes is used as a reference to which calculations using the other models are compared. This model is taken as standard because it is based on theory and experimental data and is able to accurately predict activity coefficients across a broad range of compositions and concentrations [13, 14].

The parametric study shows that use of single electrolyte models for the evaluation of activity and fugacity coefficients of mixed electrolyte solutions often results in substantially greater error than the error resulting from use of the ideal solution approximation. However, the Pitzer ion interaction model can be modified in order to achieve better agreement with the more complicated Pitzer-Kim model for mixed electrolytes. Finally, it is shown that the composition of an electrolyte solution is a significant variable in determining the least work of separation, and therefore, standard seawater properties are not appropriate to use for arbitrary electrolyte solutions.

2. Essential chemical thermodynamics

The Gibbs free energy of a mixture is

$$G \equiv \sum_i n_i \mu_i \tag{1}$$

3

Table 1: Constants and chemical data

Constant	Value	Units
e	$1.602176565 \times 10^{-19}$	C
F	96.4853365×10^3	C/mol
$M_{\mathrm{H_2O}}$	18.00988×10^{-3}	kg/mol
N_a	$6.02214129 \times 10^{23}$	1/mol
R	8.3144621	J/mol-K
ϵ_0	$8.854187817620 \times 10^{-12}$	F/m

where n_i and μ_i are the number of moles and chemical potential of species i, respectively. Chemical potential is defined as

$$\mu_i \equiv \mu_i^\circ + RT \ln a_i \tag{2}$$

Proper evaluation of Gibbs free energy requires careful treatment of the activity (a_i) of each species [13–18].

Values of constants used in the following analysis are summarized in Table 1.

2.1. Solvent

The standard state for the solvent is that of the pure liquid at the same temperature and pressure. Since the pure solvent coexists with its vapor when at equilibrium, the activity of the solvent is referenced to the pure vapor at the system temperature and atmospheric pressure. Using a modified form of Raoult's Law in which all nonidealities are assumed to occur within the liquid mixture phase [13], the ratio of the partial pressure of the vapor over the solution and the partial pressure of the vapor over pure solvent is written in terms of the mole fraction [13, 15, 16]:

$$\mu_0 = \mu_0^\circ + RT \ln \left(\gamma_{f,0} x_0 \right) \tag{3}$$

Therefore, the activity of the solvent is defined as

$$a_0 = \gamma_{f,0} x_0 \tag{4}$$

where $\gamma_{f,0}$ is the fugacity coefficient of the solvent.

2.2. Solutes

The chemical potential of a solute can be written in multiple ways, depending on the concentration scale used. For molality and mole fraction, the chemical potential is written as

$$\mu_i = \mu_{m,i}^\circ + RT \ln a_{m,i} \tag{5}$$

$$= \mu_{x,i}^\circ + RT \ln a_{x,i} \tag{6}$$

Regardless of which concentration scale is used, the chemical potential is fixed for a given state since the free energy in the standard state (μ_i°, discussed later) depends on the chosen scale [16]. Here, the solute activity is written as

$$a_{m,i} = \gamma_{m,i} m_i \tag{7}$$

$$a_{x,i} = \gamma_{x,i} x_i \tag{8}$$

Mean concentration and mean activity coefficients are often more convenient and practical to use when considering electrolyte salts. For a strong electrolyte salt, $C_{\nu_+} A_{\nu_-}$, which fully dissociates,

$$C_{\nu_+} A_{\nu_-} \longrightarrow \nu_+ C^{z+} + \nu_- A^{z-} \tag{9}$$

it can be shown that the stoichiometric coefficient (ν), the mean molal activity coeffi-

cient ($\gamma_{m,\pm}$), and the mean molal concentration ($m_\pm$) are defined as:

$$\nu \equiv \nu_+ + \nu_- \tag{10}$$

$$\gamma_{m,\pm}^\nu \equiv \gamma_{m,+}^{\nu_+} \gamma_{m,-}^{\nu_-} \tag{11}$$

$$m_\pm^\nu \equiv m_+^{\nu_+} m_-^{\nu_-} \tag{12}$$

The mean rational activity coefficient ($\gamma_{x,\pm}$) and the mean mole fraction ($x_\pm$) are similarly defined. For neutral electrolytes in which $\nu_+ = \nu_- = 1$, the mean molality of the salt is equal to the molality of the individual ions. That is, $m_{C_{\nu_+} A_{\nu_-}} = m_\pm = m_+ = m_-$.

The standard state of a solute is now defined as a hypothetical solution at a mean concentration of unity referenced to infinite dilution such that the mean activity coefficient is unity when mean concentration is zero, regardless of temperature and pressure [13, 15, 16]. Therefore, $\mu_i = \mu_i^\circ$ at standard state and $\mu_{m,i}^\circ \neq \mu_{x,i}^\circ$ [cf., Eqs. (5) and (6)]. Activity coefficients corresponding to different concentration scales are not equal, even when evaluated at equivalent concentrations on the respective scales. An equation to convert from molal to rational activity coefficient is derived by equating Eqs. (5) and (6) [13, 16]:

$$\gamma_{x,\pm} = \gamma_{m,\pm} \left(1 + M_0 \sum_s \nu_s m_s\right) \tag{13}$$

The summation in Eq. (13) is over all electrolyte salts (not solute species), m_s is the molality of each salt, and ν_s is the number of moles of ions formed per mole of salt.

For notational simplicity, the $\pm$ subscript is dropped going forward. Instead, it is understood that $\gamma_{x,s}$ and $\gamma_{m,s}$ are the rational and molal activity coefficients of salt species s while $\gamma_{x,i}$ and $\gamma_{m,i}$ are the corresponding activity coefficients of solute species i (e.g., $\gamma_{x,\text{NaCl}}$ is the rational activity coefficient of NaCl and is equal defined as $\gamma_{x,\text{NaCl}}^2 =$

$\gamma^1_{x,\text{Na}^+} \gamma^1_{x,\text{Cl}^-}$).

3. Evaluation of activity coefficients

Fluid properties are evaluated in one of two ways in this study. Gibbs free energy of mixed electrolyte solutions is evaluated using Eqs. (1) and (2), which requires evaluation of the activity and fugacity coefficients. Standard seawater properties are evaluated using a freely-available software package that is based on correlations of experimental data [4, 19].

3.1. Evaluation of activity and fugacity coefficients

Activity coefficients for various solution species can be evaluated in many ways. In order of increasing complexity, the following methods are considered: ideal solution approximation, Debye-Hückel theory and the Davies equation, the Pitzer ion interaction model, and the Pitzer-Kim model for mixed electrolytes. While there are additional mixed electrolyte models including those by Guggenheim, Bromley, Meissner, and Chen [14], only the four models listed above are considered here since they represent the most commonly used methods for evaluating the activity coefficients and also span from very simple to complex and accurate [13–16]. These models are based on a combination of statistical mechanical theory as well as curve fitting of empirical data.

Note that while it is common to evaluate single ion activity coefficients and mean molal activity constants for specific salts, single ion activity coefficients are only a useful analytical construct and not physically measurable [14, 17]. It can be shown that the use of single ion activity coefficients, at least in the instance of a single salt, gives algebraically equivalent results to the use of the mean molal activity constant.

7

3.1.1. Ideal solution

The ideal solution approximation is the simplest method for evaluating activity and fugacity coefficients. An ideal solution is defined as a solution in which the solutes do not interact with each other. Practically speaking, this means the solution is dilute and that solute long range (*e.g.*, electrostatic) forces are negligibly weak. An ideal solution has rational activity coefficients (for solutes) and fugacity coefficients (for solvent) equal to one [13, 15, 16]:

$$\gamma_{x,s}^{\text{ideal}} = 1 \qquad \gamma_{f,0}^{\text{ideal}} = 1 \qquad \text{for all species} \qquad (14)$$

Therefore, the activity (based on mole fraction) is equal to the mole fraction. Even though the rational activity coefficient is equal to one for an ideal system, the molal activity coefficient is *not* equal to one as evident from Eq. (13). Technically, the rational activity coefficient of each solute ($\gamma_{x,i}$) should be equal to one in the ideal limit; however, Eq. (11) shows that this is equivalent to setting the activity coefficient of the salt equal to one.

Due to its simplicity, the ideal solution approximation is widely used to analyze solutions. Unfortunately, it is easy to inadvertently use the model beyond its range of applicability and doing so can result in substantial error for even simple calculations [7]. Additionally, it is incorrect to equate the molal activity coefficient, rather than the rational activity coefficient, to one.

3.1.2. Debye-Hückel theory and the Davies equation

Davies proposed a modification of the basic Debye-Hückel equation that gives accurate results for low ionic strength electrolyte solutions [13–16, 20–23].

$$\log \gamma_{x,\pm} = -A|z_+z_-| \left(\frac{\sqrt{I_m}}{1 + \sqrt{I_m}} - bI_m \right) \qquad I_m < 0.5 \qquad (15)$$

The constant, A, is defined as [13, 23]:

$$A_\phi = \frac{F^3}{24\pi N_a} \left[\frac{2000\rho_0}{(\epsilon_0 \epsilon_r RT)^3} \right]^{1/2} \qquad A = 3A_\phi \log e = 1.8248 \times 10^6 \left[\frac{\rho_0}{(\epsilon_r T)^3} \right]^{1/2} \left[\frac{\text{kg}^{1/2}}{\text{mol}^{1/2}} \right]$$

At $25\,^\circ$C, the static dielectric constant (or relative permittivity) of H_2O is $\epsilon_r = 78.54$ and the density of water is $\rho_{H_2O} = 0.99705$ kg/L. Therefore, $A_\phi = 0.3903$ kg$^{\frac{1}{2}}$/mol$^{\frac{1}{2}}$ and $A = 0.5085$kg$^{\frac{1}{2}}$/mol$^{\frac{1}{2}}$. The constant b ranges from 0.2–0.3 depending on the solute. A value of $b = 0.2$ is used herein.

Molal ionic strength is defined in terms of molality and charge of each of the solute species.

$$I_m = \frac{1}{2} \sum_i m_i z_i^2 \tag{16}$$

where m_i is the molality (moles of solute per kilogram of solvent) of each solute, i. The summation is over all solute species.

While there are other commonly used forms of Debye-Hückel theory, including Debye-Hückel Limiting Law, Güntelberg equation, and others, Davies equation is the only one considered in the present study.

3.1.3. Pitzer ion interaction model for single electrolytes

The Pitzer ion interaction model for single electrolytes (referred to as the Pitzer equation or model) is developed based on the osmotic virial expansion from McMillan-Mayer theory [13]. The expansion is truncated and empirical fitting is used to specify the salt-specific coefficients in order to produce an acceptable model. The activity coefficient and osmotic coefficient for a single salt are evaluated using Eqs. (17) and (18),

respectively [13, 14, 17, 24–28]:

$$\ln \gamma_{m,\mathrm{CA}} = |z_\mathrm{C} z_\mathrm{A}| f^\gamma + m \frac{2\nu_\mathrm{C} \nu_\mathrm{A}}{\nu} B_\mathrm{CA}^\gamma + m^2 \frac{2(\nu_\mathrm{C}\nu_\mathrm{A})^{3/2}}{\nu} C_\mathrm{CA}^\gamma \tag{17}$$

$$\phi - 1 = |z_\mathrm{C} z_\mathrm{A}| f^\phi + m \frac{2\nu_\mathrm{C} \nu_\mathrm{A}}{\nu} B_\mathrm{CA}^\phi + m^2 \frac{2(\nu_\mathrm{C}\nu_\mathrm{A})^{3/2}}{\nu} C_\mathrm{CA}^\phi \tag{18}$$

where

$$f^\phi = -A_\phi \frac{\sqrt{I_m}}{1 + b\sqrt{I_m}}$$

$$f^\gamma = -A_\phi \left[\frac{\sqrt{I_m}}{1 + b\sqrt{I_m}} + \frac{2}{b} \ln\left(1 + b\sqrt{I_m}\right) \right]$$

$$B_\mathrm{CA}^\phi = \beta_0 + \sum_{k=1}^{2} \beta_k \exp\left(-\alpha_k \sqrt{I_m}\right)$$

$$B_\mathrm{CA}^\gamma = 2\beta_0 + \sum_{k=1}^{2} \frac{2\beta_k}{\alpha_k^2 I_m} \left[1 - \exp\left(-\alpha_k \sqrt{I_m}\right)\left(1 + \alpha_k \sqrt{I_m} - 0.5\alpha_k^2 I_m\right) \right]$$

$$C_\mathrm{CA}^\gamma = \frac{3}{2} C_\mathrm{CA}^\phi$$

and $b = 1.2$. Tabulated data for β_i, α_i, and C_CA^ϕ for numerous salt species is available in the literature [13, 25, 26]. The constants α_2 and β_2 are only defined for 2:2 electrolytes. For non-2:2 electrolytes, $\beta_2 = 0$ is set to zero, reducing the second term of the sums in B_CA^ϕ and B_CA^γ to zero.

Equation (17) gives the molal activity coefficient. The rational activity coefficient is obtained using Eq. (13). The molal activity of water is written in terms of the molal osmotic coefficient [13, 16, 29]:

$$\ln a_{\mathrm{H_2O}} = -\nu m M_{\mathrm{H_2O}} \phi \tag{19}$$

The fugacity coefficient of the water is evaluated using Eqs. (3) and (19):

$$\ln \gamma_{f,\mathrm{H_2O}} = -\nu m M_{\mathrm{H_2O}} \phi - \ln x_{\mathrm{H_2O}} \tag{20}$$

3.1.4. Pitzer-Kim model for mixed electrolytes

As with the single electrolyte model, the Pitzer-Kim model for mixed electrolytes (referred to as Pitzer-Kim equation or model) is based on the osmotic virial expansion from McMillian-Mayer theory. Using a similar method of combining the virial coefficients, the mean activity coefficients for electrolyte $C_{\nu_+}A_{\nu_-}$ in a mixed solution can be calculated. This model considers binary and ternary interactions between all possible salt pairs in the solution. Higher order interactions are neglected [13, 14, 17, 24–28]:

$$
\begin{aligned}
\ln \gamma_{\mathrm{CA}} = & \; |z_\mathrm{C} z_\mathrm{A}| f^\gamma + \frac{2\nu_\mathrm{C}}{\nu} \sum_a m_a \left[B_{\mathrm{C}a} + \left(\sum mz \right) C_{\mathrm{C}a} + \frac{\nu_\mathrm{A}}{\nu_\mathrm{C}} \theta_{\mathrm{A}a} \right] \\
& + \frac{2\nu_\mathrm{A}}{\nu} \sum_c m_c \left[B_{c\mathrm{A}} + \left(\sum mz \right) C_{c\mathrm{A}} + \frac{\nu_\mathrm{C}}{\nu_\mathrm{A}} \theta_{\mathrm{C}c} \right] \\
& + \sum_c \sum_a m_c m_a \left[|z_\mathrm{C} z_\mathrm{A}| B'_{ca} + \frac{1}{\nu} \left(2\nu_\mathrm{C} z_\mathrm{C} C_{ca} + \nu_\mathrm{C} \psi_{\mathrm{C}ca} + \nu_\mathrm{A} \psi_{ca\mathrm{A}} \right) \right] \\
& + \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \left[\frac{\nu_\mathrm{A}}{\nu} \psi_{cc'\mathrm{A}} + |z_\mathrm{C} z_\mathrm{A}| \theta'_{cc'} \right] \\
& + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \left[\frac{\nu_\mathrm{C}}{\nu} \psi_{\mathrm{C}aa'} + |z_\mathrm{C} z_\mathrm{A}| \theta'_{aa'} \right]
\end{aligned} \tag{21}
$$

In the last two terms, the summations over c' and a' are summations over all cations (or anions) other than the cation (or anion) from the outer sum.

$$\phi - 1 = \left(\sum_i m_i\right)^{-1} \left\{ 2I_m f^\phi + 2\sum_c \sum_a m_c m_a \left[B_{ca}^\phi + \frac{\sum mz}{\sqrt{z_c z_a}} C_{ca}^\phi \right] \right.$$
$$+ \sum_c \sum_{c'} m_c m_{c'} \left[\theta_{cc'} + I_m \theta_{cc'}' + \sum_a m_a \psi_{cc'a} \right]$$
$$\left. + \sum_a \sum_{a'} m_a m_{a'} \left[\theta_{aa'} + I_m \theta_{aa'}' + \sum_c m_c \psi_{caa'} \right] \right\} \tag{22}$$

Here, f^γ, f^ϕ are defined as above for the Pitzer Ion Interaction Model. The functions B, B', and C are defined as:

$$B_{ij} = B_{ij}^\gamma - B_{ij}^\phi = \beta_0 + \sum_{k=1}^{2} \frac{2\beta_k}{\alpha_k^2 I_m} \left[1 - \exp\left(-\alpha_k \sqrt{I_m}\right)\left(1 + \alpha_k \sqrt{I_m}\right) \right] \tag{23}$$

$$B_{ij}' = \sum_{k=1}^{2} \frac{2\beta_k}{\alpha_k^2 I_m} \left[-1 + \exp\left(-\alpha_k \sqrt{I_m}\right)\left(1 + \alpha_k \sqrt{I_m} + 0.5\alpha_k^2 I\right) \right] \tag{24}$$

$$C_{ij} = \frac{C_{ij}^\phi}{2\sqrt{z_C z_A}} \tag{25}$$

The θ and ψ terms in Eqs. (21) and (22) represent the binary and ternary interactions respectively and are tabulated [27]. The constants C_{ij}^ϕ are tabulated [25, 26]. In accordance with Pitzer's recommendation, the ionic strength dependence of θ is neglected in the present work (*i.e.*, $\theta' = 0$) [27].

Equation (21) gives the molal activity coefficient of electrolyte $C_{\nu_+} A_{\nu_-}$. The rational activity coefficient is obtained using Eq. (13) and the fugacity coefficient of the water is evaluated using a modified version of Eq. (20):

$$\ln \gamma_{f,H_2O} = -\left(\sum_s \nu_s m_s\right) M_{H_2O}\phi - \ln x_{H_2O} \tag{26}$$

3.1.5. Pitzer model with effective molality for mixed electrolytes

The Pitzer model for single electrolytes is a function of both salt molality and solution ionic strength [*cf.*, Eqs. (17) and (18)]. For a single electrolyte solution, the molality and molal ionic strength are related by Eq. (16):

$$I_m = \frac{1}{2} \left(\nu_+ m z_+^2 + \nu_- m z_-^2 \right) \tag{27}$$

In mixed electrolyte solutions, there is not a direct relationship between the molality of a single electrolyte and the overall solution ionic strength since the solution ionic strength is a function of the molalities of all electrolytes present. Therefore, the ionic strength can be significantly greater than what the single electrolyte molality would predict. In order to account for this effect, an effective molality is obtained by solving Eq. (27) for m:

$$m_{\text{effective}} = \frac{2 I_m}{\nu_+ z_+^2 + \nu_- z_-^2} \tag{28}$$

This effective molality can be used with Eq. (17) in order to more accurately evaluate the activity coefficient of a single salt in a mixed electrolyte solution. Note that an effective molality must be evaluated for each electrolyte in solution and that values of ν_+, ν_-, z_+, and z_- depend on the specific cations and anions formed from the electrolyte being considered.

In order to calculate the osmotic coefficient for a mixed electrolyte solution using Eq. (18), an effective osmotic coefficient should first be evaluated using Eq. (28) for each salt. The osmotic coefficient is the effective molality-weighted average of these effective osmotic coefficients:

$$\phi = \frac{\sum_i m_{\text{effective},i} \phi_{\text{effective},i}}{\sum_i m_{\text{effective},i}} \tag{29}$$
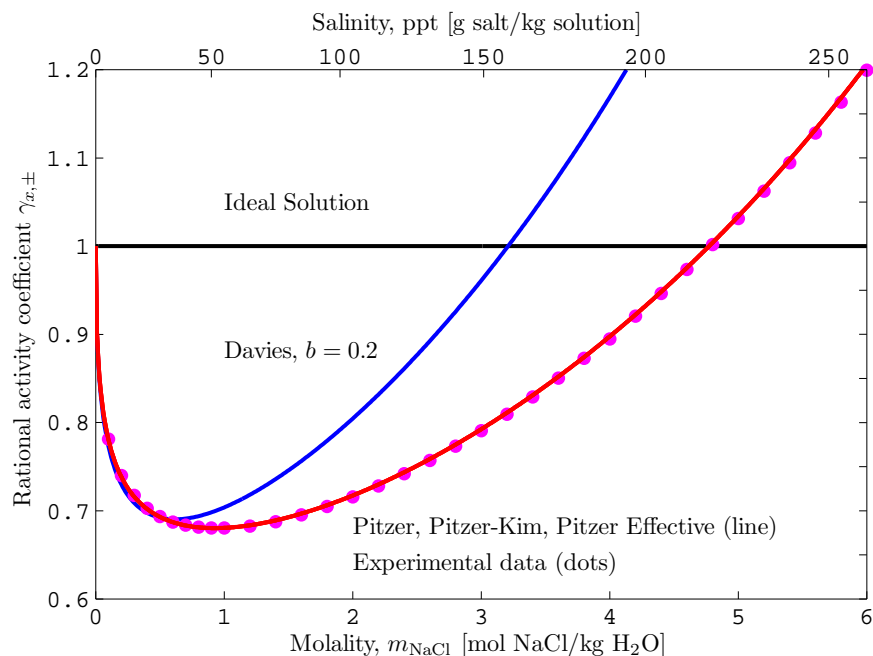
13

Figure 1: Rational activity coefficient for aqueous NaCl evaluated using ideal solution approximation, Davies equation, Pitzer's ion interaction model, and experimental data. Dots are data from [16].

Pitzer's equations with an effective molality (referred to as effective Pitzer model) is substantially easier to implement than the Pitzer-Kim model and is a good approximation for the activity and fugacity coefficients as discussed in Section 6.

Plots of the rational activity coefficient for NaCl, $MgCl_2$, and Na_2SO_4 are shown in Figs. 1 to 3 respectively. It is observed that both the Pitzer-Kim model and the effective Pitzer model reduce to the Pitzer model when they are evaluated for a single electrolyte solution in all cases. Additionally, it is observed that for molalities less than approximately 0.5, Davies equation closely approximates available data, but then quickly diverges at higher concentrations.

3.2. Empirical Correlations

There have been multiple attempts to create seawater property packages [1, 2, 4]. The work by Sharqawy et al. [4, 19] is used in this study. Correlations for properties
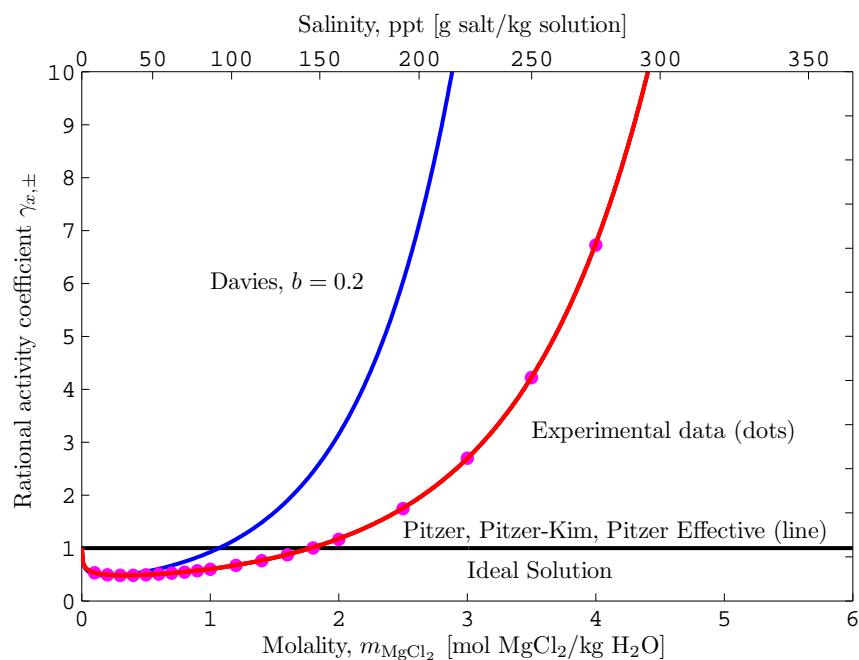
Figure 2: Rational activity coefficient for aqueous $MgCl_2$ evaluated using ideal solution approximation, Davies equation, Pitzer's ion interaction model, and experimental data. Dots are data from [16].

such as specific Gibbs free energy, osmotic coefficients, and chemical potential of water and salts in seawater are given as a function of temperature and salinity. The range of validity of the correlations varies slightly for each property, but in general, they are applicable for temperatures between 0–120 °C and salinities between 0–120 ppt. Note that this property package provides properties per kilogram of solution (seawater).

4. Least work of separation

The least work of separation ($\dot{W}_{\text{least}}$) is a commonly used metric in desalination which defines the minimum amount of work required to separate a chemical stream into two streams of differing composition in the thermodynamic limit of reversible operation [13, 30–33]. It is a benchmark to which desalination systems are compared, much as Carnot efficiency is an ideal benchmark for power plants. Typically, the least
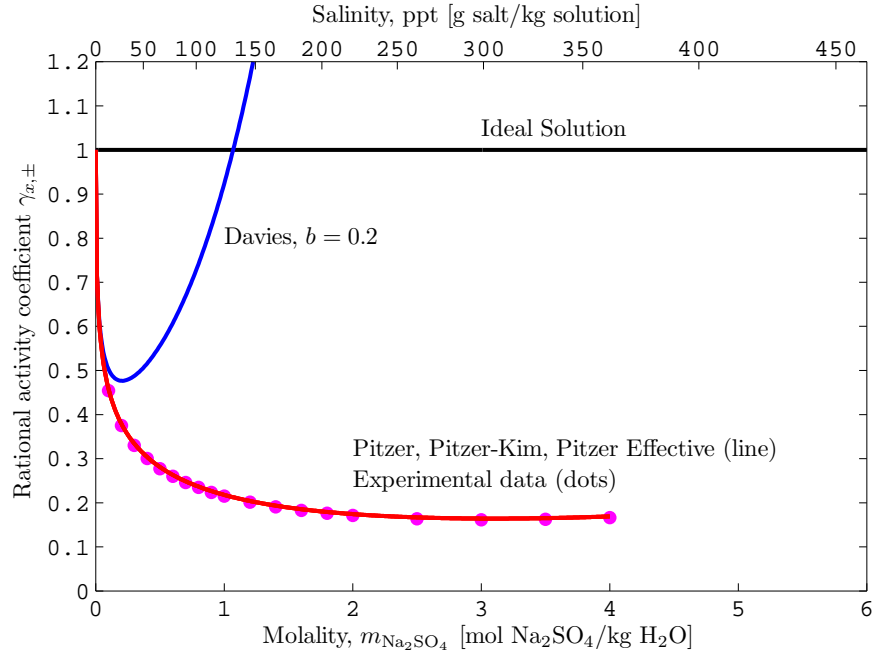
Figure 3: Rational activity coefficient for aqueous Na_2SO_4 evaluated using ideal solution approximation, Davies equation, Pitzer's ion interaction model, and experimental data. Dots are data from [16].

work of separation is evaluated per unit of product produced. In this study, all results are provided for $\dot{m}_p = 1$ kg/s and the least work is written as $\dot{W}_{\text{least}}/\dot{m}_p$ [kJ/kg]. The least work of separation is derived for a control volume containing an ideal black-box separator and then considered on both a mass and mole basis.

4.1. Derivation

Consider a simple black-box separator model for a desalination system as shown in Fig. 4. The rate of work applied to the system to drive separation is denoted by $\dot{W}_{\text{sep}}$ and the rate of heat transfer into the system is denoted by $\dot{Q}$. The feed, product, and concentrated brine streams are denoted by f, p, and b respectively. All the inlet and outlet streams enter and leave the control volume at environmental temperature, T_e, and pressure, p_e, but at different salinities, S. Heat transfer occurs at the environmental temperature. A complete discussion regarding this selection of control volume is
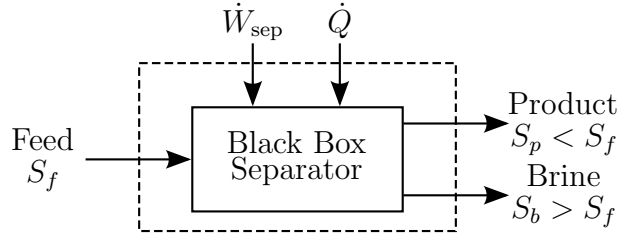
16

Figure 4: A control volume representation of a desalination system is used to derive the least work of separation.

provided by Mistry *et al.* [30].

Combining the First and Second Laws of Thermodynamics yields the rate of work of separation:

$$\dot{W}_{\text{sep}} = \dot{G}_p + \dot{G}_b - \dot{G}_f + T_e \dot{S}_{\text{gen}} \tag{30}$$

where $\dot{G}_i$ is the flow rate of Gibbs free energy of stream i and $\dot{S}_{\text{gen}}$ is the total entropy generation resulting from the separation process. In the limit of reversible operation, entropy generation is zero and Eq. (30) reduces to the reversible rate of work of separation, also known as the least work of separation:

$$\dot{W}_{\text{least}} \equiv \dot{W}_{\text{sep}}^{\text{rev}} = \dot{G}_p + \dot{G}_b - \dot{G}_f \tag{31}$$

In most real-world desalination systems, the major sources of entropy generation are viscous losses for membrane systems and heat transfer across finite temperature differences for thermal systems [30]. As a result, entropy generation is not strongly related to compositional effects in many systems. Therefore, the least work is a relevant parameter for examining the impact of nonideality on system performance.

17

4.2. Mass Basis

For property packages that evaluate properties per unit mass of solution (*e.g.*, [4]), Eq. (31) is best written on a mass flow rate basis:

$$\dot{W}_{\text{least}} = \dot{m}_p g_p + \dot{m}_b g_b - \dot{m}_f g_f \tag{32}$$

where g_j is the specific Gibbs free energy per kilogram of solution.

The recovery ratio is defined as the ratio of the mass flow rate of product water to the mass flow rate of feed seawater:

$$r \equiv \frac{\dot{m}_p}{\dot{m}_f} = \frac{\text{mass flowrate of product}}{\text{mass flowrate of feed}} \tag{33}$$

Enforcing conservation of mass for the mixture and the salts gives:

$$\frac{\dot{W}_{\text{least}}}{\dot{m}_p} = (g_p - g_b) - \frac{1}{r}(g_f - g_b) \tag{34}$$

The Gibbs free energy of each of the streams in Eq. (34) is evaluated using seawater properties, as a function of temperature and salinity, $g_j = g_j(T, S_j)$ [4]. Provided the feed and product salinities (S_f, S_p) are known, the brine salinity (S_b) is evaluated using conservation of mass:

$$S_b = \frac{S_f}{1-r} - \frac{rS_p}{1-r} \tag{35}$$

Equation (34) is a function of temperature, feed salinity, product salinity, and recovery ratio.

4.3. Mole Basis

It is more convenient to write Eq. (31) on a mole basis when physical properties are evaluated using Eq. (1). Mistry and Lienhard [7] showed that the least work for an

18

NaCl solution is given by:

$$\frac{\dot{W}_{\text{least}}}{\dot{n}_{\text{H}_2\text{O},p}RT} = \left(\ln \frac{a_{\text{H}_2\text{O},p}}{a_{\text{H}_2\text{O},b}} + m_{\text{NaCl},p}M_{\text{H}_2\text{O}} \ln \frac{a_{\text{NaCl},p}}{a_{\text{NaCl},b}} \right)$$
$$- \frac{1}{\bar{r}} \left(\ln \frac{a_{\text{H}_2\text{O},f}}{a_{\text{H}_2\text{O},b}} + m_{\text{NaCl},f}M_{\text{H}_2\text{O}} \ln \frac{a_{\text{NaCl},f}}{a_{\text{NaCl},b}} \right) \tag{36}$$

Where the molar recovery ratio $(\bar{r})$ is defined as:

$$\bar{r} \equiv \frac{\dot{n}_{\text{H}_2\text{O},p}}{\dot{n}_{\text{H}_2\text{O},f}} = \frac{\text{molar flowrate of water in product}}{\text{molar flowrate of water in feed}} \tag{37}$$

Equation (36) can be generalized to mixed electrolyte solutions:

$$\frac{\dot{W}_{\text{least}}}{\dot{n}_{\text{H}_2\text{O},p}RT} = \left(\ln \frac{a_{\text{H}_2\text{O},p}}{a_{\text{H}_2\text{O},b}} + \sum_s m_{s,p}M_{\text{H}_2\text{O}} \ln \frac{a_{s,p}}{a_{s,b}} \right)$$
$$- \frac{1}{\bar{r}} \left(\ln \frac{a_{\text{H}_2\text{O},f}}{a_{\text{H}_2\text{O},b}} + \sum_s m_{s,f}M_{\text{H}_2\text{O}} \ln \frac{a_{s,f}}{a_{s,b}} \right) \tag{38}$$

where s represents all salt species that form the electrolyte mixture recipe and the activities of the solvent and solutes are defined by Eqs. (4) and (8) respectively. As with Eq. (34), Eq. (38) is a function of temperature, feed molality, product molality, and molar recovery ratio.

Since activity is written as the product of mole fraction and activity coefficient, Eq. (38) can be easily separated into two parts: an ideal term that is a function of mole fraction of each of the species in each of the streams, and a nonideal part which is a

function of the activity coefficients of all species in each stream.

$$\frac{\dot{W}^{\text{ideal}}_{\text{least}}}{\dot{n}_{\text{H}_2\text{O},p}RT} = \left(\ln \frac{x_{\text{H}_2\text{O},p}}{x_{\text{H}_2\text{O},b}} + \sum_s \nu_{s,p} m_{s,p} M_{\text{H}_2\text{O}} \ln \frac{x_{s,p}}{x_{s,b}} \right)$$
$$- \frac{1}{\bar{r}} \left(\ln \frac{a_{\text{H}_2\text{O},f}}{a_{\text{H}_2\text{O},b}} + \sum_s \nu_{s,f} m_{s,f} M_{\text{H}_2\text{O}} \ln \frac{a_{s,f}}{a_{s,b}} \right) \tag{39}$$

$$\frac{\dot{W}^{\text{nonideal}}_{\text{least}}}{\dot{n}_{\text{H}_2\text{O},p}RT} = \left(\ln \frac{\gamma_{\text{H}_2\text{O},p}}{\gamma_{\text{H}_2\text{O},b}} + \sum_s \nu_{s,p} m_{s,p} M_{\text{H}_2\text{O}} \ln \frac{\gamma_{s,p}}{\gamma_{s,b}} \right)$$
$$- \frac{1}{\bar{r}} \left(\ln \frac{\gamma_{\text{H}_2\text{O},f}}{\gamma_{\text{H}_2\text{O},b}} + \sum_s \nu_{s,f} m_{s,f} M_{\text{H}_2\text{O}} \ln \frac{\gamma_{s,f}}{\gamma_{s,b}} \right) \tag{40}$$

The choice of electrolyte system model only affects the nonideal portion of the least work of separation, Eq. (40).

Equations (36) and (38) to (40) can all be written per unit mass flow rate of product through the use of Eq. (A.10).

5. Seawater composition

A wide variety of water sources, including brackish water (*e.g.*, ground, river, and lake water), seawater, wastewater, and produced water (such as from hydraulic fracturing) can be treated by desalination systems. Brackish water and seawater are the most common feed sources. While these water classifications are only loosely defined, water with a salinity between 1–10 ppt is typically considered brackish, seawater typically has salinities of 30–55 ppt, and water with a salinity less than 0.5 ppt is typically considered fresh [34, 35]. ASTM International provides guidelines for how to make substitute ocean water for experimental purposes and the primary components are listed in Table 2. In a previous paper [7], sodium chloride solutions were considered extensively while in the present work, various mixed electrolyte solutions are analyzed.

Table 2: Primary chemical composition of substitute ocean water [5].

Compound	Concentration [g/L]
NaCl	24.53
$MgCl_2$	5.20
Na_2SO_4	4.09
$CaCl_2$	1.16
KCl	0.695
$NaHCO_3$	0.201
KBr	0.101
H_3BO_3	0.027
$SrCl_2$	0.025
NaF	0.003

6. Parametric study of mock seawater

The effects of various electrolyte solution approximations are illustrated through a parametric study of the least work of separation. Recovery ratio and feed salinity are varied and the least work of separation is calculated while evaluating the activity coefficients using various models discussed in the preceding sections. These calculations are performed for two different types of feed waters. The first is a mock seawater based on the seawater recipe shown in Table 2. The second feed water is a two salt electrolyte solution in which both salts are composed of divalent ions. Mock seawater is analyzed in the present section.

For computational convenience, the mock seawater solution consits of only the five most predominant salts listed in Table 2 (accounting for over 99% of the dissolved salts in seawater). When the feed salinity is varied, the relative concentration of each of the five salts is held constant. That is the mass ratio of $NaCl : MgCl_2 : Na_2SO_4 : CaCl_2 :$ KCl is 24.53 : 5.20 : 4.09 : 1.16 : 0.695, regardless of feed salinity.

Before quantifying the error introduced by making various approximations, the absolute value of the least work of separation for the mock seawater solution is calculated using the Pitzer-Kim model (shown as a contour plot in Fig. 5). As expected, the re-

quired separation work increases with both increasing recovery ratio and feed salinity. Note that increasing the feed salinity has a greater effect on the required work of separation than increasing the recovery ratio. That is, producing one kilogram of product water from a higher salinity feed at lower recovery ratio will take substantially more energy than producing the same amount of product from lower salinity feed at a higher recovery ratio. Additionally, at low feed salinities, the marginal increase in the least work for increasing the recovery ratio is low. That is, $\left(\frac{\mathrm{d}(\dot{W}_{\mathrm{least}}/\dot{m}_p)}{\mathrm{d}r}\right)_{S_f}$ is small. This has important implications for those industries that require processing high salinity water and also partially explains why brackish water treatment plants operate at high recovery ratios.

The contours in Fig. 5 and all subsequent contour plots end in the upper right hand corner since those combinations of high feed salinity and recovery ratio result in a brine stream salinity that exceeds the pure salt solubility limit of any of the individual salts present in solution. While the common-ion effect does change the solubility of the salts in mixture, this effect is neglected in this analysis.

Since the ideal solution approximation is so simple to use, it is commonly taken as a first step in desalination studies. However, improper use of it has the potential to introduce significant error into calculations. Here, relative error is defined as:

$$\text{Relative error } [\%] = \left(\frac{\dot{W}_{\mathrm{least}}^{\mathrm{ideal}}}{\dot{W}_{\mathrm{least}}} - 1\right) \times 100 \qquad (41)$$

The least work of separation is evaluated for mock seawater while assuming ideal solution behavior, and the relative error is shown in Fig. 6a. Even at low salinities and low recovery ratios, significant error (approximately 10%) is introduced by assuming that the solutions behave ideally. While there is a contour at which the error is identically equal to zero, this should not be mistaken for ideal solution behavior. Rather, under
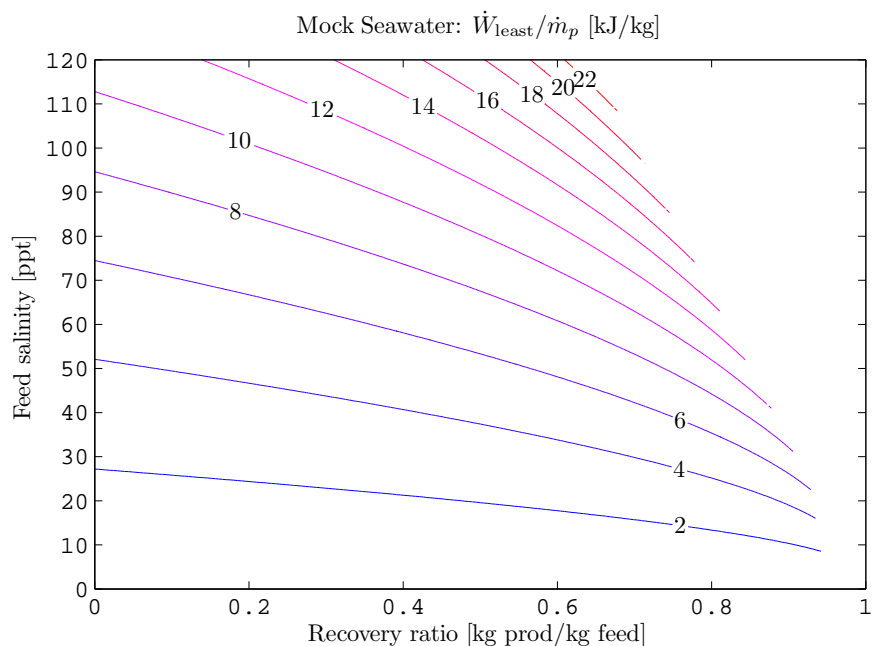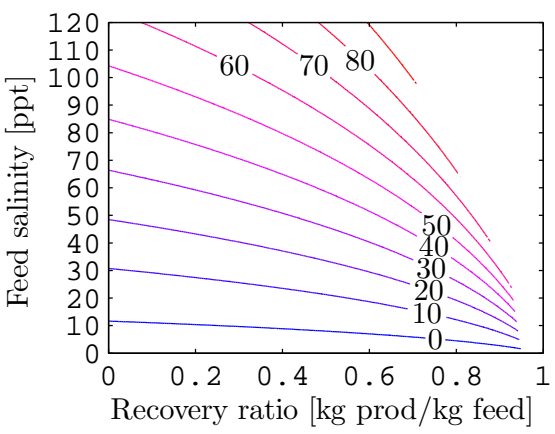
Figure 5: The least work of separation for mock seawater solution consisting of NaCl, $MgCl_2$, Na_2SO_4, $CaCl_2$, and KCl according to the proportions listed in Table 2. Required separation work increases with increasing recovery ratio and feed salinity.

those combinations of feed salinity and recovery ratio, the nonidealities in all of the streams have the net effect of canceling out. That is, Eq. (40) is equal to zero despite activity coefficients that are not equal to unity. This effect is discussed by Mistry and Lienhard [7] in regard to single electrolyte solutions.

A very common approach to electrolyte solution modeling, especially in the study of natural waters, is to approximate the solvent (water) as ideal since it is assumed to be present in high concentration and to approximate the solutes (electrolytes) as nonideal using Debye-Hückel theory since they are assumed to be relatively dilute. Figure 6b shows the percent relative error in least work of separation when the Davies equation is used for the electrolytes and ideality is assumed for water. For many naturally occurring brackish waters, this is not an unreasonable assumption, but for seawater and higher salinity waters, the approximation breaks down. Specifically, it is seen that
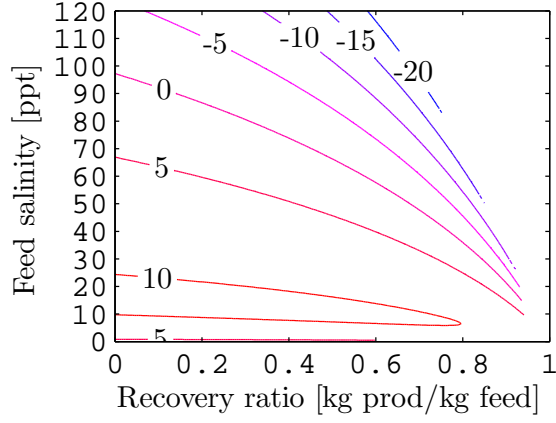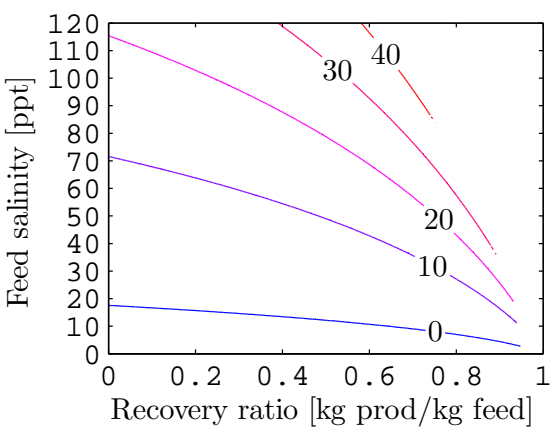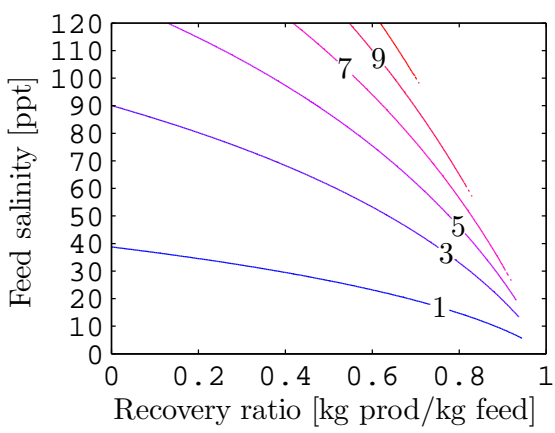
(a) Ideal solution approximation
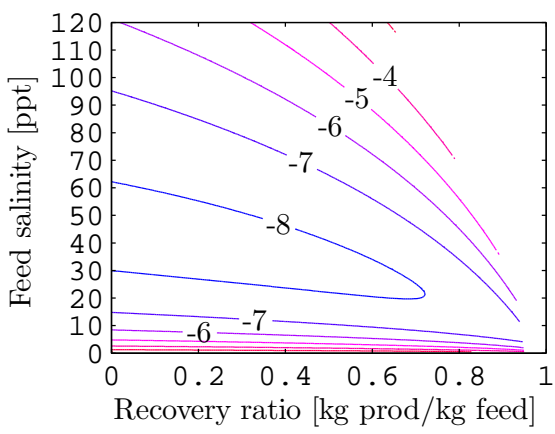
(b) Davies equation for salts, ideal water

(c) Pitzer equation for salts, ideal water

(d) Pitzer effective for salts, ideal water

(e) Pitzer effective for salts and water

Figure 6: Percent relative error in least work of separation, as a function of feed salinity and recovery ratio, resulting from various activity coefficient modeling methods for a five salt mock seawater solution.

24

for feed salinities approaching 30 ppt, the error introduced by these approximations is typically less than 10%. However, as the feed salinity increases, the error dramatically increases. The error introduced for a typical seawater desalination plant operating at 50% recovery ratio on feed at 35 ppt is nearly 20% and the error increases from there. This approximation method should only be used if all streams in the system are at low salinity (feed stream should be roughly less than 20 ppt). Note that this increase in error expected since Davies equation was derived under the dilute solution assumption.

When more accuracy is required than what is provided by use of Debye-Hückel theory, Pitzer's ion activity model is particularly useful. However, the standard Pitzer model is designed for use with single electrolyte solutions only. Given that Debye-Hückel theory is used to evaluate single ion activity coefficients which are non-physical values, some might use Pitzer's single electrolyte model for mixed electrolytes hoping to gain improved accuracy. Figure 6c shows the error introduced by assuming water is ideal and evaluating the salt activity coefficients using Pitzer's equation. Comparing Figs. 6b and 6c, it is seen that using Pitzer's equation gives better results overall, but, at lower feed salinities, the error is actually worse. This happens since the molality and ionic strength in Eqs. (17) and (18) have a one to one relationship for single electrolytes, but not for mixed electrolytes as discussed in Section 3.1.5.

In order to correct for the differences between molality and ionic strength, the effective Pitzer equation can be used to determine the activity coefficients of the salts using an effective molality. The relative error in the least work of separation when using this approximation while assuming that water behaves ideally results in reduced error at lower feed salinities as compared to the Davies equation as expected (*cf.*, Figs. 6b and 6d).

Finally, if the effective Pitzer equation for osmotic coefficient is also used, the relative error is reduced substantially (Fig. 6e). The error under the effective Pitzer model

(maximum error of approximately 9%) is an order of magnitude less than the error observed when using Davies equation (maximum error of approximately 80%; *cf.*, Figs. 6b and 6e). The effective Pitzer model works well because it better predicts the activity coefficients of the individual salts than the standard Pitzer model itself. To illustrate this, the activity and fugacity coefficients for the mock seawater solution, evaluated using the Pitzer-Kim (solid lines), Pitzer (dotted lines), and effective Pitzer (dashed lines), are shown in Fig. 7. In all cases, the effective Pitzer model is in closer agreement to the Pitzer-Kim values.

7. Parametric study of a high valence electrolyte solution

Some industrial waste waters may be dominated by higher valence salts than what is typically found in natural waters. In particular, water produced from hydraulic fracturing sometimes has a high concentration of divalent ions [36, 37]. Therefore, the same parametric study that was performed on mock seawater is performed on a 50-50 mixture (by mass) of $MgSO_4$ and $ZnSO_4$ and the effects of the various solution models are discussed. These two salts were selected since they both have high enough solubilities to allow the parametric study to be conducted over the same range of salinities and recovery ratios that was used for the mock seawater solution. The least work of separation for this mixture is evaluated and shown in Fig. 8. Comparing to Fig. 5, it is clear that the required separation work is substantially lower for this high valence electrolyte mixture. The lower separation work requirements are due to several factors: the salts considered here have a lower activity resulting in lower separation requirements, sulphate tends to participate in ion pairing (aqueous complexation), and heavier ions have a lower molality for a given salinity (weight fraction). Clearly, the specific composition, rather than simply salinity, is essential to the separation work requirements.

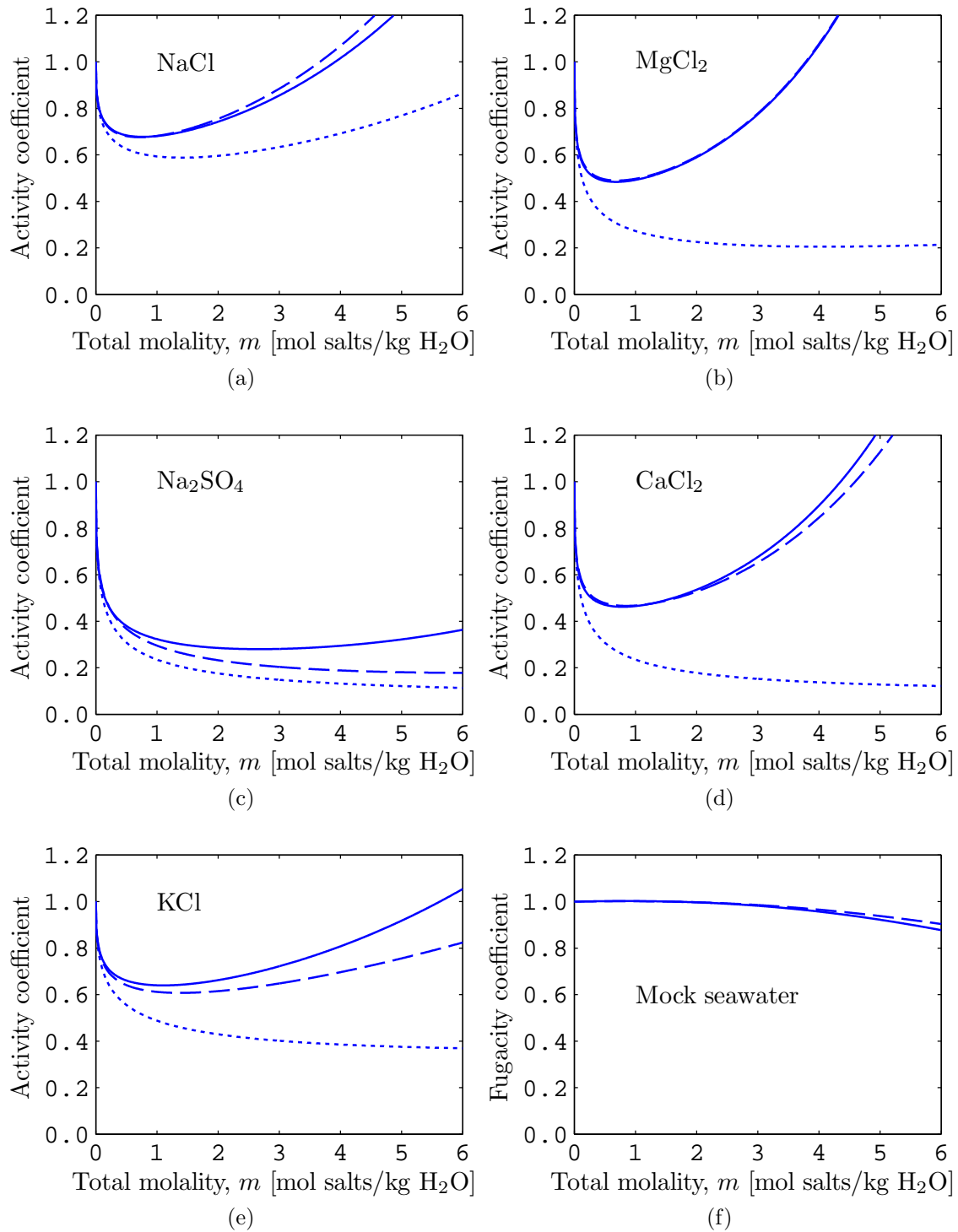The relative error in least work of separation introduced by each of the various

26

Figure 7: Rational activity and fugacity coefficient for each component in the mock seawater solution versus solution molality. Solid lines (—) are evaluated using Pitzer-Kim, dashed lines (- - -) using effective Pitzer, and dotted lines ($\cdots$) using Pitzer.
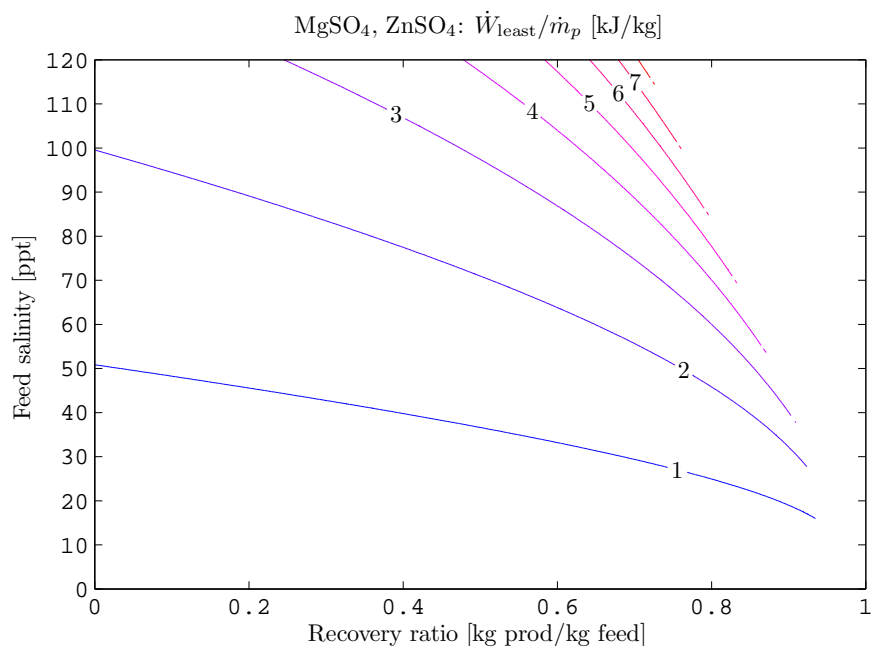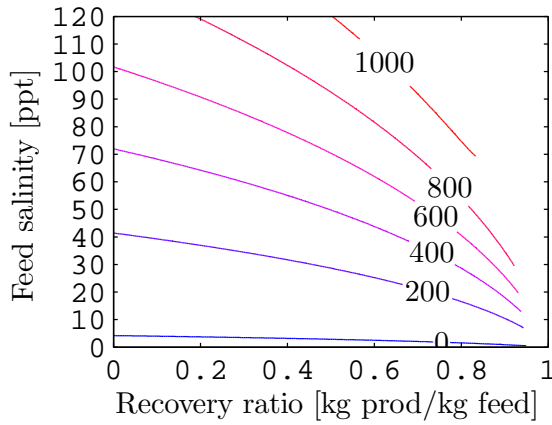
Figure 8: The least work of separation for a 50-50 mixture (by mass) of $MgSO_4$ and $ZnSO_4$. Required separation work increases with increasing recovery ratio and feed salinity.

solution models is shown in Fig. 9. Under the ideal solution approximation, the relative error reaches values in excess of 90% (Fig. 9a). Even at relatively low salinities and recovery ratios, the relative error is in excess of 50%. Therefore, for this divalent electrolyte solution, the ideal solution approximation is not valid for any solutions of reasonable salinity.

Use of Debye-Hückel theory through the Davies equation gives better results than the ideal solution model at the lowest concentrations (below approximately 5 ppt) but yields substantially worse results at higher salinities. For seawater salinities of about 35 ppt, the relative error is in excess of 200% and at the higher salinities, the error can exceed 1000% (Fig. 9b). As a result, it is not advisable to use Davies equation for high valence salts except for extremely dilute solutions. When Pitzer's single electrolyte model is used for evaluation of the salt activity coefficients while assuming that
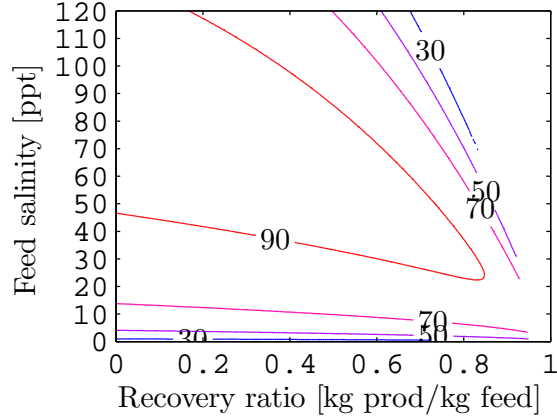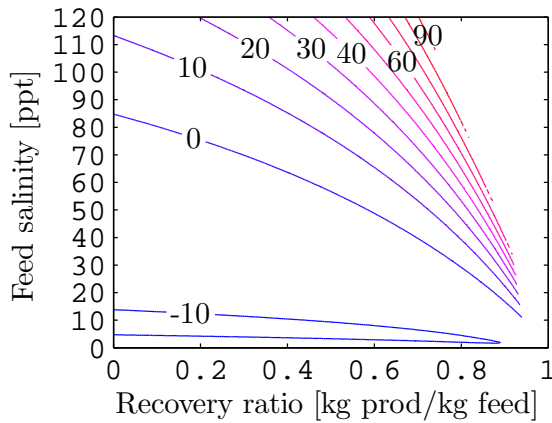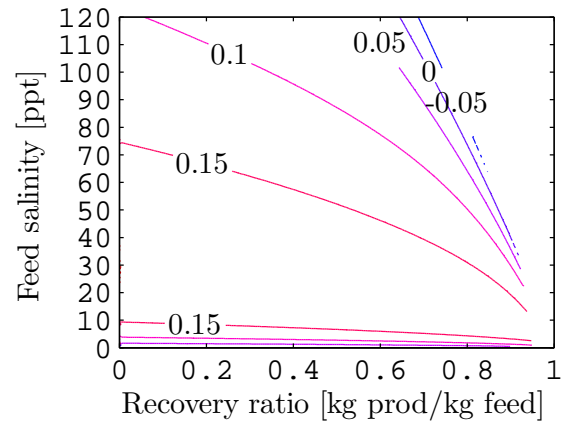
(a) Ideal solution approximation
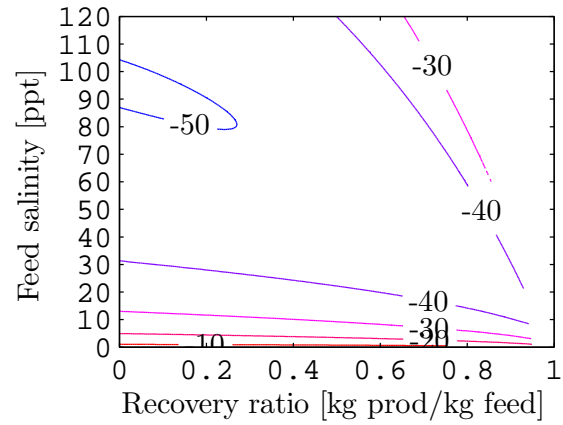
(b) Davies equation for salts, ideal water

(c) Pitzer equation for salts, ideal water

(d) Pitzer effective for salts, ideal water

(e) Pitzer effective for salts and water

Figure 9: Percent relative error in least work of separation, as a function of feed salinity and recovery ratio, resulting from various activity coefficient modeling methods for a 50-50 mixture of $MgSO_4$ and $ZnSO_4$

water behaves ideally, the relative error introduced drops substantially (Fig. 9c). The maximum relative error under the conditions considered is approximately 50%. While this is better than assuming ideality or using Debye-Hückel theory, the error is still unacceptably high for most engineering calculations.

Pitzer's model based on effective molalities for the salt activity coefficient gives reasonable accuracy for a large range of feed salinities and recovery ratios (relative error is less than 10% for most of the range of salinities and recovery ratios considered, Fig. 9d). At higher recovery ratios and very high feed salinities, the error begins to approach greater than 80% so care should be used when using this method. Finally, using the effective Pitzer model for both salts and water results in near perfect agreement with the Pitzer-Kim model (Fig. 9e). The effective Pitzer model works better on this solution than the mock seawater solution because both salts are of the same general form and are of equal proportions. That is, they are both 2:2 electrolytes and the effective molality is equal to the total molality for both salts. As a result, the approximated values obtained from the effective molality calculations closely predict the actual values from the Pitzer-Kim model.

8. Comparison to seawater

As stated in the introduction, standard seawater properties are only appropriate for solutions that have an ionic composition similar to that of the standard seawater solution. As illustrated in Figs. 5 and 8, it is clear that the least work of separation, and therefore, the Gibbs free energy, is a strong function of the composition of the solution being considered. In order to further illustrate this point, the least work of separation for the five-salt mock seawater solution and the two-salt high valence electrolyte solution are compared to the least work of separation for standard seawater [10], an NaCl solution, and an $NaCl-MgSO_4$ solution (Fig. 10).
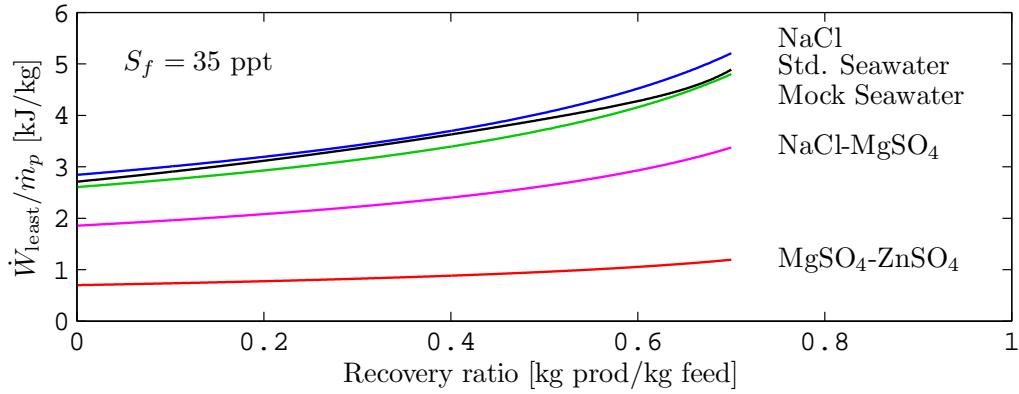
(a) Salinity of all feed streams is 35 ppt.
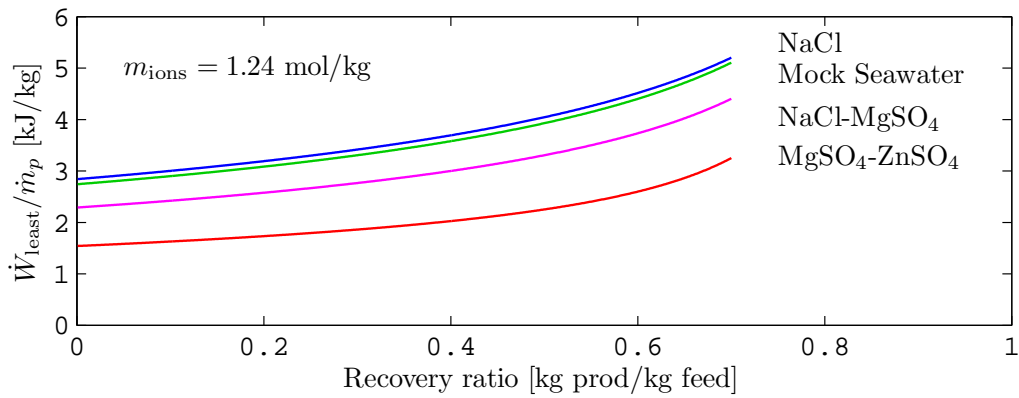
(b) Molality of all ions in all feed streams is 1.24 mol/kg, equivalent to a 35 ppt NaCl solution.
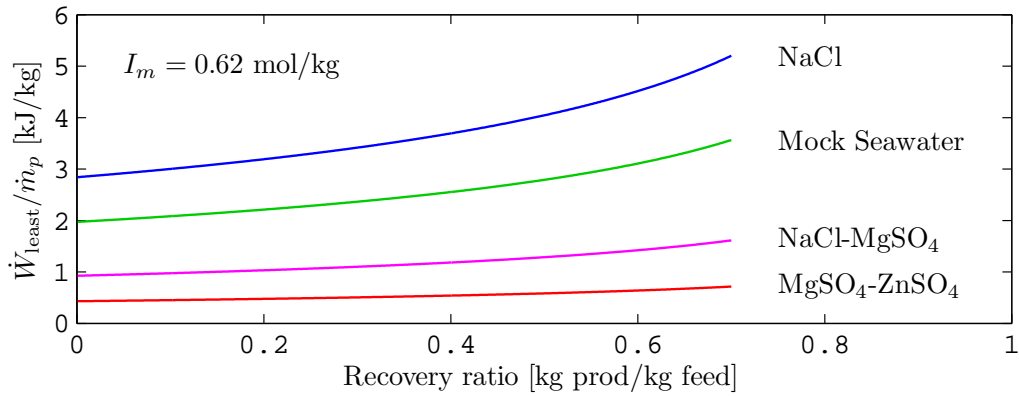
(c) Molal ionic strength of all feed streams is 0.62 mol/kg, equivalent to a 35 ppt NaCl solution.

Figure 10: The least work of separation for is a function of composition as well as feed salinity and recovery ratio.

First, all five solutions are compared when the feed salinity is 35 ppt (Fig. 10a). The NaCl solution has the highest work of separation requirements, followed by standard seawater, mock seawater, NaCl−MgSO$_4$, and MgSO$_4$−ZnSO$_4$. It is clear that the mock seawater very closely approximates the standard seawater solution. The NaCl solution has the highest work requirements and the MgSO$_4$−ZnSO$_4$ solution has the lowest work requirements for many of the reasons discussed previously: lighter salts result in higher molality for fixed salinity, differences in charge of the ions, and the role of aqueous complexation. Similarly, the mock seawater and NaCl−MgSO$_4$ solutions have intermediate work requirements between the two extreme cases.

Since the molality of the solutes in each of the streams considered in Fig. 10a is different, it is unclear whether the difference in work requirements is purely due to the molal concentration. Therefore, the least work of separation is calculated for the different solutions while holding the ionic molality of all of the feed solutions fixed at 1.24 mol/kg. Note that a 0.62 molal NaCl solution has a salinity of 35 ppt and an ionic molality of 1.24 mol/kg (Fig. 10b). Standard seawater is not shown since the ionic composition of the properties provided by [10] is unknown. Figure 10b shows the same trend observed in Fig. 10a.

Finally, the calculations are repeated again while holding the feed solution ionic strength fixed at 0.62 mol/kg which is the ionic strength of a 35 ppt NaCl solution (Fig. 10c). Again, the same trend is observed. Given that increasing concentration results in higher work requirements while increasing valence tends to reduce work requirements, it is clear that ionic strength, which is a function of both concentration and valence, cannot be used by itself to estimate the work requirements. This can be seen by noting that increasing the concentration of the NaCl solution would serve to both increase the ionic strength and the work of separation requirements.

The fact that the least work of separation is dependent on the specific ions present at

a given concentration is also apparent when considering single electrolyte solutions. In order to illustrate this, Fig. 10 is recreated for the following single electrolyte solutions in Fig. 11: NaCl, KCl, $CaCl_2$, $MgCl_2$, Na_2SO_4, $MgSO_4$, and $ZnSO_4$. Again, all of the single electrolyte solutions are compared under three different conditions: equal salinity (Fig. 11a), equal ionic molality (Fig. 11b), and equal ionic strength (Fig. 11c).

In all comparisons, it is seen that there is a wide range in the work of separation requirements, indicating that the specific ions present are an important variable in this calculation. As with the comparision of mixed electrolyte solutions, it is seen that at fixed salinity, the heavier salts tend to have lower separation requirements, due in part to lower molality, higher ionic charge, and increased ion pairing (Fig. 11a). At fixed ionic molality, the solutions are grouped roughly based on ion composition. The chloride salts all have higher requirements than the sulphate salts (Fig. 11b). Finally, at fixed ionic strength, the results group strongly based on ν_s as well as charge, which is to be expected given that ionic strength is a function of molal concentration and ionic charge. As the charge of the ions increases for fixed ionic strength, the molality of the ions necessarily decreases. Therefore, it is not surprising to see three groups: NaCl and KCl as 1:1 salts; $MgCl_2$, $CaCl_2$, and Na_2SO_4 as 2:1 salts; and $MgSO_4$ and $ZnSO_4$ as 2:2 salts (Fig. 11c).

Based on Figs. 10 and 11, it is clear that the least work of separation is a very strong function of the composition of the electrolyte solution. In all cases, the molality, molecular weight, valence of the electrolytes, and aqueous complexation serve to alter the work of separation requirements. Therefore, it is concluded that composition plays a substantial role in the overall energy requirements for desalination processes. This has important implications for both desalination and forward osmosis processes. Naturally, desalination systems' energy requirements will be a strong function of the given feed solution. Similarly, if the draw solution in a forward osmosis process is composed of
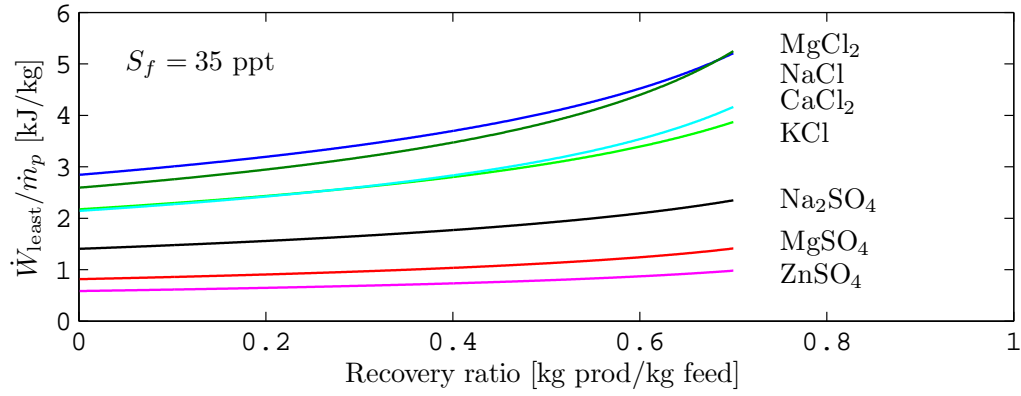
(a) Salinity of all feed streams is 35 ppt.
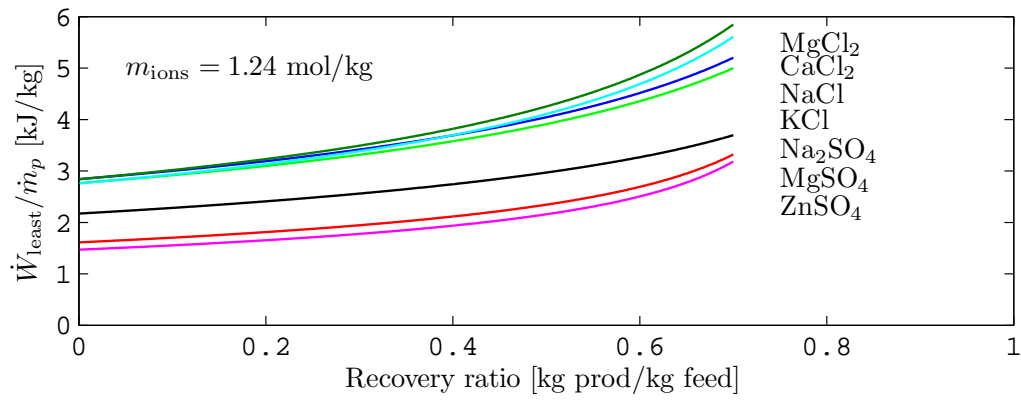
(b) Molality of all ions in all feed streams is 1.24 mol/kg, equivalent to a 35 ppt NaCl solution.
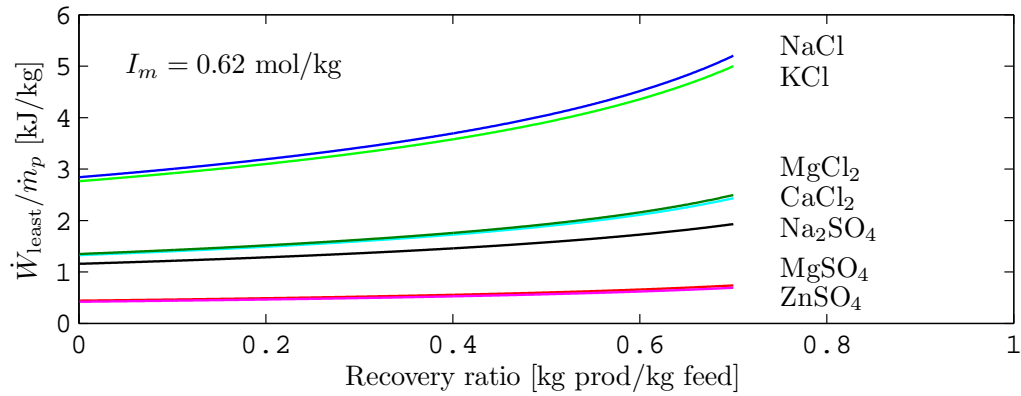
(c) Molal ionic strength of all feed streams is 0.62 mol/kg, equivalent to a 35 ppt NaCl solution.

Figure 11: The least work of separation for is a function of composition as well as feed salinity and recovery ratio.

heavy and high valence electrolytes, the required separation energy for the subsequent removal of H_2O from the draw solution will be substantially lower than what is required for the separation of H_2O from seawater, or any other solution composed mostly of lighter, single charged ions that are not prone to complexation.

9. Conclusions

Based on the parametric study of mock seawater and a high-valence electrolyte solution, the following conclusions are made:

1. Single salt models for the evaluation of salt specific activity coefficients should only be used for very dilute solutions. Using them for non-dilute solutions can result in error greater than what is caused by assuming ideal solution behavior. This is especially true for Debye-Hückel equations such as Davies equation.

2. The ideal solution approximation for mixed electrolytes sometimes yields accurate results due to happenstance cancellation, not due to a nearly ideal solution behavior.

3. Using an effective molality for each salt, defined based on the solution ionic strength, in conjunction with the Pitzer ion interaction model (single electrolyte model) gives good agreement with the more complicated Pitzer-Kim mixed electrolyte model. This method can be used as an approximation for determining both salt and water activity coefficients.

4. Error introduced through the use of single-electrolyte models and the ideal solution approximation is greatly increased when the valence of electrolytes increases.

5. The specific set of ions composing a solution has a significant impact on the least work of separation that cannot be accounted for simply by looking at overall salinity or using single variables such as ionic strength or total dissolved solids

(TDS). In particular, improper application of seawater properties to other kinds of saline water can result in substantial error.

6. Electrolyte solutions that are more prone to aqueous complexation, have higher valence, and heavier molecular weights tend to have lower work of separation requirements. Ionic strength is not strongly correlated with the least work of separation.

Acknowledgments

Nomenclature

Roman symbols		Units
A	Debye-Hückel constant	$\mathrm{kg}^{\frac{1}{2}}/\mathrm{mol}^{\frac{1}{2}}$
A_ϕ	Pitzer constant	$\mathrm{kg}^{\frac{1}{2}}/\mathrm{mol}^{\frac{1}{2}}$
a	activity	-
b	Davies constant	L/mol
F	Faraday constant	C/mol
G	Gibbs free energy	J
$\dot{G}$	Gibbs free energy flow rate	J/s
g	specific Gibbs free energy	J/kg
I_m	molal ionic strength	mol/kg
M	molecular weight	kg/mol
m	molality	$\mathrm{mol/kg_{solvent}}$

$\dot{m}$	mass flow rate	kg/s
N_a	Avogadro's number	1/mol
n	number of moles	mol
$\dot{n}$	mole flow rate	mol/s
p	pressure	Pa
$\dot{Q}$	heat rate	J/s
R	universal gas constant	J/mol-K
r	recovery ratio, mass basis	kg/kg
$\bar{r}$	recovery ratio, mole basis	mol/mol
S	salinity (TDS)	$kg_{solute}/kg_{solution}$
$\dot{S}$	entropy flow rate	J/s-K
T	temperature	K
$\dot{W}$	work rate (power)	J/s
w	mass fraction	kg/kg
x	mole fraction	mol/mol
z	valence of ion	-

Greek symbols		*Units*
ϵ_0	permittivity of free space	F/m
ϵ_r	relative permittivity/dielectric constant	-
γ_f	fugacity coefficient	-
γ_m	molal activity coefficient	-
γ_x	rational activity coefficient	-
μ	chemical potential	J/mol
ν	stoichiometric coefficient	-
ϕ	molal osmotic coefficient	-
ρ	density	kg/m^3

Subscripts

A, a	anion
C, c	cation
b	brine
f	feed
i	species
m	molal basis
x	rational (mole fraction) basis
least	reversible operation
p	product
s	electrolyte salt species
sep	separation
0	solvent
$\pm$	mean ionic property
e	environment
+	cation
−	anion

Superscripts

rev	reversible
∘	standard state

Acronyms		*Units*
ppt	parts per thousand	g/kg
ppm	parts per million	mg/kg
TDS	total dissolved solids	kg/kg

Appendix A. Useful conversions

Recovery ratios

$$\frac{r}{\bar{r}} = \frac{1 + \sum_s m_{s,p} M_s}{1 + \sum_s m_{s,f} M_s} \tag{A.1}$$

Mole fraction and molality

To convert from molality of salts to mole fraction of solutes requires a few steps. First, calculate the mole fraction of the cation and anion for each salt.

$$x_{s,+} = \frac{\nu_{s,+} m_s M_{H_2O}}{1 + M_{H_2O} \sum_s \nu_s m_s} \tag{A.2}$$

$$x_{s,-} = \frac{\nu_{s,-} m_s M_{H_2O}}{1 + M_{H_2O} \sum_s \nu_s m_s} \tag{A.3}$$

Note the sums are over all salt species. The mean mole fraction for the salt is defined analogously to the mean ionic molality [*cf.*, Eq. (12)]:

$$x_s = \left(x_{s,+}^{\nu_+} x_{s,-}^{\nu_-} \right)^{1/\nu} \tag{A.4}$$

The mole fraction of the solvent is equal to one minus the sum of all other mole fractions

$$x_{H_2O} = 1 - \sum_s x_{s,+} - \sum_s x_{s,-} \tag{A.5}$$

Mass fraction and molality

$$w_s = \frac{m_s M_s}{1 + \sum_s m_s M_s} \tag{A.6}$$

Again, the sum is over all salt species.

$$m_s = \frac{w_s}{w_{H_2O} M_s} \tag{A.7}$$

Salinity is defined as the mass fraction of all solutes in solution. Therefore,

$$S = \sum_s w_s = \frac{\sum_s m_s M_s}{1 + \sum_s m_s M_s} \tag{A.8}$$

Several units are commonly used for salinity:

$$\text{ppm} = 10^3 \text{ ppt} = 10^6 S \text{ [kg/kg]} \tag{A.9}$$

Conversion from work per mol to work per kg solution

$$\frac{\dot{W}_{\text{least}}}{\dot{m}_p} = \frac{\dot{W}_{\text{least}}}{\dot{n}_{\text{H}_2\text{O},p}} \left(\frac{1}{M_{\text{H}_2\text{O}} + M_{\text{H}_2\text{O}} \sum_s M_s m_{s,p}} \right) \tag{A.10}$$

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