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EFFECT OF NONIDEAL SOLUTION BEHAVIOR ON DESALINATION OF A SODIUM CHLORIDE (NaCl) SOLUTION AND COMPARISON TO SEAWATER

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ABSTRACT

Proper evaluation of the Gibbs free energy and other properties of seawater and other aqueous solutions is essential in the analysis of desalination systems. Standard seawater has been studied extensively and property data are readily accessible. However, many aqueous solutions requiring desalination have significantly different composition from seawater and seawater data is generally not accurate for these solutions. Experimental data for a given aqueous solution may be unavailable under the conditions of interest. Therefore, there is a need to model relevant physical properties from chemical thermodynamic principles. In particular, for solutions that are not ideal, the activity and fugacity coefficients must be considered. In this paper, the effect of nonidealities in sodium chloride (NaCl) solutions is considered through a parametric study of the least work of separation for a desalination system. This study is used to determine the conditions under which the ideal solution approximation is valid and also to determine when an NaCl solution is a good approximation to standard seawater. It is found that the ideal solution approximation is reasonable within ranges of salinities and recovery ratios typical of those found in the seawater desalination industry because many of the nonidealities cancel out, but not because the solution behaves ideally. Additionally, it is found that NaCl solutions closely approximate natural seawater only at salinities typically found in seawater and not for salinities found in typical brackish waters.

NOMENCLATURE

<i>Roman symbols</i>		<i>Units</i>
A	Debye-Hückle constant	$L^{1/2}/mol^{1/2}$
a	activity	-
b	Davies constant	L/mol
c	molarity	mol/L solution
e	electron charge	C
F	Faraday constant	C/mol
G	Gibbs free energy	J/kg
\dot{G}	Gibbs free energy flow rate	J/s
\dot{H}	enthalpy flow rate	J/s
I_c	molar ionic strength	mol/L
I_m	molal ionic strength	mol/kg
M	molecular weight	kg/mol
m	molality	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	-

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

Subscripts

a	ambient
b	brine
f	feed
i	species (solvent or solutes)
j	stream (b , f , or p)
least	reversible operation
p	product
s	solute species
sep	separation
0	solvent
\pm	mean property for anion and cation
+	cation
-	anion

Superscripts

id	ideal
nid	nonideal
rev	reversible
o	standard state

Acronyms

<i>Acronyms</i>		<i>Units</i>
DHLL	Debye-Hückle Limiting Law	
ppt	parts per thousand	g solute/kg solution
ppm	parts per million	mg solute/kg solution
TDS	total dissolved solids	kg solute/kg solution

INTRODUCTION

Desalination research is being fueled by growing water demand resulting from rising population, by increasing standards of living, and by the contamination of existing water sources. Analytical studies are a critical part of desalination research, and in order to make reliable calculations, it is essential to accurately evaluate the physical properties of the particular water source that is to be treated.

Seawater has been studied in depth and seawater physical properties are well documented [1–4]. However, these properties are only appropriate for water sources that have an ionic composition similar to standard seawater. For many natural and produced waters, including river water, ground water, flowback from hydraulic fracturing, and industrial waste waters, the composition may be substantially different from that of seawater. Additionally, when studying nanofiltration systems, which may have different permeabilities for different solutes, the brine and product streams can have substantially different compositions from the feed stream. Further, scale formation in desalination systems is a direct function of the solution composition. Therefore, for many desalination related calculations, it is essential to evaluate physical properties in detail.

Accurate evaluation of solution properties requires treatment of the activity and fugacity coefficients in order to properly address nonidealities. There are numerous ways to evaluate the activity coefficients, including Debye-Hückle theory and empirical data. For simplicity, it is common to use the ideal solution approximation, thus entirely avoiding the problem of setting the activity coefficients [5–9]. Unfortunately, it is unclear when this approximation is justifiable.

In this paper, the validity of the ideal solution approximation is analyzed through calculation of the least work of separation. Gibbs free energy for a sodium chloride (NaCl) solution is evaluated using various property models and the least work is evaluated as a function of feed salinity and recovery ratio. The NaCl solution results are also compared to the least work calculation evaluated using seawater properties because the use of aqueous NaCl solutions is common in laboratory studies of desalination systems [10–14] as well as in industry [15].

It is found that for salinities and recovery ratios typically found in desalination systems, the ideal solution approximation has lower-than-expected error due to fortuitous cancellation of terms, rather than near-ideal solution behavior.

THERMODYNAMICS AND DEFINITIONS

The Gibbs free energy of a mixture is

$$G \equiv \sum_i n_i \mu_i \quad (1)$$

where the chemical potential is defined as:

$$\mu_i \equiv \mu_i^\circ + RT \ln a_i \quad (2)$$

Proper evaluation of Gibbs free energy requires careful treatment of the activity, a_i , of each species [16–20].

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

TABLE 1: CONSTANTS AND CHEMICAL DATA

Constant	Value	Units
A	0.5115 (H ₂ O at 25 °C)	L ^{1/2} /mol ^{1/2}
b	0.2	L/mol
e	$1.602176565 \times 10^{-19}$	C
F	96.4853365×10^3	C/mol
$M_{\text{H}_2\text{O}}$	18.00988×10^{-3}	kg/mol
M_{NaCl}	$58.42176928 \times 10^{-3}$	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

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 1 bar. Therefore, the activity of the solvent is written [16, 20]:

$$\mu_0 - \mu_0^\circ = RT \ln a_0 = RT \ln \frac{\gamma_{f,0} p_0}{\gamma_{f,0}^\circ p_0^\circ(T)} \quad (3)$$

where γ_f is the fugacity coefficient, p_0 is the partial pressure of the solvent in the vapor state, and $p_0^\circ(T)$ is the partial pressure of the pure solvent at T . The reference state fugacity coefficient, γ_f° is taken to be one. Using a modified form of Raoult's Law in which all nonidealities are assumed to occur within the liquid mixture phase [18], the ratio of the actual partial pressure to the pure partial pressures is written in terms of the mole fraction:

$$\mu_0 - \mu_0^\circ = RT \ln \gamma_{f,0} x_0 \quad (4)$$

Therefore, the activity of the solvent is:

$$a_0 = \gamma_{f,0} x_0 \quad (5)$$

Solutes

Defining the activity of a solute is complicated by the fact that there are three different standard ways to measure concentration: molality, m , moles of species per kilogram solvent; molarity, c , moles of species per liter of solution; and mole fraction, x , moles of species per moles of solution. The corresponding activity

coefficients are, respectively: molal activity coefficient, γ_m ; molar activity coefficient, γ_c ; and the rational activity coefficient, γ_x . As a result, three different activities can be written for a given solute, the molal activity, molar activity, and rational activity [16]:

$$a_{m,s} = \gamma_{m,s} m_s \quad (6)$$

$$a_{c,s} = \gamma_{c,s} c_s \quad (7)$$

$$a_{x,s} = \gamma_{x,s} x_s \quad (8)$$

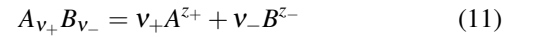
Note that the activity of a solute is a function of the concentration scale and that $a_{m,s} \neq a_{c,s} \neq a_{x,s}$. Regardless of which concentration scale is used, the chemical potential is fixed for a given state since the free energy in the standard state (μ_s° , discussed later) depends on the chosen scale. Therefore [16],

$$\mu_s = \mu_{m,s}^\circ + RT \ln a_{m,s} \quad (9)$$

$$= \mu_{x,s}^\circ + RT \ln a_{x,s} \quad (10)$$

Since molarity is not used in this paper, the molar expression is not included.

When dealing with electrolyte solutions, it is more convenient and practical to consider the free energy of the ion pairs that form from the original electrolyte salt. In order to do so, the mean concentration and mean activity coefficients are introduced. For a neutral electrolyte salt which fully dissociates as shown,



the mean activity of the dissociated salt molecule is derived from the activities of the individual ions. From Eqs. (1) and (2):

$$RT \ln a_{A_{v+} B_{v-}} = v_+ RT \ln a_+ + v_- RT \ln a_- \quad (12)$$

$$a_{A_{v+} B_{v-}} = a_+^{v_+} a_-^{v_-} \quad (13)$$

Using Eq. (6), the mean activity of the ion pair is written in terms of the mean molal activity coefficient and mean molality:

$$a_{A_{v+} B_{v-}} = (\gamma_{m,+} m_+)^{v_+} (\gamma_{m,-} m_-)^{v_-} = \gamma_{m,\pm}^v m_\pm^v \quad (14)$$

where

$$v \equiv v_+ + v_- \quad (15)$$

$$\gamma_{m,\pm}^v \equiv \gamma_{m,+}^{v_+} \gamma_{m,-}^{v_-} \quad (16)$$

$$m_\pm^v \equiv m_+^{v_+} m_-^{v_-} \quad (17)$$

$\gamma_{m,\pm}$ is the mean molal activity coefficient and m_{\pm} is the mean molal concentration. While molality and the molal activity coefficient were used in the above derivation [from Eq. (6)], mole fraction can be similarly used to define the mean mole fraction, x_{\pm} , and the mean rational activity coefficient, γ_{\pm}^x , using Eq. (8).

For neutral electrolytes in which $\nu_+ = \nu_- = 1$ [e.g., NaCl (1:1), ZnSO₄ (2:2), LaFe(CN)₆ (3:3)], the mean molality of the salt is equal to the molality of the individual ions.

$$m_{A\nu_+B\nu_-} = m_{\pm} = m_+ = m_- \quad \text{if } \nu_+ = \nu_- = 1$$

Having introduced mean concentration, the standard state 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 [16, 18, 20]. As a direct consequence of the definition of standard state, it is clear that $\mu_s = \mu_s^\circ$ at standard state and that $\mu_{m,s}^\circ \neq \mu_{x,s}^\circ$ [cf., Eqs. (9) and (10)].

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. (9) and (10) [16, 18]:

$$\gamma_{x,\pm} = \gamma_{m,\pm} (1 + \nu m M_0) \quad (18)$$

where m is the molality of the electrolyte.

MODELS FOR EVALUATING PROPERTIES

Fluid properties are evaluated in one of two ways in this study. All NaCl solution properties are evaluated using Eqs. (1) and (2), which require evaluation of the activity and fugacity coefficients. All seawater properties are evaluated using a freely-available software package that has correlated experimental data [4].

Evaluation of Activity and Fugacity Coefficients

Activity coefficients for the various solution species can be evaluated in many ways. In order of increasing accuracy, the following methods are considered: ideal solution approximation, analytical/theoretical expressions, and correlation of experimental data.

Ideal Solution The ideal solution approximation is the simplest, yet least accurate method for evaluating activity and fugacity coefficients. An ideal solution is one in which the solute molecules and ions do not interact with each other. Practically speaking, this means the solution is dilute and that solute long range (electrostatic) forces are negligibly weak. Interactions between the solute and solvent and between the solvent and solvent

occur. When a solution is ideal, the activity of each of the various species (solvent and solutes alike) is identically equal to the concentration (specifically, the mole fraction) of the respective species. Specifically, the rational activity coefficients (solutes) and the fugacity coefficient (solvent) are equal to one and the activity is equal to the mole fraction [16, 18, 20].

$$\gamma_{x,s}^{\text{id}} = 1 \quad \gamma_f^{\text{id}} = 1 \quad \text{for all species} \quad (19)$$

Even though the rational activity coefficient is equal to one for an ideal system, the molal (or molar) activity coefficient is *not* equal to one as seen in Eq. (18).

Due to its simplicity, the ideal solution approximation is widely used to analyze solutions. Unfortunately, it is easy to use the model beyond its range of applicability and doing so can result in substantial error for even simple calculations. Additionally, a common mistake is to set the molal (or molar) activity coefficient, rather than the rational activity coefficient, to one.

Analytical Equations and Correlations Debye-Hückle theory for electrolytes gives the extended Debye-Hückle equation for activity coefficients [16, 18, 21–24]:

$$\log \gamma_{x,\pm} = -\frac{A|z_+z_-|\sqrt{I_c}}{1 + Ba\sqrt{I_c}} \quad I_c < 0.1 \quad (20)$$

where the molar ionic strength is defined as

$$I_c = \frac{1}{2} \sum_s c_s z_s^2 \quad (21)$$

where c_s is the molarity of solute species s in moles per liter. The summation is over all solute species. The constant, A , is defined as [18, 24]

$$A = \frac{F^3 \log e}{8\pi N_a} \left[\frac{2000}{(\epsilon_0 \epsilon_r RT)^3} \right]^{1/2} = \frac{1.8248 \times 10^6}{(\epsilon_r T)^{3/2}} \left[\frac{\text{L}^{1/2}}{\text{mol}^{1/2}} \right]$$

At 25°C, the static dielectric constant, or relative permittivity, of H₂O is $\epsilon_r = 78.54$ and $A = 0.5092 [\text{L}^{1/2}/\text{mol}^{1/2}]$. B and a are additional parameters that are not used in this paper.

In the limit of very low ionic strength, Eq. (20) reduces to the Debye-Hückle Limiting Law (DHLL):

$$\log \gamma_{x,\pm} = -A|z_+z_-|\sqrt{I_c} \quad I_c < 10^{-2.3} \quad (22)$$

Güntelberg proposed a simplification of Eq. (20) since for most common solutes, $Ba \approx 1$.

$$\log \gamma_{\pm} = -\frac{A|z_+z_-|\sqrt{I_c}}{1 + \sqrt{I_c}} \quad I_c < 0.1 \quad (23)$$

Davies proposed a modification of Eq. (20) which extends the range of ionic strength in which the equation can be used.

$$\log \gamma_{\pm} = -A|z_+z_-| \left(\frac{\sqrt{I_c}}{1 + \sqrt{I_c}} - bI_c \right) \quad I_c < 0.5 \quad (24)$$

b is a constant that ranges from 0.2–0.3 depending on the solute. A value of $b = 0.2$ is used here.

For the low ionic strengths (and therefore, concentrations) that Debye-Hückle theory is valid ($I_c < 0.5$), molality and molarity are small and molarity may be approximated by:

$$c_i = \frac{\rho_{\text{solution}} m_i}{1 + \sum_s m_s M_s} \approx \rho_{\text{H}_2\text{O}} m_i \quad (25)$$

Further, since the density of H_2O at 25°C and 1 bar is 0.99705 kg/L, molality and molarity may be used interchangeably at low concentration (*e.g.*, from Eq. (25), a 0.1, 0.5, 1, and 6 molal NaCl solution has a molarity of 0.0995, 0.4941, 0.9790, and 5.3051 mol/L. Density data taken from Pitzer [25]. Using molality in place of molarity introduces 0.5%, 1.2%, 2.1%, and 11.5% error, respectively.). Therefore, molal ionic strength is used in place of molar ionic strength for Debye-Hückle calculations.

$$I_c = \frac{1}{2} \sum_s c_s z_s^2 \approx \frac{1}{2} \sum_s m_s z_s^2 = I_m \quad (26)$$

The error introduced by this approximation is small compared to the error resulting from the assumptions used in deriving the Debye-Hückle expressions, especially when the equations are used for solutions of ionic strength greater than 1.

Experimental Data The most accurate method for evaluating activity coefficients is to use experimental data. Robinson and Stokes [16] and Pitzer *et al.* [25] have tabulated data for the molal activity coefficient of NaCl in H_2O as a function of molality. The data was curve fitted in MATLAB [26] using a modified form of the Debye-Hückle equations:

$$\gamma_{m,\pm} = 10^{-a \left(\frac{\sqrt{m}}{1 + c\sqrt{m}} - bm \right)} + dm + em^2 + fm^3 \quad (27)$$

where $a = 0.5131$, $b = 0.17$, $c = 1.408$, $d = -0.09262$, $e = 0.002$, and $f = -0.001259$. This curve fit has a $1 - R^2$ value of 9×10^{-6} .

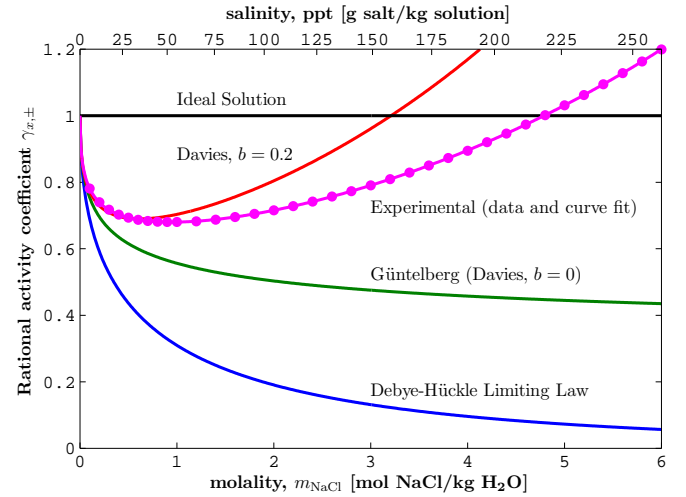


FIGURE 1: RATIONAL ACTIVITY COEFFICIENT FOR NaCl IN H_2O EVALUATED USING DEBYE-HÜCKLE THEORY FOR ELECTROLYTE SOLUTIONS AND USING EXPERIMENTAL DATA. DOTS ARE DATA FROM [16].

The rational activity coefficient is then evaluated by substituting Eq. (27) into Eq. (18).

The mean rational activity coefficient of NaCl in H_2O , evaluated using Eqs. (22) to (24) is plotted as a function of molality in Fig. 1 as solid lines. Additionally, the original data and Eq. (27) are converted to rational activity coefficient using Eq. (18) and plotted as dots and a solid line, respectively.

Osmotic Coefficient The molal activity of water can be written in terms of the molal osmotic coefficient [16, 18, 27]:

$$\ln a_{\text{H}_2\text{O}} = -vmM_{\text{H}_2\text{O}}\phi \quad (28)$$

The osmotic coefficient, ϕ , is curve fit to data provided by Robinson and Stokes [16] and Pitzer *et al.* [25] using the same functional form as Eq. (27):

$$\phi = 10^{-a \left(\frac{\sqrt{m}}{1 + c\sqrt{m}} - bm \right)} + dm + em^2 + fm^3 \quad (29)$$

where $a = 0.1924$, $b = 0.3506$, $c = 2.798$, $d = -0.1019$, $e = -0.001201$, and $f = -0.001324$. This curve fit has a $1 - R^2$ value of 5×10^{-6} .

Using the curve fit, the fugacity coefficient of the water is evaluated using Eqs. (4), (28), and (29):

$$\ln \gamma_{f,\text{H}_2\text{O}} = -vmM_{\text{H}_2\text{O}}\phi - \ln x_{\text{H}_2\text{O}} \quad (30)$$

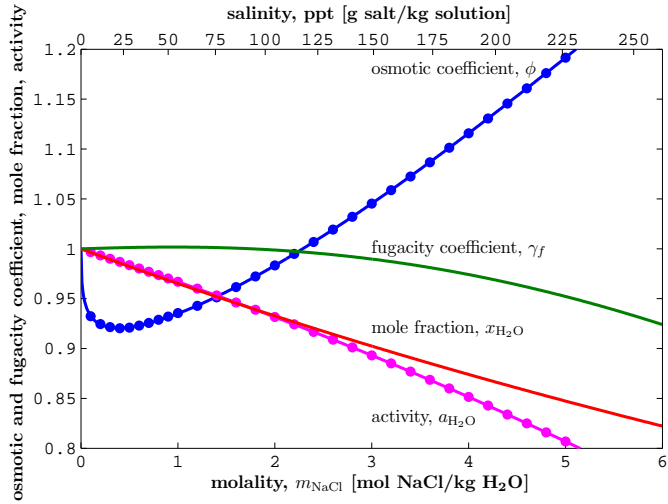


FIGURE 2: H₂O DATA FOR NaCl SOLUTION. DOTS ARE DATA [16]. SOLID LINES ARE CURVE FITS.

Osmotic coefficient, fugacity coefficient, mole fraction, and activity of H₂O is plotted versus molality in Fig. 2.

Empirical Correlations

There have been multiple attempts to create seawater property packages [1, 2, 4]. The work by Sharqawy *et al.* [4] is used in this study. Correlations for properties such as specific Gibbs free energy, osmotic coefficients, and chemical potential of water and salts in seawater have been developed as a function of temperature and salinity. The range of validity of the correlations varies slightly for each property, but in general, they are good for temperatures between 0–120°C and salinities between 0–120 ppt. Note that this property package provides properties per kilogram of solution (seawater).

LEAST WORK OF SEPARATION

The least work of separation, \dot{W}_{least} , is a commonly used metric in desalination that 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 [18, 28–31]. It is a benchmark to which desalination systems are compared, much as Carnot efficiency is an ideal benchmark for power plants. The least work of separation is derived for a control volume containing an ideal black-box separator and then considered from both a mass and mole basis.

Derivation

Consider a simple black-box separator model for a desalination system as shown in Fig. 3. The work of separation entering

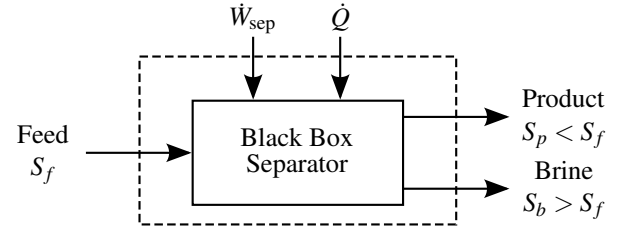


FIGURE 3: A CONTROL VOLUME REPRESENTATION OF A DESALINATION SYSTEM IS USED TO DERIVE THE LEAST WORK OF SEPARATION.

the system is denoted by \dot{W}_{sep} and the 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 ambient temperature, T_a , and pressure, p_a , but at different salinities, S . Heat transfer occurs at ambient temperature. A complete discussion regarding this selection of control volume is provided by Mistry *et al.* [28].

The First and Second Laws of Thermodynamics for the control volume are:

$$\dot{W}_{\text{sep}} + \dot{Q} + \dot{H}_f = \dot{H}_p + \dot{H}_b \quad (31)$$

$$\frac{\dot{Q}}{T_a} + \dot{S}_f + \dot{S}_{\text{gen}} = \dot{S}_p + \dot{S}_b \quad (32)$$

where the convention that work and heat input to the system are positive is used. The First and Second Laws are combined by multiplying Eq. (32) by T_a and subtracting it from Eq. (31) while noting that the Gibbs free energy rate is, $\dot{G} = \dot{H} - T\dot{S}$ (all evaluated at $T = T_a$).

$$\dot{W}_{\text{sep}} = \dot{G}_p + \dot{G}_b - \dot{G}_f + T_a \dot{S}_{\text{gen}} \quad (33)$$

In the limit of reversible operation, entropy generation is zero and the work of separation becomes the reversible work of separation, also known as the least work of separation:

$$\dot{W}_{\text{least}} \equiv \dot{W}_{\text{sep}}^{\text{rev}} = \dot{G}_p + \dot{G}_b - \dot{G}_f \quad (34)$$

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 [28]. 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.

Mass Basis

For property packages that evaluate properties per unit mass of solution (e.g., [4]), Eq. (34) is best written on a mass flow rate basis:

$$\dot{W}_{\text{least}} = \dot{m}_p g_p + \dot{m}_b g_b - \dot{m}_f g_f \quad (35)$$

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:

$$r \equiv \frac{\dot{m}_p}{\dot{m}_f} = \frac{\text{mass flowrate of product}}{\text{mass flowrate of feed}} \quad (36)$$

Conservation of mass for the mixture and the salts is written:

$$\dot{m}_f = \dot{m}_p + \dot{m}_b \quad (37)$$

$$\dot{m}_f S_f = \dot{m}_p S_p + \dot{m}_b S_b \quad (38)$$

The least work of separation per unit mass of product is obtained by rewriting Eq. (35) using Eqs. (36) and (37):

$$\frac{\dot{W}_{\text{least}}}{\dot{m}_p} = (g_p - g_b) + \frac{1}{r} (g_b - g_f) \quad (39)$$

The Gibbs free energy of each of the streams in Eq. (39) 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 Eqs. (36) and (38):

$$S_b = \frac{S_f}{1-r} - \frac{r S_p}{1-r} \quad (40)$$

Equation (39) is a function of temperature, feed salinity, product salinity, and recovery ratio.

Mole Basis

It is more convenient to write Eq. (34) on a mole basis when physical properties are evaluated using Eq. (1). Substitution gives:

$$\begin{aligned} \dot{W}_{\text{least}} = & [\dot{n}_{\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} \mu_{\text{NaCl}}]_p \\ & + [\dot{n}_{\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} \mu_{\text{NaCl}}]_b \\ & - [\dot{n}_{\text{H}_2\text{O}} \mu_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} \mu_{\text{NaCl}}]_f \end{aligned} \quad (41)$$

Conservation of mass for H₂O and NaCl is written as:

$$\dot{n}_{\text{H}_2\text{O},f} = \dot{n}_{\text{H}_2\text{O},p} + \dot{n}_{\text{H}_2\text{O},b} \quad (42)$$

$$\dot{n}_{\text{NaCl},f} = \dot{n}_{\text{NaCl},p} + \dot{n}_{\text{NaCl},b} \quad (43)$$

Substituting Eqs. (2), (42), and (43) into Eq. (41) gives:

$$\begin{aligned} \dot{W}_{\text{least}} = & [\dot{n}_{\text{H}_2\text{O}} RT \ln a_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} RT \ln a_{\text{NaCl}}]_p \\ & + [\dot{n}_{\text{H}_2\text{O}} RT \ln a_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} RT \ln a_{\text{NaCl}}]_b \\ & - [\dot{n}_{\text{H}_2\text{O}} RT \ln a_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} RT \ln a_{\text{NaCl}}]_f \end{aligned} \quad (44)$$

Note that the standard state terms (μ_j°) cancel out through conservation of H₂O and NaCl [Eqs. (42) and (43)].

The molar recovery ratio (\bar{r}) is defined as:

$$\bar{r} \equiv \frac{\dot{n}_{\text{H}_2\text{O},p}}{\dot{n}_{\text{H}_2\text{O},f}} = \frac{\text{molar flowrate of water in product}}{\text{molar flowrate of water in feed}} \quad (45)$$

Using Eqs. (42), (43), and (45), noting that

$$\frac{\dot{n}_{\text{NaCl},j}}{\dot{n}_{\text{H}_2\text{O},j}} = m_{\text{NaCl},j} M_{\text{H}_2\text{O}}$$

and normalizing the least work by $\dot{n}_{\text{H}_2\text{O},p} RT$, Eq. (44) becomes:

$$\begin{aligned} \frac{\dot{W}_{\text{least}}}{\dot{n}_{\text{H}_2\text{O},p} RT} = & \left(\ln \frac{a_{\text{H}_2\text{O},p}}{a_{\text{H}_2\text{O},b}} + m_{\text{NaCl},p} M_{\text{H}_2\text{O}} \ln \frac{a_{\text{NaCl},p}}{a_{\text{NaCl},b}} \right) \\ & + \frac{1}{\bar{r}} \left(\ln \frac{a_{\text{H}_2\text{O},b}}{a_{\text{H}_2\text{O},f}} + m_{\text{NaCl},f} M_{\text{H}_2\text{O}} \ln \frac{a_{\text{NaCl},b}}{a_{\text{NaCl},f}} \right) \end{aligned} \quad (46)$$

Like Eq. (39), Eq. (46) is a function of temperature, feed molality, product molality, and molar recovery ratio.

RAW WATER COMPOSITION

Desalination systems can be used to treat 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). 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 [32, 33]. Even though these natural waters have fairly complex compositions as shown in Table 2, sodium and chloride are the typically the dominant species [34].

TABLE 2: REPRESENTATIVE COMPOSITIONS OF BRACKISH GROUND WATER AND SEAWATER [34]. – = NOT REPORTED.

Constituent		Concentration [ppm = 1000 ppt]		
Name	Symbol	Brackish Water	Normal Seawater	Arabian Gulf At Kuwait
Bicarbonate	HCO ₃ ⁻	385	140	142
Boric Acid	H ₃ BO ₃	–	26	–
Bromide	Br ⁻	–	65	80
Calcium	Ca ²⁺	258	400	500
Chloride	Cl ⁻	870	18,980	23,000
Fluoride	F ⁻	–	1	–
Iodide	I ⁻	–	<1	–
Iron	Fe ²⁺	<1	–	–
Magnesium	Mg ²⁺	90	1,262	1,765
Manganese	Mn ²⁺	1	–	–
Nitrate	NO ₃ ⁻	1	–	–
Phosphate	PO ₄ ³⁻	<1	–	–
Potassium	K ⁺	9	380	460
Silica	SiO ₂	25	–	–
Silicate	SiO ₃ ²⁻	–	1	1.5
Sodium	Na ⁺	739	10,556	15,850
Strontium	Sr ²⁺	3	13	–
Sulfate	SO ₄ ²⁻	1,011	2,649	3,200
Total Dissolved Solids		3,394	34,483	45,000

The recovery ratio with which a desalination plant can operate is strongly dependent upon the feed water salinity. Scaling, membrane durability, and energy costs all serve to limit the maximum salinity allowable in the system [32, 35]. Brackish water plants can operate at higher recovery ratios than can seawater plants due to the lower feed salinity [32, 33]. As part of the parametric study, the least work of separation is evaluated for two different systems: System A has brackish feed with a salinity of 5 ppt and a recovery ratio of 75%; System B has seawater feed at 35 ppt and a recovery ratio of 50%. Both the brackish water and seawater systems are evaluated using various NaCl solutions

models and the seawater package.

PARAMETRIC STUDY

Equation (46) can be modified to facilitate a direct examination of nonideal solution behavior on the least work of separation. Writing the activity of water as $a_{\text{H}_2\text{O},j} = \gamma_{f,\text{H}_2\text{O},j} x_{\text{H}_2\text{O},j}$ and the activity of NaCl as $a_{\text{NaCl},j} = \gamma_{x,\text{NaCl},j}^v x_{\text{NaCl},j}^v$, Eq. (46) is broken into ideal and nonideal parts:

$$\frac{\dot{W}_{\text{least}}}{\dot{n}_{\text{H}_2\text{O},p}RT} = \frac{\dot{W}_{\text{least}}^{\text{id}}}{\dot{n}_{\text{H}_2\text{O},p}RT} + \frac{\dot{W}_{\text{least}}^{\text{nid}}}{\dot{n}_{\text{H}_2\text{O},p}RT} \quad (47)$$

where

$$\begin{aligned} \frac{\dot{W}_{\text{least}}^{\text{id}}}{\dot{n}_{\text{H}_2\text{O},p}RT} = & \left(\ln \frac{x_{\text{H}_2\text{O},p}}{x_{\text{H}_2\text{O},b}} + v_{\text{NaCl}} m_{\text{NaCl},p} M_{\text{H}_2\text{O}} \ln \frac{x_{\text{NaCl},p}}{x_{\text{NaCl},b}} \right) \\ & + \frac{1}{\bar{r}} \left(\ln \frac{x_{\text{H}_2\text{O},b}}{x_{\text{H}_2\text{O},f}} + v_{\text{NaCl}} m_{\text{NaCl},f} M_{\text{H}_2\text{O}} \ln \frac{x_{\text{NaCl},b}}{x_{\text{NaCl},f}} \right) \end{aligned} \quad (48)$$

$$\begin{aligned} \frac{\dot{W}_{\text{least}}^{\text{nid}}}{\dot{n}_{\text{H}_2\text{O},p}RT} = & \left(\ln \frac{\gamma_{f,\text{H}_2\text{O},p}}{\gamma_{f,\text{H}_2\text{O},b}} + v_{\text{NaCl}} m_{\text{NaCl},p} M_{\text{H}_2\text{O}} \ln \frac{\gamma_{x,\text{NaCl},p}}{\gamma_{x,\text{NaCl},b}} \right) \\ & + \frac{1}{\bar{r}} \left(\ln \frac{\gamma_{\text{H}_2\text{O},b}}{\gamma_{\text{H}_2\text{O},f}} + v_{\text{NaCl}} m_{\text{NaCl},f} M_{\text{H}_2\text{O}} \ln \frac{\gamma_{x,\text{NaCl},b}}{\gamma_{x,\text{NaCl},f}} \right) \end{aligned} \quad (49)$$

The ideal part of the least work, Eq. (48), is a function of composition, while the nonideal part of the least work, Eq. (49) is a function of fugacity and activity coefficients.

In order to explore the role of nonideality, a parametric study is performed in which Eqs. (46), (48), and (49) are evaluated while varying feed molality ($m_{\text{NaCl},f}$) and molal recovery ratio (\bar{r}) at 25 °C and assuming pure product water ($m_{\text{NaCl},p} = 0$). All results, however, are given in kJ/kg product as a function of feed salinity (S_f) and recovery ratio (r) since these units are more typical for the desalination industry. Relevant unit conversions are provided in the Appendix [Eqs. (51), (55), and (60)]. In order to avoid extrapolating beyond the available data ranges, calculations are only considered in which all streams are 6 molal or less ($S_j < 260$ ppt).

Least Work for an NaCl Solution

The least work of separation for an NaCl solution, evaluated using Eq. (46), is a strong function of feed salinity, regardless of recovery ratio. As the feed salinity increases, it becomes a strong function of recovery ratio as well (Fig. 4). For the brackish plant, System A, the least work of separation is 0.73 kJ/kg product at a recovery ratio of 75%. For the seawater plant, System B, the

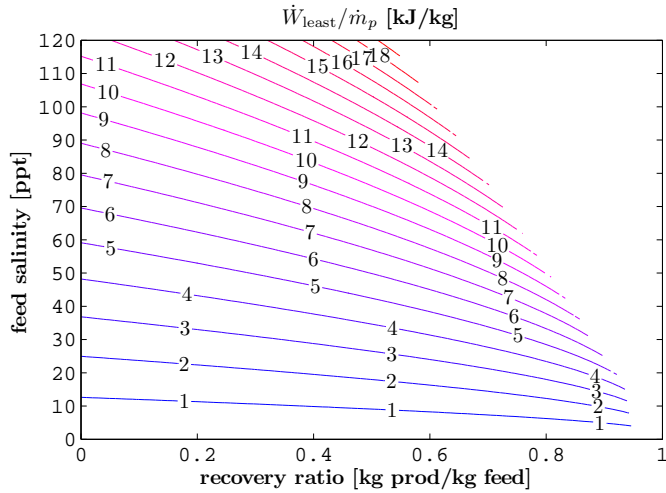


FIGURE 4: LEAST WORK OF SEPARATION FOR AN NaCl SOLUTION [EQ. (46)] IN WHICH ACTIVITY AND FUGACITY COEFFICIENTS ARE EVALUATED USING DATA FROM [16].

least work of separation is 4.04 kJ/kg product at a recovery ratio of 50%. Values of least work of separation for both Systems A and B evaluated using various activity coefficient models are summarized in Table 3.

The ideal part of the least work of separation is shown in Fig. 5. By comparing Figs. 4 and 5, it is clear that the ideal part of the least work is the dominant part. The ideal part is a slightly weaker function of recovery ratio. The ideal part of the least work of separation is 0.79 kJ/kg for System A and 4.27 kJ/kg for System B. These values are 7.7% and 5.5% greater than the actual values.

Unlike the ideal part, the nonidealities are only significant in the least work calculation when the feed salinity and recovery ratio are large (Fig. 6). The results of Eq. (49), as shown in Fig. 6, appear to imply that the NaCl solution behaves approximately ideally for most feed salinities and recovery ratios that are found within the desalination industry and that the nonidealities may reasonably be neglected. However, while it is true that for this particular calculation, the net effect of nonideality is small, it is not because the system is behaving ideally, but rather, because the nonidealities tend to cancel one another, as is shown below.

Error Associated with Ideal Behavior Approximation

The effect of the nonidealities can be visualized by considering the relative error between an ideal NaCl solution (least work values shown in Fig. 5) and an actual NaCl solution (least work

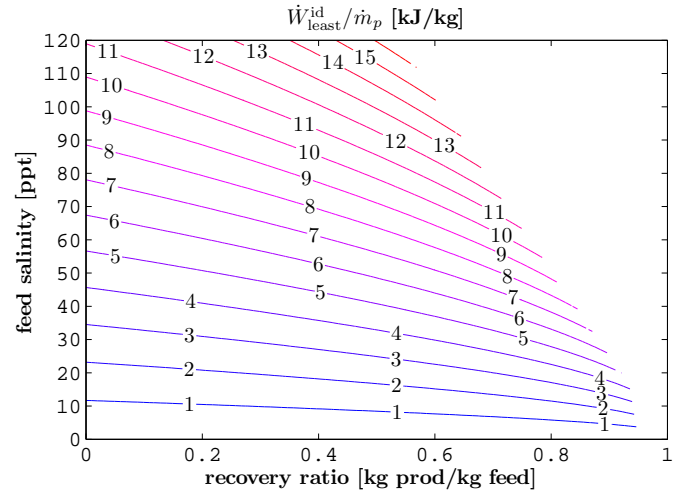


FIGURE 5: IDEAL PART OF THE LEAST WORK OF SEPARATION FOR AN NaCl SOLUTION [EQ. (48)].

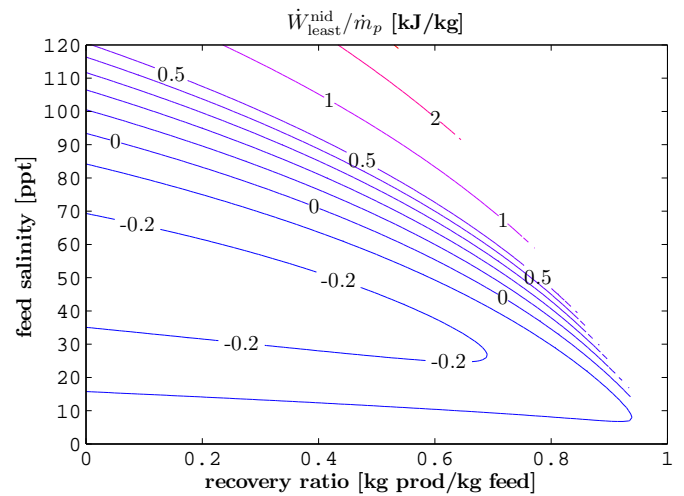


FIGURE 6: THE NONIDEAL PART OF THE LEAST WORK OF SEPARATION FOR AN NaCl SOLUTION [EQ. (49)] ONLY BECOMES SIGNIFICANT AT HIGH FEED SALINITIES AND HIGH RECOVERY RATIOS. ACTIVITY AND FUGACITY COEFFICIENTS ARE EVALUATED USING DATA FROM [16].

values shown in Fig. 4). Relative error, defined as

$$\text{Error [\%]} = \left(\frac{\dot{W}_{\text{least}}^{\text{id}}}{\dot{W}_{\text{least}}^{\text{(actual)}}} - 1 \right) \times 100 \quad (50)$$

between the ideal and actual cases is shown in Fig. 7. As the feed salinity increases at fixed recovery ratio, the magnitude of the

TABLE 3: VALUES FOR THE IDEAL PART, NONIDEAL PART, AND TOTAL LEAST WORK OF SEPARATION FOR TWO DESALINATION SYSTEMS SEPARATING AQUEOUS NaCl SOLUTIONS EVALUATED USING VARIOUS PROPERTY MODELS. NOTE THAT THE DEBYE-HÜCKLE MODELS ARE MORE ACCURATE FOR LOWER SALINITIES AND THAT NaCl SOLUTION IS A BETTER APPROXIMATION FOR SEAWATER AT HIGH SALINITIES. LEAST WORK VALUES ARE IN KJ/KG PRODUCT.

Property Model		Brackish Feed, $S_f = 5$ ppt, $r = 0.75$				Seawater Feed, $S_f = 35$ ppt, $r = 0.5$			
NaCl	H ₂ O	$\dot{W}_{\text{least}}^{\text{id}}$	$\dot{W}_{\text{least}}^{\text{nid}}$	\dot{W}_{least}	Error [%]	$\dot{W}_{\text{least}}^{\text{id}}$	$\dot{W}_{\text{least}}^{\text{nid}}$	\dot{W}_{least}	Error [%]
data	data	0.79	-0.06	0.73	0	4.27	-0.22	4.04	0
ideal	ideal	0.79	0	0.79	7.66	4.27	0	4.27	5.47
ideal	data	0.79	0.01	0.80	8.38	4.27	-0.21	4.06	0.36
data	ideal	0.79	-0.06	0.73	-0.74	4.27	-0.01	4.25	5.11
DHLL	data	0.79	-0.19	0.60	-18.52	4.27	-2.62	1.64	-59.39
Güntelberg	data	0.79	-0.09	0.70	-4.70	4.27	-0.84	3.43	-15.29
Davies	data	0.79	-0.06	0.73	0.05	4.27	0.09	4.36	7.68
Seawater [4]		-	-	0.33	-	-	-	3.93	-

relative error first decreases and then begins to increase once a critical feed salinity is reached. This behavior is not intuitive and in order to properly understand the behavior of the nonidealities in the given system, the nonideality associated with the dissolved species and those associated with the solvent are isolated and considered independently.

First, the nonidealities associated with NaCl are considered by looking at the least work evaluated while approximating NaCl as ideal and treating H₂O as nonideal. The relative error under these approximations is shown in Fig. 8. Even when it is assumed that NaCl is ideal, it is clear that there are certain conditions when this assumption has no effect on the overall calculation — these conditions are illustrated by the zero relative error contour line in Fig. 8.

Since the nonidealities for saline solutions are non-zero, the only way for the nonidealities to be zero is if they cancel out. Since it is assumed that the product stream is pure H₂O, the nonidealities due to salt appear as the final term of Eq. (49):

$$\frac{V_{\text{NaCl}} m_{\text{NaCl},f} M_{\text{H}_2\text{O}}}{\bar{r}} \ln \frac{\gamma_{x,\text{NaCl},b}}{\gamma_{x,\text{NaCl},f}}$$

When the activity coefficient of salt in the brine stream equals the activity coefficient of salt in the feed stream, the ln term equals zero and the salt nonidealities exactly cancel out. Figure 1 shows that except when $\gamma > 1$, there are two molalities that will give the same value of the activity coefficient. As long as the feed and brine concentrations are such that the resulting activity

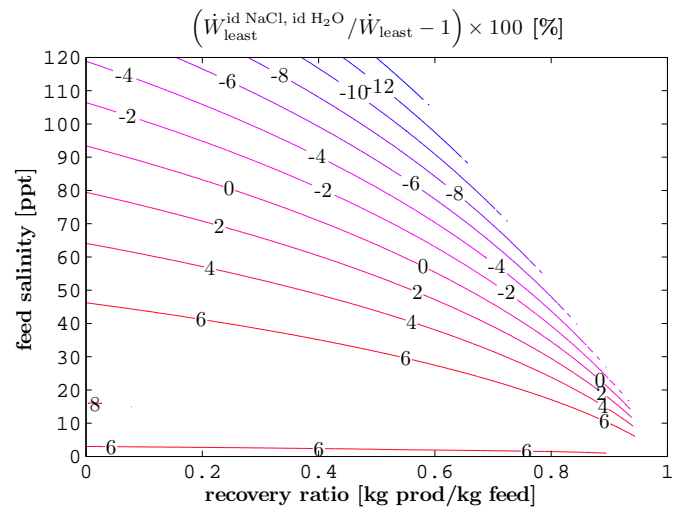


FIGURE 7: RELATIVE ERROR BETWEEN THE IDEAL SOLUTION AND ACTUAL VALUES OF LEAST WORK OF SEPARATION IS LARGE WHEN SALINITY IS EITHER VERY LOW OR VERY HIGH.

coefficients are equal, the nonidealities cancel and the relative error goes to zero as seen in Fig. 8. Any deviation in molality from either stream from this condition will result in error. The least work of separation, when only salt is approximated as ideal, is 0.80 kJ/kg for System A and 4.06 kJ/kg for System B (8.4% and 0.36% error, respectively).

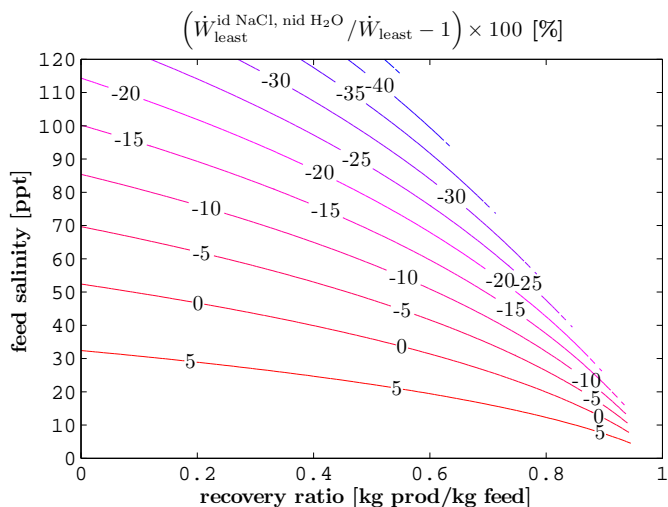


FIGURE 8: RELATIVE ERROR WHEN ONLY NaCl IS APPROXIMATED AS IDEAL GOES TO ZERO WHEN THE ACTIVITY COEFFICIENTS OF SALT IN THE FEED AND BRINE ARE EQUAL.

Nonidealities associated with H₂O are considered by looking at the least work evaluated while approximating H₂O as ideal and treating NaCl as nonideal. From Eq. (49), it is seen that when

$$\ln \frac{\gamma_{f,H_2O,p}}{\gamma_{f,H_2O,b}} + \frac{1}{\bar{r}} \ln \frac{\gamma_{H_2O,b}}{\gamma_{H_2O,f}} = 0$$

the nonidealities associated with H₂O in all three streams cancel out. Figure 2 shows that as long as the molality of the NaCl solution is less than 3 ($S_j < 150$ ppt), the fugacity coefficient is within 1% of unity. Therefore, it is expected that except for combinations of feed salinity and recovery ratio that result in brine streams with greater than 3 molal (149 ppt) concentrations, the error introduced by assuming the water is ideal should be negligible. This is clearly seen to be the case in Fig. 9. The least work of separation, when only water is approximated as ideal, is 0.73 kJ/kg for System A and 4.25 kJ/kg for System B (-0.74% and 5.1% error, respectively).

Figures 8 and 9 both show that there is significant error introduced when it is assumed that either water or salt is ideal. However, the error associated with assuming salt is ideal decreases with increasing feed salinity while the error associated with assuming water is ideal increases with increasing feed salinity. As a result of these reverse trends, the net effect of assuming both the solutes and the solvent are ideal is less than the individual errors. For this reason, it appears that the effect of nonidealities on the least work of separation is small (Fig. 7).

The error introduced by using each of the analytical models for the NaCl activity coefficient is now considered. Unsurpris-

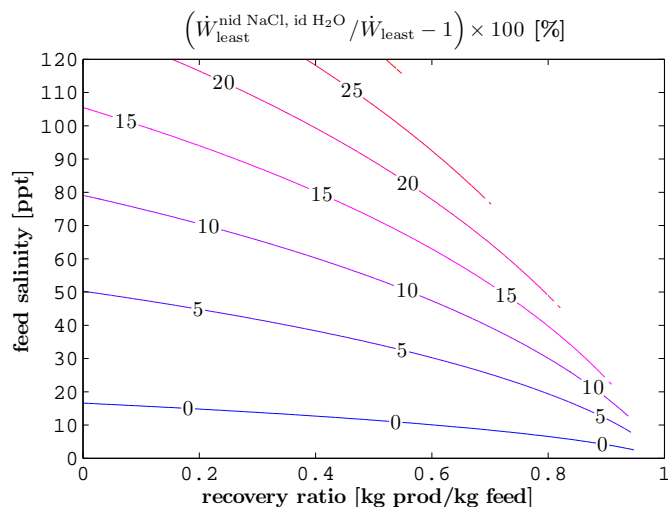


FIGURE 9: RELATIVE ERROR WHEN ONLY H₂O IS APPROXIMATED AS IDEAL GOES TO ZERO WHEN THE FUGACITY COEFFICIENTS OF ALL THE STREAMS CANCEL.

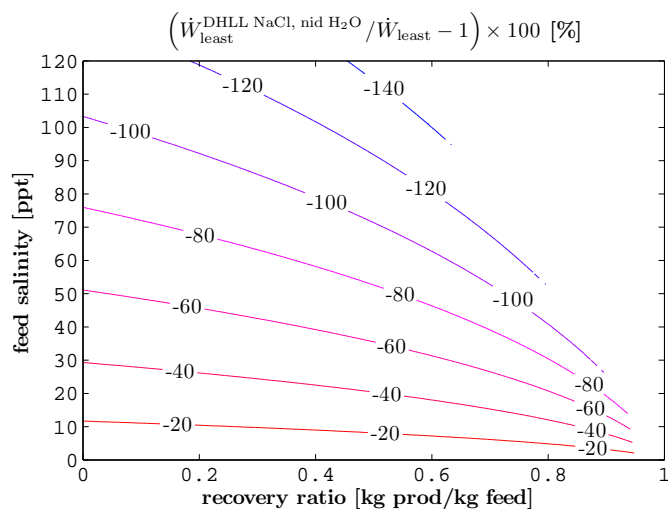


FIGURE 10: THE DEBYE-HÜCKLE LIMITING LAW INTRODUCES SIGNIFICANT ERROR FOR ALL BUT THE LOWEST FEED SALINITIES.

ingly, the error introduced by using the Debye-Hückle Limiting Law [Eq. (22)] is substantial except at the lowest salinities (Fig. 10). This is because the limiting law is only applicable at very low molalities, typically less than $10^{-2.3}$. The least work of separation, when the salt activity coefficient is evaluated using the limiting law, is 0.60 kJ/kg for System A and 1.64 kJ/kg for System B (-19% and -59% error, respectively).

The Güntelberg equation [Eq. (23)] is substantially more

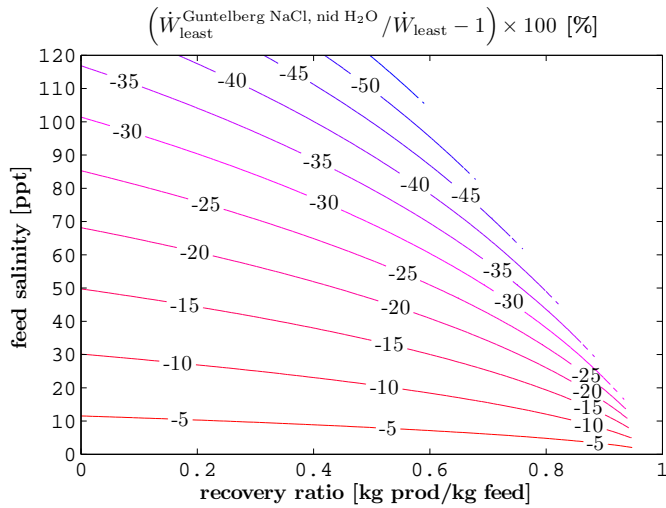


FIGURE 11: THE GÜNTEMBERG EQUATION IS ACCURATE FOR LOW SALINITIES, BUT EVEN FOR SEAWATER SALINITIES, THE RELATIVE ERROR IS AT LEAST 10%.

accurate than the limiting law. However, even at seawater feed salinities, the relative error is at least 10% (Fig. 11). The least work of separation, when the salt activity coefficient is evaluated using Güntelberg equation, is 0.70 kJ/kg for System A and 3.43 kJ/kg for System B (-4.7% and -15% error, respectively).

Finally, the Davies equation [Eq. (24)] is quite accurate for all but the highest salinities. For seawater salinities, the error does not exceed 10% except at extremely high recovery ratios (Fig. 12). The least work of separation, when the salt activity coefficient is evaluated using the Davies equation, is 0.73 kJ/kg for System A and 4.36 kJ/kg for System B (-0.05% and -7.7% error, respectively).

NaCl Solution Compared to Seawater

As a final comparison, the least work of separation for an NaCl solution is compared to the least work of separation for seawater. Seawater is composed of many different species, including chlorine (55.3%), sodium (30.8%), sulfate (7.7%), magnesium (3.7%), calcium (1.2%), potassium (1.1%), and others [36]. Unlike the NaCl solution, several of the species in seawater are divalent (*e.g.*, calcium, sulfate, *etc.*). Larger species, such as the multivalent and multiatomic ions, are generally easier to remove from solution than small monovalent, monatomic species such as sodium and chloride. As a result, it is expected that an NaCl solution will have higher work of separation than seawater of equal salinity. This trend is seen in Fig. 13. The least work of separation, when seawater properties are used, is 0.33 kJ/kg for System A and 3.93 kJ/kg for System B.

It is also seen that as feed salinity increases, the NaCl solution begins to more closely approximate the seawater solution. This

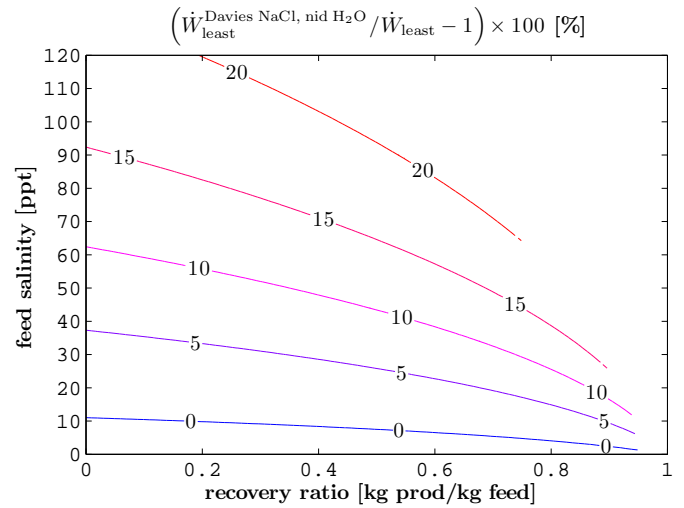


FIGURE 12: THE DAVIES EQUATION ACCURATELY EVALUATES THE SALT NONIDEALITIES AND RESULTS IN MINIMAL ERROR EXCEPT AT VERY HIGH SALINITIES.

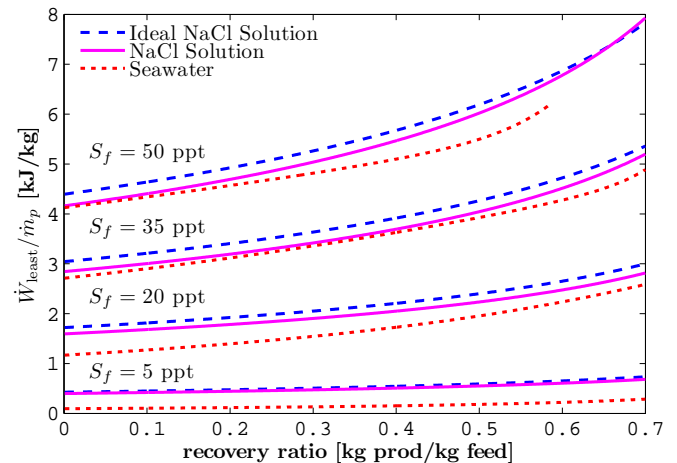


FIGURE 13: THE LEAST WORK OF SEPARATION FOR AN NaCl SOLUTION IS GREATER THAN THE LEAST WORK OF SEPARATION FOR AN AQUEOUS SOLUTION WITH SEAWATER COMPOSITION.

phenomena is explained by the fact that for very low salinities, the activity coefficient is close to one. However, as salinity increases, the activity coefficient quickly drops to approximately 0.7 and then begins to slowly increase (Fig. 1). This general trend is observable in many salt species. As a result, when the feed is at slightly higher salinities (about 35 ppt or higher), the nonidealities associated with the salts tend to become smaller and the least work

is dominated by the compositional effects that are captured in the ideal work of separation. Therefore, the difference in nonidealities between NaCl solutions and seawater solutions tend to become less significant at higher concentrations.

CONCLUSIONS

In this paper, the following conclusions have been reached:

1. The least work of separation can be divided into ideal and nonideal parts. The ideal part is a function of composition (specifically, mole fraction). The nonideal part is a function of the fugacity coefficients of the solvent and the rational activity coefficients of the solutes in the feed, product, and brine streams. Both are functions of temperature, feed and product molality, and molar recovery ratio.
2. Approximating a sodium chloride solution as ideal introduces small error in calculating the least work of separation for salinities and recovery ratios representative of seawater and brackish water desalination systems since the effects of the nonidealities of water and salt tend to have opposite signs, thus partially canceling out. The relatively low error is *not* attributable to near-ideal behavior of the solution itself.
3. Nonidealities associated with the salts become negligible in evaluating least work under certain operating conditions because they cancel out, not because they are insignificant. The nonidealities associated with water are negligible except for highly concentrated solutions.
4. Sodium chloride solutions tend to approximate seawater more accurately at higher salinities.

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APPENDIX: SOME USEFUL CONVERSIONS

Recovery Ratios

$$\frac{r}{\bar{r}} = \frac{1 + m_{\text{NaCl},p} M_{\text{NaCl}}}{1 + m_{\text{NaCl},f} M_{\text{NaCl}}} \quad (51)$$

Mass Fraction and Mole Fraction

$$w_i = \frac{x_i M_i}{x_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}} + \sum_s x_s M_s} \quad (52)$$

Note: i is the particular species (solute or solvent) of interest, s is any solute species (but not solvent species).

Mass Fraction and Molality

General:

$$w_i = \frac{m_i M_i}{1 + \sum_s m_s M_s} \quad (53)$$

For NaCl:

$$w_i = \frac{m_i M_i}{1 + m_{\text{NaCl}} M_{\text{NaCl}}} \quad i = \text{Na}^+, \text{Cl}^- \quad (54)$$

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

$$S = \sum_s w_s = w_{\text{Na}^+} + w_{\text{Cl}^-} = \frac{m_{\text{NaCl}} M_{\text{NaCl}}}{1 + m_{\text{NaCl}} M_{\text{NaCl}}} \quad (55)$$

Several units are commonly used for salinity:

$$\text{ppm} = 10^3 \text{ ppt} = 10^6 S \quad (56)$$

Mole Fraction and Molality

General:

$$x_i = \frac{m_i M_{\text{H}_2\text{O}}}{1 + M_{\text{H}_2\text{O}} \sum_s m_s} \quad (57)$$

For NaCl:

$$x_{\text{Na}^+} = x_{\text{Cl}^-} = \frac{m_{\text{NaCl}} M_{\text{H}_2\text{O}}}{1 + 2m_{\text{NaCl}} M_{\text{H}_2\text{O}}} \quad (58)$$

$$x_{\text{H}_2\text{O}} = 1 - 2x_{\text{Na}^+} \quad (59)$$

Conversion From Work per mol to Work per kg Solution

$$\frac{\dot{W}_{\text{least}}}{\dot{m}_p} = \frac{\dot{W}_{\text{least}}}{\dot{m}_{\text{H}_2\text{O},p}} \left(\frac{1}{M_{\text{H}_2\text{O}} + m_p M_{\text{H}_2\text{O}} M_{\text{NaCl}}} \right) \quad (60)$$