Effect of nonideal solution behavior on desalination of a sodium chloride (NaCl) solution and comparison to seawater

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

Citation

As Published

Publisher
American Society of Mechanical Engineers

Version
Author's final manuscript

Accessed
Fri Dec 07 14:58:01 EST 2018

Citable Link
http://hdl.handle.net/1721.1/76752

Terms of Use
Creative Commons Attribution-Noncommercial-Share Alike 3.0

Detailed Terms
http://creativecommons.org/licenses/by-nc-sa/3.0/
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 nonidealties 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 nonidealties 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

Roman symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>L^{1/2} mol^{1/2}</td>
</tr>
<tr>
<td>a</td>
<td>L/mol</td>
</tr>
<tr>
<td>b</td>
<td>mol/L solution</td>
</tr>
<tr>
<td>c</td>
<td>C</td>
</tr>
<tr>
<td>e</td>
<td>J/kg</td>
</tr>
<tr>
<td>F</td>
<td>mol/L</td>
</tr>
<tr>
<td>G</td>
<td>J/L</td>
</tr>
<tr>
<td>H</td>
<td>J/L</td>
</tr>
<tr>
<td>I_c</td>
<td>mol/L</td>
</tr>
<tr>
<td>I_m</td>
<td>mol/kg</td>
</tr>
<tr>
<td>M</td>
<td>kg/mol</td>
</tr>
<tr>
<td>m</td>
<td>mol/kg solvent</td>
</tr>
<tr>
<td>n</td>
<td>kg/s</td>
</tr>
<tr>
<td>N_a</td>
<td>1/mol</td>
</tr>
<tr>
<td>n</td>
<td>mol</td>
</tr>
<tr>
<td>n</td>
<td>mol/s</td>
</tr>
<tr>
<td>p</td>
<td>Pa</td>
</tr>
<tr>
<td>Q</td>
<td>J/s</td>
</tr>
<tr>
<td>R</td>
<td>J/mol-K</td>
</tr>
<tr>
<td>r</td>
<td>kg/kg</td>
</tr>
<tr>
<td>r</td>
<td>mol/mol</td>
</tr>
<tr>
<td>S</td>
<td>kg solute/kg solution</td>
</tr>
<tr>
<td>S</td>
<td>J/s-K</td>
</tr>
<tr>
<td>T</td>
<td>K</td>
</tr>
<tr>
<td>W</td>
<td>J/s</td>
</tr>
</tbody>
</table>
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

\[ G = \sum_i n_i \mu_i \quad (1) \]

where the chemical potential is defined as:

\[ \mu_i = \mu_i^\circ + RT \ln a_i \quad (2) \]

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.
where \( \gamma \) is the fugacity coefficient, \( p_0 \) is the partial pressure of the solvent in the vapor state, and \( p_0^0(T) \) is the partial pressure of the pure solvent at \( T \). The reference state fugacity coefficient, \( \gamma^0_f \) 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:

\[
\mu_0 - \mu_0^0 = RT \ln a_0 = RT \ln \left( \frac{\gamma_f,0 p_0}{\gamma_f,0 p_0^0(T)} \right) 
\]  
(3)

where \( \gamma_f \) is the fugacity coefficient, \( p_0 \) is the partial pressure of the solvent in the vapor state, and \( p_0^0(T) \) is the partial pressure of the pure solvent at \( T \). The reference state fugacity coefficient, \( \gamma_f^0 \) 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:

\[
\mu_0 - \mu_0^0 = RT \ln \gamma_f,0 x_0 
\]  
(4)

Therefore, the activity of the solvent is:

\[
a_0 = \gamma_f,0 x_0 
\]  
(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, \( \gamma_m \); molar activity coefficient, \( \gamma_c \); and the rational activity coefficient, \( \gamma_r \). As a result, three different activities can be written for a given solute, the molal activity, molar activity, and rational activity [16]:

\[
a_{m,s} = \gamma_m,0 m_s 
\]  
(6)

\[
a_{c,s} = \gamma_c,0 c_s 
\]  
(7)

\[
a_{x,s} = \gamma_{x,s} x_s 
\]  
(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 (\( \mu_0^0 \), discussed later) depends on the chosen scale. Therefore [16],

\[
\mu_v = \mu_{m,s}^0 + RT \ln a_{m,s} 
\]  
(9)

\[
= \mu_{x,s}^0 + RT \ln a_{x,s} 
\]  
(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,

\[
A_{v,+} B_{v,-} = v_+ A^{z+} + v_- B^{z-} 
\]  
(11)

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

\[
RT \ln a_{A_{v,+} B_{v,-}} = v_+ RT \ln a_{v,+} + v_- RT \ln a_{v,-} 
\]  
(12)

\[
a_{A_{v,+} B_{v,-}} = a_{v,+}^{v_+} a_{v,-}^{v_-} 
\]  
(13)

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

\[
a_{A_{v,+} B_{v,-}} = \left( \gamma_{m,+} m_{v,+} \right)^{v_+} \left( \gamma_{m,-} m_{v,-} \right)^{v_-} = \gamma_{v,+}^{v_+} \gamma_{v,-}^{v_-} m_{v,+} m_{v,-} 
\]  
(14)

where

\[
v \equiv v_+ + v_- 
\]  
(15)

\[
\gamma_{v,+}^{v_+} = \gamma_{m,+}^{v_+} \gamma_{v,-}^{v_-} 
\]  
(16)

\[
m_{v,+} m_{v,-} 
\]  
(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, \( \gamma_{id}^{\pm} \), using Eq. (8).

For neutral electrolytes in which \( \nu_+ = \nu_- = 1 \) [e.g., NaCl (1:1), ZnSO\(_4\) (2:2), LaFe(CN)\(_6\) (3:3)], the mean molality of the salt is equal to the molality of the individual ions.

\[
m_{A_{\nu_+,B_{\nu_-}}} = m_{\pm} = m_+ = m_- \quad \text{if} \quad \nu_+ = \nu_- = 1
\]

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 \( \mu_i = \mu_i^s \) at standard state and that \( \mu_{m,s}^0 \neq \mu_{m,s}^0 \) [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]:

\[
\gamma_{id}^{\pm} = \gamma_{m,\pm} (1 + \nu m M_0) \tag{18}
\]

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 (solute) and the fugacity coefficient (solvent) are equal to one and the activity is equal to the mole fraction [16, 18, 20].

\[
\gamma_{id}^{\pm} = 1 \quad \gamma_f^{id} = 1 \quad \text{for all species} \tag{19}
\]

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]:

\[
\log \gamma_{id}^{\pm} = -\frac{A|z_+ z_-|\sqrt{T_c}}{1 + Ba\sqrt{T_c}} \quad I_c < 0.1 \tag{20}
\]

where the molar ionic strength is defined as

\[
I_c = \frac{1}{2} \sum_s c_s z_s^2 \tag{21}
\]

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]

\[
A = \frac{F^3 \log e}{8\pi N_a} \left[ \frac{2000}{(\varepsilon_0 \varepsilon_r RT)^3} \right]^{1/2} = 1.8248 \times 10^6 \frac{I_c^{1/2}}{(\varepsilon_r T)^{3/2}} \left[ \frac{\text{L}^{1/2}}{\text{mol}^{1/2}} \right]
\]

At 25°C, the static dielectric constant, or relative permittivity, of H\(_2\)O is \( \varepsilon_r = 78.54 \) and \( A = 0.5092 \left[ \text{L}^{1/2}/\text{mol}^{1/2} \right] \). \( B \) 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):

\[
\log \gamma_{id}^{\pm} = -A|z_+ z_-|\sqrt{T_c} \quad I_c < 10^{-2.3} \tag{22}
\]

4 Copyright © 2012 by ASME
Güntelberg proposed a simplification of Eq. (20) since for most common solutes, \( Ba \approx 1 \).

\[
\log \gamma_{c_m} = \frac{A |z_+z_-| \sqrt{I_c}}{1 + \sqrt{I_c}} \quad I_c < 0.1 \tag{23}
\]

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

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

\( b \) 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:

\[
c_i = \frac{\rho_{\text{solution}} m_i}{1 + \sum m_j M_j} \approx \rho_{H_2O} m_i \tag{25}
\]

Further, since the density of \( H_2O \) at 25\(^\circ\)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.

\[
I_c = \frac{1}{2} \sum_i c_i^2 \approx \frac{1}{2} \sum m_i c_i^2 = I_m \tag{26}
\]

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:

\[
\gamma_{m_m} = 10^{-a \left( \frac{\sqrt{m}}{1 + \sqrt{m}} - b m \right)} + dm + em^2 + fm^3 \tag{27}
\]

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 \( 9 \times 10^{-6} \).

![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].](image)

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]:

\[
\ln a_{H_2O} = -\nu m M_{H_2O} \phi \tag{28}
\]

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

\[
\phi = 10^{-a \left( \frac{\sqrt{m}}{1 + \sqrt{m}} - b m \right)} + dm + em^2 + fm^3 \tag{29}
\]

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 \( 5 \times 10^{-6} \).

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

\[
\ln \gamma_{f,H_2O} = -\nu m M_{H_2O} \phi - \ln x_{H_2O} \tag{30}
\]
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, \( W_{\text{least}} \), 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 the system is denoted by \( W_{\text{sep}} \) 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:

\[
W_{\text{sep}} + \dot{Q} + \dot{H}_f = \dot{H}_p + \dot{H}_b
\]

(31)

\[
\frac{\dot{Q}}{T_a} + \dot{S}_f + \dot{S}_{\text{gen}} = \dot{S}_p + \dot{S}_b
\]

(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, \( \dot{G} = \dot{H} - T S \) (all evaluated at \( T = T_a \)).

\[
W_{\text{sep}} = \dot{G}_p + \dot{G}_b - \dot{G}_f + T_a \dot{S}_{\text{gen}}
\]

(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:

\[
W_{\text{least}} = W_{\text{rev}} = \dot{G}_p + \dot{G}_b - \dot{G}_f
\]

(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:

\[
\dot{W}_{\text{least}} = \dot{m}_p g_p + \dot{m}_b g_b - \dot{m}_f g_f 
\]  \hspace{1cm} (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:

\[
r \equiv \frac{\dot{m}_p}{\dot{m}_f} = \frac{\text{mass flowrate of product}}{\text{mass flowrate of feed}} 
\]  \hspace{1cm} (36)

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

\[
\dot{m}_f = \dot{m}_p + \dot{m}_b 
\]  \hspace{1cm} (37)

\[
\dot{m}_f S_f = \dot{m}_p S_p + \dot{m}_b S_b 
\]  \hspace{1cm} (38)

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

\[
\frac{\dot{W}_{\text{least}}}{\dot{m}_p} = (g_p - g_b) + \frac{1}{r} (g_b - g_f) 
\]  \hspace{1cm} (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):

\[
S_b = S_f \frac{r}{1 - r} - \frac{r S_p}{1 - r} 
\]  \hspace{1cm} (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:

\[
\dot{W}_{\text{least}} = [\dot{n}_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} M_{\text{NaCl}}]_{\rho} 
\]  
\[+ [\dot{n}_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} M_{\text{NaCl}}]_{b} 
\]  
\[- [\dot{n}_{\text{H}_2\text{O}} M_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} M_{\text{NaCl}}]_{f} \]  \hspace{1cm} (41)

Conservation of mass for \( \text{H}_2\text{O} \) and \( \text{NaCl} \) is written as:

\[
\dot{n}_{\text{H}_2\text{O},f} = \dot{n}_{\text{H}_2\text{O},\rho} + \dot{n}_{\text{H}_2\text{O},b} \]  \hspace{1cm} (42)

\[
\dot{n}_{\text{NaCl},f} = \dot{n}_{\text{NaCl},\rho} + \dot{n}_{\text{NaCl},b} \]  \hspace{1cm} (43)

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

\[
\dot{W}_{\text{least}} = [\dot{n}_{\text{H}_2\text{O}} RT \ln a_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} RT \ln a_{\text{NaCl}}]_{\rho} 
\]  
\[+ [\dot{n}_{\text{H}_2\text{O}} RT \ln a_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} RT \ln a_{\text{NaCl}}]_{b} 
\]  
\[- [\dot{n}_{\text{H}_2\text{O}} RT \ln a_{\text{H}_2\text{O}} + \dot{n}_{\text{NaCl}} RT \ln a_{\text{NaCl}}]_{f} \]  \hspace{1cm} (44)

Note that the standard state terms (\( \mu^c \)) cancel out through conservation of \( \text{H}_2\text{O} \) and \( \text{NaCl} \) [Eqs. (42) and (43)].

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

\[
\bar{r} \equiv \frac{n_{\text{H}_2\text{O},\rho}}{n_{\text{H}_2\text{O},f}} = \frac{\text{molar flowrate of water in product}}{\text{molar flowrate of water in feed}} 
\]  \hspace{1cm} (45)

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

\[
\dot{n}_{\text{NaCl},f} = m_{\text{NaCl},f} M_{\text{H}_2\text{O}} 
\]  \hspace{1cm} (46)

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

\[
\frac{\dot{W}_{\text{least}}}{\dot{n}_{\text{H}_2\text{O},\rho} RT} = \left( \ln \frac{a_{\text{H}_2\text{O},\rho}}{a_{\text{H}_2\text{O},b}} + m_{\text{NaCl},\rho} M_{\text{H}_2\text{O}} \ln \frac{a_{\text{NaCl},\rho}}{a_{\text{NaCl},b}} \right) 
\]  
\[+ \bar{r} \left( \ln \frac{a_{\text{H}_2\text{O},b}}{a_{\text{H}_2\text{O},f}} + m_{\text{NaCl},f} M_{\text{H}_2\text{O}} \ln \frac{a_{\text{NaCl},b}}{a_{\text{NaCl},f}} \right) \]  \hspace{1cm} (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].
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, 33]. 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 $a_{H_2O}$ and assuming pure product water ($x_{NaCl}$ = 0), the activity of NaCl as $a_{NaCl} = \gamma_{NaCl}^x x_{NaCl}$, and the activity of H2O as $a_{H_2O} = \gamma_{H_2O}^x x_{H_2O}$, Eq. (46) is broken into ideal and nonideal parts:

$$\frac{W_{\text{least}}}{n_{H_2O,p}RT} = \frac{W_{\text{id least}}}{n_{H_2O,p}RT} + \frac{W_{\text{nid least}}}{n_{H_2O,p}RT} \quad (47)$$

where

$$\frac{W_{\text{id least}}}{n_{H_2O,p}RT} = \left( \ln \frac{x_{H_2O,b}}{x_{H_2O,f}} + \sum_{j \neq NaCl} m_{NaCl} M_{H_2O} \ln \frac{x_{NaCl,p}}{x_{NaCl,b}} \right)$$

$$+ \frac{1}{\dot{r}} \left( \ln \frac{\gamma_{H_2O,b}}{\gamma_{H_2O,f}} + \sum_{j \neq NaCl} m_{NaCl} M_{H_2O} \ln \frac{\gamma_{NaCl,b}^x}{\gamma_{NaCl,f}^x} \right) \quad (48)$$

$$\frac{W_{\text{nid least}}}{n_{H_2O,p}RT} = \left( \ln \frac{\gamma_{H_2O,b}}{\gamma_{H_2O,f}} + \sum_{j \neq NaCl} m_{NaCl} M_{H_2O} \ln \frac{\gamma_{NaCl,b}^x}{\gamma_{NaCl,f}^x} \right)$$

$$+ \frac{1}{\dot{r}} \left( \ln \frac{\gamma_{H_2O,b}}{\gamma_{H_2O,f}} + \sum_{j \neq NaCl} m_{NaCl} M_{H_2O} \ln \frac{\gamma_{NaCl,b}^x}{\gamma_{NaCl,f}^x} \right) \quad (49)$$

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 ($m_{NaCl}$) and molal recovery ratio ($\dot{r}$) at 25°C and assuming pure product water ($m_{NaCl,p} = 0$). All results, however, are given in kJ/kg product as a function of feed salinity ($S_f$) and recovery ratio ($\dot{r}$) 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 ($S_f < 260$ 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

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

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration [ppm = 1000 ppt]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Brackish Water</td>
</tr>
<tr>
<td>Name</td>
<td>Symbol</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>HCO$_3^-$</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>H$_3$BO$_3$</td>
</tr>
<tr>
<td>Bromide</td>
<td>Br$^-$</td>
</tr>
<tr>
<td>Calcium</td>
<td>Ca$^{2+}$</td>
</tr>
<tr>
<td>Chloride</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td>Fluoride</td>
<td>F$^-$</td>
</tr>
<tr>
<td>Iodide</td>
<td>I$^-$</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe$^{2+}$</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Mg$^{2+}$</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn$^{2+}$</td>
</tr>
<tr>
<td>Nitrate</td>
<td>NO$_3^-$</td>
</tr>
<tr>
<td>Phosphate</td>
<td>PO$_4^{3-}$</td>
</tr>
<tr>
<td>Potassium</td>
<td>K$^+$</td>
</tr>
<tr>
<td>Silica</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Silicate</td>
<td>SiO$_2^{2-}$</td>
</tr>
<tr>
<td>Sodium</td>
<td>Na$^+$</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr$^{2+}$</td>
</tr>
<tr>
<td>Sulfate</td>
<td>SO$_4^{2-}$</td>
</tr>
</tbody>
</table>

Total Dissolved Solids 3,394 34,483 45,000
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 values shown in Fig. 4). Relative error, defined as

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

between the ideal and actual cases is shown in Fig. 7. As the feed salinity increases at fixed recovery ratio, the magnitude of the
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 H\(_2\)O 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 H\(_2\)O, the nonidealities due to salt appear as the final term of Eq. (49):

\[
\frac{V_{NaCl} M_{NaCl} f_{H_2O}}{F} \ln \frac{\gamma_{NaCl,b}}{\gamma_{NaCl,f}}
\]

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 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).
Nonidealities associated with H$_2$O are considered by looking at the least work evaluated while approximating H$_2$O as ideal and treating NaCl as nonideal. From Eq. (49), it is seen that when

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

the nonidealities associated with H$_2$O in all three streams cancel out. Figure 2 shows that as long as the molality of the NaCl solution is less than 3 (S$_f < 150$ 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. Unsurprisingly, 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
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 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 typical 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.

ACKNOWLEDGMENT
The authors would like to thank the King Fahd University of Petroleum and Minerals in Dhahran, Saudi Arabia, for funding the research reported in this paper through the Center for Clean Water and Clean Energy at MIT and KFUPM under project number R13-CW-10.

REFERENCES


APPENDIX: SOME USEFUL CONVERSIONS

**Recovery Ratios**

\[
\frac{\bar{r}}{r} = \frac{1 + m_{NaCl} \rho M_{NaCl}}{1 + m_{NaCl} M_{NaCl}}
\]  

(51)

**Mass Fraction and Mole Fraction**

\[
w_i = \frac{x_i M_i}{x_{H_2O} M_{H_2O} + \sum x_i M_i}
\]  

(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:**

\[
w_i = \frac{m_i M_i}{1 + \sum s m_s M_s}
\]  

(53)

For NaCl:

\[
w_i = \frac{m_i M_i}{1 + m_{NaCl} M_{NaCl}} \quad i = Na^+, Cl^- 
\]  

(54)

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

\[
S = \sum s w_s = w_{Na^+} + w_{Cl^-} = \frac{m_{NaCl} M_{NaCl}}{1 + m_{NaCl} M_{NaCl}}
\]  

(55)

Several units are commonly used for salinity:

\[
ppm = 10^3 \text{ ppt } = 10^6 S
\]  

(56)


Mole Fraction and Molality

General:

\[ x_i = \frac{m_i M_{H_2O}}{1 + M_{H_2O} \sum m_s} \]  

(57)

For NaCl:

\[ x_{Na^+} = x_{Cl^-} = \frac{m_{NaCl} M_{H_2O}}{1 + 2m_{NaCl} M_{H_2O}} \]  

(58)

\[ x_{H_2O} = 1 - 2x_{Na^+} \]  

(59)

Conversion From Work per mol to Work per kg Solution

\[ \frac{\dot{W}_{\text{least}}}{m_p} = \frac{\dot{W}_{\text{least}}}{\dot{n}_{H_2O,p}} \left( \frac{1}{M_{H_2O} + m_p M_{H_2O} M_{NaCl}} \right) \]  

(60)