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FORMULATION OF SEAWATER FLOW EXERGY USING ACCURATE THERMODYNAMIC DATA

Mostafa H. Sharqawy

Department of Mechanical Engineering
 Massachusetts Institute of Technology
 Cambridge, MA, USA
mhamed@mit.edu

John H. Lienhard V

Department of Mechanical Engineering
 Massachusetts Institute of Technology
 Cambridge, MA, USA
lienhard@mit.edu

Syed M. Zubair

Department of Mechanical Engineering
 King Fahd University of Petroleum and Minerals
 Dhahran, Saudi Arabia
smzubair@kfupm.edu.sa

ABSTRACT

Seawater is a complex electrolyte solution of water and salts with sodium chloride as the major constituent. However, the thermodynamic properties of seawater are considerably different from those of aqueous sodium chloride solution. In the literature, exergy analyses of seawater desalination systems have sometimes modeled seawater by sodium chloride solutions of equivalent salt content or salinity; however, such matching does not bring all important properties of the two solutions into agreement. Further, some published studies attempt to represent sodium chloride solutions as a specific model for an ideal mixture of liquid water and solid sodium chloride, which is shown to have serious shortcomings. In this paper, the most up-to-date thermodynamic properties of seawater are compared with those of aqueous sodium chloride solution as well as the ideal mixture model. The flow exergy is calculated using various models and the results are compared. In addition, the minimum desalination work required to produce a unit mass of fresh water from seawater of varying salinity is calculated using these models. A difference of about 50% in the minimum desalination work is observed when calculating separation work using the ideal mixture model. This consequently shows that exergy analysis and the second law efficiency calculations performed using the ideal mixture model in question are comparatively far from the actual values.

NOMENCLATURE

a_f	specific flow exergy	J kg ⁻¹
c	specific heat at constant pressure	J kg ⁻¹ K ⁻¹
G	Gibbs energy	J
g	specific Gibbs energy	J kg ⁻¹
h	specific enthalpy	J kg ⁻¹
M	molecular weight	g mol ⁻¹
m	molality	mol kg ⁻¹
m^o	mass flow rate	kg s ⁻¹
m_w	mass of water	kg
m_s	mass of salt	kg
n	number of species in mixture	
P	Pressure	Pa
R	gas constant	J kg ⁻¹ K ⁻¹
s	specific entropy	J kg ⁻¹ K ⁻¹
S_A	absolute salinity	kg kg ⁻¹
T	temperature	°C
w	mass fraction	
W_{min}	minimum separation work	J kg ⁻¹
x	mole fraction	
Greek Symbols		
ϕ	osmotic coefficient	
γ	activity coefficient	
μ	chemical potential	J kg ⁻¹
ν	number of ions	
Subscripts		
O	environmental dead state	
s	Salt	
w	pure water	
Superscripts		
*	restricted dead state	
•	standard state	

INTRODUCTION

Increasing attention is being given to energy conservation, and this has resulted in increasing use of exergy analysis. This concept is widely recognized as a necessary tool to quantify the thermodynamic losses in a system or process. One important application of exergy analysis is to seawater desalination systems because there is a large difference between the theoretical minimum power requirement for seawater desalination and the practical requirements, owing to the irreversible losses in real systems. Therefore, a number of exergy analyses have been carried out to determine the inefficiencies and to give relevant recommendations for improvement of desalination systems.

Determination of the flow exergy requires knowledge of the thermodynamic properties of the working fluid involved in a given process. These properties are available for many pure substances and some aqueous solutions. However, for seawater applications, relatively little data is available in the literature. In this regard, different models have been adopted to estimate the thermodynamic properties of seawater. Frequently, seawater has been represented by aqueous sodium chloride solutions of equivalent salt content or salinity [1-3].

Although sodium chloride is the major constituent in seawater, such matching does not bring all important properties of the two solutions into agreement. Bromley [4] investigated the differences between the heat capacity of seawater and sodium chloride at increasing concentrations. He showed that sodium chloride solution has a slightly higher heat capacity than natural seawater. No concentration frame of reference—weight percent, ionic strength, equal number of ions, or equal number of equivalents—was available for which the heat capacities of seawater and those of sodium chloride solutions could be matched. Thus, Bromley [4] concluded that sodium chloride solution thermodynamic properties data cannot be substituted for seawater.

Some researchers have further represented seawater as an ideal mixture of pure water and solid sodium chloride salt [5-13]. In this model, the thermodynamic properties of pure water were determined from steam tables and those of the salt were calculated by using the thermodynamic relations for solids. It is claimed [5] that seawater can be approximated as an ideal [dilute] solution of sodium chloride and water if the salt concentration is less than 5%. Dilute solutions closely approximate the behavior of an ideal solution, in which the effect of dissimilar solute molecules is negligible. It is, however, important to note that aqueous sodium chloride solution and seawater are strong electrolyte solutions, and that the long-range electrostatic interactions of charged solutes in water cause the ideal solution model to breakdown at much

lower concentrations than for non-charge solutes [14]. It is thus important to emphasize that assuming an ideal mixture model for an electrolyte solution, results in significant deviations in the thermodynamic properties.

The objective of this paper is to calculate the flow exergy of seawater by using three different thermodynamic property models to represent seawater. The three models are: seawater itself; aqueous sodium chloride solution; and the ideal mixture model of Cerci [5]. The most recent thermodynamic properties of seawater and accurate properties for aqueous sodium chloride solution are used in these calculations. The enthalpy and entropy of the three models are calculated and compared. The effect of the dead state selection is also examined. In addition, the minimum separation work required to produce a unit mass of fresh water from seawater is calculated using the three exergy models.

FLOW EXERGY

Flow exergy is the maximum amount of work obtainable when a flow stream is brought into equilibrium, from its initial state to the environmental (dead) state. In this regard, the environment state must be specified: the system is considered to be at zero exergy when it reaches this state. The flow exergy consists of a thermomechanical exergy and a chemical exergy. The thermomechanical exergy is the maximum work obtained when the pressure and temperature of the flow stream changes to the environment pressure and temperature (T_0, P_0) with no change in the concentration of any substance incorporated in the flow stream. Consequently, we say that thermomechanical equilibrium with the environment is attained.

The chemical exergy is the maximum work obtained when the concentration of each substance in the flow stream changes to its concentration in the environment at the environment pressure and temperature (T_0, P_0). Consequently, the chemical potential of each substance in the flow stream will be equal to the corresponding one in the environment; hence chemical equilibrium occurs. This description of the flow exergy, a_f , can be mathematically expressed as [15, 16],

$$a_f = (h - h^*) - T_0(s - s^*) + \sum_{i=1}^n w_i (\mu_i^* - \mu_i^0) \quad (1)$$

where h , s , μ and w are the specific enthalpy, specific entropy, chemical potential and mass fraction, respectively. The first two terms of Eq. (1) represent the thermomechanical exergy and the last term is the chemical exergy. Properties with “*” in the above equation are determined at the temperature and pressure of the environment (T_0, P_0) but at the same composition or concentration of the initial flow stream state. This is referred to as the restricted dead state, in which only the temperature and pressure are changed to the environmental values. However, the properties with “0” in the above equation (i.e., μ^0) are determined at the temperature, pressure and concentration of

the environment (T_0, P_0, w_0), which is called the global dead state. If the temperature and pressure of the system is equal to that of the environment (i.e. $T = T_0$ and $P = P_0$) but the concentration is different than that of the environment, the flow exergy will be nonzero due to the chemical exergy, which is the difference between the chemical potentials at the restricted dead state (μ^*) and at the global dead state (μ^0).

It is important to note that if the system and environment are both pure substances (e.g. pure water), the chemical exergy (last term in Eq. 1) will vanish. However, for a multi-component system (e.g. seawater) the chemical exergy term in Eq. (1) must be considered. Ignoring it may lead to unrealistic and illogical results for the exergy variation with the concentration as will be seen in the following sections.

SEAWATER THERMODYNAMIC MODELS

In this section, the thermodynamic properties (enthalpy, entropy and chemical potential) are determined for seawater using three different models that represent seawater. The first model is the seawater as defined by the International Association for the Physical Sciences of the Oceans, IAPSO [17] where a fundamental equation for the Gibbs energy as a function of temperature, pressure and salinity is used to calculate the thermodynamic properties of seawater. Details of this fundamental equation can be found in a recent release issued by the International Association of Properties of Water and Steam, IAPWS 2008 [18].

The second model for seawater is the aqueous sodium chloride solution, where seawater is represented by a sodium chloride solution of an equivalent salt concentration by mass (i.e. equivalent absolute salinity). The thermodynamic properties of aqueous sodium chloride solutions are given by Pitzer et al. [19] in terms of tabulated data for various temperature, pressure and molality. The third model is the ideal solution of sodium chloride and pure water as given in Cerci [5]. This model has been used in many subsequent seawater exergy analysis papers [6-13].

To calculate the specific enthalpy and specific entropy of seawater, the correlations provided by Sharqawy et al. [20] are used. These correlations fit the specific enthalpy and specific entropy data extracted from the seawater Gibbs energy function of IAPWS 2008 [18]. These are polynomial equations given as functions of temperature and salinity at atmospheric pressure (or saturation pressure for temperatures over normal boiling temperature). The chemical potentials of water in seawater and salts in seawater are determined by differentiating the total Gibbs energy function with respect to the composition:

$$\mu_w = \frac{\partial G}{\partial m_w} = g - w_s \frac{\partial g}{\partial w_s} \quad (2)$$

$$\mu_s = \frac{\partial G}{\partial m_s} = g + (1 - w_s) \frac{\partial g}{\partial w_s} \quad (3)$$

where w_s is the mass fraction of salts in seawater which is equal to the absolute salinity in kg_s/kg; g is the specific Gibbs energy of seawater calculated from the enthalpy and entropy correlation given in Sharqawy et al. [20]. The Gibbs energy itself is defined as

$$g = h - Ts \quad (4)$$

The differentiation of Gibbs energy with respect to salt mass fraction (or absolute salinity) is carried out using the enthalpy and entropy correlations as,

$$\frac{\partial g}{\partial w_s} = \frac{\partial h}{\partial w_s} - T \frac{\partial s}{\partial w_s} \quad (5)$$

For aqueous sodium chloride solution, the thermodynamic properties provided by Pitzer et al. [19] are used. They provided accurate tabulated data for the thermodynamic properties of sodium chloride solution including specific enthalpy and specific entropy as well as osmotic and activity coefficients. The later are used to determine the chemical potential of water and sodium chloride in the solution, which are described as,

$$\mu_w - \mu_w^* = -\nu m R_w T M_w \phi \quad (6)$$

$$\mu_s - \mu_s^* = \nu R_s T \ln(m \gamma) \quad (7)$$

where μ_w^* and μ_s^* are the chemical potential of pure water and sodium chloride salt, respectively at a standard state. The definition of the standard state used by Pitzer et al. [19] is pure liquid for water and a hypothetical one molal ideal solution for sodium chloride. Here, m is the molality and ν is number of ions generated on complete dissociation, for sodium chloride, $\nu = 2$. The osmotic coefficient, ϕ and activity coefficient γ are tabulated in Pitzer et al. [19] based on molality concentration. Therefore, to convert from the salt mass fraction to the molality, we can write as

$$m = \frac{1000 \times w_s}{M_s \times (1 - w_s)} \quad (8)$$

where M_s is the molecular weight of the sodium chloride salt.

For the ideal mixture model of Cerci [5], the enthalpy and entropy of the sodium chloride solution were calculated [5-13] as;

$$h = w_w h_w + w_s c_s (T - T_0) \quad (9)$$

$$s = w_w s_w + w_s c_s \ln(T/T_0) - R_m [x_w \ln(x_w) + x_s \ln(x_s)] \quad (10)$$

where h_w and s_w are the specific enthalpy and specific entropy of pure water determined from IAPWS 1996 [21], c_s is the specific heat of solid sodium chloride salt (anhydrous) which was taken as 0.8368 kJ/kg.K [5], x_w and x_s are the mole fractions of water and sodium chloride, respectively. R_m is the gas constant for the mixture taking the molecular weights of water and sodium chloride as $M_w = 18.02$ and $M_s = 58.44$ g/mol, respectively. It is important to mention here that the specific enthalpy and specific entropy of the salt calculated in Eqs. (9) – (10) by using the specific heat of anhydrous sodium chloride, do not accurately represent the thermodynamic properties of an ideal aqueous solution. Instead, the apparent specific heat of the salt should be used [19] which, when multiplied by the salt mass fraction and added to the mass weighted specific heat of pure water, gives the equivalent specific heat of the solution. A second shortcoming of this model is the omission of the chemical exergy component of the flow exergy. To calculate the chemical exergy, the chemical potential should be determined first which is given for water and sodium chloride in the ideal mixture by

$$\mu_w - \mu_w^\bullet = R_w T \ln(x_w) \quad (11)$$

$$\mu_s - \mu_s^\bullet = R_s T \ln(x_s) \quad (12)$$

RESULTS AND DISCUSSION

The three models of seawater thermodynamic properties discussed above are used to calculate and compare enthalpy, entropy and flow exergy of seawater. Because the absolute enthalpy and absolute entropy reference states are different for each model, the differences in enthalpy and entropy from a selected reference state are calculated and compared. This reference state is taken at $P = 101.325$ kPa, $T_0 = 25$ °C and $S_{A,0} = 0.035$ kg_s/kg. Figure 1 shows the changes in specific enthalpy calculated for seawater, aqueous sodium chloride solution and the sodium chloride ideal mixture model [5] as it varies with the salinity. At the reference salinity ($S_{A,0} = 0.035$ kg_s/kg), the enthalpy is zero for all three models. There are large differences between the enthalpy of seawater and the aqueous sodium chloride solution. This is due to a large difference in the heats of solution between the seawater and sodium chloride, averaging up to a factor of ten according to Tribus and Evans [22]. It is important to emphasize that the accurate estimation of the seawater specific enthalpy obtained by using the ideal mixture model [5] is coincidental, as the enthalpy should be close to aqueous sodium chloride solution rather than seawater.

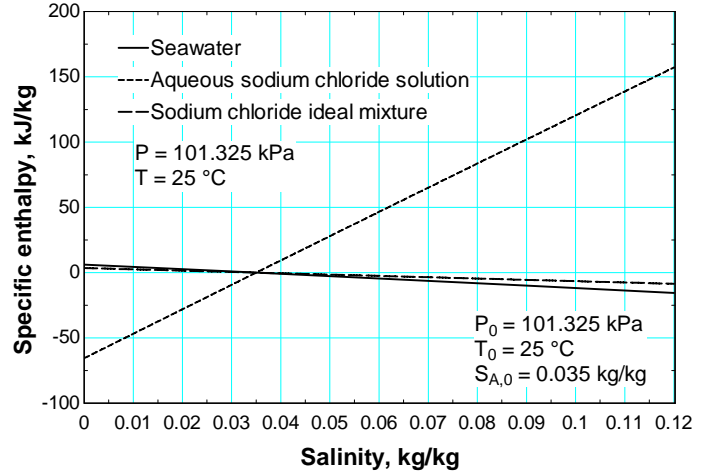


Fig. 1 The specific enthalpy as a function of salinity

On the other hand, the specific entropy calculated for the three models is shown in Figure 2. As shown in this figure, there is no agreement between any of the three models. However, the trend of seawater and the aqueous sodium chloride solution is the same: the entropy decreases as the salinity increases.

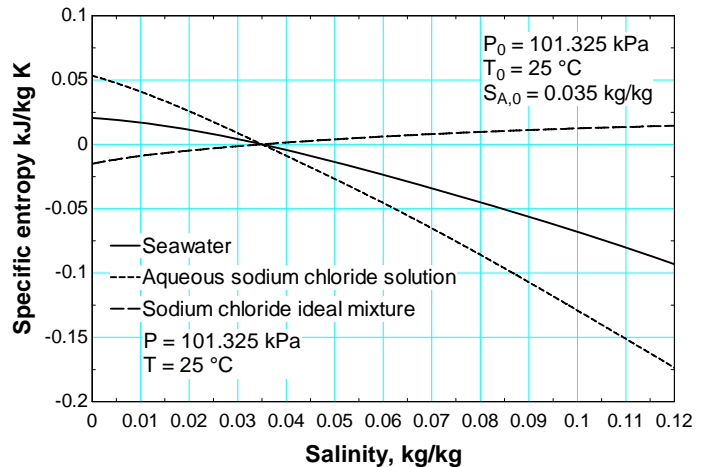


Fig. 2 The specific entropy as it varies with salinity

To calculate the flow exergy, a reference environment state should be specified. However the choice of this reference state should not affect the results of an exergy analysis. Figure 3 shows the specific flow exergy of seawater calculated for the three models. The dead state is selected as $T_0 = 25$ °C, $P_0 = 101.325$ and $S_{A,0} = 0.035$ kg/kg. In the case when the temperature and pressure are kept at the environmental state, the results for seawater and aqueous sodium chloride solution have very good agreement; however the flow exergy of the ideal mixture model for sodium chloride is about 50% less than that of seawater at any salinity.

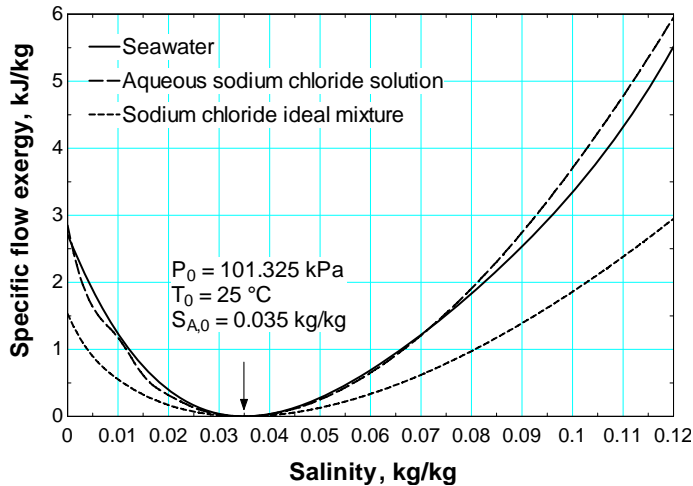


Fig. 3 The specific flow exergy as a function of salinity

As shown in Fig 3, at the dead state, flow exergy is zero. It is *always positive* at any concentration other than the dead state. This is true for all models because whenever there is a difference in concentration between the system and environment, there will be a chemical potential difference that makes the chemical exergy positive. This will be further explained in the next section. However, the ideal mixture model of [5] ignores the chemical exergy term resulting in a negative flow exergy at salinities higher than the dead state as shown in Figure 4.

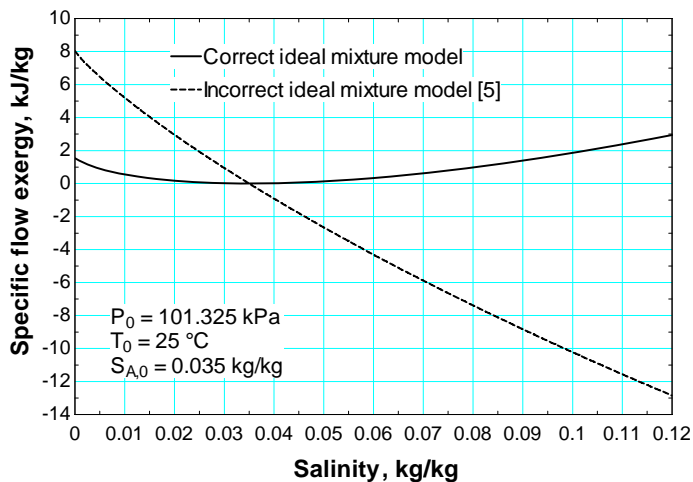


Fig. 4 The correct and incorrect ideal mixture flow exergy

The negative flow exergy due to the incorrect ideal mixture model has been explained improperly in the literature. Cerci [5] and Kahraman and Cengel [9] concluded that the exergy of the seawater at the environmental state is zero, since this state is taken to be the dead state, which is obviously correct. However, the negative exergy at salinities higher than the dead state was attributed to the work required to reduce the salinity to the dead state level, and thus justifying a negative exergy. This explanation is questionable, since the added work

will separate salts from the flow stream to reduce its salinity to the dead state but it also will produce a brine of higher salinity. This brine, according to the above explanation, has lower exergy than the initial state. Therefore, the flow exergy of the system as a whole will never reach the dead state level.

As another example of the positive flow exergy rule, assume pure water at a temperature T and pressure $P = P_0$. Let the dead state be selected as $T_0 = 25 \text{ }^\circ\text{C}$, $P_0 = 101.325 \text{ kPa}$. If the water has a temperature equal to the dead state, the flow exergy is zero (see Fig. 5). However if the temperature is higher or lower than the dead state temperature, the flow exergy is always positive. The positive exergy is due to the heat that can be transferred between the flow stream temperature and the dead state temperature, in one direction or the other as appropriate, to operate a heat engine cycle that can produce positive work. Therefore, any temperature difference between the flow stream state and the dead state will result in positive exergy due to heat transfer [16].

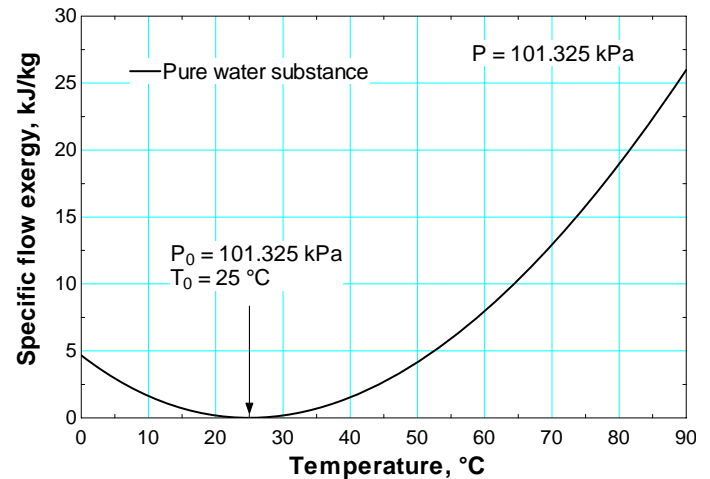


Fig. 5 The specific flow exergy of pure water as a function of temperature

Similarly, any difference in the concentration can be used to produce work through mass transfer. For instance, if the salt concentration (or salinity) of the flow stream is higher than the salt concentration at the dead state, pure water can flow from the environment to the flow stream through a semi-permeable membrane because of the chemical potential difference or the osmotic pressure. This will increase the static head of the flow stream and can produce positive work (exergy) through a hydropower turbine. This fact has been discussed since 1970s [23 - 25] and recently was applied in a pilot osmotic power plant in Norway [26]. The same thing will happen if the salt concentration of the flow stream is lower than that of the environment dead state, but the flow of water in this case will be from the flow stream to the environment. This is clearly illustrated in Figures 6 and 7, which is applicable to any selected dead state. In Figures 5 and 6, the flow exergy of seawater is plotted versus salinity for the seawater, the aqueous

sodium chloride solution as well as the correct sodium chloride ideal mixture models. The reference salinity in Figure 6 is selected as $S_{A,0} = 0.050$ kg/kg and for 0.070 kg/kg in Figure 7.

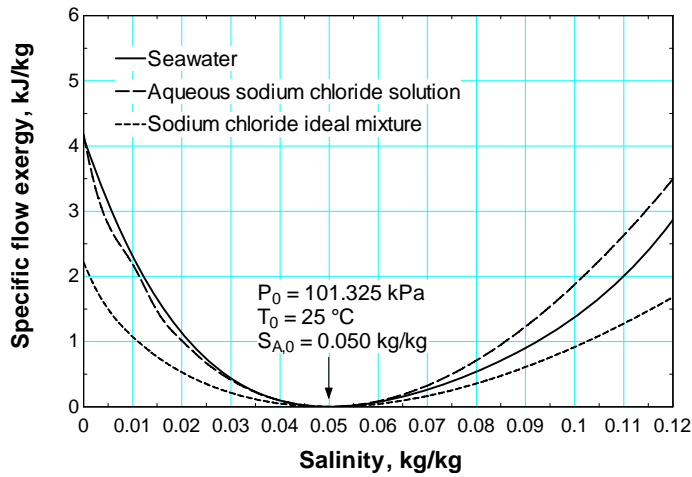


Fig. 6 The specific flow exergy as a function of salinity when $S_{A,0} = 0.050$ kg/kg

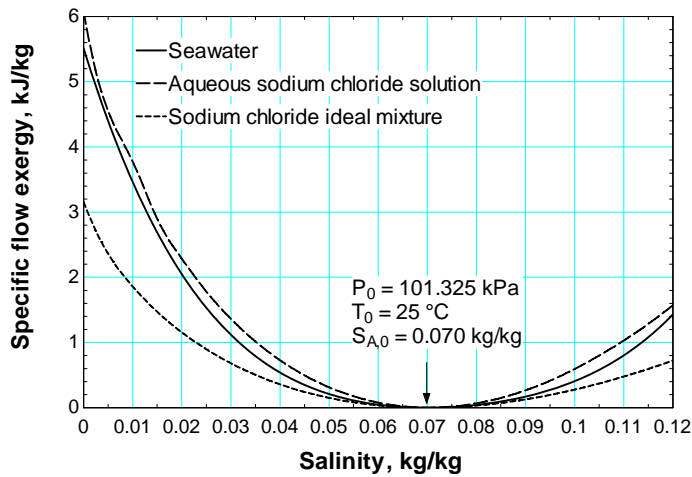


Fig. 7 The specific flow exergy as a function of salinity when $S_{A,0} = 0.070$ kg/kg

It is important to note that the ideal mixture model, even when used correctly, gives significant deviations in the thermodynamic properties and flow exergy of seawater. This model follows Raoult’s law and Henry’s law which are laws that describe the thermodynamic behavior of dilute solutions of non-electrolytes. It is strictly valid in the limit of infinite dilution [27, 28]. The ideal mixture model led to a simple linear dependence of the chemical potential on the logarithm of the mole fraction of solvent and solute. However, such a model does not describe the behavior of real solutions or electrolytes over the entire range of composition [27]. Therefore the activity coefficient (for solute) and osmotic coefficient (for solvent) are introduced to calculate the chemical potential of real solutions. These experimentally determined coefficients depend on the mole fraction, temperature and pressure of the

solution. The deviation of these coefficients from one (the value for an ideal mixture) describes how far real solution differs from ideal behavior. For the aqueous sodium chloride solution, the activity coefficient may go down to 0.2 and the osmotic coefficient may go up to 1.3 [19]. Therefore, it is important to emphasize that the ideal mixture model should not be considered for strong electrolyte solutions like sodium chloride solution or seawater.

MINIMUM SEPARATION WORK

In this section, the seawater flow exergy models presented above will be used to calculate the minimum work required for separation of pure water from salt water. This work has been calculated by many past researchers (Spiegler and El-Sayed [3], Tribus and Evans [22], Bromley et al. [28]) using both sodium chloride solution and seawater data. The minimum separation work can also be calculated using the exergy balance. The three models of seawater will be used in the calculations and compared with previous calculations in the literature.

Consider Figure 8 which shows a general seawater separation process in which inlet feed of seawater at state 1 is converted into pure water at state 2 and brine at state 3. Let the rate of fresh water production be 1 kg/s. By applying a mass balance on the water and salts in the flow streams, the following relations can be obtained:

$$w_{w,1} \dot{m}_1 = w_{w,2} \dot{m}_2 + w_{w,3} \dot{m}_3 \quad (13)$$

$$w_{s,1} \dot{m}_1 = w_{s,2} \dot{m}_2 + w_{s,3} \dot{m}_3 \quad (14)$$

To calculate the minimum work required for this process, assume a reversible system in which the exergy destruction is zero:

$$\dot{W}_{min} = \dot{m}_2 a_{f,2} + \dot{m}_3 a_{f,3} - \dot{m}_1 a_{f,1} \quad (15)$$

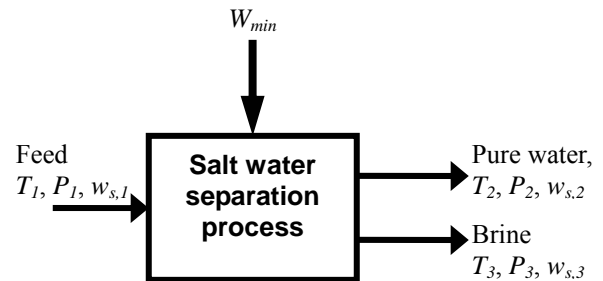


Fig. 8 Schematic diagram of a seawater separation process

The extraction ratio is defined as the ratio of the mass of pure water produced per unit mass of pure water in the feed.

This ratio is limited to the solubility of salts in the brine and can not reach 100% because at the saturation concentration, salts will precipitate from the solution. The saturation concentration of aqueous sodium chloride solution at 25 °C is at molality of 6.149 [19] which corresponds to a salinity of 0.264 kg_s/kg. If the salinity of the inlet feed stream is 0.035 kg_s/kg, this will limit the extraction ratio to 89%. However, the correlations that are used here for seawater (Sharqawy et al. [20]) are valid only up to a salinity of 0.120 kg/kg, corresponding to an extraction ratio of 74%. Therefore, the analysis here will be limited to an extraction ratio of 70%.

By assuming constant temperature and pressure for the inlet and outlet streams and changing the extraction ratio from 0 to 70%, the minimum required work is found, which is shown in Figure 9 for the three seawater models. As seen in this figure, the seawater model gives slightly less work than the sodium chloride solution model. The minimum work values for the seawater and sodium chloride solution were found to be nearly identical to those given by Tribus and Evans [22] and by Spiegler and El-Sayed [3]. It is very important to note that these values do not change when changing the reference dead state of the environment.

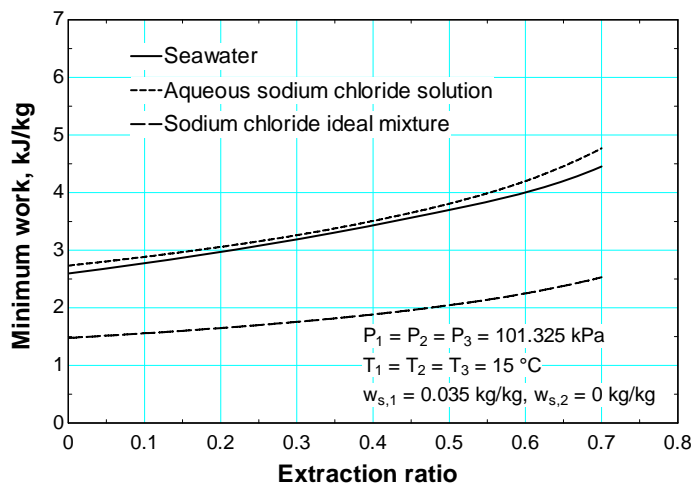


Fig. 9 Minimum separation work

On the other hand, using the ideal mixture model of [5] yields values for the minimum work which are almost 50% less than the reported values in the literature and those that are calculated here for seawater and the real sodium chloride solution. It is important to note that the values of the minimum separation work calculated using the ideal mixture model in the present work are the same as that of Cerci [5]. This indicates that this ideal mixture model for aqueous sodium chloride solution gives significant errors when applied to exergy analysis or the calculation of second law efficiencies. In addition, the negative exergy values obtained by this ideal mixture model are not physically justified.

CONCLUSION

Three models for seawater thermodynamic properties are presented in this paper, namely; the seawater, sodium chloride aqueous solution and a widely used ideal mixture model for aqueous sodium chloride solution. The flow exergy is calculated using these models. The thermodynamic properties of sodium chloride and seawater are different; however, the flow exergy is very similar. The ideal mixture model gives incorrect values of flow exergy. It is found that the minimum separation work calculated using the ideal mixture model is about 50% less than the values reported in the literature as well as those calculated using the seawater and aqueous sodium chloride solution models discussed in this paper. This ideal mixture model of sodium chloride solution model, which has been used in a number of times in the literature, should not be used in exergy and energy analysis of desalination or seawater thermal systems.

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