

# Electrolyte Thermodynamic Models in Aspen Process Simulators and Their Applications

Shu Wang,\* Yuhua Song, Ying Zhang, and Chau-Chyun Chen



Cite This: *Ind. Eng. Chem. Res.* 2022, 61, 15649–15660



Read Online

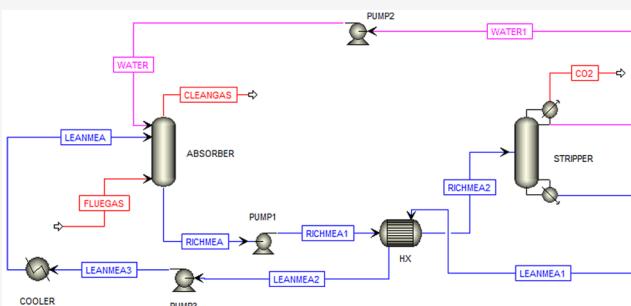
ACCESS |

Metrics & More

Article Recommendations

Supporting Information

**ABSTRACT:** Electrolyte systems are becoming increasingly important as the process industries transition to better address environmental sustainability and climate change. Industrial processes such as carbon capture and sequestration, brine water treatment, lithium refining, and many others require accurate and rigorous electrolyte thermodynamic models to support process simulation and design of chemical processes involving electrolyte systems. Distinctly different from nonelectrolyte systems, the solution nonideality of electrolyte systems is primarily characterized by the electrolyte solution chemistry and secondly impacted by the subsequent physical interactions and associations of true species in solutions. This Article presents the methodology in Aspen process simulators to address the solution chemistry with true species and apparent component approaches together with the two electrolyte thermodynamic models, Pitzer and Electrolyte Nonrandom Two-Liquid equations. Also covered are experimental data compilation, best practice in data regression, and industrial applications highlighted with CO<sub>2</sub> capture with amine solutions and high salinity brine solutions. We further present our perspectives in current challenges and emerging opportunities with thermodynamic modeling for electrolyte systems with high charge density ions, transport property estimation, and systematic data collection and verification.



Downloaded via UNIV SCIENCE AND TECHNOLOGY CHINA on October 15, 2024 at 11:13:09 (UTC).  
See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

dissociation and the resulting long-range electrostatic ion–ion interactions and the short-range van der Waals interactions between ion–ion, ion–molecule, and molecule–molecule pairs contribute to the solution nonideality of electrolyte solutions.

Current widely practiced thermodynamic models to address the electrolyte solution nonideality are primarily based on the activity coefficient approach. Notable examples are the Pitzer model,<sup>2–4</sup> the electrolyte versions of the Nonrandom Two-Liquid (eNRTL) model,<sup>5,6</sup> the electrolyte Universal Quasi-chemical (UNIQUAC) model,<sup>7</sup> and a hybrid model of Pitzer and UNIQUAC called the mixed-solvent electrolyte (MSE) model by OLI.<sup>8</sup> The strengths and weaknesses of these models have been extensively reviewed in the literature.<sup>9,10</sup> There are also recent efforts to develop electrolyte models based on equations of state, such as PC-SAFT and CPA EoS.<sup>11</sup>

The purpose of this work is to present the electrolyte thermodynamic modeling methodology to address the solution

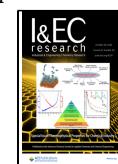
**Special Issue:** Thermophysical Properties for Chemical Industry

**Received:** May 28, 2022

**Revised:** September 15, 2022

**Accepted:** September 16, 2022

**Published:** September 30, 2022



chemistry together with the two electrolyte thermodynamic models, Pitzer and eNRTL, implemented in Aspen process simulators, namely, Aspen Properties. Also covered are an experimental data compilation, best practice in data regression, and successful industrial applications for various electrolyte systems. Also discussed are our perspectives on some of the challenges and emerging opportunities.

## 2. THERMODYNAMIC FRAMEWORK

A rigorous thermodynamic framework for electrolyte systems must include both solution chemistry and electrolyte thermodynamic models. While the importance of electrolyte thermodynamic models is well understood, one often overlooks the fact that the solution chemistry and the resulting compositions of true species present in the solution, ionic and molecular, play the dominant role in the solution non-ideality.<sup>9,10</sup> In other words, accurate thermodynamic modeling for electrolyte systems starts with physically verifiable solution chemistry and completes with parameter tuning of versatile thermodynamic models that capture the various interactions, physical or otherwise, between and among the true species. One should avoid subjectively proposing hypothetical solution chemistry reactions and species for the purpose of overcoming inadequacies of electrolyte thermodynamic models by incorporating extra model parameters associated with imaginary solution chemistry reactions and species to correlate experimental data.

**2.1. Solution Chemistry.** The solution chemistry refers to the various types of chemical reactions when electrolytes dissolve in the liquid phase. Strong electrolytes such as NaCl and MgCl dissociate completely into ionic species. Weak electrolytes such as CO<sub>2</sub> dissociate partially into mixtures of molecular species and ionic species. Ionic species in solutions may further react to form different ions and solid salts or hydrates if the saturation limit is reached. These chemical reactions occur instantaneously in solution and reach chemical equilibrium conditions. The solution chemistry has profound effects on electrolyte solution thermodynamic properties, calorimetric properties, and fluid phase equilibria. For typical nonelectrolyte systems, chemical reaction considerations are restricted to reactor modeling. For electrolyte systems, computations of the solution chemistry are inherent to the material stream properties calculations, and they are integrated with phase equilibrium calculations for every material stream and unit operation of the entire process flowsheet.

The solution chemistry reactions in chemical equilibrium dictate the true species and their compositions in solution. The chemical equilibrium relationship for reaction *j* is expressed as

$$\ln K_j = \sum_i \nu_{i,j} \ln a_i \quad (1)$$

where  $K_j$  is the chemical equilibrium constant for reaction *j*,  $\nu_{i,j}$  is the reaction stoichiometric coefficient of component *i* in reaction *j*, and  $a_i$  is the activity of component *i*.

The temperature dependence of chemical equilibrium constant is usually expressed in the form

$$\ln K_j(T) = a_j + (b_j/T) + (c_j \ln T) + (d_j T) \quad (2)$$

where  $T$  is the system temperature; and  $a_j$ ,  $b_j$ ,  $c_j$ , and  $d_j$  are the temperature coefficients. The chemical equilibrium constant can also be calculated from the Gibbs–Helmholtz equation for Gibbs energy of reaction,  $\Delta G^\circ(T)$ , which is further calculated

from the Gibbs energy of formation of the reactants and the products at their respective reference state together with the reaction stoichiometry. The commonly adopted reference state for solvents is pure liquid, and for ionic species, the infinite dilution ideal aqueous solution extrapolated to unity molality.

$$\begin{aligned} \ln K_j(T) &= -\frac{\Delta G_j^\circ(T)}{RT} \\ &= -\frac{\Delta G_j^\circ(T_{\text{ref}})}{RT_{\text{ref}}} + \frac{\Delta H_j^\circ(T_{\text{ref}})}{R} \left[ \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right] \\ &\quad + \frac{\Delta C_{p,j}^\circ(T_{\text{ref}})}{R} \left[ \frac{T_{\text{ref}}}{T} - 1 + \ln \left( \frac{T}{T_{\text{ref}}} \right) \right] \end{aligned} \quad (3)$$

where  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta C_{p,j}^\circ$  are the Gibbs free energy, the enthalpy, and the heat capacity change of reaction *j*.  $T_{\text{ref}}$  is the reference temperature, i.e., 298.15 K.

To simulate an electrolyte system, all relevant chemical reactions must be properly identified for the solution chemistry. It could never be overemphasized that the chemical theory of solutions should only be used for real chemical reactions. Postulating strong physical interactions or associations in solutions as chemical reactions in equilibrium generates unsubstantiated species. For example, hypothesizing the presence of molecular NaCl in the aqueous NaCl single electrolyte solution treats the binary system as a ternary system of solvent water, fully dissociated NaCl, and molecular NaCl. While it would help solve the short-term problem of correlating experimental data, the practice would be noted with poorly identified model parameters, excessively high computational loads, baseless extrapolations for higher order systems, and further delay in advancing thermodynamic models.

## 2.2. Apparent Components and True Species.

Apparent components are molecular solvents, molecular solutes, and electrolytes that are fed to an electrolyte system. For example, the Benfield process for CO<sub>2</sub> absorption has three apparent components: solvent water, molecular solute CO<sub>2</sub> as a weak acid electrolyte, and strong electrolyte K<sub>2</sub>CO<sub>3</sub>. In the aqueous solution, the solution chemistry of the Benfield process involves the following complete and partial dissociation reactions:



From the solution chemistry, five ionic species, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, H<sub>3</sub>O<sup>+</sup>, and OH<sup>-</sup>, are thereby generated. The five ionic species, the solvent H<sub>2</sub>O, and the molecular solute CO<sub>2</sub> together are considered the true species of the electrolyte system. The concentration of the H<sub>3</sub>O<sup>+</sup> ion determines the solution pH. The fugacities or partial pressures of volatile species, whether calculated with Raoult's law for solvents or Henry's law for molecular solutes, are proportional to their true species concentrations at chemical equilibrium conditions and strongly affected by the solution chemistry, i.e., ionization of CO<sub>2</sub> as a weak acid electrolyte.

Both sets of components, i.e., apparent components and true species, describe the same electrolyte system. Whether one chooses to use apparent components or true species in process simulation is a matter of convenience. For example, apparent components are used to express the extent of CO<sub>2</sub> loading in chemical absorption of CO<sub>2</sub> with amine solutions. In contrast, concentrations of true ionic species are reported for high salinity brines generated from oil and gas production. Aspen Properties supports thermodynamic properties and process simulation calculations with both apparent component and true species approaches, and they are interchangeable.

In summary, apparent molecular solvents, solutes, and electrolytes may be present in electrolyte systems. In the liquid phase, the solution chemistry yields additional ionic and molecular species, and solid salts may also exist as true species. Therefore, true species may include molecular solvents, molecular solutes, ionic species, and solid salts. Treated with Raoult's law with pure liquid as the reference state, water is the solvent for aqueous electrolyte systems. For mixed-solvent and nonaqueous electrolyte systems, there are other solvent components in addition to or in lieu of water. Treated with Henry's law with infinite dilution ideal solution extrapolated to unity concentration as the reference state, molecular solutes are components with low critical temperature, such as CO<sub>2</sub> and N<sub>2</sub>. Ionic species are nonvolatile and remain only in the liquid phase. Salts are nonvolatile molecular species that exist as pure solid crystals. All thermodynamic properties of electrolyte systems are always calculated based on the true species approach. If the process simulation is to be performed with the apparent component approach, then the thermodynamic properties are converted for the apparent components.

To support fluid phase equilibria calculations and heat and mass balances in process simulators, key thermodynamic properties that must be computed beyond thermodynamic chemical equilibrium constants for solution chemistry reactions are activity coefficients, solution enthalpy, and solution Gibbs free energy as functions of temperature, pressure, and solution composition. Among them, activity coefficients are the most critical thermodynamic properties as they are essential to accurately account for the solution nonideality in fluid phase equilibria calculations. In addition, activity coefficients are the basis for solution enthalpy required in heat balance calculations and for solution Gibbs free energy required in phase and chemical equilibrium calculations, entropy calculations, and exergy analysis calculations.

**2.3. Electrolyte Thermodynamic Models.** With the solution chemistry properly established, the accuracy of electrolyte process calculations depends on the underlying electrolyte thermodynamic models and the experimental data used to tune the model parameters. The questions to consider for the thermodynamic models include the rigor of model formulation, the plausibility of underlying theory and assumptions, and the usability of model parameters to correlate experimental data. Given the inevitably limited availability of experimental data and the associated data uncertainties, use of rigorous and thermodynamically consistent models developed from a proper understanding of physical phenomena and sound engineering assumptions is the only way to meaningfully correlate and reconcile with available experimental data and to reliably extrapolate and predict thermodynamic properties of multicomponent electrolyte systems. Advances in electrolyte thermodynamics over the past decades have yielded several successful semiempirical excess Gibbs energy models to

support accurate calculations for activity coefficients. Due to their thermodynamic rigor, model simplicity, and practical usability, the Pitzer model and the eNRTL model are the two most widely adopted equations in process simulators including Aspen Properties.

**2.3.1. Pitzer Activity Coefficient Model.** Developed for aqueous electrolyte thermodynamics, the Pitzer model<sup>2</sup> represents an improvement over the earlier model of Guggenheim<sup>3,4</sup> valid only at electrolyte concentrations less than 0.1 molal. Incorporating virial expansion up to third-order terms, the Pitzer model extends the model validity up to 6 molal ionic strength. Based on the McMillan–Mayer theory for aqueous electrolyte solutions, it expresses the solution excess Gibbs energy per unit mass of solvent water with solute concentrations in molality as follows:

$$\frac{G^{\text{ex},*}}{n_s RT} = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk}(I) m_i m_j m_k \quad (8)$$

where G<sup>ex,\*</sup> is the solution excess Gibbs energy, n<sub>s</sub> is the mass in kg of solvent water, R is the gas constant, T is the system temperature in K, f(I) is the Pitzer–Debye–Hückel formula for long-range electrostatic interactions and a function of the ionic strength I in molality and temperature, λ<sub>ij</sub>(I) accounts for the two-body intermolecular interactions of solute species, μ<sub>ijk</sub>(I) represents the three-body intermolecular interactions, and m<sub>i</sub>, m<sub>j</sub>, and m<sub>k</sub> are the molalities of solute species i, j, and k, respectively. The reference state for the Pitzer model is pure liquid for solvent water and infinite dilution ideal solution extrapolated to unity molality for ionic and molecular solutes. From eq 8, one could derive the molality scale unsymmetric activity coefficient for solute species, γ<sub>i</sub><sup>\*(m)</sup>.

$$\ln \gamma_i^{*,\text{aq}(m)} = \frac{1}{RT} \left( \frac{\partial G^{\text{ex},*}}{\partial m_i} \right)_{T,P,m_j \neq i} \quad (9)$$

The Pitzer model provides accurate calculations of thermodynamic properties including mean ionic activity coefficients for aqueous electrolytes up to 6 molal ionic strength. Numerous literature articles reported Pitzer model parameters for wide varieties of aqueous electrolyte solutions, and the Pitzer model parameters for close to 200 cation–anion pairs have been captured in Aspen Properties.<sup>12</sup> From the process modeling perspective, the Pitzer model provides high accuracy representation of the experimental data, and it is widely practiced in modeling geochemical systems. However, the use of the Pitzer model in process industries remains limited because its extrapolations into high electrolyte concentrations may diverge and are not reliable.<sup>13</sup> Furthermore, the Pitzer model parameter tuning is cumbersome as it requires an excessive amount of literature data due to the inclusion of ternary interaction parameters for three-body interactions and the use of an empirical polynomial expression for temperature dependence of interaction parameters.<sup>14</sup>

**2.3.2. Electrolyte NRTL Activity Coefficient Model.** Initially developed<sup>5,6</sup> as an excess Gibbs energy expression for aqueous electrolyte solutions, the eNRTL model has been extended for mixed-solvent electrolytes and nonaqueous electrolytes.<sup>15–20</sup> The model considers two contributions to the solution excess Gibbs energy: one related to the long-range ion–ion interactions modeled with the symmetric Pitzer–Debye–

Hückel (PDH) formula<sup>21</sup> with the other resulting from the short-range ion–ion, ion–molecule, and molecule–molecule interactions formulated with the NRTL local composition theory while incorporating the local electroneutrality and like-ion repulsion hypotheses. Based on the Lewis–Randall theory, the model formulation is expressed in terms of moles of molecular solvents, molecular solutes, and hypothetical pure liquid electrolytes. To maintain the commonly used aqueous solution infinite dilution ideal solution reference state for mixed-solvent electrolytes, the electrostatic solvation Born term<sup>22,23</sup> is introduced to account for the Gibbs energy of transfer due to the change in the dielectric constant for the change of the reference state from the mixed-solvent infinite dilution state to the aqueous solution infinite dilution state for the PDH term.

Here we present the basic equations of the most recent version of the eNRTL model in Aspen Properties. The details of the eNRTL model are given in **Appendix A** in the Supporting Information. The model expresses the excess Gibbs energy of electrolyte systems in terms of number of molecules of each true species as follows:

$$G^{\text{ex}} = G^{\text{ex,lc}} + G^{\text{ex,PDH}} + \Delta G^{\text{Born}} \quad (10)$$

where  $G^{\text{ex,lc}}$  and  $G^{\text{ex,PDH}}$  represent the contributions from the short-range and the long-range interactions, respectively;  $\Delta G^{\text{Born}}$  is the Born correction term. The mole fraction scale activity coefficient of species  $i$ ,  $\gamma_i$ , can be derived from  $G^{\text{ex}}$  as follows:

$$\begin{aligned} \ln \gamma_i &= \frac{1}{RT} \left( \frac{\partial G^{\text{ex}}}{\partial n_i} \right)_{T,P,n_j \neq i} \\ &= \frac{1}{RT} \left( \frac{\partial G^{\text{ex,lc}}}{\partial n_i} \right)_{T,P,n_j \neq i} + \frac{1}{RT} \left( \frac{\partial G^{\text{ex,PDH}}}{\partial n_i} \right)_{T,P,n_j \neq i} \\ &\quad + \frac{1}{RT} \left( \frac{\partial \Delta G^{\text{Born}}}{\partial n_i} \right)_{T,P,n_j \neq i} \end{aligned} \quad (11)$$

or

$$\ln \gamma_i = \ln \gamma_i^{\text{lc}} + \ln \gamma_i^{\text{PDH}} + \Delta \ln \gamma_i^{\text{Born}} \quad (12)$$

where  $T$  is the temperature,  $P$  is the pressure,  $n_i$  and  $n_j$  are the mole numbers of components  $i$  and  $j$ , and both  $i$  and  $j$  are used as component indices for all components including solvents and solutes.

The reference state is pure liquid for solvent species and infinite dilution ideal aqueous solution extrapolated to unity mole fraction for ionic and molecular solutes. Water must be present as a solvent of the solution when the infinite dilution aqueous solution reference state is used. Note that, given the condition of the infinite dilution aqueous solution as the reference state for ionic species, the unsymmetric activity coefficient of an ionic species,  $\gamma_i^{*,\text{aq}}$ , can be calculated as follows:

$$\ln \gamma_i^{*,\text{aq}} = \ln \gamma_i - \ln \gamma_i^{\infty,\text{aq}} \quad (13)$$

$$n\gamma_i^{\infty,\text{aq}} = \ln \gamma_i (x_w \rightarrow 1) \quad (14)$$

where  $\gamma_i^{\infty,\text{aq}}$  is the activity coefficient of ionic species  $i$  at the infinite dilution aqueous solution;  $x_w$  is the water mole

fraction. The above condition applies to all ionic species in the solution.

Unlike the Pitzer model which is limited to the ionic strength of 6 molal, the eNRTL model has been successfully applied to wide varieties of electrolyte systems up to salt saturation concentration or to pure liquid electrolytes.<sup>20</sup> Recent studies have further shown that the eNRTL model extrapolates reliably into high concentrations,<sup>13</sup> and the weak temperature dependence of eNRTL binary interaction parameters is well-behaving and follows the Gibbs–Helmholtz equation.<sup>24</sup> Moreover, the eNRTL binary interaction parameters are related to species diameter, interaction energy, and the local domain radius around the center species that can be obtained from molecular simulations.<sup>13,25</sup> However, due to the inherent assumption of local composition models which only accounts for the van der Waals type physical interactions between interacting species, the use of the eNRTL model is less satisfactory for electrolyte systems with strongly hydrated high charge density ions such as lithium ions and magnesium ions.<sup>26</sup> From the process modeling perspective, the use of the eNRTL model is a good first choice because of its reliable extrapolation into high concentrations, its practical requirement of two binary interaction parameters per electrolyte–molecule pair, and the weak temperature dependence of the binary interaction parameters.

**2.4. Solution Enthalpy and Gibbs Free Energy Calculations.** Enthalpy and Gibbs free energy of liquid mixtures are related to activity coefficients. Specifically, the liquid enthalpy of electrolyte systems consists of contributions from the pure component liquid enthalpy of each true species in its reference state and the excess enthalpy of mixing:

$$H_{\text{mix}}^1 = \sum_s x_s H_s^1 + \sum_i x_i H_i^{\infty,\text{aq}} + H_{\text{mix}}^{*,\text{ex}} \quad (15)$$

where  $H_{\text{mix}}^1$  is the molar enthalpy of liquid mixture,  $H_s^1$  is the molar enthalpy of solvent  $s$ ,  $H_i^{\infty,\text{aq}}$  is the molar enthalpy of solute species  $i$  at the aqueous phase infinite dilution reference state, and  $H_{\text{mix}}^{*,\text{ex}}$  is the molar excess enthalpy of liquid mixture calculated from the activity coefficients:

$$H_{\text{mix}}^{*,\text{ex}} = -RT^2 \left( \sum_s x_s \frac{\partial \ln \gamma_s}{\partial T} + \sum_i x_i \frac{\partial \ln \gamma_i^{*,\text{aq}}}{\partial T} \right) \quad (16)$$

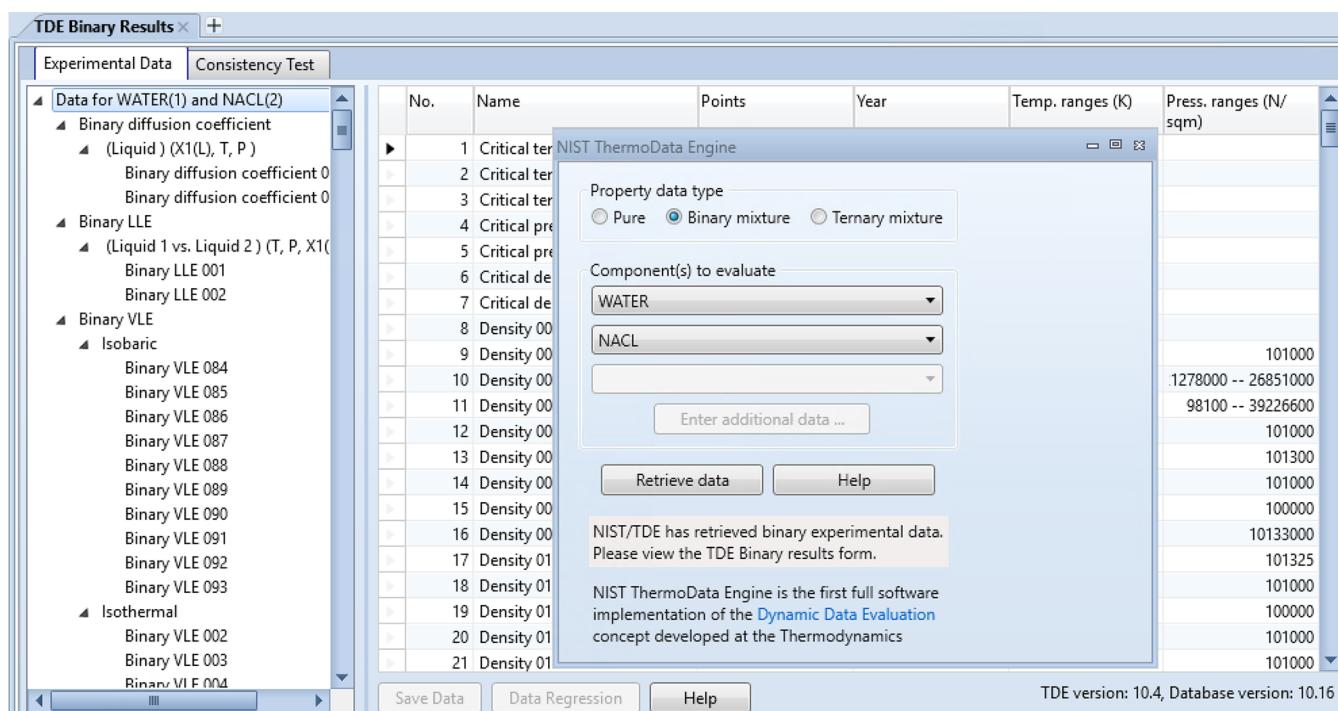
where  $\gamma_s$  is the activity coefficient of solvent  $s$ , and  $\gamma_i^{*,\text{aq}}$  is the unsymmetric activity coefficient of solute species  $i$  with the aqueous phase infinite dilution reference state.

Similarly, the molar Gibbs free energy of liquid mixture,  $G_{\text{mix}}^1$ , can be calculated from the activity coefficients as follows:

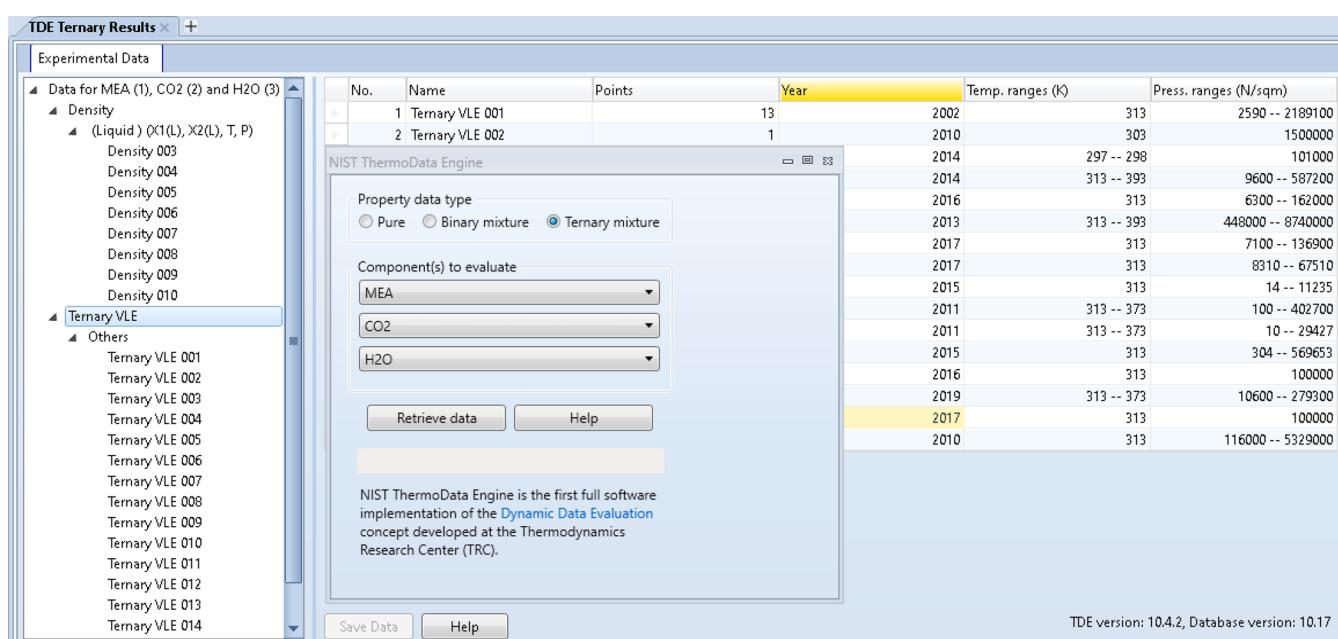
$$G_{\text{mix}}^1 = RT \sum_j x_j \ln x_j + \sum_s x_s G_s^1 + \sum_i x_i G_i^{\infty,\text{aq}} + G_{\text{mix}}^{*,\text{ex}} \quad (17)$$

$$G_{\text{mix}}^{*,\text{ex}} = RT \left( \sum_s x_s \ln \gamma_s + \sum_i x_i \ln \gamma_i^{*,\text{aq}} \right) \quad (18)$$

where  $j$  is the component index for all species including solvents  $s$  and solutes  $i$ ,  $G_s^1$  is the molar Gibbs energy of solvent  $s$ ,  $G_i^{\infty,\text{aq}}$  is the molar Gibbs energy of solute species  $i$  at the aqueous phase infinite dilution reference state, and  $G_{\text{mix}}^{*,\text{ex}}$  is the molar excess Gibbs energy of liquid mixture.



**Figure 1.** Experimental data of the  $\text{NaCl} + \text{H}_2\text{O}$  binary system from NIST ThermoData Engine in Aspen Properties.



**Figure 2.** Experimental data of the  $\text{CO}_2-\text{MEA}-\text{H}_2\text{O}$  ternary system from NIST ThermoData Engine in Aspen Properties.

### 3. EXPERIMENTAL DATA AND DATA REGRESSION

Electrolyte thermodynamical models such as the Pitzer model and the eNRTL model provide rigorous thermodynamic framework and adjustable model parameters to correlate experimental data and to interpolate, extrapolate, and predict thermodynamic properties and fluid phase equilibria for multicomponent electrolyte systems. Proper identification of the model parameters from experimental data in turn depends on the data types, the availability, the uncertainties, and the ranges of temperature, pressure, and composition of the data used to tune the model parameters.

Aspen Properties Data Regression System supports data regression of electrolyte systems from a wide variety of data types for pure components and mixtures. The built-in property data types for mixtures include mean ionic activity coefficients, osmotic coefficients, boiling point elevation, freezing point depression, heat capacity, heat of mixing, excess enthalpy, mixture enthalpy, vapor–liquid equilibrium, liquid–liquid equilibrium, salt solubility, etc. In addition, users can define user properties calculated by user subroutines and then use them in data regression. Examples of such user-defined data types include heat of  $\text{CO}_2$  absorption in aqueous MEA

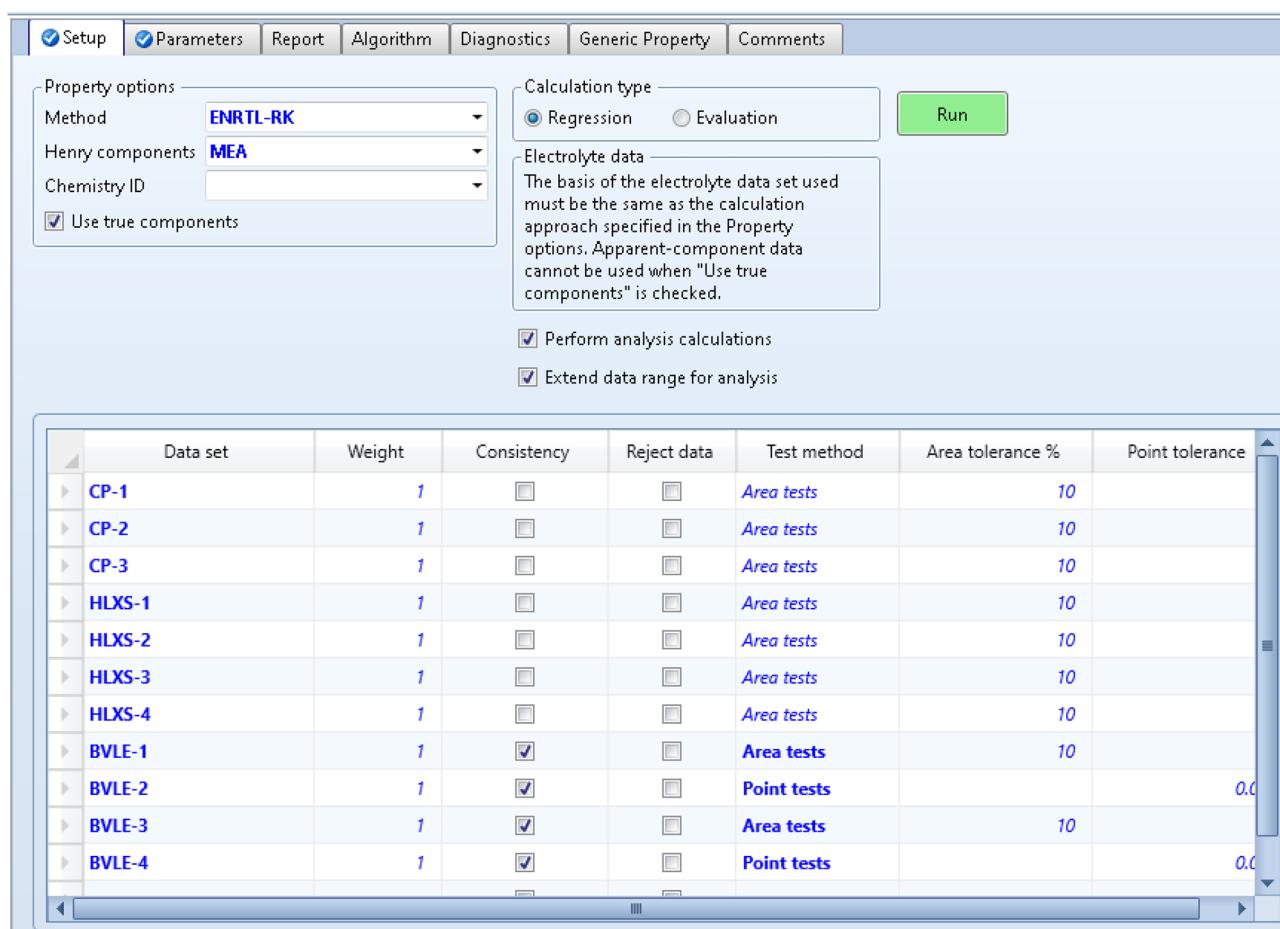


Figure 3. Set up regression within Aspen Properties.

The screenshot shows the 'Parameters' tab of the Aspen Properties software. It lists various parameters to be regressed, grouped by their properties like Type, Name, Element, Component or Group, and Usage. Parameters include DGAQFM, DHAQFM, CPAQ0, GMENCC, GMENCC, GMENCC, GMENCD, MEAH+, H2O, MEAH+, H2O, MEAH+, H2O, MEACOO-, HCO3-, MEACOO-, HCO3-, MEAH+, HCO3-, and Exclude. Each parameter has associated values for Initial value, Lower bound, Upper bound, Scale factor, and Set Aji = Aij. Buttons for Copy, Paste, and Clear are at the bottom.

Type	Parameter	Parameter	Parameter	Pair parameter				
Name	DGAQFM	DHAQFM	CPAQ0	GMENCC	GMENCC	GMENCC	GMENCC	GMENCD
Element			1					
Component or Group	MEACOO-	MEACOO-	MEACOO-	H2O	MEAH+	H2O	MEAH+	H2O
					HCO3-		MEACOO-	
					MEAH+	H2O	MEAH+	HCO3-
					HCO3-		MEACOO-	
Usage	Regress	Regress	Regress	Regress	Regress	Regress	Regress	Exclude
Initial value	-4.9e+08	-6.9e+08	-100000	8	-4	8	-4	0
Lower bound	-9e+08	-9e+08	-1e+08	0	-36	0	-36	-10000
Upper bound	0	0	1e+08	72	0	72	0	10000
Scale factor	1	1	1	1	1	1	1	1
Set Aji = Aij	No	No	No	No	No	No	No	No

Figure 4. Specify model parameters to be regressed with Aspen Properties.

solutions and true species concentrations in  $\text{CO}_2 + \text{MEA} + \text{H}_2\text{O}$  solutions.<sup>27</sup>

Aspen Properties provides a treasure of evaluated experimental data published in the literature. To perform data regression, users collect experimental data from experiments of their own and literature such as journal articles; technical

reports; data collections such as Perry's Chemical Engineer's Handbook, CRC Handbook, and DECHEMA Chemistry Data Series; and online databases such as DETHERM database and ThermoData Engine (TDE) from the National Institute of Standards and Technology (NIST). With newly published data captured constantly from year to year, the NIST TDE database

covers millions of evaluated experimental data points compiled from published thermodynamic literature for over 30 000 pure organic and inorganic compounds and their mixtures.<sup>28</sup> For pure components, the data include critical temperature and pressure; thermophysical properties such as normal boiling point, vapor pressure, and density; as well as transport properties such as viscosity and thermal conductivity. For mixtures, it provides phase equilibrium (vapor–liquid and liquid–liquid) data for binary and ternary systems. In addition, it also hosts various built-in thermodynamic consistency tests for VLE data sets based on the Gibbs–Duhem equation, including Herington test, Van Ness test, Point test, Infinite dilution test, etc. These tests quantify the quality of the experimental data, so that these data sets can be properly weighted during data regression. NIST TDE has been fully integrated into Aspen Properties. Users can easily search, retrieve, evaluate, and regress the experimental data from NIST TDE for pure, binary, and ternary mixtures. Figures 1 and 2 show a partial list of available experimental data for the NaCl + H<sub>2</sub>O binary system and the CO<sub>2</sub> + MEA + H<sub>2</sub>O ternary system in NIST TDE, respectively. Note that NIST TDE does not yet cover solution chemistry data nor electrolyte-specific thermodynamic properties such as mean ionic activity coefficients and osmotic coefficients.

With the availability of a comprehensive thermodynamic framework that covers all thermodynamic properties and fluid phase equilibria including salt solubility, users can and shall regress model parameters from experimental data of all data types simultaneously. To set up a regression within Aspen Properties Data Regression System, users should specify the thermodynamic property model and method, select the experimental data sets, and identify the model parameters to be regressed as shown in Figures 3 and 4. The Aspen data regression algorithm is based on the Maximum Likelihood Principles estimation method<sup>29</sup> with two built-in thermodynamic consistency tests (Redlich–Kister area test and Van Ness point test) available for the binary VLE data. Users can remove the inconsistent data from the regression to avoid convergence issues or model parameters with high uncertainties.<sup>12</sup>

The Maximum Likelihood Principles objective function is defined as

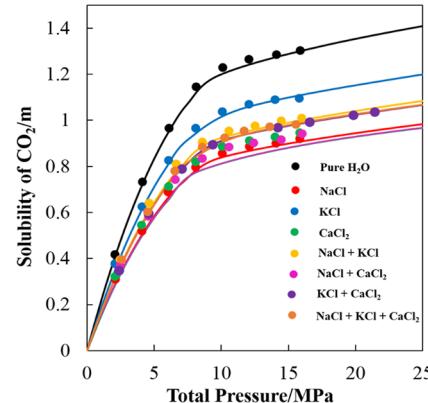
$$\text{Obj} = \frac{\sum_{i=1}^k w_i \sum_{j=1}^m [(Z_{ij} - Z\text{M}_{ij})/\sigma_{ij}]^2}{k - n} \quad (19)$$

where  $Z$  is the calculated value,  $Z\text{M}$  is the experimentally measured value,  $\sigma$  is the standard deviation of the data,  $w$  is the weighting factor,  $i$  is the index of the data point,  $j$  is the measured variable for each data point (such as temperature, pressure, or composition),  $k$  is the total number of data points,  $m$  is the total number of measured variables for each data point, and  $n$  is the total number of adjustable parameters.

#### 4. INDUSTRIAL APPLICATIONS

The eNRTL model in Aspen Properties has been used to model many industrial electrolyte systems and processes to support calculations of thermodynamic properties, calorimetric properties, fluid phase equilibria including salt solubilities, and heat and mass balances. Some prominent industrial applications includes acid gas removal, sour water stripping, sulfuric acid production,<sup>30</sup> caustic brine evaporation, nitric acid dehydration,<sup>31–33</sup> trona processing, hybrid sulfur cycle process

for hydrogen production,<sup>34</sup> high salinity brines treatment and desalination,<sup>35,36</sup> CO<sub>2</sub> capture with aqueous amine solutions<sup>37–43</sup> and with aqueous potassium carbonates,<sup>44</sup> and, most recently, CO<sub>2</sub> solubility in brine solutions for sequestration in deep saline aquifers,<sup>45,46</sup> etc. As an illustration, Figure 5 shows the experimental data<sup>47</sup> and the eNRTL model



**Figure 5.** CO<sub>2</sub> solubility in pure water, 10 wt % of single salt solutions, and 10 wt % of mixed salt solutions of NaCl + KCl (1:1 weight ratio), NaCl + CaCl<sub>2</sub> (1:1 weight ratio), KCl + CaCl<sub>2</sub> (1:1 weight ratio), and NaCl + KCl + CaCl<sub>2</sub> (1:1:1 weight ratio) at 318.15 K. The symbols are experimental data;<sup>47</sup> the solid lines are eNRTL model results.<sup>45</sup>

results for CO<sub>2</sub> solubility in pure water, 10 wt % single salt solutions, and 10 wt % mixed salt solutions of NaCl + KCl (1:1 weight ratio), NaCl + CaCl<sub>2</sub> (1:1 weight ratio), KCl + CaCl<sub>2</sub> (1:1 weight ratio), and NaCl + KCl + CaCl<sub>2</sub> (1:1:1 weight ratio) at 318.15 K. The applications on CO<sub>2</sub> capture with aqueous amine solutions and high salinity brine treatments are briefly summarized below.

Removing acid gases such as CO<sub>2</sub> and H<sub>2</sub>S with aqueous amine solutions is one of the most proven technologies for gas treating and CO<sub>2</sub> capture. Comprehensive and accurate thermodynamic models of the aqueous amine plus acid gas systems are essential for the simulation and optimization of industrial amine units. Indeed, many aqueous amine solutions have been accurately modeled with Aspen Properties for use in Aspen Plus and Aspen HYSYS.<sup>12</sup> Figure 6 shows the amine solvents supported in Aspen HYSYS including MDEA, MEA, DEA, DGA, DIPA, TEA, PZ, and their blends. Developed based on the eNRTL model, these amine solvent models have been developed from and validated with available experimental data including VLE, heat of solution, and true species compositions over wide ranges of temperature, pressure, and concentration.<sup>41</sup> The list of model parameters and experimental measurements for data regression for the CO<sub>2</sub> + MEA + H<sub>2</sub>O system is given in Appendix B in the Supporting Information. Figure 7 shows the experimental data and the model results for CO<sub>2</sub> partial pressure as a function of CO<sub>2</sub> to MEA molar ratio at 313, 353, and 393 K.<sup>27</sup> Of particular interest is the calculation of true species compositions and activities used in the reaction kinetics rate expressions within the rate-based absorption/desorption simulation models for accurate simulation of amine units.<sup>37</sup> The technical details for the modeling and simulation of amine units have been elaborated in our previous works.<sup>27,38–42</sup>

With the widespread implementation of hydraulic fracking, unconventional shale gas extraction from tight rock has

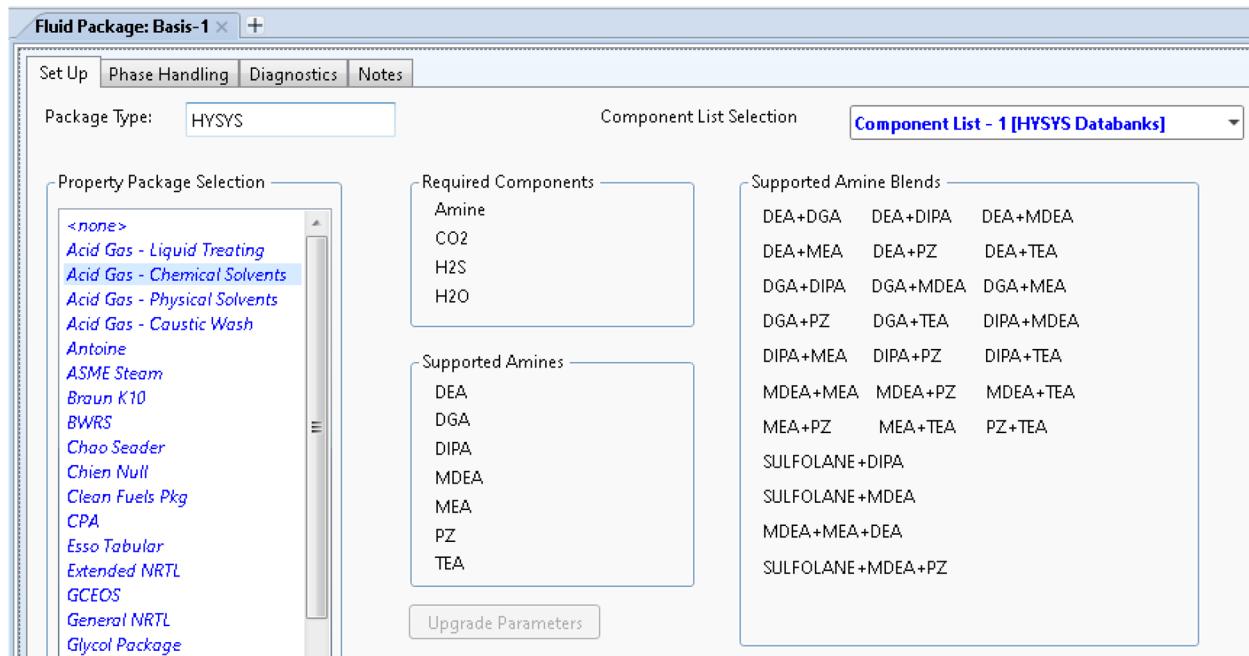


Figure 6. Supported amine solvents in Aspen HYSYS.

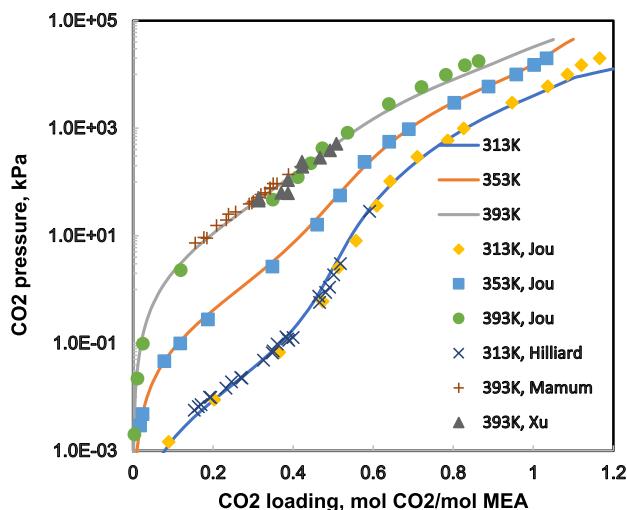


Figure 7. Experimental data and the eNRTL model results for  $\text{CO}_2$  partial pressure as a function of  $\text{CO}_2$  to MEA molar ratio at 313, 353, and 393 K.<sup>27</sup>

become a significant contributor to the oil and gas production in the United States. However, the production process generates a massive amount of high salinity brines called “produced water” during fracking and subsequent oil and gas production. While most of the produced water is disposed of via underground injection,<sup>48</sup> a major risk factor for seismic activity in the areas near the disposal well,<sup>49</sup> development of novel technology to treat and reuse high salinity produced water has gained heightened interest. To support development and innovation of these novel treatment processes, a comprehensive thermodynamic model based on the eNRTL model in Aspen Properties has been developed for high salinity brines.<sup>50–61</sup> The dominant ionic species in high salinity brines that contribute to the salinity include  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ . However, the ionic species that cause most of the scaling in the treatment processes are the trace species such as

$\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . The model covers all these dominant and trace species, and it has been shown to provide satisfactory estimation and reliable prediction for various thermodynamic properties, salt solubilities, and scaling behaviors for high salinity brines and its subsystems with temperature from 273.15 to 473.15 K and salt concentrations up to saturation. As an illustration, Figure 8 shows the experimental data<sup>62</sup> and the eNRTL model results for the solubilities of various salt forms in the aqueous  $\text{Na}^+ + \text{Mg}^{2+} + \text{SO}_4^{2-}$  system.<sup>53</sup>

## 5. CHALLENGES AND EMERGING OPPORTUNITIES

Despite tremendous success of the current electrolyte thermodynamic models, many challenges remain from the perspective of process modeling and simulation of electrolyte

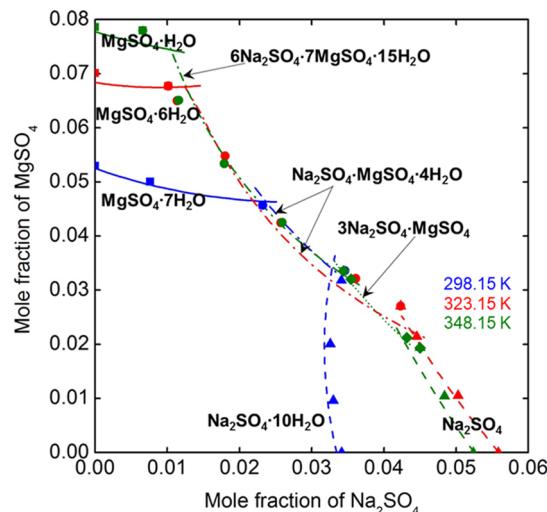


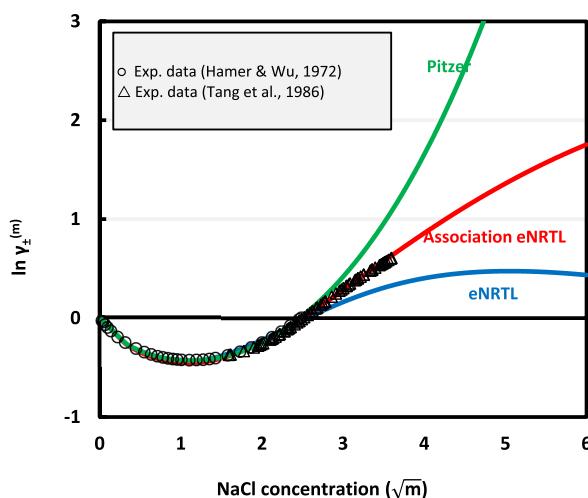
Figure 8. Experimental data<sup>63</sup> and the eNRTL model results for the solubilities of various salt forms in the aqueous  $\text{Na}^+ + \text{Mg}^{2+} + \text{SO}_4^{2-}$  system.<sup>54</sup>

systems. Among them, three challenges stand out: (1) the need for advanced electrolyte thermodynamic models capable of accurately describing electrolyte systems of high charge density ions, (2) the need for accurate and robust engineering models for transport properties of electrolyte solutions, and (3) the need for accurate experimental thermodynamic and phase equilibrium data for single and multicomponent electrolyte systems.

While the eNRTL model has proven to be an effective and versatile thermodynamic model for a wide variety of electrolyte systems such as high salinity brines and for CO<sub>2</sub> capture with amine solutions, thermodynamic modeling of electrolyte solutions with high charge density ions remains unsatisfactory with the eNRTL model. Examples of high charge density ions are the lithium ion, magnesium ion, hydroxide ion, rare earth element ions, etc. As strong electron acceptors, high charge density cations exhibit a strong hydration tendency with electron donor sites of solvent water and a strong ion-pairing tendency with anions that are strong electron donors. Without explicitly addressing such hydration and ion-pairing behavior, eNRTL is incapable of accurately representing the thermodynamic properties of these electrolyte systems with high charge density ions. This deficiency in eNRTL model formulation may have been addressed with the recent advent of the association eNRTL model.<sup>63</sup> Incorporating an association term based on the Wertheim association theory<sup>64–66</sup> as formulated by Fu et al.<sup>67</sup> for activity coefficient models, this association eNRTL model is capable of accurately describing thermodynamic properties of electrolyte systems involving high charge density ions. A distinct feature of the association model is the adoption of species-specific association site numbers and dimensionless association strengths with the water self-association strength as the reference.<sup>63,68,69</sup> Given the association sites and the association strengths identified for true species, the association model is capable of reliably predicting association behavior of electrolyte solutions such as ion hydration and ion-pairing without the additional burden to quantify binary association parameters.<sup>63</sup> As many mixed-solvent electrolyte systems involve solvents that self-associate and/or cross-associate, i.e., water and alcohols, the association model should also facilitate more accurate thermodynamic representations of mixed-solvent and nonaqueous electrolyte systems. Extensive investigations are being pursued to validate the association model for aqueous lithium salt solutions, aqueous rare earth elements salt solutions, and mixed-solvent electrolyte solutions.

A high charge density ion, the sodium ion is known to hydrate extensively in aqueous solutions. Figure 9 shows both the Pitzer model and the eNRTL model are capable of accurately describing the mean ionic activity coefficient data of aqueous NaCl solution<sup>70,71</sup> up to 6 molal at 298.15 K. However, the Pitzer model extrapolations to higher salt concentrations overestimate the mean ionic activity coefficients and in fact diverge while the eNRTL model extrapolations underestimate the mean ionic activity coefficients. In contrast, the association model accurately correlates all the mean ionic activity coefficient data even at the supersaturation concentration of ~12 molal, and further extrapolation into higher salt concentrations remains reasonable.

In addition to the association eNRTL model, notable association-based equation-of-state models for electrolyte systems include various CPA<sup>72</sup> and SAFT<sup>73</sup> implementations



**Figure 9.** Pitzer model, the eNRTL model, and the association eNRTL model results for the mean ionic activity coefficient data<sup>71,72</sup> of aqueous NaCl solution at 298.15 K.

for electrolytes. However, these models do not yet explicitly account for ion hydration nor ion-pairing.

Beyond the association eNRTL model, it is worth mentioning that the eNRTL model has also been extended for thermodynamic modeling of aqueous ionic liquid solutions<sup>74</sup> and aqueous polyelectrolyte solutions<sup>75,76</sup> including mobile ion partitioning in ion exchange membranes.<sup>77</sup> In addition, the eNRTL model has been used to investigate swelling of hydrogels in aqueous brine solutions.<sup>78</sup> There should be many more opportunities for further refinement of the eNRTL model as scientists and engineers explore innovative electrolyte systems and processes to address environmental sustainability and climate change.

While active research continues for the development of advanced electrolyte thermodynamic models, research and development of transport properties models for electrolyte solutions have been virtually nonexistent, and the current models in Aspen Properties remain empirical, are applicable only to very dilute electrolyte concentrations, and are largely polynomial in nature for concentration dependence. A rare development, a recent percent-level accuracy universal correlation made it possible to estimate the density of aqueous single and multicomponent electrolyte solutions at room temperature by grouping electrolytes as either structure making, structure breaking, or structure superbreaking.<sup>79</sup> The transport properties of interest include density, viscosity, surface tension, diffusivity, and thermal conductivity. These transport properties are required for rate-based process simulation calculations such as hydraulics correlations for effective packing surface area, heat transfer coefficients, and mass transfer coefficients. A list of transport properties models available in Aspen Properties is given in **Appendix C** of the Supporting Information. Clearly much more work is needed to bring physical insights into transport properties models to allow for robust estimation and extrapolation into higher electrolyte concentrations for multicomponent electrolyte systems.

Finally, it is without question that accurate experimental thermodynamic and phase equilibrium data for both single and multicomponent electrolyte systems remain the foundation for thermodynamic model development, robust parameter tuning, and ultimately accurate process modeling and simulation. With

the expensive and laborious efforts to measure, validate, and evaluate experimental data, the scientific community at large should recognize those scientists dedicated to experimental measurement and compilation of thermodynamic and phase equilibrium data. As the society pivots to green energy for sustainability, a few high impact areas are thermodynamic data related to electrolyte systems of lithium salts and rare earth element salts. Moreover, with the incorporation of the NIST TDE database in Aspen Properties, the availability of millions of evaluated experimental data at the fingertips of scientists and engineers has proven to be an invaluable asset for people dedicated to thermodynamic model development. It would be even more impactful if the NIST TDE database could be further expanded to cover electrolyte-specific thermodynamic properties such as mean ionic activity coefficient and osmotic coefficient for single and multicomponent electrolyte systems. In addition, data for solid–liquid equilibria or salt solubility should be captured in NIST TDE in addition to data for vapor–liquid equilibria and liquid–liquid equilibria.

## 6. CONCLUSIONS

This Article presents an overview of the electrolyte thermodynamic framework currently implemented in Aspen Properties and discusses successful applications, current challenges, and emerging opportunities. The thermodynamic framework builds on physically verifiable solution chemistry for electrolyte systems and an accurate description of electrolyte thermodynamic properties with rigorous thermodynamic models for excess Gibbs energy of aqueous and mixed-solvent electrolyte solutions. Aspen Properties supports thermodynamic model parameters tuning with evaluated literature data from ThermoData Engine and best practice data regression methodology in Aspen Properties Data Regression System. The Pitzer model provides an accurate representation of thermodynamic properties for aqueous electrolyte solutions with ionic strength up to six molal while the electrolyte NRTL model proves its versatility in accurate modeling of wide varieties of industrial electrolyte systems such as aqueous amine solutions for CO<sub>2</sub> capture and high salinity brines. Looking forward, the advent of the association electrolyte NRTL model should facilitate accurate thermodynamic modeling of electrolyte systems with high charge density ions such as lithium ions and rare earth element ions. In contrast to electrolyte thermodynamic models, accurate and robust engineering models for transport properties of electrolyte solutions are lacking and remain grossly underdeveloped. Finally, the industry is in great need of systematic data measurements for single and multicomponent electrolyte systems in general and in particular for high impact systems such as lithium salts and rare earth element salts, to support future development of thermodynamic models and process simulation of innovative electrolyte systems to address environmental sustainability and climate change.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.2c01881>.

Details of the eNRTL model, list of model parameters and experimental measurements for data regression for the CO<sub>2</sub> + MEA + H<sub>2</sub>O system, and a list of transport property models available in Aspen Properties ([PDF](#))

## ■ AUTHOR INFORMATION

### Corresponding Author

Shu Wang – Aspen Technology, Inc., Bedford, Massachusetts 01730, United States; [orcid.org/0000-0002-7070-5095](https://orcid.org/0000-0002-7070-5095); Email: [shu.wang@aspentech.com](mailto:shu.wang@aspentech.com)

### Authors

Yuhua Song – Aspen Technology, Inc., Bedford, Massachusetts 01730, United States

Ying Zhang – AspenTech Shanghai, Pudong, Shanghai 2012010, China

Chau-Chyun Chen – Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409-3121, United States

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.iecr.2c01881>

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

C.-C.C. gratefully acknowledges the financial support of the Jack Maddox Distinguished Engineering Chair Professorship in Sustainable Energy sponsored by the J.F. Maddox Foundation.

## ■ REFERENCES

- (1) Chen, C.-C.; Mathias, P. M. Applied Thermodynamics for Process Modeling. *AICHE J.* **2002**, *48*, 194–200.
- (2) Guggenheim, E. A. The specific thermodynamic properties of aqueous solutions of strong electrolytes. *London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1935**, *19* (7), 588–643.
- (3) Guggenheim, E. A.; Turgeon, J. C. Specific interaction of ions. *Trans. Faraday Soc.* **1955**, *51*, 747–761.
- (4) Pitzer, K. S. Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **1973**, *77*, 268–277.
- (5) Chen, C.-C.; Britt, H. L.; Boston, J. F.; Evans, L. B. Local Composition Model for Excess Gibbs Energy of Electrolyte Systems. Part I: Single Solvent, Single Completely Dissociated Electrolyte Systems. *AICHE J.* **1982**, *28*, 588–596.
- (6) Chen, C.-C.; Evans, L. B. A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems. *AICHE J.* **1986**, *32*, 444–454.
- (7) Prausnitz, J. M.; et al. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall: Upper Saddle River, NJ, 1998.
- (8) Wang, P.; et al. A Speciation-Based Model for Mixed-Solvent Electrolyte Systems. *Fluid Phase Equilibrium* **2002**, *203*, 141–176.
- (9) Chen, C.-C.; et al. Modeling Aqueous Electrolyte Systems. *Chemical Engineering Progress* **2015**, *111* (3), 65–75.
- (10) Wang, M.; Chen, C.-C.; et al. Modeling Mixed-Solvent Electrolyte Systems. *Chemical Engineering Progress* **2016**, *112* (2), 34–42.
- (11) Kontogeorgis, G. M.; Schlaikjer, A.; Olsen, M. D.; Maribom-Mogensen, B.; Thomsen, K.; von Solms, N.; Liang, X. A Review of Electrolyte Equations of State with Emphasis on Those Based on Cubic and Cubic-Plus-Association (CPA) Models. *Int. J. Thermophys.* **2022**, *43* (4), 54.
- (12) *Aspen Physical Property System, version 12.1*; Aspen Technology Inc.: Bedford, MA, 2021.
- (13) Hossain, N.; Ravichandran, A.; Khare, R.; Chen, C.-C. Revisiting Electrolyte Thermodynamic Models: Insights from Molecular Simulations. *AICHE J.* **2018**, *64*, 3728–3734.
- (14) Voigt, W. Solubility equilibria in multicomponent oceanic salt systems from t = 0 to 200 °C. Model parameterization and databases. *Pure Appl. Chem.* **2001**, *73*, 831–844.

- (15) Mock, B.; Evans, L. B.; Chen, C.-C. Thermodynamic Representation of Phase Equilibria of Mixed-Solvent Electrolyte Systems. *AICHE J.* **1986**, *32*, 1655–1664.
- (16) Chen, C.-C.; Mathias, P. M.; Orbey, H. Use of Hydration and Dissociation Chemistries with the Electrolyte-NRTL Model. *AICHE J.* **1999**, *45*, 1576–1586.
- (17) Chen, C.-C.; Bokis, C. P.; Mathias, P. M. Segment-Based Excess Gibbs Energy Model for Aqueous Organic Electrolytes. *AICHE J.* **2001**, *47*, 2593–2602.
- (18) Chen, C.-C.; Song, Y. Generalized Electrolyte-NRTL Model for Mixed-Solvent Electrolyte Systems. *AICHE J.* **2004**, *50*, 1928–1941.
- (19) Bollas, G. M.; Chen, C.-C.; Barton, P. I. Refined Electrolyte-NRTL Model: Activity Coefficient Expressions for Application to Multi-Electrolyte Systems. *AICHE J.* **2008**, *54*, 1608–1624.
- (20) Song, Y.; Chen, C.-C. Symmetric Electrolyte Nonrandom Two-Liquid Activity Coefficient Model. *Ind. Eng. Chem. Res.* **2009**, *48*, 7788–7797.
- (21) Pitzer, K. S.; Simonson, J. M. Thermodynamics of Multi-component, Miscible, Ionic Systems: Theory and Equations. *J. Phys. Chem.* **1986**, *90*, 3005–3009.
- (22) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*, 2nd ed.; Butterworths, 1970.
- (23) Rashin, A. A.; Honig, B. Reevaluation of the Born Model of Ion Hydration. *J. Phys. Chem.* **1985**, *89*, 5588–5593.
- (24) Hossain, N.; Bhattacharia, S. K.; Chen, C.-C. Temperature Dependence of Interaction Parameters in Electrolyte NRTL Model. *AICHE J.* **2016**, *62*, 1244–1253.
- (25) Saravi, S. H.; Ravichandran, A.; Khare, R.; Chen, C.-C. Bridging Two-Liquid Theory with Molecular Simulations for Electrolytes: An Investigation of Aqueous NaCl Solution. *AICHE J.* **2019**, *65*, 1315–1324.
- (26) Kirkes, T. E.; Saravi, S. H.; Chen, C.-C. Thermodynamic Modeling of Aqueous LiCl, LiBr, LiI and LiNO<sub>3</sub> Solutions. *Fluid Phase Equilibr.* **2021**, *531*, 112914.
- (27) Zhang, Y.; Que, H.-L.; Chen, C.-C. Thermodynamic modeling for CO<sub>2</sub> absorption in aqueous MEA solution with electrolyte NRTL model. *Fluid Phase Equilibr.* **2011**, *311*, 67–76.
- (28) Diky, V.; Muzny, C. D.; Lemmon, E. W.; Chirico, R. D.; Frenkel, M. ThermoData Engine (TDE): Software Implementation of the Dynamic Data Evaluation Concept. 2. Equations of State on Demand and Dynamic Updates over the Web. *J. Chem. Inf. Model.* **2007**, *47*, 1713–1754.
- (29) Britt, H. L.; Luecke, R. H. The Estimation of Parameters in Nonlinear, Implicit Models. *Technometrics* **1973**, *15* (2), 233–247.
- (30) Que, H.; Song, Y.; Chen, C.-C. Thermodynamic Modeling of the Sulfuric Acid-Water-Sulfur Trioxide System with the Symmetric Electrolyte NRTL Model. *J. Chem. Eng. Data* **2011**, *S6*, 963–977.
- (31) Wang, M.; Kaur, H.; Chen, C.-C. Thermodynamic Representation of Nitric Acid-Sulfuric Acid-Water Ternary System. *AICHE J.* **2017**, *63*, 3310–3317.
- (32) Wang, M.; Gorensen, M.; Chen, C.-C. Thermodynamic Representation of Aqueous Sodium Nitrate and Nitric Acid Solution with Electrolyte NRTL Model. *Fluid Phase Equilibr.* **2016**, *407*, 105–116.
- (33) Ghuge, P. D.; Mali, N. A.; Joshi, S. S. Extractive Distillation Configuration for Nitric Acid Dehydration Using Sulfuric Acid as a Solvent. *Ind. Eng. Chem. Res.* **2020**, *59*, 6183–6193.
- (34) Kaur, H.; Wang, M.; Gorensen, M. B.; Chen, C.-C. Thermodynamic Modeling of the Hybrid Sulfur (HyS) Cycle for Hydrogen Production. *Fluid Phase Equilibr.* **2018**, *460*, 175–188.
- (35) Islam, M. R.; Hsieh, I.-M.; Lin, B.; Thakur, A.; Chen, C.-C.; Malmali, M. Molecular Thermodynamics for Scaling Prediction: Case of Membrane Distillation. *Sep. Purif. Technol.* **2021**, *276*, 119231.
- (36) Thakur, A. K.; Hsieh, I.-M.; Islam, M. R.; Lin, B.; Chen, C.-C.; Malmali, M. Performance of Sweeping Gas Membrane Distillation for Treating Produced Water: Modeling and Experiments. *Desalination* **2020**, *492*, 114597.
- (37) Yu, C.-H.; Lin, Y.; Wong, D. S.-H.; Chen, C.-C. Process Modeling of CO<sub>2</sub> Absorption with Monoethanolamine Aqueous Solutions Using Rotating Packed Beds. *Ind. Eng. Chem. Res.* **2022**, *61* (33), 12142–12152.
- (38) Zhang, Y.; Chen, C.-C. Modeling CO<sub>2</sub> Absorption and Desorption by Aqueous Monoethanolamine Solution with Aspen Rate-Based Model. *Energy Procedia* **2013**, *37*, 1584–1596.
- (39) Zhang, Y.; Chen, H.; Plaza, J.; Dugas, R.; Rochelle, G.; Chen, C.-C. Rate-Based Process Modeling Study of CO<sub>2</sub> Capture with Aqueous MEA Solution. *Ind. Eng. Chem. Res.* **2009**, *48*, 9233–9246.
- (40) Zhang, Y.; Chen, C.-C. Modeling Gas Solubilities in Aqueous Methyldiethanolamine Solution. *Ind. Eng. Chem. Res.* **2011**, *50*, 6436–6446.
- (41) Zhang, Y.; Chen, C.-C. Thermodynamic Modeling of CO<sub>2</sub> Absorption in Aqueous Methyldiethanolamine Solution with Electrolyte NRTL Model. *Ind. Eng. Chem. Res.* **2011**, *50*, 163–175.
- (42) Zong, L.; Chen, C.-C. Thermodynamic Modeling of CO<sub>2</sub> and H<sub>2</sub>S Solubilities in Aqueous DIPA Solution, Aqueous Sulfolane-DIPA Solution, and Aqueous Sulfolane-MDEA Solution with Electrolyte NRTL Model. *Fluid Phase Equilibr.* **2011**, *306*, 190–203.
- (43) Que, H.; Chen, C.-C. Thermodynamic Modeling of the NH<sub>3</sub>-CO<sub>2</sub>-H<sub>2</sub>O System with Electrolyte NRTL Model. *Ind. Eng. Chem. Res.* **2011**, *50*, 11406–11421.
- (44) Kaur, H.; Chen, C.-C. Thermodynamic Modeling of CO<sub>2</sub> Absorption in Aqueous Potassium Carbonate Solution with Electrolyte NRTL Model. *Fluid Phase Equilibr.* **2020**, *505*, 112339.
- (45) Kaur, H.; Abedi, S.; Chen, C.-C. Estimating CO<sub>2</sub> Solubility in Aqueous Na<sup>+</sup>-K<sup>+</sup>-Mg<sup>2+</sup>-Ca<sup>2+</sup>-Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup> Solutions with Electrolyte NRTL - PC-SAFT Model. *Journal of Chemical & Engineering Data* **2022**, *67* (8), 1932–1950.
- (46) Yan, Y.; Chen, C.-C. Thermodynamic Modeling of CO<sub>2</sub> Solubility in Aqueous Solutions of NaCl and Na<sub>2</sub>SO<sub>4</sub>. *J. Supercrit. Fluids* **2010**, *55*, 623–634.
- (47) Liu, Y.; Hou, M.; Yang, G.; Han, B. Solubility of CO<sub>2</sub> in aqueous solutions of NaCl, KCl, CaCl<sub>2</sub> and their mixed salts at different temperatures and pressures. *J. Supercrit. Fluids* **2011**, *56*, 125–129.
- (48) Produced Water R&D. <https://www.energy.gov/fecm/science-innovation/oil-gas/shale-gas-rd/produced-water-rd> (accessed on 2022/08/22).
- (49) Understanding Seismicity Associated with Saltwater Disposal Wells. <https://www.api.org/~media/Files/Oil-and-Natural-Gas/Hydraulic-Fracturing/seismicity-and-saltwater-wells.pdf> (accessed on 2022/08/22).
- (50) Chen, T.; Honarpourvar, S.; Reible, D.; Chen, C.-C. Thermodynamic Modeling of Calcium Carbonate Scale Precipitation: Aqueous Na<sup>+</sup>-Ca<sup>2+</sup>-Cl<sup>-</sup>-HCO<sub>3</sub><sup>2-</sup>-CO<sub>3</sub><sup>2-</sup>-CO<sub>2</sub> System. *Fluid Phase Equilibr.* **2022**, *552*, 113263.
- (51) Tanveer, S.; Chen, C.-C. Extended Thermodynamic Model for High Salinity Produced Waters. *Chem. Eng. Sci.* **2021**, *243*, 116754.
- (52) Tanveer, S.; Chen, C.-C. A Comprehensive Thermodynamic Model for High Salinity Produced Waters. *AICHE J.* **2020**, *66* (1), No. e16818.
- (53) Tanveer, S.; Chen, C.-C. Molecular Thermodynamic Modeling of Aqueous Na<sup>+</sup>-K<sup>+</sup>-Mg<sup>2+</sup>-Ca<sup>2+</sup>-SO<sub>4</sub><sup>2-</sup> Quinary System. *Fluid Phase Equilibr.* **2019**, *491*, 77–87.
- (54) Honarpourvar, S.; Saravi, S. H.; Reible, D.; Chen, C.-C. Comprehensive Thermodynamic Modeling of Saline Water with Electrolyte NRTL Model: A Study of the Aqueous Sr<sup>2+</sup>-Na<sup>+</sup>-Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup> Quaternary System. *Fluid Phase Equilibr.* **2018**, *470*, 221–231.
- (55) Honarpourvar, S.; Saravi, S. H.; Reible, D.; Chen, C.-C. Comprehensive Thermodynamic Modeling of Saline Water with Electrolyte NRTL Model: A Study on Aqueous Ba<sup>2+</sup>-Na<sup>+</sup>-Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup> Quaternary System. *Fluid Phase Equilibr.* **2017**, *447*, 29–38.
- (56) Tanveer, S.; Zhou, H.; Chen, C.-C. Thermodynamic Modeling of Mg<sup>2+</sup>-Na<sup>+</sup>-K<sup>+</sup>-Cl<sup>-</sup> Quaternary System. *Fluid Phase Equilibr.* **2017**, *437*, 56–68.
- (57) Tanveer, S.; Chen, C.-C. Thermodynamic Modeling of Ca<sup>2+</sup>-Na<sup>+</sup>-K<sup>+</sup>-Cl<sup>-</sup> Quaternary System. *Fluid Phase Equilibr.* **2016**, *409*, 193–206.

- (58) Bhattacharia, S. K.; Tanveer, S.; Hossain, N.; Chen, C.-C. Thermodynamic Modeling of  $\text{Na}^+$ - $\text{K}^+$ - $\text{Mg}^{2+}$ - $\text{SO}_4^{2-}$  Quaternary System. *Fluid Phase Equilib.* **2015**, *404*, 141–149.
- (59) Bhattacharia, S. K.; Hossain, N.; Chen, C.-C. Thermodynamic Modeling of  $\text{Na}^+$ - $\text{K}^+$ - $\text{Cl}^-$ - $\text{SO}_4^{2-}$  Quaternary System with Electrolyte NRTL Model. *Fluid Phase Equilib.* **2015**, *403*, 1–9.
- (60) Bhattacharia, S. K.; Chen, C.-C. Thermodynamic Modeling of  $\text{KCl} + \text{H}_2\text{O}$  and  $\text{KCl} + \text{NaCl} + \text{H}_2\text{O}$  Systems Using Symmetric Electrolyte NRTL Model. *Fluid Phase Equilib.* **2015**, *387*, 169–177.
- (61) Yan, Y.; Chen, C.-C. Thermodynamic Representation of the  $\text{NaCl}$ - $\text{Na}_2\text{SO}_4$ - $\text{H}_2\text{O}$  System with Electrolyte NRTL Model. *Fluid Phase Equilib.* **2011**, *306*, 149–161.
- (62) Deng, T. L.; Zhou, H.; Xia, C.; *Salt-Water System Phase Diagram and Its Application*; Chemical Industry Press: Beijing, 2013.
- (63) Lin, Y. J.; Hsieh, C. J.; Chen, C.-C. Association-based activity coefficient model for electrolyte solutions. *AIChE J.* **2021**, *68*, No. e17422.
- (64) Wertheim, M. Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations. *J. Stat. Phys.* **1984**, *35*, 35–47.
- (65) Wertheim, M. Fluids with highly directional attractive forces. IV. Equilibrium polymerization. *J. Stat. Phys.* **1986**, *42*, 477–492.
- (66) Wertheim, M. Fluids of dimerizing hard spheres, and fluid mixtures of hard spheres and dispheres. *J. Chem. Phys.* **1986**, *85*, 2929–2936.
- (67) Fu, Y.-H.; Sandler, S. I.; Orbey, H. A modified UNIQUAC model that includes hydrogen bonding. *Ind. Eng. Chem. Res.* **1995**, *34*, 4351–4363.
- (68) Hao, Y.; Chen, C.-C. Nonrandom two-liquid segment activity coefficient model with association theory. *Ind. Eng. Chem. Res.* **2019**, *58*, 12773–12786.
- (69) Hao, Y.; Chen, C.-C. Nonrandom two-liquid activity coefficient model with association theory. *AIChE J.* **2020**, *67*, No. e17061.
- (70) Hamer, W. J.; Wu, Y. C. Osmotic Coefficients and Mean Activity Coefficients of Uni-univalent Electrolytes in Water at 25°C. *Journal of Physical and Chemical Reference Data*. **1972**, *1*, 1047–1100.
- (71) Tang, I. N.; Munkelwitz, H. R.; Wang, N. Water activity measurements with single suspended droplets: the  $\text{NaCl}$ - $\text{H}_2\text{O}$  and  $\text{KCl}$ - $\text{H}_2\text{O}$  systems. *J. Colloid Interface Sci.* **1986**, *114*, 409–415.
- (72) Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An equation of state for associating fluids. *Ind. Eng. Chem. Res.* **1996**, *35*, 4310–4318.
- (73) Gross, J.; Sadowski, G. Application of the Perturbed-Chain SAFT Equation of State to Associating Systems. *Ind. Eng. Chem. Res.* **2002**, *41*, 5510–5515.
- (74) Lin, Y.; Hossain, N.; Chen, C.-C. Modeling Dissociation of Ionic Liquids with Electrolyte NRTL Model. *J. Mol. Liq.* **2021**, *329*, 115524.
- (75) Yu, Y.; Li, Y.; Hossain, N.; Chen, C.-C. Nonrandom Two-Liquid Activity Coefficient Model for Aqueous Polyelectrolyte Solutions. *Fluid Phase Equilib.* **2019**, *497*, 1–9.
- (76) Li, Y.; Yu, Y.; Chen, C.-C. Modeling Aqueous Multivalent Polyelectrolytes Systems with Polyelectrolyte NRTL Model. *J. Mol. Liq.* **2021**, *336*, 116237.
- (77) Yu, Y.; Yan, N.; Freeman, B. D.; Chen, C.-C. Mobile Ion Partitioning in Ion Exchange Membranes Immersed in Saline Solutions. *J. Membr. Sci.* **2021**, *620*, 118760.
- (78) Tanveer, S.; Chen, C.-C. Thermodynamic Analysis of Hydrogel Swelling in Aqueous Sodium Chloride Solutions. *J. Mol. Liq.* **2022**, *348*, 118421.
- (79) Nguyen, N. H.; Hussain, F.; Chen, C.-C. Correlations for Densities of Aqueous Electrolyte Solutions. *Journal of Chemical & Engineering Data* **2016**, *61*, 740–747.

## □ Recommended by ACS

### Design Water Networks through MINLP Formulation: An Algorithm to Find the Stability Region of Parameters

Fernando Arenas-Araya, Felipe A. Díaz-Alvarado, et al.

OCTOBER 11, 2022

INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH

READ ▶

### Experimental Study on Catalytic Action of Intrinsic Metals in Coal Spontaneous Combustion

Ling Qiao, Yansheng Wang, et al.

APRIL 06, 2023

ACS OMEGA

READ ▶

### Deciphering Fast Ion Transport in Glasses: A Case Study of Sodium and Silver Vitreous Sulfides

Mohammad Kassem, Eugene Bychkov, et al.

AUGUST 01, 2022

INORGANIC CHEMISTRY

READ ▶

### Electrochemical Analysis of High-Performance Flow-Electrode Capacitive Mixing (F-CapMix) under Different Operating Conditions

Hanki Kim, SeungCheol Yang, et al.

JULY 08, 2021

ACS SUSTAINABLE CHEMISTRY & ENGINEERING

READ ▶

Get More Suggestions >