



Thermodynamic model of aqueous $\text{Mg}^{2+} - \text{Na}^+ - \text{K}^+ - \text{Cl}^-$ quaternary system



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ABSTRACT

We present a thermodynamic model for the aqueous $\text{Mg}^{2+} - \text{Na}^+ - \text{K}^+ - \text{Cl}^-$ quaternary system based on symmetric electrolyte Non-Random Two Liquid (eNRTL) theory. This work is a continuation of our previous study on the aqueous $\text{Ca}^{2+} - \text{Na}^+ - \text{K}^+ - \text{Cl}^-$ quaternary system and part of a larger effort to develop a comprehensive engineering thermodynamic model for high salinity produced water in oil and gas production. The eNRTL theory requires two binary interaction parameters for each molecule-molecule, molecule-electrolyte, and electrolyte-electrolyte pair to correlate composition dependence of the solution nonideality. The binary interaction parameters, including their temperature coefficients, are identified for the $(\text{Mg}^{2+} - \text{Cl}^-) : \text{H}_2\text{O}$ pair, $(\text{Mg}^{2+} - \text{Cl}^-) : (\text{K}^+ - \text{Cl}^-)$ pair, and $(\text{Mg}^{2+} - \text{Cl}^-) : (\text{Na}^+ - \text{Cl}^-)$ pair using available thermodynamic data. The binary parameters for the other pairs are taken directly from the literature. Together, the eNRTL model and the binary parameters yield a satisfactory thermodynamic model for the quaternary system and its subsystems with temperatures ranging from 273.15 to 473.15 K and salt concentrations up to saturation.

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1. Introduction

Oil and gas production plays a major role in the US economy. Along with hydrocarbons, a vast amount of waste-water, known as produced water, is also generated. Produced water consists of mainly (a) salts (expressed as salinity, conductivity or total dissolved solid, TDS) (b) organic hydrocarbons termed as “oil and grease”, (c) metals, (d) naturally active radioactive materials, and (e) chemical additives [1]. Among these, salts are the primary content of produced water in onshore production [2] and are the focus for our present work.

In western regions of the US, specifically in drought prone areas, reusing and treating produced water is important for both economic and environmental reasons [3]. To support research and development of novel treatment processes for produced water, it is essential that we have a comprehensive engineering thermodynamic model for high salinity produced water that could reliably compute thermodynamic and calorimetric properties over wide ranges of temperature and salt concentration. However, no such thermodynamic model exists to date [4].

Sodium, potassium, calcium, and magnesium are the major cations that are present in produced water, while major anions include chloride, sulfate and bicarbonate [5]. Based on the symmetric electrolyte Non-random Two-Liquid (eNRTL) model [6], we are in the process of developing a complete engineering thermodynamic model for the major electrolytes in produced water. As a part of that we previously presented a thermodynamic modeling study for the aqueous $\text{Ca}^{2+} - \text{Na}^+ - \text{K}^+ - \text{Cl}^-$ quaternary system [7]. The current study presents thermodynamic modeling of the aqueous $\text{Mg}^{2+} - \text{Na}^+ - \text{K}^+ - \text{Cl}^-$ quaternary system with a focus on the $\text{MgCl}_2 + \text{H}_2\text{O}$ binary.

Several research groups have made efforts to establish thermodynamic models for the $\text{MgCl}_2 + \text{H}_2\text{O}$ binary. These modeling studies have been based on the Pitzer's ion interaction model [8–13] and the REUNQUAC model [14].

Holmes et al. [8] reported isopiestic vapor pressure data for the $\text{MgCl}_2 + \text{H}_2\text{O}$ binary and fit the data with the Pitzer equation with MgCl_2 concentrations up to 3.54 mol/kg. They accounted for the concentration dependence of the binary with three temperature-dependent adjustable parameters at 382, 413.8, 445.4, and 474 K. While observing the osmotic coefficient plot, they reported that MgCl_2 showed “anomalous” behavior above 2 molal electrolyte concentration. de Lima and Pitzer [9] used nine adjustable

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parameters to describe the binary with MgCl_2 concentrations of (1–6) mol/kg and temperatures of (298–473) K. Phutela et al. [10] used eleven adjustable parameters to model liquid molar heat capacity at temperatures (298–453) K and concentrations (0–0.9) mol/kg. Wang et al. [11] also developed a Pitzer equation for the binary which is valid for temperatures from 240 to 627 K, from saturation pressure to 100 MPa, and salt concentration up to 25 mol/kg. The model considers up to fourth virial coefficients and requires 126 adjustable parameters. Later on, Pitzer et al. [12] proposed empirical ionic-strength dependence functions for third, fourth, and higher virial coefficients to represent the thermodynamic properties of the binary up to 5.9 mol/kg salt concentration. The Pitzer model, while successful in modeling the $\text{MgCl}_2 + \text{H}_2\text{O}$ binary, requires many adjustable parameters and so is too complicated for practical engineering calculations.

Recently, Hingerl et al. [14] proposed a revised Extended Universal QUAsiChemical (REUNIQUAC) activity coefficient model for geothermal brines for temperatures of (298–573) K and salt concentrations up to 5 molal. In the model for the $\text{MgCl}_2 + \text{H}_2\text{O}$ binary, they modified Debye-Hückel equation by introducing an “effective ionic radii of solute species”. They further introduced a quadratic temperature dependence and a quadratic concentration dependence for the UNIQUAC interaction parameters. The REUNIQUAC model is of limited use for the binary because it is applicable only up to 4 molal while requiring 18 binary interaction parameters, including concentration-dependent parameters.

The eNRTL model [6] is well-suited for thermodynamic modeling of aqueous electrolyte systems including the $\text{Mg}^{2+} - \text{Na}^+ - \text{K}^+ - \text{Cl}^-$ quaternary system. It requires only two binary interaction parameters to account for the solution nonideality of each binary system. The temperature dependence can be further correlated to three temperature coefficients through a Gibbs-Helmholtz type equation [15]. Wang et al. [16] recently reported a thermodynamic model for the $\text{MgCl}_2 + \text{H}_2\text{O}$ binary based on the eNRTL model. Unfortunately, the authors erroneously fitted the molecule-electrolyte binary interaction parameters to MgCl_2 solubility data and failed to identify proper temperature dependence of the binary interaction parameters.

In this work, we first identify the eNRTL binary interaction parameters for the $(\text{Mg}^{2+}-\text{Cl}^-):\text{H}_2\text{O}$ pair by regressing experimental phase equilibrium and calorimetric data of the $\text{MgCl}_2 + \text{H}_2\text{O}$ binary. We retrieve available eNRTL binary interaction parameters for the $(\text{Na}^+-\text{Cl}^-):\text{H}_2\text{O}$ pair [17] and the $(\text{K}^+-\text{Cl}^-):\text{H}_2\text{O}$ pair [18] from the literature. We then use salt solubility data of the $\text{MgCl}_2 + \text{NaCl} + \text{H}_2\text{O}$ ternary to regress the binary interaction parameters for the $(\text{Mg}^{2+}-\text{Cl}^-):(\text{Na}^+-\text{Cl}^-)$ pair and salt solubility data of the $\text{MgCl}_2 + \text{KCl} + \text{H}_2\text{O}$ ternary to regress the binary interaction parameters for the $(\text{Mg}^{2+}-\text{Cl}^-):(\text{K}^+-\text{Cl}^-)$ pair. These interaction parameters are then integrated with the binary interaction parameters for the $(\text{Na}^+-\text{Cl}^-):(\text{K}^+-\text{Cl}^-)$ pair [18] to complete the thermodynamic model for the $\text{Mg}^{2+} - \text{Na}^+ - \text{K}^+ - \text{Cl}^-$ quaternary. We use ASPEN software (version 8.4) as the regression tool to identify the parameters. Tables 1–3 summarize the thermodynamic constants and eNRTL binary interaction parameters. All experimental data used in this work are listed in Tables 4–6.

2. Thermodynamic framework

Vapor-liquid equilibrium of the system can be described by the isofugacity relationship:

$$\varphi_i y_i P = x_i \gamma_i f_i^0 \quad (1)$$

where φ_i is the vapor phase fugacity coefficient of component i calculated with the Redlich-Kwong equation of state, y_i is the vapor

Table 1

Thermodynamic constants for water and ions at 298.15 K and 0.1 MPa [33].

| Component | State | $\Delta_f G$ (kJ.mol ⁻¹) | $\Delta_f H$ (kJ.mol ⁻¹) | C_p (J.mol ⁻¹ K ⁻¹) |
|----------------------|---------------|--------------------------------------|--------------------------------------|----------------------------------------------|
| H_2O | ig | -228.57 | -241.82 | 33.6 |
| Mg^{2+} | ∞ , aq | -454.8 | -466.85 | -18.2 ^a |
| Na^+ | ∞ , aq | -261.91 | -240.12 | 46.4 |
| K^+ | ∞ , aq | -283.27 | -252.38 | 21.8 |
| Cl^- | ∞ , aq | -131.23 | -167.16 | -116.2 |

For Mg^{2+} ion, $C_1 = 104385$, $C_2 = -411.028$, $C_3 = 0$.

For Cl^- ion, $C_1 = -710737.41$, $C_2 = 3714.987$, $C_3 = -5.772$ [17].

^a C_p for Mg^{2+} are obtained in this study.

$$C_p^{\infty, aq} (\text{J.kmol}^{-1}\text{K}^{-1}) = C_1 + C_2 T(K) + C_3 (T(K))^2;$$

phase mole fraction, P is the system pressure, x_i is the liquid phase mole fraction, γ_i is the liquid phase activity coefficient, and f_i^0 is the fugacity at reference state.

Water is the only component that exists in both the vapor and liquid phases in the quaternary system. We use the steam tables equation of state [19] to estimate the water saturation vapor pressure.

The activity coefficient of component i , γ_i , is derived from excess Gibbs free energy, G^{ex} :

$$\ln \gamma_i = \frac{1}{RT} \left(\frac{\partial G^{ex}}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (2)$$

Here, n is number of moles, R is universal gas constant, and T is system temperature. The reference state for ions is aqueous phase infinite dilution and for solvent water is pure liquid.

The eNRTL model is used to calculate the liquid phase activity coefficients. Details of the model are readily available in literature [6] and not reproduced here. Briefly, the eNRTL model expresses G^{ex} of electrolyte solutions as the sum of short-range and long-range interaction contributions:

$$G^{ex} = G^{ex,lc} + G^{ex,PDH} \quad (3)$$

Here, $G^{ex,lc}$ is the short-range interaction contribution expressed as a function of an asymmetric binary interaction energy parameter, τ_{ij} . τ_{ij} is further described by three temperature coefficients through a form of the Gibbs-Helmholtz equation [15,20]:

$$\tau_{ij} = C_{ij} + \frac{D_{ij}}{T} + E_{ij} \left[\frac{T_{ref} - T}{T} + \ln \left(\frac{T}{T_{ref}} \right) \right] \quad (4)$$

where C_{ij} , D_{ij} , E_{ij} are temperature coefficients, T_{ref} is the reference temperature chosen as 298.15 K, and i, j are indices representing molecules and electrolytes.

$G^{ex,PDH}$ is the long-range ion-ion interaction term, represented by the symmetric Pitzer-Debye-Hückel (PDH) formula. It requires no adjustable parameters.

In high salinity water, salts are in equilibrium with liquid. Solid-liquid equilibrium, or salt solubility, is described by the solubility product constant, K_{sp} . K_{sp} can be calculated from the change in Gibbs free energy for the formation of solid crystal k from ionic species in the aqueous phase:

$$\ln K_{sp}(T) = -\frac{\Delta G_k^0}{RT} \quad (5)$$

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