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Thermodynamic modeling of $KCl + H_2O$ and $KCl + NaCl + H_2O$ systems using electrolyte NRTL model

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ABSTRACT

A comprehensive thermodynamic model based on electrolyte NRTL activity coefficient model is developed for $KCl + H_2O$ binary and $KCl + NaCl + H_2O$ ternary systems. To model $KCl + H_2O$ binary systems, we identify required binary interaction parameters for (K^+Cl^-):H_2O pair by regressing experimental thermodynamic data including mean ionic activity coefficient, osmotic coefficient, vapor pressure, enthalpy, and heat capacity. To model $KCl + NaCl + H_2O$ ternary systems, we obtain required binary interaction parameters for (Na^+Cl^-):H_2O pair from the literature and (K^+Cl^-):(Na^+Cl^-) pair by regressing available thermodynamic data including osmotic coefficient, vapor pressure, and solubility for $KCl + NaCl + H_2O$ ternary systems. The model accurately represents all thermodynamic properties with temperature from 273.15 to 473.15 K and electrolyte concentration up to saturation. This model should be useful for process modeling and simulation of aqueous electrolyte solutions involving KCl.

1. Introduction

Increased demand for petroleum and natural gas has driven an increase of the production by hydraulic fracturing and horizontal drilling from deeper geologic formations. In this process, a very high volume of water, known as "produced water" is generated along with the oil and gas produced [1]. This produced water contains oil, grease, chemicals, suspended organics and solid, naturally occurring radioactive materials, and total dissolved solid (TDS) [2]. Reduction of TDS is a major step towards reuse or remediation of produced water. Treatment of total dissolved solid is the most challenging step because of the presence of multiple electrolytes. It has been reported that concentration of TDS ranges from ~3000 to 400,000 mg/L [3]. Sodium, potassium, calcium, and magnesium are the major cations present as TDS in produced water, along with major counters ions, chloride, bicarbonate, and sulfate [4]. A very high concentration of TDS in produced water challenges designers of chemical processes with proper understanding of thermodynamics and kinetics of the system. A comprehensive and accurate thermodynamic model for $KCl + H_2O$ binary and $KCl + NaCl + H_2O$ ternary is highly desirable for process modeling and simulation of treatment processes for produced water as well as for other chemical processes such as water desalination, chemical and nuclear waste treatment, potash processing etc.

Recent developments in molecular thermodynamics make it possible to develop accurate electrolyte thermodynamic models with fewer parameters. The symmetric electrolyte NRTL (eNRTL) model was proposed by Song and Chen for thermodynamic modeling of aqueous and nonaqueous electrolyte solutions [5]. This model has been proposed as a generalization of the local composition models [6,7]. Key advantages of this model are: (1) it requires only two binary interaction parameters to model electrolytes up to saturation, and (2) three temperature coefficients are sufficient for the required binary interaction parameters to cover temperatures up to 473 K. Based on the eNRTL model, a comprehensive thermodynamic model has been developed for aqueous solutions of sodium chloride (NaCl) and sodium sulfate (Na_2SO_4) [8]. Comprehensive thermodynamic models based on eNRTL have also been reported for aqueous sulfuric acid solution [9] and for CO_2 capture in amine and ammonia solutions [10–13]. Moreover, CO_2 solubility in aqueous solutions of NaCl, Na_2SO_4, and KCl, H_2S solubility in various solvents, burkeite solubility in water, [HAE]Cl solubility in aqueous solution of $MgCl_2$, and solubility of xylitol and sorbitol in various ionic liquids, were modeled with eNRTL [14–19]. Recently, Li and Li applied the eNRTL model to study vapor–liquid equilibrium of binary, ternary, and quaternary systems containing sulfuric acid, octane, ethanol, and water [20].

Many literature studies are available on modeling $KCl + H_2O$ binary systems. Notable efforts include those by Wood [21,22] and

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Pabalan and Pitzer [23]. Wood modeled solubility of KCl + NaCl + H_2O systems using the Scatchard–Harned model with temperature up to 473 K and estimated enthalpy and heat capacities [22]. Pabalan and Pitzer modeled KCl + H_2O binary using the Pitzer model with a maximum temperature of 573 K and KCl concentration up to 6 molal [23]. Archer extended the works of Pabalan and Pitzer of modeling KCl + H_2O binary and presented the baseline parameters for evaluating 'near ambient' data [24]. Although both Wood [21,22] and Pabalan and Pitzer [23] presented thermodynamic models of the aqueous solution of KCl, for the purpose of process modeling and simulation of treatment processes for produced water from hydraulic fracturing these models fall short due to the very large number of adjustable model parameters required to cover temperatures and electrolyte concentrations of interest [25,26].

In this article, we present a comprehensive thermodynamic model for KCl + H_2O binary and KCl + NaCl + H_2O ternary systems. We use the 2009 version of the electrolyte NRTL model [5] as the thermodynamic framework to account for liquid phase non-ideality and Redlich–Kwong equation-of-state [27] for vapor phase fugacity. We obtain the necessary eNRTL binary interaction parameters for (K^+Cl^-):H_2O pair and (K^+Cl^-):(Na^+Cl^-) pair by regressing available thermodynamic property data from literature. We use ASPEN (version 8.2) software for regressing the data. Literature values for the eNRTL binary interaction parameters for (Na^+Cl^-):H_2O pair [8] are used directly. We show that the model requires only a minimal number of adjustable model parameters and is capable of accurately calculating all thermodynamic properties including mean ionic activity coefficient, osmotic coefficient, vapor pressure, liquid enthalpy, heat capacity, and salt solubility in water across wide ranges of temperature and concentration.

2. Thermodynamic framework

In KCl + H_2O binary and KCl + NaCl + H_2O ternary systems, only H_2O participates in vapor–liquid equilibrium (VLE). To model the VLE, we used the following equation

$$\mathrm{P}y_i\varphi_i = x_i\gamma_i f_i^o \tag{1}$$

where P is the system pressure; y_i is the vapor phase mole fraction of component i, φ_i is the vapor phase fugacity coefficient, x_i is the liquid phase mole fraction, γ_i is the liquid phase activity coefficient, and f_i^o is the liquid phase reference fugacity which is calculated using the following equations,

$$f_i^o = p_i^o\varphi_i^o\theta_i^o \tag{2}$$

$$\theta_i^o = \exp\left(\frac{1}{RT}\int_{p_i^o}^{p} \nu_i^o \mathrm{d}p\right) \tag{3}$$

$$\nu_i^o = \frac{RT_c\left(Z_i^{RA}\right)^{\left[1+(1-T_r)^{2/7}\right]}}{P_c} \tag{4}$$

where p_i^o is the vapor pressure of component i; φ_i^o is the vapor fugacity coefficient at p_i^o and the system temperature T; R is the gas constant; T_c and P_c are the critical temperature and pressure, respectively; $T_r = T/T_c$ is the reduced temperature; Z_i^{RA} is the correlation parameter. For water, Z_i^{RA} is fixed at 0.243.

The electrolyte NRTL model [5] is used to calculate γ_i. The model expresses excess Gibbs energy (G^{ex}) as the sum of two contributions:

$$G^{\mathrm{ex}} = G^{\mathrm{ex,lc}} + G^{\mathrm{ex,PDH}} \tag{5}$$

where $G^{\mathrm{ex,lc}}$ is the contribution from the short range ion–ion, ion–molecule, and molecule–molecule interactions while $G^{\mathrm{ex,PDH}}$ is the contribution from the long range ion–ion interactions.

The short range interactions that exist at the immediate neighborhood of any species are represented with the electrolyte NRTL local composition formulation:

$$\frac{G^{\mathrm{ex,lc}}}{nRT} = \sum_m n_m\left(\frac{\sum_i X_i G_{im}\tau_{im}}{\sum_i X_i G_{im}}\right) + \sum_c z_c n_c\left(\frac{\sum_{i\neq c} X_i G_{ic}\tau_{ic}}{\sum_{i\neq c} X_i G_{ic}}\right) + \sum_a z_a n_a\left(\frac{\sum_{i\neq a} X_i G_{ia}\tau_{ia}}{\sum_{i\neq a} X_i G_{ia}}\right) \tag{6}$$

$$X_i = C_i x_i = C_i\left(\frac{n_i}{n}\right), i = m, c, a \tag{7}$$

$$n = \sum_i n_i = \sum_m n_m + \sum_c n_c + \sum_a n_a \tag{8}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{9}$$

$$\tau_{ij} = C_{ij} + \frac{D_{ij}}{T} + E_{ij}\left(\frac{T_{\mathrm{ref}} - T}{T} + \ln\frac{T}{T_{\mathrm{ref}}}\right) \tag{10}$$

where i is the species index including molecular species m, cationic species c, and anionic species a; n_i and x_i are the mole number and the mole fraction of species i in the system, respectively; C_i is the absolute charge number for ionic species and unity for molecular species; α_{ij} is the non-randomness factor (fixed at 0.2 in this study); τ_{ij} is the binary interaction energy parameter in which C_{ij}, D_{ij}, and E_{ij} are the temperature coefficients of τ_{ij} with T_{ref} = 298.15 K.

The long range ion–ion interactions are represented with the extended Pitzer–Debye–Hückel (PDH) formula for multicomponent electrolytes:

$$\frac{G^{\mathrm{ex,PDH}}}{nRT} = -\frac{4A_\varphi I_x}{\rho}\ln\left[\frac{1+\rho I_x^{1/2}}{1+\rho\left(I_x^0\right)^{1/2}}\right] \tag{11}$$

$$A_\varphi = \frac{1}{3}\left(\frac{2\pi N_A}{\nu}\right)^{1/2}\left(\frac{Q_e^2}{\varepsilon k_B T}\right)^{3/2} \tag{12}$$

$$I_x = \frac{1}{2}\sum_i z_i^2 x_i = \frac{1}{2}\sum_c z_c^2 x_c + \frac{1}{2}\sum_a z_a^2 x_a \tag{13}$$

$$\varepsilon = A + B\left(\frac{1}{T} - \frac{1}{C}\right) \tag{14}$$

where A_φ is the Debye–Hückel parameter; I_x is the ionic strength in mole fraction; ρ is the closest approach parameter; I_x^0 is I_x at the fused salt reference state; N_A is Avogadro's number; Q_e is the electron charge; k_B is Boltzmann constant; ν and ε are the molar volume and dielectric constant of solvent water, respectively; z_i is the charge number of species i; z_c and z_a are the charge numbers of cation and anion, respectively. ε is correlated with temperature as