Fluid Phase Equilibria 417 (2016) 187-196

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Modeling hydrate-containing phase equilibria for mixtures with sulfur dioxide or alkali halides



Department of Chemical and Biological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul, 02841, Republic of Korea

ARTICLE INFO

Article history: Received 11 December 2015 Received in revised form 23 February 2016 Accepted 24 February 2016 Available online 3 March 2016

Keywords: Hydrate-containing phase equilibria Electrolyte equation of state Sulfur dioxide Electrolytes

ABSTRACT

Gas hydrate-containing phase behaviors are essentially required for flow assurance in carbon dioxide sequestrations and resources recovery. To model effects of weak electrolyte such as SO₂ and strong electrolytes such as alkali halides on phase equilibria of hydrate systems, an electrolyte equation of state is used, which is based on hydrogen-bonding nonrandom lattice fluid equation of state for fluid phases and van der Waals and Platteeuw model for hydrate phases. A guest gas of SO₂ is modeled as partially dissociating component in aqueous solution. Various phase behaviors of water and SO₂ mixtures for hydrate-free and hydrate-forming conditions are analyzed by comparing the model results with experimental data. An improvement in accuracy of liquid—liquid equilibria for the mixture is achieved by the inclusion of cross-association between water and SO₂. The proposed model has been also found to provide with reliable predictions of hydrate-containing phase equilibria for a binary guest of CO₂ and SO₂. In the presence of NaCl or KCl as an inhibitor of formed hydrate, predicted incipient hydrate-forming conditions of single guests such as methane, ethane, propane, and CO₂ are compared with experimental data and available models, showing good agreement with the data.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Hydrate-containing phase behaviors are essential information required for flow assurance in carbon dioxide or gas/oil transportation in offshore processes. Sulfur dioxide is a common impurity in recovered combustion products and it can be a guest component when hydrates are formed in the gas stream. Unlike the other possible impurities like nitrogen or oxygen, SO₂ partially dissociates into ions in water and forms electrolyte solution. The dissociation of SO₂ shows complex behavior in hydrate-containing phase equilibria due to interactions between various species, and very few modeling studies have been successful to model such systems within a single framework. Such a model can be also used to predict inhibition effect of electrolytes like NaCl and KCl, which are common compounds found in the offshore applications, on the hydrate formation.

A recent comprehensive modeling study [1] for hydratecontaining phase equilibria was reported by present authors but was limited to nonelectrolyte systems. Chassefiere et al. [2]

* Corresponding author. E-mail address: jwkang@korea.ac.kr (J.W. Kang). optimized Kihara potential parameters of SO₂ below the freezing point of water without considering the dissociation. Edwards et al. [3,4] and Jin and Donohue [5] calculated vapor—liquid equilibria of weak electrolyte solutions containing ammonia, hydrogen sulfide, CO₂ and SO₂ by introducing a contribution of long-range interactions between dissociated ions to their models. Pereda et al. [6] used extended UNIQUAC model combined with Soave–Relich–Kwong equation of state to describe complex equilibria with the dissociation reactions of SO₂ in electrolyte solutions. However, above mentioned modeling studies [3–6] are restricted to the calculation of solubility of SO₂ in aqueous solutions.

Modeling studies on inhibition effects of electrolytes have been presented by several researchers. Haghtalab et al. [7] calculated hydrate equilibrium conditions of various guests in the presence of single and mixed electrolytes using electrolyte cubic square-well equation of state and they compared their results with those of HWHYD model [8] and the predictive Soave—Redlich—Kwong equation of state [9]. Modified versions of the HWHYD model, which are based on Valderrama modification of a Patel-Teja equation of state with nondensity-dependent mixing rules, were proposed to predict the inhibition effects of NaCl and KCl on hydrate dissociation conditions of methane and CO₂ [10,11]. Haghighi et al. [12] measured incipient hydrate-forming conditions of methane in





CrossMark

the presence of electrolytes and compared the data with predictions using Cubic-Plus-Association equation of state. Mohammadi et al. [13] used an extended-UNIQUAC approach for modeling the incipient hydrate-forming conditions of hydrogen sulfide in the presence of various thermodynamic inhibitors such as salts, alcohols and ethylene glycol. CSMGem program [14] is available for calculating hydrate-containing phase equilibria of various guests with representative electrolyte inhibitors such as NaCl, KCl and CaCl₂.

Lee et al. [1] recently reported a comprehensive modeling study for incipient hydrate-forming conditions of single and binary guests and solubility in hydrate-containing two-phase equilibria. They used a nonrandom hydrogen-bonding lattice fluid (NLF-HB) equation of state for fluid phases and van der Waals and Platteeuw model [15] for hydrate phases as in previous studies [16–18]. Crossassociation interactions between water and CO₂ as well as the selfassociation of water molecules are included in the NLF-HB equation of state. The combined model was applied to hydrate-containing phase equilibria of single and binary guest systems of methane, ethane, propane, isobutane, CO₂, nitrogen and hydrogen sulfide. Kim and Lee [19] extended the NLF-HB equation of state to electrolyte solutions by adding a long-range contribution from the mean spherical approximation theory [20]. With this extension the model is now formally applicable to gas hydrate systems containing SO₂ and electrolytes. In the present work, the applicability of the extended model to water and SO₂ mixtures with and without CO₂ is studied. Inhibition effects of NaCl and KCl on gas hydrate formation of guest species such as methane, ethane, propane and CO₂ are also examined.

2. Model and parameters

Conditions of equal chemical potential or fugacity for each component in all stable phases are required for phase equilibrium calculations. Hydrate-containing phase equilibria involve hydrate (*H*), vapor (*V*), water-rich liquid (L_w), and/or guest-rich liquid phases (L_g) above the freezing point of water. Calculations of the property in fluid phases (V, L_w , and L_σ) are based on a hydrogenbonding nonrandom lattice fluid (NLF-HB) model, which accounts for contributions of physical and association interactions. Kim and Lee [19] extended the model to aqueous electrolyte solutions by including a long-range contribution from the mean spherical approximation theory [20]. Recently Lee et al. [1] used the NLF-HB model with a revised association contribution but without the long-range contribution in modeling hydrate-containing phase equilibria for nonelectrolyte systems. Hydrate phase was modeled by van der Waals and Platteeuw theory [15] with newly determined parameters. In the present application, the long-range contribution is added to the framework of Lee et al. for calculations of hydrateforming conditions in the presence of electrolytes. Working equations for both fluid and hydrate phases are summarized in the Appendix.

2.1. Parameters for nonelectrolyte systems

Parameters for the physical interaction are temperaturedependent segment number r_i (r_{ai} , r_{bi} and r_{ci}), interaction energy parameter ε_{ii} (ε_{ai} , ε_{bi} and ε_{ci}) and binary interaction parameter k_{ij} .

$$r_i = r_{ai} + r_{bi}(T - T_0) + r_{ci}[T \ln(T_0/T) + (T - T_0)]$$
(1)

$$\varepsilon_{ii}/k = \varepsilon_{ai} + \varepsilon_{bi}(T - T_0) + \varepsilon_{ci}[T \ln(T_0/T) + (T - T_0)]$$
⁽²⁾

where $T_0 = 298.15$ K. Temperature-dependent coefficients of the segment number and the interaction energy for nonelectrolyte

species are given in Table 1 from Lee et al. [1]. The physical interaction parameters of SO₂ were fitted to saturated vapor pressure and saturated liquid density of pure SO₂, which are generated from REFPROP [21] program in a temperature range between 273.15 and 323.15 K, and very good agreement is found within 0.1% deviation. The interaction energy between segments of unlike species ε_{ij} is expressed as

$$\varepsilon_{ij} = \left(\varepsilon_{ii}\varepsilon_{jj}\right)^{1/2} \left(1 - k_{ij}\right) \tag{3}$$

with the binary interaction parameter k_{ij} (= k_{ji}) that is regressed as a function of temperature.

$$k_{ij} = A_{ij} + B_{ij} / T + C_{ij} / T^2$$

$$\tag{4}$$

Temperature-dependent coefficients of the binary interaction parameter between nonelectrolytes are taken from Lee et al. [1] as listed in Table 2. Binary interaction parameters between CO₂ and SO₂ were fitted to vapor-liquid phase equilibrium data of the binary mixture [22,23] with average deviations of 4.1% for equilibrium pressures. For the association interaction, hydrogen-bonding energy U_{kl} and hydrogen-bonding entropy S_{kl} are needed between k-type donor and l-type acceptor together with the numbers of donor (d_i^k) and of acceptor sites (a_i^l) in a molecule of component *i*. Interaction parameters for self-association of water and crossassociation between water and CO₂ were determined by Lee et al. [1] and the values are given in Table 3. SO₂ is assumed to have only acceptor sites like CO₂. Considering the dissociation of SO₂ in aqueous solution, binary interaction parameters and association interaction parameters between water and SO₂ are determined in the present study after the ionic parameters of H₂SO₃ are set. Kihara potential parameters (ε_j , σ_j , and a_j) are needed for each guest component *j* in modeling the hydrate phase. In Table 4 the values for the guest components except for SO₂ are taken from Lee et al. [1] where the Kihara potential parameters were carefully determined by fitting to incipient hydrate-forming conditions of single and binary guests and solubility data in hydrate-containing two-phase equilibria together with structure-type dependent parameters.

2.2. Parameters for water and SO₂ system

Water and SO₂ are in equilibrium with H₂SO₃ as represented by

$$H_2O + SO_2 \leftrightarrow H^+ + HSO_3^-$$
(5)

The physical interaction parameters of ionic species are differently determined from those of molecular component, which are fitted to the pure property data, since a pure ion cannot exist.

Table 1	
Physical interaction parameters for NLF-HB equation of state.	

Comp.	r _a	$r_b/10^{-3}$	$r_c/10^{-3}$	ε_a [K]	$\varepsilon_b/10^{-2}$	$\varepsilon_c/10^{-2}$
Water ^a	1.770	-0.139	-2.140	112.97	8.46	12.60
CO_2^a	3.816	7.060	-23.20	84.99	-14.40	-12.70
CH_4^a	4.203	-0.679	8.720	53.80	7.200	-0.206
$C_2H_6^a$	5.366	1.230	2.670	75.70	-0.225	-0.102
$C_3H_8^a$	6.813	-0.445	4.980	84.87	0.981	-8.810
SO ₂	4.361	2.632	5.046	126.65	-14.61	-32.68
H^+	0.0125	_	_	80.11	-	_
HSO_3^-	6.176	_	_	80.11	-	_
Na ⁺	0.488	_	_	118.84	_	_
K^+	1.339	_	_	3.475	_	_
Cl-	3.375	_	_	234.91	-	_
Br	4.220	_	_	179.72	-	_
I-	5.736	—	—	141.43	—	—

^a Values from Lee et al. [1].

Download English Version:

https://daneshyari.com/en/article/200822

Download Persian Version:

https://daneshyari.com/article/200822

Daneshyari.com