

Contents lists available at [ScienceDirect](#)

Chemical Engineering Research and Design

journal homepage: [www.elsevier.com/locate/cherd](http://www.elsevier.com/locate/cherd)

IChemE

# Thermodynamic modeling of the dissociation conditions of hydrogen sulfide clathrate hydrate in the presence of aqueous solution of inhibitor (alcohol, salt or ethylene glycol)

Abolfazl Mohammadi<sup>a</sup>, Mehrdad Manteghian<sup>b,\*</sup>, Amir H. Mohammadi<sup>c,d</sup>, Arash Kamran-Pirzaman<sup>e</sup>

<sup>a</sup> Faculty of Engineering, University of Bojnord, Bojnord, Iran

<sup>b</sup> Department of Chemical Engineering, Tarbiat Modares University, Tehran, Iran

<sup>c</sup> Institut de Recherche en Génie Chimique et Pétrolier (IRGCP), Paris Cedex, France

<sup>d</sup> Thermodynamics Research Unit, School of Chemical Engineering, University of KwaZulu-Natal, Howard College Campus, King George V Avenue, Durban, South Africa

<sup>e</sup> Chemical Engineering Department, Mazandaran University of Science and Technology, Behshahr, Iran

## ABSTRACT

Hydrate dissociation conditions of hydrogen sulfide in the presence of aqueous solution of thermodynamic inhibitor (methanol, ethanol, ethylene glycol, NaCl, KCl and CaCl<sub>2</sub>) is modeled in this communication. A thermodynamic model is developed to correlate the hydrate dissociation conditions for the systems of H<sub>2</sub>S + water + salt (single and mixed salts of NaCl, KCl and CaCl<sub>2</sub>), H<sub>2</sub>S + water + alcohol (methanol or ethanol), H<sub>2</sub>S + water + ethylene glycol and H<sub>2</sub>S + water + mixed salt, and methanol/ethylene glycol. Extended-UNIQUAC (e-UNIQUAC) approach is used for modeling of the activity coefficient of water in aqueous phase. The structural parameters of e-UNIQUAC model are extracted from literature but interaction parameters of this model are obtained by fitting the model with experimental data. The results of the present model are in satisfactory agreement with experimental data.

© 2014 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

**Keywords:** Gas hydrates; Hydrogen sulfide; Thermodynamic inhibitor; Thermodynamic modeling; Phase equilibria

## 1. Introduction

Clathrate hydrates or gas hydrates are crystalline compounds formed by contacting the small molecules (typically gases and volatile liquids) as guests with water as host at low temperatures and high pressures. The hydrate structures are stabilized because of the physical forces between water/guest molecules. There is no chemical interaction between guest and water in hydrate formation process. The van der Waals forces are the only interaction between host/guest molecules (Sloan and Koh, 2008). Three typical types of hydrate crystalline structures are I, II and H with different numbers and sizes of cavities in each type (Sloan and Koh, 2008). Since 1934 when Hammerschmid found that hydrate formation causes plugging in

natural gas pipelines (Hammerschmid, 1934), many scientists have directed their research toward hydrate formation process and they have investigated the pressure/temperature (P/T) condition of this process (Bond and Russell, 1948; Cady, 1981; Carroll, 1990; Carroll and Mather, 1989; Javanmardi and Moshfeghian, 2000; Javanmardi et al., 2000, 2001; Mahadev and Bishnoi, 1999; Mahmoodaghdam, 2001; Majumdar et al., 2000; Mohammadi and Richon, 2009, 2010, 2012a,b; Ng and Robinson, 1983; Ng et al., 1985; Platteeuw and Van der Waals, 1959; Selleck et al., 1952; Von Stackelberg, 1949). Increasing the temperature, decreasing the pressure, and using the inhibitors in the system are traditionally considered for preventing the hydrate formation. Thermodynamic inhibitors (such as alcohol, glycol and salt) are compounds that decrease the hydrate

\* Corresponding author at: P.O. Box 14115-311, Iran. Tel.: +98 21 82883333.

E-mail address: [manteghi@modares.ac.ir](mailto:manteghi@modares.ac.ir) (M. Manteghian).

Received 15 May 2013; Received in revised form 6 January 2014; Accepted 7 January 2014

0263-8762/\$ – see front matter © 2014 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

<http://dx.doi.org/10.1016/j.cherd.2014.01.010>

### Symbols

$a, b$ and $d$	Langmuir constant parameters
$A, B, C, D, A', B'$	Henry constant parameters
AAD	average absolute deviation
$C_{ij}$	Langmuir constant
$f$	fugacity
$H$	Henry's constant
$I$	ionic strength
$K$	Boltzmann constant
$m_i$	molality
$M_w$	molecular weight
$N$	number of water molecule per cell
$N_{\text{cavity}}$	number of cavity types in the hydrate lattice
$N_A$	Avogadro's number
$P$	pressure
$q_i$	surface area parameter in UNIQUAC model
$r_i$	volume parameter in UNIQUAC model
$R$	gas constant
$S$	UNIQUAC parameter
$T$	temperature
$u_{ij}$	interaction parameter in UNIQUAC model
$v$	molar volume
$x$	mole fraction in liquid phase
$Z_i$	ionic charge

### Greek letters

$\Delta$	change in property
$\gamma$	activity coefficient
$\mu$	chemical potential
$\nu_m$	the number of cages of type $m$ per water molecule in the unit cell
$\theta$	UNIQUAC parameter
$\Phi$	UNIQUAC parameter
$\tau$	UNIQUAC parameter

### Superscripts and subscripts

$i, j, m$	counter
$H$	hydrate
$L$	liquid
$NH$	number of hydrate former
sat	saturation condition
$w$	water
$\beta$	empty hydrate phase

dissociation temperature at a specified pressure or increase the pressure needed for hydrate formation at a specified temperature (Mahmoodaghdam, 2001; Sloan and Koh, 2008). Modeling of these systems for predicting the hydrate dissociation condition is very important (Chen and Guo, 1996, 1998; Parrish and Prausnitz, 1972; Van der Waals and Platteeuw, 1959). Nevertheless, extra efforts are thought to be needed before these models could be applied for the cases when inhibitors are present at high concentrations or when a mixture of inhibitors is present.

Since the systems of water + gas + alcohol, water + gas + glycol, and water + gas + salt (electrolyte) are non-ideal, one must use an appropriate activity model for increasing the precision of the predictions. There are many models for predicting the activity coefficient of non-ideal systems. The most common of these models are NRTL, UNIFAC, and UNIQUAC but the precision of these models for predicting

electrolyte systems is low. Thomsen and his coworkers added the Debye-Hückel term to the UNIQUAC model in order to develop a new model called Extended-UNIQUAC model (Thomsen and Rasmussen, 1999; Thomsen et al., 1996). It is believed that the Extended-UNIQUAC (e-UNIQUAC) model can predict the activity coefficients of electrolyte systems with a satisfactory accuracy. In this study, the principle of equality of the fugacity of water in the hydrate and aqueous (liquid) phases for the system of water + hydrogen sulfide + inhibitor is first used to obtain the binary interaction parameters. After determining the binary interaction parameters for e-UNIQUAC model, the equilibrium conditions for the hydrate of hydrogen sulfide in the presence of aqueous solution of alcohol, salt and/or ethylene glycol are estimated.

## 2. Thermodynamic model

The equality of the fugacity of water in aqueous and hydrate phases is the basis of the proposed model, as mentioned earlier:

$$f_w^H = f_w^L \quad (1)$$

$f_w^H$  and  $f_w^L$  are the fugacity of water in hydrate and liquid phases, respectively. Fugacity of water in hydrate phase can be determined as (Sloan and Koh, 2008)

$$f_w^H = f_w^\beta \exp \left[ -\frac{\Delta\mu_w^{\beta-H}}{RT} \right] \quad (2)$$

In this equation,  $f_w^\beta$  is the fugacity of water molecules in the empty lattice of hydrate structure,  $R$  is the universal constant of gases,  $T$  is temperature, and  $\Delta\mu_w^{\beta-H}$  is the chemical potential difference of water in the filled and empty hydrate lattice that is given as (Mahmoodaghdam, 2001; Sloan and Koh, 2008)

$$\Delta\mu_w^{\beta-H} = \mu_w^\beta - \mu_w^H = RT \sum_{m=1}^{N_{\text{cavity}}} \nu_m \left( \ln \left( 1 + \sum_{j=1}^{NH} C_{jm} f_j \right) \right) \quad (3)$$

where  $\mu_w^\beta$  and  $\mu_w^H$  are the chemical potential of water in empty hydrate lattice and hydrate phase, respectively,  $\nu_m$  is the number of cages of type  $m$  per water molecule in the unit cell of hydrate,  $NH$  is the number of components that can form hydrate,  $N_{\text{cavity}}$  is the number of cavity types in the hydrate lattice (that is 2, 2 and 3 for structures I, II and H, respectively),  $C_{jm}$  is the Langmuir constant, and  $f_j$  represents the fugacity of guest component in the gas/vapor phase calculated by Peng-Robinson (PR) equation of state (Peng and Robinson, 1976). Due to the low vapor pressure of water and inhibitors, the amounts of water and inhibitor in gas phase are negligible and it is assumed that the gas phase consists of pure hydrogen sulfide only.

The Langmuir constant can be obtained from Eq. (4) (Ma et al., 2008; Munck et al., 1988):

$$C_{ij} = \frac{a_{ij}}{T} \exp \left( \frac{b_{ij}}{T} + \frac{d_{ij}}{T^2} \right) \quad (4)$$

The unit of  $T$  is Kelvin and the adsorption parameters ( $a_{ij}$ ,  $b_{ij}$  and  $d_{ij}$ ) are determined by fitting the model with experimental

Download English Version:

<https://daneshyari.com/en/article/10385045>

Download Persian Version:

<https://daneshyari.com/article/10385045>

[Daneshyari.com](https://daneshyari.com)