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Hydrate dissociation conditions for gas mixtures containing carbon dioxide, hydrogen, hydrogen sulfide, nitrogen, and hydrocarbons using SAFT

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Abstract

A new method, a molecular thermodynamic model based on statistical mechanics, is employed to predict the hydrate dissociation conditions for binary gas mixtures with carbon dioxide, hydrogen, hydrogen sulfide, nitrogen, and hydrocarbons in the presence of aqueous solutions. The statistical associating fluid theory (SAFT) equation of state is employed to characterize the vapor and liquid phases and the statistical model of van der Waals and Platteeuw for the hydrate phase. The predictions of the proposed model were found to be in satisfactory to excellent agreement with the experimental data.

Keywords: Hydrate; SAFT; Equation of state; Phase equilibria; Gas mixture

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1. Introduction

Gas hydrates are crystalline inclusion compounds that consist of water and at least one other compound, usually small molecules like methane, nitrogen, and carbon dioxide. Water molecules are connected by hydrogen bonds and form various types of cavities. Low molecular-weight gas molecules are captured into these cavities. Hydrates are non-stoichiometric compounds that form generally in either of three distinct structures, namely structures I, II, and H, which differ in cavity size and shape [1].

It is of great importance to understand the hydrate dissociation conditions for the rational and economic design of processes in the chemical, oil, gas, and other industries where hydrate formation is encountered. Hence, obviously, predicting the conditions in which hydrates are dissociated would be valuable. van der Waals and Platteeuw [2] were the first who developed the basic statistical theory for computation of gas hydrate dissociation pressure. Later, Parrish and Prausnitz [3] developed a generalized method based on the statistical model of van der Waals and Platteeuw [2] to predict the hydrate dissociation conditions in the presence of pure water. To expand the range of applicability, Ng and Robinson [4], Holder *et al.* [5] and John *et al.* [6] improved this model. To predict the effects of inhibitors on the hydrate formation conditions, Hammerschmidt developed the first method used in the industry for predicting the inhibiting effect of methanol [7]. Anderson and Prausnitz [8] developed a method based on the identity of fugacities to predict hydrate dissociation conditions with methanol. Englezos *et al.* presented a methodology based on the Trebble–Bishnoi equation of state to calculate the inhibition effects of methanol [9,10].

So far, there are various thermodynamic models dealing with the phase equilibria for hydrate systems developed or modified to accommodate specific requirements appeared in a variety of hydrate mixtures [2–13]. In short, in these

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List of symbols

A	Helmholtz free energy (J)
C	Langmuir constant (MPa^{-1})
C_p	heat capacity ($\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)
d	hard-sphere diameter (1×10^{-10} m)
f	fugacity (MPa)
g	radius distribution function
k	Boltzmann constant ($\mathrm{J \cdot K^{-1}}$)
m_i	effective number of segments in component i ($i = 1, 2, \ldots, n$)
M	number of associate sites
n	number of components in mixture
nc	number of hydrate forming substances
N	number of molecules
N_{A}	Avogadro constant ($6.02217 \times 10^{23}\ \mathrm{mol}^{-1}$)
r	radial distance from center of hydrate cavity (m)
R	gas constant ($8.3143\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$)
R_m	type m spherical cavity radius (m)
P	pressure (MPa)
T	absolute temperature (K)
v	molar volume ($\mathrm{m^3 \cdot mol^{-1}}$)
$W(r)$	cell potential function (J)
x_i	mole fraction of component i in liquid phase ($i = 1, 2, \ldots, n$)
X_i^A	mole fraction of molecule i not bonded at site A
y_i	mole fraction of component i in vapor phase ($i = 1, 2, \ldots, n$)
Z	compressibility factor

Greek letters

β	$1/kT$
ε/k	energy parameter of dispersion (K)
ε^{AB}/k	energy parameter of association between sites A and B (K)
κ^{AB}	bonding volume
Δ^{AB}	association strength between sites A and B
μ	chemical potential
ρ	molar density ($\mathrm{mol \cdot m^{-3}}$)
ρ_n	number density ($\mathrm{m^{-3}}$)
σ	soft-sphere diameter (1×10^{-10} m)
v_m	number of cavities of type m

Subscripts

i, j, k	components
m	type of cavity
w	water

Superscripts

assoc	association interaction
A, B	association site
chain	hard-sphere chain
disp	dispersion interaction
hs	hard-sphere
res	residual term
H	hydrate
L	liquid
L°	pure liquid water
MT	empty lattice
°	reference conditions of 273.15 K and zero absolute pressure
V	vapor

traditional models as well as ones developed in recent years, most of them applied either cubic equations of state or activity coefficient models, which all are empirical or semi-empirical models, for vapor and liquid phases. The parameters in the models usually have little physical meaning. The statistical associating fluid theory (SAFT) based on Wertheim's first-order thermodynamic perturbation theory for associating fluid [14] has been developed very rapidly in recent years [15]. The molecular-based equations of states with salient physical meaningful parameters are generally more reliable than empirical models for extrapolation and prediction. Consequently, the SAFT has been used to calculate successfully a wide variety of the thermodynamic properties and phase equilibria for industrially important fluids containing *n*-alkane mixtures, alcoholic aqueous solutions and other mixture systems [15–18]. Recently, we first successfully used the SAFT equation in conjunction with the van der Waals–Platteeuw model to predict the thermodynamic inhibiting effect of methanol and glycols on single gas hydrate formation [19]. It is noted that the vapor and liquid phases were modeled using SAFT, and the solid hydrate phase was modeled with the van der Waals–Platteeuw model. In the present work, with predictive success of our previous work, the above model was extended to the prediction of the hydrate dissociation conditions for binary gas mixtures.

2. Thermodynamic model

For the three phase vapor (V)/liquid (L)/solid hydrate (H) system, the thermodynamic equilibrium condition is described by:

$$f_i^{\mathrm{L}} = f_i^{\mathrm{V}} \quad (i = 1, \ldots, N), \tag{1}$$

$$f_j^{\mathrm{H}} = f_j^{\mathrm{V}} \quad (j = 1, \ldots, n_c), \tag{2}$$

where f is the fugacity of component i or j; N is all the components; n_c is the hydrate forming components including water.

In the above equations, the fugacities in vapor, liquid and solid phases may be calculated using a suitable thermodynamic model. In this work, the SAFT equation of state is employed for vapor and liquid phases. The van der Waals–Platteeuw model is used for the solid hydrate phase.