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Experimental measurement of phase equilibrium for gas hydrates of refrigerants, and thermodynamic modeling by SRK, VPT and CPA EOSs

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ABSTRACT

In this study, three-phase equilibrium conditions of hydrate-liquid–vapor, (VL_WH), were experimentally determined for chlorodifluoromethane and 1,1,1,2-tetrafluoroethane gas hydrates at temperatures ranging from (278 to 290) K and (280 to 285) K respectively, at pressures ranging from (0.2 to 0.8) MPa. Then the different models were presented for estimating of the hydrate dissociation conditions of chlorodifluoromethane, 1,1,1,2-tetrafluoroethane and 1,1-difluoroethane refrigerants. The cubic simple equations of state (SRK and VPT) and the cubic plus association equation of state (CPA) were employed for modeling the vapor and liquid phases, also van der Waals–Platteeuw statistical model was used for the solid hydrate phase. In this paper, the binary interaction parameters of classic and modified mixing rules were optimized by using two-phase equilibrium data (VL_WH). The Kihara potential parameters in each refrigerant were estimated using obtained experimental equilibrium data (VL_WH) and based on the optimization scheme by the Nelder Mead optimization method. The agreement between the experimental and the predicted pressure is acceptable by using these models. The average deviation of models for chlorodifluoromethane, 1,1,1,2-tetrafluoroethane, and 1,1-difluoroethane hydrates is about 3%, 4.3%, and 3.6%, respectively.

1. Introduction

Clathrate hydrates are crystalline solid compounds. These crystals are composed of hydrogen-bonded water molecules (host molecules), and some other gas species (guest molecules). Water molecules form a cage-like structure at high pressure and low temperature conditions. The guest molecules such as methane, ethane and others hydrocarbons are trapped in the lattice and stabilize the structure [1–2].

In recent years, gas hydrates have been increasingly involved in the development of energy storage and environmental-related technologies. For purpose of problem solving related to natural gas pipelines by hydrate formation, the scientific and technical study of hydrate-related problems are urgent. These subjects contain kinetics, thermodynamics and also mass and heat transfer of hydrate formation and dissociation and using of clathrate hydrate in gas transportation, energy storage and water desalination [1–4].

Gas hydrates of refrigerants have been proposed in the past decade. Refrigerant hydrates can be formed at a temperature above the freezing point of water and under different pressures [3–7]. In general the most common refrigerants used in the industry belong to the three categories of CFC (chlorofluorocarbon), HCFC (hydrochlorofluorocarbon) and HFC (hydrofluorocarbon). Development of alternatives to replace CFCs is necessary to protect the world's environment. Hydrofluorocarbons (HFCs) are a group of compounds containing no chlorin and are selected as good candidates for replacing of CFC [7,8]. Refrigerant gas hydrates, which are formed above 273.15 K at moderate pressure, can be considered as promising materials for energy storage and desalination, and they are especially suitable for air conditioning systems [3]. Refrigerant hydrates have the proper melting temperature ranging from (277.15 to 280.15) K, high volumetric storage density about (302.4 to 464) kJ/kg, and fair heat transfer coefficients [9]. The cooling technology was expanded by Ogawa et al. [10] and Watanable et al. [11] based on gas hydrate formation and dissociation

Gas hydrates are divided into three distinct structures, I, II, and H, which differ in cavity size and shape [1–3]. The chlorodifluoromethane ($CHClF_2$, HCFC22) hydrate is characterized by crystal structure I. Chlorodifluoromethane molecules are too large to fit into the small cavities, therefore they occupy only large cavities that the hydrate crystals are stabilized [12,13]. The 1,1,1,2-tetrafluoroethane (CH_2FCF_3, HFC134a) refrigerant can form hydrate structure II and fill big cavities of this structure [9]. The 1,1-difluoroethane (CHF_2CH_3, HFC152a) hydrate is structure I [9,14].

To use refrigerant gas hydrates in cool storage systems, it is important to have reliable equilibrium data for these systems. Linag et al. presented the equilibrium data of 1,1,1,2-tetrafluoroethane, 1,1-dichloro-1-fluoroethane and 1,1-difluoroethane hydrate dissociation [9]. Also the equilibrium conditions of difluoromethane

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Nomenclature

f_i^v	fugacity of component i in the vapor phase
f_i^L	fugacity of component i in the liquid phase
f_i^H	fugacity of component i in the hydrate phase
f_i	fugacity of a gas component i
T	temperature (K)
T_0	ice point of water (K)
P	pressure (Pa)
R	gas constant ($\text{Pa} \cdot \text{L} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
v	molar volume ($\text{L} \cdot \text{mol}^{-1}$)
a	energy term in SRK and VPT EoSs ($\text{Pa} \cdot \text{L}^2 \cdot \text{mol}^{-2}$)
b	co-volume parameter in SRK and VPT EoSs ($\text{L} \cdot \text{mol}^{-1}$)
c	co-volume parameter in VPT EoS ($\text{L} \cdot \text{mol}^{-1}$)
P_c	critical pressure (Pa)
T_c	critical temperature (K)
T_r	reduced temperature
Z_c	critical compressibility factor
a^c	energy term for mixture – classic term ($\text{Pa} \cdot \text{L}^2 \cdot \text{mol}^{-2}$)
a^A	energy term for mixture – asymmetric term ($\text{Pa} \cdot \text{L}^2 \cdot \text{mol}^{-2}$)
b_{mix}	co-volume term for mixture ($\text{L} \cdot \text{mol}^{-1}$)
k_{ij}	binary interaction parameter
l_{pi}	binary interaction parameter in modified mixing rule
A_i	site A in molecule i
B_j	site B in molecule j
X_{Ai}	the mole fraction of the molecule i not bonded at site A
x_i	the superficial mole fraction of component i
n_j	mole fraction of substance j
$g(\rho)^{ref}$	radial distribution function
v_m	number of type m cavities per water molecule
C_{jm}	Langmuir constant
K	Boltzmann constant ($\text{J} \cdot \text{K}^{-1}$)
$w(r)$	spherically symmetric cell potential function
Z	coordination number of the cavity
$O.F$	objective function
Greek letters:$\Delta^{A_iB_j}$	
	association strength between site A and site B
$\varepsilon^{A_iB_j}$	association energy between site A and site B ($\text{J} \cdot \text{mol}^{-1}$)
$\beta^{A_iB_j}$	volume of interaction between site A and site B
α	hard core radius (A°)
σ	collision diameter (A°)
ε	depth of energy ($\text{J} \cdot \text{mol}^{-1}$)
ρ_i	molar density of component i ($\text{mol} \cdot \text{L}^{-1}$)
ω	acentric factor

refrigerant were given by Imai et al. [15]. Formation conditions of several refrigerant gas hydrates have been studied; however, there is not much information on the hydrate phase boundaries, especially for those with three-phase (ice + hydrate + vapor) equilibrium.

In this study, a series of equilibrium tests containing three-phase of liquid water–hydrate–vapor for chlorodifluoromethane and 1,1,1,2-tetrafluoroethane were performed over temperatures ranging from (278.6 to 289.5) K and (280.9 to 285.0) K and pressures ranging from (0.2 to 0.8) and (0.3 to 0.8) MPa, respectively. Also the experimental dissociation data were used for optimizing the Kihara potential parameters in the hydrate phase model, and a set of Kihara potential parameters of these refrigerant hydrates were obtained based on the Nelder Mead optimization method. The hydrate formation conditions were calculated by Van der Waals–Platteeuw statistical model for the hydrate phase, and using both the classic and associated equations of state for vapor and liquid phases. The cubic equations of state play an important role in the phase equilibrium in mixtures.

Most phase equilibrium calculations are accomplished using the classic equation of state. Despite simplicity, Soave–Redlich–Kwong (SRK) and Valderama–Patel–Teja (VPT) equations of state have high applicability in industry. Using the modified Van der Waals mixing rule for simple equations of SRK and VPT is one of the novel features of this study. Also applicability of the Cubic-Plus-Association (CPA) equation with a simple mixing rule (Van der Waals) was evaluated to predict the formation conditions of hydrate. CPA equation of state describes systems containing polar compounds successfully.

2. Experimental

2.1. Apparatus and materials

The experiments were conducted in a system consisting of a reactor, a jacket for heat transfer, and a data acquisition system. The apparatus is shown in figure 1.

Hydrate decomposition was conducted in a stirred batch reactor that is capable of operating pressures between 0 and 9 MPa; the volume of the reactor is 990 cm^3. The reactor is equipped by a jacket which is used for heating and cooling. The temperature of jacketed cell is controlled by flowing ethanol in the jacket. The cell pressure was measured by a Druck PTX1400 pressure transmitter (0 to 20 MPa, ±0.01). The temperature was measured using PT100 thermometers (±0.1 K). Pressure and temperature readings were acquired by a data acquisition system which was driven by a personal computer. For mixing, the experimental cell includes a magnetically, which is coupled stirrer shaft and a stirring motor speed controller. The experiments were conducted at a stirrer speed of 910 rpm. The purities and suppliers of materials (hydrate formers) are provided in table 1.

2.2. Experimental procedures

Firstly, the hydrate formation reactor was evacuated and 650 cm^3 of distilled water was charged to the reactor cell. Then the gas hydrate former was fed into the cell from the liquefied gas reservoir. The heterogeneous mixture of two liquid and gas phases, distilled water and liquefied HCFC22 (or HFC134a), were mixed at 283 K with mechanical agitation at 910 rpm. Then the mixture was slowly cooled at 0.3 $\text{K} \cdot \text{min}^{-1}$. The pressure and temperature of two liquid phases were recorded. After the hydrate formation (when the pressure of reactor was not changed), the mixture was slowly heated at 0.2 $\text{K} \cdot \text{min}^{-1}$ until the hydrate crystals disappear. The intersection of cooling and heating curves was recorded as the pressure and temperature of hydrate formation condition. The attainment time of equilibrium state was about 8 h for each experiment. The experiments were performed three times and the obtained equilibrium data are reliable and confirmable. The quantity of uncertainty on pressure and temperature measurements is about ±0.01 MPa and ±0.1 K respectively.

3. Thermodynamic modeling

3.1. Liquid and vapor phases modeling

At phase equilibrium, the fugacity or chemical potential of species in the various phases must be equal. For three-phase