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Statistical-Thermodynamics Modeling of Clathrate-Hydrate-Forming Systems Suitable as Working Media of a Hydrate-Based Refrigeration System

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Abstract Attempts to develop a novel hydrate-based refrigeration system have been carried out in recent years. It was reported that the vapor/liquid/liquid/hydrate four-phase equilibrium conditions in the systems of cyclopentane and water plus difluoromethane satisfy the required conditions of the working media of a hydrate-based refrigeration system for residential air-conditioning use. When a statistical-thermodynamic model is applied to the above-mentioned hydrate-forming systems, the Kihara potential parameters of these guest substances need to be determined. In this study, an attempt was made to determine the Kihara potential parameters of difluoromethane and cyclopentane based on phase equilibrium data for difluoromethane + water, cyclopentane + water, and difluoromethane + cyclopentane + water systems. The absolute average deviations of the predicted equilibrium pressure at a given temperature from the corresponding experimental values are 0.043 for the HFC-32 + water system, 0.12 for the cyclopentane + water, and 0.031 for the HFC-32 + cyclopentane + water.

Keywords Clathrate hydrate · Heat pump · Phase equilibrium · Refrigeration

1 Introduction

Clathrate hydrates are crystalline solid compounds that consist of water molecules forming cages via a hydrogen-bonding network containing guest molecules. Depending on the size and shape of the guest molecules, water molecules form different cages that combine to form the hydrates of the three different crystallographic structures, structures I, II, and H. Recently, a novel design of a heat pump or refrigeration

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system utilizing formation and dissociation of a hydrate was proposed [1]. This system is expected to extract heat from a cooler region (i.e., a space to be refrigerated) by endothermic hydrate dissociation at a lower pressure and to discharge heat to a warmer region by exothermic hydrate formation at a higher pressure. The performance of this hydrate-based refrigeration system may exceed that of the conventional vapor-compression type refrigeration system [1].

To apply this hydrate-based refrigeration technology to residential air-conditioning systems, their working media must satisfy the following characteristics:

(1) It must have a wide temperature range of phase equilibrium conditions.
(2) The temperature of the hydrate formation must be higher than ∼298 K, or more favorably higher than 303 K.
(3) The pressure of the hydrate formation must be less than 5 MPa.

The high pressure or low temperature required to form hydrates is a major obstacle to developing this hydrate-based refrigeration system. Specifically, an increase in the hydrate equilibrium temperature is the key for development of the refrigeration system. Several experimental phase equilibrium studies in the literature have reported an increase in the hydrate equilibrium temperature by searching for the appropriate guest substances and by selecting the appropriate combination of guest substances [2–5]. Imai et al. [2] was the first to report phase equilibrium conditions of hydrate-forming systems that may be practically used as the working media of the refrigeration system. They reported phase equilibrium pressure–temperature conditions for the four phases, HFC-32-rich vapor (V) + cyclopentane-rich liquid (L_g) + water-rich liquid (L_w) + hydrate (H), as illustrated in Fig. 1. The pair of HFC-32 (difluoromethane; CH_2F_2) and cyclopentane is one of the promising guest candidates suitable for a hydrate-based refrigerant. No thermodynamic modeling study has been reported for candidates suitable for a hydrate-based refrigeration system. This article reports a thermodynamic modeling study of hydrate-forming systems containing HFC-32

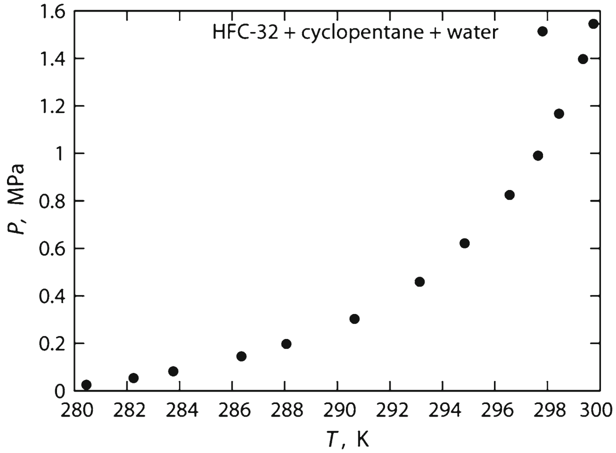


Fig. 1 Experimental data for V + $L_g + L_W +$ H four-phase equilibrium in the system of HFC-32 + cyclopentane + water [2]

and cyclopentane as guest substances based on a statistical thermodynamic model developed by van der Waals and Platteeuw [6] and Parrish and Prausnitz [7]. We determined the Kihara parameters of HFC-32 and cyclopentane by comparing model predictions to relevant experimental phase equilibrium data.

2 Modeling

For calculating the equilibrium temperature–pressure conditions for the guest-rich vapor + water-rich liquid or ice + hydrate three phases, or the guest-rich vapor + guest-rich liquid + water-rich liquid or ice + hydrate four phases, this study generally follows the approach of Parrish and Prausnitz [7] and Chap. 5.1 of [8].

The temperature is first specified at an arbitrary value in the range from 273 K to 295 K over which the experimental data are available, and then the pressure is also set at a prescribed value. The selection of this pressure is arbitrary, but in this study we set the pressure at 5 MPa as an initial value. Under this temperature–pressure condition, the chemical potentials of water in the hydrate and water-rich liquid phases are calculated. If the chemical potentials coincide within eleven digits, the temperature and pressure are determined to be an equilibrium condition. If equality of the chemical potentials was not obtained, a similar calculation of the chemical potentials was repeated with a new set value of the pressure until the equilibrium condition was determined.

The difference between the chemical potential of water in the hydrate phase and that in the hypothetical empty hydrate lattice ($\Delta\mu_{\mathrm{w}}^{\mathrm{H}}$) is expressed as

$$\Delta\mu_{\mathrm{w}}^{\mathrm{H}} = -RT\sum_{i}\nu_i \ln\left(1-\sum_{k}\theta_{ki}\right), \tag{1}$$

where R is the universal gas constant, T is the absolute temperature, ν_i is the number of type i cavities per water molecule in the hydrate, and θ_{ki} is the fraction of the type i cavity occupied by the guest molecule k. This fractional occupancy of the cavity is expressed as

$$\theta_{ki} = \frac{C_{ki} f_k}{1+\sum_j C_{ji} f_j}, \tag{2}$$

where f_k is the fugacity of the guest component k and C_{ki} is the Langmuir constant of component k in cavity i. The Soave–Redlich–Kwong equation of state [9] was used to calculate the fugacity of the guest substances in the vapor and liquid phases. The Langmuir constant is expressed as

$$C_{ki} = \frac{4\pi}{k_{\mathrm{B}}T}\int_{0}^{R-a}\exp\left(-\frac{\omega_{ki}(r)}{k_{\mathrm{B}}T}\right)r^2\mathrm{d}r, \tag{3}$$

where k_B is the Boltzmann constant, r is the distance from the center of the cavity, R is the empty cavity radius, $\omega_{ki}(r)$ is the cell potential, and a is the core radius defined in the Kihara potential. The cell potential is expressed as

$$\omega_{ki}(r) = 2z\varepsilon\left[\frac{\sigma^{12}}{R^{11}r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^{6}}{R^{5}r}\left(\delta^{4} + \frac{a}{R}\delta^{5}\right)\right], \tag{4}$$

$$\delta^N = \frac{1}{N}\left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N}\right], \tag{5}$$

where z is the coordination number of the cavity, σ is the distance between the cores at zero potential energy, and ε is the depth of the intermolecular potential well in the Kihara potential. The Kihara potential is expressed as follows:

$$\phi(r) = \begin{cases} \infty & \text{for} \quad r \le 2a \\ 4\varepsilon\left[\left(\frac{\sigma}{r-2a}\right)^{12} - \left(\frac{\sigma}{r-2a}\right)^{6}\right] & \text{for} \quad r > 2a \end{cases} \tag{6}$$

where $\varphi(r)$ is the intermolecular potential energy.

On the other hand, the difference between the chemical potential of water in the ice (α) or the liquid (L) and that in the hypothetical empty hydrate lattice ($\Delta\mu_w^{\alpha/L}$) is expressed as

$$\frac{\Delta\mu_w^{\alpha/L}}{RT} = \frac{\Delta\mu_w^0}{RT} - \int_{T_0}^{T}\left(\frac{\Delta h_w}{RT^2}\right)dT + \int_0^P\left(\frac{\Delta v_w}{RT}\right)dP - \ln\gamma_w x_w, \tag{7}$$

where P is the pressure, $\Delta\mu_w^0$ is the difference in the chemical potential of water between the empty hydrate lattice and ice at T_0 (273.15 K), Δh_w and Δv_w are the differences in the enthalpy and the volume between the empty hydrate and pure ice/liquid water phases, respectively, γ_w is the activity coefficient, and x_w is the mole fraction of water in the ice/liquid water phase. The molar enthalpy difference between an empty hydrate lattice and liquid water is described as follows:

$$\Delta h_w = \Delta h_w^0 + \int_{T_0}^{T}\Delta C_{PW}dT, \tag{8}$$

where Δh_w^0 is the molar enthalpy difference between the empty hydrate lattice and ice at the ice point and zero pressure, and ΔC_{pw} is the heat-capacity difference between the empty hydrate lattice and the pure liquid water phase. ΔC_{pw} is also temperature-dependent and is given by

$$\Delta C_{pw} = \Delta C_{pw}^0 + b(T - T_0), \tag{9}$$

Table 1 Parameters used for the hydrate-phase equilibrium calculations

	Structure				
	I			II	
$\Delta\mu^0_{\mathrm{W}}(\mathrm{J \cdot mol^{-1}})$	1263.60			883.82	
$\Delta h^0_{\mathrm{W\,liquid}}(\mathrm{J \cdot mol^{-1}})$	−4623.27			−4987.27	
$\Delta h^0_{\mathrm{W\,ice}}(\mathrm{J \cdot mol^{-1}})$	1389.08			1025.08	
$\Delta\nu_{\mathrm{W,liquid}}(\mathrm{cm^3 \cdot mol^{-1}})$	4.6			5.0	
$\Delta\nu_{\mathrm{W,ice}}(\mathrm{cm^3 \cdot mol^{-1}})$	3.0			3.4	
$\Delta C^0_{\mathrm{PW}}(\mathrm{J \cdot mol^{-1} \cdot K^{-1}})$			−38.12		
b			0.141		
Cavity type	Small	Large		Small	Large
R (nm)	0.395	0.433		0.391	0.473

where ΔC^0_{pw} is the value of the reference state heat-capacity difference and b is the constant reported by Parrish and Prausnitz [7].

Table 1 specifies the following parameters used in this study: the difference in the chemical potential of water between the empty hydrate lattice and ice, $\Delta\mu^0_{\mathrm{w}}$; the molar enthalpy differences between the empty hydrate lattice and pure ice/liquid water phases, Δh^0_{w}; the differences in the volume between empty hydrate and pure ice/liquid water phases, $\Delta\nu_{\mathrm{w}}$; the value of the reference state heat-capacity difference between the empty hydrate lattice and the pure liquid water phase, ΔC^0_{PW}; and the average cavity radius, R. The properties were reported by Sloan [8].

3 Results and Discussion

There are three different Kihara parameters to be determined for a guest substance: the spherical hard core radius (a), the zero potential energy distance (σ), and the maximum attractive potential (ε). We determined the value of a based on the second virial coefficient of HFC-32 and cyclopentane based on the method described by Tee et al. [10]. The new Kihara parameters of σ and ε for HFC-32 and cyclopentane were determined by fitting the model predictions to experimental data. In this study, we defined the absolute average deviation (*AAD*) as follows:

$$AAD = \frac{1}{n}\sum_{i=1}^{n}\left|\frac{P_{i,\mathrm{cal}} - P_{i,\mathrm{exp}}}{P_{i,\mathrm{exp}}}\right|, \tag{10}$$

where n is the number of data points, $P_{i,\mathrm{cal}}$ is the calculated equilibrium pressure, and $P_{i,\mathrm{exp}}$ is the experimentally measured equilibrium pressure. In the fitting procedure, σ is fixed at an arbitrary value in the range from 0.17 nm to 0.34 nm for HFC-32, and from 0.25 nm to 0.37 nm for cyclopentane. The ε value, which provides the smallest *AAD* in combination with the fixed σ value is then determined. As a result, in each

Table 2 Kihara parameters for methane and nitrogen used in this study

Guest substance	a (nm)	σ (nm)	ε/k_B (K)
Methane	0.03834	0.31650	154.54
Nitrogen	0.03526	0.30124	125.15

The parameters were reported by Sloan [8]

hydrate-forming system, an infinite set of $\sigma-\varepsilon$ pairs can be determined by comparison of the model predictions to a set of experimental equilibrium data. If there are two sets of experimental data for the two hydrate-forming systems that commonly contain a guest substance, the two infinite sets may have an intersection. The σ–ε pair at the intersection may be considered as an optimal pair, because the experimental data in the two different hydrate-forming systems may be well reproduced with the $\sigma-\varepsilon$ pair. In this study, the effect of the solubility of HFC-32 and cyclopentane in liquid water on the water chemical potential in the liquid water phase was neglected, because the solubility is known to be negligibly small [11,12].

To determine the Kihara parameters for cyclopentane, we adopted the following experimentally measured equilibrium data:

(1) cyclopentane + water system (V–L_w–H three-phase equilibrium) [13]
(2) cyclopentane + methane + water system (V–L_g–L_w–H four-phase equilibrium) [14]
(3) cyclopentane + methane + nitrogen + water system (V–L_g–L_w–H four-phase equilibrium) [14]

We utilized the previously determined Kihara parameters for methane and nitrogen as listed in Table 2. Figure 2 indicates the infinite set of $\sigma-\varepsilon$ pairs of cyclopentane that were determined by comparison of the modeling results and experimental phase equilibrium data obtained in the previously mentioned three systems. As the infinite set was obtained by determining the ε value that provides the smallest *AAD* at a prescribed σ value (as described in the above paragraph), the experimental data can be well reproduced using any σ–ε pair of the infinite set. As seen in Fig. 2, the infinite sets of σ–ε pairs, each obtained by modeling using the experimental data of each of the three systems, almost overlap, and the experimental data can be well reproduced by any $\sigma-\varepsilon$ pair of the three infinite sets. Thus, in the following part of this article, we utilize the infinite set obtained for the cyclopentane + water system (and the infinite sets obtained for the methane and nitrogen systems are disregarded).

To determine the Kihara parameters for HFC-32, we adopted the following experimentally measured equilibrium data:

(1) HFC-32 + water system (V–L_w–H three-phase equilibrium) [2]
(2) HFC-32 + cyclopentane + water system (V–L_g–L_w–H four-phase equilibrium) [2]

We first tested the four sets of Kihara parameters for cyclopentane as listed in Table 3 that are selected from the infinite set shown in Fig. 2. Figure 3 shows an infinite set of $\sigma-\varepsilon$ pairs for HFC-32 fitted by the equilibrium data in the above-mentioned two

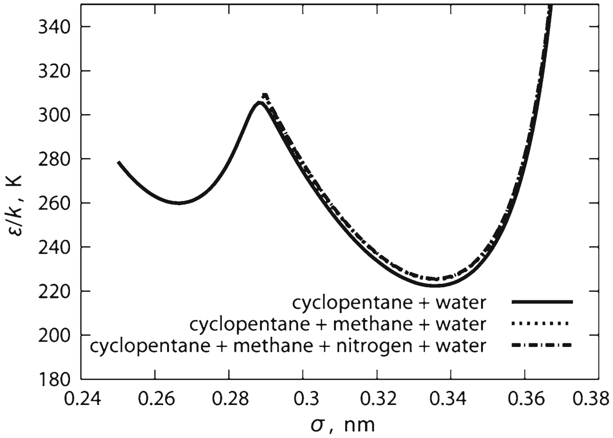


Fig. 2 Infinite sets of Kihara parameters determined by fitting the model predictions to the hydrate-phase equilibrium data in the systems containing cyclopentane

Table 3 Sets of Kihara parameters for cyclopentane used in this study

	Set 1	Set 2	Set 3	Set 4
a (nm)	0.08968	0.08968	0.08968	0.08968
σ (nm)	0.3200	0.3400	0.3500	0.3600
ε/k_B (K)	236.9	226.7	239.7	281.2

hydrate-forming systems. The infinite set of σ–ε pairs for HFC-32, with which the phase-equilibrium data in the HFC-32 + water system were reproduced, was determined in a relatively wide range of σ and ε. The set of σ–ε pairs for HFC-32 with which the equilibrium data in the HFC-32 + cyclopentane + water system were reproduced was determined in a limited range of σ from 0.291 nm to 0.299 nm. As seen in Fig. 3, these two sets have no intersection. This indicates that there is no appropriate Kihara parameter set for HFC-32 with which the equilibrium data in the two hydrate-forming systems can be satisfactorily reproduced. We considered that the optimal Kihara parameters might not have been determined because the vapor–liquid equilibrium of HFC-32 and cyclopentane cannot be accurately calculated. Our attempt to improve the modeling is described below.

In the calculations described in the above paragraphs, we calculated the vapor–liquid equilibrium conditions for HFC-32 and cyclopentane by utilizing the Soave–Redlich–Kwong equation of state together with the following simple combining rule:

$$a_{ij} = \sqrt{a_{ii}a_{jj}}, \tag{11}$$

where a_{ii} is the constant for the pure component obtained from the critical properties and a_{ij} is the constant defined in the Soave–Redlich–Kwong equation of state as follows:

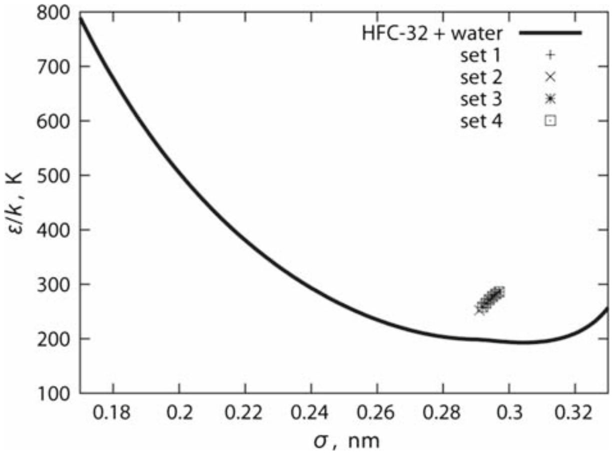


Fig. 3 Infinite sets of Kihara parameters determined by fitting the model predictions to the hydrate-phase equilibrium data in the systems containing HFC-32

$$P = \frac{RT}{\underline{V} - b} - \frac{a}{\underline{V}(\underline{V} + b)}, \tag{12}$$

$$a = \sum_{i=1}^{n} \sum_{j=1}^{n} y_i y_j a_{ij}, \tag{13}$$

$$b = \sum_{i=1}^{n} y_i b_i, \tag{14}$$

where R is the universal gas constant, T is the temperature, $\underline{V}$ is the molar volume, y_i is the mole fraction of species i, and b_i is the constant obtained from the critical properties. For details of the equation of state, see [15].

We then introduced the following combining rule to improve the calculation of the vapor-liquid equilibrium conditions for HFC-32 and cyclopentane:

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - k_{ij}), \tag{15}$$

where k_{ij} is the binary interaction parameter.

The value of k_{ij} should generally be determined by fitting measured vapor–liquid equilibrium data. However, there are no experimental vapor–liquid equilibrium data for HFC-32 and cyclopentane reported in the literature. Thus, in this study, we treated k_{ij} as a fitting parameter to match the model predictions of the hydrate-phase equilibria with the corresponding experimental data. Figure 4 indicates that the calculated vapor–liquid equilibrium for HFC-32 and cyclopentane at the temperature of 286.35 K varied with the binary interaction parameter. With the binary interaction parameter k_{ij} higher than 0.17, a set of σ–ε pairs for the HFC-32 + cyclopentane hydrate was calculated over a wider range of σ. Figure 5 shows the parameter sets of the σ–ε pairs for HFC-32

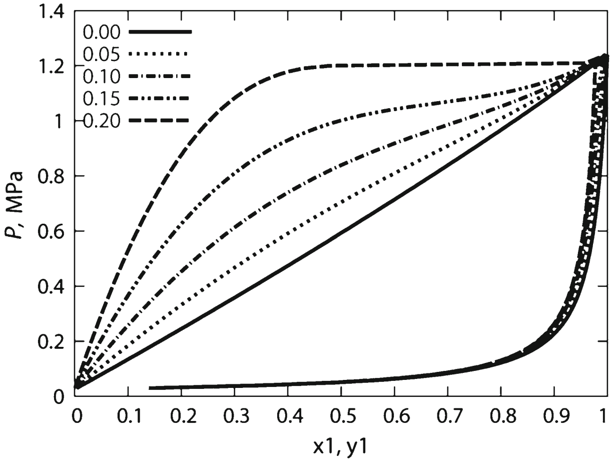


Fig. 4 Predicted vapor–liquid equilibrium for the HFC-32 + cyclopentane system by varying the binary interaction parameter

that were obtained using the fixed values of $\sigma = 0.3400$ nm and $\varepsilon/k_B = 226.7$ K for cyclopentane (set 2 in Table 3), and the binary interaction parameter, $k_{ij} = 0.20$. As a result of the fitting procedure with varying σ for HFC-32 from 0.17 nm to 0.34 nm, σ for cyclopentane from 0.25 nm to 0.37 nm, and k_{ij} from 0.15 to 0.21, we determined the optimal set to minimize the summation of the *AAD* in the three hydrate-forming systems, i.e.,

$$AAD_{\text{sum}} = AAD_{\text{HFC}-32} + AAD_{\text{cyclopentane}} + AAD_{(\text{HFC}-32+\text{cyclopentane})}, \tag{16}$$

The determined Kihara parameters for HFC-32 and cyclopentane and their binary interaction parameters are shown in Table 4. Figure 6 compares the experimentally measured equilibrium data and the relevant calculated results by the parameters newly determined in this study.

The validity of the newly determined Kihara parameters for HFC-32 and cyclopentane was examined in terms of the crystallographic structures of the stable hydrates that were predicted using the Kihara parameters. The Kihara parameters were determined on the basis of the assumption that the crystallographic structures of the HFC-32 simple hydrate, cyclopentane simple hydrate, and HFC-32 + cyclopentane double hydrate were structure I, structure II, and structure II, respectively. We calculated the equilibrium pressures at selected temperatures for the specified crystallographic structures of the hydrates. The hydrate with the lowest equilibrium pressure is considered as the stable hydrate. Figure 7 shows the calculated equilibrium pressures for the specified crystallographic structures of the hydrates. Figure 8 shows the $\sigma - \varepsilon$ pairs that were deduced to determine the parameters for HFC-32 and cyclopentane specified in Table 4. In this figure, different lines are used to depict the infinite sets of $\sigma - \varepsilon$ pairs and to indicate the crystallographic structures that are predicted with the sets of $\sigma - \varepsilon$ pairs. On the basis of the molecular size and shape of HFC-32 and cyclopentane, the crystallographic structure of the HFC-32 simple, the cyclopentane simple, and the

Fig. 5 Infinite sets of Kihara parameters determined by fitting the model predictions to the hydrate-phase equilibrium data in the systems containing cyclopentane. The binary interaction parameter k_{ij} is set to 0.20

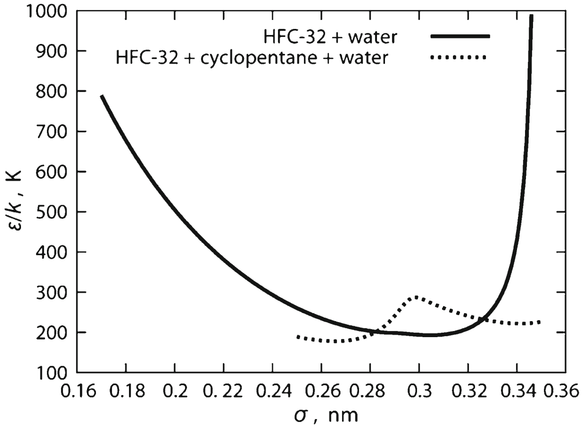


Table 4 Kihara parameters and binary interaction parameter determined in this study

	a (nm)	σ (nm)	ε/k_B (K)	k_{ij}
HFC-32	0.08292	0.2806	203.1	0.1790
Cyclopentane	0.08968	0.2870	303.9	

HFC-32 + cyclopenatne double hydrates should be structure I, structure II, and structure II, respectively. The $\sigma-\varepsilon$ pairs that predict crystallographic structures other than the above-mentioned ones should be excluded from the fitting procedure. Figure 8a shows that the crystallographic structure of the cyclopentane simple hydrate is not correctly predicted by the $\sigma-\varepsilon$ pairs indicated in Table 4. The crystallographic structure of the HFC-32 simple hydrate can be correctly predicted by the $\sigma-\varepsilon$ pairs indicated in Fig. 8b, while the crystallographic structure of the HFC-32 + cyclopentane double hydrate cannot be correctly predicted. To avoid these erroneous predictions, we limited the range of σ of cyclopentane from 0.3138 nm to 0.3300 nm that provides the correct prediction of the crystallographic structure of the simple hydrate and determined the Kihara parameters and binary interaction parameters with this limitation. The newly determined Kihara parameters and binary interaction parameter of HFC-32 and cyclopentane are indicated in Table 5. Figure 9 shows the p–T equilibrium conditions calculated using the parameters indicated in Table 5. With these Kihara parameters, $AAD_{\mathrm{HFC-32}}$ is 0.043, $AAD_{\mathrm{cyclopentane}}$ is 0.12, and $AAD_{(\mathrm{HFC-32+cyclopentane})}$ is 0.031.

4 Conclusions

Thermodynamic modeling based on the van der Waals–Platteeuw theory was performed for hydrate-forming systems containing HFC-32 and cyclopentane that is expected to be a working medium in a hydrate-based refrigeration system.

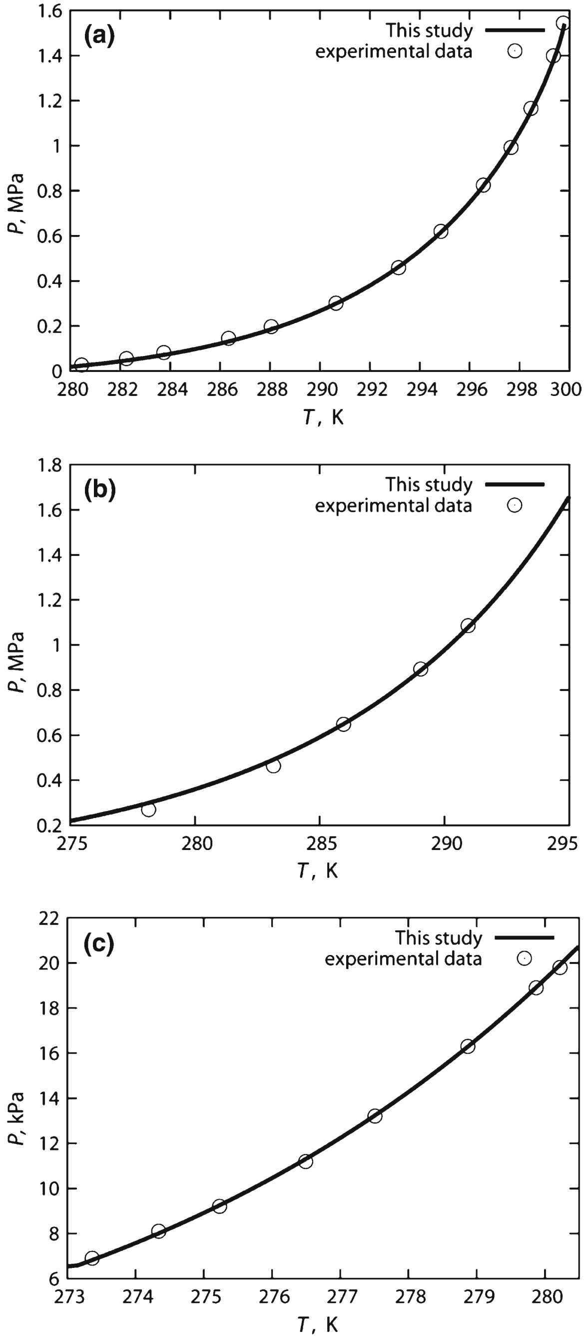
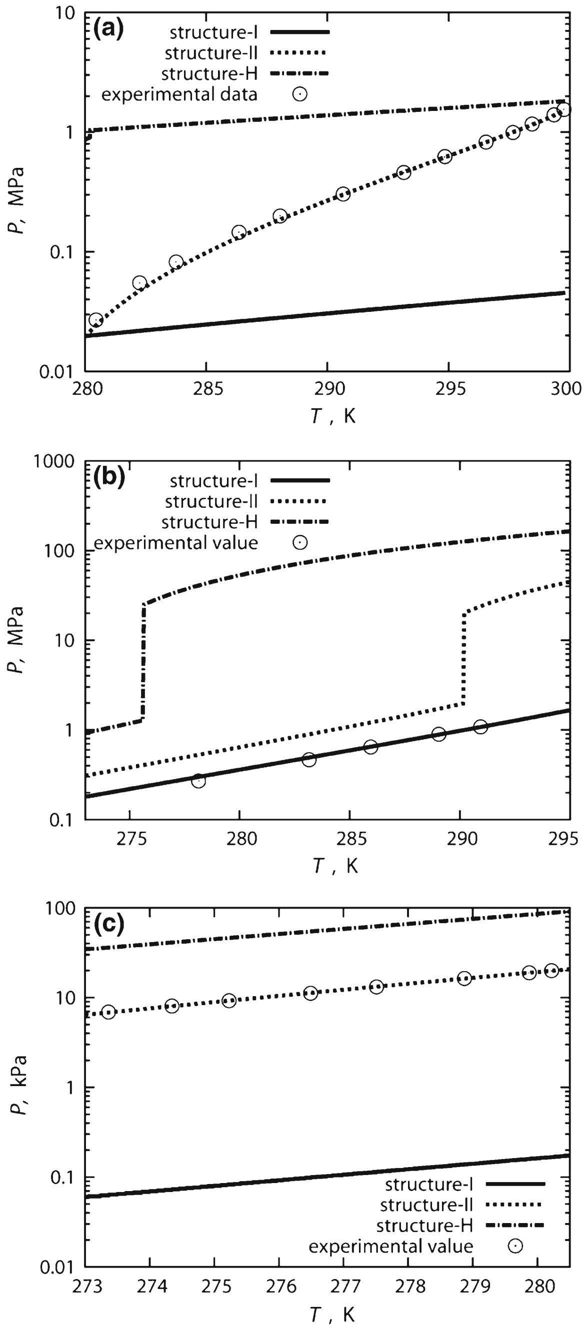


Fig. 6 Calculated equilibrium *p*–*T* conditions and the relevant experimental data:
(**a**) HFC-32 + cyclopentane + water system,
(**b**) HFC-32 + water system, and
(**c**) cyclopentane + water system

Fig. 7 Calculated equilibrium p–T conditions for specified crystallographic structures of the hydrates and the relevant experimental data:
(**a**) HFC-32 + cyclopentane + water system,
(**b**) HFC-32 + water system, and
(**c**) cyclopentane + water system



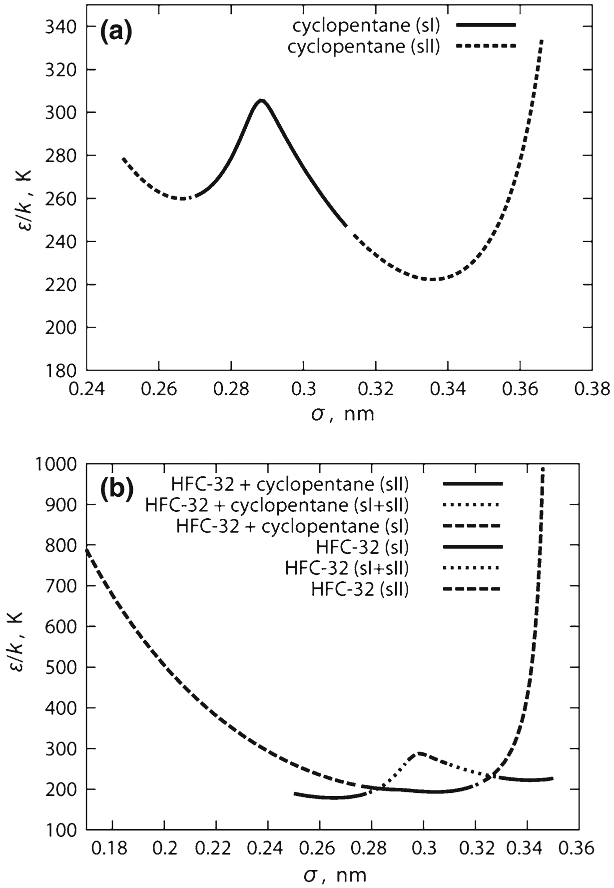


Fig. 8 Infinite sets of Kihara parameters determined by fitting the model predictions to the hydrate-phase equilibrium data in the systems containing cyclopentane. The stable crystallographic structures predicted using the parameters are indicated by the *different lines*

Table 5 Kihara parameters and binary interaction parameter with which the crystallographic structures of the hydrates are correctly predicted

	a (nm)	σ (nm)	ε/k_B (K)	k_{ij}
HFC-32	0.08292	0.2756	208.1	0.1950
Cyclopentane	0.08968	0.3138	243.5	

The phase equilibrium pressure–temperature conditions and stable hydrate structure conditions in the HFC-32 + cyclopentane + water system are well reproduced using the newly determined Kihara parameters for HFC-32 and cyclopentane with an *AAD* of 0.031.

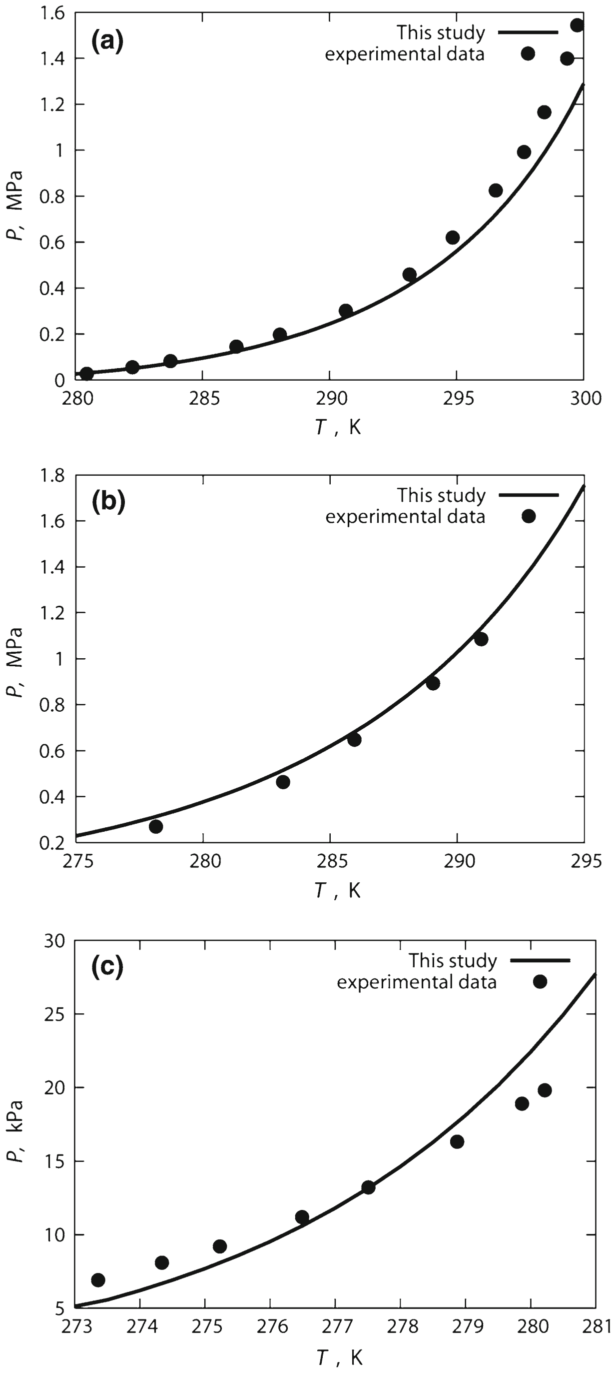


Fig. 9 Calculated equilibrium *p*–*T* conditions calculated using the parameters indicated in Table 5, and the relevant experimental data: (**a**) HFC-32 + cyclopentane + water system, (**b**) HFC-32 + water system, and (**c**) cyclopentane + water system

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