Three-Phase Equilibrium Relations and Hydrate Dissociation Enthalpies for Hydrofluorocarbon Hydrate Systems: HFC-134a, -125, and -143a Hydrates

Shunsuke Hashimoto,*,‡ Takashi Makino,† Yoshiro Inoue,‡ and Kazunari Ohgaki‡

Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan, and Research Center for Compact Chemical System, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan

The three-phase equilibrium (pressure−temperature) relations were measured for the hydrofluorocarbon (HFC) (1,1,1,2-tetrafluoroethane (-134a), pentafluoroethane (-125), or 1,1,1-trifluoroethane (-143a)) + water binary systems containing gas hydrate. The measurements were performed in the pressure range up to 10.0 MPa and the temperature range of (273.15 to 295.15) K. The invariant quadruple points (gaseous HFC, liquid HFC, aqueous, and hydrate phases) were located at 283.19 K and 0.416 MPa (HFC-134a), 283.95 K and 0.930 MPa (HFC-125), and 283.33 K and 0.838 MPa (HFC-143a), respectively. The enthalpies of hydrate dissociation to gaseous HFC and water were calculated with the Clapeyron equation, and the value was about 140 kJ·mol^{-1} for all HFC hydrate systems.

Introduction

Gas hydrate is a clathrate inclusion compound. It consists of host water molecules and appropriate relatively small guest molecules. The water molecules are hydrogen-bonded and constitute the hydrate frameworks with cavities, in which guest molecules are encaged. In general, the van der Waals interaction (attractive and repulsive forces) operates on the guest and water molecules, and the guest molecules encaged in the clathrate hydrate do not join in hydrogen bonds of water molecules.[1] There are several types of hydrate unit-cells, and in particular, two types, which are called structure-I (s-I) and structure-II (s-II), are well-known. Both the hydrate unit cells include the pentagonal dodecahedron (5^{12}, S-cage). In addition to the S-cage, the s-I and s-II hydrates have the tetrakaidecahedron ($5^{12}6^2$, M-cage) and the hexakaidecahedron ($5^{12}6^4$, L-cage), respectively. The unit cell of s-I is composed of two S-cages and six M-cages, while that of s-II consists of 16 S-cages and 8 L-cages. The hydrate structure mainly depends on temperature, pressure, and the physical and chemical properties of guest species.

Some of the unique properties of gas hydrate are the large dissociation enthalpy and proper melting temperature for refrigerating and air-conditioning. Therefore, the gas hydrate has attracted considerable attention as a promising phase change material (PCM) for the refrigerating and air-conditioning systems. Especially in the case of the gas hydrate being stable at relatively low pressures and (278 to 284) K (the temperature range of the chilled water),[2] the gas hydrate thermal storage system can work with higher coefficient of performance than the ice thermal storage system.[3] Consequently, it is possible to save about 40 % energy by the use of gas hydrate as a refrigerant.[2,3]

The equilibrium pressures of some hydrofluorocarbon (HFC) hydrates are relatively lower (less than 1 MPa) than those of conventional hydrocarbon gas hydrates. On the other hand, the dissociation enthalpies of the HFC hydrate are comparable with those of ordinary hydrocarbon gas hydrates. Some HFCs have been used as alternative refrigerants for the air-conditioning system to replace chlorofluorocarbons (CFCs) and chlorohydrofluorocarbons (CHFCs), which have high ozone depletion and global warming potentials.[4] The HFC has specific thermal and chemical characteristics that are favorable as a refrigerant material. However, the reduction of HFC use is required by Kyoto Protocol because of its relatively high global-warming potential. In our recent study,[5] based on the phase-equilibrium relation, we have estimated that the dissociation enthalpy of difluoromethane (HFC-32) hydrate (gas hydrate to gaseous HFC and water) is about 70 kJ·mol^{-1} near the freezing point. The dissociation enthalpy per mole of gas of the HFC-32 hydrate is higher than the vaporization enthalpy per mole of gas of HFC-32. Therefore, the employment of the slurry containing gas hydrate is considered as an effective technique to decrease the amount of HFC in the cool energy storage system.

Phase change data and hydrate dissociation enthalpies, especially for simple HFC hydrate systems, are surely essential to develop the air-conditioning and refrigerating processes with HFC hydrates. Some previous studies[6−10] reported the equilibrium (pressure−temperature) relations and dissociation enthalpies of the halogenated−hydrocarbon hydrate systems. However, the number of investigated systems is very limited, and an appropriate HFC hydrate system for the cool energy storage system is still unclear. Therefore, further fundamental studies such as phase equilibrium measurement for HFC hydrates should be performed.

In the present study, three-phase equilibrium (pressure−temperature) relations for three binary systems (1,1,1,2-tetrafluoroethane (HFC-134a), pentafluoroethane (HFC-125), or 1,1,1-trifluoroethane (HFC-143a) + water systems) have been investigated accurately by phase-equilibrium measurement. In addition, the hydrate dissociation enthalpies (gas hydrate to gaseous HFC and water) have been calculated with the Clapeyron equation.

* Corresponding author. Telephone & Fax: +81-6-6850-6277. E-mail: shunsuke@cheng.es.osaka-u.ac.jp.
† National Institute of Advanced Industrial Science and Technology (AIST).
‡ Osaka University.

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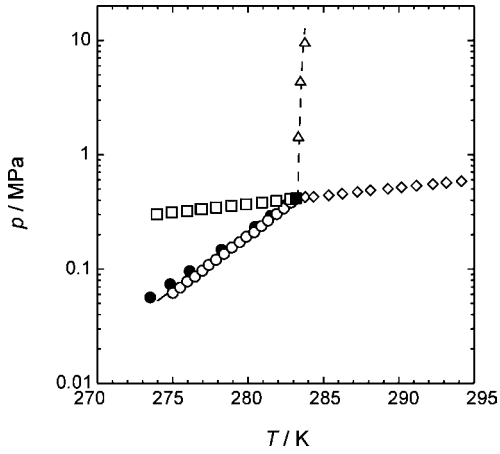

Figure 1. Three-phase equilibrium relation (temperature T−pressure p projection) for the HFC-134a (2) + water (1) binary system. ●, HL_1G (Liang et al., 2001); ○, HL_1G (present study); □, HL_2G (present study); △, HL_1L_2 (present study); ◇, L_1L_2G (present study); ■, quadruple point (Q_2, present study); −, the reference data (Akiya et al., 1999).

Experimental Methods

Experimental Apparatus. The experimental equipment including a high-pressure glass cell was the same as a previous one.[5] The inner volume and maximum working pressure of the high-pressure glass cell were 10 cm^3 and 5 MPa, respectively.

The temperature was measured within an uncertainty of 0.02 K using a thermistor probe (model: Takara D-632). The probe was calibrated with a Pt resistance thermometer (25 Ω) defined by ITS-90. The pressure was measured by a pressure gauge (model: Valcom VPRT) calibrated by a RUSKA quartz Bourdon tube gauge (model: direct reading pressure gauge, series 6000). The estimated uncertainty of equilibrium pressure was 0.001 MPa (p < 1 MPa) or 0.01 MPa (p > 1 MPa).

Experimental Procedure. Almost all procedures of phase equilibrium measurements in the present study were the same as a previous one.[5] In advance, the dissolved air in water was sufficiently degassed and replaced by a bubbling method with each HFC gas. After that, the degassed water was introduced into the evacuated high-pressure glass cell. The cell was immersed in a thermo-controlled water bath to control the temperature. Then, the contents were pressurized by supplying HFC gas up to a desired pressure and subcooled and agitated to generate the gas hydrate. A magnetic stirrer was manipulated in a vertical direction to agitate the contents. The phase behavior was observed directly under the transmitted light. After the formation of gas hydrate, the pressure dropped and reached a plateau, which meant the three-phase equilibrium state of hydrate (H), gas (G), and water (L_1) was established. Then, the pressure and temperature were determined as the three-phase equilibrium pressure and temperature, respectively. In the present study, in addition to the three-phase equilibrium curve of HL_1G, other curves of HL_2G and L_1L_2G were also measured by means of similar procedures. The symbol L_2 stands for the liquid HFC phase.

Unlike the equilibrium measurement for HL_1G, HL_2G, and L_1L_2G conditions, the three-phase equilibrium curve of HL_1L_2 was measured with another high-pressure cell (maximum working pressure was 100 MPa).[5] A certain amount of gaseous HFC was introduced into the evacuated high-pressure optical cell, and then the distilled water was charged up to a desired pressure by use of the high-pressure pump. After the pressurization, the two-phase coexistence state of HFC hydrate + water appeared immediately under the experimental conditions. Thereafter, the temperature was increased gradually to generate the liquid HFC phase by dissociation of the gas hydrate. The gas hydrate was annealed by giving temperature perturbations to avoid a hysteresis effect. The contents were agitated intermittently for at least half a day. After the pressure change per hour was within 0.01 MPa, the pressure and temperature were determined as the three-phase equilibrium pressure and temperature, respectively.

In the present study, to confirm the experimental reproducibility without a hysteresis phenomenon, we repeated each equilibrium measurement using fresh water.

Materials. HFC-134a (mole fraction purity, > 99.6 %) and HFC-125 (mole fraction purity, > 99.5 %) were purchased from Daikin Industries, Ltd. HFC-143a (mole fraction purity, > 99.5 %) was obtained from Du pont-Mitsui Fluorochemicals Co., Ltd. The critical temperature and pressure of HFC-134a, HFC-125, and HFC-143a were (374.21 K and 4.06 MPa), (339.17 K

Table 1. Three-Phase Equilibrium Data (Temperature T, Pressure p) of the HFC-134a (2) + Water (1) Binary System

T/K	p/MPa
HL_1G	
275.00	0.062
275.48	0.069
275.96	0.078
276.47	0.086
276.96	0.097
277.39	0.109
277.87	0.121
278.40	0.136
278.92	0.155
279.45	0.172
279.88	0.192
280.41	0.210
280.88	0.238
281.32	0.266
281.89	0.304
282.38	0.341
282.86	0.383
283.17	0.412
HL_2G	
273.95	0.302
274.94	0.313
275.95	0.323
276.86	0.335
276.93	0.335
277.88	0.346
278.90	0.358
279.87	0.370
280.92	0.382
281.88	0.395
282.81	0.410
L_1L_2G	
283.81	0.424
284.36	0.427
285.37	0.441
286.27	0.455
287.28	0.471
288.15	0.486
289.30	0.502
290.20	0.518
291.19	0.534
292.28	0.552
293.18	0.569
294.19	0.586
HL_1L_2	
283.34	1.45
283.49	4.42
283.78	9.68
Q_2 (HL_1L_2G)	
283.19	0.416

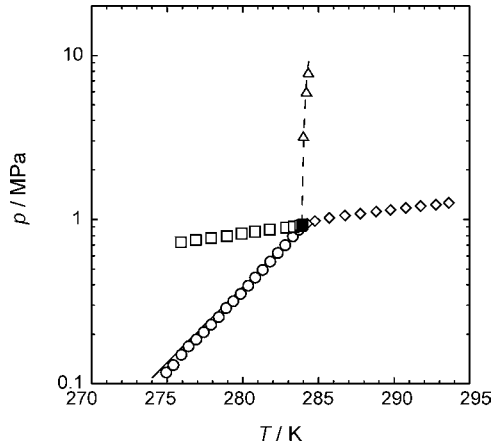

Figure 2. Three-phase equilibrium relation (temperature T−pressure p projection) for the HFC-125 (2) + water (1) binary system. ○, HL_1G (present study); □, HL_2G (present study); △, HL_1L_2 (present study); ◇, L_1L_2G (present study); ■, quadruple point (Q_2, present study). −, the reference data (Akiya et al., 1999).

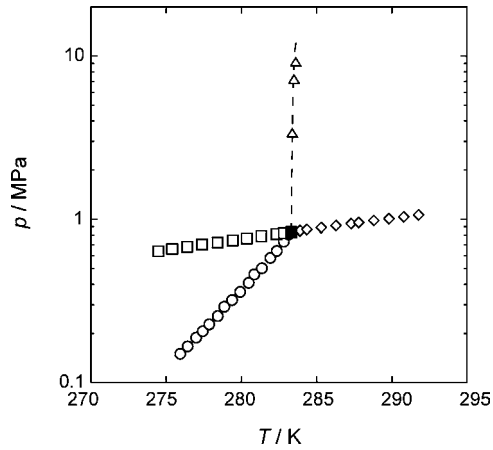

Figure 3. Three-phase equilibrium relation (temperature T−pressure p projection) for the HFC-143a (2) + water (1) binary system. ○, HL_1G (present study); □, HL_2G (present study); △, HL_1L_2 (present study); ◇, L_1L_2G (present study); ■, quadruple point (Q_2, present study).

and 3.62 MPa), and (345.86 K and 3.76 MPa), respectively.[11] Distilled water was obtained from Wako Pure Chemical Industries, Ltd. All the materials were used without further purification.

Results and Discussion

Figure 1 shows the three-phase equilibria for the HFC-134a + water binary system. Table 1 summarizes the three-phase equilibrium (pressure (p)−temperature (T)) relations of HL_1G, HL_2G, HL_1L_2, and L_1L_2G. A filled square is located at the invariant quadruple point (Q_2) of HL_1L_2G. As shown in Figure 1, the HL_1G curve agrees well with the reported equilibrium relations.[7,8] Four three-phase equilibrium curves converge at the Q_2, and the quadruple point is determined as (283.19 K and 0.416 MPa).

The three-phase equilibrium ($p-T$) relations of HL_1G, HL_2G, HL_1L_2, and L_1L_2G for the HFC-125 or -143a + water binary systems are also shown in Figures 2 and 3 and summarized in Tables 2 and 3, respectively. The phase behaviors of the HFC-125 and HFC-143a hydrate systems are similar to that of the simple HFC-134a hydrate system. The quadruple points for the HFC-125 + water and HFC-143a + water systems are located at (283.95 K and 0.930 MPa) and (283.33 K and 0.838 MPa),

Table 2. Three-Phase Equilibrium Data (Temperature T, Pressure p) of the HFC-125a (2) + Water (1) Binary System Containing Gas Hydrates

T/K	p/MPa
HL_1G	
274.94	0.117
275.40	0.130
275.94	0.150
276.41	0.169
276.92	0.186
277.41	0.206
277.91	0.229
278.41	0.255
278.90	0.289
279.37	0.318
279.86	0.353
280.35	0.396
280.82	0.444
281.31	0.495
281.81	0.556
282.31	0.628
282.80	0.701
283.31	0.792
283.70	0.870
HL_2G	
275.90	0.730
276.89	0.752
277.90	0.772
278.94	0.794
279.93	0.820
280.81	0.843
281.79	0.867
282.86	0.892
283.37	0.904
283.79	0.918
L_1L_2G	
284.27	0.941
284.78	0.976
285.73	1.02
286.76	1.05
287.78	1.08
288.81	1.11
289.77	1.14
290.78	1.17
291.76	1.20
292.78	1.23
293.63	1.26
HL_1L_2	
284.01	3.21
284.21	6.00
284.34	7.87
Q_2 (HL_1L_2G)	
283.95	0.930

respectively. Additionally, as shown in Figure 4, the isothermal equilibrium pressure of the HFC-125 hydrate is almost the same as that of the HFC-143a hydrate under HL_1G conditions, while the HFC-134a hydrate is stable under lower pressures than the HFC-125 and HFC-143a hydrates. The HFC-134a hydrate slurry has a larger prospect as a refrigerant for air-conditioning than the other systems measured in the present study. In addition, all the present hydrate systems have similar gradients of HL_1G curves.

The slope of the three-phase equilibrium curve ($(dp/dT)_{eq}$) was calculated at each equilibrium data point on the HL_1G curve. From the combination of $(dp/dT)_{eq}$, molar volumes of HFC hydrate (v^H), water (v^{L}_{H2O}), and gaseous HFC (v^{G}_{HFC}), the hydrate dissociation enthalpy per unit hydrate ($\Delta_{hyd}H$) was calculated with the Clapeyron equation as follows

$$(dp/dT)_{eq} = \Delta_{hyd}H/(\Delta_{hyd}VT) \quad (1)$$

Table 3. Three-Phase Equilibrium Data (Temperature *T*, Pressure *p*) of the HFC-143a (2) + Water (1) Binary System Containing Gas Hydrates

T/K	*p*/MPa
HL_1G	
275.94	0.150
276.43	0.167
276.99	0.189
277.43	0.207
277.86	0.228
278.43	0.256
278.86	0.292
279.38	0.321
279.92	0.360
280.48	0.409
280.85	0.461
281.36	0.503
281.93	0.582
282.35	0.642
282.82	0.732
283.13	0.810
HL_2G	
274.49	0.640
275.41	0.660
276.40	0.680
277.39	0.702
278.42	0.723
279.42	0.745
280.36	0.766
281.32	0.789
282.33	0.811
282.84	0.824
283.32	0.836
L_1L_2G	
283.90	0.849
283.91	0.851
284.36	0.863
285.31	0.887
286.30	0.912
287.31	0.938
287.80	0.952
288.82	0.978
289.82	1.01
290.80	1.03
291.79	1.06
HL_1L_2	
283.39	3.37
283.51	7.21
283.62	9.20
Q_2 (HL_1L_2G)	
283.33	0.838

where the total molar volume change for hydrate formation or dissociation, $\Delta_{hyd}V$, is defined by eq 2

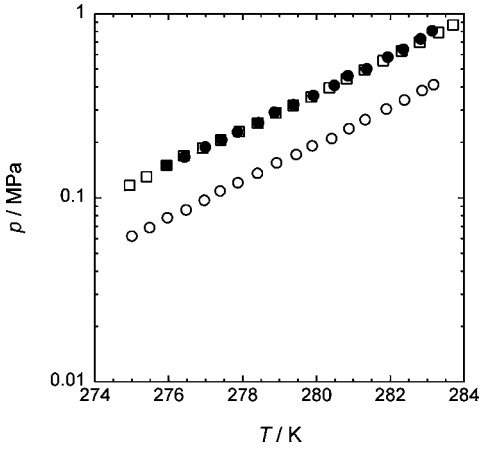

Figure 4. Three-phase (HL_1G) equilibrium curves of HFC-134a, -125, and -143a + water systems. ○, HFC-134a; □, HFC-125; ●, HFC-143a.

$$\Delta_{hyd}V = v^{G}_{HFC} + qv^{L}_{H2O} - v^{H} \quad (2)$$

$$HFC\ (G) + qH_2O\ (L_1) \leftrightarrow HFC \cdot qH_2O\ (H) \quad (3)$$

On the basis of the molecular size of HFC obtained from reference data,[6] all HFCs investigated in the present study are the s-II former and occupy only the L-cages of s-II. Therefore, v^{H} was 390 $cm^3 \cdot mol^{-1}$, which was calculated from the lattice constant of s-II (1.73 nm),[12] and the hydration number, *q*, was assumed to be 17 (ideal hydration, $HFC \cdot 17H_2O$). v^{L}_{H2O} was calculated from the equation proposed by Saul and Wagner.[13] In addition, v^{G}_{HFC} was obtained from the Lee−Kesler equation of state[14] (for details, refer to Supporting Information).

Table 4. Hydrate Dissociation Enthalpy (Gas Hydrate to Gaseous HFC and Water), $\Delta_{hyd}H$, of the Three HFC (HFC-134a, -125, and -143a) Hydrates

T	v_{HFC}	v_{H2O}	$\Delta_{hyd}V$	$(dp/dT)_{eq}$	$\Delta_{hyd}H$
K	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$cm^3 \cdot mol^{-1}$	$MPa \cdot K^{-1}$	$kJ \cdot mol^{-1}$
		HFC-134a			
275.00	36276	18.0175	36192	0.014	142.32
275.48	32594	18.0172	32510	0.016	143.07
275.96	28817	18.0169	28733	0.018	141.51
276.47	26131	18.0167	26048	0.020	144.57
276.96	23144	18.0176	23060	0.023	143.57
277.39	20564	18.0164	20480	0.025	141.03
277.87	18499	18.0164	18416	0.028	141.91
278.40	16427	18.0164	16343	0.031	142.60
278.92	14369	18.0164	14285	0.035	140.80
279.45	12916	18.0166	12833	0.040	143.21
279.88	11527	18.0167	11444	0.044	141.26
280.41	10510	18.0170	10426	0.050	145.72
280.88	9219	18.0172	9136	0.056	142.55
281.32	8199	18.0174	8115	0.061	140.38
281.89	7113	18.0178	7030	0.070	138.98
282.38	6286	18.0181	6203	0.079	137.55
282.86	5538	18.0185	5455	0.088	135.36
283.17	5110	18.0187	5026	0.094	134.13
		HFC-125			
274.94	19061	18.0171	18977	0.027	138.74
275.40	17138	18.0167	17054	0.030	138.60
275.94	14820	18.0163	14736	0.033	135.61
276.41	13124	18.0160	13040	0.037	133.71
276.92	11905	18.0168	11821	0.042	136.31
277.41	10723	18.0156	10640	0.047	137.32
277.91	9617	18.0154	9534	0.052	138.05
278.41	8605	18.0153	8521	0.058	138.44
278.90	7550	18.0153	7467	0.065	135.78
279.37	6831	18.0153	6747	0.073	136.71
279.86	6117	18.0153	6032	0.081	136.84
280.35	5411	18.0153	5327	0.091	135.22
280.82	4781	18.0154	4697	0.101	132.86
281.31	4245	18.0154	4161	0.113	131.75
281.81	3731	18.0155	3647	0.126	129.55
282.31	3250	18.0156	3166	0.141	126.17
282.80	2862	18.0157	2778	0.158	123.90
283.31	2474	18.0157	2390	0.177	119.89
283.70	2204	18.0157	2120	0.193	116.32
		HFC-143a			
275.94	14818	18.0163	14734	0.034	138.01
276.43	13286	18.0160	13202	0.038	138.74
276.99	11709	18.0157	11625	0.043	139.33
277.43	10667	18.0155	10584	0.048	140.65
277.86	9657	18.0154	9573	0.053	140.73
278.43	8567	18.0153	8484	0.060	142.56
278.86	7464	18.0152	7380	0.067	137.18
279.38	6760	18.0152	6676	0.075	140.20
279.92	5987	18.0153	5903	0.085	140.72
280.48	5222	18.0153	5138	0.097	139.69
280.85	4583	18.0152	4499	0.106	133.40
281.36	4167	18.0154	4083	0.119	136.45
281.93	3538	18.0155	3455	0.136	131.98
282.35	3163	18.0155	3079	0.149	129.83
282.82	2711	18.0154	2628	0.167	123.70
283.13	2398	18.0152	2314	0.179	117.14

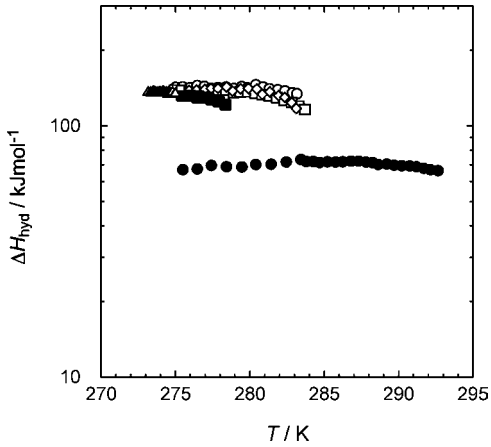

Figure 5. Temperature dependence of hydrate dissociation enthalpies (gas hydrate to gaseous HFC and water), $\Delta_{hyd}H$, for the each HFC hydrate. ●, HFC-32 hydrate (Hashimoto et al., in press); ■, C_3H_8 hydrate (Kubota et al., 1984); △, *i*-C_4H_{10} hydrate (Rouher and Barduhn, 1969); ○, HFC-134a hydrate; □, HFC-125 hydrate; ◇, HFC-143a hydrate.

The values of $(dp/dT)_{eq}$ were obtained from the fitting data of three-phase (HL_1G) equilibrium curve on the $p-T$ relation. Hence, the hydrate dissociation enthalpies, $\Delta_{hyd}H$, can be calculated and are summarized in Table 4, and the temperature dependencies of the enthalpy are shown in Figure 5. The dissociation enthalpies of the investigated HFC hydrates decrease very gradually with an increase of temperature. Each of the investigated HFC hydrates shows a similar value of dissociation enthalpy, about 140 kJ·mol^{-1} near the freezing point. This heat quantity is comparable with the dissociation enthalpies of the simple C_3H_8 hydrate[15] and *i*-C_4H_{10} hydrate[16] and larger than that of the simple HFC-32 hydrate.[5]

Conclusion

Four three-phase equilibrium curves of HL_1G, HL_2G, HL_1L_2, and L_1L_2G (without hydrate phase) for the binary systems of HFC-134a, -125, or -143a + water have been measured in the temperature range from (273.15 to 295.15) K and pressure range up to 10.0 MPa. The HFC-134a hydrate has the lowest equilibrium pressure under the HL_1G conditions in the tested hydrate systems. The invariant quadruple points, Q_2 (HL_1L_2G), are determined as follows: HFC-134a system (283.19 K and 0.416 MPa), HFC-125 system (283.95 K and 0.930 MPa), and HFC-143a system (283.33 K and 0.838 MPa). The dissociation enthalpies of the present HFC hydrates (gas hydrate to gaseous HFC and water), which were calculated with the Clapeyron equation, are about 140 kJ·mol^{-1} near the freezing point and larger than that of the simple HFC-32 hydrate.

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Supporting Information Available:

Details of the Lee−Kesler method. This material is available free of charge via the Internet at http://pubs.acs.org.

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