Vapor−Liquid Equilibria for Hydrogen Fluoride + 1,1-Difluoroethane at 288.23 and 298.35 K

Jongcheon Lee and Hwayong Kim

Department of Chemical Engineering, Seoul National University, 56-1, Shinlimdong,
Kwanak-ku, Seoul 151-742, Korea

Jong Sung Lim,* Jae-Duck Kim, and Youn Yong Lee

Division of Environmental and CFC Alternatives Technology, Korea Institute of Science and Technology (KIST),
P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Isothermal vapor−liquid equilibria for hydrogen fluoride + 1,1-difluoroethane at 288.23 and 298.35 K were measured using a circulation type apparatus equipped with an equilibrium view cell. The compositions of both vapor and liquid phases were analyzed by an on-line gas chromatographic method. They were compared with *PTx* equilibrium data measured by the total pressure method. The experimental data were correlated with Anderko's equation of state using the Wong−Sandler mixing rule as well as the van der Waals one-fluid mixing rule. The Wong−Sandler mixing rule gives better results, and the relevant parameters are presented.

Introduction

Hydrogen fluoride (HF) is widely used in the HF alkylation process, manufacture of refrigerants, and synthesis of other halogenated compounds. The production of refrigerants involves the separation of multicomponent mixtures containing HF, hydrogen chloride, and various chlorinated and fluorinated hydrocarbons. Therefore it is indispensable to know the phase behavior of these mixtures. Because of the toxic and corrosive nature of HF, the vapor−liquid equilibrium data in HF-containing systems are limited.

HF association in the vapor phase has been well-known, and there have been many conflicting models proposed for the description of the self-associating HF vapor. Discontinuous association models such as monomer−hexamer (Simons and Hildebrand, 1924), monomer−dimer−hexamer (Maclean et al., 1962), monomer−trimer−hexamer (Beckerdite et al., 1983), and monomer−dimer−hexamer−octamer (Schotte, 1980), as well as continuous model (Redington, 1982), were used to facilitate the fitting of empirical equations to gas phase data. The association of HF manifests itself in its significantly reduced gas phase compressibility factor and the strong nonideality of mixtures containing HF and either hydrocarbons or halocarbons. Owing to this gas phase association, it is difficult to describe the properties of HF-containing systems. The ability to describe the properties of HF with an equation of state is an important step in the proper design and operation of these industrial processes. Modeling the properties of HF is especially important in the final separation and purification of HF.

Two equations of state for HF have been proposed. One is an association model, which was developed by Anderko and co-workers (Lencka and Anderko, 1993; Anderko and Prausnitz, 1994), in which the probability of consecutive association reactions is considered and combined with an equation of state and extended to mixtures. The other one is proposed by Twu et al. (1993). Twu et al. have proposed a closed-form equation of state which is written in terms of monomer parameters and the monomer−hexamer chemical equilibrium constant.

In this work, a newly designed circulating type apparatus equipped with a equilibrium view cell and connected directly to a gas chromatograph has been constructed to obtain the equilibrium *PTxy* data for the HF-containing system. We measured *PTxy* vapor−liquid equilibria for the binary system of HF + 1,1-difluoroethane (HFC-152a) using this apparatus, and they were compared with *PTx* equilibrium data obtained in this work. Experimental data were correlated with Anderko's equation of state (Lencka and Anderko, 1993) and two mixing rules, the van der Waals one-fluid mixing rule and the Wong−Sandler mixing rule (Wong and Sandler, 1992; Wong et al., 1992).

Experimental Section

Chemicals. HF was supplied by ULSAN chemical company, Korea, with a guaranteed purity of not less than 99.9%. HFC-152a from Du Pont has a certified purity of minimum 99.9%. Both chemicals were used without further purification.

Experimental Apparatus. The schematic diagram of the apparatus is shown in Figure 1. This vapor−liquid circulating type apparatus was designed to obtain vapor−liquid equilibrium data in the temperature range from 253.15 to 333.15 K and pressure up to 100 bar. The equilibrium cell was made of 316 stainless steel and had an internal volume of approximately 60 cm^3. In the middle part of the cell, Pyrex glass windows of 10 mm thickness protected by a translucent perfluoroalkoxy (PFA) sheets of 10 mm thickness were placed to allow the observation for mixing, circulating conditions, and phase separation of cell contents. PFA sheets were used to prevent the direct contact of HF and Pyrex glass. A magnetic stirrer was also installed to accelerate the attainment of the equilibrium state. To circulate the vapor and liquid phase, we manufactured the piston pump which consists of 316 stainless steel cylinder, an iron piston with Cr coating, stainless steel ball, and an electromagnet. It operated as a check valve and withstood corrosive materials, such as HF. Monel

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* Author to whom all correspondence should be addressed.

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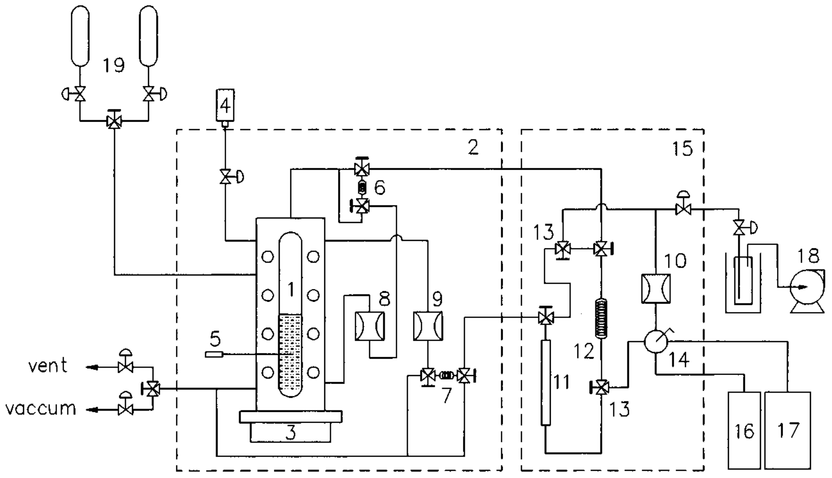

1. Equilibrium View Cell
2. Water Bath
3. Magnetic Stirrer
4. Pressure Transducer
5. RTD Thermostat
6. Vapor Sampling Loop
7. Liquid Sampling Loop
8. Vapor Circulation Pump
9. Liquid Circulation Pump
10. Circulation Pump
11. Liquid Expansion Loop
12. Vapor Expansion Loop
13. Expansion Loop Changing Valve
14. Sampling Valve
15. Air Bath
16. Gas Chromatograph
17. Helium Gas
18. Vacuum Pump
19. Charging Cylinder

Figure 1. Flow diagram of the apparatus.

tubes were used for the vapor and liquid circulation lines. We used an electromagnet pump in the expansion loop to obtain uniform concentration.

The apparatus was placed in steel housing for safety. During operation the cell was submerged in a constant temperature water bath. The bath temperature was maintained constant by a temperature-controlled circulator (Haake model F3-K) with the fluctuation of ±0.02 K. The pressure in the cell was measured by a pressure transducer (SENSOTEC Model TJE-AP122-DTS) and digital indicator (SENSOTEC Model GM) which was calibrated by a dead weight gauge (NAGANO KEIKI PD12) with the measuring accuracy of ±0.01 bar. The temperature in the cell was measured by a standard platinum resistance thermometer and a digital indicator (OMEGA Co.) which was calibrated by KRISS (Korea Institute of Standards and Science) with an uncertainty of ±0.05 K. The accuracies of temperature and pressure measurements were estimated to be ±0.05 K and ±0.01 bar, respectively. A gas chromatograph (Gow-Mac Co.) with a thermal conductivity detector was used for analysis of composition. A Teflon column ($^1/_8$ in. o.d. and 17 ft long) packed with chromosorb T, on which was coated 5% halocarbon oil, was used with helium as a carrier gas. During the analysis, the column temperature was fixed at 288 K, the carrier gas flow rate was 30 cm^3/min, the detector temperature was 393 K, and the detector current was 170 mA.

Experimental Procedure. After the whole system was evacuated with a vacuum pump, HF was introduced into the cell from a charging cylinder and then HFC-152a was charged. After the samples were completely introduced, the vapor and liquid circulation pumps and the magnetic stirrer were started to accelerate the vapor−liquid equilibrium. To measure the vapor and liquid composition with the gas chromatograph, the following steps were required. For vapor composition, the vapor samples were taken and expanded into the pre-evacuated expansion loop. The expansion loop temperature was maintained at 333 K. After being recirculated in the expansion loop by the electromagnet piston pump for 30−60 min to obtain uniform concentration, the vapor samples were led to the gas chromatograph for on-line analysis. For the liquid composition, liquid samples were taken, followed by the same steps as for the vapor samples. Both vapor and liquid samples were analyzed three times, and the average value was reported.

Modeling of Phase Behavior of HF-Containing Systems

Species, such as HF, that form hydrogen bonds often exhibit unusual thermodynamic behavior. Representation of the properties for the self-associating substances like HF and their mixtures by an equation of state without considering chemical theory is not successful. Therefore, it is not surprising that numerous approaches have been tried to describe the thermodynamic properties and phase behavior of the associating systems with chemical theory. Among these approaches, we have taken Anderko's method to correlate the phase behavior of HF-containing systems. The general framework of Anderko's approach was presented earlier (Anderko, 1989, 1991). Lencka and Anderko (1993) also have proposed a closed-form equation of state for HF and extended their equation to the HF-containing mixtures. Their derivation was based on the assumption that the compressibility factor z can be decomposed into physical (z^{ph}) and chemical (z^{ch}) contributions

$$z = z^{ph} + z^{ch} - 1 \qquad (1)$$

where the z^{ch} contribution is defined as the ratio of the total number of moles of all species in an associated mixture (n_T) to the number of moles of all species that would exist in

Table 1. Parameters of Equations 3 and 18

c_1	7.829 1	c_5	55.955 7	d_1	0.890 73	d_5	983.589 41
c_2	−7.582 1	c_6	−2.944 3	d_2	−5.659 92	d_6	−1404.988 08
c_3	113.579 3	c_7	1.650 0	d_3	71.951 46	d_7	1022.387 30
c_4	−88.229	c_8	0.109 27	d_4	−369.355 51	d_8	−296.660 23

the absence of association (n_0)

$$z^{\mathrm{ch}} = \frac{n_{\mathrm{T}}}{n_0} \tag{2}$$

The z^{ph} contribution is equivalent to an equation of state for nonassociating monomeric species and can be expressed by a simple cubic equation of state, such as the Peng−Robinson equation of state.

Lencka and Anderko suggested that the z^{ch} term has the following expression

$$z^{\mathrm{ch}}_{\mathrm{pure}} = \frac{(1 + \sum_{k=1}^{8} c_k q^k)}{(1+q)^8} \tag{3}$$

with

$$q = \frac{RTK}{v} \tag{4}$$

where R is the gas constant, T is the absolute temperature, v is the molar volume, K is the dimerization constant of HF, and the parameters c_k ($k = 1, 2, \cdots, 8$) are listed in Table 1. The temperature dependence of the dimerization constant K is expressed by

$$\ln K = \frac{(-\Delta h^\circ + \Delta C_P^\circ T_0)}{RT} + \frac{(\Delta s^\circ - \Delta C_P^\circ - \Delta C_P^\circ \ln(T_0))}{R} + \frac{\Delta C_P^\circ \ln(T)}{R} \tag{5}$$

where h°, s°, and C_P° are the standard enthalpy, entropy, and heat capacity of association, respectively, and the reference temperature T_0 is 273.15 K. These parameters were given by Lencka and Anderko, and their values are $h^\circ = -35.069$ kJ·mol^{-1}, $s^\circ = -133.67$ J·mol^{-1}·K^{-1}, and $C_P^\circ = 52.68$ J·mol^{-1}·K^{-1}.

For the physical contribution z^{ph}, the Peng−Robinson (Peng and Robinson, 1976) equation of state was used

$$z^{\mathrm{ph}} = \frac{v}{(v-b)} - \frac{a(T)v}{RT[v(v+b) + b(v-b)]} \tag{6}$$

The parameters of the z^{ph} contribution are given by Lencka and Anderko as the following

$$b\ (\mathrm{cm^3/mol}) = 9.69 \tag{7}$$

$$a\ (\mathrm{bar{\cdot}cm^6/mol^2}) = 10^6[0.7187 + 0.2734 \exp(-0.6232((T/\mathrm{K})/100 - 4.02)^2)] \tag{8}$$

Then, eqs 1, 3, and 6 determine the equation of state for pure HF.

The Peng−Robinson equation of state has been applied to the mixtures using mixing rules for the z^{ph} contribution. Here we applied Peng−Robinson equation of state to mixtures containing HF using two mixing rules.

The van der Waals one-fluid mixing rule is represented as

$$b_{\mathrm{mix}} = \sum_i x_i b_i \tag{9}$$

$$a_{\mathrm{mix}} = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij}) \tag{10}$$

where k_{ij} is the binary interaction parameter.

Wong and Sandler (Wong and Sandler, 1992a; Wong et al., 1992) have developed a theoretically correct mixing rule for cubic equation of state, which is represented as

$$b_{\mathrm{mix}} = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{\left(1 - \frac{A^{\mathrm{E}}}{CRT} - \sum_i x_i \frac{a_i}{RTb_i}\right)} \tag{11}$$

and

$$\frac{a_{\mathrm{mix}}}{b_{\mathrm{mix}}} = \sum_i x_i \frac{a_i}{b_i} + \frac{A^{\mathrm{E}}}{C} \tag{12}$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{\left(b - \frac{a}{RT}\right)_i + \left(b - \frac{a}{RT}\right)_j}{2}(1 - k_{ij}) \tag{13}$$

where A^{E} is the Helmholtz excess free energy term, a and b are equation of state parameters, R is the gas constant, T is the absolute temperature, and C is a constant dependent on the equation of state selected; $1/\sqrt{2}\ \ln(\sqrt{2} - 1)$ for the Peng−Robinson equation of state is used here.

Equation 3 has been applied to mixtures for the z^{ch} contribution

$$z^{\mathrm{ch}}_{\mathrm{mix}} = x_{\mathrm{A}} \frac{(1 + \sum_{k=1}^{8} c_k q^k_{\mathrm{mix}})}{(1 + q_{\mathrm{mix}})^8} + x_{\mathrm{B}} \tag{14}$$

with

$$q_{\mathrm{mix}} = \frac{RTKx_{\mathrm{A}}}{v} \tag{15}$$

where x_{A} is the analytical (apparent) mole fraction for HF and x_{B} is the analytical (apparent) mole fraction for the nonassociating component.

The fugacity coefficient is calculated through classical thermodynamics according to the following equation

$$\ln \phi_i = \int_V^{\infty} \left(\frac{1}{RT}\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{j\neq i}} - \frac{1}{V}\right) \mathrm{d}V - \ln z \tag{16}$$

and from the separation of the physical and chemical contribution to the compressibility factor that

$$\ln(\phi_i z) = \ln(\phi_i^{\mathrm{ph}} z^{\mathrm{ph}}) + \ln(\phi_i^{\mathrm{ch}} z^{\mathrm{ch}}) \tag{17}$$

The coefficient ϕ_i^{ph} is identical with the fugacity coefficient for the equation of state representing the physical

Table 2. Vapor–Liquid Equilibria by *PTxy* Measurements for the HFC-152a (1) + HF (2) System at 288.23 and 298.35 K

P/bar	T/K	x_1	y_1
0.84	288.23	0.0000	0.0000
2.80	288.23	0.1278	0.5267
3.49	288.23	0.2563	0.6740
3.50	288.23	0.2616	0.6756
3.65	288.23	0.3123	0.7178
3.84	288.23	0.4072	0.7520
3.92	288.23	0.4638	0.7801
4.13	288.23	0.6783	0.8512
4.40	288.23	1.0000	1.0000
1.23	298.35	0.0000	0.0000
3.72	298.35	0.1276	0.5125
4.42	298.35	0.2088	0.6257
4.70	298.35	0.2563	0.6664
4.75	298.35	0.2685	0.6709
5.40	298.35	0.4968	0.7865
5.52	298.35	0.5682	0.8121
5.65	298.35	0.6629	0.8509
5.67	298.35	0.6729	0.8595
5.69	298.35	0.6977	0.8754
6.03	298.35	1.0000	1.0000

contribution to z whereas ϕ_i^{ph} for the associating component is given by

$$\ln(\phi_i^{\mathrm{ph}}) = -d_1 \ln(1 + q_{\mathrm{mix}}) + \sum_{i=1}^{8} d_i\left(\frac{1}{(1 + q_{\mathrm{mix}})^i} - 1\right) - \ln(z_{\mathrm{mix}}^{\mathrm{ch}}) \quad (18)$$

The parameters d_i ($i = 1, 2, ..., 8$) are listed in Table 1.

Results and Discussion

Table 2 present the results of *PTxy* measurements by gas chromatograph analysis for the HFC-152a + HF system at 288.23 and 298.35 K. We also measured the phase equilibria for the same system and at the same temperatures with *PTx* measurements to compare the results with each other. The experimental apparatus and procedure used in the PTx measurements are the same as those used in the previous work (Lee et al., 1995). After the whole system was evacuated by vacuum pump, a known mass of HF was introduced into the cell from a charging cylinder. The cell was allowed to equilibrate, and the pressure was measured. Known masses of the refrigerant were then charged to the cell. After each increment, the contents were allowed to equilibrate before the pressure was measured. The mass of the charge in the cell was measured by the mass change of the charging cylinder for each increment. During the run, the total liquid volume of two components was more than 60% of the cell volume. The liquid composition is determined from the charged amounts of each compound. Then the vapor composition is calculated by using Schotte's method (1980). The calculation methods are also shown in our previous work (Lee et al., 1995). Table 3 represents the results of *PTx* measurements. The $P-x$ diagrams at 288.23 and 298.35 K are shown in Figure 2. The empty circles represent the experimental values by the *PTx* method, and filled circles represent the experimental values by *PTxy* measurements. As shown in Figure 2, the liquid compositions calculated by charged amounts of each compound agree well with the analyzed values by gas chromatograph. The uncertainty of the liquid composition analysis is usually within 1%, but it is assumed that the uncertainty of the vapor analysis can be as large as 3%.

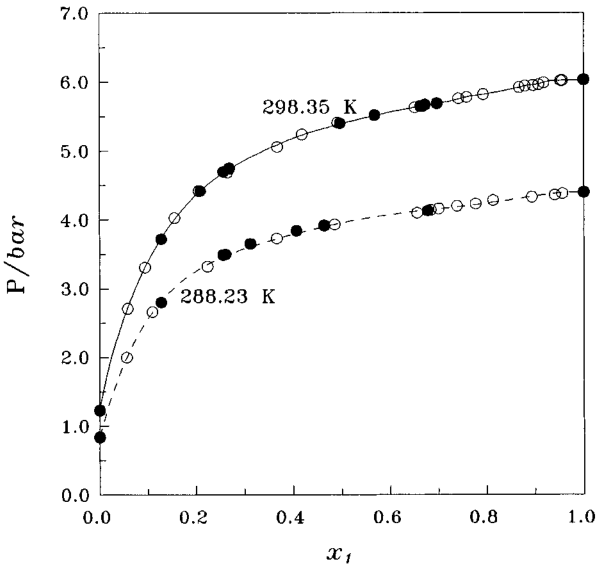

Figure 2. $P-x$ diagram for the HFC-152a (1) + HF (2) system at 288.23 and 298.35 K: (●) Experimental data by *PTxy* measurement; (○) experimental data by *PTx* measurement.

Table 3. Vapor–Liquid Equilibria by *PTx* Measurements for the HFC-152a (1) + HF (2) System at 288.23 and 298.35 K

x_1	y_1(calcd)	P/bar exptl	P/bar calcd	γ_1	γ_2
		$T = 288.23$ K			
0.0000	0.0000	0.84	0.84	7.5448	1.0000
0.0561	0.3661	2.00	2.01	5.4194	1.0092
0.1094	0.5145	2.66	2.64	4.2340	1.0318
0.1095	0.5147	2.66	2.65	4.2322	1.0318
0.2240	0.6614	3.32	3.34	2.8501	1.1154
0.3665	0.7474	3.73	3.74	2.0206	1.2867
0.4857	0.7944	3.93	3.93	1.6302	1.5088
0.6563	0.8502	4.10	4.11	1.2897	2.0643
0.6845	0.8593	4.14	4.14	1.2488	2.2041
0.7013	0.8648	4.16	4.16	1.2261	2.2975
0.7394	0.8775	4.20	4.19	1.1786	2.5439
0.7779	0.8908	4.23	4.23	1.1360	2.8564
0.8139	0.9038	4.28	4.26	1.1008	3.2298
0.8939	0.9353	4.33	4.33	1.0386	4.5572
0.9406	0.9566	4.36	4.37	1.0139	5.9731
0.9564	0.9653	4.38	4.39	1.0079	6.6615
1.0000	1.0000	4.40	4.40	1.0000	9.6337
		$T = 298.35$ K			
0.0000	0.0000	1.23	1.23	6.6172	1.0000
0.0583	0.3463	2.71	2.72	4.9359	1.0086
0.0942	0.4574	3.31	3.31	4.2419	1.0212
0.1558	0.5750	4.03	4.01	3.3966	1.0540
0.2057	0.6354	4.42	4.40	2.9146	1.0901
0.2650	0.6861	4.69	4.72	2.4890	1.1443
0.3675	0.7454	5.06	5.09	1.9842	1.2704
0.4187	0.7676	5.24	5.23	1.8021	1.3521
0.4919	0.7949	5.41	5.38	1.5947	1.4975
0.6515	0.8461	5.63	5.63	1.2848	2.0010
0.6688	0.8515	5.65	5.65	1.2595	2.0797
0.7423	0.8752	5.76	5.75	1.1661	2.5030
0.7593	0.8809	5.78	5.78	1.1474	2.6279
0.7938	0.8929	5.82	5.82	1.1126	2.9249
0.8679	0.9207	5.92	5.92	1.0519	3.8615
0.8800	0.9256	5.94	5.94	1.0439	4.0730
0.8966	0.9327	5.95	5.96	1.0337	4.4022
0.9077	0.9376	5.96	5.97	1.0275	4.6523
0.9182	0.9424	5.99	5.99	1.0222	4.9149
0.9526	0.9608	6.02	6.02	1.0082	6.0102
0.9563	0.9631	6.02	6.02	1.0070	6.1554
1.0000	1.0000	6.03	6.03	1.0000	8.5187

We correlated phase behavior of the HFC-152a + HF system using Anderko's equation of state for HF with the van der Waals one-fluid mixing rule as well as the Wong–Sandler mixing rule.

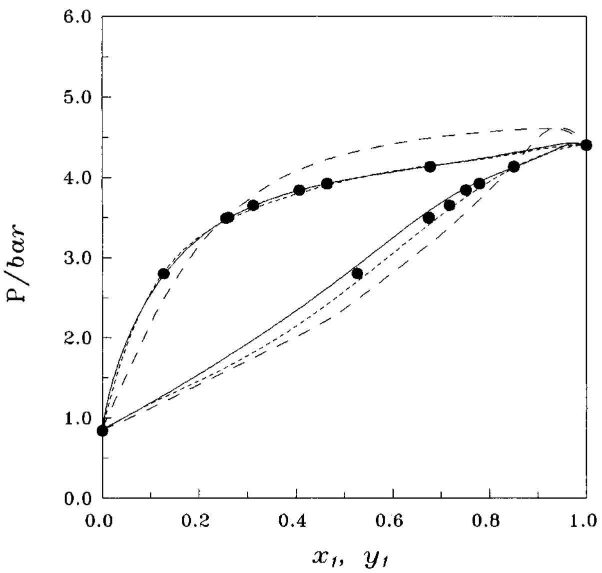

Figure 3. $P-x-y$ diagram for the HFC-152a (1) + HF (2) system at 288.23 K: (●) Experimental data by *PTxy* measurement; (···) calculated by Schotte's method; (- - -) calculated by the van der Waals one-fluid mixing rule; (—) calculated by the Wong–Sandler mixing rule.

For the z^{ph} contribution of Anderko's equation of state, we used the original Peng–Robinson equation of state. The pure component parameters a and b for compounds other than HF have been calculated from critical temperature, critical pressure, and vapor pressure using an expression for the temperature dependence of a proposed by Melhem et al. (1989). The modified NRTL expression was used for the A^{E} term of eqs 11 and 12

$$\frac{A^{\text{E}}}{RT} = \sum_i x_i \frac{(\sum_j x_j G_{ji} \tau_{ji})}{\sum_k x_k G_{ki}} \tag{19}$$

with

$$G_{ji} = b_j \exp(-\alpha_{ij} \tau_{ji}) \tag{20}$$

where b_j is the volume parameter in the equation of state for species j. This modified NRTL form was suggested earlier by Huron and Vidal (1979) for the excess Gibbs free energy for use in their model and used by Orbey and Sandler (1995) for correlating binary nonideal mixtures. After some preliminary trials, we found that we could choose $\alpha_{ij} = 0.3$ for the HFC-152a + HF system. The parameters of mixing rules were obtained by a nonlinear optimization technique using the Marquardt algorithm (Kuester and Mize, 1973). Since the uncertainty of vapor analysis is assumed larger than that of liquid analysis, we used as following object function:

$$\text{obj} = \left[100 \times \sum_i \left(\frac{P_{\text{exptl},i} - P_{\text{calcd},i}}{P_{\text{exptl},j}} \right) \right]^2 \tag{21}$$

The results are shown in Figures 3 and 4. These figures show the calculated results at 288.23 and 298.35 K, respectively, compared with the experimental measurements of this work. The solid lines are predictions using Anderko's equation of state with the Wong–Sandler mixing rule, and the long dashed lines are predictions with the van der Waals one-fluid mixing rule. The binary interaction parameter for the van der Waals one-fluid mixing rule, k_{ij}, is −0.1679 at two temperatures. Parameters for the Wong–Sandler mixing rule are $k_{ij} = 0.429$, $\tau_{21} = 0.01$, and $\tau_{12} = -0.23$ at two temperatures. The short dashed lines are predictions using Schotte's method. Predictions with the Wong–Sandler mixing rule and with Schotte's method show good agreement with experimental values. According to prediction of Lencka and Anderko (1993) for HCl + HF, R-113 + HF, and R-22 + HF systems, the van der Waals one-fluid mixing rule gives good results, but the calculated results are not good for the HFC-152a + HF system as shown in Figures 3 and 4.

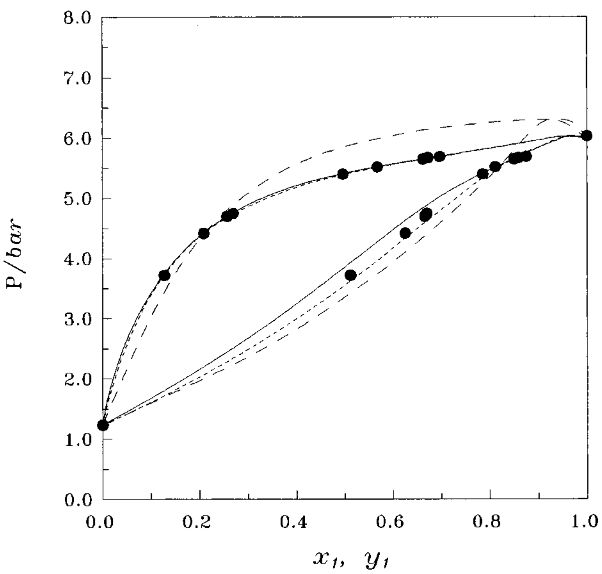

Figure 4. $P-x-y$ diagram for the HFC-152a (1) + HF (2) system at 298.35 K: (●) Experimental data by PTxy measurement; (···) calculated by Schotte's method; (- - -) calculated by the van der Waals one-fluid mixing rule; (—) calculated by the Wong–Sandler mixing rule.

Conclusions

A newly designed circulating type apparatus with a view cell was constructed to measure the vapor–liquid equilibrium data for HF-containing systems. Equilibrium *PTxy* data for the HFC-152a + HF system at 288.23 and 298.35 K were obtained with this equipment. *PTx* equilibrium data were also measured by the total pressure method to compare the results with each other. We have correlated the experimental data with several methods. Results show that Schotte's method and Anderko's equation of state with the Wong–Sandler mixing rule can be used to predict the phase behavior of the HFC-152a + HF system in the range of temperatures studied.

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