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High Pressure Vapor-Liquid Equilibria of Binary System 1,1,1-trifluoroethane (HFC-143a)+Propane (HC-290)

Jong Sung Lim[†], Ji-Young Park* and Byung-Gwon Lee*

Department of Chemical & Biomolecular Engineering, Sogang University, C.P.O. Box 1142, Seoul 100-611, Korea
*Division of Environmental and Process Technology, KIST, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

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Abstract−Isothermal vapor-liquid equilibrium data were measured for the binary mixture of 1,1,1-trifluoroethane (HFC-143a)+propane (HC-290) at six equally spaced temperatures between 268.15 and 318.15 K by using a circulation-type equilibrium apparatus. The phase composition at equilibrium was measured by gas chromatography. The experimental data were compared with the calculated data based on the Carnahan-Starling-De Santis (CSD) equation of state. Good agreement between experimental and calculated data indicates that the CSD equation of state can be used to estimate thermodynamic properties for the mixture of HFC-143a+propane in the range of temperatures between 268.15 and 318.15 K. The binary system of HFC-143a+propane exhibits azeotropes.

Key words: Vapor-Liquid Equilibria, HFC-143a, Propane (HC-290), Carnahan-Starling-De Santis (CSD) EOS, Azeotropes

INTRODUCTION

For nearly sixty years, chlorofluorocarbons (CFCs) have been widely used as solvents, foam blowing agents, aerosols and especially refrigerants due to their stability, non-toxicity, non-flammability, good thermodynamic properties and so on. However, they also have a harmful effect on the earth's protective ozone layer. So, they have been being regulated internationally by Montreal Protocol since 1989. Subsequently, it was discovered that CFCs also contributed significantly to the global warming problem. The result was that CFCs have been forbidden to be developed from January of 1996. In 2010, production and use of CFCs will be prohibited completely all over the world. In consequence, much research has been done to find a suitable replacement for CFCs. Initial alternatives included some hydrochloroflourocarbons (HCFCs), but they will also be phased out internationally around 2020-2030 because their ozone depletion potentials and global warming potentials are in relative high levels though less than those of CFCs. Hydrofluorocarbons (HFCs) - synthetic refrigerants which have zero ozone depletion potentials - were proposed as promising replacements for CFCs and HCFCs. Hydrofluorocarbons such as difluoroethane (HFC-32), pentafluoroethane (HFC-125), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1-trifluoroethane (HFC-143a), 1,1-difluoro-ethane (HFC-152a), and 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) are promising alternative refrigerants in place of dichlorodifluoromethane (CFC-12) and chlorodifluoromethane (HCFC-22). Their global warming potential (GWP) is less than that of CFC-12 and HCFC-22 because they contain more hydrogen atoms and thus have a shorter atmospheric lifetime. Unfortunately, HFCs are stable but very expensive and the manufacture of these HFCs is high-tech process; consequently, their cost is high, which would create a burden for poor countries. On the other hand, the utilization of hydrocarbons such as propane, n-butane, iso-butane, propylene, etc., as effective refrigerants is believed as an alternative solution because these hydrocarbons are environmentally benign chemicals (due to their zero ozone depletion potential and near zero global warming potential) and have many outstanding properties. They are also common components of natural gas, so they are cheap and plentiful. Their flammability has caused some concerns but all tests done so far have indicated that they are quite safe in small applications such as domestic refrigerators and car air-conditioners because of the very small amounts involved. Therefore, the mixture of the two compounds may have a good potential for alternative refrigerants. Vapor-liquid equilibrium data are required as one of the most important types of basic information in evaluating the performance of refrigeration cycles and determining their optimal compositions [Nishiumi and Ohno, 2000; Nishiumi et al., 1997].

In this work, VLE data for HFC-143a+propane were measured, and the experimental data were correlated with the Carnahan-Starling-De Santis (CSD) equation of state (EOS). Almost all the calculated values using this model give good agreement with the experimental data. This mixture exhibits azeotropes. In the range of experimental temperature, the average absolute deviations of pressures and vapor phase compositions between experimental and calculated values were determined and the relevant parameters were presented.

EXPERIMENTAL SECTION

1. Chemicals

High-grade chemicals of HFC-143a and propane were used for this investigation. HFC-143a of purity higher than 99.8% mass was supplied by DuPont Industries, U.S.A. Propane supplied by MG Industry, UK had purity higher than 99.5% mass. The purities of the chemicals were guaranteed from the manufacturers and they were used without any further purification.

2. Experimental Apparatus

The vapor-liquid equilibrium apparatus used in this work was a circulation-type in which both liquid and vapor phases were continuously recirculated. This apparatus was explained well in our

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[†] To whom correspondence should be addressed.
E-mail: limjs@sogang.ac.kr

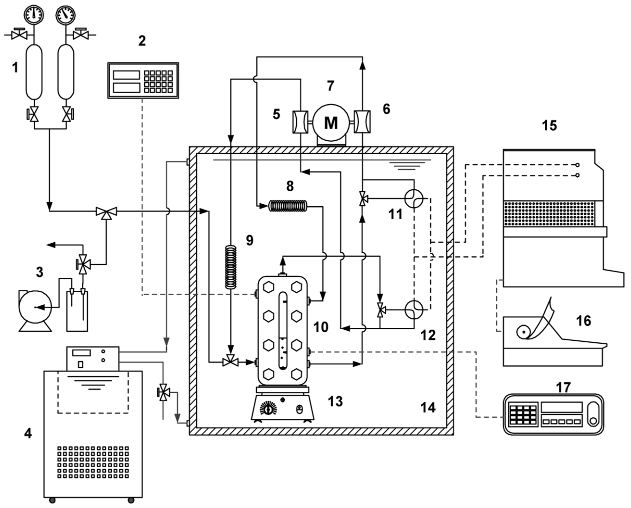

Fig. 1. Schematic diagram of the vapor liquid equilibrium apparatus.

1. Sample reservoir
2. Pressure indicator
3. Vacuum pump
4. Bath circulator
5. Vapor circulation pump
6. Liquid circulation pump
7. Electric motor
8. Liquid/Liquid heat exchanger
9. Gas/Liquid heat exchanger
10. Equilibrium cell
11. Liquid auto-sampler
12. Vapor auto-sampler
13. Magnetic stirrer
14. Bath containing heat carrier
15. Gas chromatograph
16. Computing integrator
17. Temperature indicator

previous papers [Lim et al., 2000, 2004]. A schematic diagram of this apparatus is in Fig. 1. The equilibrium cell is a 316 stainless steel vessel with an inner volume of about 85 cm^3. In its middle part, a pair of Pyrex glass windows of 20 mm thickness was installed so that the liquid level, mixing and circulating behaviors, and critical phenomena could be observed during operation. A stirrer, rotated at variable speeds by an external magnet, was used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in both phases. The temperature of the equilibrium cell in the water bath was maintained by a circulator from Jeio Tech, Korea. The temperature in the cell was measured with a platinum resistance sensor and a digital temperature indicator model F250MkII precision thermometer from Automatic Systems Laboratories Ltd., United Kingdom. They were calibrated by NAMAS accredited calibration laboratory. The total uncertainty in temperature measurements is estimated to be within ±0.01 K, including sensor uncertainty, ±0.01 K, temperature resolution, ±0.001 K, and measurement uncertainty, ±0.001 K. The pressure was measured with a pressure transducer, Model XPM60, and digital pressure calibrator, Model PC 106, from Beamax, Finland. Pressure calibrations are traceable to National Standards (Center for Metrology and Accreditation Cert. no. M-95P077, 14.11.1995, M-M 730, 16.11.1995 and M-95P078, 16.11.1995), and calibrator uncertainty was ±0.0005 MPa, sensor uncertainty was ±0.001 MPa, measurement uncertainty was ±0.001 MPa. Therefore, total uncertainties were estimated to be within ±0.001 MPa. The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump from the Milton Roy Company. After equilibrium was reached, the vapor and liquid samples were withdrawn from the recycling loop and injected on-line into a Gow-Mac Model 550P gas chromatograph. The gas chromatograph was equipped with a thermal conductivity detector (TCD) and a Porapak Q column from Alltech Company.

3. Experimental Procedures

Experiments for measuring VLE of HFC-143a(1)+propane(2) were performed by the following procedure. The system was first evacuated by a vacuum pump (3) to make sure that all inert gases were removed. An adequate amount of propane (less volatile than HFC-143a) contained in sample reservoir was introduced into the cell, and then the temperature of the entire system was maintained by controlling the temperature of the heat medium in the bath (14). After the desired temperature was attained, the vapor pressure of the pure propane was measured. After that, a targeted amount of HFC-143a was supplied into the cell from a charging cylinder. The mixture in the cell was stirred continuously with a magnetic stirrer for over 1 hr. Both vapor and liquid phases were circulated by the dual-head high-pressure pump until an equilibrium state was established. According to our experience, 1 hr or more is sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath. After equilibration, the pressure in the equilibrium cell was measured and then vapor and liquid samples were withdrawn from the recycling lines by the vapor and liquid sampling valves, respectively. The compositions of the samples were measured by immediately injecting them into the GC, which was connected online to vapor and liquid sampling valves. The GC was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. At least three analyses were performed for each phase and the average value was considered as corresponding to the equilibrium.

4. Correlation

The experimental VLE data were correlated with the Canahan-Starling-De Santis (CSD) equation of state using the approach of Morrison and McLinden [1986].

$$\frac{PV_M}{RT}=\frac{1+y+y^2-y^3}{(1-y)^3}-\frac{a}{RT(V_M+b)} \tag{1}$$

$$y=b/4V_M,\ V_M\text{: molar volume} \tag{2}$$

In case of pure component, the temperature dependence of ‘a’ and ‘b’ is represented by the following forms:

$$a=a_0\exp(a_1T+a_2T^2) \tag{3}$$

$$b=b_0+b_1T+b_2T^2 \tag{4}$$

The coefficient of a_0, a_1, a_2, in Eq. (3) and b_0, b_1, b_2 in Eq. (4) were cited from REFPROP 5.0 [Huber et al., 1996] and listed in Table 1.

In application of the CSD equation of state to mixtures, there exist the effective molecular parameters a_m and b_m (the m subscript refers to the mixture) defined by using the following mixing rules:

$$a_m=\sum_{i=1}^{n}\sum_{j=1}^{n}x_ix_ja_{ij} \tag{5}$$

$$b_m=\sum_{i=1}^{n}\sum_{j=1}^{n}x_ix_jb_{ij} \tag{6}$$

where n is the number of components in mixture. When i=j, the values of a_{ii} and b_{ii} are those of ‘a’ and ‘b’ of the pure components

Table 1. Pure fluid coefficients of CSD equation of state (Source: RERPROP 5.0)

Component	α_0 /kJm^{3}kg^{-1}mol^{-2}	$\alpha_1\times10^3$ /kJm^{3}kg^{-1}mol^{-2}K^{-1}	$\alpha_2\times10^6$ /kJm^{3}kg^{-1}mol^{-2}K^{-2}	β_0 /m^{3}kg^{-1}mol^{-1}	$\beta_1\times10^4$ /m^{3}kg^{-1}mol^{-1}K^{-1}	$\beta_2\times10^7$ /m^{3}kg^{-1}mol^{-1}K^{-2}
HFC-143a	2763.909	−2.509056	−1.7971077	0.1331526	−1.5895379	−0.5833105
Propane	2988.277	−2.629020	−1.097062	0.1429625	−1.7651912	−0.5785137

which are determined by Eqs. (3) and (4). The values of a_{ij} and b_{ij} can be obtained if nearly any experimental property of the mixture is known. For the binary systems, the values of a_{12} and b_{12} can be expressed as the following forms:

$$a_{12}=(1-f_{12})(a_{11}a_{22})^{1/2} \tag{7}$$

$$b_{12}=\frac{1}{8}(b_1^{1/3}+b_2^{1/3})^3 \tag{8}$$

the mixing rule for the ‘a’ parameter for a mixture involves the interaction parameter, f_{12}, which must be determined from experimental data. The approach is to find the value of f_{12}, which minimizes the sum of square Γ of relative deviation between measured and calculated quantities:

$$\Gamma(T,x,f_{12})=\omega_P\left(\frac{P_{exp.}-P_{cal.}}{P_{exp.}}\right)^2+\omega_L\left(\frac{V_{L,exp.}-V_{L,cal.}}{V_{L,exp.}}\right)^2+\omega_v\left(\frac{V_{v,exp.}-V_{v,cal.}}{V_{v,exp.}}\right)^2+\omega_y(y_{exp.}-y_{cal.})^2 \tag{9}$$

Because the vapor composition must be between zero and unity, the last term in Eq. (9) is expressed as an absolute error. Because the experimental data of vapor and liquid specific volume indicated in this equation are not available, the corresponding weighting factors in the expression of Γ are set to zero.

$$\Gamma(T,x,f_{12})=\omega_P\left(\frac{P_{exp.}-P_{cal.}}{P_{exp.}}\right)^2+\omega_y(y_{exp.}-y_{cal.})^2 \tag{10}$$

RESULTS AND DISCUSSION

Some characteristic properties of pure HFC-143a and propane from the database REFPROP 6.01 [McLinden et al., 1998] which is considered to be reliable for the pure compounds considered here and consistent with other literature data are summarized in Table 2.

The saturated vapor pressures of HFC-143a and propane at various temperatures that were experimentally measured and obtained from database REFPROP 6.01 are shown in Table 3. A comparison between experimental and calculated values indicates that the absolute deviations of vapor pressure for both HFC-143a and propane were within ±0.005 MPa, and the average relative deviations

Table 2. Characteristic properties

Component	Chemical formula	M.W.	T_c/K	P_c/MPa	ω	Source
HFC-143a	CF_3CH_3	84.04	346.04	3.776	0.2611	RERPROP 6.01
Propane	C_3H_8	44.10	369.85	4.248	0.1524	

Table 3. Comparison of the measured pure components vapor pressures with data from the database REFPROP 6.01 and ASHRAE

T (K)	Measured	REFPROP	ΔP^a (MPa)	ΔP/P (%)	ASHRAE	ΔP^a (MPa)	ΔP/P (%)^b
				HFC-143a			
268.15	0.5292	0.5284	0.0008	0.1512	-	-	-
278.15	0.7224	0.7217	0.0007	0.0969	-	-	-
288.15	0.9620	0.9637	0.0017	0.1767	-	-	-
298.15	1.2618	1.2618	0.0000	0.0000	-	-	-
308.15	1.6198	1.6244	0.0046	0.2840	-	-	-
318.15	2.0548	2.0596	0.0048	0.2336	-	-	-
Average deviation			0.0021	0.1570			
				Propane			
268.15	0.4079	0.4059	0.0020	0.4903	0.4061	0.0018	0.4413
278.15	0.5494	0.5510	0.0016	0.2912	0.5512	0.0018	0.3276
288.15	0.7350	0.7314	0.0036	0.4898	0.7316	0.0034	0.4626
298.15	0.9548	0.9519	0.0029	0.3037	0.9521	0.0027	0.2828
308.15	1.2130	1.2180	0.0050	0.4122	1.2179	0.0049	0.4039
318.15	1.5308	1.5340	0.0032	0.2090	1.5343	0.0035	0.2286
Average deviation			0.0030	0.3660		0.0030	0.3578

$^a\Delta P=P_{exp}-P_{cal}$, $^b\Delta P/P(\%)=100\times\frac{P_{exp}-P_{cal}}{P_{exp}}$

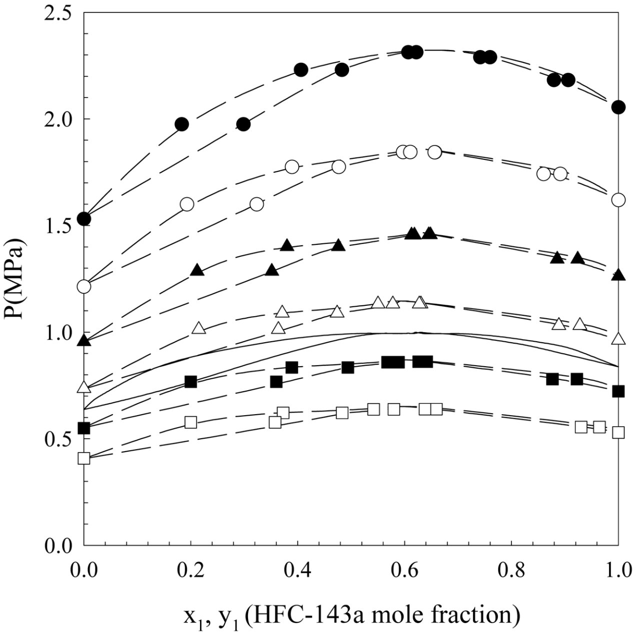

Fig. 2. P-x-y diagram for HFC-143a+propane mixtures at various temperatures: (□) 268.15 K, (■) 278.15 K, (△) 288.15 K, (▲) 298.15 K, (○) 308.15 K, (●) 318.15 K, (– –) calculated value by using CSD EOS, (—) S. Bobbo's work at 283.15 K.

(DP/P(%)) were 0.157% for HFC-143a and 0.366% for propane from database REFPROP 6.01 and 0.357% for propane from ASHRAE [ASHRAE Handbook, 1993].

Fig. 2 shows P-x-y diagram for a mixture of HFC-143a+propane at various temperatures such as at 268.15, 278.5, 288.15, 298.15, 308.15, and 318.15 K. The black dashed line represents the calculated data by CSD equation of state and the calculated diagram shows relatively good agreement with the corresponding experimental one. The black solid line represents the Bobbo's work [Stryjek et al., 1998] at 283.15 K. The experimental VLE data of HFC-143a(1)+propane (2) mixture including mole fraction of HFC-143a in the liquid and vapor phases, pressures in equilibrium at 268.15, 278.5, 288.15, 298.15, 308.15, and 318.15 K are listed in Table 3.

Figs. 3 and 4 show the deviations of pressure and vapor composition between experimental data and calculated value using the CSD equation of state, point by point. As can be seen in these figures, the average deviations of pressure and vapor phase composition are relatively small and acceptable in the temperature range from 268.15 to 318.15 K. That is, the calculated values from using the CSD equations of state give a good agreement with the experimental data. Interaction parameters, f_{12}, of the CSD equation of state with various temperatures were obtained by using VLE data. The values of f_{12} determined at 268.15, 278.5, 288.15, 298.15, 308.15, and 318.15 K were 0.1166, 0.1069, 0.1181, 0.1161, 0.1155, and 0.1166. The data calculated by using the CSD equation of state and the deviations of pressure and vapor phase composition between experimental and calculated data at various temperatures are listed in Table 5.

Table 4. Vapor-liquid equilibrium data for HFC-143a(1)+propane (2) system

P(MPa)	x_1	y_1
	T=268.15 K	
0.4079	0.000	0.000
0.5767	0.200	0.358
0.6216	0.373	0.483
0.6376	0.542	0.580
0.6382	0.660	0.638
0.5549	0.964	0.930
0.5292	1.000	1.000
	T=278.15 K	
0.5494	0.000	0.000
0.7674	0.200	0.360
0.8340	0.389	0.494
0.8590	0.568	0.589
0.8614	0.642	0.626
0.7794	0.922	0.877
0.7224	1.000	1.000
	T=288.15 K	
0.7350	0.000	0.000
1.0126	0.215	0.364
1.0890	0.371	0.474
1.1322	0.550	0.578
1.1322	0.631	0.627
1.0308	0.928	0.889
0.9620	1.000	1.000
	T=298.15 K	
0.9548	0.000	0.000
1.2848	0.212	0.352
1.4004	0.380	0.476
1.4554	0.613	0.618
1.4566	0.648	0.645
1.3418	0.924	0.886
1.2618	1.000	1.000
	T=308.15 K	
1.2130	0.000	0.000
1.5990	0.193	0.323
1.7746	0.390	0.477
1.8446	0.597	0.611
1.8432	0.657	0.656
1.7414	0.891	0.860
1.6198	1.000	1.000
	T=318.15 K	
1.5308	0.000	0.000
1.9744	0.183	0.299
2.2296	0.406	0.483
2.3124	0.607	0.622
2.2888	0.760	0.742
2.1822	0.906	0.879
2.0548	1.000	1.000

This mixture exhibited the azeotropes and Figs. 5 and 6 show the azeotropic compositions and pressures of this mixture. Azeotropic data of this mixture determined in the temperature range of 268.15-318.15 K were 0.591 to 0.637 mole fraction in composition, and 0.639 to 2.314 MPa in pressure. It was revealed that azeotropic composition and pressures depended on the temperature. In the experimental temperature range, azeotropic compositions were cor-

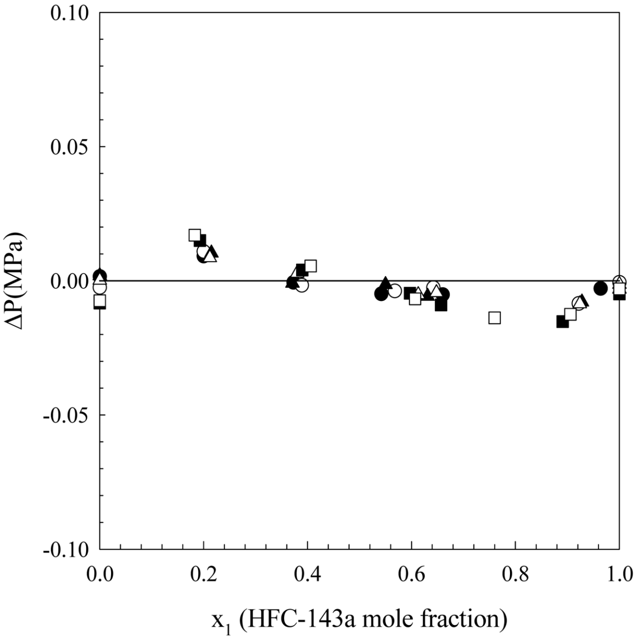

Fig. 3. Deviation of pressure for HFC-143a+propane mixture at various temperatures: (●) 268.15 K, (○) 278.15 K, (▲) 288.15 K, (△) 298.15 K, (■) 308.15 K, and (□) 318.15 K.

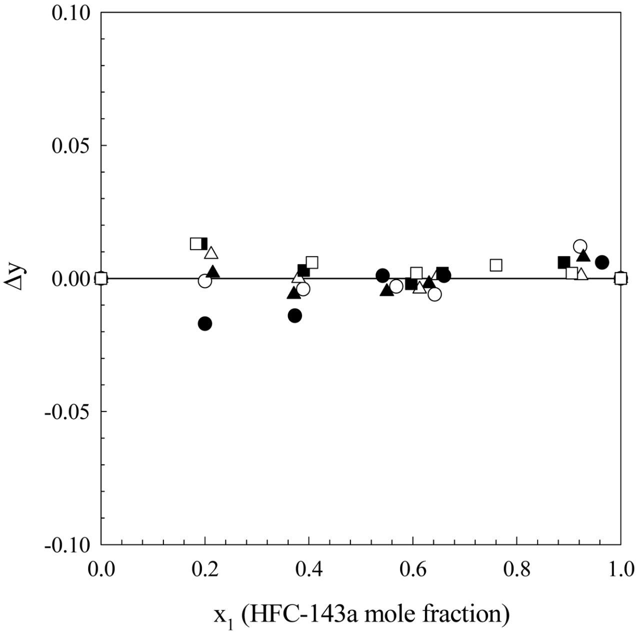

Fig. 4. Deviation of vapor phase composition for HFC-143a+propane mixture at various temperatures: (●) 268.15 K, (○) 278.15 K, (▲) 288.15 K, (△) 298.15 K, (■) 308.15 K, and (□) 318.15 K.

related by the empirical equation, x_{azeo} (mole fraction)=0.334+9.591 $\times 10^{-4} \times$T (K), and azeotropic pressures were correlated by the empirical equation, P_{azeo} (MPa)=17.88+20.146×T (K)+3.067$\times 10^{-4}$ T (K)^2. Azeotropic compositions and pressures are reported in Table 6.

CONCLUSIONS

Table 5. Values of binary parameters and average deviations of P and y

T (K)	CSD EOS			
	f_{12}[a]	δP[a] (MPa)	$\delta P/P$[b] (%)	δy[c]
268.15	0.1166	0.0036	0.61	0.0056
278.15	0.1169	0.0044	0.57	0.0037
288.15	0.1181	0.0045	0.44	0.0033
298.15	0.1161	0.0044	0.33	0.0021
308.15	0.1155	0.0087	0.54	0.0037
318.15	0.1166	0.0094	0.46	0.0040

[a] $\delta P = \frac{1}{N}\sum|(P_{exp} - P_{cal})|$

[b] $\delta P/P = \frac{1}{N}\sum|(P_{exp} - P_{cal})/P_{exp}| \times 100$

[c] $\delta y = \frac{1}{N}\sum|(y_{exp} - y_{cal})|$

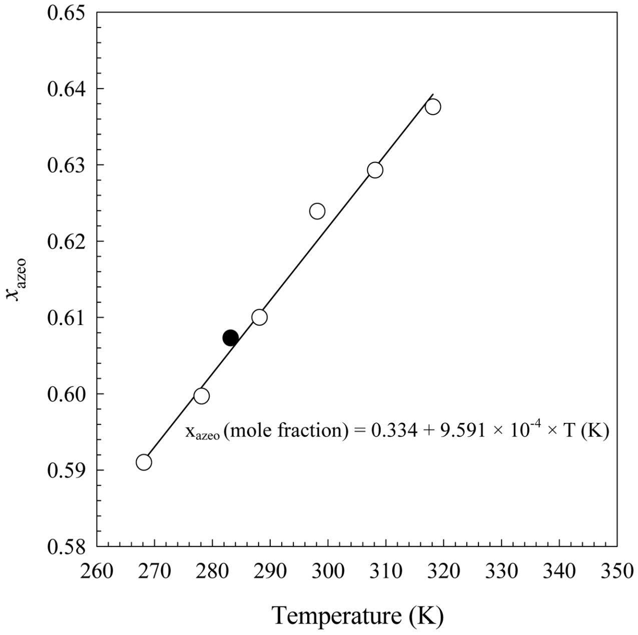

Fig. 5. Variation of the azeotropic composition for HFC-143a+propane mixture: (○) this work, and (●) S. Bobbo's work at 283.15 K.

Measurements of the vapor-liquid equilibria for the mixture of HFC-143a+propane at six equally spaced temperatures between 268.15 and 318.15 K were made by using a circulation-type equilibrium apparatus. It was found that this mixture shows azeotropic behavior in the experimental temperature range. The experimental VLE data were correlated with calculated values by using the CSD equation of state and the interaction parameters, f_{12}, were obtained. The calculated data from the CSD equation of state show good agreement with the experimental data. This result indicates that the CSD equation of state can be used to estimate the thermodynamic properties for the mixture of HFC-143a(1)+propane(2) in the temperature range between 268.15 and 318.15 K and can be applied to other ranges, but additional experiments are needed to confirm this.

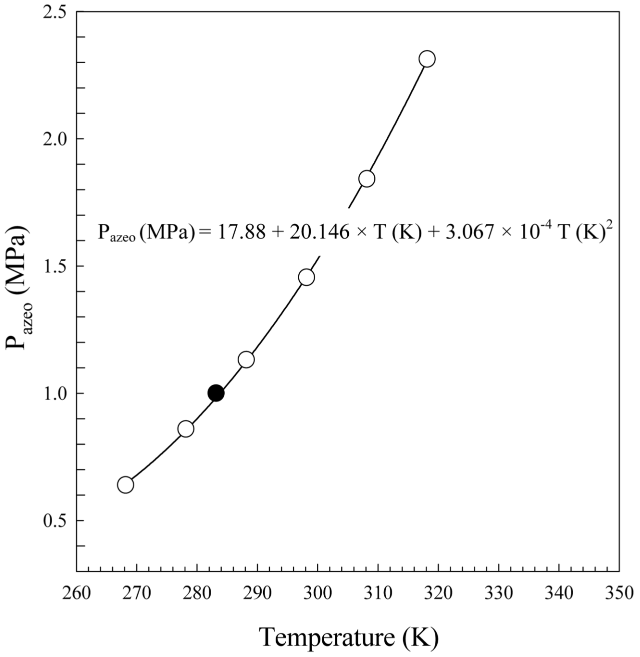

Fig. 6. Variation of the azeotropic pressure for HFC-143a+propane mixture: (○) this work, and (●) S. Bobbo's work at 283.15 K.

Table 6. Azeotropic composition and pressure of HFC-143a+propane system

	T(K)	x_{azeo}	P_{azeo} (MPa)
This work	268.15	0.5910	0.6397
	278.15	0.5997	0.8594
	288.15	0.6100	1.1320
	298.15	0.6239	1.4551
	308.15	0.6293	1.8426
	318.15	0.6376	2.3139
S. Bobbo's work	283.18	0.6073	1.0003

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