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Vapor–Liquid Equilibrium Measurements for Binary Mixtures Containing 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea)[1]

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Isothermal vapor–liquid equilibrium data for two binary mixtures of alternative refrigerants were determined by using an apparatus applying recirculating vapor and liquid. The difluoromethane (HFC-32) + 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) and 1,1,1,2-tetrafluoroethane (HFC-134a) + 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) systems were studied at 298.15 and 312.65 K. The pressure and vapor and liquid compositions were measured at each temperature. The experimental data were correlated with the Peng–Robinson equation of state using the van der Waals one-fluid mixing rule. Calculated results show that this equation yields good agreement with the experimental data.

KEY WORDS: HFC-134a; HFC-227ea; HFC-32; Peng–Robinson equation of state; vapor–liquid equilibrium.

1. INTRODUCTION

1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) is one of the promising alternative replacements for dichlorodifluoromethane (CFC-12) and 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114). It has been recently reported

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that this substance has several advantages such as low enthalpy rise, low toxicity, and inflammability, but it has not been widely used [1]. Difluoromethane (HFC-32) is mainly used as a component of a refrigerant blend to substitute for CFC-12, chlorodifluoromethane (HCFC-22), or R502. 1,1,1,2-Tetrafluoroethane (HFC-134a) has been commercially used in automotive air conditioners, refrigerators, etc., mainly as a pure substitute for CFC-12, but also as a component of mixtures to substitute for HFC-22 and R502.

Vapor–liquid equilibria are basic data essential for evaluating the thermodynamic properties, and then the efficiency, for refrigeration systems, and for selecting the optimal compositions for design and operation. Little information about these properties for systems containing HFC-227ea has been previously reported in the literature.

In this work, isothermal vapor–liquid equilibria for the HFC-32 + HFC-227ea and HFC-134a + HFC-227ea systems were experimentally investigated at 298.15 and 312.65 K with a vapor and liquid recirculation apparatus. The experimental data were correlated with the Peng–Robinson equation of state using the van der Waals one-fluid mixing rule.

2. EXPERIMENTS

2.1. Compounds

The purities and sources of the compounds used in this work are shown in Table I. They were used without further purification. The purity was tested with a gas chromatograph with a flame ionization detector. The oven, injector, and detector temperatures were 50, 100, and 120°C, respectively. After the compounds were introduced into the feed vessel, the vessel was heated and the valve of the vessel was opened for a few seconds to vent air. We ensured that there were negligible amounts of impurities by comparing the vapor pressure of pure refrigerants measured in this study with literature values. The critical properties and acentric factor of each component are shown in Table II.

Table I. Origin and Purity of the Components

Component	Origin	Purity (mass %)
HFC-227ea	Great Lakes Chemical Corp.	>99.9
HFC-32	Ulsan Chemical Co., Korea	>99.9
HFC-134a	DuPont	>99.95

Table II. Critical Properties and Acentric Factor of the Pure Components

Component	T_c (K)	P_c (bar)	ω	Source
HFC-227ea	375.0	29.1	0.356	[a]
HFC-32	351.3	57.8	0.277	6
HFC-134a	374.3	40.7	0.326	6

[a] Great Lakes Chemical Corp. data sheet.

2.2. Apparatus

Vapor–liquid equilibria were measured using a recirculation-type apparatus that is similar to that of Lee et al. [2]. A schematic diagram of the apparatus is shown in Fig. 1. The system consists of five major parts: an equilibrium cell, a magnetic pump for circulation, vapor and liquid sampling valves, constant-temperature air bath, and an analysis system. The equilibrium cell, whose internal volume is about 320 cm^3, was made of 316 stainless steel. It is equipped with a glass window so that the phases at vapor–liquid equilibrium and the circulation behavior could be observed. In the vapor circulation mode, the vapor is taken from the upper part of the cell and recirculated into the bottom and bubbles up through the liquid phase so that the two phases are in contact with each other. On the other hand, in the liquid circulation mode, liquid from the bottom of the cell is circulated in the opposite direction and brought into the cell in the shape of droplets. A magnetic pump was used to circulate the mixture. To switch the circulation mode from vapor to liquid, a reverse four-port valve was used.

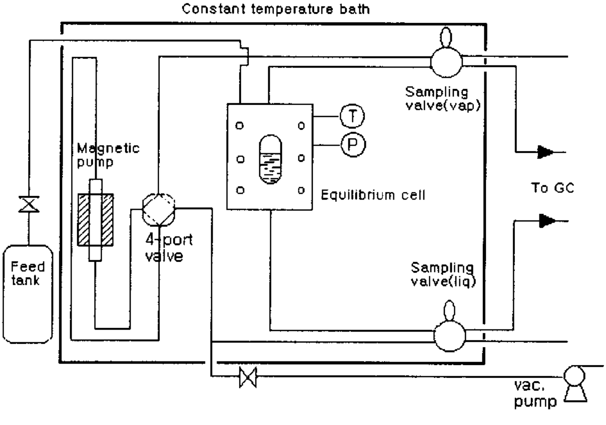

Fig. 1. Schematic diagram of the apparatus.

Vapor and liquid samples were analyzed on-line using the gas chromatograph with a flame ionization detector and a packed column with carbopak B + 5 % fluorocol. The conditions of the gas chromatograph were as follows: detector temperature was 423.15 K and oven temperature was 323.25 K. Nitrogen was used as a carrier gas, and the flow rate was set to 25 $\text{cm}^3 \cdot \text{min}^{-1}$. Although the internal calibration method generally gives a more accurate analysis result than the absolute method, the latter was used to determine vapor and liquid compositions because a standard gas for HFC-227ea is not available. In this method the compositions of the samples are determined with the peak area according to a known accurate amount of each pure component. Varying the amount with several sampling loops, each pure component was analyzed to generate calibration curves. Considering the fluctuations in areas of pure components and mixtures, the uncertainty of liquid and vapor compositions is estimated to be within 0.002 mole fraction.

The temperature was measured using a 100-Ω platinum resistance thermometer calibrated against ITS-90, and the uncertainty was estimated to be within ±0.05 K. The pressure was measured with a strain-type pressure transducer (Model Super TJE, Sensotec), and the uncertainty of the pressure measurement was estimated to be ±0.5 psia. Two six-port sampling valves (Valco Instruments, Rheodyne Instruments) were equipped to withdraw the vapor and liquid samples. They were connected to a gas chromatograph for on-line analysis. Except for the data analysis system, all parts were located in the forced convection air oven, which operates from room temperature to 473 K with an error of ±0.05 K.

2.3. Experimental Procedure

A targeted amount of HFC-227ea in the reservoir was charged into the equilibrium cell after the whole system was evacuated by a vacuum pump to remove impurities. The temperature of the system was maintained by controlling the temperature of the air bath. The pressure of the pure component was measured when the desired temperature was reached. A targeted amount of HFC-32 or HFC-134a was introduced into the cell. The coexistence of the vapor and liquid phases was observed through the glass windows, and the magnetic pump was turned on to circulate the mixture. The pressure was measured when vapor–liquid equilibrium was accomplished. In the vapor circulation mode, the vapor sample was taken with a vapor sampling valve while the vapor was circulated. The procedure of liquid sampling was the same as that for vapor sampling. The samples trapped in the sampling valve were injected on-line to the gas chromatograph. After the analysis for one data point, incrementa amounts of HFC-32

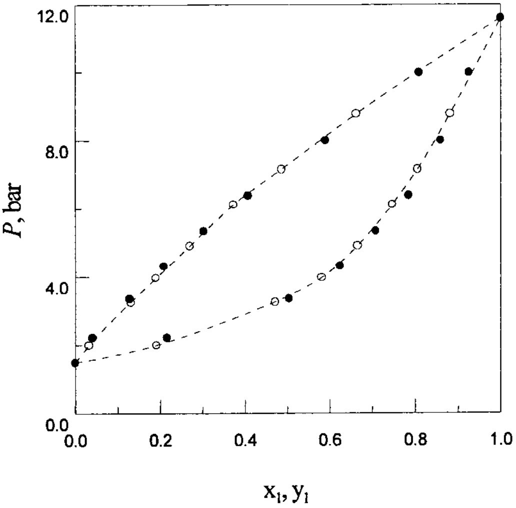

Fig. 2. Thermodynamic consistency test of the experimental apparatus: Comparison of the present experimental data (●) with the literature [3] data (○) for HFC-134a (1) + HCFC-141b (2) at 318.15 K.

or HFC-134a were introduced in to the cell to attain another equilibrium condition.

To verify the performance of the apparatus used in this study, vapor–liquid equilibria for HFC-134a + HCFC-141b were measured and compared with literature data [3]. This experiment was carried out at 318.15 K, and the experimental results are shown in Fig. 2. The deviation in pressure of the measurements from the reference was about 0.33 % for the P, T, x measurement and 1.2 % for the P, T, y measurement. The maximum absolute deviation in vapor composition is estimated to be about 0.02 mole fraction. The deviation has a maximum when pressure increases from 6 to 8 bar. Except for this pressure range, the deviations are smaller than 0.01 mole fraction.

3. RESULTS

The experimental vapor–liquid equilibria data were obtained for the binary systems of HFC-32 + HFC-227ea and HFC-134a + HFC-227ea at 298.15 and 312.65 K. The results are given in Tables III and IV, respectively. The measured temperatures, pressures, and liquid and vapor mole fractions are presented in these tables.

Table III. Isothermal Vapor–Liquid Equilibrium Data for HFC-32 (1) + HFC-227ea (2) System[a]

P (bar)			y_1	
Exp	Calc	x_1	Exp	Calc
		$T = 298.15$ K		
4.56	4.52	0.000	0.000	0.000
6.07	5.93	0.102	0.294	0.281
7.64	7.53	0.219	0.486	0.482
8.96	8.91	0.321	0.603	0.601
10.25	10.25	0.423	0.693	0.690
11.14	11.14	0.492	0.753	0.740
13.00	13.13	0.652	0.846	0.833
14.53	14.70	0.786	0.908	0.898
15.52	15.71	0.877	0.949	0.940
16.86	17.02	1.000	1.000	1.000
		$T = 312.65$ K		
6.93	6.90	0.000	0.000	0.000
8.83	8.50	0.084	0.232	0.220
10.01	9.75	0.150	0.354	0.344
13.22	13.08	0.327	0.576	0.572
14.99	15.00	0.430	0.670	0.664
16.54	16.66	0.520	0.740	0.730
17.50	17.76	0.581	0.782	0.769
20.82	21.11	0.773	0.897	0.878
22.33	22.68	0.869	0.943	0.927
24.37	24.70	1.000	1.000	1.000

[a] x_1, y_1 in mole fractions.

4. CORRELATION OF DATA

The measured data for the HFC-32 + HFC-227ea system were correlated with the Peng–Robinson equation of state [4], which is expressed as follows:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \tag{1}$$

with

$$a(T) = (0.457235\ R^2T_c^2/P_c)\alpha \tag{2}$$

$$b = 0.077796\ RT_c/P_c \tag{3}$$

Table IV. Isothermal Vapor–Liquid Equilibrium Data for HFC-134a (1) + HFC-227ea (2) System[a]

P (bar)			y_1	
Exp	Calc	x_1	Exp	Calc
		$T = 298.15$ K		
4.56	4.52	0.000	0.000	0.000
4.87	4.89	0.123	0.190	0.177
5.18	5.18	0.228	0.307	0.307
5.47	5.46	0.337	0.414	0.426
5.70	5.69	0.438	0.518	0.526
5.92	5.90	0.533	0.604	0.612
6.17	6.23	0.705	0.747	0.757
6.36	6.40	0.809	0.837	0.842
6.64	6.65	1.000	1.000	1.000
		$T = 312.65$ K		
6.93	6.90	0.000	0.000	0.000
7.36	7.35	0.106	0.143	0.148
7.80	7.78	0.213	0.279	0.280
8.26	8.25	0.340	0.418	0.419
8.67	8.66	0.458	0.541	0.536
8.94	8.92	0.539	0.619	0.610
9.34	9.39	0.704	0.773	0.753
9.58	9.63	0.800	0.851	0.832
9.69	9.72	0.838	0.880	0.864
9.98	10.04	1.000	1.000	1.000

[a] x_1, y_1 in mole fractions.

$$\alpha = [1 + \kappa(1 - T_{\mathrm{r}}^{0.5})]^2 \tag{4}$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

where P (in bar) is the pressure, v (in $\mathrm{cm^3 \cdot mol^{-1}}$) is the molar volume, R (in $\mathrm{bar \cdot cm^3 \cdot mol^{-1} \cdot K^{-1}}$) is the universal gas constant, the parameter a (in $\mathrm{bar \cdot cm^3 \cdot mol^{-2}}$) is a function of temperature, b (in $\mathrm{cm^3 \cdot mol^{-1}}$) is a constant, ω is the acentric factor, κ is a function of the acentric factor characteristic of each component, and α is a function of reduced temperature and acentric factor. In the calculation procedure the van der Waals one-fluid mixing rule was used. It is known that vapor–liquid equilibria data are correlated well with the Peng–Robinson equation of state using only one adjustable parameter for ideal mixtures,

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

$$b = \sum_i x_i b_i \tag{7}$$

$$a_{ij} = (1 - k_{ij})\, a_i^{1/2} a_j^{1/2} \tag{8}$$

The objective function that was utilized to calculate the binary interaction parameters was set as follows.

$$\mathrm{OF} = 100 \sum_i \left| \frac{P(\exp) - P(\mathrm{calc})}{P(\exp)} \right|^2 \tag{9}$$

The Marquardt algorithm [5] was applied to calculate the interaction parameter by minimizing the objective function. The results of calculations are given in Table III and compared with the experimental values as shown in Fig. 3. The binary interaction parameters obtained at each temperature and the average absolute deviations (AAD) between measured and calculated values are given in Table V. As shown in this table, the calculated values gave quite good agreement with the experimental results and the values of the binary interaction parameters were close to zero. It

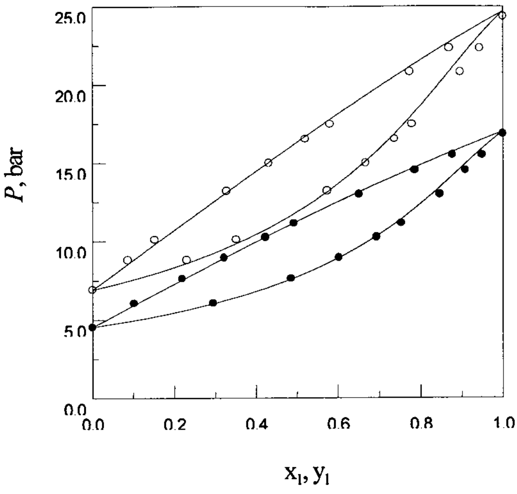

Fig. 3. Pressure vs. composition diagram for the HFC-32 (1) + HFC-227ea (2) system: (●) experimental data at 298.15 K; (○) experimental data at 312.65 K; (—) calculated.

Table V. Interaction Parameters and AAD (%) of Pressure

System	T (K)	k_{12}	Dev. P[a]	Dev. y[b]
HFC-32 + HFC-227ea	298.15	0.0191	0.952	1.42
	312.65	0.0254	1.442	2.05
HFC-134a + HFC-227ea	298.15	0.0121	0.377	2.08
	312.65	0.0121	0.325	1.64

[a] dev.P (%) = $(100/N) \sum_i^n |P_i(\text{exp}) - P_i(\text{calc})|/P_i(\text{exp})$.
[b] dev.y (%) = $(100/N) \sum_i^n |y_i(\text{exp}) - y_i(\text{calc})|/y_i(\text{exp})$.

was found that the HFC-32 + HFC-227ea system forms a nearly ideal mixture.

The same equation of state and optimization algorithm are applied to the HFC-134a + HFC-227ea system. The results of the calculation are given in Table IV and compared with experimental values as shown in Fig. 4. The binary interaction parameters are nearly constant over the range of the experimental measurements.

It is a very important characteristic whether a mixture is azeotropic or not when this mixture is used as a refrigerant. The two systems in this study were shown to be nonazeotropic mixtures. It can be seen easily that

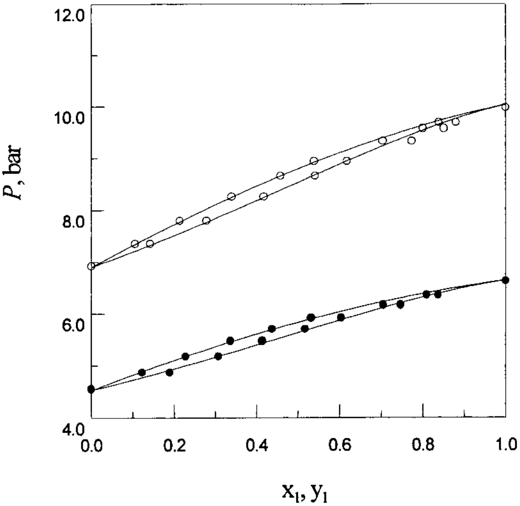

Fig. 4. Pressure vs. composition diagram for the HFC-134a (1) + HFC-227ea (2) system: (●) experimental data at 298.15 K; (○) experimental data at 312.65 K; (—) calculated.

the HFC-32 + HFC-227ea system is nonazeotropic, but it is quite difficult to state definitely that HFC-134a + HFC-227ea is nonazeotropic. In general, an azeotrope is likely to be formed when the difference of vapor pressure of each component is small or the nonideality of the mixture is sufficienty large. As the HFC-134a + HFC-227ea system has a very small difference of vapor pressure, this system is highly likely to form an azeotrope with some nonideality. But this system was found to show nearly ideal behavior, and it was concluded that this system is a nonazeotropic mixture. Though the possibility of near-azeotropic conditions was also considered for this system, it seems that the phase diagram would not be a smooth curve in the case of a near-azeotropic system. We calculated the difference of the Scatchard–Hildebrandt solubility parameter to determine the degree of nonideality assuming that this system is a regular solution because HFC-134a and HFC-227ea are not so different in shape and size. As a result of calculations, the difference of solubility parameter was too small to form an azeotropic mixture. Thus we concluded that the HFC-134a + HFC-227ea system forms a nonazeotropic mixture.

5. CONCLUSION

Vapor–liquid equilibria for HFC-32 + HFC-227ea and HFC-134a + HFC-227ea system were experimentally investigated using a recirculation-type apparatus. Neither of the two systems forms an azeotropic mixture over the range of these measurements. The experimental data are correlated with the Peng–Robinson equation of state with one adjustable parameter using the van der Waals one-fluid mixing rule. This equation yields satisfactory results in comparison with the experimental data.

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