J. Chem. Eng. Data **1996,** *41,* 745−747 **745**

Vapor−Liquid Equilibria for 1,1,1,2-Tetrafluoroethane + 1-Chloro-1,2,2,2-tetrafluoroethane and 1-Chloro-1,2,2,2-tetrafluoroethane + 1-Chloro-1,1-difluoroethane Systems

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Isothermal vapor−liquid equilibria were determined for two binary mixtures of refrigerants with a circulation type apparatus. The 1,1,1,2-tetrafluoroethane (HFC-134a) + 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124) system was studied at 296.45, 302.25, and 307.25 K. The 1-chloro-1,2,2,2-tetrafluoroethane (HCFC-124) + 1-chloro-1,1-difluoroethane (HCFC-142b) system was studied at 298.15 and 312.15 K. At each temperature, the pressure and vapor and liquid compositions were measured. Results were correlated with the Peng−Robinson equation of state.

Introduction

Several hydrofluorocarbons and hydrochlorofluorocarbons are now considered as alternative refrigerants that are harmless or less harmful to the ozone layer. HFC-134a is one of the promising candidates as an alternative refrigerant. There are disadvantages in using pure HFC-134a, so leading to studies on mixtures of HFC-134a with other refrigerants. HFC-134a has a poor compatibility with lubricants due to the absence of chlorine atoms. This disadvantage can be eliminated by mixtures with HCFC-124 which has a good compatibility with lubricants.

Azeotropic mixtures have merit when used as refrigerants because they show behavior similar to pure components. It has been predicted that the HCFC-124 + HCFC-142b system might have an azeotropic point (Lee and Sun, 1992).

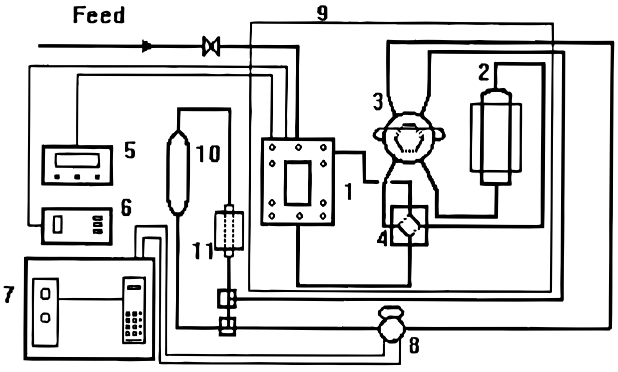
Vapor−liquid equilibria for mixtures are necessary to evaluate the efficiency for refrigeration and selecting the optimal composition for design and operation. In this work, we have measured the *P*, *T*, *x*, *y* data for HFC-134a + HCFC-124 and HCFC-124 + HCFC-142b and correlated the results with the Peng−Robinson equation of state.

Experimental Section

Chemicals. HFC-134a and HCFC-124 were supplied by DuPont, and the purities were 99.70 mass % and 99.95 mass %, repectively. HCFC-142b was supplied by Ulsan Chemical Co. with a minimum purity of 99.90 mass %.

Apparatus. The schematic diagram of the apparatus is shown in Figure 1. This experimental setup is a recirculation type similar to that of Kubota et al. (1990).

The mixture is circulated with a magnetic pump. The change in the circulation mode from vapor to liquid or the reverse is achieved by using a four-port valve. The sample trapped in a six-port valve is introduced into the pre-evacuated expansion loop. The expansion loop has a volume sufficient for the liquid sample to vaporize. The liquid sample is circulated in the expansion loop with a magnetic pump and homogenized. Vapor and liquid samples were analyzed chromatographically with a Yanaco 1800G gas chromatograph with a thermal conductivity detector and a carbowax 20M WHP 100/200 column for HFC-134a + HCFC-124. For the analysis of HCFC-124 + HCFC-142b, a Carbosieve B column was used. Helium was used as the carrier gas and the flow rate was set to 25 cm^3·min^{-1} for both systems. The absolute calibration method was used for determining the vapor and liquid compositions. The compositions of the samples are determined by the peak areas of an accurate amount of the pure components. The uncertainty of composition was estimated to be within ±0.002 mole fraction.



1. Equilibrium Cell 2. Magnetic Pump 3. 6-port Valve
4. 4-port Valve 5. Pressure Gauge 6. Thermocouple
7. Gas Chromatograph 8. Sampling Valve
9. Constant Temperature Bath 10. Expansion Vessel
11. Magnetic Pump (in Expansion Loop)

Figure 1. Experimental apparatus.

The temperature was measured with a Pt-100 Ω transmeter, and the uncertainty was estimated to be within ±0.05 K. Pressure was measured with a pressure transducer, and the uncertainty was estimated to be within ±0.01 bar.

The performance of the apparatus was tested by comparing some measurements with published results. The reference used was HFC-134a + HCFC-141b (Zheng et al., 1990). At 318.15 K, we measured the vapor−liquid equilibria, and the results are compared in Figure 2. The deviation of the measurement from the reference in pres-

S0021-9568(96)00018-0 CCC: $12.00

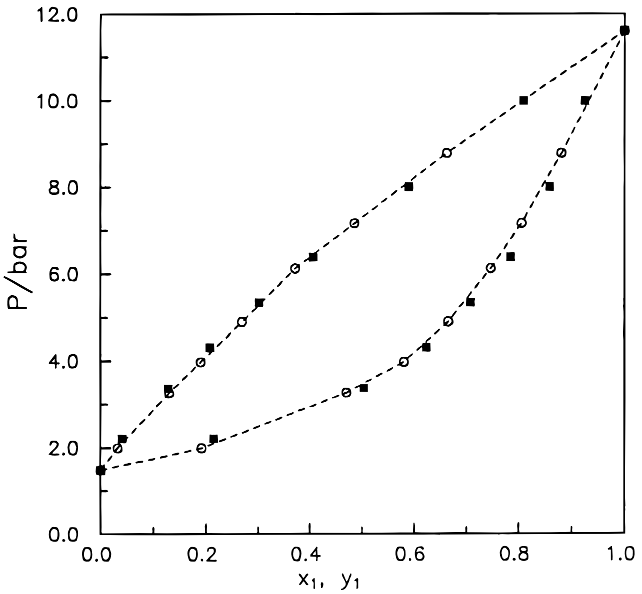


Figure 2. Thermodynamic consistency test of experimental apparatus. Comparison of Experimental Data (- - ○ - -) with the literature (Zheng et al., 1990) (■) for HFC-134a (1) + HCFC-142b (2) at 318.15 K.

Table 1. Critical Temperature, Critical Pressure, and Acentric Factor of the Pure Component

	HFC-134a	HCFC-124	HCFC-142b
/K	374.3[a]	395.7[a]	410.26[b]
/bar	40.7[a]	36.3[a]	40.4[b]
	0.327[a]	0.286[a]	0.230[c]

Poling et al. (1987). [b] Sato et al. (1994). [c] Calculated with the vapor pressures of Silva and Weber (1993).

sure ($\delta P/P$) was about 0.33% for the P, T, x measurement and 1.2% for the P, T, y measurement, respectively.

Results

Experimental vapor–liquid equilibria were measured for HFC-134a + HCFC-124 at 296.45, 302.25, and 307.25 K and for HCFC-124 + HCFC-142b at 298.15 and 312.15 K. The results are given in Tables 2 and 3. Neither HFC-134a + HCFC-124 nor HCFC-124 + HCFC-142b shows azeotropic behavior at the temperatures studied.

Correlation of Results

Results for HFC-134a + HCFC-124 were correlated with the Peng–Robinson equation of state (Peng and Robinson, 1976) using the van der Waals one fluid mixing rule. Results of calculation are also given in Table 2 and compared with the experimental values in Figure 3. With only one parameter, the Peng–Robinson equation of state correlates the experimental data very well. Interaction parameters (k_{12}) obtained at each temperature are given in Table 4.

To obtain the binary interaction parameters, we set the objective function as follows.

$$F = 100\sum_i \left|\frac{P(\mathrm{exp}) - P(\mathrm{calc})}{P(\mathrm{exp})}\right|^2 \qquad (1)$$

The Marquardt algorithm was used to minimize the objective function. The values of the binary interaction parameters are close to zero. From the results of the calculations, it was found that HFC-134a + HCFC-124 forms a nearly ideal mixture.

Table 2. Pressure (P) and Liquid and Vapor Mole Fraction (x, y) for HFC-134a (1) + HCFC-124 (2)[a]

P/bar			y_1	
exp	calc	x_1	exp	calc
		T = 296.45 K		
3.70	3.65	0.000	0.000	0.000
4.21	4.22	0.193	0.297	0.288
4.85	4.86	0.409	0.542	0.521
5.27	5.22	0.558	0.663	0.669
5.72	5.76	0.755	0.835	0.826
6.21	6.32	1.000	1.000	1.000
		T = 302.25 K		
4.31	4.36	0.000	0.000	0.000
4.73	4.76	0.102	0.171	0.167
5.06	5.06	0.180	0.286	0.276
5.26	5.26	0.237	0.354	0.346
5.72	5.71	0.368	0.488	0.490
6.67	6.64	0.678	0.766	0.761
6.88	6.89	0.761	0.825	0.825
7.16	7.17	0.865	0.901	0.901
7.48	7.50	1.000	1.000	1.000
		T = 307.25 K		
4.98	5.05	0.000	0.000	0.000
5.36	5.36	0.071	0.122	0.118
5.69	5.74	0.161	0.256	0.246
6.22	6.22	0.266	0.387	0.376
7.07	7.04	0.486	0.605	0.598
7.79	7.77	0.711	0.793	0.785
8.52	8.47	0.937	0.955	0.954
8.65	8.66	1.000	1.000	1.000

[a] Calculated values are from the Peng–Robinson equation of state with parameters from Table 4.

Table 3. Pressure (P) and Liquid and Vapor Mole Fraction (x, y) for HCFC-124 (1) + HCFC-142b (2)[a]

P/bar			y_1	
exp	calc	x_1	exp	calc
		T = 298.15 K		
3.38	3.37	0.000	0.000	0.000
3.39	3.38	0.039	0.041	0.042
3.39	3.39	0.050	0.0530	0.054
3.43	3.43	0.189	0.196	0.202
3.45	3.44	0.240	0.263	0.256
3.51	3.52	0.431	0.452	0.456
3.56	3.56	0.540	0.566	0.567
3.59	3.58	0.587	0.611	0.615
3.62	3.63	0.684	0.703	0.710
3.69	3.68	0.783	0.800	0.804
3.77	3.77	0.947	0.949	0.954
3.79	3.80	1.000	1.000	1.000
		T = 312.15 K		
5.08	5.07	0.00	0.000	0.000
5.10	5.09	0.035	0.037	0.038
5.14	5.13	0.124	0.134	0.133
5.20	5.19	0.240	0.257	0.256
5.26	5.24	0.329	0.346	0.350
5.36	5.36	0.508	0.536	0.534
5.46	5.47	0.664	0.692	0.690
5.53	5.55	0.770	0.792	0.792
5.55	5.57	0.791	0.817	0.811
5.61	5.63	0.867	0.890	0.881
5.73	5.74	1.000	1.000	1.000

[a] Calculated values are from the Peng–Robinson equation of state with parameters from Table 4.

It has been reported that HCFC-124 + HCFC-142b forms an azeotropic mixture almost irrelevant to temperature. Lee and Sun (1992) correlated the vapor–liquid equilibrium data of various refrigerant mixtures using the Teja–Patel equation of state and regressed the binary interaction parameters to the difference of acentric factors and the ratio of critical compressibility factors of each pure component.

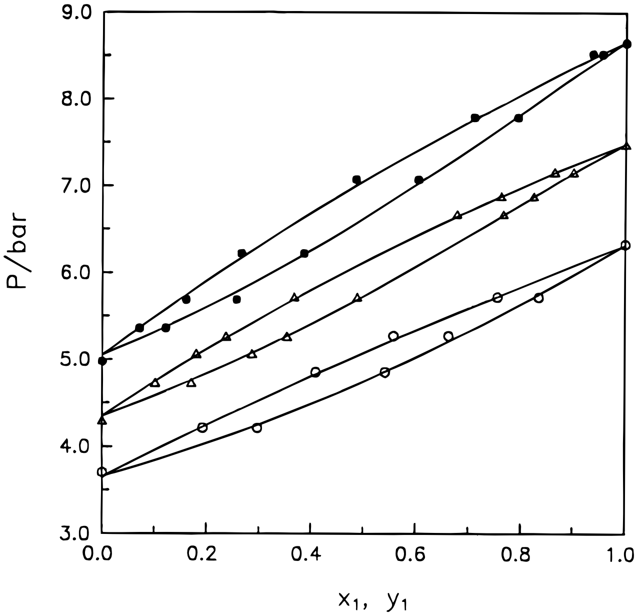


Figure 3. Pressure vs composition diagram for HFC-134a (1) + HCFC-124 (2): (○) experimental at 296.45 K; (△) 302.25 K; (●) 307.25 K; (—) P−R EOS.

Table 4. Interaction Parameters and AAD (%) of *P* and y_1

system	*T*/K	k_{12}	dev[a]	
			P	y_1
HFC-134a + HCFC-124	296.45	0.0089	0.878	3.19
	302.25	0.0166	0.330	1.28
	307.25	0.0152	0.458	1.94
HCFC-124 + HCFC-142b	298.15	−0.0059	0.161	1.42
	312.15	−0.0055	0.210	0.593

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

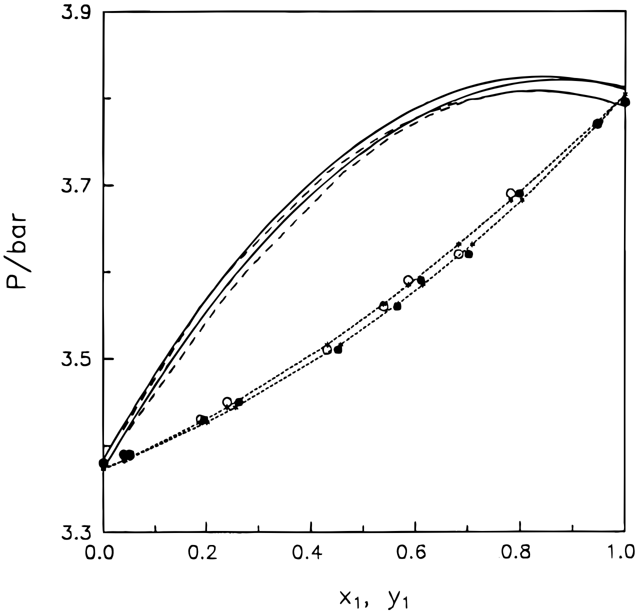


Figure 4. Predictions of vapor−liquid equilibria of HCFC-124 (1) + HCFC-142b (2) by Lee and Sun (1992) (- - -) and UNIFAC (Kleiber, 1995) (—) at 298.15 K. Comparison of experimental data [(○) liquid composition; (●) vapor composition] with the predictions (···) P−R EOS].

UNIFAC also predicts azeotropic behavior for this system. The energy parameters of the UNIFAC model for refrigerants were obtained by Kleiber (1995).

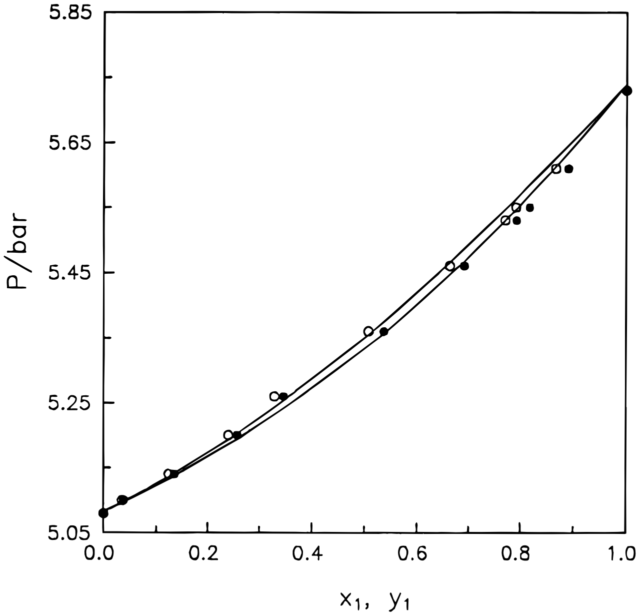


Figure 5. Pressure vs composition diagram for HCFC-124 (1) + HCFC-142b (2) at 312.15 K: (○) liquid composition; (●) vapor composition; (—) P−R EOS.

But it is found that this system does not form an azeotropic mixture from experiment. Results at 298.15 K are compared with two predictions in Figure 4. The equation of state and the optimization algorithm are the same as those used in the correlation of the HFC-134a + HCFC-124 system. Results of the calculations are given in Table 3 and compared with experimental values in Figures 4 and 5.

Conclusions

We measured vapor−liquid equilibrium data for HFC-134a + HCFC-124 and HCFC-124 + HCFC-142b using a circulation type apparatus. Neither of these systems form azeotropic mixtures. The experimental data were correlated by the Peng−Robinson equation of state with one adjustable parameter.

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Received for review January 22, 1996. Accepted March 23, 1996.[⊗]

JE960018I

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1996.