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Vapor−Liquid Equilibria for the Difluoromethane (HFC-32) + 1,1,1,2-Tetrafluoroethane (HFC-134a) System

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Isothermal vapor−liquid equilibrium data of the binary mixture of difluoromethane (HFC-32) + 1,1,1,2-tetrafluoroethane (HFC-134a) have been measured in the temperature range between 263 K and 323 K. The experiment was carried out with a circulation type apparatus with the measurement of temperature, pressure, and compositions of the liquid and vapor phases. The experimental data were correlated with the Peng−Robinson and Redlich−Kwong−Soave equations of state, and comparison with literature results has been made.

Introduction

In this paper, isothermal vapor−liquid equilibrium data (P, T, x, y) of the binary mixture of HFC-32/134a have been measured in the temperature range from 263 K to 323 K and correlated with the Peng−Robinson and Redlich−Kwong−Soave equations of state.

Experimental Section

Chemicals. HFC-32 with a purity of 99.9% was supplied by Ulsan Chemical Co., and HFC-134a with a purity of 99.8% was supplied by Showa Denko Co.

Apparatus. The schematic diagram of the experimental apparatus is shown in Figure 1. The equilibrium cell is made of SUS316 with an inner volume of about 150 cm^3 and a height of the cell of about 120 mm. It is immersed in the isothermal bath filled with ethylene glycol and water solution. Temperature fluctuations in the isothermal bath were limited within ±0.02 K by a temperature control system, which is composed of platinum resistance thermometer, power controller, two individual heaters, and one refrigerator. The refrigerant mixture is circulated with a magnetic pump. Vapor samples were analyzed with a gas chromatograph (Hewlett-Packard, 5890 series II plus) with a thermal conductivity detector, and a Chromosorb 102 column was used. To analyze the liquid composition, liquid samples were trapped in a space between two valves and introduced into a preevacuated expansion cell. The volume of expansion cell is sufficient for the liquid sample to evaporate. Helium gas was used as a carrier gas, and the flow rate was set to 25 cm^3 min^{-1}. The uncertainty of composition analysis was estimated to be within ±0.005 in mole fraction. Temperatures were measured with a Pt-100 Ω resistance thermometer (Automatic Systems Laboratories, F250) calibrated against an ITS-90 scale, and the uncertainty of temperature measurement was estimated to be within ±0.02 K. The pressure was measured with a pressure transducer (Sensotec, super TJE-AP112), and the uncertainty of pressure measurement was estimated to be within ±0.3%.

Results and Correlation

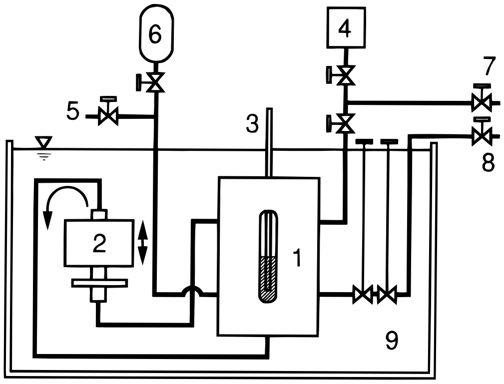

Figure 1. Schematic diagram of experimental apparatus: 1, equilibrium cell; 2, magnetic pump; 3, resistance thermometer; 4, pressure transducer; 5, vacuum pump; 6, charging cylinder; 7, vapor sampling port; 8, liquid sampling port; 9, isothermal bath.

Vapor−liquid equilibria and vapor pressures of pure components were measured for the HFC-32 + HFC-134a mixture at temperatures from 263 K to 323 K, and the results are given in Table 1. The vapor pressure data of pure HFC-32 and HFC-134a are compared with those given in REFPROP 5.0 (Huber et al., 1996) and JAR Thermodynamic Tables (Sato et al., 1994). The relative deviation of our experimental data for HFC-32 from REFPROP 5.0 is about 0.38% and that from the JAR Table is about 0.27%. The relative deviation for HFC-134a from REFPROP 5.0 is about 0.20%, and that from the JAR Table is about 0.30%, respectively.

The experimental results were correlated with the Peng−Robinson (Peng and Robinson, 1976) and Redlich−Kwong−Soave (Soave, 1972) equations of state using the van der Waals one-fluid mixing rule. The critical properties and acentric factors used are given in Table 2.

Optimal binary interaction parameters were obtained to make the relative pressure deviation between measured and calculated values minimized. In Figure 2, it is evident that the binary interaction parameter decreases as temperature increases for both equations of state. In Figure 3, relative pressure deviation between measured and calculated values was shown when the constant binary interaction parameter and the temperature dependent binary interaction parameter were used. As shown in Figure 3, the relative pressure deviation for two cases was generally less than 0.2% for the temperature range investigated, and the difference is not significant considering the uncertainty of pressure measurements. For this reason, optimized binary interaction parameters shown in Table 3 were used regardless of temperature, and the

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Table 1. Vapor−Liquid Equilibrium for HFC-32 + HFC-134a

P/kPa	mole fraction of HFC−32		P/kPa	mole fraction of HFC−32	
	liquid	vapor		liquid	vapor
T = 263.15 K					
199.7	0.0000	0.0000	467.7	0.7001	0.8538
288.9	0.2245	0.4510	579.8	1.0000	1.0000
345.0	0.3919	0.6179			
T = 273.15 K					
291.6	0.0000	0.0000	653.8	0.7104	0.8474
408.4	0.2326	0.4322	810.7	1.0000	1.0000
484.9	0.3837	0.6004			
T = 283.15 K					
414.0	0.0000	0.0000	929.2	0.7447	0.8683
570.7	0.2411	0.4188	1104.0	1.0000	1.0000
797.0	0.5715	0.7383			
T = 293.15 K					
570.9	0.0000	0.0000	1234.9	0.7599	0.8568
769.6	0.2376	0.4034	1471.4	1.0000	1.0000
1061.5	0.5757	0.7217			
T = 303.15 K					
769.3	0.0000	0.0000	1607.9	0.7541	0.8499
1008.5	0.2270	0.3760	1922.7	1.0000	1.0000
1380.4	0.5646	0.7114			
T = 313.15 K					
1015.3	0.0000	0.0000	1938.7	0.6709	0.7808
1288.6	0.2140	0.3409	2474.9	1.0000	1.0000
1625.4	0.4470	0.6077			
T = 323.15 K					
1316.4	0.0000	0.0000	2467.4	0.6742	0.7708
1642.7	0.2079	0.3209	3136.1	1.0000	1.0000
2050.7	0.4453	0.5850			

Table 2. Critical Properties and Acentric Factor of Pure Components

	HFC-32	HFC-134a
critical temperature, T_c/K	351.255[a]	374.110[b]
critical pressure, P_c/kPa	5780.0[c]	4052.0[b]
acentric factor	0.277[d]	0.326[d]

[a] Kuwabara et al. (1995). [b] Higashi (1994). [c] Nishimura et al. (1992). [d] Sato et al. (1994).

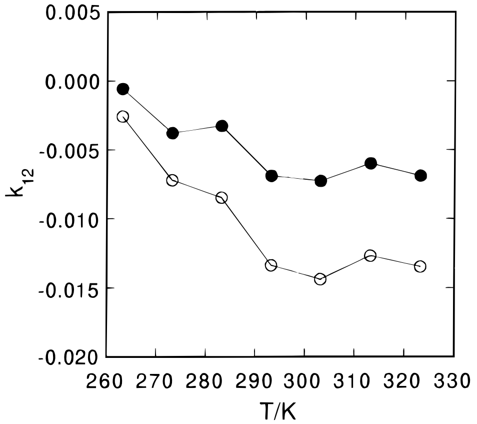

Figure 2. Optimized binary interaction parameter k_{12} in Peng−Robinson and Redlich−Kwong−Soave equations of state for the HFC-32 + HFC-134a mixture at several temperatures: (●) PR; (○) RKS.

deviations of measured pressure and vapor composition from the equations of state are also given in Table 3. As a result, the Peng−Robinson (PR) equation of state correlates the experimental data better than the Redlich−Kwong−Soave (RKS) equation of state. Our experimental data were in good agreement with the calculated values using the PR equation, and the deviations were less than 1% except one point at low temperature. In Figure 4, comparison of the relative pressure deviation of available data in the open literature from the results calculated by the PR equation was shown. In Figure 4, the absolute average deviation of relative pressure from Fujiwara et al. (1992) is 2.1% and the maximum deviation is 3.5%. Compared with the data by Higashi (1995), the absolute average deviation of relative pressure was 1.2% except the data at 283 K. Considerably larger difference exists at 283 K, and the maximum deviation is nearly 10% . The experimental results of Nagel and Bier (1995) are in good agreement with our results in the temperature range of this study with absolute average deviation of 1.0%. The results from

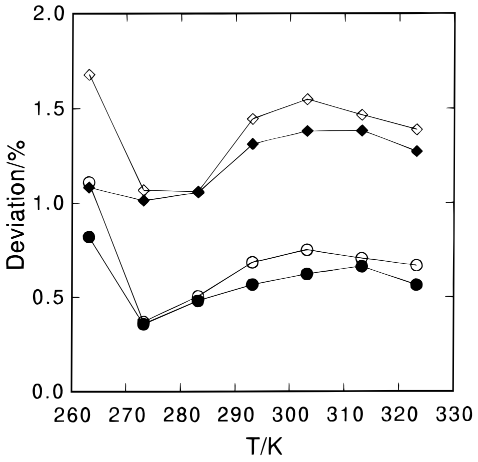

Figure 3. Comparison of pressure deviation when constant binary interaction parameter k_{12} and temperature-dependent binary interaction parameter $k_{12}(T)$ are used: (●) PR, k_{12}(T); (○) PR, k_{12}; (◆) RKS, k_{12}(T); (◇) RKS, k_{12}; deviation (%) = $(100/N)\Sigma(|P_{exp} - P_{cal}|/P_{exp})$.

Table 3. Optimized Binary Interaction Parameters for HFC-32 + HFC-134a and Deviations of Pressure and Vapor Mole Fraction of HFC-32 from Equations of State

		δ[a]	
equation of state	k_{12}	pressure	vapor mole fraction
Peng−Robinson	−0.0043	0.55	0.76
Redlich−Kwong−Soave	−0.0091	1.18	0.86

[a] $\delta = (100/N)\Sigma(|P_{exp} - P_{cal}|/P_{exp})$ or $(100/N)\Sigma(|y_{exp} - y_{cal}|/y_{exp})$.

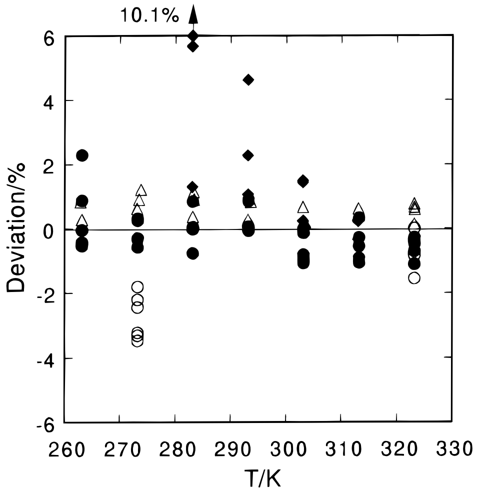

Figure 4. Deviation of bubble point pressure for the HFC-32 + HFC-134a mixture from the Peng−Robinson equation of state: (●) this study; (○) Fujiwara et al.; (◆) Higashi; (△) Nagel and Bier; deviation (%) = $(100/N)\Sigma(|P_{exp} - P_{cal}|/P_{exp})$.

REFPROP (Huber et al., 1996) were also in good agreement with the present results with absolute average deviation of 1.0%.

Conclusions

Isothermal vapor−liquid equilibrium data of the binary mixture of HFC-32 and HFC-134a have been measured, and 56 data points along seven isotherms in the temperature range between 263 K and 323 K were obtained, including the vapor pressure data for pure components. The experimental data were correlated by the Peng−Robinson and Redlich−Kwong−Soave equations of state with one binary interaction parameter. Comparison with the data in available literature has been made.

Acknowledgment

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