HIGH-PRESSURE VAPOR-LIQUID EQUILIBRIA FOR THE SYSTEM HFC134a + HFC143a

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Introduction

Increasing concern about ozone depletion in the stratosphere will accelerate the regulation of uses of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs).

This paper presents the vapor-liquid equilibrium data for the binary mixture of 1,1,1,2-tetrafluoroethane (HFC134a) + 1,1,1-trifluoroethane (HFC143a). Neither component contains chlorine atom in its molecule, and

the mixture has no ozone depletion potential. Experimental temperatures were fixed at 278.15, 288.15, 303.15, 318.15, and 333.15 K while pressures ranged from 0.35 to 2.9 MPa.

This new fluorocarbon mixture is now being considered as an alternative to chlorodifluoromethane (HCFC22), and the mixture forms a non-azeotropic mixture that is a prospective working fluid for refrigeration and heat pump cycles.

To analyze the condition of a mixture in a refriger-

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Table 1. Isothermal Vapor-Liquid Equilibrium Data for HFC134a(2) + HFC143a(1) System

Pressure [MPa]	mole fraction of HFC143a		equilibrium ratio	
	x_1	y_1	K_1	K_2
$T = 278.15 \text{ K}$				
0.350	0	0	-	1
0.419	0.168	0.268	1.595	0.880
0.486	0.354	0.502	1.418	0.771
0.553	0.534	0.682	1.277	0.682
0.606	0.672	0.782	1.164	0.665
0.666	0.841	0.902	1.073	0.616
0.721	1	1	1	-
$T = 288.15 \text{ K}$				
0.489	0	0	-	1
0.547	0.116	0.199	1.715	0.906
0.627	0.279	0.427	1.530	0.795
0.673	0.386	0.545	1.412	0.741
0.747	0.534	0.677	1.268	0.693
0.788	0.629	0.754	1.199	0.663
0.835	0.733	0.831	1.134	0.633
0.963	1	1	1	-
$T = 303.15 \text{ K}$				
0.770	0	0	-	1
0.911	0.191	0.293	1.534	0.874
1.004	0.330	0.457	1.385	0.810
1.068	0.440	0.570	1.295	0.768
1.148	0.572	0.685	1.198	0.736
1.207	0.667	0.763	1.144	0.712
1.308	0.838	0.890	1.062	0.679
1.434	1	1	1	-
$T = 318.15 \text{ K}$				
1.160	0	0	-	1
1.300	0.130	0.193	1.485	0.928
1.408	0.257	0.345	1.342	0.869
1.500	0.368	0.470	1.277	0.839
1.586	0.475	0.574	1.208	0.811
1.663	0.578	0.671	1.161	0.780
1.730	0.660	0.740	1.121	0.765
1.798	0.724	0.794	1.097	0.746
2.062	1	1	1	-
$T = 333.15 \text{ K}$				
1.681	0	0	-	1
1.824	0.109	0.150	1.376	0.954
1.954	0.227	0.298	1.313	0.908
2.147	0.411	0.493	1.200	0.861
2.300	0.553	0.625	1.130	0.839
2.404	0.641	0.707	1.103	0.816
2.511	0.720	0.778	1.081	0.793
2.667	0.855	0.889	1.040	0.766
2.879	1	1	1	-

ation circuit, it is necessary to obtain the mixture's thermodynamic properties through its vapor-liquid equilibria data. In this work, experimental data were fitted to the Soave-Redlich-Kwong (S-R-K) and Peng-Robinson (P-R) equations of state by using a mixing rule. Optimum corresponding binary interaction parameters for these equations of state were obtained.

1. Experimental

A detailed description of the experimental apparatus used in this work was presented in our previous paper^{2,6}. In the experimental procedure, special attention was paid to diminishing the uncertainty of measurements. Since the temperature inside the equilibrium cell was not measured, more than 2 hours was deemed necessary to ensure complete thermal equilibrium between the

Table 2. Binary interaction parameters and deviations between experimental and calculated results for HFC134a(2) + HFC143a(1) System

Peng-Robinson eq.

Temp. [K]	k_{ij}	Δx_1	Δy_1
278.15	0.007	0.004	0.006
288.15	0.002	0.004	0.006
303.15	0.003	0.011	0.009
318.15	0.003	0.012	0.013
333.15	-0.003	0.009	0.009

Soave-Redlich-Kwong eq.

Temp. [K]	k_{ij}	Δx_1	Δy_1
278.15	0.000	0.007	0.009
288.15	-0.005	0.010	0.008
303.15	-0.001	0.020	0.019
318.15	-0.003	0.015	0.016
333.15	-0.009	0.010	0.010

$\Delta x = \sum |x_{\text{calc}} - x_{\text{exp}}| / n$, $\Delta y = \sum |y_{\text{calc}} - y_{\text{exp}}| / n$
where n is number of data.

sample in the cell and the thermostated bath fluid. The bath temperature controlled by a Haake circulator was checked at each experimental temperature by a standard quartz thermometer in the 1968 International Practical Temperature Scale (IPTS-68).

At 303.15 K, vapor and liquid compositions were measured in the case of either elevation or reduction of pressure. Both values in both cases were confirmed to agree with each other. This probably indicates that complete equilibrium was achieved throughout the whole experiment.

The uncertainty of temperature measurements is estimated to be within 0.05K, including the precision of the standard thermometer and the fluctuation of the temperature controller. The maximum uncertainty of pressure measurements is estimated to be within 2.0 kPa. The analysis uncertainty of liquid compositions is estimated to be within 0.7 mol%, while that of vapor compositions is below 0.8 mol%, including the uncertainty of the calibration curve. The purity of the HFC134a was greater than 99.8 mol% and that of HFC143a not less than 99.5 mol%.

2. Experimental Results

The experimental equilibrium data of pressure, temperature and mole fraction for both liquid and vapor phases of HFC143a, including the equilibrium ratios $K_i = y_i/x_i$, are listed in **Table 1**. The equilibrium pressures were plotted against mole fractions of both phases of HFC143a for the five isotherms as shown in **Fig. 1**. Literature values were used for the vapor pressures of pure sample fluids^{1,5}. This figure showed that the mixture almost obeys Raoult's law under this experimental condition.

As expected, experimental results indicated that this mixture exhibits no azeotropic phenomena in the

Fig. 1 Pressure vs. Composition Diagram for HFC134a + HFC143a System

pressure and temperature range of this investigation.

Data were tested to be thermodynamically consistent by methods described in our previous paper²⁾. As an example, plots of the equilibrium ratios versus pressure are shown in Fig. 2. The equilibrium ratios changed smoothly with pressure.

3. Data Correlation

Experimental data for five isotherms were correlated with the S-R-K⁴⁾ and P-R³⁾ equations of state with the conventional mixing rule.

The binary interaction parameters, k_{ij} , obtained for each isotherm are listed in Table 2. This table also shows the absolute average deviations obtained by minimizing the following objective function:

$$OF = \sum \{ |x_{1,calc} - x_{1,exp}|^2 + |y_{1,calc} - y_{1,exp}|^2 \}$$

The vapor-liquid relations calculated by the P-R equation of state with the corresponding interaction parameters k_{ij} by the P-R equation are also shown in Fig. 1. Both equations correlate the experimental data very satisfactorily.

The acentric factors of HFC134a and HFC143a employed in this calculation were taken from the litera-

Fig. 2 Pressure vs. Equilibrium Ratio Diagram for HFC134a + HFC143a System

□ 278.15K ▲ 288.15K ■ 303.15K
○ 318.15K ● 333.15K

ture⁷⁾.

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Nomenclature

K	= equilibrium ratio (= y/x)	[-]
k_{ij}	= binary interaction parameter	[-]
T	= absolute temperature	[K]
x	= mole fraction of liquid phase	[-]
y	= mole fraction of vapor phase	[-]

<Subscripts>

i, j	= component
calc	= calculated
exp	= experimental

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