

HIGH PRESSURE VAPOR-LIQUID EQUILIBRIA OF THE HFC134a + HCFC123 SYSTEM

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Introduction

This paper presents vapor-liquid equilibrium data for the system of 1,1,1,2-tetrafluoroethane (HFC-134a) + 1,1-dichloro-2,2,2-trifluoroethane (HCFC-123). Temperatures were fixed at 289.17, 303.15, 318.15, and 332.74 K while pressures ranged from 0.1 to 1.5 MPa.

These new fluorocarbons are now regarded as refrigerants. HFC-134a, for example, is regarded as an alternative to dichlorodifluoromethane (CFC-12), and HCFC-123 as that to trichlorofluoromethane (CFC-11). The mixture of these new compounds forms a non-azeotropic mixture which is a prospective working fluid for refrigeration and heat pump cycles.

In view of various operation conditions in a refrigeration system, a predictive method is desirable for interpolating the available data. In this work, experimental data were correlated by the Soave-Redlich-Kwong (S-R-K) and Peng-Robinson (P-R) equations of state to evaluate the corresponding binary interaction parameters. It was found that these parameters of both equations were linear functions of temperature.

1. Experimental

The experimental apparatus used in this work was described in detail in our previous paper^{1,5}). In the experimental procedure, special attention was paid to diminish the uncertainty of measurement. Since the temperature inside the equilibrium cell was not measured, more than 2 hours was deemed necessary to ensure complete thermal equilibrium between the 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 either case were confirmed to agree with each other. This probably indicates that complete equilibrium was achieved throughout the experiment.

The uncertainty of temperature measurements is estimated to be within ± 0.05 K 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 ± 1.0 kPa. The analysis uncertainty of liquid compositions is estimated to be within ± 0.05 mol%, while that of vapor compositions is below 0.1 mol% including the uncertainty of the calibration curve. The purity of the HCFC123 was greater than 99.9 mol% and that of the HFC134a not less than 99.8 mol%.

2. Experimental Results

The experimental values of pressure, temperature and mole fraction for both liquid and vapor phases of HFC-134a including the equilibrium ratios $K_i = y_i/x_i$ are listed in **Table 1**. The equilibrium pressures are plotted against mole fractions of both phases of HFC-134a for the four isotherms in **Fig. 1**.

As expected, the experimental results show that this mixture exhibits no azeotropic phenomena in the pressure and temperature ranges of this investigation.

Data were found by testing to be thermodynamically consistent by methods used in our previous paper¹).

3. Data Correlation

Experimental data for four isotherms were correlated with the S-R-K⁴) and P-R²) equations of state by the conventional mixing rule.

Values of the binary interaction parameters, k_{ij} , obtained for each isotherm are listed in **Table 2** including the absolute average deviations obtained by minimizing the following objective function:

$$OF = \sum_j^N \{ |X_{1,calc} - Y_{1,exp}|_j + |Y_{1,calc} - Y_{1,exp}|_j \}$$

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Table 1. Isothermal Vapor-Liquid Equilibrium Data for the HFC134a(1)+HCFC123(2) System

Pressure [MPa]	Mole fraction		Equilibrium ratio	
	x_1	y_1	K_1	K_2
$T=289.17\text{ K}$				
0.120	0.103	0.495	4.818	0.563
0.145	0.153	0.593	3.882	0.480
0.195	0.244	0.720	2.952	0.370
0.249	0.361	0.802	2.221	0.311
0.312	0.510	0.860	1.687	0.286
0.393	0.740	0.926	1.304	0.287
$T=303.15\text{ K}$				
0.201	0.108	0.481	4.461	0.582
0.264	0.191	0.629	3.294	0.459
0.356	0.317	0.736	2.320	0.387
0.464	0.487	0.822	1.693	0.347
0.553	0.636	0.880	1.383	0.330
0.594	0.709	0.897	1.266	0.353
0.628	0.766	0.915	1.194	0.370
$T=318.15\text{ K}$				
0.278	0.076	0.339	4.443	0.716
0.404	0.193	0.571	2.968	0.531
0.556	0.343	0.718	2.092	0.430
0.653	0.441	0.779	1.768	0.395
0.792	0.590	0.849	1.438	0.369
0.897	0.712	0.899	1.264	0.349
1.019	0.836	0.942	1.127	0.355
1.096	0.921	0.968	1.051	0.406
$T=332.74\text{ K}$				
0.476	0.118	0.402	3.421	0.678
0.601	0.203	0.566	2.791	0.544
0.714	0.284	0.651	2.289	0.488
0.874	0.397	0.740	1.862	0.432
0.992	0.489	0.791	1.617	0.410
1.126	0.580	0.830	1.432	0.398
1.217	0.654	0.860	1.314	0.405
1.328	0.740	0.894	1.208	0.409
1.446	0.829	0.930	1.121	0.412
1.495	0.860	0.941	1.094	0.420

Calculated results with the corresponding interaction parameters k_{ij} by the S-R-K equation are shown in Fig. 1. Both equations correlate the experimental data very satisfactorily.

The acentric factors of HFC-134a and HCFC 123 were estimated by methods suggested by Reid *et al.*³⁾

In addition, the binary interaction parameters obtained by both S-R-K and P-R equations of state were found to be a linear function of temperature.

By the least-squares method, the following empirical equations were obtained:

For the S-R-K equation

$$k_{ij} = -2.788 \times 10^{-2} + 2.024 \times 10^{-4} T$$

For the P-R equation

$$k_{ij} = -6.544 \times 10^{-2} + 3.362 \times 10^{-4} T$$

Vapor-liquid equilibria of this mixture in a temperature range close to that in this experiment may probably be predicted with confidence by using the

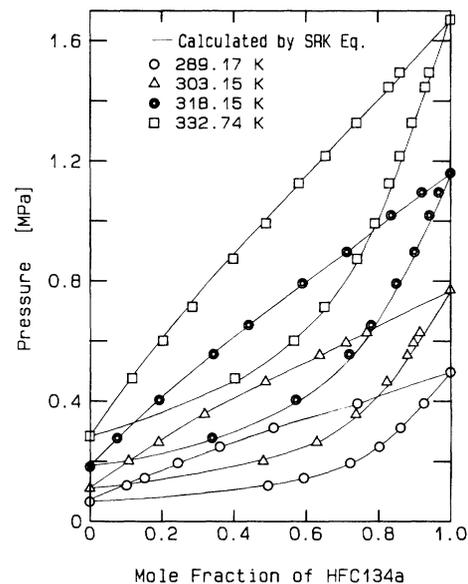


Fig. 1. Total pressure against mole fraction of HFC134a

Table 2. Binary interaction parameters and mean deviations between experimental and calculated results

Temp. [K]	Peng-Robinson eq.			Soave-Redlich-Kwong eq.		
	k_{ij}	Δx	Δy	k_{ij}	Δx	Δy
289.17	0.0318	0.007	0.008	0.0308	0.008	0.008
303.15	0.0367	0.001	0.012	0.0340	0.004	0.014
318.15	0.0410	0.006	0.018	0.0356	0.003	0.019
332.74	0.0467	0.008	0.011	0.0400	0.004	0.013

$$\Delta x = \frac{1}{n} \sum_{i=1}^n |x_{\text{calc}} - x_{\text{exp}}|_i, \quad \Delta y = \frac{1}{n} \sum_{i=1}^n |y_{\text{calc}} - y_{\text{exp}}|_i$$

where n is number of data

temperature-dependent interaction parameters.

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Nomenclature

K	= equilibrium ratio (= x/y)	[—]
k_{ij}	= binary interaction parameter	[—]
P	= pressure	[MPa]
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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