

High Pressure Vapor-liquid Equilibria and Critical Loci for the HFC125-HFC134a System

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Abstract—We measured vapor-liquid equilibria (VLE) ranging from 303.75 to 363.15 K and the critical locus for the system of pentafluoroethane (HFC125)-1,1,1,2-tetrafluoroethane (HFC134a). The critical locus exhibited type I behavior by van Konynenberg and Scott. Correlating the VLE data with an extended BWR equation of state, we found the optimum binary interaction parameter for this system 1.0081 and estimated coefficients of performance (C.O.P.) as a mixture refrigerant. As a result of the correlation, we found that the HFC125-HFC134a system is a potential alternative refrigerant when mole fraction of HFC125 is lower than 0.6. Calculations showed a 4.9% saving energy in the cycle compared with chlorodifluoromethane (HCFC22), for a composition of 30 mole percent HFC125.

Key words: Vapor-Liquid Equilibria, Critical Locus, HFC125-HFC134a, Equation of State, C.O.P.

INTRODUCTION

Although HCFC22 has been widely used in industry, its use as a refrigerant is limited due to its ozone-depleting potential. Fluorocarbon mixtures without chlorine atoms are expected to be the new generation of viable replacements. However, for many of these mixtures, thermodynamic data are not available. We chose the system of HFC125-HFC134a as one of the substituted fluorocarbons. The objectives of this paper are to report VLE and the critical locus for this system, and to provide a thermodynamic possibility as a mixture refrigerant.

EXPERIMENTS

1. Materials

HFC125 and HFC134a supplied by Daikin Kogyo had a purity more than 98% and 99.8%, respectively.

2. Critical Locus Measurement

2-1. Apparatus

The equilibrium cell used for critical locus measurement had a volume that could be varied with a movable piston from 250 to 1,000 ml. Two rectangular (20×50 mm) glass windows allowed interface observation. Mixing was provided by a rotating magnetic stirrer in the cell coupled with an external rotating permanent magnet and by a circulating pump. The cell was mounted in an air bath.

Temperature in the air bath was measured with a digital platinum resistance thermometer based on IPTS-68 whose values were finally converted to ITS90. Temperature in the cell was maintained at a desired value to within 0.2 K over a three-day period. System pressure was measured with a 10 MPa bourdon pressure gauge that had a full scale accuracy of 0.15%. More details can be found in

Nishiumi et al. [1997].

2-2. Procedure

The cell was evacuated and brought to near the desired temperature. The heavier component HFC134a was introduced, and then the lighter component HFC125 was charged to a desired pressure. Volume was varied with a movable piston. The critical point was taken to be the maximum in scattering light as observed with transmitted light. The composition was analyzed by gas chromatography.

2-3. Results of Critical Locus Measurement

Results are listed in Table 1. The deviation of composition at the critical point was ± 0.003 in mole fraction. Fig. 1 shows the critical locus for the system of HFC125-HFC134a. It was found to be type I according to the classification system of van Konynenberg and Scott [1968].

3. VLE Measurement

3-1. Apparatus

The equilibrium cell used for vapor-liquid equilibrium measurement had a constant volume of about 150 ml. Eight uniformly spaced 250 watt electrical heaters mounted vertically were con-

Table 1. Critical locus data for the system of HFC125-HFC134a in this work

Temperature [K]*	Pressure [MPa]	HFC125 mole fraction [-]
339.38	3.612**	1.0000
343.13	3.669	0.9070
348.27	3.753	
353.13	3.822	0.6490
358.39	3.890	
363.16	3.942	0.3095
367.22	3.983	
374.27	4.065	0.0000

*Based on ITS90.

**Value from Nishiumi et al. [1997]. The value 3.16 MPa of Table 2 in the paper was a typographical error as can be seen in Table 1 of that work.

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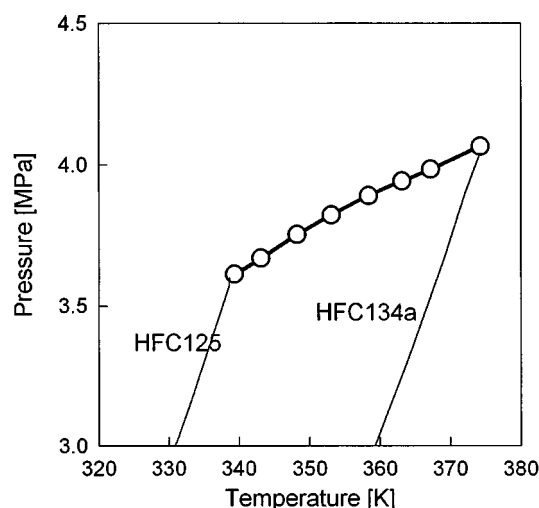


Fig. 1. Critical locus for the HFC125-HFC134a system.

trolled with a commercial temperature controller. Temperature in the cell was gradually cycled over 0.2 K over a 24 hour period. System pressures were measured with a 10 MPa bourdon pressure gauge that had a full scale accuracy of 0.15%. Composition analysis of vapor and liquid samples was done with a thermal conductivity detector and a 2 m long column of Gaskuropack 54. More details can be found in Nishiumi et al. [1997].

3-2. Experimental Method

A sample was introduced with the same procedure as the critical locus measurement. The mixture was magnetically stirred until equilibrium was attained. Vapor or liquid samples were taken and expanded in an evacuated manifold, where heated helium was circulated to prevent condensation prior to analysis. Their composition was analyzed with gas chromatography.

3-3. Results of VLE Measurement

Experimental VLE results are shown in Table 2. Fig. 2 shows the VLE for the system of HFC125-HFC134a ranging from 303.74 to 363.12 K together with the critical locus and solid lines which are calculations from an extended BWR equation of state.

DISCUSSION FROM EXTENDED BWR EQUATION OF STATE

1. Polar Parameters

Fitting to the compiled vapor pressure data of HFC134a [Tiller-Roth et al., 1998], the polar parameters are determined with an extended BWR equation of state [Nishiumi et al., 1997]. The values are listed in Table 3 together with those of HFC125 [Nishiumi et al., 1998].

2. Binary Interaction Parameter

Fig. 3 shows optimum binary interaction parameters m_{ij} values for an extended BWR equation of state in this work together with the results already reported by one of the authors [Nishiumi et al., 1998]. In this work, the value of m_{ij} for the system of HFC125-HFC134a was correlated as follows,

$$m_{ij} = 1.1303 - 0.325 \times 10^{-3} T \quad \text{for } T \geq 337.91 \text{ K} \\ = 1.0171 \quad T < 337.91 \text{ K} \quad (1)$$

Table 2. Experimental vapor-liquid equilibria for the system of HFC125-HFC134a

Temperature* [K]	Pressure [MPa]	HFC125 mole fraction [-]	
		Liquid	Vapor
303.74	0.920	0.188	0.297
	1.009	0.316	0.442
	1.136	0.461	0.59
	1.245	0.595	0.707
	1.339	0.721	0.818
	1.472	0.862	0.921
314.04	1.118	0.075	0.1183
	1.230	0.202	0.2888
	1.295	0.279	0.3636
	1.472	0.430	0.5359
	1.594	0.599	0.7052
	1.725	0.743	0.8157
323.13	1.878	0.871	0.9168
	1.336	0.0450	0.0725
	1.444	0.1380	0.2065
	1.571	0.2365	0.3465
	1.846	0.4595	0.5475
	1.953	0.5515	0.6525
333.13	2.047	0.6250	0.7080
	2.174	0.7530	0.8190
	2.243	0.8005	0.8755
	1.865	0.0715	0.1705
	1.963	0.1685	0.3130
	2.042	0.2660	0.3680
343.13	2.169	0.3650	0.4755
	2.356	0.4910	0.5865
	2.571	0.6435	0.7170
	2.846	0.8050	0.8505
	3.042	0.9380	0.9510
	2.248	0.0990	0.1366
353.13	2.412	0.2023	0.2670
	2.630	0.3210	0.3940
	2.802	0.4200	0.4910
	2.980	0.5153	0.5870
	3.138	0.6032	0.6643
	3.274	0.6748	0.7237
363.12	3.444	0.7688	0.7995
	3.542	0.8199	0.8410
	2.823	0.1120	0.1449
	2.851	0.1240	0.1585
	3.007	0.2050	0.2548
	3.160	0.2760	0.3320
363.12	3.356	0.3700	0.4260
	3.537	0.4550	0.5050
	3.709	0.5395	0.5757
	3.494	0.1132	0.1371
	3.577	0.1483	0.1766
	3.719	0.2022	0.2333
363.12	3.807	0.2366	0.2677
	3.925	0.2892	0.3095

*Temperature is based on ITS90.

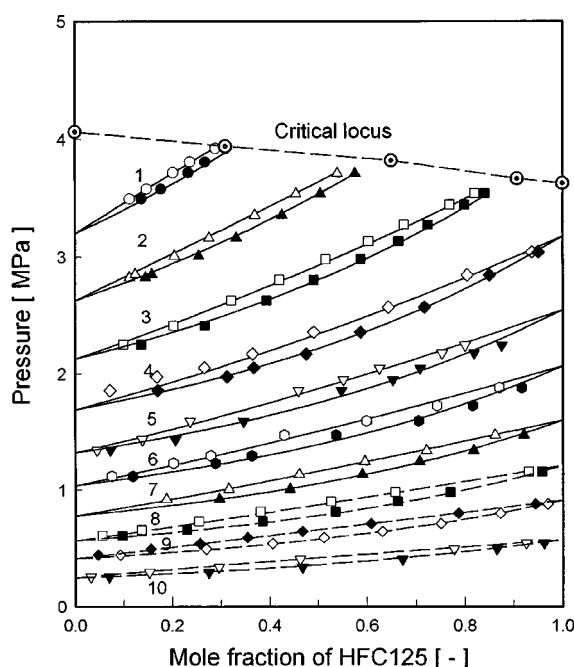


Fig. 2. VLE measurements and critical locus for the system of HFC125-HFC134a. broken line: critical locus. exponential temperatures 1: 363.12 K, 2: 353.13 K, 3: 343.13 K, 4: 333.13 K, 5: 323.13 K, 6: 314.04 K, 7: 303.74 K, 8: 293.15 K, 9: 283.15 K, 10: 268.15 K (8 to 10 [Nishiumi and Kobayashi, 1998]). solid lines: estimation from an extended BWR equation of state.

Table 3. Critical properties and polar parameters for fluorocarbons

Component	Pc [MPa]	Tc [K]	Vc [l/mol]	ω [-]
HFC125	3.617	339.27	0.2113	0.2770
HFC134a	4.064	374.30	0.2000	0.3360
Ψ_A^*	Ψ_E^*	S_3^*	S_1^*	S_2
-0.13	-0.0110	-0.0689	-0.0896	3.175
-0.60	0.4694	-0.5243	0.3565	6.130

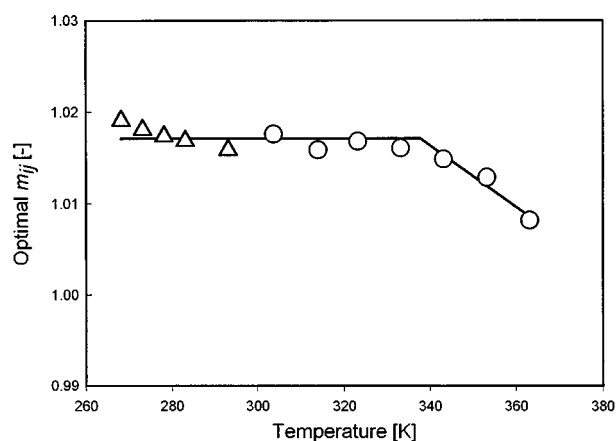


Fig. 3. Temperature dependence of binary interaction parameters, m_{ij} with an extended BWR equation of state for the system of HFC125-HFC134a.

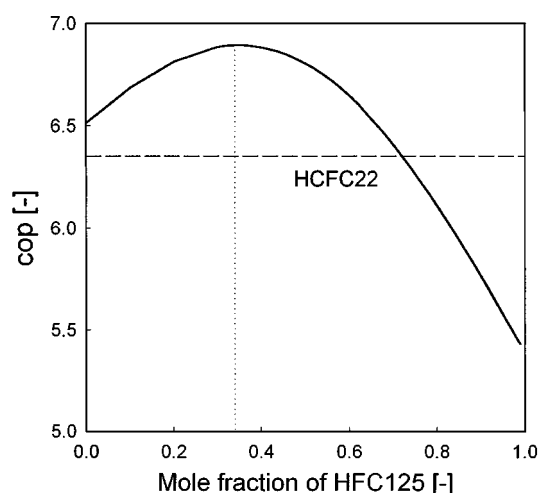


Fig. 4. Comparison of calculated COP for the system of HFC125-HFC134a with HCFC22 using an extended BWR equation of state. broken line: HCFC22

VLE estimation using the correlated binary interaction parameter m_{ij} value agreed well with experimental values as shown in Fig. 2.

3. C.O.P. Comparison

To examine the possibility of a mixture as a refrigerant, we estimated the C.O.P. values for the HFC125-HFC134a system under the conditions that temperatures changed from 285.15 to 280.15 K for heat radiation and 305.15 to 310.15 K for heat absorption with 3 K minimum temperature difference for each heat exchanger. As shown in Fig. 4, the C.O.P.c. values of this mixture were found to be higher than that of HCFC22 below 0.7 in mole fraction. Calculation showed an 8.5% energy-saving in comparison with chlorodifluoromethane (HCFC22), when the composition was 34 mole percent of HFC125. A C.O.P.c. value can be obtained as the ratio of enthalpy between B and C to that of A-B in Fig. 5 of P-h diagrams for 0, 34, 60 and 100 mole% of HFC125.

CONCLUSIONS

1. We measured seven isothermal vapor-liquid equilibria rang-

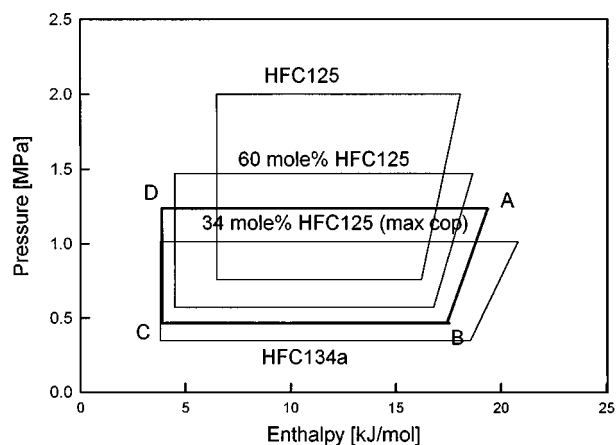


Fig. 5. Comparison of P-h diagram of 0, 34, 60 and 100 mole per cent HCFC125 for the system of HFC125-HFC134a.

ing from 303.75 to 363.15 K for HFC125-HFC134a mixture.

2. The critical locus was found to be continuous between the pure component critical points.

3. Using an extended BWR equation of state, coefficient of performance C.O.P.c. values of the HFC125-HFC134a system were found to be higher than that of HCFC22 when the mole fraction of HFC125 was below 0.7 with a maximum 8.5% energy-saving at 34 mole percent of HFC125. Systems can be designed for HFC125-HFC134a mixtures that will require less energy than the HCFC22 system.

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