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Vapor–Liquid Equilibrium of HFC-32/134a and HFC-125/134a Systems

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A vapor–liquid equilibrium apparatus has been developed and used to obtain data for the binary HFC-32/134a and HFC-125/134a systems. Twenty-two equilibrium data are obtained for the HFC-32/134a system over the temperature range from 258.15 to 283.15 K at 5 K intervals and the composition range from 0.2 to 0.8 liquid mole fraction. Twenty-five equilibrium data are obtained for the HFC-125/134a system over the temperature range from 263.15 to 303.15 K at 10 K intervals and the composition range from 0.18 to 0.81 liquid mole friction. These data have been tested and found to be thermodynamically consistent. Based upon the present data, the binary interaction parameters of the Carnahan–Starling–De Santis (CSD) and Redlich–Kwong–Soave (RKS) equations of state are calculated for five isotherms for the HFC-125/134a mixture and six isotherms for the HFC-32/134a mixture. The calculated results from the CSD equation are compared with data in the open literature.

KEY WORDS: *activity coefficients; binary interaction parameters; equation of state; fugacity coefficients; HFC-32/134a mixture; HFC-125/134a mixture; thermodynamic consistency; vapor–liquid equilibrium.*

1. INTRODUCTION

As a result of the regulation of CFCs and HCFCs, pure HFCs and HCs and mixtures of these fluids are being investigated as alternative refrigerants [1]. It is very important to obtain accurate and reliable information on the thermophysical properties of these refrigerants. This paper reports vapor–

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liquid equilibrium (VLE) data for the HFC-32/134a and HFC-125/134a systems.

2. MEASUREMENT OF VAPOR–LIQUID EQUILIBRIUM

Phase equilibrium experimental methods are classified as either static, flow, or circulation, depending upon how the mixture is equilibrated [2]. In this study the circulation method is used, and the apparatus for measuring the vapor–liquid equilibrium is shown schematically in Fig. 1. The apparatus consists of an equilibrium unit, sampling and analysis unit, and supply unit. The most important unit is the equilibrium unit that consists of an equilibrium cell, magnetic pump, and constant temperature bath.

The equilibrium cell consists of a Pyrex tube. The inner diameter is 20 mm, and the length is 80 mm. The cell volume is about 25 cm^3. The magnetic pump circulates the vapor phase to ensure proper mixing and to reach equilibrium quickly. The equilibrium cell and the magnetic pump are installed in the constant temperature bath. An external controller maintains the bath temperature at its set point. The heat transfer medium is silicon oil.

The temperature is measured with a 25-Ω standard platinum resistance thermometer (ISOTECH) and a precision thermometry bridge (Model F700, Automatic Systems Laboratories) with a precision of 0.001 K. The thermometer is calibrated against the ITS-90 scale. The uncertainty of the temperature measurement is estimated to be within ± 0.02 K.

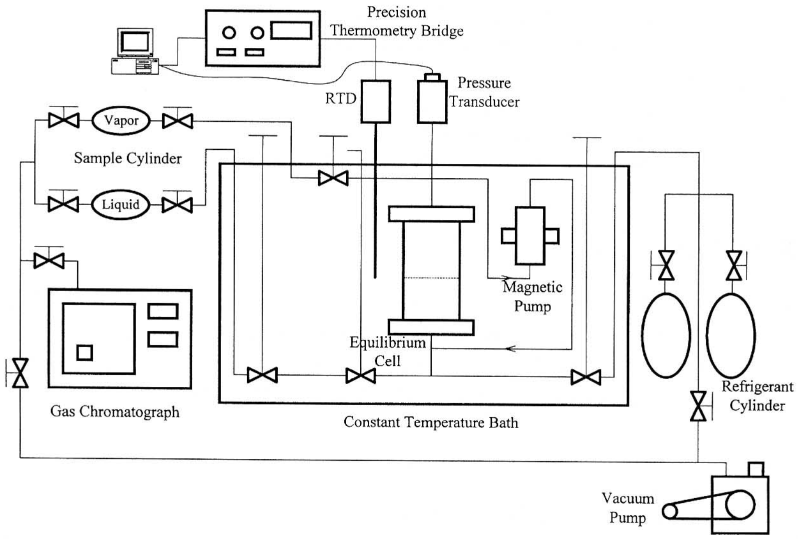

Fig. 1. Schematic diagram of the vapor–liquid equilibrium apparatus.

The pressure is measured with a pressure transducer (Model ATS, Heise) with a precision of 0.07 kPa. The uncertainty of the pressure measurement is estimated to be within ±0.2% (about 2.1 kPa).

The compositions of the vapor and liquid samples are determined using a gas chromatograph (HP 5890II) equipped with a thermal conductivity detector. The column is a Porapak-Q column (1.83 m long; 3.18 mm in diameter; mesh range, 80/100). The gas chromatograph is calibrated with a standard mixture, resulting in an estimated uncertainty of ±0.3 mol%.

3. RESULTS AND DISCUSSION

3.1. Sample Purity

The manufacturer's stated purity for the samples of HFC-32, HFC-125, and HFC-134a was 99.9%. These samples were used without further purification.

3.2. Vapor Pressure of Pure Refrigerants

Before starting the VLE measurements on mixtures, the vapor pressures of pure refrigerants HFC-134a and HFC-125 were measured and compared with data in a ASHRAE handbook [3]. The results are shown in Fig. 2. The deviations for both refrigerants are within ±0.5%.

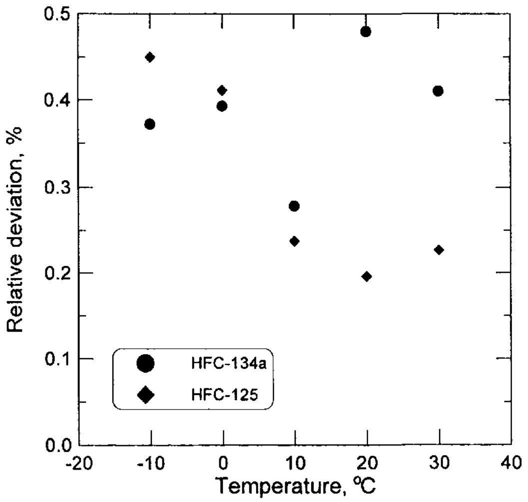

Fig. 2. Comparisons of the measured vapor pressures of HFC-134a and HFC-125 with data in the ASHRAE handbook [3].

3.3. Vapor–Liquid Equilibrium

The VLE data for HFC-32/134a measured over the temperature range from 258.15 to 283.15 K at 5 K intervals with compositions of about 0.2, 0.4, 0.6, and 0.8 liquid mole fraction of HFC-32 are presented in Fig. 3 and Table I. These data are compared with both CSD [4] and RKS [5] models. These results are also shown in Fig. 3.

The VLE data for HFC-125/134a measured over the temperature range from 263.15 to 303.15 K at 10 K intervals with compositions of about 0.18, 0.34, 0.50, 0.64, and 0.81 liquid mole fraction of HFC-125 are presented in Fig. 4 and Table II. These data are compared to both the CSD and the RKS models.

3.4. Interaction Parameters

On the basis of the present VLE data, the binary interaction parameters of the CSD and RKS equations for the HFC-32/134a and HFC-125/134a systems are determined. These results are shown in Table III.

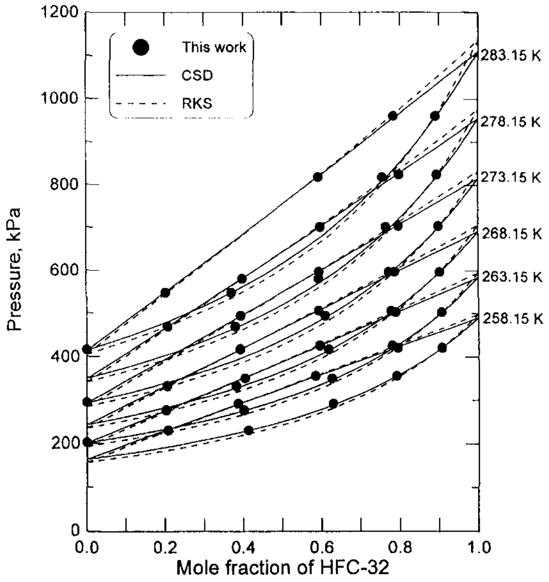

Fig. 3. Vapor–liquid equilibrium data for the HFC-32/134a system compared with results from the CSD and RKS equations of state.

Table I. Vapor–Liquid Equilibrium Data for the HFC-32/134a System

		Mole fraction of HFC-32	
Temperature (K)	Pressure (kPa)	Liquid	Vapor
258.15	229.455	0.2070	0.4121
	290.424	0.3865	0.6279
	354.546	0.5835	0.7910
	420.146	0.7938	0.9066
263.15	201.265	0.0000	0.0000
	275.818	0.2021	0.4004
	349.036	0.4035	0.6249
	425.026	0.5946	0.7798
	502.088	0.7876	0.9053
268.15	331.250	0.2045	0.3810
	416.683	0.3915	0.6163
	505.227	0.5915	0.7768
	596.825	0.7865	0.9015
273.15	293.839	0.0000	0.0000
	493.330	0.3923	0.6080
	596.784	0.5938	0.7724
	703.556	0.7966	0.8984
278.15	468.673	0.2059	0.3789
	580.657	0.3978	0.5927
	700.902	0.5967	0.7649
	823.856	0.7987	0.8944
283.15	415.646	0.0000	0.0000
	547.511	0.2019	0.3704
	817.642	0.5923	0.7563
	960.186	0.7844	0.8917

In Table III, no clear temperature dependence is evident for the binary interaction parameters for the HFC-32/134a system for either equation. The interaction parameters scatter around constant values (about −0.0115 and 0.0046, respectively, for the CSD and RKS equations) along six isotherms. In REFPROP [6], a constant value of −0.01 is used for the binary interaction parameter of the CSD equation for the HFC-32/134a system. And no clear temperature dependence is evident for the binary interaction parameters of the CSD equation for the HFC-125/134a system. However, as the temperature increases, the binary interaction parameters of the RKS equation decrease.

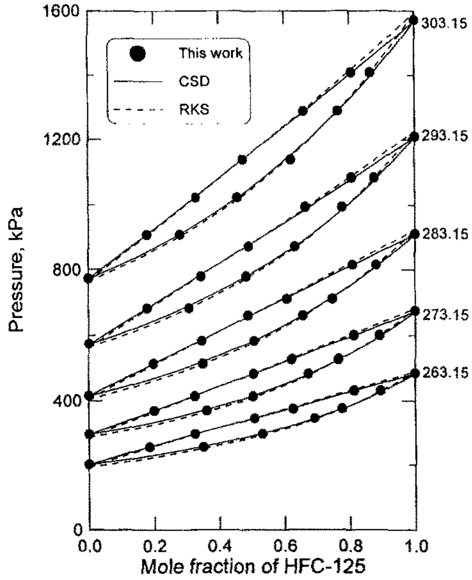

Fig. 4. Vapor–liquid equilibrium data for the HFC-125/134a system compared with results from the CSD and RKS equations of state.

3.5. Data Reduction Method

To verify vapor–liquid equilibrium data, these data are tested for thermodynamic consistency. There are three types of methods to verify consistency: (a) the method of integral forms of the Gibbs–Duhem equation, (b) the method of data reduction, and (c) the method of the Gibbs–Helmholtz equation [7]. In this work, the data reduction method is used.

The criterion, which must be satisfied for equilibrium between a liquid and a vapor phase at the same T and P, is given by Eq. (1) [8]:

$$y_i \varphi_i P = x_i \gamma_i P_i^{\mathrm{sat}} \varphi_i^{\mathrm{sat}} \tag{1}$$

where x_i and y_i are the liquid and vapor mole fractions, φ_i and φ_i^{sat} are the fugacity coefficients, γ_i is the activity coefficient, and P_i^{sat} is the vapor pressure of the pure refrigerants.

The vapor pressures of the pure refrigerants, the fugacity coefficients, and the activity coefficients must be calculated in order to verify the consistency of the experimental data. The vapor pressures of the pure

Table II. Vapor–Liquid Equilibrium Data for the HFC-125/134a System

Temperature (K)	Pressure (kPa)	Mole fraction of HFC-125	
		Liquid	Vapor
263.15	201.265	0.0000	0.0000
	253.732	0.1853	0.3513
	294.551	0.3258	0.5324
	345.038	0.5084	0.6921
	374.961	0.6265	0.7770
	431.725	0.8136	0.8947
	485.707	1.0000	1.0000
273.15	293.839	0.0000	0.0000
	368.922	0.2000	0.3622
	413.794	0.3258	0.5043
	483.250	0.5061	0.6734
	527.251	0.6228	0.7663
	600.363	0.8120	0.8910
	674.784	1.0000	1.0000
283.15	415.646	0.0000	0.0000
	513.862	0.1992	0.3516
	582.588	0.3466	0.5064
	659.685	0.4884	0.6562
	709.878	0.6084	0.7482
	816.401	0.8102	0.8819
	912.596	1.0000	1.0000
293.15	574.357	0.0000	0.0000
	681.304	0.1794	0.3081
	779.253	0.3461	0.4836
	871.814	0.4898	0.6324
	993.449	0.6646	0.7782
	1083.778	0.8078	0.8767
	1208.965	1.0000	1.0000
303.15	773.277	0.0000	0.0000
	908.287	0.1786	0.2802
	1021.985	0.3298	0.4562
	1138.136	0.4737	0.6215
	1288.985	0.6597	0.7657
	1408.670	0.8075	0.8648
	1572.957	1.0000	1.0000

Table III. Binary Interaction Parameters of the CSD and RKS Equations of State for the HFC-32/134a and HFC-125/134a Systems

Temperature (K)	Interaction parameter	
	CSD	RKS
	HFC-32/134a	
258.15	−0.0108	0.0062
263.15	−0.0132	0.0031
268.15	−0.0113	0.0051
273.15	−0.0114	0.0035
278.15	−0.0123	0.0038
283.15	−0.0103	0.0059
	HFC-125/134a	
263.15	0.0000	0.0027
273.15	−0.0006	0.0008
283.15	0.0006	0.0010
293.15	−0.0013	−0.0023
303.15	0.0000	−0.0016

refrigerants, P_i^{sat}, are determined by the correlation of McLinden et al. [9] expressed as a function of temperature.

$$\ln(P/P_c) = \frac{1}{(1-\tau)} \sum_{i=0} a_i \tau^{k_i} \tag{2}$$

where $\tau = (1 - T/T_c)$, P_c is the critical point pressure, and a_i's are the fitting parameters. The fugacity coefficients, ϕ_i and ϕ_i^{sat}, are determined using the RKS equation of state.

Activity coefficients, γ_i, are determined from the Margules [10] and the Van Ness and Abbott [10] equations. The constants in the Margules and the Van Ness and Abbott equations for activity coefficients are calculated by the method of bubble-point pressure calculations and given along isotherms in Table IV. The relative deviations of the bubble-point pressures and vapor mole fractions between measured and calculated results using the data reduction method for the HFC-32/134a and HFC-125/134a systems are given in Table V.

In Table V, when the activity coefficients are determined by the Margules equation, the average deviations of the mole fraction difference between measured and calculated results for the vapor mole fraction for the

Table IV. Constants for Equations of Activity Coefficients for the HFC-32/134a and HFC-125/134a Systems

	Margules equation[a]		Van Ness and Abbott equation[b]		
Temperature (K)	A_{12}	A_{21}	A'	B'	D'
	HFC-32/134a				
258.15	−0.0062	0.1272	0.4996	0.3726	0.2467
263.15	−0.0011	0.0746	−0.5102	−0.1761	−0.2492
268.15	−0.0131	0.1213	−0.1102	0.0719	−0.0486
273.15	0.0253	0.0952	0.0063	0.0841	−0.0104
278.15	0.0224	0.0804	−0.0391	0.0495	−0.0309
283.15	−0.0053	0.1415	−0.5532	−0.1387	−0.2735
	HFC-125/134a				
263.15	0.0660	0.0576	−0.1735	−0.0610	−0.1204
273.15	0.0363	0.0684	−0.1433	−0.0240	−0.0926
283.15	0.0490	0.0771	−0.0600	0.0198	−0.0574
293.15	−0.0029	0.0899	−0.2709	−0.0621	−0.1455
303.15	0.0407	0.0700	−0.0233	0.0438	−0.0320

[a] $G^E/x_1x_2RT = A_{21}x_1 + A_{21}x_2$.

[b] $G^E/x_1x_2RT = A'x_1 + B'x_2 - D'x_1x_2$.

Table V. Average Deviations Between Calculated and Measured Data for the HFC-32/134a and HFC-125/134a Systems from the Data Reduction Method

	RMS[a]			
Equation of activity coefficient	ΔP_{bub} (kPa)	P_{bub} (%)	Δy	y (%)
	HFC-32/134a			
Margules [10]	2.2046	0.32	0.0153	2.86
Van Ness et al. [10]	0.9134	0.21	0.0203	3.98
	HFC-125/134a			
Margules [10]	2.5484	0.37	0.0096	1.96
Van Ness et al. [10]	2.1719	0.32	0.0119	2.27

[a] $\text{RMS}(\%) = \sqrt{\frac{1}{n}\sum_{i=1}\left(\frac{x_{i,\text{cal}} - x_{i,\text{exp}}}{x_{i,\text{exp}}}\right)^2} \times 100$, $\text{RMS}(\Delta) = \sqrt{\frac{1}{n}(x_{i,\text{cal}} - x_{i,\text{exp}})^2}$.

HFC-32/134a and HFC-125/134a systems are 0.0153 and 0.0096, respectively. And when determined by the Van Ness and Abbott equation, the average deviations of the mole fraction difference are 0.0203 and 0.0119, respectively.

3.6. Equations of State

The CSD and RKS equations of state are used to calculate the pressure and vapor mole fraction for the HFC-32/134a and HFC-125/134a systems. These results are then compared with experimental data in the open literature and the calculated results of REFPROP.

The relative deviations between measured data and calculated results from the CSD and RKS equations are given in Table VI. The average deviation between the experimental data and calculated results from the CSD equation for the HFC-32/134a system is very small. The deviations of the calculated results from the RKS equation for the HFC-32/134a system are larger than those from the CSD equation. And the results from the CSD and RKS equations for HFC-125/134a are in good agreement with the present data.

The average deviations of the mole fraction difference between measured data and calculated results from the CSD equation for the HFC-32/134a and HFC-125/134a systems are 0.0084 and 0.0081, respectively. And the average deviations of the mole fraction difference from the RKS equation are 0.0185 and 0.0099, respectively.

The calculated results from the CSD equation are compared with experimental data from the open literature and with the calculated results of REFPROP. These results are shown in Figs. 5 and 6 for the HFC-32/134a and HFC-125/134a systems, respectively.

Table VI. Deviations Between Calculated and Measured Data for the HFC-32/134a and HFC-125/134a Systems from the CSD and RKS Equations of State

	RMS			
Equation of state	ΔP_{bub} (kPa)	P_{bub} (%)	Δy	y (%)
	HFC-32/134a			
CSD	2.2763	0.38	0.0084	1.85
RKS	5.4217	1.56	0.0185	3.65
	HFC-125/134a			
CSD	3.2545	0.41	0.0081	1.93
RKS	3.7541	0.63	0.0099	1.86

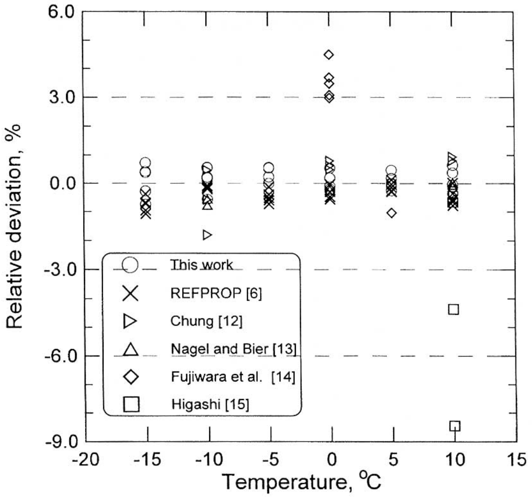

Fig. 5. Relative deviations of bubble-point pressures of HFC-32/134a system from the CSD equation of state with respect to temperature.

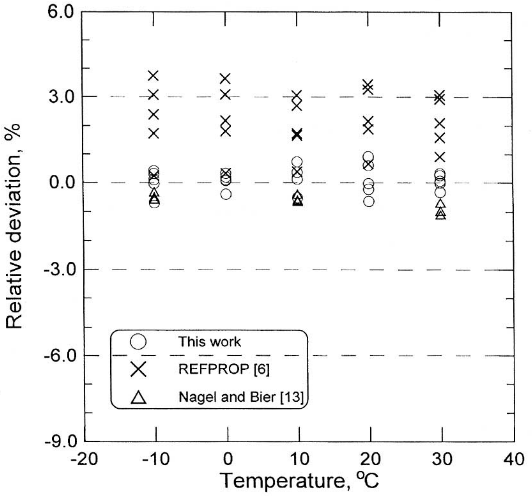

Fig. 6. Relative deviations of bubble-point pressures of HFC-125/134a system from the CSD equation of state with respect to temperature.

In Fig. 5 for the HFC-32/134a system, the results of Chung [12] and Nagel and Bier [13] are in good agreement with the present results. The deviations are within −1.81 to 0.94 and −0.78 to 0.04%, respectively. On the other hand, the results of Fujiwara et al. [13] and Higashi [14] are somewhat different from the present results. The deviations of the results of Fujiwara et al. and Higashi are within −1.04 to 4.49 and −8.45 to 0.66%, respectively. The calculated results of REFPROP are in good agreement; the deviations are within ±1.0%.

In Fig. 6 for the HFC-125/134a system, the results of Nagel and Bier [13] are in good agreement with the present results; the deviations are within 0.32 to 1.11%. But the calculated results of REFPROP show larger deviations, ranging from −0.22 to 3.74%. The deviation patterns are the same for all isotherms. Maximum deviations occur at about 0.3 liquid mole fraction of HFC-125.

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REFERENCES

1. M. H. Kim and Y. S. Park, *Soc. Air-Condition. Refrig. Eng. Korea* **25**:489 (1996).
2. W. R. Adams, Ph.D. thesis (Cornell University, Ithaca, NY, 1986).
3. *ASHRAE Handbook, Fundamentals*, SI ed. (ASHRAE, Atlanta, GA, 1997).
4. G. Morrison and M. O. McLinden, NBS Tech. Note 1226 (U.S. Government Printing Office, Washington, DC, 1986).
5. G. Soave, *Chem. Eng. Sci.* **27**:1197 (1972).
6. M. Huber, J. Gallagher, M. McLinden, and G. Morrison, *NIST Thermodynamic Properties of Refrigerants and Refrigerant Mixtures (REFPROP 5.0)* (National Institute of Standards and Technology, Boulder, CO, 1996).
7. S. Malanowski and A. Anderko, *Modelling Phase Equilibria: Thermodynamic Background and Practical Tools* (John Wiley, New York, 1992).
8. J. M. Smith and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, 4th ed. (McGraw-Hill, London, 1987).
9. M. O. McLinden, M. L. Huber, and S. L. Outcalt, *ASME Winter Annual Meeting*, New Orleans, LA, Paper No. 93-WA/HT-29 (1993).
10. J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd ed. (Prentice-Hall, Englewood Cliffs, NJ, 1986).
11. H. C. Van Ness and M. M. Abbott, *AIChE J.* **21**:62 (1975).
12. E. Y. Chung, Master's thesis (Seoul University, Seoul, 1997).
13. M. Nagel and K. Bier, *Int. J. Refrig.* **18**:534 (1995).
14. K. Fujiwara, H. Momoto, and M. Noguchi, *Proc. 13th Japan. Symp. Thermophys. Prop.* (1992), p. 61.
15. Y. Higashi, *Int. J. Thermophys.* **16**:1175 (1995).