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Vapor–Liquid Equilibrium, Coexistence Curve, and Critical Locus for Binary HFC-32/HFC-134a Mixture[1]

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Two kinds of equilibrium measurements of binary R-32/134a mixtures were carried out. The vapor–liquid equilibria were measured by the static method in the temperature range between 283 and 313 K. On the basis of the present experimental data, the temperature dependence of the binary interaction parameter k_{12} for two equations of state, namely, the Soave–Redlich–Kwong equation and Carnahan–Starling–De Santis equation, was discussed. The vapor–liquid coexistence curve near the critical point was also measured by the observation of meniscus disappearance. The critical temperatures and critical densities of 30 and 70 wt% R-32 mixtures were determined on the basis of the saturation densities along the coexistence curve in the critical region. In addition, a correlation of the critical locus for this mixture is proposed as a function of composition.

KEY WORDS: binary interaction parameter; critical density; critical temperature; equation of state; R-32/134a mixture; vapor–liquid coexistence curve; vapor–liquid equilibrium.

1. INTRODUCTION

As the result of the regulation of CFCs and HCFCs, HFC mixtures, for example, R-32/134a, R-32/125, and R-32/125/134a, are expected to be the main candidates for future refrigeration and heat pump systems. It is presently very difficult, however, to obtain accurate and reliable information on thermophysical properties for these mixtures. This paper reports the measurements of two kinds of equilibrium properties for binary R-32

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(CH_2F_2; difluoromethane) and R-134a (CF_3CH_2F; 1,1,1,2-tetrafluoroethane) mixtures. The first measurement is that of the vapor–liquid equilibrium, and the second is that of densities of the vapor–liquid coexistence curve near the critical point.

2. MEASUREMENTS OF THE VAPOR–LIQUID EQUILIBRIUM

The apparatus for measuring the vapor–liquid equilibrium by the static method is shown schematically in Fig. 1. The vapor–liquid equilibrium cell **A** is a cylindrical pressure vessel made of stainless steel, whose inner volume is about 150 cm^3. It is immersed in the thermostated bath **C**. Water was used as the heat transfer medium. Temperature fluctuations in the thermostated bath were kept constant within ±10 mK by a temperature control system composed of platinum resistance thermometer **I**, PID controller **J**, thyristor regulator **K**, and two individual heaters **M** and **N**. Temperatures were measured with a 100-Ω platinum resistance thermometer **D** calibrated against ITS-90 using a 25-Ω standard platinum

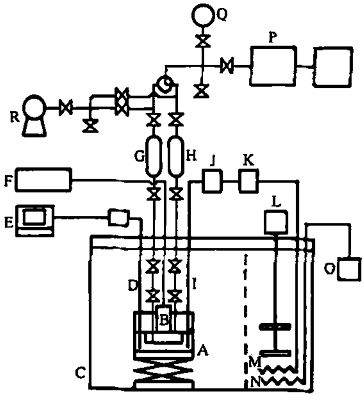

Fig. 1. Experimental apparatus for the measurement of vapor–liquid equilibrium. (A) Vapor–liquid equilibrium cell; (B) pressure transducer; (C) thermostated bath; (D) platinum resistance thermometer; (E) computer; (F) digital multimeter; (G) cylinder I; (H) cylinder II; (I) platinum resistance thermometer; (J) PID controller; (K) thyristor regulator; (L) stirrer; (M) heater (300 W); (N) main heater (1.5 kW); (O) voltage convecter; (P) gas chromatograph; (Q) pressure gauge; (R) vacuum pump.

resistance thermometer. The uncertainty of temperature measurements is estimated to be within ±10 mK.

The pressure of the sample was measured with a diaphragm semiconductor strain-gauge pressure transducer **B** installed in this equilibrium cell. This pressure transducer was calibrated against another quartz crystal pressure transducer after every series of experiments. The uncertainty of pressure measurements is estimated to be within ±0.3%.

Compositions of the vapor and liquid samples were determined with a gas chromatograph **P** (Shimadzu GC-7AG) equipped with a thermal conductivity detector. In the present study, the chromatograph was equipped with a Porapak-Q column (2 m long; ID, 3 mm; mesh range, 50/80). Peak areas were determined with an electronic integrator. The gas chromatograph was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. The uncertainty of the composition measurements is estimated within ±0.4 mol%.

3. MEASUREMENTS OF THE VAPOR–LIQUID COEXISTENCE CURVE NEAR THE CRITICAL POINT

The present apparatus for measuring the vapor–liquid coexistence curve and determining the critical parameters of fluid mixtures was described in detail in previous publications [1, 2]. The present measurements of the coexistence curve in the critical region of R-32/134a mixtures were made by the visual observation of the meniscus disappearance and of the critical opalescence. The temperature measurement was conducted with a 25-Ω standard platinum resistance thermometer calibrated against ITS-90. The uncertainty of the temperature measurements was estimated within to be ±10 mK. The sample density was calculated by the sample mass and the inner volumes of the pressure vessels. The uncertainty of the sample density was estimated to be within ±0.5–1.5 $\mathrm{kg \cdot m^{-3}}$. The composition of the mixtures was not determined by using the gas chromatograph. The procedure for determining the composition of a mixture has been described previously [3]. The estimated uncertainty of the composition is no greater than 0.05%.

4. RESULTS

4.1. Sample Purity

The samples of pure R-32 and pure R-134a were furnished by Asahi Glass Co. Ltd. The manufacturer stated that the sample purities were

99.98 wt% R-32 and 99.99 wt% R-134a. These samples were used without further purification.

4.2. Vapor–Liquid Equilibrium

The experimental results for the vapor–liquid equilibria (VLE) of the R-32/134a mixture are shown in Fig. 2. Thirty-two data points along four isotherms, i.e., 283.07, 293.06, 303.05, and 313.04 K, including the vapor-pressure data for each pure component were obtained. The vapor-pressure data of R-32 and R-134a are given in Tables I and II, respectively, whereas the VLE data are given in Table III. The available VLE data of R-32/134a at 273.15 K by Fujiwara et al. [4] were obtained from previous publication. In Fig. 2, the isotherms calculated from the computer program package REFPROP, Version 4.0 [5] are also indicated. The calculation results from REFPROP were good agreement with the present results except the data of 283 K.

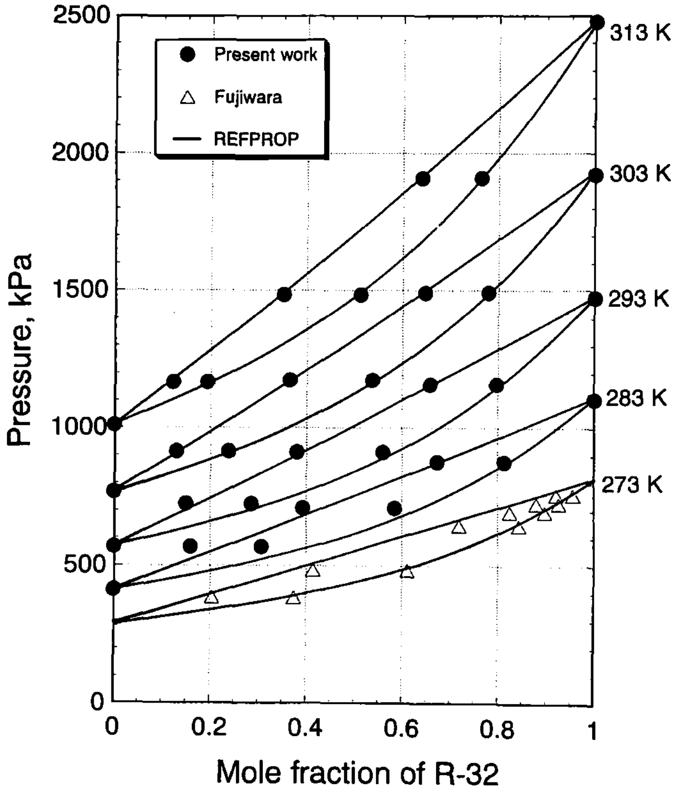

Fig. 2. Vapor–liquid equilibrium for the R-32/134a mixture.

Table I. Vapor-Pressure Data for R-32

Temperature (K)	Pressure (kPa)
283.10	$1104._7$
293.10	$1474._2$
302.99	$1922._4$
313.06	$2477._7$

Table II. Vapor-Pressure Data for R-134a

Temperature (K)	Pressure (kPa)
283.07	$412._5$
293.14	$568._2$
303.12	$768._1$
312.95	$1009._8$

Table III. Vapor–Liquid Equilibrium Data for the R-32/134a Mixture

Pressure (kPa)	Mole fraction of R-32	
	Liquid	Vapor
	$T = 283.07$ K	
$567._2$	0.159_1	0.306_3
$708._9$	0.392_9	0.584_8
$878._5$	0.673_0	0.813_5
	$T = 293.06$ K	
$724._5$	0.149_1	0.285_9
$911._3$	0.379_9	0.559_7
$1158._3$	0.658_8	0.797_4
	$T = 303.05$ K	
$914._3$	0.128_6	0.237_9
$1173._9$	0.364_7	0.537_0
$1490._3$	0.646_9	0.779_1
	$T = 313.04$ K	
$1166._0$	0.121_5	0.193_0
$1482._9$	0.351_2	0.512_0
$1908._0$	0.639_8	0.764_1

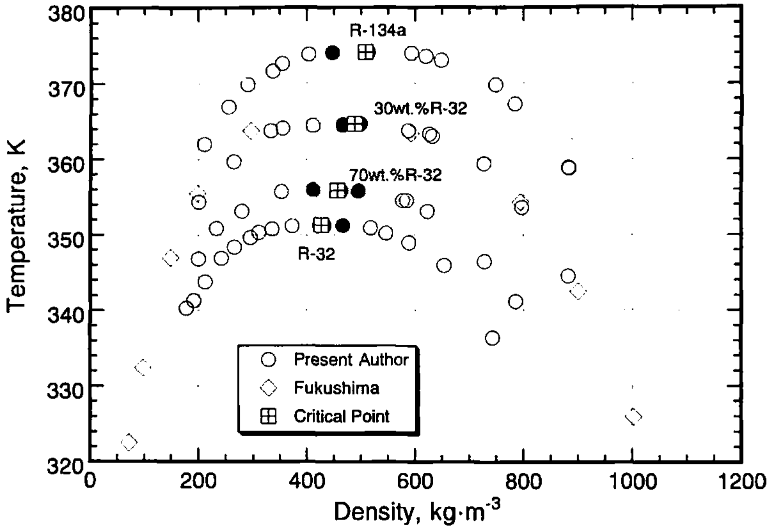

Fig. 3. Vapor–liquid coexistence curve for the R-32/134a mixture in the critical region; filled circles indicates the observation of critical opalescence.

Table IV. Experimental Data of the Saturated Densities for the R-32/134a Mixture

Temperature (K)	Sat. liquid density ($kg \cdot m^{-3}$)	Temperature (K)	Sat. vapor density ($kg \cdot m^{-3}$)
	45.67 mol% (30.00 wt%) R-32		
344.48	$882._1$	354.37	$201._4$
353.61	$797._3$	359.71	$264._4$
359.39	$726._8$	363.79	$333._1$
363.02	$632._4$	364.11	$355._3$
363.34	$627._1$	364.49	$411._7$
363.80	$587._9$	364.64	$466._6$
364.74	$499._3$		
364.65	$497._6$		
364.66	$490._8$		
	82.07 mol% (70.00 wt%) R-32		
341.20	$785._6$	346.84	$200._0$
346.50	$727._5$	350.88	$233._4$
353.11	$623._0$	353.13	$280._1$
354.50	$584._2$	355.75	$352._9$
354.51	$577._0$	355.99	$412._0$
355.79	$494._3$		
355.89	$463._5$		

Table V. Critical Parameters for the R-32/134a Mixture

Mole fraction of R-32 (mol%)	Mass fraction of R-32 (wt%)	Critical temperature (K)	Critical density ($kg \cdot m^{-3}$)	Critical molar volume ($cm^3 \cdot mol^{-1}$)
0	0	374.11 ± 0.02	508 ± 5	201 ± 2
45.67	30.00	364.66 ± 0.02	489 ± 3	162 ± 1
82.07	70.00	355.89 ± 0.02	457 ± 7	133 ± 2
100	100	351.26 ± 0.02	427 ± 5	122 ± 2

4.3. Vapor–Liquid Coexistence Curve

The experimental results for the vapor–liquid coexistence curve of the R-32/134a mixture near the critical point are shown in Fig. 3. The experimental temperature versus density data along the coexistence curve for two compositions, 45.67 mol% (30.00 wt%) and 82.07 mol% (70.00 wt%) R-32, are given in Table IV. The results of the measurements for both pure components were published previously [2]. The measurements at which critical opalescence was observed are indicated by filled symbols in Fig. 3. The coexistence data of 45.67 mol% R-32 of Fukushima et al. [6] are also indicated in Fig. 3.

The critical temperature and critical density for two compositions of the R-32/134a mixture were determined by analyzing the present coexistence curve, taking into consideration the disappearing meniscus level and the intensity of the critical opalescence. The critical parameters thus obtained for the R-32/134a mixture are given in Table V.

5. DISCUSSION

5.1. Correlation of the Critical Locus

On the basis of the present measurements for the critical parameters, the correlation of the critical locus of the R-32/134a mixture was formulated by the following functions [7]:

$$T_{cm} = \theta_1 T_{c1} + \theta_2 T_{c2} + 2\theta_1 \theta_2 \Delta_T \tag{1}$$

$$V_{cm} = \theta_1 V_{c1} + \theta_2 V_{c2} + 2\theta_1 \theta_2 \Delta_V \tag{2}$$

Here T_{cm} and V_{cm} denote the critical temperature of mixture in K and critical molar volume of mixture in $cm^3 \cdot mol^{-1}$, respectively. Δ_T and Δ_V

are the adjustable parameters for the critical temperature and critical molar volume, respectively. θ denotes the surface fraction given by Eq. (3) and subscripts 1 and 2 correspond to each component of the mixture.

$$\theta_i = x_i V_{ci}^{2/3} \Big/ \sum x_j V_{cj}^{2/3} \tag{3}$$

Here x denotes the mole fraction. Equations (1) and (2) with $\Delta_T = -1.89$ K and $\Delta_V = -20.2 \, \text{cm}^3 \cdot \text{mol}^{-1}$ reproduce the present critical parameters within the experimental accuracy.

5.2. Binary Interaction Parameter

On the basis of the present VLE data, the binary interaction parameter, k_{12}, for two equations of state, i.e., the Soave–Redlich–Kwong equation (SRK equation) [8] and the Carnahan–Staring–De Santis equation of

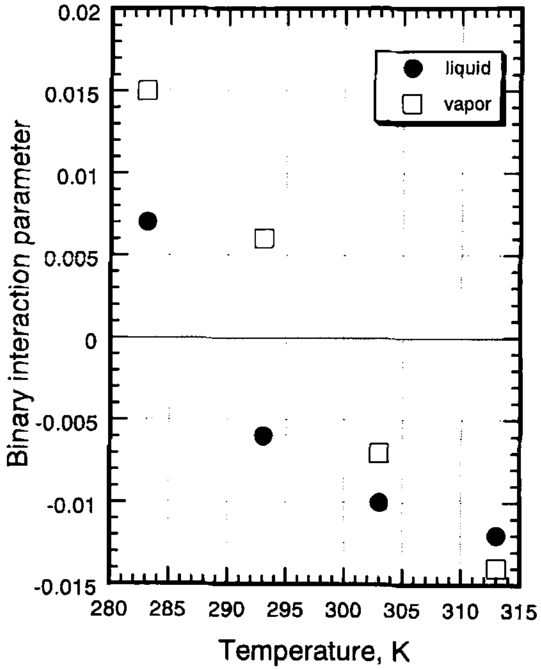

Fig. 4. Temperature dependence of the binary interaction parameter of the Soave–Redlich–Kwong equation of state for the R-32/134a mixture.

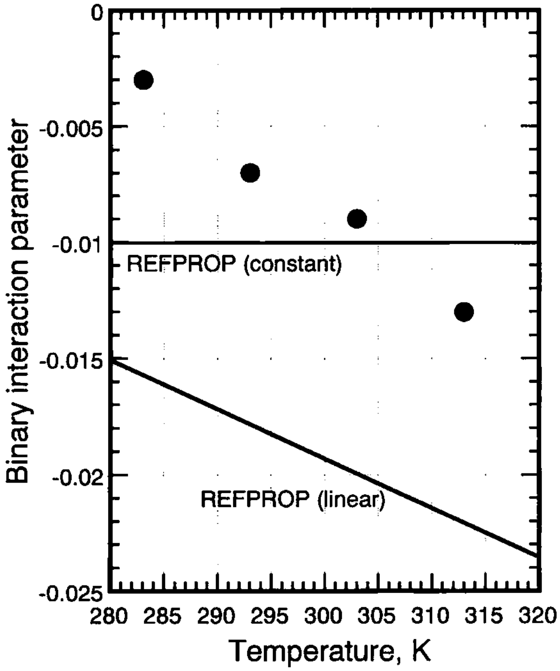

Fig. 5. Temperature dependence of the binary interaction parameter of the Carnahan–Starling–De Santis equation of state for the R-32/134a mixture.

state (CSD equation) [9], were determined. The temperature dependence of the binary interaction parameters for the SRK and CSD equations is shown in Figs. 4 and 5, respectively.

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