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High-Pressure Vapor–Liquid Equilibrium Data of the HFC 134a + HCFC 141b System

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Isothermal vapor–liquid equilibrium data for the 1,1,1,2-tetrafluoroethane (HFC 134a) + 1,1-dichloro-1-fluoroethane (HCFC 141b) system were determined by using an optical cell with a vapor and liquid alternatively recirculating apparatus. Temperatures were set to 278.15, 288.15, 303.15, 318.15, and 333.15 K, and pressures ranged from 0.1 to 1.5 MPa. Experimental data were correlated with the Soave–Redlich–Kwong equation of state and the density-dependent local-composition-equation of state (DDLC–EOS) unified model. Calculated results show that both equations yield rather good agreements with the experimental values.

Introduction

Several hydrofluorocarbons and hydrochlorofluorocarbons are now considered as alternative refrigerants that are nondestructive to ozone in the stratosphere. 1,1-Dichloro-1-fluoroethane (HCFC 141b) may be regarded as one of the alternatives for trichlorofluoromethane (CFC 11), while 1,1,1,2-tetrafluoroethane (HFC 134a) as that for dichlorodifluoromethane (CFC 12).

These alternative refrigerants usually form a nonazeotropic mixture, which has recently been considered as the prospective working fluid for refrigeration and heat pump systems. Their thermodynamic properties, especially vapor–liquid equilibria, are the basic data essential for selecting the optimal composition for design and operation purposes. On the other hand, binary interaction parameters obtained from precise vapor–liquid equilibrium data can be utilized to predict both saturated liquid and vapor densities, as well as other thermodynamic properties of the mixture, when an adequate equation of state capable of accurately describing volumetric behaviors is applied. However, scarce information concerning these properties is available to date.

In this investigation, isothermal vapor–liquid equilibrium data for the 1,1,1,2-tetrafluoroethane + 1,1-dichloro-1-fluoroethane system were determined by using an optical cell connected with a vapor and liquid alternatively recirculating apparatus at 278.15, 288.15, 303.15, 318.15, and 333.15 K with atmospheric pressures up to 1.5 MPa.

In addition, experimental data were correlated with the Soave–Redlich–Kwong equation of state (*1*) and the DDLC–EOS unified model (*2*), i.e. the density-dependent local-composition model combined with the cubic equation of state. Results show that both equations predict the present data rather satisfactorily.

Experimental Section

*1. **Apparatus***. An apparatus similar to that used by Kubota et al. (*3*) and Wu et al. (4) was newly constructed with some minor modifications. The schematic diagram of the apparatus used in this work is shown in Figure 1.

The equilibrium cell is a 304 stainless steel cylindrical vessel with a 128-mm outside diameter, 28-mm inner diameter, and 205-mm height, as shown in Figure 2. In its middle part, a pair of Pyrex glass windows of 20-mm thickness and 21-mm diameter was installed so that the liquid level, mixing and circulating behaviors, and critical phenomena could be observed. A stirrer rotated with variable speeds by an external magnet was also installed to accelerate the attainment of the equilibrium state and reduce any concentration gradient in both phases, as shown in that figure.

Two small holes of 3.2-mm diameter were provided on the side wall of the cell as the inlet and outlet of the circulating fluid. The open arrows shown in Figure 2 denote the liquid recirculation mode, i.e. the liquid is drawn out from the bottom of the cell and returned to the upper part, falling as liquid droplets back into the cell. For the vapor recirculation mode, the vapor is sucked off from the upper hole and recirculated to the bottom, bubbling up through the liquid phase, to attain close contact between the liquid and vapor phases.

A high-pressure six-port ball valve was used to switch the recirculation mode from liquid to vapor and vice versa.

Since the sample temperature in the cell is not measured directly, full attention must be paid to confirm thermal equilibrium between the sample fluid and the thermostated bath fluid during the measurement.

The bath temperature was kept constant by a Haake circulator Model F3 with the fluctuation of ±0.02 K, which had been calibrated by a standard quartz thermometer in the 1968 International Practical Temperature Scale (IPTS-68). The possible uncertainty in temperature measurements is estimated to be within ±0.05 K, including the precision of the standard thermometer used and the fluctuation of the temperature controller.

Pressures were measured with a digital pressure transducer Model TD-300 of TEAC Instruments Corp., which had been calibrated by standardized dead-weight gauges. The uncertainty of pressure measurements is estimated to be within ±1.0 kPa.

*2. **Experimental Procedure***. After the whole system had been evacuated to 0.1 Pa by a vacuum pump, HCFC 141b was introduced into the cell from a feed reservoir. HFC 134a was then charged therein, while the high pressure recirculating pump was turned on to increase the rate of HFC 134a solving in HCFC 141b until the desired pressure was achieved and an acceptable liquid level appeared within the optical window.

The temperature controller of the Haake circulator Model F3 in the thermostatics was then switched on. When the experimental temperature was below room temperature, a small refrigerator was used to cool the thermostated bath.

When the experimental temperature was above 303.15 K and the cell pressure greater than the saturated pressure of HFC 134a at room temperature, a small cylindrical vessel would be used to fill HFC 134a from the sample bomb by ice-cooling the vessel, if it was necessary. Then, it was transferred to the equilibrium cell by heating the vessel.

The mixture in the cell was then stirred continuously by the magnetic stirrer for over 1 h. The vapor was recirculated by the high-pressure pump until the equilibrium state was estab-

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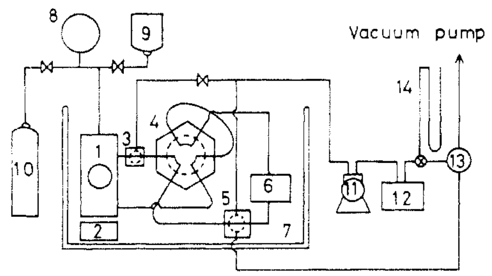

Figure 1. Schematic diagram of the apparatus: (1) equilibrium cell; (2) magnetic stirrer; (3) two-way (three-port) ball valve; (4) six-way (six-port) ball valve; (5) two-way (four-port) ball valve; (6) high-pressure recirculating pump; (7) constant-temperature bath; (8) pressure transducer; (9) HCFC 141b reservoir; (10) HFC 134a bomb; (11) low-pressure diaphragm pump; (12) gas chromatograph; (13) expansion vessel; (14) mercury manometer.

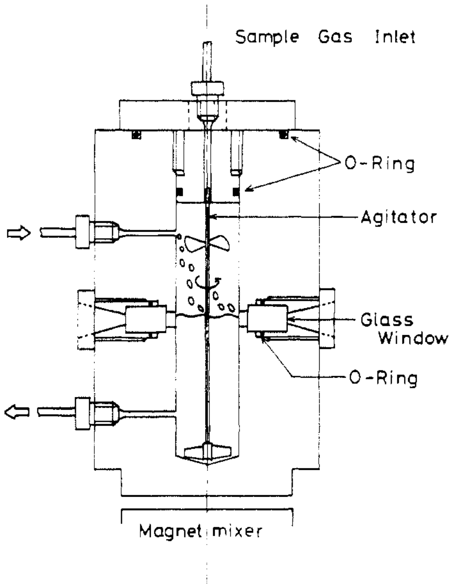

Figure 2. Optical equilibrium cell.

lished. It is believed that 1 h or more is sufficient to obtain thermal equilibrium between the cell fluid and the thermostated bath.

Before sampling, it is often necessary to wait for 5 min in order to allow some of small liquid drops, if there are any, to be separated from the vapor stream. The vapor sample was taken from the top of the cell and expanded into the low-pressure system, which had been evacuated to vacuum beforehand. After being recirculated in the low-pressure system by a diaphragm pump for over 15 min to obtain a uniform concentration, the vapor sample was led to the gas chromatograph for on-line analysis.

Then the high-pressure six-ports ball valve was switched to the liquid recirculation mode. The same procedure was performed as that used in the case of vapor sampling, except that the liquid sample was taken directly from the four-port valve and flashed to the low-pressure circulation system to avoid any disturbance to the equilibrium condition during the withdrawal of the liquid sample. However, if the vapor sample is also taken directly from the four-port valve, it may contain some liquid droplets, which would probably cause serious errors according to our experimental results.

After the measurement of one datum point was completed, more HFC 134a was charged into the cell from the sample bomb until the desired pressure and a suitable liquid level were attained. However, it must be noted that the liquid level should not be too high. For instance, when the vapor–liquid interface is only about 10 mm below the top edge of the optical window, serious errors in measurement may occur due to the carrying-over of liquid droplets into the vapor phase. In that case, a little liquid was discharged from the cell and more HFC 134a was recharged into the cell until the desired pressure was attained and an appropriate liquid level appeared in the optical window.

In the measurement of both vapor- and liquid-phase compositions, each sample was analyzed three times, and the disparity of results was usually within 0.5 mol % or less, so the average value was adopted.

The same procedure was performed for another datum point.

3. Calibration and Analysis Methods. Because HCFC 141b is in a liquid state while HFC 134a is a vapor at room temperature under atmospheric pressure, a gravity method has been used for the preparation of synthetic mixtures to determine the response factor of this binary system for the gas chromatographic analysis.

Samples were weighed on a precision chemical balance (Jupiter CT2-200, Chyo Balance Corp.) with an uncertainty of ±0.3 mg. Samples of both liquid and vapor components were frozen separately by liquefied nitrogen and trapped in a U-tube of the low-pressure system, which had been evacuated to around 0.1 Pa. The synthetic mixture trapped in the U-tube was then evaporated by heating and circulated by the diaphragm pump in the low-pressure system. After a uniform concentration was obtained, the synthetic mixture was led to the gas chromatograph for analysis.

According to the Lambert–Beer's law, the peak area is proportional to the amount of the solute, the response factor can be determined. When the ratios of the peak areas are plotted against the ratios of moles of both components, a straight line passing through the origin can be obtained. The response factor for this system was determined by the least-squares method to be 0.897.

Samples of both vapor and liquid phases were analyzed on-line by a Yanaco gas chromatograph Model G1880T with a thermal conductivity detector. A column packed with Porapak QS 80 was used at 423 K with helium as a carrier gas. An integrator of SIC Chromatocorder Model 12 was used to calculate the analysis results. Analysis procedures were performed three times for each sample to confirm reproducibility. The analysis uncertainty of liquid compositions is estimated to be within ±0.05% while that of vapor compositions is not greater than 0.1%.

Source and Purity of Chemicals

HCFC 141b and HFC 134a used in this work were provided by Daikin Industries, Ltd., Osaka, Japan. The purities were determined by the manufacturer: HCFC 141b was greater than 99.9 mol % and HFC 134a greater than 99.8 mol %. Both compounds were tested by the gas chromatograph, and no traces of impurity were detected, so they were used without further purification.

Experimental Results

The measured pressures, temperatures, and mole fractions of both liquid and vapor phases of HFC 134a including the equilibrium ratios are presented in Table I. The pressures vs mole fractions of both phases of HFC 134a for 278.15, 303.15, and 333.15 K isotherms are shown in Figure 3 and those for 288.15 and 318.15 K in Figure 4. Experimental results indicate that this mixture does not exhibit an azeotropic phenomenon in the pressure and temperature ranges of this investigation.

The saturated vapor pressures of pure HFC 134a at five temperatures and pure HCFC 141b at four temperatures of this experiment were measured by Yamashita et al. (*5*) with another apparatus.

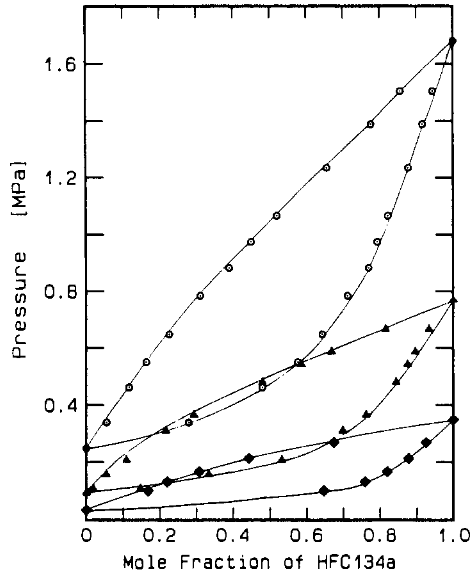

Figure 3. Phase diagram of the HFC 134a + HCFC 141b system. Temperature conditions and DDLC–EOS model parameters C_{12} and C_{21}: (♦) 278.15 K, $C_{12} = 0.096$, $C_{21} = -0.010$; (▲) 303.15 K, $C_{12} = -0.042$, $C_{21} = 0.221$; (⊙) 333.15 K, $C_{12} = -0.007$, $C_{21} = 0.115$.

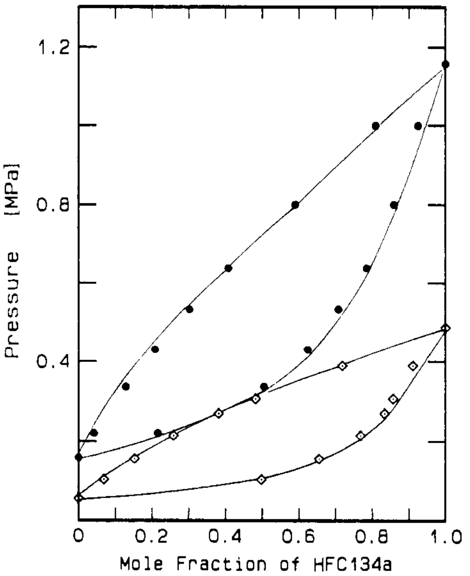

Figure 4. Phase diagram of the HFC 134a + HCFC 141b system. Temperature condition and DDLC–EOS model parameters C_{12} and C_{21}: (◈) 288.15 K, $C_{12} = 0.007$, $C_{21} = 0.109$; (●) 318.15 K, $C_{12} = -0.112$, $C_{21} = 0.381$.

Data Correlation

The two-constant cubic equation of state with the conventional mixing rule is not usually capable of accurately describing the liquid volumetric behavior, which is also of importance in refrigerating process design. It was found that Soave's modified version of the Redlich–Kwong equation of state failed to predict the saturated liquid density of 1,1-difluoroethane (*6*).

In this work, the DDLC-EOS model (density-dependent local-composition model combined with the cubic equation of state) proposed in the previous work (*2*) and the Soave–Redlich–Kwong equation (*1*) were applied to correlate the present experimental data. Calculated results were compared with the experimental values. Results calculated by the DDLC-EOS model were also plotted in full lines as shown in Figures 3 and 4. Rather satisfactory results were obtained except for the vapor mole fractions of the 303.15 K isotherm.

Table I. Isothermal Vapor–Liquid Equilibrium Data for the HFC 134a (1) + HCFC 141b (2) System

	mole fraction		equilibrium ratio	
pressure, MPa	x	y	K_1	K_2
		T = 278.15 K		
0.101	0.168	0.647	3.844	0.425
0.132	0.221	0.759	3.441	0.309
0.167	0.308	0.819	2.663	0.261
0.213	0.443	0.877	1.982	0.220
0.269	0.674	0.925	1.372	0.231
		T = 288.15 K		
0.101	0.069	0.498	7.225	0.539
0.154	0.152	0.655	4.303	0.407
0.215	0.258	0.768	2.976	0.313
0.270	0.384	0.834	2.169	0.207
0.306	0.482	0.857	1.776	0.277
0.389	0.718	0.911	1.268	0.317
		T = 303.15 K		
0.108	0.019	0.147	7.872	0.869
0.157	0.054	0.333	6.148	0.706
0.207	0.109	0.532	4.883	0.525
0.311	0.217	0.698	3.226	0.385
0.366	0.293	0.762	2.600	0.337
0.479	0.480	0.844	1.758	0.301
0.541	0.586	0.875	1.494	0.302
0.587	0.668	0.896	1.341	0.313
0.667	0.816	0.934	1.145	0.360
		T = 318.15 K		
0.221	0.041	0.215	5.205	0.818
0.336	0.128	0.504	3.947	0.568
0.431	0.208	0.624	3.007	0.475
0.534	0.302	0.708	2.344	0.419
0.638	0.407	0.785	1.927	0.363
0.800	0.590	0.859	1.457	0.343
0.999	0.809	0.925	1.143	0.395
		T = 333.15 K		
0.340	0.056	0.278	5.002	0.764
0.461	0.117	0.479	4.100	0.590
0.550	0.164	0.576	3.521	0.507
0.649	0.226	0.643	2.840	0.462
0.785	0.311	0.712	2.290	0.418
0.883	0.390	0.769	1.973	0.378
0.975	0.450	0.793	1.764	0.376
1.066	0.520	0.822	1.581	0.370
1.236	0.657	0.878	1.337	0.356
1.389	0.777	0.917	1.180	0.373
1.504	0.857	0.944	1.102	0.388

Mathematical formulations of the two equations with their mixing rules used for data correlation are expressed as follows:

DDLC–EOS model (*2*)

$$P = RT/(v - b) - a(T,v)/v(v + b) \tag{1}$$

$$a_m = \sum x_i \sum x_j \, a^\circ{}_{ji}(1 - C_{ji} E_{ji}/\sum x_k E_{ki})$$

$$b_{\mathrm{m}} = \sum x_i \, b_i, \quad a^\circ{}_{ji} = (a_{ii} \, a_{jj})^{0.5}$$

$$E_{ji} = \exp[-C_{ji} \, a^\circ{}_{ji} \ln (1 + b/v)/RTb]$$

SRK equation (*1*)

$$P = RT/(v - b) - a(T)/v(v + b) \tag{2}$$

$$a_m = \sum x_i \sum x_j \, a_{ij}(1 - k_{ji})$$

$$b_m = \sum x_i \, b_i$$

The Simplex method of Nelder and Mead (*7*) was applied to obtain the optimal binary interaction parameters with the following objective function:

$$\mathrm{OF} = \sum_j^m [(x_{1,\mathrm{exp}} - x_{1,\mathrm{cal}})_j^2 + (y_{1,\mathrm{exp}} - y_{1,\mathrm{cal}})_j^2]$$

The acentric factors of both components were estimated by the methods of Reid et al. (*8*).

Conclusion

1. The apparatus used in this investigation is capable of measuring reliable vapor–liquid equilibrium data for process design purposes.

2. Both the Soave–Redlich–Kwong equation of state and the DDLC-EOS model yield satisfactory results in comparison with the experimental data.

Glossary

a	attractive parameter, J·m^3·mol^{-2}
b	repulsive parameter, m^3·mol^{-1}
C_{ji}	binary interaction parameter
E_{ji}	nonconformal parameter
m	number of datum points
P	pressure, MPa
R	gas constant, J·mol^{-1}·K^{-1}
T	absolute temperature, K
v	molar volume, m^3·mol^{-1}
x	mole fraction of liquid phase
y	mole fraction of vapor phase

Superscripts

°	conformal reference state

Subscripts

i,j,k	component
cal	calculated
exp	experimental

Registry No. HFC 134a, 811-97-2; HCFC 141b, 1717-00-6.

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Excess Volumes of Isobutanol with Toluene or *o*-Xylene at 303.15 and 308.15 K

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Excess molar volumes for the binary mixtures of isobutanol with toluene and *o*-xylene have been measured at 303.15 and 308.15 K with use of a continuous dilution dilatometer. The excess volumes are positive for both the systems at these temperatures.

Introduction

Brown and Smith (*1*) have studied the excess volumes of mixing for isobutanol (2-methyl-1-propanol) with benzene in the temperature range of 298.15–318.15 K. Swamy et al. (*2*) and Raman et al. (*3*) have reported excess volumes of isobutanol with toluene at 303.15 K. Here we report the excess volumes of isobutanol with toluene and *o*-xylene at 303.15 and 308.15 K. The excess volumes are positive over the entire composition range and increase with temperature.

Experimental Section

A continuous dilution dilatometer of the type used by Kumaran and McGlashan (*4*) was fabricated to carry out the present study. The dilatometer was immersed in a water bath. Temperature of the bath was controlled by a proportional controller and measured to ±0.01 K with a K-3 universal potentiometer (Leeds and Nothrup Inc.) A precision cathetometer (Gartener Scientific Co., Chicago, IL) readable to 0.01 mm was used to measure the mercury levels in the dilatometer. The estimated uncertainty in the volume measurement was ±0.004 cm^3/mol^{-1}. The experimental procedure is similar to the one followed by Kumaran and McGlashan (*4*) and Pickerell and Plank (*5*). The details of the experiment are described elsewhere (*6*).

Table I. Normal Boiling Points T_b and Densities ρ of Pure Components

	T_b/K		ρ/(kg m^{-3})		
component	this work	lit.	T/K	this work	lit.
isobutanol	380.30	380.81 (*7*)	303.15	795.93	793.8 (*7*)
			308.15	791.84	789.8 (*7*)
toluene	383.65	383.78 (*8*)	303.15	857.79	857.6 (*8*)
			308.15	852.93	852.9 (*8*)
o-xylene	417.25	417.58 (*8*)	303.15	866.08	871.7 (*8*)
			308.15	861.93	867.5 (*8*)

Purification of Materials

Analytical grade chemicals were purified in a 22-plate distillation column. The middle cut from the distillation product was taken for the experiments. Triple-distilled mercury was used in the experiments. Measured values for normal boiling point and densities of the purified components are presented in Table I, along with literature values (*7*, *8*). The details of the distillation of the chemicals and measurement of physical properties were described earlier (*9*).

Results and Discussion

The experimental excess molar volumes V^E of isobutanol with toluene and *o*-xylene are presented in Table II. The

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