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Vapor−Liquid Equilibrium (VLE) Data for the Carbon Dioxide (CO_2) + 1,1,1,2-Tetrafluoroethane (R134a) System at Temperatures from 252.95 K to 292.95 K and Pressures up to 2 MPa

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Isothermal vapor−liquid equilibrium data of the binary mixture of carbon dioxide (CO_2)−1,1,1,2-tetrafluoroethane (R134a) at temperatures between 252.95 K and 292.95 K and pressures up to 2 MPa are measured and correlated. To obtain experimental data, we have used the static-analytic method with liquid and vapor phase sampling. The data are correlated using the Peng−Robinson (PR) equation of state and the classical mixing rules.

Introduction

Replacement of the conventional refrigerant chlorodifluoromethane is one of the urgent issues to be solved within the scheduled time frame of the amended Montreal Protocol. The vapor−liquid equilibrium (VLE) data are essential for the selection of mixtures with suitable thermodynamic properties for replacing conventional refrigerants with new, more environmentally benign alternatives. Another use of the data is to improve the parameters available for use in equations of state or group contribution methods to represent or predict the physical properties and equilibrium phase behavior of multicomponent systems containing selected binary pairs.

The R134a is an acceptable refrigerant by its environmental impact. It has been used to replace the CFC-12 (dichlorodifluoromethane) in a wide variety of applications, especially in conditioned air; this implies the design of new equipment, using accurate thermodynamic properties.[1] On the other hand, carbon dioxide has received special attention as a fluid that can be used in combination with other refrigerants to minimize flammability and/or toxicity hazards. In this scope, mixtures of refrigerants such as R134a with CO_2 are of great importance.

In this paper, isothermal vapor−liquid equilibrium data of the binary mixture carbon dioxide (CO_2)−1,1,1,2-tetrafluoroethane (R134a) have been measured in the temperature range from 252.95 K to 293.95 K. They were fitted using the Peng−Robinson equation of state to determine the binary interaction parameter. The experimental method used in this work is based on the static-analytic method.

Experimental Section

Materials. The carbon dioxide is from Air Liquide with a certified purity higher than 99.995%. 1,1,1,2-Tetrafluoroethane (R134a) is from Dehon Service with purity higher than 99.9 wt %; no further purification was performed before use.

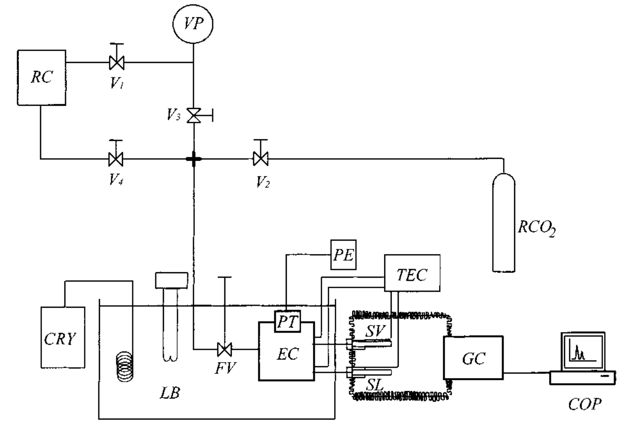

Figure 1. Schematic diagram of experimental apparatus: *RCO_2*, carbon dioxide reservoir; *RC*, 1,1,1,2-tetrafluoromethane reservoir; *V*, valve (Autoclave Engineers); *TEC*, temperature control; *FV*, feeding valve; *EC*, equilibrium cell; *LB*, liquid bath; *PT*, pressure transducer; *SV*, sampling vapor; *SL*, sampling liquid; *GC*, gas chromatograph; *PE*, pressure electronic display; *VP*, vacuum pump; *CRY*, cryocool unit; *COP*, computer.

Apparatus and Procedures. The experimental method used in this work to determine the VLE data is the static-analytic method with liquid and vapor phase sampling and analysis. A schematic diagram of the apparatus is shown in Figure 1. This apparatus is similar to that described by Laugier and Richon.[2] The way of feeding the binary mixture is different, however.

The equilibrium cell is immersed inside a controlled temperature liquid bath. It contains an efficient magnetic stirrer to ensure fast equilibrium, and it is equipped with two sampling systems. In both cases small size withdrawn samples guarantee a negligible disturbance of the thermodynamic equilibrium at each working pressure. The working volume of the cell is about 50 cm^3. To know the average temperature, two type J thermocouples (iron−constantan) are inserted in holes machined inside the body of the equilibrium cell. They are close to the vapor and liquid phases, respectively. Their calibrations were achieved using a 25 Ω platinum probe. The temperature data were

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Table 1. Vapor−Liquid Equilibrium Data for the CO_2 (1)−R134a (2) System

			mole fraction		
T/K	P/MPa	ΔP ($P_{cal} - P_{exp}$)	liquid x_1	vapor y_1	Δy ($y_{cal} - y_{exp}$)
252.95	0.131	0.000	0.000	0.000	0.000
252.95	0.301	−0.007	0.099	0.572	0.013
252.95	0.508	0.022	0.223	0.772	0.003
252.95	0.683	0.048	0.326	0.848	−0.001
252.95	0.800	0.043	0.393	0.878	0.000
252.95	1.003	−0.003	0.506	0.919	−0.004
252.95	1.202	−0.123	0.611	0.943	−0.004
252.95	1.357	−0.117	0.697	0.954	0.001
252.95	1.576	−0.208	0.810	0.974	−0.001
252.95	1.685	−0.204	0.867	0.983	−0.002
272.75	0.288	0.001	0.000	0.000	0.000
272.75	0.394	−0.037	0.038	0.260	0.010
272.75	0.534	−0.107	0.087	0.468	−0.003
272.75	0.644	0.027	0.132	0.565	0.011
272.75	0.698	−0.043	0.149	0.607	0.001
272.75	0.862	0.099	0.213	0.695	0.003
272.75	0.977	0.104	0.254	0.738	0.002
272.75	1.155	0.034	0.314	0.793	−0.006
272.75	1.454	0.010	0.416	0.849	−0.005
272.75	1.607	−0.036	0.466	0.871	−0.006
272.75	1.821	−0.061	0.536	0.895	−0.005
272.75	2.033	−0.015	0.606	0.916	−0.006
292.95	0.566	0.001	0.000	0.000	0.000
292.95	0.823	−0.104	0.062	0.307	−0.001
292.95	0.932	0.212	0.097	0.419	−0.007
292.95	1.127	−0.071	0.138	0.524	−0.019
292.95	1.397	0.088	0.207	0.607	0.007
292.95	1.716	−0.042	0.279	0.691	0.000
292.95	1.916	−0.087	0.324	0.731	−0.003
292.95	2.048	−0.084	0.354	0.755	−0.005

acquired through a digital electronic unit (Fluke, type 2190A, LT479). The uncertainty of the temperature measurements is estimated to be within ±0.15 K.

Pressures are measured by means of a pressure transducer (Duck, type PTX611, 16 bar, accepting an overpressure of 30%). The uncertainty of the pressure measurement was estimated to be within ±0.006 MPa, following a calibration against a dead weight balance (Desgranges & Huot 5202S, CP 0.3 to 40 MPa, France).

All analytical work was carried out on a gas chromatograph (Stang Intruments type ST200) coupled to a data acquisition system. A thermal conductivity detector (TCD) is used to analyze both components. The measurement column is a Porapak Q (length, 2 m; granulometry 80/100 mesh; $^1/_8$ in. stainless steel; from Restek). The TCD was repeatedly calibrated by introducing pure compounds through a syringe in the injector of the gas chromatograph. The uncertainty of composition analysis was estimated to be within ±1% in mole fraction, taking into account the deviations on the calibration plots and the repeatability of samples and analyses. At least five samples of each phase are taken for analyses so that the reported compositions are the result of averaging five measurements.

The process to load the equilibrium cell is the following (see Figure 1): before feeding the binary system, the circuit is kept under a vacuum to prevent air from coming inside the equilibrium cell. The liquid component [1,1,1,2-tetrafluoroethane (R134a)] is introduced directly into the equilibrium cell from its storage container by gravity under a vacuum (valves 4 and FV are opened, V_1, V_2, and V_3 are closed). Then at constant temperature, the vapor pressure of R134a is measured. The pressure in the equilibrium cell is adjusted by adding CO_2 from its gas storage cylinder. When the equilibrium is reached under efficient stirring of the studied mixture, samples of liquid and vapor are withdrawn using the pneumatic samplers and analyzed by gas chromatography. At the completion of each measurement, a new set of conditions is established by adding more CO_2. The equilibration and sampling sequence is then repeated to cover the whole mole fraction range.

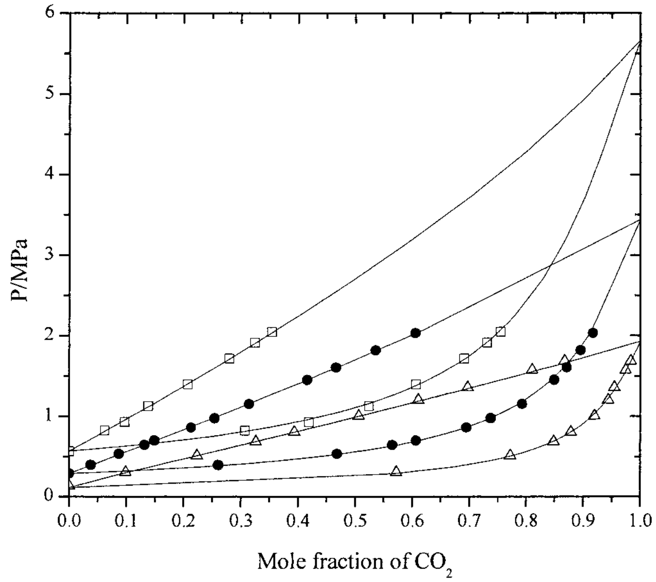

Figure 2. $P-x-y$ phase equilibrium diagram for CO_2 (1)−R134a (2) at different temperatures: Δ, 252.95 K; ●, 272.75 K; □, 292.95 K; solid lines are calculated with the PR-EoS and δ_{ij} from Table 3.

Results and Discussion

Isothermal vapor−liquid equilibrium results are presented in Table 1 and are shown graphically in Figure 2. The isothermal VLE data are correlated using the Peng−Robinson[3] (PR) equation of state and the classical mixing rules,

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

where

$$a(T) = 0.45724\frac{R^2 T_c^{\,2}}{P_c}\alpha(T) \tag{2}$$

$$b = 0.07780\frac{RT_c}{P_c} \tag{3}$$

$\alpha(T)$ comes from the original Soave[4] function,

$$\alpha(T) = [1 + m(1 - T_r^{\,1/2})]^2 \tag{4}$$

where

$$m = 0.3746 + 1.54226\omega - 0.26992\omega^2 \tag{5}$$

For mixtures, the parameters are expressed in terms of the pure component parameters by the combining rules,

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{6}$$

with

$$a_{ij} = (a_i a_j)^{1/2}(1 - \delta_{ij}) \tag{7}$$

$$b = \sum_i x_i b_i \tag{8}$$

Table 2. Critical Parameters and Acentric Factors (ω) (from Dortmund Data Bank version 97)[5]

component	T_c/K	P_c/MPa	ω
carbon dioxide (CO_2)	304.20	7.377	0.2250
1,1,1,2-tetrafluoroethane (R134a)	374.25	4.064	0.3259

Table 3. δ_{ij} Binary Interaction Parameter for the CO_2 (1)−R134a (2) System

T/K	δ_{ij}
252.95	0.0132
272.75	0.0164
292.95	0.0181

where δ_{ij} is the binary interaction parameter. Table 2 shows the values T_c and P_c and the acentric factors (ω) used in this work. The optimal δ_{ij} values determined from each isothermal binary VLE data set are presented in Table 3. The Levenberg−Marquardt method is applied for the data reduction, while the objective function (F) used is

$$F = \sum_{i=1}^{N}\left(\frac{P_{i,\mathrm{cal}} - P_{i,\mathrm{exp}}}{P_{i,\mathrm{exp}}}\right)^2 + \sum_{i=1}^{N}\left(\frac{y_{i,\mathrm{cal}} - y_{i,\mathrm{exp}}}{y_{i,\mathrm{exp}}}\right)^2 \qquad (9)$$

where N is the total number of data points ($i = 1, ..., N$), $P_{i,\mathrm{cal}}$ and $P_{i,\mathrm{exp}}$ are the calculated and the experimental total pressures, and $y_{i,\mathrm{cal}}$ and $y_{i,\mathrm{exp}}$ are the calculated and the experimental CO_2 vapor mole fractions.

The solid isothermal lines in Figure 2 are calculated from the Peng−Robinson equation with the corresponding binary interaction parameters reported in this work (Table 3).

The δ_{ij} binary interaction parameter is slightly temperature dependent in the 253 to 293 K temperature range; see Figure 3. It can be represented by

$$\delta_{ij} = -15.89 \times 10^{-2} + (1.16 \times 10^{-3})T/\mathrm{K} - (1.90 \times 10^{-6})(T/\mathrm{K})^2 \qquad (10)$$

Equation 10 can be used to generate data at any temperatures between 252.95 and 293.95 K.

The mean relative deviations (Δ) and the standard relative deviation (STRD) for pressures and vapor phase compositions are given in Table 4. They are defined as

$$\Delta P(\%) = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{P_{\mathrm{cal}} - P_{\mathrm{exp}}}{P_{\mathrm{exp}}}\right|_i \times 100 \quad \text{and}$$

$$\Delta y(\%) = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{y_{\mathrm{cal}} - y_{\mathrm{exp}}}{y_{\mathrm{exp}}}\right|_i \times 100$$

$$\mathrm{STRD}\ P = 100\left(\frac{1}{N-1}\sum_{i=1}^{N}\left[\frac{P_{\mathrm{cal}} - P_{\mathrm{exp}}}{P_{\mathrm{exp}}}\right]_i^2\right)^{0.5} \quad \text{and}$$

$$\mathrm{STRD}\ y = 100\left(\frac{1}{N-1}\left[\frac{y_{\mathrm{cal}} - y_{\mathrm{exp}}}{y_{\mathrm{exp}}}\right]_i^2\right)^{0.5}$$

Vapor pressures of R134a have been measured at three temperatures and compared to literature values[6] in Table 5.

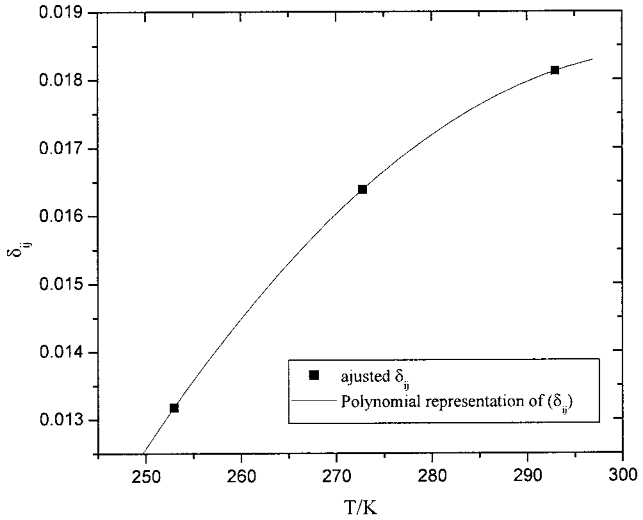

Figure 3. Binary interaction parameter δ_{ij} for the CO_2 (1)−R134a (2) system.

Table 4. Mean Relative Deviations and Standard Relative Deviations on Pressures and Vapor Phase Compositions for the CO_2 (1)−R134a (2) System

T/K	$\Delta y(1)$ (%)	ΔP (%)	STRD $y(1)$	STRD P
252.95	0.41	0.59	0.76	0.82
272.75	0.94	0.65	1.43	0.90
292.95	1.11	0.84	1.74	1.15

Table 5. Comparison of Experimental and Literature Vapor Pressures of R134a

experimental		literature[a]		REFPROP[b]	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
252.95	0.131			252.95	0.132
272.75	0.288	272.17	0.282	272.75	0.289
292.95	0.566	292.10	0.553	292.95	0.568

[a] Kobayashi and Nishiumi.[6] [b] REFPROP version 6.01.[7]

Conclusion

Vapor−liquid equilibrium data for the carbon dioxide (1)−R134a (2) system have been determined at three different temperatures: 252.95, 272.75, and 292.95 K. No experimental data were previously available on this system. The modeling using the PR equation of state is satisfactory (ΔP and Δy are around 1%). The δ_{ij} parameter is temperature dependent.

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