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Isothermal Vapor−Liquid Equilibria for 1,1,1,2-Tetrafluoroethane + Propane and Propane + 1,1,1-Trifluoroethane at 283.18 K

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Isothermal vapor−liquid equilibria (VLE) for the binary systems 1,1,1,2-tetrafluoroethane (R134a) + propane (R290) and propane + 1,1,1-trifluoroethane (R143a) were measured at 283.18 K using a recirculation apparatus in which the vapor phase was forced through the liquid. The phase composition at equilibrium was measured by gas chromatography, calibrating its response using gravimetrically prepared mixtures. The data were correlated using the Carnahan−Starling−De Santis and Peng−Robinson equations of state. We found positive homoazeotropes for R134a (1) + R290 (2) at a pressure $P = 1000.5$ kPa and a composition $x_1 = 0.386$, and for R290 (1) + R143a (2) at $P = 796$ kPa and $x_1 = 0.363$. For the R134a + R290 there was a valid consistency with the values reported in the literature.

Introduction

Due to the need to substitute traditional CFCs with new environment-friendly compounds, a research effort has been dedicated in recent years to studying the thermodynamic properties of fluorinated derivatives of methane and ethane and their mixtures. For binary or ternary mixtures with other similar compounds or with hydrocarbons, vapor−liquid equilibrium (VLE) data are particularly important to verify the quality of the models and to design or retrofit currently operating refrigeration plants. The present work reports on the results of VLE measurements and data reduction on the binary systems 1,1,1,2-tetrafluoroethane (R134a) + propane (R290) and propane (R290) + 1,1,1-trifluoroethane (R143a). For the former system, a valid consistency was found with the literature (Kleiber, 1994). To our knowledge, there are no data available in the literature on the latter.

Experimental Section

Reagents. R143a, with 0.01% impurities detected by gas chromatography (see Table 1) using the flame ionization detector (FID) and 0.2% using the thermal conductivity detector (TCD) (assessed as a percentage of area), R290, with 0.01% total impurities detected by the FID and about 0.2% by the TCD, and R134a, with 0.01% and 0.3% total impurities detected by the FID and TCD, respectively, were used with no further purification. All the compounds were donated by AUSIMONT SpA, Italy. The difference in the proportion of impurities detected by the FID and TCD is probably due to the presence of inorganic compounds in the samples that are not detected by the FID.

Experimental Apparatus. The recirculation VLE apparatus and the procedures used in this work are described only briefly here as they have already been presented in more detail elsewhere (Bobbo et al., 1997). The VLE is reached in a stainless steel cell of about 50 cm^3 capacity equipped with a magnetic pump and two glass windows. The glass windows are sealed to the cell body with gold O-rings. The VLE cell, together with a magnetic pump, was immersed in a liquid thermostat of about 100 L capacity. Water was used as a thermostating fluid. The VLE cell, magnetic pump, and thermostat were built by the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.

Temperature was measured by a 100 Ω platinum resistance thermometer connected to a multimeter (HP3458) and was recorded continuously using a data acquisition software (LABVIEW). The temperature in the bath was stabilized (±1 mK) by means of a PID-controlled system governing a 1.5 kW heater immersed in the thermostating bath. An auxiliary cooler (LAUDA RK8CP) was used both to compensate for the heat produced by the PID-controlled system and to keep the temperature below or close to ambient temperature.

Pressure was measured by means of one of the two (RUSKA 6000) pressure gauges with a full scale of 600 kPa and 3500 kPa, respectively, depending on the actual pressure being measured. A differential pressure cell (RUSKA 2413) immersed in the thermostat was used to separate the reagents from the quartz sensors of the pressure gauges. A control box (RUSKA 2461) connected to a null detector (RUSKA 2416) was used to balance the pressure on both sides of the differential pressure cell diaphragm.

With this apparatus the margins of error in the pressure and temperature measurements are estimated to be within ±0.3 kPa and ±0.005 K, respectively.

The composition of the vapor and liquid phases was established by gas chromatographic analysis. A gas chromatograph (Hewlett-Packard 6890) was connected on-line to the VLE cell. The gas chromatographic parameters are given in Table 1.

The response of the detector was carefully calibrated using gravimetrically prepared mixtures. The calibrating

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Table 1. Gas Chromatography Parameters

system	column				oven temp./K	detector
	length/m	internal diameter/mm	carrier (N_2) flow rate/$cm^3 \cdot min^{-1}$	packing		
R134a (1) + R290 (2)	2	2.1	45	Porapak N	383	FID
R290 (1) + R143a (2)	2	2.1	45	Porapak Q	363	FID

Table 2. Experimental Vapor–Liquid Equilibrium Data for the R134a (1) + R290 (2) System at 283.18 K

P/kPa	x_1	P/kPa	x_1
414.7	1.0000	795.6	0.3327
683.5	0.8051	792.9	0.2761
748.8	0.6770	787.3	0.2271
771.1	0.5958	775.6	0.1761
785.2	0.5063	756.2	0.1257
786.0	0.5011	723.9	0.0742
793.1	0.4418	681.0	0.0288
797.4	0.3360	637.2	0.0000

Table 3. Vapor–Liquid Equilibrium Data for the R290 (1) + R143a (2) System at 283.18 K

P/kPa	x_1	y_1	P/kPa	x_1	y_1
637.2	1.0000	1.0000	994.5	0.3940	0.3935
685.8	0.9794	0.9176	994.9	0.3787	0.3837
685.5	0.9757		998.9	0.3686	0.3785
760.9	0.9277	0.8072	992.8	0.3405	0.3606
760.7	0.9272		993.0	0.2940	0.3293
871.6	0.8172	0.6631	977.5	0.2168	0.2717
970.9	0.6058	0.5115	945.1	0.1285	0.1867
994.4	0.4713	0.4376	912.6	0.0764	0.1264
994.1	0.4279	0.4135	837.5[a]	0.0000	0.0000

[a] Value calculated with the CSD EOS.

mixtures were prepared in stainless steel vessels with a capacity of 240 cm^3 pretested up to 5 MPa. An analytical balance with a resolution of 0.1 mg was used, and the accuracy in the composition of the calibrating mixture was estimated at ±0.0001 of the mole fraction. Considering the margin of error and the reproducibility of gas chromatography, we estimated the accuracy in composition measurements to be within ±0.0015 of the mole fraction for both the liquid and the vapor phases.

Results and Discussion

The P, x equilibrium data for the R134a + R290 mixtures and the P, x, y equilibrium data for the R290 + R143a mixtures (both measured at 283.18 K) are presented in Tables 2 and 3, respectively. The vapor and liquid-phase envelopes are shown in Figures 1 and 2. Throughout the paper, x and y indicate the liquid and vapor mole fractions, respectively, while P is the pressure in kPa.

Among the many EOS, expressions for the dependence of their parameters on temperature and combining rules proposed in the literature, for data reduction we considered the Carnahan–Starling–De Santis (CSD) EOS in the form proposed by De Santis et al. (1976)

$$P = \frac{RT}{V}\left[\frac{1 + Y + Y^2 - Y^3}{(1 - Y)^3}\right] - \frac{a}{V(V + b)} \tag{1}$$

where

$$Y = \frac{b}{4V} \tag{2}$$

with the following expressions for the temperature-dependent a and b parameters

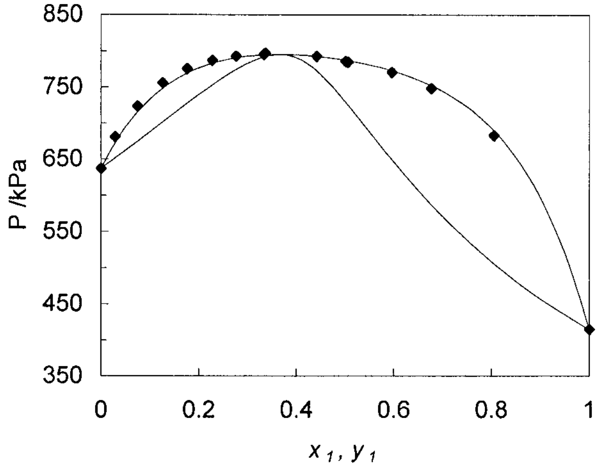

Figure 1. Vapor–liquid equilibrium for R134a (1) + R290 (2) at 283.18 K. Solid lines represent CSD EOS fit.

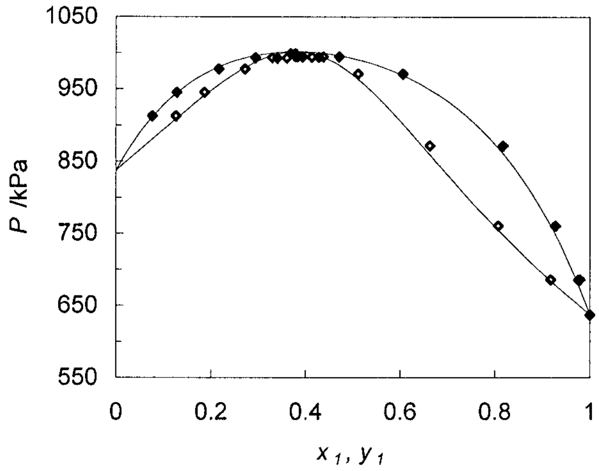

Figure 2. Vapor–liquid equilibrium for R290 (1) + R143a (2) at 283.18 K. Solid lines represent CSD EOS fit.

$$a(T) = a_0 \exp(a_1 T + a_2 T^2) \tag{3}$$

$$b(T) = b_0 + b_1 T + b_2 T^2 \tag{4}$$

and the Peng–Robinson (PR) EOS (Peng and Robinson, 1976)

$$P = \frac{RT}{V - b} - \frac{a}{V^2 + 2bV - b^2} \tag{5}$$

where

$$a = 0.457\,24\left(\frac{R^2 T_c^2}{P_c}\right)\alpha(T) \tag{6}$$

$$b = 0.077\,80\left(\frac{RT_c}{P_c}\right) \tag{7}$$

Table 4. Parameters of the CSD EOS (Eq 1) Used for Data Correlation (Huber et al., 1996)

	compound		
parameter	R134a	R143a	R290
a_0/kPa·L^2·mol^{-2}	3582.1714	2763.9092	2988.277
a_1/K^{-1}	$-2.811\,136\,2 \times 10^{-3}$	$-2.509\,055\,9 \times 10^{-3}$	$-2.629\,019\,5 \times 10^{-3}$
a_2/K^{-2}	$-1.446\,788\,8 \times 10^{-6}$	$-1.797\,107\,7 \times 10^{-6}$	$-1.097\,062 \times 10^{-6}$
b_0/L·mol^{-1}	0.141 750 31	0.133 152 59	0.142 962 5
b_1/L·mol^{-1}·K^{-1}	$-1.627\,631\,0 \times 10^{-4}$	$-1.589\,537\,9 \times 10^{-4}$	$-1.765\,191\,2 \times 10^{-4}$
b_2/L·mol^{-1}·K^{-2}	$-0.628\,932\,64 \times 10^{-7}$	$-0.583\,310\,54 \times 10^{-7}$	$-5.785\,137 \times 10^{-8}$

Table 5. Critical Parameters and R_m, R_n Parameters of Pure Compounds Used in the PR EOS (Eq 5)

compound	T_c/K	P_c/kPa	reference	R_m	R_n
R134a	374.18	4056.0	ASHRAE (1993)	0.268 770	0.603 161
R143a	345.97	3776.0	Fukushima (1993)	0.192 830	0.598 612
R290	369.80	4242.0	ASHRAE (1993)	0.184 545	0.422 918

Table 6. Results of the VLE Data Reduction with the PR and CSD EOS at 283.18 K

	R134a + R290		R290 + R143a	
system EOS	PR	CSD	PR	CSD
δP (%)	0.12	0.16	0.14	0.17
abs(δP) (%)	0.39	0.53	0.48	0.68
δy			−0.001 6	0.000 2
abs(δy)			0.004 2	0.006 2
k_{12}	0.166 16	0.153 37	0.130 21	0.120 52

V is the molar volume in (L·mol^{-1}), T is the temperature in (K), and $R = 8.314\,45$ is the universal gas constant in (J·mol^{-1}·K^{-1}). Consequently, the a and b parameters in eqs 1 and 5 are expressed in (kPa·L^2·mol^{-2}) and (L·mol^{-1}), respectively. The subscript c (as in eqs 6 and 7) denotes a property in a critical state.

For the temperature dependence of the α parameter, the expression

$$\alpha(T) = 1 + (1 - T_r)\left(R_m + \frac{R_n}{T_r}\right) \tag{8}$$

proposed by Soave (1976) was used with two compound characteristic adjustable dimensionless parameters R_m and R_n, which gave a valid representation of the vapor pressure for $T_r > 0.6$, where $T_r = T/T_c$ is the reduced temperature.

The coefficients a and b of the CSD EOS for pure compounds were adopted from the Huber et al. (1996) database. They are listed in Table 4.

The R_n and R_m parameters for α in the PR EOS were found from the fit of the vapor pressure data. For R134a and R290, the data were taken from the ASHRAE Handbook (1993). For the latter compound, the data were truncated below 101 kPa. Saturated pressure data for R143a have been published recently by various authors (Giuliani et al., 1995; Widiatmo et al., 1994; Zheng et al., 1995); all show similar deviations from the fit, but we ultimately used the data from Giuliani et al. (1995) because they cover the widest temperature range. The resulting coefficients R_m and R_n are shown in Table 5.

The vapor pressure of the pure compounds established in this work were compared with data in the literature and findings produced by the EOS with the coefficients shown in Tables 4 and 5. We found a strong consistency with the data in the literature (ASHRAE Handbook, 1993), the deviations being −0.05% and −0.2% for R134a and R290, respectively.

The same form of combining rules was used for both EOS

$$a = \sum\sum \xi_i \xi_j a_{ij} \tag{9}$$

where ξ_i is the mole fraction of the ith component and

$$b = \sum \xi_i b_i \tag{10}$$

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - k_{ij}) \tag{11}$$

where k_{ij} is a dimensionless adjustable parameter for $i \neq j$.

The VLE data were reduced using the above equations and minimizing the objective function

$$\text{obf} = \sum_{i=1}^{N_p} [(\delta P/P)]^2 \tag{12}$$

where N_p is the number of experimental points. $\delta P = P_{exp} - P_{EOS}$ and $\delta y = y_{1,exp} - y_{1,EOS}$ are defined throughout the paper. The results of data reduction are given in Table 6.

For the R134a + R290 system, our findings were compared with those published elsewhere (Kleiber, 1994). For the comparison, Kleiber's data at 275 and 298 K (the closest to our measurements) were fitted to the CSD. We found $k_{12} = 0.150\,49$, with abs(δP) = 0.42% and abs(δy) = 0.0062. At maximum pressure, where the difference is greatest, the resulting value of k_{12} gives a −0.8% pressure deviation from our measurement.

Azeotropic parameters can be found from the EOS involving either the condition

$$\partial P/\partial x_1 = 0 \tag{13}$$

or equivalently

$$x_1 = y_1 \tag{14}$$

Here, the latter procedure was used, and the azeotropic composition and pressure findings are given in Table 7.

The differences between the results of the two EOS are minimal and may result from the differences in the vapor pressure representation by the EOS. Here, we have adopted the mean values given above.

Conclusions

Both systems show a positive deviation from Raoult's law and form positive homogeneous azeotropes: R134a (1) +

Table 7. Azeotropic Composition and Pressure for R134a (1) + R290 (2) and R290 (1) + R143a (2) at 283.18 K from PR and CSD EOS

	PR		CSD		recommended values	
EOS system	P/kPa	x_1	P/kPa	x_1	P/kPa	x_1
R134a (1) + R290 (2)	796.4	0.3613	795.9	0.3658	796	0.363
R290 (1) + R143a (2)	1000.3	0.3928	1002.0	0.3800	1000.5	0.386

R290 (2) at $P = 796$ kPa and $x_1 = 0.363$ and R290 (1) + R143a (2) at $P = 1000.5$ kPa and $x_1 = 0.386$.

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