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Isothermal Vapor−Liquid Equilibria for the Binary System 1,1,1-Trifluoroethane (R143a) + 1,1,1,3,3,3-Hexafluoropropane (R236fa) at 283.11, 298.16, and 313.21 K

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A recirculation apparatus in which the vapor phase was forced through the liquid was used to measure isothermal vapor−liquid equilibria (VLE) for the binary system 1,1,1-trifluroethane (R143a) + 1,1,1,3,3,3-hexafluoropropane (R236fa) at 283.11, 298.16, and 313.21 K. The phase composition at equilibrium was measured with a gas chromatograph that was calibrated with gravimetrically prepared mixtures. The system shows a small deviation from Raoult's law. The data were reduced with the Carnahan−Starling−De Santis (CSD) equation of state. The deviations observed in vapor composition suggest a relatively good consistency of the experimental findings and the model used for their reduction.

Introduction

An extensive study of the vapor−liquid equilibria of binary systems with 1,1,1,3,3,3-hexafluoropropane (R236fa) has been performed by our group within a European Community Project aimed at the substitution of 1,2-dichlorotetrafluorethane (R114) in high-temperature industrial heat pumps. In the past, mixtures with isobutane (R600a) (Bobbo et al., 1998a), 1,1,1,2-tetrafluorethane (R134a) (Bobbo et al., 1998a), difluoromethane (R32) (Bobbo et al., 1999), pentafluoroethane (R125) (Bobbo et al., 1999), and dimethyl ether (Bobbo et al., 1998b) have been studied. To complete the study of the behavior at equilibrium of R236fa mixed with the most relevant hydrofluorocarbons, the present work reports on the results of VLE measurements and data reduction on the binary system 1,1,1-trifluoroethane (R143a) + R236fa. The interest in this system is from both the chemical (to improve the comprehension of intermolecular interaction in the series of systems combining a highly fluorinated propane derivative (R236fa) with fluoroderivatives of methane and ethane) and the technological points of view (R143a and R236fa are possible components of mixtures to be proposed as substitutes for R114 in high-temperature heat pumps).

Experimental Section

Chemicals. R236fa was supplied by Du Pont with a declared purity >99%. R143a was donated by Ausimont with a declared purity >99.9%. For both fluids, no impurities were detected by gas chromatography used with a flame ionization detector (FID). The fluids were used with no further purification.

Apparatus and Procedures. The recirculation VLE apparatus (Figure 1) and the procedures used in this study are described only briefly here, since they have already been presented in more detail by Bobbo et al. (1998a). The VLE is reached in a stainless steel cell of about 50 cm^3 capacity equipped with a magnetic pump and two glass windows sealed to the cell body with gold O-rings. The VLE cell, together with a magnetic pump, was immersed in a thermostatic water bath of about 100 L capacity.

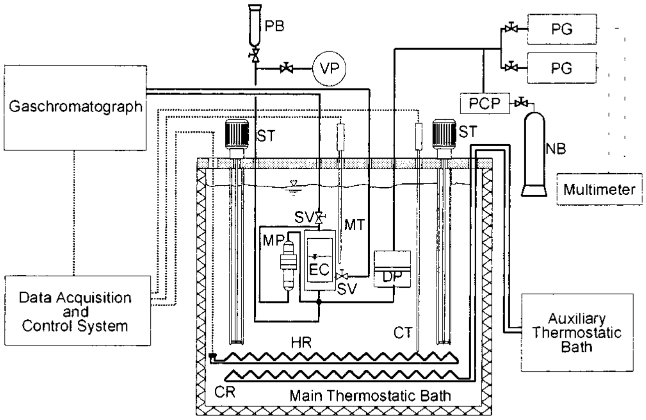

Figure 1. Schematic diagram of the apparatus: cooler (CR); resistance thermometer for temperature control (CT); diaphragm (DP); equilibrium cell (EC); heating resistor (HR); magnetic pump (MP); resistance thermometer for temperature measurement (MT); nitrogen bottle (NB); pure refrigerant bottle (PB); pressure control pack (PCP); pressure gauge (PG); stirrer (ST); sampling valve (SV); vacuum pump (VP).

Temperature was measured with a 100 Ω platinum resistance thermometer (ISOTECH 909/100). The temperature in the bath was stabilized (±1 mK) by means of a PID-controlled system governing a heater immersed in the thermostatic bath. An auxiliary cooler was used to compensate for the heat produced by the PID-controlled system and to keep the temperature below or near ambient temperature.

Pressure was measured by means of a Bourdon type pressure gauge (RUSKA 6000) with a full scale pressure

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Table 1. Gas Chromatography Parameters

	column				detector (FID)	
oven temperature/K	length/m	internal diameter/mm	packing	nitrogen flow rate/cm^3·min^{-1}	hydrogen flow rate/cm^3·min^{-1}	air flow rate/cm^3·min^{-1}
423	2	2.1	Porapak T	30.5	40	400

Table 2. Vapor−Liquid Equilibrium Data for R143a (1) + R236fa (2) Systems

$T_{\exp}$/K	$P_{\exp}$/kPa	$x_{1,\exp}$	$y_{1,\exp}$	P_{calc}/kPa	$y_{1,\text{calc}}$	$10^{-2}\Delta y^a$	δP^b
283.11	160.9	0.0000	0.0000	159.2			1.03
283.11	200.1	0.0752	0.2460	200.1	0.2514	−0.54	0.02
283.11	293.9	0.2399	0.5543	294.6	0.5672	−1.29	−0.25
283.11	348.6	0.3292	0.6642	349.1	0.6716	−0.74	−0.15
283.11	448.0	0.4799	0.7897	446.7	0.7951	−0.54	0.29
283.11	552.3	0.6302	0.8753	551.3	0.8789	−0.36	0.18
283.11	648.1	0.7608	0.9288	647.9	0.9321	−0.33	0.03
283.11	731.4	0.8658	0.9634	729.1	0.9658	−0.24	0.31
283.11	834.8	1.0000	1.0000	836.5			−0.21
298.16	272.5	0.0000	0.0000	272.2			0.10
298.16	383.0	0.1410	0.3618	383.5	0.3657	−0.39	−0.14
298.16	495.9	0.2746	0.5672	496.4	0.5705	−0.33	−0.11
298.16	610.8	0.4009	0.6983	610.6	0.7013	−0.30	0.04
298.16	729.7	0.5231	0.7905	728.5	0.7939	−0.34	0.17
298.16	840.3	0.6312	0.8536	839.2	0.8575	−0.39	0.13
298.16	974.6	0.7563	0.9122	975.1	0.9163	−0.41	−0.05
298.16	1099.6	0.8649	0.9545	1099.8	0.9577	−0.32	−0.02
298.16	1260.7	1.0000	1.0000	1263.5			−0.22
313.21	439.3	0.0000	0.0000	438.6			0.17
313.21	558.9	0.1158	0.2800	561.6	0.2818	−0.18	−0.48
313.21	746.8	0.2774	0.5319	747.1	0.5336	−0.17	−0.04
313.21	944.6	0.4319	0.6900	941.5	0.6927	−0.27	0.33
313.21	1132.5	0.5694	0.7922	1130.3	0.7959	−0.37	0.19
313.21	1388.3	0.7409	0.8890	1388.8	0.8932	−0.42	−0.04
313.21	1567.6	0.8518	0.9395	1570.8	0.9435	−0.40	−0.20
313.21	1629.4	0.8869	0.9548	1630.9	0.9578	−0.30	−0.09
313.21	1832.5	1.0000	1.0000	1834.4			−0.10

[a] $\Delta y = y_{1,\exp} - y_{1,\text{calc}}$. [b] $\delta P = 100[(P_{\exp} - P_{\text{calc}})/P_{\exp}]$.

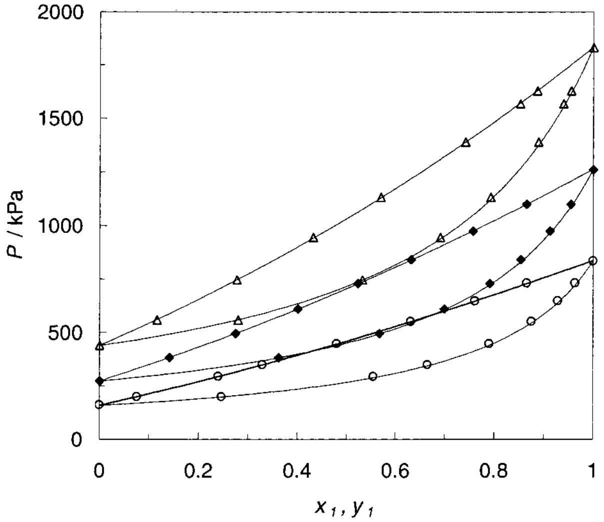

Figure 2. Vapor−liquid equilibrium for R143a (1) + R236fa (2) at three temperatures: 283.11 K (○); 298.16 K (♦); 313.21 K (△). (—) CSD EOS fit.

of 3500 kPa. A differential pressure cell immersed in the thermostatic bath was used to separate the chemicals from the quartz sensors of the pressure gauges. The accuracies in the pressure and temperature measurements are estimated to be ±1 kPa and ±0.02 K, respectively.

The compositions of the vapor and liquid phases were established by gas chromatographic analysis. A gas chromatograph (Hewlett-Packard 6890) was connected on-line to the VLE cell. Gas chromatographic analyses of the phase equilibrium composition for both systems were performed under the conditions shown in Table 1. The response of the detector was carefully calibrated using gravimetrically prepared mixtures. Considering the residuals of the calibration curve, the margin of error, and the reproducibility of gas chromatography and the stability of the composition during the measurements, we estimated the accuracy in composition measurements to be within ±0.002 of the mole fraction for both the liquid and the vapor phases.

Results and Discussion

The *P*, *x*, *y* equilibrium data for the mixture R143a + R236fa at 283.11 K, 298.16 K, and 313.21 K are presented in Table 2. The vapor- and liquid-phase envelopes are shown in Figure 2. Throughout the paper, *x* and *y* indicate the liquid and vapor mole fractions, respectively, while *P* stands for the pressure in kPa.

The experimental vapor pressures of pure compounds measured in this work were compared with data reported in the literature. The vapor pressure was calculated at our experimental temperatures by using either our vapor pressure equations of various authors or the equation proposed by Tillner-Roth et al. (1998), who fitted the data in the literature with a Wagner equation in the form shown by Reid et al. (1988). The results are shown in Table 3. For R-236fa, there is consistency between the present experimental data and data in the literature. Slightly higher deviations were found in the case of R-143a, with a systematic positive deviation of the data in the literature from ours. The best agreement was found with data from Weber et al. (1996), with absolute deviations <2 kPa.

Table 3. Vapor Pressure of Pure Compounds and a Comparison between Experimental Data from the Present Work and Values Calculated from the Literature

		283.11 K			298.16 K			313.21 K		
fluid	ref[a]	P/kPa	$P_{\exp} - P$/kPa	δP^b	P/kPa	$P_{\exp} - P$/kPa	δP^b	P/kPa	$P_{\exp} - P$/kPa	δP^b
R-236fa	(1)	160.9			272.5			439.3		
	(2)	159.3	1.6	0.98	271.8	0.7	0.27	437.3	2.0	−0.46
	(3)	159.5	1.4	0.87	272.5	0.0	0.00	438.6	0.7	−0.16
R-143a	(1)	834.8			1260.7			1832.5		
	(3)	835.7	−0.9	−0.11	1262.6	−1.9	−0.15	1834.8	−2.3	−0.13
	(4)	835.7	−0.9	−0.11	1263.1	−2.4	−0.19	1836.3	−3.8	−0.21
	(5)	835.7	−0.9	−0.11	1262.8	−2.1	−0.16	1835.4	−2.9	−0.16
	(6)	835.3	−0.5	−0.06	1262.1	−1.4	−0.11	1834.5	−2.0	−0.11

[a] References: (1) this work (exp); (2) Di Nicola et al. (1999); (3) McLinden et al. (1998); (4) Giuliani et al. (1995); (5) Tillner-Roth et al. (1998); (6) Weber et al. (1996). [b] $\delta P = 100[(P_{\exp} - P)/P_{\exp}]$.

Table 4. Parameters of the CSD EOS (Eq 1) Used for Data Correlation

	R143a	R236fa
a_0/kPa·L^2·mol^{-2}	2763.9092	5812.833
a_1/K^{-1}	$-2.5090559 \times 10^{-3}$	-2.860835×10^{-3}
a_2/K^{-2}	$-1.7971077 \times 10^{-6}$	-1.409685×10^{-6}
b_0/L·mol^{-1}	1.3315259×10^{-1}	1.976126×10^{-1}
b_1/L·mol^{-1}·K^{-1}	$-1.5895379 \times 10^{-4}$	-1.906306×10^{-4}
b_2/L·mol^{-1}·K^{-2}	$-0.58331054 \times 10^{-7}$	-1.462412×10^{-7}

Table 5. Results of VLE Data Reduction for the System R143a (1) + R236fa (2) Using the CSD EOS at *T*/K = 283.11, 298.16, and 313.21 K

T/K	283.11	298.16	313.21
δP^{a}	0.14	−0.01	−0.03
abs(δP)	0.27	0.11	0.18
Δy^{b}	−0.0058	−0.0035	−0.0030
abs(Δy)	0.0058	0.0034	0.0030
k_{12}	−0.0159	−0.0157	−0.0171

[a] $\delta P = \frac{100}{N_{\mathrm{P}}}\sum_{i=1}^{N_{\mathrm{P}}}[(P_{i,\mathrm{exp}} - P_{i,\mathrm{calc}})/P_{i,\mathrm{exp}}]$.

[b] $\Delta y = \frac{1}{N_{\mathrm{P}}}\sum_{i=2}^{N_{\mathrm{P}}-1}(y_{i,1,\mathrm{exp}}y_{i,1,\mathrm{calc}})$.

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:

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

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

where V is the molar volume in L·mol^{-1} and R = 8.31445 J·mol^{-1}·K^{-1} is the universal gas constant. Consequently, the a and b parameters in eq 1 are expressed in kPa·L^2·mol^{-2} and L·mol^{-1}, respectively. The a_i and b_i coefficients for the compounds studied were taken from Huber et al. (1996) and are given in Table 4.

The following combining rules were used for the CSD EOS:

$$a = \sum\sum \xi_i \xi_j a_{ij} \tag{5}$$

$$b = \sum \xi_i b_i \tag{6}$$

where x_i is the mole fraction of the i-th component and

$$a_{ij} = (a_{ii}a_{jj})^{0.5}(1 - k_{ij}) \tag{7}$$

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

The VLE data were reduced by using the CSD EOS and minimizing the objective function

$$\mathrm{obf} = \sum_{i=1}^{N_{\mathrm{p}}}(\Delta P/P_{\mathrm{exp}})^2 \tag{8}$$

where N_{p} is the number of experimental data points, $\Delta P = P_{\mathrm{exp}} - P_{\mathrm{calc}}$, P_{exp} is the experimental saturation pressure, and P_{calc} is the saturation pressure calculated with the CSD EOS. The results of data reduction are summarized in Table 5. Scatter diagrams of pressure and vapor-phase composition deviations are presented in Figures 3 and 4. The outcome of data reduction shows a deviation in saturated pressure and vapor-phase composition slightly higher than the experimental uncertainties for the isotherms at 298.16 K and 313.21 K, while higher deviations are calculated for the isotherm at 283.16 K. However, the S-shaped diagrams of deviations as a function of liquid composition suggest that these deviations are mostly due to the model rather than to inaccuracies in the experimental data.

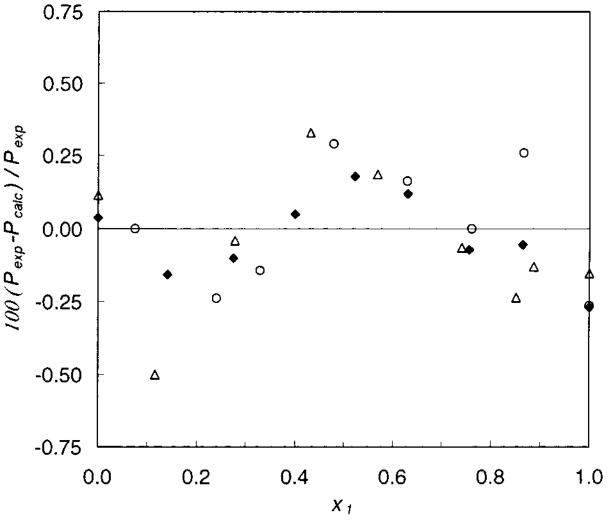

Figure 3. Scatter diagram of saturated pressure deviations for R143a (1) + R236fa (2) at three temperatures: 283.11 K (○); 298.16 K (◆); 313.21 K (△).

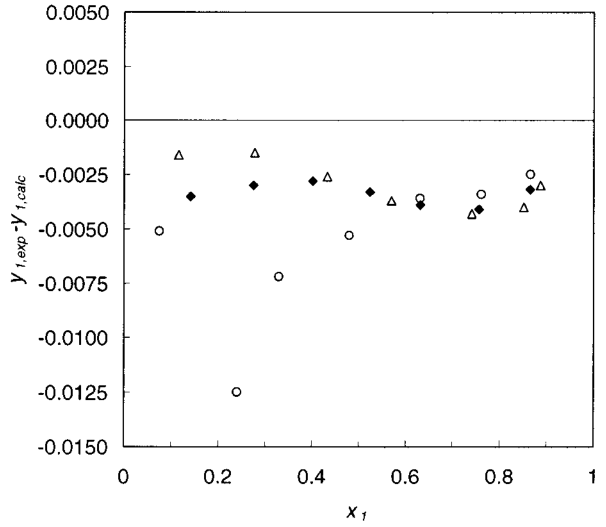

Figure 4. Scatter diagram of deviations in the vapor-phase composition for R143a (1) + R236fa (2) at three temperatures: 283.11 K (○); 298.168 K (◆); 313.21 K (△).

Conclusions

The system shows a small deviation from Raoult's law, confirming the behavior at equilibrium of binary mixtures formed by R236fa with HFCs. The experimental data are quite well represented by the CSD EOS.

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