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Vapor−Liquid Equilibria for Difluoromethane (R32) + and Pentafluoroethane (R125) + 1,1,1,3,3,3-Hexafluoropropane (R236fa) at 303.2 and 323.3 K

Sergio Bobbo* and Roberto Camporese

Institute of Refrigeration, National Research Council, corso Stati Uniti 4, 35127 Padova, Italy

Roman Stryjek

Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

Isothermal vapor−liquid equilibria (VLE) for the binary systems difluoromethane (R32) + 1,1,1,3,3,3-hexafluoropropane (R236fa) and pentafluoroethane (R125) + 1,1,1,3,3,3-hexafluoropropane (R236fa) were measured at 303.2 and 323.3 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. Both systems show a slight deviation from Raoult's law. The data were reduced by the Carnahan−Starling−De Santis EOS. The deviations observed in vapor composition, averaging below 0.003 in mole fraction, confirm the consistency of the experimental findings and the model used for their reduction. Calculated excess Gibbs energy functions reveal values to be within ±40 J mol^{-1} at $T = 303$ K. The margins of error in pressure, temperature, and composition of vapor and liquid-phase measurements were estimated to be less than ±0.15%, ±0.005 K, and ±0.0015 of mole fraction, respectively.

Introduction

In our previous studies on the VLE of binary systems with 1,1,1,3,3,3-hexafluoropropane (R236fa), a new azeotrope with 2-methylpropane (isobutane) (Bobbo et al., 1997) and a strong hydrogen bonding with dimethyl ether (Bobbo et al., 1998) were found. The present work reports on the results of VLE measurements and data reduction on the binary systems difluoromethane (R32) + (R236fa) and pentafluoroethane (R125) + (R236fa). These systems are of interest in pure chemistry terms, since they provide information on the intermolecular interaction in the series of systems combining a highly fluorinated propane derivative (R236fa) with fluoroderivatives of methane and ethane. They are also of considerable technological interest for high-temperature heat pump applications; a prototype heat pump is currently being tested in which the heat output is controlled by varying the concentration of a refrigerant mixture containing the components considered.

Experimental Section

Materials. R236fa, with no impurities detected by gas chromatography using both the flame ionization detector (FID) and the thermal conductivity detector (TCD), was supplied by Du Pont.

R125, with 0.2% total impurities detected by the FID and about 0.4% by the TCD (assessed as a percentage of area), and R32, with no impurities detected by either the FID or the TCD, were supplied by ICI. The R125 was used with no further purification.

The difference in the proportion of impurities detected by the FID and TCD is probably due to the presence of inorganic compounds in R125, which are not detected by the FID.

Apparatus. The recirculation VLE apparatus and the procedures used in this study are described only briefly here, since they have already been presented in more detail elsewhere (Bobbo et al., 1997; Stryjek et al., 1998). 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 thermostatic water bath of about 100 L capacity. The VLE cell, magnetic pump, and thermostat were built by the Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland.

Temperature was measured with a 100 Ω platinum resistance thermometer connected to a multimeter (HP3458) and was recorded continuously using 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 thermostatic bath. An auxiliary cooler (LAUDA RK8CP) 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 pressure gauge (RUSKA 6000) with a range up to 3500 kPa. A differential pressure cell (RUSKA 2413) immersed in the thermostatic bath was used to separate the chemicals 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

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* Corresponding author. E-mail: sergio@itef.pd.cnr.it. Fax: 0039.49.8295728.

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Table 1. Vapor−Liquid Equilibrium Data for R32 (1) + R236fa (2) System, $\Delta y = y_{1,\mathrm{exp}} - y_{1,\mathrm{EOS}}$, and $\delta P = 100(\Delta P/P_{\mathrm{exp}})$

T_{exp}/K	P_{exp}/kPa	$x_{1,\mathrm{exp}}$	$y_{1,\mathrm{exp}}$	P_{EOS}/kPa	$y_{1,\mathrm{EOS}}$	$\Delta y \times 10^2$	δP
303.20	322.2	0	0	321.20	0	0	0.31
303.20	553.1	0.1710	0.4769	554.30	0.4815	-0.46	-0.22
303.20	694.9	0.2710	0.6177	697.63	0.6217	-0.40	-0.39
303.20	897.3	0.4054	0.7443	899.68	0.7462	-0.19	-0.27
303.19	1098.0	0.5320	0.8250	1100.90	0.8273	-0.23	-0.26
303.19	1294.0	0.6494	0.8817	1297.44	0.8842	-0.25	-0.27
303.19	1496.9	0.7658	0.9273	1501.39	0.9294	-0.21	-0.30
303.19	1695.2	0.8769	0.9635	1703.16	0.9654	-0.19	-0.47
303.19	1926.6	1	1	1933.37	1	0	−0.35
323.27	584.2	0	0	586.35	0	0	−0.37
323.26	890.8	0.1516	0.3930	889.66	0.3903	0.27	0.13
323.26	1251.4	0.3173	0.6161	1248.03	0.6159	0.02	0.27
323.26	1250.8	0.3154	0.6141	1243.74	0.6139	0.02	0.56
323.26	1601.5	0.4634	0.7408	1592.50	0.7422	-0.14	0.56
323.26	1818.5	0.5490	0.7964	1808.82	0.7991	-0.27	0.53
323.26	2306.1	0.7281	0.8905	2300.71	0.8935	-0.30	0.23
323.26	2524.4	0.8061	0.9240	2532.30	0.9274	-0.34	-0.31
323.26	2765.8	0.8863	0.9556	2780.87	0.9592	-0.36	-0.54
323.26	3154.1	1	1	3148.86	1	0	0.17

Table 2. Vapor−Liquid Equilibrium Data for R125 (1) + R236fa (2) System, $\Delta y = y_{1,\mathrm{exp}} - y_{1,\mathrm{EOS}}$, and $\delta P = 100(\Delta P/P_{\mathrm{exp}})$

T_{exp}/K	P_{exp}/kPa	$x_{1,\mathrm{exp}}$	$y_{1,\mathrm{exp}}$	P_{EOS}/kPa	$y_{1,\mathrm{EOS}}$	$\Delta y \times 10^2$	δP
303.19	322.3	0	0	321.20	0	0	0.34
303.19	449.9	0.1183	0.3392	450.27	0.3417	-0.25	-0.08
303.19	604.0	0.2564	0.5604	604.64	0.5631	-0.27	-0.11
303.19	743.0	0.3767	0.6861	743.16	0.6863	-0.02	-0.02
303.19	894.7	0.5040	0.7784	894.85	0.7801	-0.17	-0.02
303.20	896.9	0.5054	0.7791	896.55	0.7810	-0.19	0.04
303.20	1049.3	0.6277	0.8487	1048.83	0.8500	-0.13	0.04
303.19	1205.8	0.7474	0.9042	1205.13	0.9052	-0.10	0.06
303.19	1389.9	0.8797	0.9565	1388.78	0.9573	-0.08	0.08
303.19	1568.5	1	1	1569.91	1	0	−0.09
323.26	585.7	0	0	586.35	0	0	−0.11
323.26	757.1	0.1065	0.2691	757.10	0.2712	-0.21	0.00
323.27	959.9	0.2298	0.4696	960.86	0.4732	-0.36	-0.10
323.27	1221.3	0.3807	0.6348	1221.06	0.6380	-0.32	0.02
323.27	1488.3	0.5272	0.7487	1488.19	0.7520	-0.33	0.01
323.26	1675.8	0.6239	0.8099	1674.51	0.8126	-0.27	0.08
323.26	1984.0	0.7696	0.8891	1977.18	0.8913	-0.17	0.34
323.26	2539.3	1	1	2525.72	1	0	0.53

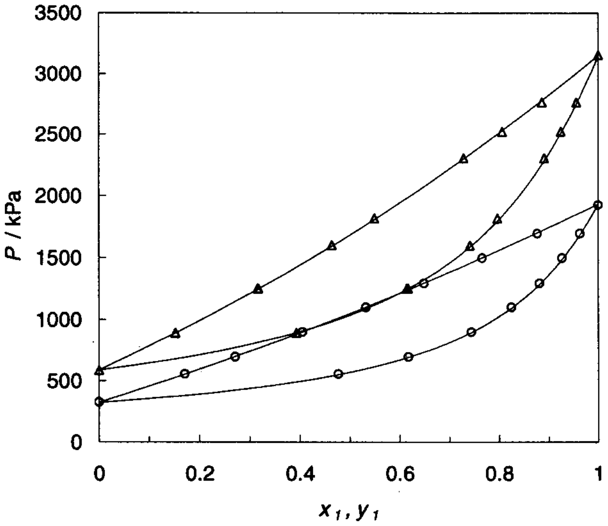

Figure 1. Vapor−liquid equilibrium for R32 (1) + R236fa (2) at T = 303.2 K (○) and 323.3 K (△); (−) CSD EOS fit.

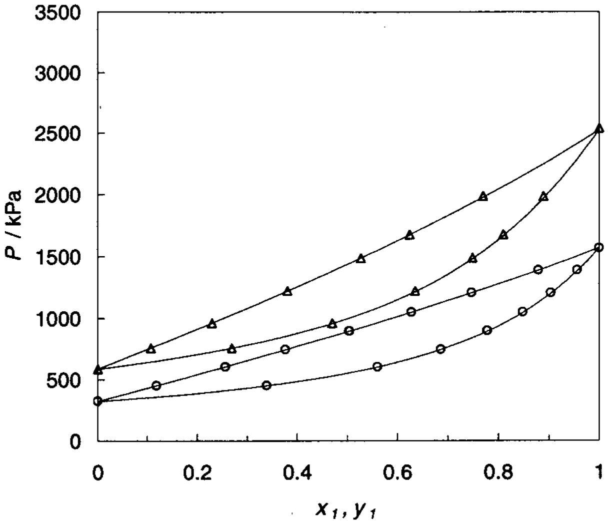

Figure 2. Vapor−liquid equilibrium for R125 (1) + R236fa (2) at T = 303.2 K (○) and 323.3 K (△); (−) CSD EOS fit.

±0.15% 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. Gas chromatographic analyses of the phase equilibrium composition for both systems were performed under the following conditions: column, 2 m × 2.1 mm ID, packed with Porapak T 80/100 mesh; flow rate, nitrogen at 30.5 $\mathrm{cm}^3\ \mathrm{min}^{-1}$; oven temperature, 423 K; an FID was used. The response of the detector was carefully calibrated using gravimetrically prepared mixtures. The calibrating 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 to be ±0.0001 in units of 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 for the mole fraction of both the liquid and the vapor phases.

Results and Discussion

The P, x, y equilibrium data for the mixtures R32 + R236fa and R125 + R236fa, measured at temperatures 303.3 K and 323.3 K, are presented in Tables 1 and 2, 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 stands for the pressure in kPa.

For data reduction we considered the Carnahan−Starling−De Santis (CSD) EOS in the form proposed by

Table 3. Parameters of the CSD EOS (Eq 1) Taken from Huber et al. (1996) Used for Data Correlation

	compound		
parameter	R32	R125	R236fa
a_0/kPa L^2 mol^{-2}	1662.2699	3427.9219	5812.833
a_1/K^{-1}	$-2.1975227 \times 10^{-3}$	$-3.1746132 \times 10^{-3}$	-2.860835×10^{-3}
a_2/K^{-2}	-1.889027×10^{-6}	$-1.7572861 \times 10^{-6}$	-1.409685×10^{-6}
b_0/L mol^{-1}	0.077987924	0.14938043	0.1976126
b_1/L mol^{-1} K^{-1}	$-0.75238102 \times 10^{-4}$	$-1.8085107 \times 10^{-4}$	-1.906306×10^{-4}
b_2/L mol^{-1} K^{-2}	$-0.5301071 \times 10^{-7}$	$-1.1881331 \times 10^{-7}$	-1.462412×10^{-7}

Table 4. Results of VLE Data Reduction as a Combined Set Using the CSD EOS, $\delta P = 100(\Delta P/P_{\mathrm{exp}})$, $\Delta y = y_{1,\mathrm{exp}} - y_{1,\mathrm{EOS}}$

	R32 + R236fa	R125 + R236fa
δP	−0.05	0.15
Abs(δP)	0.34	0.20
Δy	−0.0020	−0.0014
Abs(Δy)	0.0024	0.0025
k_{12}	−0.0325	−0.0008

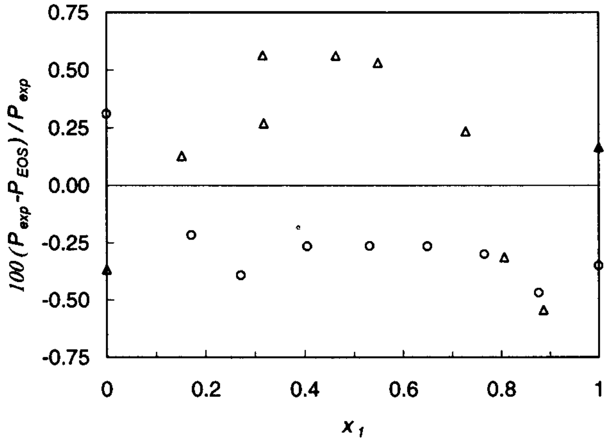

Figure 3. Scatter diagram of saturated pressure deviations for R32 (1) + R236fa (2) at T = 303.2 K (○) and 323.3 K (△).

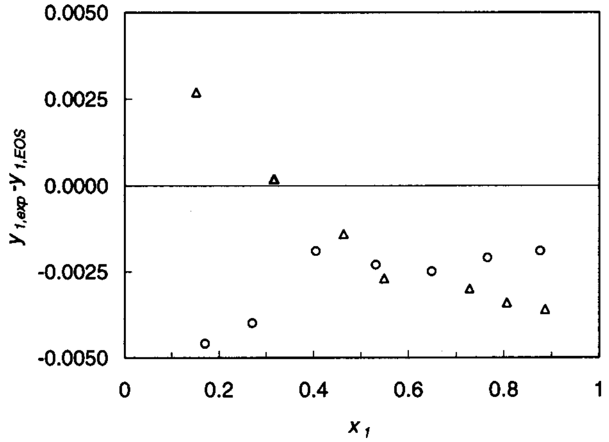

Figure 4. Scatter diagram of deviations in vapor phase composition for R32 (1) + R236fa (2) at T = 303.2 K (○) and 323.3 K (△).

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:

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

$$b(T) = b_0 + b_1 T + b_2 T_2 \tag{4}$$

V is the molar volume in L mol^{-1} and R = 8.314 45 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 3.

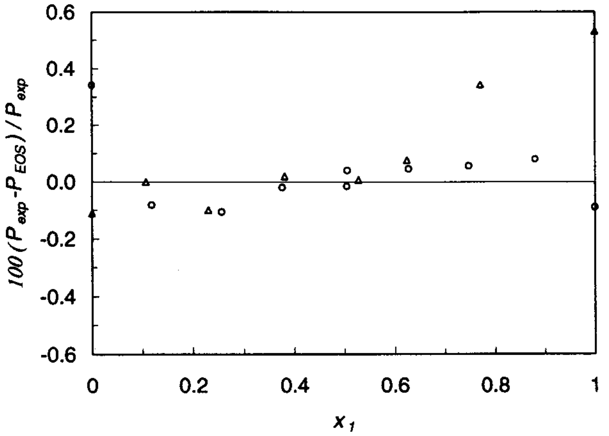

Figure 5. Scatter diagram of saturated pressure deviations for R125 (1) + R236fa (2) at T = 303.2 K (○) and 323.3 K (△).

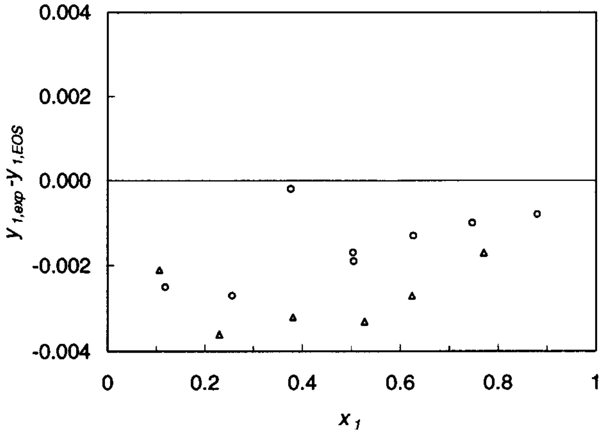

Figure 6. Scatter diagram of deviations in vapor phase composition for R125 (1) + R236fa (2) at T = 303.2 K (○) and 323.3 K (△).

The vapor pressures of the pure compounds established in this study were compared with data reported in the literature (McLinden et al., 1998), and a valid consistency was found.

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 ξ_i is the mole fraction of the ith 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 as a set combined from two isotherms for each system and simply assuming that k_{ij} is independent of temperature, using the CSD EOS and minimizing the objective function

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

where N_{p} is the number of experimental points and $\Delta P = P_{\mathrm{exp}} - P_{\mathrm{EOS}}$ and $\Delta y = y_{1,\mathrm{exp}} - y_{1,\mathrm{EOS}}$ are defined throughout the paper. The outcome of data reduction shows a deviation

Table 5. Results of VLE Data Reduction Using the CSD EOS at T = 303.2 K and 323.3 K, $\delta P = 100(\Delta P/P_{exp})$, $\Delta y = y_{1,exp} - y_{1,EOS}$

	R32 + R236fa		R125 + R236fa	
T/K	302.3	323.3	302.3	323.3
δP	−0.05	−0.10	0.04	0.008
Abs(δP)	0.16	0.26	0.09	0.17
Δy	−0.0024	−0.0016	−0.0015	−0.0028
Abs(Δy)	0.0024	0.0020	0.0015	0.0028
k_{12}	−0.0338	−0.0311	−0.0009	−0.0007

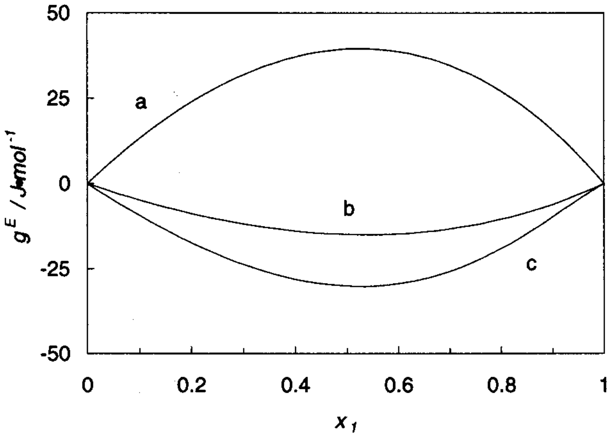

Figure 7. Excess Gibbs energy at T = 303 K for (a) R125 (1) + R236fa (2), (b) R134a (1) + R236fa (2), and (c) R32 (1) + R236fa (2).

in both saturated pressure and vapor-phase composition, which is small enough for the data and the adopted model to be considered consistent. The results of data reduction are summarized in Table 4. Scatter diagrams of pressure and vapor-phase composition deviations are presented in Figures 3−6. A small improvement in the saturated pressure representation was obtained by reducing the data for each isotherm separately; by use of the same procedure, there was no noticeable improvement in the vapor-phase representation, and the respective results are shown in Table 5.

The excess Gibbs energy g^E in J mol^{-1} was calculated using the fundamental relationship

$$g^E = RT\,(\ln \varphi - \sum x_i \ln \varphi_i) \qquad (9)$$

where φ and φ_i were calculated for the liquid phase at the same temperature and pressure, using k_{12} values reported in Table 4 for the studied binaries. The corresponding results for the R134a (1,1,1,2-tetrafluoroethane) + R236fa system (Bobbo et al., 1997) were included for comparison. The courses of the g^E are shown in Figure 7. All systems show very small g^E values at 303 K, being within ±40 J mol^{-1} at most.

Conclusions

Both systems show a minute deviation from Raoult's law. The experimental data are well represented by the CSD EOS, assuming that k_{ij} is independent of temperature.

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