

Vapor–Liquid Equilibria for the Binary System Difluoromethane (HFC-32) + Propane (HC-290) at Seven Temperatures [(268.15, 278.15, 283.15, 288.15, 298.15, 308.15, and 318.15) K]

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Isothermal vapor–liquid equilibria for the binary mixtures of difluoromethane (HFC-32) + propane (HC-290) were measured at (268.15, 278.15, 283.15, 288.15, 298.15, 308.15, and 318.15) K. The experiments were carried out using a circulation-type equilibrium apparatus with the measurement of temperature, pressure, and the compositions of the liquid and vapor phases. The experimental data were correlated with the Peng–Robinson equation of state using the Wong and Sandler mixing rules and the Carnahan–Starling–Desantis equation of state. Calculated results with these equations showed good agreement with the experimental data, but the Peng–Robinson equation of state gave more accurate calculations for the binary systems. It was found that this system has a very strong positive azeotrope for all the temperature range studied here.

Introduction

Chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents, propellants, or cleaning agents due to their outstanding properties. However, production and use of CFCs are currently being phased out under an international agreement, the Montreal Protocol, because of global environment concerns. Hydrofluorocarbons (HFCs) are promising alternative refrigerants to replace CFCs, and hydrocarbons (HCs) such as propane (HC-290) are widely used in Europe. The ozone depletion potentials (ODPs) of HFCs and HCs are zero, since they do not contain chlorine. Their global warming potentials (GWPs) are less than those of CFCs because they contain more hydrogen atoms and thus have a shorter atmospheric lifetime.¹ HFCs are stable but very expensive; on the other hand, hydrocarbons are flammable but very cheap. Mixtures of the two compounds may have good potential as alternative refrigerants. There are two other reasons for studying refrigerant mixtures containing propane. One of the difficulties with the chlorine-free alternative refrigerants is their immiscibility with the oils used in refrigeration cycles. The addition of propane to the mixture to enhance oil solubility is under investigation. Another reason for studying propane is the complex phase behavior exhibited by propane mixtures which allows the models to be rigorously tested.²

Vapor–liquid equilibrium (VLE) data are required as one of the most important types of information in evaluating the performance of refrigeration cycles and determining their optimal compositions. Azeotropic mixtures have merit, since their behaviors are similar to those of pure compounds. However, very few experimental data^{2,3} have been reported previously in the literature. In this study, we measured VLE data for the binary system difluoromethane (HFC-32) + propane (HC-290) at seven temperatures [(268.15, 278.15, 283.15, 288.15, 298.15, 308.15, and 318.15) K]. Experimental data were correlated with the Peng–Robinson equation of state⁴ using the Wong and

Sandler mixing rules⁵ and the Carnahan–Starling–Desantis (CSD) equation of state.⁶

Experimental Section

Chemicals. The high-grade chemicals HFC-32 (provided by Dupont, USA, with a declared purity of >99.9 mass %) and propane (provided by MG Industry, U.K., with a declared purity of >99.5 mass %) were used for the measurements of VLE. The purities of the chemicals were guaranteed from the manufacturers, and they were used without any further purification.

Experimental Apparatus. Vapor–liquid equilibria were measured in an apparatus in which both vapor and liquid phases were continuously recirculated. The experimental apparatus used in this work is the same as that used in previous work^{7–13} and is briefly summarized here. The equilibrium cell is a 316 stainless steel vessel with an inner volume of about 85 cm³. In its middle part, a pair of Pyrex glass windows of 20 mm thickness was installed, so that the liquid level, mixing and circulating behaviors, and critical phenomena could be observed during operation. A stirrer, rotated at variable speeds by an external magnet, was used to accelerate the attainment of the equilibrium state and to reduce concentration gradients in both phases.

The temperature of the equilibrium cell in the water bath was maintained by a circulator from Jeio Tech, Korea. The temperature in the cell was measured with a platinum resistance sensor and a digital temperature indicator model F250MkII precision thermometer from Automatic Systems Laboratories Ltd., United Kingdom. They were calibrated by the NAMAS accredited calibration laboratory. The total uncertainty in temperature measurements is estimated to be within ± 0.01 K, including sensor uncertainty, ± 0.01 K, temperature resolution, ± 0.001 K, and measurement uncertainty, ± 0.001 K. The pressure was measured with a pressure transducer, model XPM60, and a digital pressure calibrator, model PC 106, from Beamax, Finland. Pressure calibrations are traceable to National Standards (Center for Metrology and Accreditation Cert. no. M-95P077,

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Table 1. Characteristic Properties of the Chemicals

component	chemical formula	MW	T_c/K	P_c/MPa	ω	source
HFC-32	CH ₂ F ₂	52.02	351.26	5.782	0.2768	REFPROP 6.01 ¹⁸
propane	C ₃ H ₈	44.10	369.85	4.248	0.1524	REFPROP 6.01 ¹⁸

Table 2. Comparison of the Measured Pure Component Vapor Pressures with the Values from the Database REFPROP 6.01¹⁸

component	T/K	P/MPa		$\Delta P^a/MPa$	$(\Delta P/P)^b/\%$
		exp	REFPROP ¹⁸		
HFC-32	268.15	0.6954	0.6901	0.0053	0.7622
	278.15	0.9520	0.9509	0.0011	0.1155
	283.15	1.1022	1.1060	0.0038	0.3448
	288.15	1.2812	1.2800	0.0012	0.0937
	298.15	1.6856	1.6890	-0.0034	0.2017
	308.15	2.1852	2.1890	-0.0038	0.1739
	318.15	2.7948	2.7940	0.0008	0.0286
propane	268.15	0.4079	0.4059	0.0020	0.4903
	278.15	0.5494	0.5510	-0.0016	0.2912
	283.15	0.6364	0.6365	-0.0001	0.0157
	288.15	0.7350	0.7314	0.0036	0.4898
	298.15	0.9548	0.9519	0.0029	0.3037
	308.15	1.2130	1.2180	-0.0050	0.4122
	318.15	1.5308	1.5340	-0.0032	0.2090

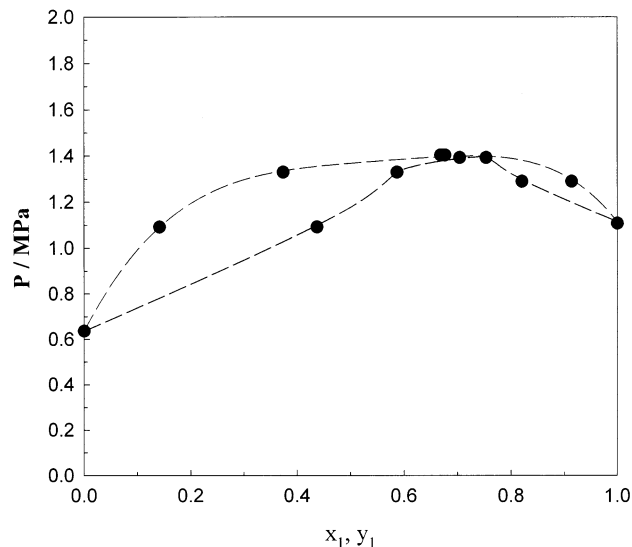
$$^a \Delta P = P_{\text{exp}} - P_{\text{cal}}, \quad ^b \Delta P/P = |(P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}| \times 100.$$

14.11.1995, M-M 730, 16.11.1995 and M-95P078, 16.11.1995), and the calibrator uncertainty was ± 0.0005 MPa, the sensor uncertainty was ± 0.001 MPa, and the measurement uncertainty was ± 0.001 MPa. Therefore, the total uncertainty of the pressure is estimated to be within ± 0.001 MPa.

The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump from the Milton Roy Company. After equilibrium was reached, the vapor and liquid samples were withdrawn from the recycling loop and injected on-line into a Gow-Mac model 550P gas chromatograph. The gas chromatograph was equipped with a thermal conductivity detector (TCD) and a Porapak Q column from Alltech Company.

Experimental Procedures. Experiments for a binary system were performed by the following procedure. The system was first evacuated to remove all inert gases. A certain amount of propane was introduced into the cell, and then the temperature of the entire system was maintained constant by controlling the temperature of the water bath. After the desired temperature was attained, the pressure of the pure component was measured. A proper amount of HFC-32 was supplied to the cell from a charging cylinder. The mixture in the cell was stirred continuously with the magnetic stirrer for over 1 h. Both vapor and liquid phases were circulated by the dual-head high-pressure pump until an equilibrium state was established. It was believed that 1 h or more is sufficient to obtain thermal equilibrium between the cell fluid and the thermostatic bath. After equilibration, the pressure in the equilibrium cell was measured and then vapor and liquid samples were withdrawn from the recycling lines by the vapor and liquid sampling valves, respectively. The compositions of the samples were measured by immediately injecting them into the gas chromatograph, which was connected on-line to vapor and liquid sampling valves. The gas chromatograph was calibrated with pure components of known purity and with mixtures of known composition that were prepared gravimetrically. At least five analyses were performed for each phase, and the average value was considered as corresponding to the equilibrium.

Considering the margin of error and the reproducibility of GC, we generally estimated an overall accuracy in the

**Figure 1.** P - x - y Diagram for the HFC-32 (1) + propane (2) system at 283.15 K: ●, this work; ---, ref. 3.

measurements of the composition of ± 0.002 in the mole fraction for both the liquid and the vapor phases.

Correlation

Isothermal vapor-liquid equilibria were measured for the binary systems of HFC-32 + propane at the temperature range from 268.15 to 318.15 K. The VLE data were correlated with the Peng-Robinson equation of state⁴ and the CSD equation of state.⁶ The Peng-Robinson equation of state is expressed as follows:

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

with

$$a(T) = (0.457235R^2T_c^2/P_c)\alpha(T) \quad (2)$$

$$b = 0.077796RT_c/P_c \quad (3)$$

$$\alpha(T) = [1 + k(1 - T_r^{0.5})]^2 \quad (4)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

where the parameter a is a function of temperature, b is constant, κ is a constant characteristic of each substance, ω is the acentric factor, P/MPa is pressure, P_c/MPa is the critical pressure, T/K is the absolute temperature, T_c/K is the critical temperature, T_r is the reduced temperature, and $v/\text{cm}^3 \cdot \text{mol}^{-1}$ is the molar volume. The Wong-Sandler mixing rules⁵ were used to obtain equation of state parameters for a mixture from those of the pure components. These mixing rules for a cubic equation of state can be written as

$$b_m = \frac{\sum_i \sum_j x_i x_j (b - a/RT)_{ij}}{(1 - A_\infty^E/CRT - \sum_i x_i a_i/RTb_i)} \quad (6)$$

with

$$(b - a/RT)_{ij} = \frac{1}{2}[(b - a/RT)_i + (b - a/RT)_j](1 - k_{ij}) \quad (7)$$

Table 3. Vapor–Liquid Equilibrium Measurements for the HFC-32 (1) + Propane (2) System

experimental data			Peng–Robinson EoS				CSD EoS			
$P_{\text{exp}}/\text{MPa}$	$x_{1,\text{exp}}$	$y_{1,\text{exp}}$	$P_{\text{cal}}/\text{MPa}$	$y_{1,\text{cal}}$	$\Delta P^a/\text{MPa}$	Δy_1^b	$P_{\text{cal}}/\text{MPa}$	$y_{1,\text{cal}}$	$\Delta P^a/\text{MPa}$	Δy_1^b
$TK = 268.15$										
0.408	0.000	0.000	0.405	0.000	0.003	0.000	0.406	0.000	0.002	0.000
0.747	0.143	0.498	0.747	0.474	0.000	0.024	0.682	0.442	0.065	0.056
0.892	0.422	0.634	0.891	0.600	0.001	0.034	0.901	0.636	-0.009	-0.002
0.907	0.590	0.660	0.908	0.634	-0.001	0.026	0.929	0.630	-0.001	0.030
0.902	0.737	0.689	0.905	0.671	-0.003	0.018	0.935	0.684	-0.033	0.005
0.867	0.867	0.747	0.867	0.741	0.000	0.006	0.922	0.713	0.055	0.034
0.695	1.000	1.000	0.693	1.000	0.002	0.000	0.691	1.000	0.004	0.000
$TK = 278.15$										
0.549	0.000	0.000	0.550	0.000	-0.001	0.000	0.552	0.000	0.003	0.000
0.946	0.130	0.438	0.946	0.428	0.000	0.010	0.872	0.397	-0.010	0.041
1.148	0.341	0.584	1.149	0.563	-0.001	0.021	1.147	0.591	0.000	-0.007
1.214	0.589	0.657	1.216	0.639	-0.002	0.018	1.245	0.670	-0.042	-0.013
1.223	0.726	0.703	1.216	0.683	0.007	0.020	1.255	0.693	-0.019	0.010
1.139	0.898	0.788	1.142	0.792	-0.003	-0.004	1.208	0.759	-0.011	0.029
0.952	1.000	1.000	0.957	1.000	-0.005	0.000	0.953	1.000	0.125	0.000
$TK = 283.15$										
0.636	0.000	0.000	0.636	0.000	0.010	0.000	0.638	0.000	0.003	0.000
1.092	0.142	0.437	1.092	0.428	0.000	0.009	1.014	0.401	-0.010	0.036
1.329	0.374	0.587	1.330	0.572	-0.001	0.015	1.328	0.598	0.000	-0.011
1.403	0.668	0.677	1.400	0.666	0.003	0.011	1.433	0.687	-0.042	0.010
1.392	0.753	0.704	1.392	0.700	0.000	0.004	1.434	0.706	-0.019	-0.002
1.289	0.914	0.821	1.291	0.823	-0.002	-0.002	1.359	0.790	-0.011	0.031
1.102	1.000	1.000	1.114	1.000	-0.012	0.000	1.109	1.000	0.125	0.000
$TK = 288.15$										
0.735	0.000	0.000	0.731	0.000	0.004	0.000	0.733	0.000	0.001	0.000
1.228	0.135	0.420	1.228	0.406	0.000	0.014	1.140	0.382	0.088	0.038
1.502	0.356	0.576	1.501	0.550	0.001	0.026	1.499	0.582	0.003	-0.006
1.601	0.664	0.678	1.606	0.667	-0.005	0.011	1.645	0.687	-0.044	-0.009
1.603	0.724	0.698	1.602	0.693	0.001	0.005	1.648	0.702	-0.045	-0.004
1.506	0.898	0.811	1.505	0.812	0.001	-0.001	1.581	0.790	-0.075	-0.021
1.281	1.000	1.000	1.290	1.000	-0.009	0.000	1.283	1.000	-0.002	0.000
$TK = 298.15$										
0.955	0.000	0.000	0.952	0.000	0.003	0.000	0.955	0.000	0.000	0.000
1.632	0.168	0.436	1.632	0.422	0.000	0.014	1.546	0.406	0.086	-0.030
1.961	0.380	0.580	1.960	0.559	0.001	0.021	1.950	0.578	0.001	0.002
2.093	0.618	0.667	2.088	0.654	0.005	0.013	2.121	0.674	-0.028	-0.007
2.075	0.749	0.738	2.084	0.711	-0.009	0.027	2.137	0.717	-0.062	0.021
1.973	0.895	0.820	1.969	0.820	0.004	0.000	2.050	0.796	-0.077	0.024
1.686	1.000	1.000	1.705	1.000	-0.019	0.000	1.693	1.000	-0.007	0.000
$TK = 308.15$										
1.213	0.000	0.000	1.220	0.000	-0.007	0.000	1.221	0.000	-0.008	0.000
1.961	0.158	0.397	1.961	0.369	0.000	0.028	1.874	0.364	0.087	0.033
2.339	0.327	0.538	2.336	0.498	0.003	0.040	2.321	0.525	0.018	0.013
2.631	0.660	0.691	2.637	0.676	-0.006	0.015	2.682	0.690	-0.051	0.001
2.629	0.732	0.724	2.637	0.717	-0.008	0.007	2.693	0.720	-0.064	0.004
2.471	0.920	0.867	2.457	0.867	0.014	0.000	2.533	0.843	-0.062	0.024
2.185	1.000	1.000	2.212	1.000	-0.027	0.000	2.194	1.000	-0.027	0.000
$TK = 318.15$										
1.531	0.000	0.000	1.539	0.000	-0.008	0.000	1.538	0.000	-0.007	0.000
2.387	0.158	0.373	2.388	0.356	-0.001	0.017	2.291	0.338	0.096	0.035
2.929	0.344	0.530	2.931	0.517	-0.002	0.013	2.877	0.512	0.052	0.018
3.265	0.627	0.677	3.258	0.662	0.007	0.015	3.313	0.673	-0.048	0.004
3.271	0.740	0.739	3.269	0.724	0.002	0.015	3.353	0.731	-0.082	0.008
3.107	0.895	0.858	3.116	0.851	-0.009	0.007	3.222	0.835	-0.115	0.023
2.795	1.000	1.000	2.824	1.000	-0.029	0.000	2.797	1.000	-0.002	0.000

$$^a \Delta P = P_{\text{exp}} - P_{\text{cal}}, \quad ^b \Delta y_1 = y_{\text{exp}} - y_{\text{cal}}$$

and

NRTL model¹⁵ given by

$$\frac{a_m}{b_m} = \sum_i x_i \frac{a_i}{b_i} + \frac{A_\infty^E}{C} \quad (8)$$

$$\frac{A_\infty^E}{RT} = \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_k x_k G_{ki}} \quad (9)$$

and where C is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the Peng–Robinson equation used in this work. Also, A_∞^E is an excess Helmholtz free energy model at infinite pressure which can be equated to a low-pressure excess Gibbs free energy model;¹⁴ in this study we use the

with

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad \text{and} \quad \tau_{ij} = A_{ij}/(RT) \quad (10)$$

where G_{ij} is the local composition factor for the NRTL

model, τ_{ij} is the NRTL model binary interaction parameter, $A_{ij} = (g_{ij} - g_{ji})$, g_{ij} is an interaction energy parameter of i - j , α_{ij} is a nonrandomness parameter, and R is the universal gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The critical properties (T_c , P_c) and acentric factors (ω) of HFC-32 and propane used to calculate the parameters for the Peng–Robinson equation of state are given in Table 1. We have set the nonrandomness parameter, α_{ij} , equal to 0.3 for all the binary mixtures studied here. The Carnahan–Starling–Desantis equation of state⁶ is expressed as follows:

$$\frac{PV}{RT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} - \frac{a}{RT(V + b)} \quad (11)$$

with

$$y = \frac{b}{4V} \quad (12)$$

$$a = \alpha_0 \exp(\alpha_1 T + \alpha_2 T^2) \quad (13)$$

$$b = \beta_0 + \beta_1 T + \beta_2 T^2 \quad (14)$$

where a is an attraction parameter and b is a molecular volume. The following mixing rules¹⁶ were used to obtain equation of state parameters for a mixture.

$$a_{12} = (1 - f_{12})(a_1 a_2)^{1/2} \quad (15)$$

$$b_{12} = \frac{1}{8}(b_1^{1/3} + b_2^{1/3})^3 \quad (16)$$

where f_{12} is the interaction parameter and a_i and b_i are properties of pure components. The coefficients α_i and β_i for pure components were cited from REFPROP 5.0.¹⁷ The parameters of these equations were obtained by minimizing the objective function

$$\text{objective function} = \frac{1}{N} \sum_j^n \left[\left(\frac{P_{j,\text{exp}} - P_{j,\text{cal}}}{P_{j,\text{exp}}} \right) \times 100 \right]^2$$

Results and Discussion

Table 2 reports a comparison of measured vapor pressures of pure HFC-32 and propane with those calculated from the database REFPROP 6.01,¹⁸ which is considered to be reliable for the pure compounds considered and consistent with literature data. The average deviation ($\Delta P/P$) between measured and calculated values from the data of REFPROP 6.01¹⁸ is 0.2458% for HFC-32 and 0.3160% for propane.

The performance of the experimental system was tested by comparing the measured data with published results of Higashi.³ As can be seen in Figure 1, our experimental measurements for the HFC-32 + propane system show good agreement with the published results. At 283.15 K, the average absolute deviation of pressure (δP) from the measurements of Higashi³ was found to be 0.40% for the P , T , x measurements. The experimental vapor pressure data for the pure components and isothermal vapor liquid equilibria for the HFC-32 + propane mixtures are shown in Table 3. This table lists the measured mole fraction of the liquid and vapor phases, pressures, and temperatures in equilibrium and the deviations between measured and calculated pressures (ΔP) and vapor compositions (Δy), point by point. The interaction parameters of binary mixtures for each isotherm, the binary parameters of the NRTL model with the Wong–Sandler mixing rules, and

Table 4. Values of Binary Parameters and Average Deviations of P and y of the HFC-32 (1) + Propane (2) System

T/K	Peng–Robinson EoS ^a			CSD EoS		
	binary parameters	$\delta P^b/\%$	δy^c	binary parameters	$\delta P^b/\%$	δy^c
268.15	$k_{ij} = 0.2182$ $A_{ij} = 3.777$ $A_{ji} = 3.482$	0.266	0.0154	$f_{ij} = 0.1632$	3.2670	0.0183
278.15	$k_{ij} = -0.1827$ $A_{ij} = 0.3739$ $A_{ji} = 0.3820$	0.256	0.0107	$f_{ij} = 0.1662$	2.8090	0.0141
283.15	$k_{ij} = 0.2118$ $A_{ij} = -0.3512$ $A_{ji} = 0.3486$	0.236	0.0059	$f_{ij} = 0.1656$	2.5852	0.0129
288.15	$k_{ij} = 0.1674$ $A_{ij} = 0.3893$ $A_{ji} = 0.3814$	0.261	0.0079	$f_{ij} = 0.1688$	2.6145	0.0112
298.15	$k_{ij} = 0.2543$ $A_{ij} = -0.3213$ $A_{ji} = 0.3220$	0.328	0.0110	$f_{ij} = 0.1738$	2.0822	0.0118
308.15	$k_{ij} = 0.1683$ $A_{ij} = 0.3359$ $A_{ji} = 0.3999$	0.442	0.0128	$f_{ij} = 0.1723$	1.8860	0.0105
318.15	$k_{ij} = 0.3689$ $A_{ij} = -0.3074$ $A_{ji} = 1.0861$	0.319	0.0095	$f_{ij} = 0.1715$	2.0100	0.0125

^a The unit of A_{ij} and A_{ji} is $\text{kJ}\cdot\text{mol}^{-1}$. ^b $\delta P = (1/N)\sum|(P_{\text{exp}} - P_{\text{cal}})/P_{\text{exp}}| \times 100$. ^c $\delta y = (1/N)\sum|y_{\text{exp}} - y_{\text{cal}}|$.

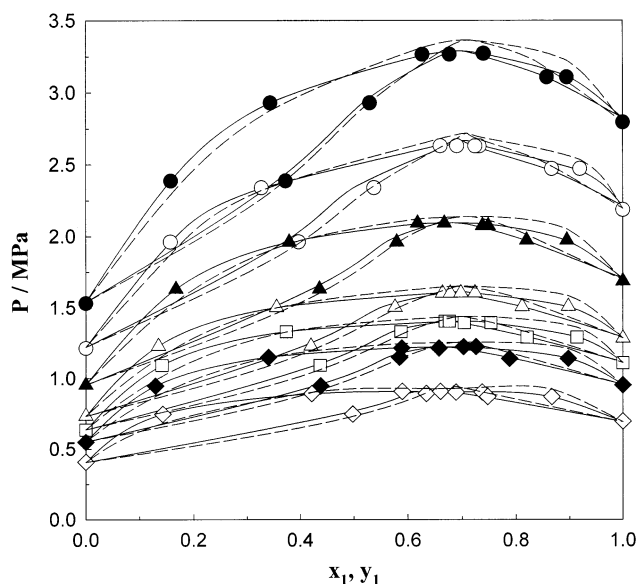


Figure 2. P - x - y Diagram for the HFC-32 (1) + propane (2) system at 268.15 to 318.15 K: \diamond , exp at 268.15 K; \blacklozenge , at 278.15 K; \square , at 283.15 K; \triangle , at 288.15 K; \blacktriangle , at 298.15 K; \circ , at 308.15 K; \bullet , at 318.15 K; —, calc with PR EoS; ---, calc with CSD EoS.

the average absolute deviations of pressure (δP) and vapor-phase composition (δy) between measured and calculated values are reported in Table 4. Figure 2 shows the comparison of measured and calculated values for HFC-32 + propane at (268.15, 278.15, 283.15, 288.15, 298.15, 308.15, and 318.15) K. The deviations of pressure and vapor-phase mole fraction of HFC-32 between the measured data and the calculated values are compared in Figures 3 and 4, respectively. From these figures and the low average absolute deviations of P and y in Table 4, we concluded that the calculated values using the Peng–Robinson equation of state and the CSD equation of state give good agreement with the experimental data, but the Peng–Robinson equation of state yielded more accurate predictions for this binary system. This binary system is a

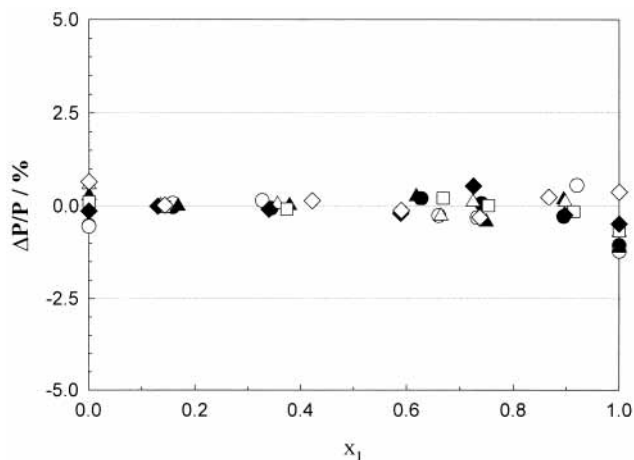


Figure 3. Deviation of pressure for the system HFC-32 (1) + propane (2) from the Peng–Robinson EoS using the Wong–Sandler mixing rules: \diamond , exp at 268.15 K; \blacklozenge , exp at 278.15 K; \square , exp at 283.15 K; \triangle , exp at 288.15 K; \blacktriangle , exp at 298.15 K; \circ , exp at 308.15 K; \bullet , exp at 318.15 K.

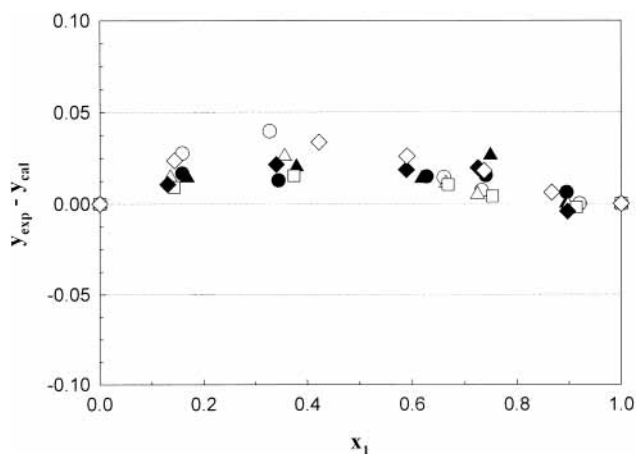


Figure 4. Deviation of vapor composition for the system HFC-32 (1) + propane (2) from the Peng–Robinson EoS using the Wong–Sandler mixing rules: \diamond , exp at 268.15 K; \blacklozenge , exp at 278.15 K; \square , exp at 283.15 K; \triangle , exp at 288.15 K; \blacktriangle , exp at 298.15 K; \circ , exp at 308.15 K; \bullet , exp at 318.15 K.

Table 5. Azeotropic Data of the HFC-32 (1) + Propane (2) System

T/K	x_1	P/MPa
268.15	0.665	0.909
278.15	0.671	1.224
283.15	0.678	1.405
288.15	0.684	1.610
298.15	0.688	2.097
308.15	0.697	2.667
318.15	0.701	3.288

mixture of a very polar molecule (HFC-32) and a nonpolar molecule (HC-290). These two molecules have repulsive interactions and exhibit a strong positive azeotrope. The azeotropic compositions and pressures were obtained graphically from a P - x - y diagram with experimental data. The azeotropic data (temperature, composition, and pressure) of the HFC-32 + propane system are listed in Table 5. Figure 5 represents the variation of the azeotropic composition with pressure for the HFC-32 + propane system. As can be seen in Figure 5, a logarithmic plot shows a linear relationship between the mole fraction of HFC-32 at the azeotropic point and the pressure. The liquid-phase separation

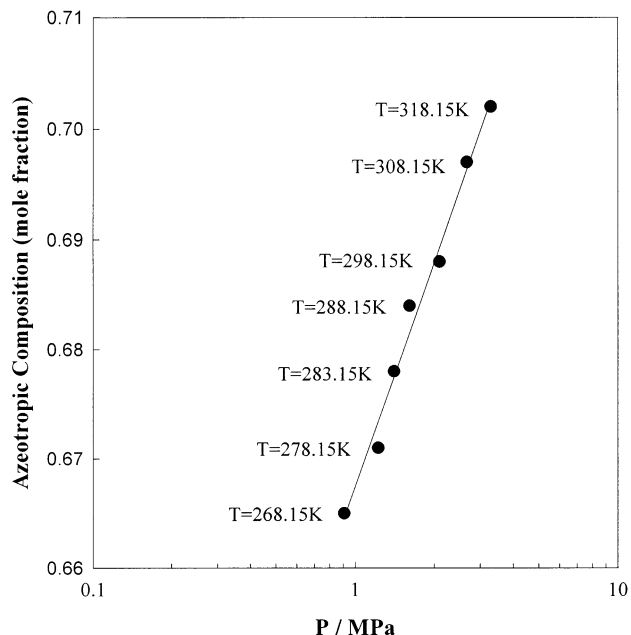


Figure 5. Variation of the azeotropic composition with pressure for the HFC-32 (1) + propane (2) binary system.

into two phases reported by Holcomb et al.² was not observed in the temperature range of the present work.

Conclusions

The vapor–liquid equilibrium data for binary systems of HFC-32 + propane were measured at seven temperatures between (268.15 and 318.15) K using a circulation-type equilibrium apparatus. The experimental data were correlated with the Peng–Robinson equation of state using the Wong and Sandler mixing rules and the Carnahan–Starling–Desantis (CSD) equation of state. Calculated results with these equations showed good agreement with the experimental data, but the Peng–Robinson equation of state gave a more accurate prediction for this binary system. This system shows a strong positive azeotrope for all the temperature range studied here.

List of Symbols

- $a(T)$ = temperature-dependent equation of state constant
- A_∞^E = excess Helmholtz free energy model at infinite pressure
- b = equation of state constant
- G_{ij} = local composition factor for the NRTL model
- g_{ij} = interaction energy parameter of i - j
- P, P_c = pressure, critical pressure (MPa)
- R = gas constant, $8.3144 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
- T, T_c, T_r = absolute temperature, critical temperature, reduced temperature (K)
- v = molar volume
- x = liquid mole fraction
- y = vapor mole fraction

Greek Letters

- $\alpha(T)$ = temperature-dependent equation of state parameter
- α_{ji} = nonrandomness parameter
- κ = Peng–Robinson equation of state parameter
- τ_{ij} = NRTL model binary interaction parameter
- ω = acentric factor
- Δ = deviation (experimental – calculated)

Subscripts

c = critical property

cal = calculated

exp = experimental

 $i, j = i$ th, j th component of the mixture**Literature Cited**

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