

Measurement of Vapor–Liquid Equilibria for the Binary Mixture Difluoromethane (HFC-32) + Propylene (R-1270)

Quang Nhu Ho, Byung Gwon Lee,* Jong Sung Lim, and Kye Sang Yoo

Division of Environment and Process Technology, Korea Institute of Science and Technology (KIST), P.O. Box 131, Cheongryang, Seoul 130-650, South Korea

Isothermal vapor–liquid equilibria data for the binary mixture of difluoromethane (HFC-32) + propylene (R-1270) at five equally spaced temperatures between (273.15 and 313.15) K were measured by using a circulation-type equilibrium apparatus. The experimental data were correlated with the Peng–Robinson equation of state (PR-EOS) combined with the Wong–Sandler mixing rule. It is confirmed that the data calculated by this equation of state are in good agreement with experimental data. Azeotropes of this mixture were found experimentally for all of the temperatures studied here.

Introduction

Chlorofluorocarbons (CFCs) have been widely used in a variety of industrial, commercial, and household applications such as refrigerants, blowing agents, propellants, and cleaning agents because of their outstanding properties. However, CFCs also have a negative effect on the earth's environment, particularly the ozone layer. For this reason, the production and use of CFCs will be completely prohibited within a decade. Initially, some hydrochlorofluorocarbons (HCFCs) were considered as an alternative to CFCs, but they will be phased out around 2030 because their ozone depletion potentials (ODPs) and global warming potentials (GWPs) are relatively high. Hence, much effort has been expended to find suitable replacement for CFCs and HCFCs. Hydrofluorocarbons (HFCs)—synthetic refrigerants with zero ODPs—were proposed as promising replacements for these materials. Unfortunately, HFCs have been included in the basket of greenhouse gases to be regulated by Kyoto Protocol 1997 because their GWPs are several thousand times higher than that for CO₂. Furthermore, the high manufacturing cost of these HFCs will gradually lead to reductions in the use and production of HFCs.

In recent years, the utilization of light hydrocarbons, such as propane, butane, propylene, and so forth, as effective refrigerants is believed to be an alternative solution because these hydrocarbons are rather cheap, plentiful, and environmentally benign chemicals (zero ODPs and near-zero GWPs) and possess many outstanding properties. Although the flammability of these materials has caused some concern, it was found that hydrocarbons are quite safe in small applications such as domestic refrigeration and car air-conditioning because very small amounts are involved. Consequently, the combination of hydrocarbons and HFCs is expected to be a good solution for developing CFC alternative refrigerants in the future.

To use a mixture of hydrocarbons combined with HFCs as multicomponent refrigerants, vapor–liquid equilibrium (VLE) data are required to evaluate the performance of refrigeration cycles and to determine their optimal compositions. In this work, isothermal VLE data for the binary mixture (HFC-32) + propylene (R-1270), which supply very

important basic information in evaluating the performance of refrigeration cycles and in determining the optimal composition of this mixture, were measured at five equally spaced temperatures between (273.15 and 313.15) K by using a circulation-type equilibrium apparatus. The experimental data were correlated with the Peng–Robinson¹ equation of state combined with the Wong–Sandler² mixing rule. The interaction parameters and average deviations in pressures and in vapor-phase compositions obtained from this equation of state are presented.

Experimental Section

Chemicals. High-grade chemicals of difluoromethane (HFC-32) and propylene were used for this investigation. Propylene of purity higher than 99.5% by mass was supplied by Conley Gas Ltd. HFC-32 produced by Ulsan Chemical Co. (UCC), Ltd., Korea, had a purity higher than 99.8% by mass. The purity of each chemical was validated by using a gas chromatograph.

Vapor–Liquid Equilibrium Apparatus. The vapor–liquid equilibrium apparatus used in this work was a circulation-type instrument in which both the liquid and vapor phase were continuously recirculated. A description of the experimental apparatus has been reported in our previous work³ and is only briefly discussed here.

The equilibrium cell was made of 316 stainless steel with an inner volume of about 85 mL. A pair of Pyrex glass windows was installed on two sides of the cell to observe the inside during operation. Inside the cell, a stirring bar rotating at variable speed 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 bath was maintained by a bath circulator (RCB-20, Jeio Tech, Korea). The temperature in the cell was measured with a platinum resistance sensor connected to a digital temperature indicator (F250 precision thermometer, Automatic Systems Laboratories Ltd., U.K.). They were calibrated by the NAMAS accredited calibration laboratory. The total uncertainty is estimated to be within ± 0.01 K, including the sensor uncertainty (± 0.01 K), the temperature resolution (± 0.001 K), and the measurement uncertainty (± 0.001 K). The pressure was measured with a pressure transducer (model XPM60) and a digital pressure calibrator indicator (C106 model, Beamax, Finland).

* Corresponding author. E-mail: bglee@kist.re.kr. Tel: 82-2-958-5857. Fax: 82-2-958-5809.

Table 1. Characteristic Properties of HFC-32 and R-1270^a

characteristic properties	HFC-32	R-1270
critical temperature, T_c /K	351.26	365.57
critical pressure, P_c /MPa	5.782	4.665
acentric factor, ω	0.2768	0.1408

^a Source: database REFPROP 6.01.⁶**Table 2. Comparisons of the Vapor Pressure (P_v) of Pure Components between Experimental Data and Data Obtained from the Database REFPROP 6.01**

component	T /K	$P_{v,exptl}$ /MPa	$P_{v,REF}$ /MPa	$ \Delta P_v $ /MPa ^a	$(\Delta P_v /P_{exptl})/\%$
HFC-32	273.15	0.8168	0.8131	0.0037	0.45
	283.15	1.1118	1.1070	0.0048	0.43
	293.15	1.4802	1.4750	0.0052	0.35
	303.15	1.9304	1.9280	0.0024	0.12
	313.15	2.4780	2.4780	0.0000	0.00
	AAD% - $P_v = 0.27$				
R-1270	273.15	0.5878	0.5859	0.0019	0.32
	283.15	0.7812	0.7809	0.0003	0.04
	293.15	1.0202	1.0200	0.0002	0.02
	303.15	1.3082	1.3080	0.0002	0.02
	313.15	1.6508	1.6520	0.0012	0.07
	AAD% - $P_v = 0.09$				

^a $\Delta P_v = P_{v,exptl} - P_{v,REF}$.**Table 3. Comparison of Deviations in Pressure and in Vapor-Phase Composition between Experimental and Calculated VLE Data for the Binary Mixture of HFC-32 (1) + R-1270 (2) at 273.15 K**

experimental data			calculated data		$(P_{exptl} - P_{calcd})/P_{exptl}/\%$	δy^a
$x_{1,exptl}$	$y_{1,exptl}$	P_{exptl}/MPa	$y_{1,calcd}$	P_{calcd}/MPa		
0.000	0.000	0.5878	0.000	0.5847	0.52	0.000
0.089	0.240	0.7328	0.238	0.7323	0.07	0.001
0.176	0.363	0.8248	0.357	0.8246	0.03	0.006
0.262	0.443	0.8828	0.432	0.8857	-0.33	0.011
0.338	0.497	0.9244	0.484	0.9251	-0.08	0.013
0.420	0.544	0.9568	0.533	0.9563	0.05	0.011
0.490	0.575	0.9764	0.570	0.9749	0.16	0.005
0.558	0.598	0.9878	0.606	0.9868	0.10	-0.008
0.625	0.639	0.9928	0.640	0.9927	0.01	-0.001
0.652	0.653	0.9950	0.654	0.9933	0.17	-0.001
0.665	0.661	0.9948	0.660	0.9932	0.16	0.001
0.674	0.668	0.9930	0.665	0.9931	-0.01	0.002
0.710	0.684	0.9914	0.684	0.9912	0.03	0.000
0.768	0.718	0.9830	0.717	0.9835	-0.05	0.001
0.827	0.760	0.9670	0.757	0.9681	-0.11	0.003
0.879	0.804	0.9446	0.800	0.9454	-0.08	0.004
0.923	0.833	0.9136	0.850	0.9150	-0.15	-0.017
1.000	1.000	0.8168	1.000	0.8166	0.02	0.000

^a $\delta y = y_{1,exptl} - y_{1,calcd}$.

Pressure calibrations are traceable to national standards (Center for Metrology and Accreditation Certificate nos. M-95P077 dated 14-11-1995, M-M730 dated 16-11-1995, and M-95P078 dated 16-11-1995), and the total uncertainty was estimated to be within ± 1 kPa, including the calibration uncertainty of ± 0.5 kPa, the sensor uncertainty of ± 1 kPa, and the measurement uncertainty of ± 1 kPa. The vapor and liquid phases in the equilibrium cell were continuously recirculated by a dual-head circulation pump (Milton Roy Co.). After equilibrium was reached, the vapor and liquid samples were withdrawn from the recycling loop and injected on-line into a gas chromatograph (Gow-Mac model 550P) equipped with a thermal conductivity detector (TCD) and an 80/100 Chromosorb-102 column (Restek Co.).

Experimental Procedures. Experiments to measure VLE data for the binary mixture HFC-32 + R-1270 at a certain temperature were performed by the following procedures. First, the system was evacuated to remove all inert gases. A certain amount of R-1270 (less volatile than

Table 4. Comparison of Deviations in Pressure and in Vapor-Phase Composition between Experimental and Calculated VLE Data for the Binary Mixture of HFC-32 (1) + R-1270 (2) at 283.15 K

experimental data			calculated data		$(P_{exptl} - P_{calcd})/P_{exptl}/\%$	δy
$x_{1,exptl}$	$y_{1,exptl}$	P_{exptl}/MPa	$y_{1,calcd}$	P_{calcd}/MPa		
0.000	0.000	0.7812	0.000	0.7797	0.20	0.000
0.078	0.207	0.9448	0.208	0.9423	0.26	-0.001
0.185	0.361	1.0932	0.367	1.0987	-0.50	-0.006
0.263	0.438	1.1810	0.441	1.1772	0.32	-0.003
0.326	0.484	1.2262	0.487	1.2245	0.14	-0.003
0.407	0.533	1.2702	0.535	1.2677	0.20	-0.002
0.502	0.584	1.3064	0.583	1.3003	0.47	0.001
0.567	0.618	1.3086	0.613	1.3135	-0.37	0.004
0.615	0.643	1.3106	0.636	1.3186	-0.61	0.007
0.644	0.658	1.3182	0.650	1.3200	-0.13	0.008
0.674	0.674	1.3226	0.665	1.3198	0.21	0.009
0.703	0.691	1.3150	0.680	1.3180	-0.23	0.011
0.753	0.721	1.3082	0.710	1.3103	-0.16	0.011
0.802	0.756	1.2960	0.743	1.2964	-0.03	0.013
0.843	0.789	1.2792	0.777	1.2779	0.10	0.012
0.882	0.824	1.2566	0.815	1.2532	0.27	0.009
0.911	0.855	1.2330	0.849	1.2296	0.28	0.006
1.000	1.000	1.1118	1.000	1.1140	-0.20	0.000

Table 5. Comparison of Deviations in Pressure and in Vapor-Phase Composition between Experimental and Calculated VLE Data for the Binary Mixture of HFC-32 (1) + R-1270 (2) at 293.15 K

experimental data			calculated data		$(P_{exptl} - P_{calcd})/P_{exptl}/\%$	δy
$x_{1,exptl}$	$y_{1,exptl}$	P_{exptl}/MPa	$y_{1,calcd}$	P_{calcd}/MPa		
0.000	0.000	1.0202	0.000	1.0192	0.10	0.000
0.071	0.184	1.2102	0.181	1.2088	0.12	0.003
0.169	0.332	1.3860	0.322	1.3902	-0.30	0.011
0.244	0.403	1.4928	0.393	1.4884	0.30	0.009
0.311	0.458	1.5572	0.446	1.5576	-0.03	0.012
0.387	0.511	1.6180	0.499	1.6195	-0.09	0.012
0.478	0.569	1.6752	0.556	1.6735	0.10	0.013
0.569	0.623	1.7032	0.611	1.7077	-0.26	0.012
0.610	0.645	1.7132	0.636	1.7169	-0.21	0.010
0.651	0.670	1.7196	0.660	1.7218	-0.13	0.010
0.673	0.680	1.7240	0.674	1.7227	0.08	0.006
0.696	0.697	1.7362	0.689	1.7222	0.81	0.007
0.732	0.716	1.7156	0.712	1.7184	-0.16	0.004
0.754	0.731	1.7154	0.728	1.7139	0.09	0.003
0.776	0.747	1.7064	0.743	1.7082	-0.10	0.004
0.837	0.792	1.6816	0.790	1.6822	-0.03	0.003
0.893	0.846	1.6388	0.842	1.6414	-0.16	0.004
1.000	1.000	1.4802	1.000	1.4866	-0.43	0.000

Table 6. Comparison of Deviations in Pressure and in Vapor-Phase Composition between Experimental and Calculated VLE Data for the Binary Mixture of HFC-32 (1) + R-1270 (2) at 303.15 K

experimental data			calculated data		$(P_{exptl} - P_{calcd})/P_{exptl}/\%$	δy
$x_{1,exptl}$	$y_{1,exptl}$	P_{exptl}/MPa	$y_{1,calcd}$	P_{calcd}/MPa		
0.000	0.000	1.3082	0.000	1.3092	-0.08	0.000
0.102	0.224	1.6214	0.219	1.6164	0.31	0.005
0.153	0.294	1.7246	0.288	1.7315	-0.40	0.006
0.251	0.394	1.8994	0.386	1.9005	-0.06	0.008
0.322	0.450	1.9934	0.442	1.9933	0.01	0.008
0.425	0.527	2.0966	0.515	2.0968	-0.01	0.013
0.512	0.587	2.1592	0.572	2.1575	0.08	0.015
0.599	0.643	2.1942	0.629	2.1961	-0.09	0.014
0.638	0.668	2.2056	0.654	2.2052	0.02	0.014
0.676	0.693	2.2076	0.680	2.2094	-0.08	0.013
0.709	0.711	2.2084	0.702	2.2089	-0.02	0.009
0.717	0.716	2.2238	0.708	2.2082	0.70	0.008
0.763	0.746	2.2004	0.741	2.1992	0.06	0.005
0.787	0.771	2.1924	0.760	2.1906	0.08	0.012
0.817	0.794	2.1766	0.783	2.1767	0.00	0.010
0.859	0.819	2.1422	0.820	2.1482	-0.28	-0.001
0.899	0.868	2.1010	0.859	2.1112	-0.48	0.008
1.000	1.000	1.9304	1.000	1.9459	-0.80	0.000

HFC-32) was introduced into the cell, and then the temperature of the entire system was maintained by controlling the temperature of the water bath system. After the desired temperature was achieved, the vapor pressure of R-1270 was measured. Then, a targeted amount of HFC-32 was supplied to the cell. Both the dual-head pump and

Table 7. Comparison of Deviations in Pressure and in Vapor-Phase Composition between Experimental and Calculated VLE Data for the Binary Mixture of HFC-32 (1) + R-1270 (2) at 313.15 K

experimental data			calculated data		$[(P_{\text{expt}} - P_{\text{calcd}})/P_{\text{expt}}]/\%$	δy
$x_{1,\text{expt}}$	$y_{1,\text{expt}}$	$P_{\text{expt}}/\text{MPa}$	$y_{1,\text{calcd}}$	$P_{\text{calcd}}/\text{MPa}$		
0.000	0.000	1.6508	0.000	1.6558	-0.30	0.000
0.080	0.173	1.9314	0.169	1.9378	-0.33	0.003
0.199	0.339	2.2724	0.330	2.2612	0.49	0.008
0.299	0.436	2.4664	0.424	2.4598	0.27	0.012
0.375	0.492	2.5718	0.484	2.5763	-0.17	0.009
0.434	0.539	2.6465	0.526	2.6502	-0.14	0.013
0.480	0.571	2.6930	0.557	2.6969	-0.15	0.014
0.550	0.618	2.7447	0.603	2.7519	-0.26	0.015
0.608	0.654	2.7780	0.640	2.7829	-0.17	0.014
0.675	0.696	2.7960	0.684	2.8015	-0.20	0.011
0.705	0.715	2.7970	0.704	2.8035	-0.23	0.011
0.715	0.723	2.7990	0.712	2.8032	-0.15	0.011
0.745	0.745	2.8240	0.733	2.7995	0.87	0.012
0.772	0.765	2.7965	0.754	2.7920	0.16	0.011
0.827	0.806	2.7670	0.798	2.7636	0.12	0.008
0.890	0.863	2.7045	0.857	2.7049	-0.02	0.006
0.932	0.908	2.6420	0.905	2.6446	-0.10	0.004
1.000	1.000	2.4780	1.000	2.5042	-1.06	0.000

Table 8. Interaction Parameters k_{12} , NRTL Parameters (τ_{12} , τ_{21}), and Average Absolute Deviations in Pressures (AAD% - P) and in Vapor-Phase Composition (AAD% - y)

T/K	k_{12}	τ_{12}	τ_{21}	AAD% - P^a	AAD - y^b
273.15	-0.09283	1.17504	2.03138	0.12	0.005
283.15	0.22315	0.55843	0.91569	0.26	0.006
293.15	-0.01541	0.97475	1.55235	0.19	0.007
303.15	0.01602	0.91363	1.34720	0.20	0.008
313.15	0.16713	0.45658	1.00574	0.29	0.009

$$^a \text{AAD\%} - P = \frac{100}{N} \sum_{i=1}^N \frac{|P_{\text{expt},i} - P_{\text{calcd},i}|}{P_{\text{expt},i}} \quad ^b \text{AAD} - y = \frac{1}{N} \sum_{i=1}^N |y_{\text{expt},i} - y_{\text{calcd},i}|$$

stirrer should be turned on continuously until the equilibrium state of the mixture in the cell is established. As soon as the equilibrium state was confirmed, the compositions of the sample and the pressure in the cell were measured. The uncertainty in the composition measurement was estimated to be within ± 0.002 mole fraction for both the liquid and vapor phase. Finally, the vapor pressure of pure HFC-32 was measured using the same procedure mentioned above for R-1270.

Correlation

In this work, the experimental VLE data were correlated with the Peng–Robinson equation of state (PR-EOS) combined with the Wong–Sandler mixing rule. The Peng–Robinson equation¹ of state is expressed by

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

$$a(T) = \left(0.457235 \frac{R^2 T_c^2}{P_c}\right) \alpha(T) \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha(T) = [1 + k(1 - \sqrt{T/T_c})]^2 \quad (4)$$

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

where the parameter a is a function of temperature, b is a constant, k is a constant characteristic of each substance, ω is the acentric factor, P and P_c (MPa) are the absolute and critical pressures, respectively, T and T_c (K) are the

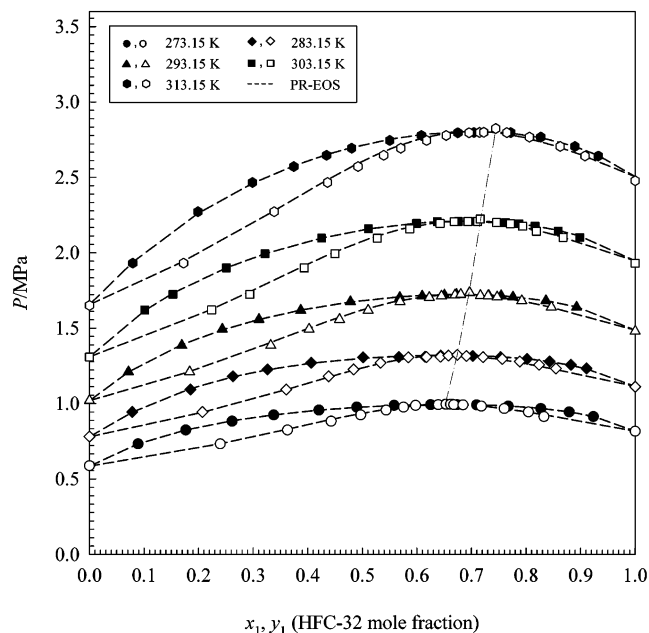


Figure 1. P - x - y diagrams for the mixture HFC-32 + R-1270 at various temperatures.

absolute and critical temperatures, respectively, T_r is the reduced temperature, and V_M is the molar volume.

The Wong–Sandler mixing rule² was used in this work to obtain equation-of-state parameters for a mixture from those of the pure components. Wong and Sandler equated the excess Helmholtz free energy at infinite pressure from an equation of state to the excess Helmholtz free energy from any activity coefficient model in such a way that a mixing rule is obtained that simultaneously satisfies the quadratic composition dependence of the second virial coefficient but also behaves like an activity coefficient model at high density. This mixing rule 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

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

and

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

where C is a constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR-EOS used in this work and k_{ij} is binary interaction parameter. Also, A_∞^E is an excess Helmholtz free energy model at infinite pressure that can be equated to a low-pressure excess Gibbs free energy.⁴ In this study, we use the NRTL model⁵ given by

$$\frac{A_\infty^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{ji} \tau_{ji}}{\sum_r x_r G_{ri}} \quad (9)$$

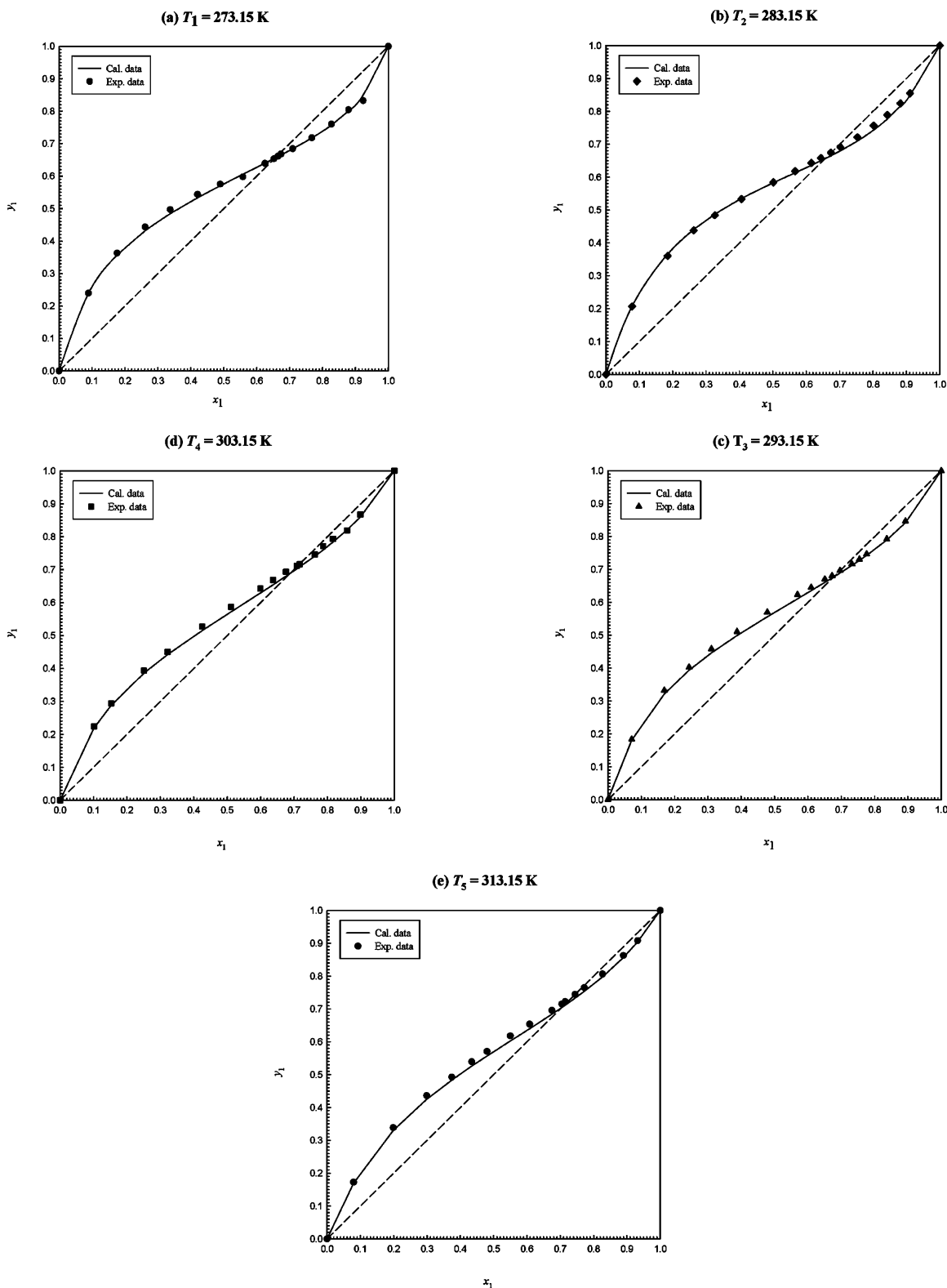


Figure 2. y - x diagrams for the binary mixture HFC-32 + R-1270 at various temperatures.

with

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

where G_{ji} is the local composition factor for the NRTL model, τ_{ji} is the NRTL model binary interaction parameter,

$A_{ji} = (g_{ji} - g_{ii})$, g_{ji} is interaction energy between an i - j pair of molecules, α_{ji} is a nonrandomness parameter, and R is the universal gas constant ($8.314 \text{ J K}^{-1}\text{mol}^{-1}$). The critical properties (T_c , P_c) and acentric factors (ω) of HFC-32 and R-1270 used to calculate the parameters for the PR-EOS are summarized in Table 1. We have set the nonrandomness parameter, α_{ij} , equal to 0.3 for the binary mixture investigated here. The parameters of these equations

wereobtained by minimizing the objective function

$$\text{objective function} = \frac{1}{N} \sum_{i=1}^N \left[\left(\frac{|P_{i,\text{exptl}} - P_{i,\text{calcd}}|}{P_{i,\text{exptl}}} \right) 100 \right]^2 \quad (11)$$

where N is the number of experimental points; P_{exptl} and P_{calcd} are experimental and calculated pressures.

Results and Discussion

Comparison of measured saturated vapor pressures (P_v) of pure HFC-32 and R-1270 at various temperatures with the data calculated from the database REFPROP 6.01⁶ are illustrated in Table 2. The result indicates that the absolute deviations of vapor pressure (ΔP_v) between experimental and cited data are within ± 0.005 and ± 0.002 MPa for HFC-32 and R-1270, respectively, and that the average absolute deviations ($\text{AAD}\% - P_v$) are 0.09% for R-1270 and 0.27% for HFC-32. All values are low and acceptable.

The measured and calculated VLE data for the binary mixture HFC-32 (1) + R-1270 (2) at (273.15, 283.15, 293.15, 303.15, and 313.15) K as well as their deviations in pressure and in vapor-phase composition are presented in Tables 3–7. The results of correlation including all of the values of determined k_{12} , the NRTL parameters τ_{12} and τ_{21} , and the average absolute deviations in pressure and in vapor-phase composition ($\text{AAD}\% - P$ and $\text{AAD} - y$) between calculated and experimental data for this binary mixture are reported in Table 8. The P - x - y diagrams for this system are shown in Figure 1, where the experimental data are presented as symbols and the dashed lines represent the calculated values by PR-EOS. Both experimental and calculated diagrams clearly indicated that the mixture HFC-32 + R-1270 exhibited a positive deviation from Raoult's law as well as azeotropic behavior. On the y - x diagrams shown in Figure 2, the azeotropic points of the investigated system are located where the equilibrium lines crosses the corresponding diagonals. Generally, its azeotrope composition varies by way of decreasing R-1270 mole fraction with increasing temperature. From Figures 1 and 2, it can be realized that there was a small difference between experimental and calculated diagrams. The difference can be also demonstrated clearly in Figures 3 and 4 by the deviations in the vapor-phase composition and pressure of the calculated data compared with experimental values at each point. From the results summarized in Table 8, it was found that in the temperature range between (273.15 and 313.15) K the values of $\text{AAD}\% - P$ varied within (0.12 to 0.29)%; meanwhile, the values of $\text{AAD} - y$ varied within 0.005 to 0.009 mole fraction. Generally, all values are relatively small and acceptable, and the data calculated by using PR-EOS combined with the Wong–Sandler mixing rule are in good agreement with the experimental data.

As mentioned above, the binary mixture HFC-32 + R-1270 exhibited azeotropic behavior. In this work, the azeotropic point of this mixture was measured at (273.15, 283.15, 293.15, 303.15, and 313.15) K, with the difference between the azeotropic composition in the vapor and the liquid phase considered to be within 0.001 of the R-32 mole fraction. The experimental azeotrope data including pressure and composition are reported in Table 9. The experimental azeotropic locus of this mixture over the range of temperature between (273.15 and 303.15) K is shown as the dashed-dotted line in Figure 1. All azeotropes in this range of temperature were found at a mole fraction of R-32 higher than 0.65.

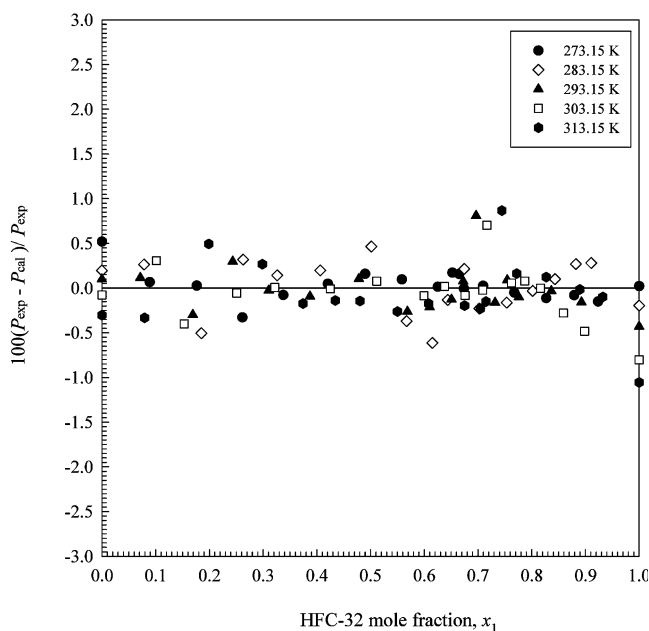


Figure 3. Deviations in pressure between experimental and calculated data for the binary mixture HFC-32 + R-1270 at various temperatures.

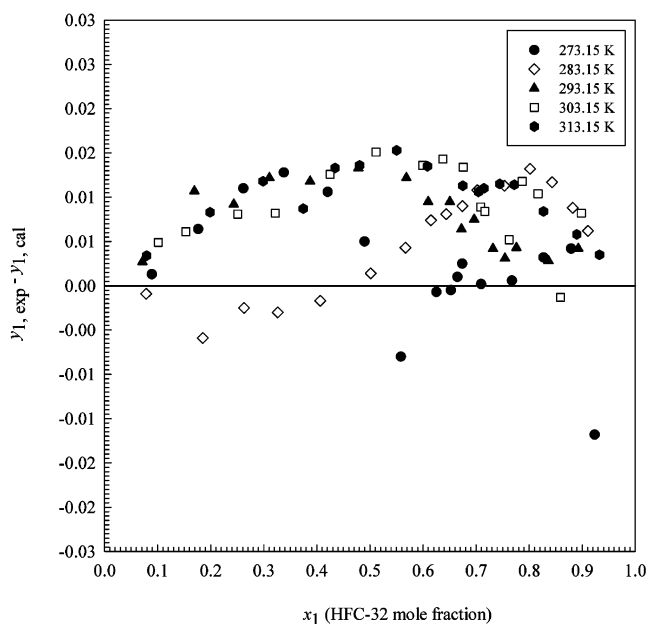


Figure 4. Deviations in the vapor-phase composition between experimental and calculated data for the binary mixture HFC-32 + R-1270 at various temperatures.

Table 9. Experimental Azeotropic Points of the Binary Mixture HFC-32 (1) + R-1270 (2) at Various Temperatures

T/K	measured azeotropic composition		P_a/MPa
	liquid phase, $x_{1,a}$	vapor phase, $y_{1,a}$	
273.15	0.652	0.653	0.9950
283.15	0.674	0.674	1.3226
293.15	0.696	0.697	1.7362
303.15	0.717	0.716	2.2238
313.15	0.745	0.745	2.8240

Conclusions

Measurements of the vapor–liquid equilibria for the binary mixture HFC-32 + R-1270 at (273.15, 283.15, 293.15, 303.15, and 313.15) K were carried out by using a

circulation-type equilibrium apparatus. The results showed that this mixture exhibited a positive deviation from Raoult's law in the presence of an azeotrope at a mole fraction of R-32 higher than 0.65 over this range of temperature.

The experimental VLE data were correlated with the PR-EOS combined with the Wong–Sandler mixing rule. The calculated data obtained from the equation of state are in good agreement with experimental data. This result means that the model equation used in this study can be used to estimate the thermodynamic properties of the binary mixture of HFC-32 + R-1270 in the range of temperature from (273.15 to 313.15) K.

List of Symbols

A^E_∞	an excess Helmholtz free energy
$a(T)$	function of temperature
b	constant
C	a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$ for the PR-EOS
k_{12}	interaction parameter between species 1 and 2
g_{ij}	an interaction energy parameter of the i - j component
G_{ij}	the local composition factor for the NRTL model
k	a constant characteristic of each substance
n	number of components in a mixture
N	number of experiments
P, P_c, P_v	pressure, critical pressure, vapor pressure (MPa)
R	gas constant, $R = 8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$
T, T_c	absolute temperature, critical temperature (K)
T_r	reduced temperature
V_M	molar volume
x, y	mole fraction in liquid phase, vapor phase

Greek Letters

$\alpha(T)$	temperature dependence
α_{12}	nonrandomness parameter
g	activity coefficient
Δ, δ	change in a quantity
w	acentric factor

Subscripts

a	azeotropic property
c	critical property
calcd	calculated
exptl	experimental
i, j	i th, j th components of the mixture
m	mixture
v	vapor phase

Literature Cited

- (1) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59–64.
- (2) Wong, D. S. H.; Sandler, S. I. A Theoretically Correct Mixing Rule for Cubic Equations of State. *AIChE J.* **1992**, *38*, 671–680.
- (3) Lim, J. S.; Ho, Q. N.; Park, J. Y.; Lee, B. G. Measurement of Vapor–Liquid Equilibria for the Binary Mixture of Propane (R-290) + Isobutane (R-600a). *J. Chem. Eng. Data* **2004**, *49*, 192–198.
- (4) Wong, D. S. H.; Orbey, H.; Sandler, S. I. Equation of State Mixing Rule for Nonideal Mixtures Using Available Activity Coefficient Model Parameter and That Allows Extrapolation over Large Ranges of Temperature and Pressure. *Ind. Eng. Chem. Res.* **1992**, *31*, 2033–2039.
- (5) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135–144.
- (6) McLinden, M. O.; Klein, S. A.; Lemmon, E. W.; Peskin, A. P. *Thermodynamic Properties of Refrigerants and Refrigerant Mixtures Database, REFPROP V.6.01*; National Institute of Standards and Technology: Gaithersburg, MD, 1998.

Received for review June 21, 2004. Accepted November 4, 2004.

JE0497698