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Isothermal Vapor−Liquid Equilibrium of (Pentafluoroethane + Fluoroethane) at Temperatures between (265.15 and 303.15) K Obtained with a Recirculating Still

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The binary mixture refrigerant with (pentafluoroethane + fluoroethane),which in refrigeration nomenclature is R125 + R161, can be considered an alternative refrigerant because it is environmental friendly, has excellent thermodynamic performance, and is safe. (Vapor + liquid) equilibrium (VLE) data for (pentafluoroethane + ethyl fluoride) have been obtained at temperatures of (265.15, 275.15, 283.15, 293.15, 303.15, and 313.15) K. The experimental method used for this study is of the circulation type. Using the Peng−Robinson equation of state combined with the linear combination of the Vidal and Michelsen (LCVM) mixing rules, the modified LCVM mixing rules, and the NRTL model, the VLE data have been correlated. The results reveal that both models have good agreement with existing experimental data obtained by the apparatus. In comparison with the LCVM model, the modified LCVM mixing rule gives much better correlations for the VLE of the binary system (pentafluoroethane + fluoroethane).

Introduction

The investigation of the "ozone hole" above the Antarctic established the relationship between chlorine and ozone content in the stratosphere. In particular, the chlorine oxide (CLO^-) radical is mainly responsible for the ozone depletion. This radical is formed by chlorine atoms released by chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), which are refrigerants. However, concern about the depletion of the stratospheric ozone layer by chlorine derived from CFCs and HCFCs has led to the Montreal Protocol. These require the phase-out of chlorine-containing CFCs and HCFCs. HCFCs and mixtures with HCFCs are still used at present. It is important to use refrigerants that are environmental friendly and have excellent thermodynamic and safety performances. Investigations show that a pure alternative refrigerant is rare with the correct properties. Hence, mixtures of refrigerants are being used as a replacement. Fluoroethane is acceptable but also flammable, which will impede application to some extent. To overcome the latter weakness, pentafluoroethane instead of 1,1,1,2-tetrafluoroethane is mixed with fluoroethane.[1] The main reasons for this are as follows: (i) Fluoroethane is more flammable, and pentafluoroethane is inflammable relative to 1,1,1,2-tetrafluoroethane.[2] (ii) The cooling capacity of pentafluoroethane is greater than that of 1,1,1,2-tetrafluoroethane and thus can add to the unit volume capacity of mixtures. (iii) By comparison with 1,1,1,2-tetrafluoroethane, pentafluoroethane is mixed with fluoroethane. The variation in the vaporation temperature of the mixture (pentafluoroethane + fluoroethane) is less.[3] Thus, by substituting the working fluid (pentafluoroethane + fluoroethane), few modifications are required for the refrigerator components, which brings little additional cost. Accurate values of the VLE data of (pentafluoroethane + fluoroethane) are required to evaluate the vapor compression cycle for it. Here were report VLE measurements on (pentafluoroethane + fluoroethane) at temperatures from (265.15 to 313.15) K.

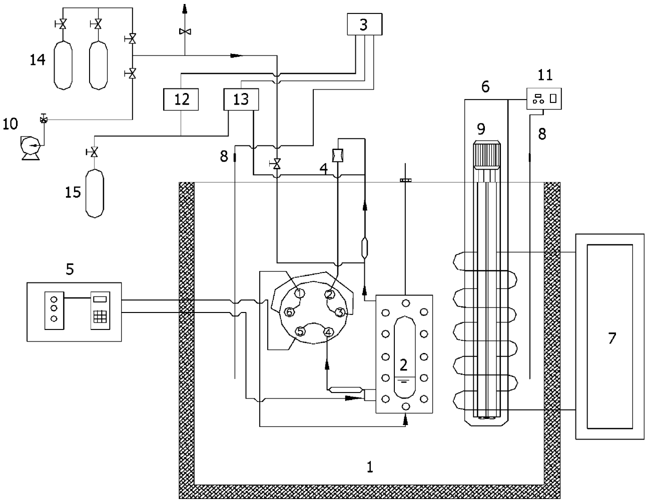

Figure 1. Schematic diagram of the VLE apparatus: 1, thermostated bath; 2, equilibrium cell; 3, multi-meter; 4, circulation pump; 5, gas chromatograph; 6, heater; 7, refrigeration system; 8, calibrated platinum resistance thermometer; 9, stirrer; 10, vacuum pump; 11, temperature control meter; 12, pressure transfer; 13, differential pressure transmitter; 14, samples; 15, high-pressure nitrogen.

Experimental Section

Materials. Pentafluoroethane and fluoroethane were supplied by the Chemical Engineering Company of Zhejiang, China, with a minimum stated purity of 99.98 % and 99.7 %, respectively. The samples were used without further purification.

Experimental Equipment and Procedures. Pressure, temperature, and liquid and vapor compositions were obtained from

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Table 1. VLE ($T-p-x_1-y_1$) Data for the System Pentafluoroethane (1) + Fluoroethane (2) at Temperatures of (265.15 and 275.15) K

T/K	x_1	y_1	p/Pa	T/K	x_1	y_1	p/Pa
265.15	0.0000	0.0000	336000	275.15	0.0000	0.0000	468900
	0.3234	0.4248	392800		0.4516	0.5712	578800
	0.4020	0.5227	410900		0.5511	0.6706	599900
	0.4254	0.5498	414700		0.5999	0.7124	624600
	0.5563	0.6703	438800		0.7319	0.8134	651000
	0.6740	0.7743	461700		0.7724	0.8404	659400
	0.7257	0.8022	471647		0.8075	0.8633	666300
	0.7590	0.8232	480500		0.8260	0.8759	679000
	0.7936	0.8507	485100		0.8385	0.8840	681600
	0.8129	0.8616	488700		0.8551	0.8889	690800
	0.8202	0.8744	495800		0.8800	0.9196	702400
	0.8575	0.8873	502300		1.0000	1.0000	714300
	1.0000	1.0000	517000				

Table 2. VLE ($T-p-x_1-y_1$) Data for the System Pentafluoroethane (1) + Fluoroethane (2) at Temperatures of (283.15 and 293.15) K

T/K	x_1	y_1	p/Pa	T/K	x_1	y_1	p/Pa
283.15	0.0000	0.0000	602900	293.15	0.0000	0.0000	808200
	0.1165	0.1577	632500		0.3293	0.4234	955900
	0.1437	0.1938	636500		0.5383	0.6383	1038700
	0.2370	0.3131	663700		0.5620	0.6609	1053300
	0.3229	0.4156	690500		0.6053	0.7060	1079700
	0.466	0.5776	737400		0.6859	0.7689	1093300
	0.5438	0.6520	766600		0.7551	0.8128	1118900
	0.6332	0.7311	809100		0.7856	0.8328	1123400
	0.6806	0.7786	812800		0.7966	0.8409	1133600
	0.7348	0.8140	830500		0.8094	0.8596	1134400
	0.7558	0.8323	839800		0.8320	0.8730	1140100
	0.7990	0.8613	849200		0.8464	0.8818	1156100
	0.8335	0.8849	863570		1.0000	1.0000	1205000
	0.8837	0.9191	880935				
	1.0000	1.0000	908800				

Table 3. VLE ($T-p-x_1-y_1$)data for the System Pentafluoroethane (1) + Fluoroethane (2) at Temperatures of (303.15 and 313.15) K

T/K	x_1	y_1	p/Pa	T/K	x_1	y_1	p/Pa
303.15	0.0000	0.0000	1051400	313.15	0.0000	0.0000	1348600
	0.4527	0.5030	1393000		0.4452	0.4830	1812600
	0.5591	0.6045	1422100		0.5154	0.5558	1833600
	0.6068	0.6444	1442600		0.5844	0.6161	1857300
	0.7289	0.7536	1487800		0.6592	0.6845	1872700
	0.7596	0.7839	1491900		0.7184	0.7471	1899900
	0.7832	0.8039	1506900		0.7236	0.7548	1907300
	0.7968	0.8214	1514700		0.7749	0.8043	1917000
	0.8451	0.8595	1529300		0.8322	0.8529	1928000
	0.8602	0.8738	1539300		0.8695	0.8900	1944000
	1.0000	1.0000	1567000		1.0000	1.0000	2006000

Table 4. Critical Parameters and Acentric Factors

		M	T_c	p_c	V_c		
substance	chemicals	g·mol^{-1}	K	MPa	cm^3·mol^{-1}	Z_c	ω
pentafluoroethane	C_2HF_5	120.03	339.20	3.59	210.099	0.270	0.303
fluoroethane	CH_3-CH_2F	48.06	375.30	5.02	169.00	0.261	0.215

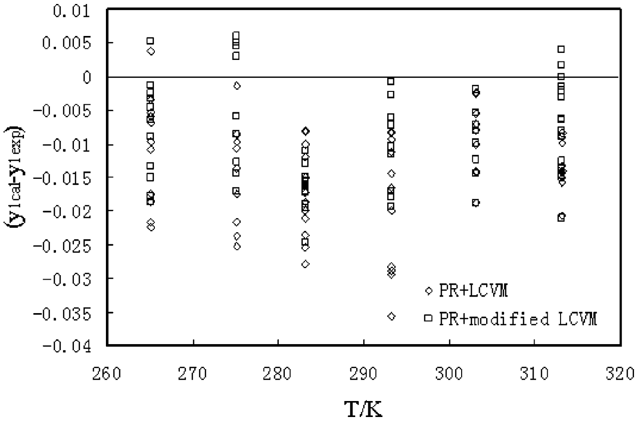

Figure 2. Deviations of vapor molar composition for the binary mixture (pentafluoroethane + fluoroethane).

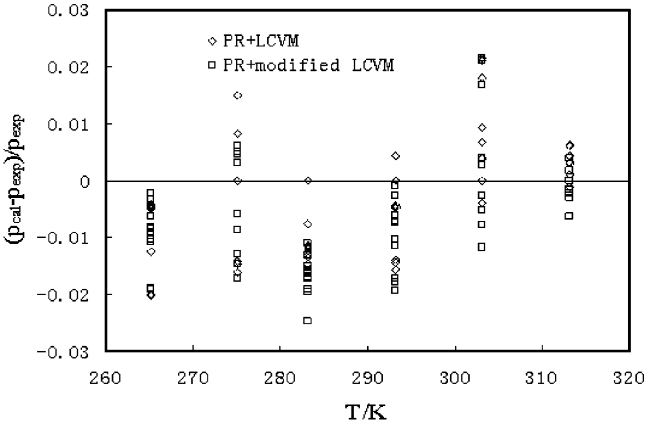

Figure 3. Deviations of vapor pressure for the binary mixture (pentafluoroethane + fluoroethane)

measurements with a recirculating still (shown in Figure 1). It consists of a stainless steel equilibrium cell volume of 80 mL. By visual observation of the solution in the cell, the phase behavior can be determined. The cell is thermostated in a bath, fitted with glass windows and insulated with polyurethane foam. The bath temperature stability has been determined as ± 0.01 K at temperatures in the range of (243.15 to 313.15) K. The temperature is measured with a platinum resistance thermometer (model WZP-II) with a precision of ± 0.01 K. The pressure of the fluid within the cell is on one side of a differential pressure transmitter (model 1151DP) that is kept balanced with nitrogen, the pressure of which is determined with a model PMP4010 from Druck Co. with an accuracy of ± 0.0014 MPa.

A circulation loop is used to promote equilibration and sample the liquid phase. The liquid is circulated through the gas. The vapor outlet from the cell penetrates the cover of the thermostatic bath and then connects to the vapor pump. The pump head and other parts outside the thermostat are trace heated and insulated. The liquid sample is collected via the sampling port, and the vapor sample is taken on-line by a six-port sampling valve with a 15 μL sampling loop. Both vapor and liquid samples are analyzed by gas chromatograph (GC) equipped with a flame ionization detector (FID) (model GC112A, China). The reproducibility of the composition results was verified by several measurements under the same conditions of pressure and temperature with gravimetrically prepared mixtures, which allow us to estimate their uncertainty of the mole fraction to be ± 0.002.

The experimental procedure is as follows: (1) the system was first evacuated; (2) (pentafluoroethane + fluoroethane) was introduced into cell, and then the temperature of the entire system was maintained by the thermostatic bath; (3) the vapor in the cell was circulated continuously with the magnetic activated circulation pump until an equilibrium state was established; (4) about 1 h is sufficient to obtain the thermal equilibrium state between the cell fluid and the thermostatic bath; (5) after the desired temperature was attained, the pressure in the equilibrium cell was measured and the (vapor + liquid) samples were withdrawn from the recycling lines for analysis; and (6) the compositions of the samples were measured by immediately injecting them into the GC. The experimental data at the equilibrium state were measured at least three times in order to ensure the reproducibility. The isothermal VLE data for the binary mixture (pentafluoroethane + fluoroethane) are listed in Tables 1 to 3.

Table 5. Correlated Results of the VLE Data for the Binary Mixture (Pentafluoroethane + Fluoroethane) at Different Temperatures Using PR + LCVM and PR + Modified LCVM Models

		PR + LCVM				PR + modified LCVM				interaction parameters	
T/K	N_p	Δy	δp	max Δy	max δp	Δy	δp	max Δy	max δp	τ_{12}	τ_{21}
265.15	12	0.0115	0.8063	0.0217	2.0168	0.0088	0.9223	0.0186	1.8912	1.5835	−1.0083
275.15	11	0.0146	0.6806	0.0253	1.6011	0.0111	0.8339	0.0195	1.7083	1.9084	−1.1599
283.15	12	0.0171	1.1365	0.0278	1.5809	0.0136	1.6653	0.0222	1.9566	1.6420	−1.1159
293.15	14	0.0191	0.6841	0.0357	1.5692	0.0145	0.9210	0.0296	1.9450	1.0306	−0.7210
303.15	11	0.0092	0.9404	0.0188	2.1536	0.0089	1.0384	0.0186	2.1036	−0.9732	2.5019
313.15	10	0.0133	0.4005	0.0207	0.6408	0.0127	0.3460	0.0211	0.6316	−1.0968	2.9440

Correlations

The Peng−Robinson equation of state[4] is given by

$$p = \frac{RT}{v - b} - \frac{a}{v^2 + 2vb - b^2} \tag{1}$$

$$a = 0.45724R^2T_c^{\ 2}/p_c\alpha(T) \tag{2}$$

and

$$b = 0.07780RT_c/p_c \tag{3}$$

where p is the pressure, v is the molar volume, T is the absolute temperature, R is the universal gas constant, a and b are adjustable parameters, T_c is the critical temperature, p_c is the critical pressure, and ω is the acentric factor. The values of T_c, p_c, and ω for each pure substance are listed in Table 4, and these were obtained from refs 5 and 6.

The mixing rules used to correlate the VLE data are the LCVM mixing rule:[6]

$$\frac{a_m}{b_mRT} = \lambda\alpha_v + (1-\lambda)\alpha_M = \left(\frac{\lambda}{C^{HV}} + \frac{1-\lambda}{C^{MHV1}}\right)\frac{G_\gamma^{\ E}}{RT} + \frac{1-\lambda}{C^{MHV1}}\sum_i x_i \ln\left(\frac{b_m}{b_i}\right) + \sum_i x_i\frac{a_i}{b_iRT} \tag{4}$$

$$b_m = \sum_i x_ib_i \tag{5}$$

where G is the Gibbs free energy; $\alpha = a/(bRT)$; the subscript m stands for mixture; the superscripts E, HV, and MHV1 are excess property, Huron−Vidal mixing rule, first Modified Huron−Vidal mixing rule, respectively; x_i is the liquid mole fraction; λ is a parameter that determines the relative contributions of MHV1 and HV models and was obtained by fitting bubble point pressure for a variety of binary mixtures at high and low pressure. The empirical value of parameter λ is set equal to 0.36.[7]

The second set of mixing rules used are the modified LCVM mixing rule proposed by Han and Chen,[8] its expressions are

$$\frac{a_m}{b_mRT} = \left(\frac{\lambda}{C^{HV}} + \frac{1-\lambda}{C^{MHV1}}\right)\frac{A_\gamma^{\ E}}{RT} + \frac{1-\lambda}{C^{MHV1}}\sum_i x_i \ln\left(\frac{b_m}{b_i}\right) + \sum_i x_i\frac{a_i}{b_iRT} \tag{6}$$

$$b_m = \frac{\sum_i^{x_i}\left(b_i - \frac{a_i}{RT}\right)}{1 - \sum_i x_i\frac{a_i}{b_iRT} - \left(\frac{\lambda}{C^{HV}} + \frac{1-\lambda}{C^{MHV1}}\right)\frac{A_\gamma^{\ E}}{RT} - \frac{1-\lambda}{C^{MHV1}}\sum x_i \ln\frac{b_m}{b_i}} \tag{7}$$

Where A^E is the excess Helmholtz energy, obtained by the excess Gibbs model,[9] and the subscript γ is the activity coefficient.

The excess Gibbs energy and excess Helmholtz energy are calculated using the NRTL local composition model:[10]

$$\frac{G_{(T,P)}^E}{RT} = \sum_i x_i \sum_j \frac{x_j \exp\left(-\alpha_{j,i}\frac{\tau_{j,i}}{RT}\right)}{\sum_k x_k \exp\left(-\alpha_{k,i}\frac{\tau_{k,i}}{RT}\right)}\tau_{j,i} \tag{8}$$

where $\alpha_{j,i}$, $\tau_{j,i}$, and $\tau_{i,j}$ are adjustable parameters; $\tau_{i,i} = 0$; and $\alpha_{i,i} = 0$. For the system in this work, the third parameter α_{ij} in the NRTL model was set equal to 0.3.

Results and Discussion

Using the models of the LCVM and the modified LCVM mixing rule with PR EOS, respectively, VLE data of the binary mixture (pentafluoroethane + fluoroethane) were correlated in which the NRTL activity coefficient model is used to calculate the excess Gibbs free energy. For the correlation of the experimental data, a computer program has been developed applying the least-squares method. The correlated results are shown in Table 3 and Figures 2 and 3. The deviations, δp (%) and Δy listed in the tables are defined by

$$\delta p = 1/N_p\sum_i |(p_{cal} - p_{exp})/p_{exp}|_i \times 100 \tag{9}$$

$$\Delta y = 1/N_p\sum_i |y_{cal} - y_{exp}|_i \tag{10}$$

where N_p is the number of components; p_{cal} and p_{exp} are calculated pressure, experimental pressure, respectively; y_{cal} and y_{exp} are calculated vapor mole fraction, and experimental vapor mole fraction, respectively.

From the results listed in Table 5 and Figures 2 and 3, we can see that within a wide range of temperatures and pressures, both models have the better agreement with existing experimental data. In comparison with the LCVM model, the modified LCVM mixing rule gives much better predictions for the VLE of (pentafluoroethane + fluoroethane).

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