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Vapor−Liquid Equilibrium Measurements and Correlation of the Binary Refrigerant Mixture Propane (HC-290) + 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea) at 278.15, 293.15, and 308.15 K

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Isothermal vapor−liquid equilibria for the binary system propane (HC-290) + 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) were measured at 278.15, 293.15, and 308.15 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; calibration of the response was made with gravimetrically prepared mixtures. The system shows a major deviation from Raoult's law, with the formation of a homogeneous azeotrope at a mole fraction of propane of about 0.8. The uncertainties in pressure, temperature, and vapor- and liquid-phase composition measurements were estimated to be no more than ±1 kPa, ±0.02 K, and ±0.002 in the mole fraction, respectively. The data were reduced using the Carnahan Starling De Santis (CSD) equation of state (EoS) and the Lemmon−Jacobsen (LJ) Helmholtz energy mixture model. A comparison was made with VLE calculations from REFPROP 6.0 for both the experimental data and the data reduction models.

Introduction

This paper presents measurements of isothermal VLE *P*, *T*, *x*, *y* data for the binary refrigerant system HC-290 + HFC-227ea, ranging from 278.15 K and 308.15 K, to increase our knowledge of the thermodynamic properties of binary mixtures that are considered to be substitutes for CFCs in refrigeration, air-conditioning, and heat pump applications. Mixtures of hydrocarbons and HFCs are interesting in view of their simultaneous containment of global warming impact (HFCs) and flammability (HCs). Moreover, this mixture has been selected as the system that is homomorphic to the mixture dimethyl ether (RE170) + HFC-227ea, currently being measured, to evaluate the hydrogen bonding interaction between HFCs and RE170.[1−3] This work will provide a better understanding of the molecular interaction between HFCs and ethers, which provides a basis for predicting the solubility of refrigerants in lubricant oils. To our knowledge, no data are currently available on the thermodynamic properties of this binary mixture.

Experimental Section

Materials. HFC-227ea (Solvay) had 0.2% impurities detected by gas chromatography using both the flame ionization detector (FID) and the thermal conductivity detector (TCD). HC-290 (Air Liquide) had a declared purity greater than 99.95%, and no impurities were detected by the FID or TCD. To eliminate the noncondensable gases, each sample underwent several cycles of freezing with liquid nitrogen, evacuation, thawing, and ultrasound.

Apparatus. The recirculation VLE apparatus and the procedures used in this study have already been presented in detail.[4] The VLE was reached in a stainless steel cell of about 50 cm^3 capacity equipped with a magnetic pump. The VLE cell and the magnetic pump were immersed in a thermostatic water bath of about 100 L capacity.

The temperature in the bath was kept stable at ±1 mK throughout the measurements by means of a proportional, integral, derivative (PID) control system governing a heater immersed in the bath. An auxiliary cooler was used to compensate for the heat produced by the PID control system and to keep the temperature below or near ambient temperature.

Temperature was measured with a 100 Ω platinum resistance thermometer (ISOTECH 909/100), and the uncertainty in the temperature measurements was estimated to be ±0.02 K.

Pressure was measured by means of a pressure gauge (RUSKA 6000) with a full scale reading of 3500 kPa. A differential pressure cell (RUSKA 2413) immersed in the thermostatic bath was used to separate the chemicals from the quartz sensor of the pressure gauge. The uncertainty in the pressure measurement was estimated to be within ±1 kPa, estimated by taking into account the accuracy of the pressure transducer and the stability of the pressure during the measurements.

The compositions of the vapor and liquid phases were measured 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 were performed under the conditions shown in Table 1. The detector's response was carefully calibrated using gravimetrically prepared mixtures. Considering the reproducibility of gas chromatography, the stability of the composition during the measurements, and the uncertainty in calibration, we estimated the accuracy of composition measurements to be within ±0.002 for the mole fraction of both the liquid and the vapor phases.

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Table 1. Gas Chromatography Parameters

	Column				Detector		
oven temp/K	length/m	i.d./mm	carrier (N_2) flow rate/$cm^3 \cdot min^{-1}$	packing	type	air flow rate/$cm^3 \cdot min^{-1}$	hydrogen flow rate/$cm^3 \cdot min^{-1}$
403	2	3.175	130	Poropak N	FID	400	40

Table 2. Experimental Vapor−Liquid Equilibrium Data for the HC-290 (1) + HFC-227ea (2) System at T = 278.15 K, 293.15 K, and 308.15 K

T = 278.15 K			T = 293.15 K			T = 308.15 K		
$x_{1,\text{exp}}$	$y_{1,\text{exp}}$	P_{exp}/kPa	$x_{1,\text{exp}}$	$y_{1,\text{exp}}$	P_{exp}/kPa	$x_{1,\text{exp}}$	$y_{1,\text{exp}}$	P_{exp}/kPa
0.0000	0.0000	234.6	0.0000	0.0000	389.1	0.0000	0.0000	610.5
0.0471	0.2176	297.6	0.0295	0.1286	443.7	0.1069	0.2851	822.9
0.0978	0.3601	351.7	0.1002	0.3225	550.1	0.2887	0.5015	1059.4
0.1799	0.4968	423.3	0.1964	0.4621	655.6	0.3968	0.5783	1151.8
0.3224	0.6122	497.6	0.3249	0.5691	752.6	0.4799	0.6264	1205.9
0.4992	0.6913	549.8	0.4888	0.6579	831.1	0.5984	0.6881	1259.7
0.6667	0.7521	578.5	0.6857	0.7459	882.9	0.7116	0.7474	1291.9
0.7251	0.7760	584.5	0.7061	0.7553	885.7	0.7907	0.7943	1300.2
0.7552	0.7873	586.6	0.7516	0.7774	890.8	0.8394	0.8272	1298.2
0.7757	0.7966	587.8	0.7915	0.7983	892.9	0.8622	0.8458	1294.6
0.8489	0.8363	588.1	0.8395	0.8280	892.5	0.9534	0.9333	1257.8
0.9173	0.8881	580.3	0.9253	0.8996	876.9	1.0000	1.0000	1216.1
1.0000	1.0000	550.9	0.9660	0.9464	859.1			
			1.0000	1.0000	835.7			

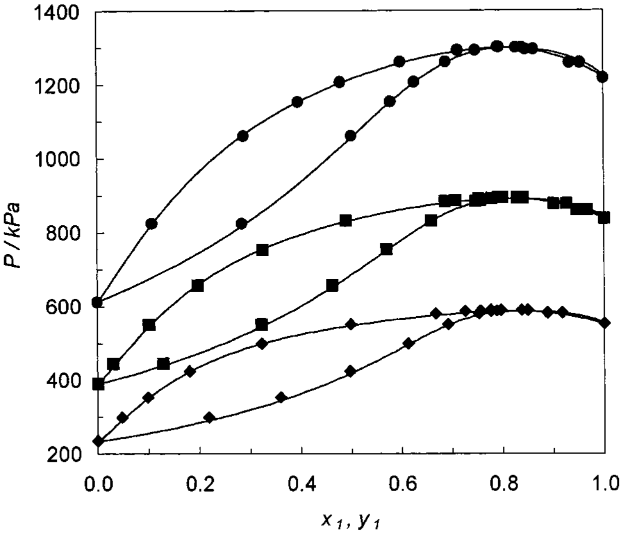

Figure 1. Vapor−liquid equilibrium experimental data for HC-290 (1) + HFC-227ea (2): T = 278.15 K (◆), 293.15 K (■), and 308.15 K (●); Lemmon−Jacobsen model fit (—).

Table 3. Azeotropic Points for the Mixture HC-290 + HFC-227ea Extrapolated from Experimental Data by Zeroing an Analytical Equation Expressing ($y - x$) as a Function of (x)

T/K	x_{azeo}	P_{azeo}/kPa
278.15	0.822	588.7
293.15	0.811	893.3
308.15	0.804	1300.2

Table 4. Critical Parameters of HC-290 and HFC-227ea

compd	T_c/K	P_c/kPa	source
HC-290	369.80	4242.0	ASHRAE[5]
HFC-227ea	375.95	2987.7	Shi et al.[6]

Results and Discussion

In total, 39 P, x, y equilibrium data points (including pure compound vapor pressures) for the mixture under study were measured along three isotherms at temperatures of 278.15 K, 293.15 K, and 308.15 K. The experimental data are presented in Table 2 and Figure 1. Throughout the paper, x and y indicate the liquid and vapor mole fractions, respectively, while P stands for the pressure in kilopascals.

The system shows a marked positive deviation from Raoult's law with the presence of a homogeneous azeotrope. The composition of the azeotrope at each temperature was evaluated by setting equal to zero an analytical equation expressing the difference between the dew point and the bubble point composition ($y - x$) as a function of the bubble point composition (x). Azeotropic pressure was evaluated as the maximum of a polynomial function interpolating the experimental bubble points. The results are shown in Table 3.

Pure Fluid Vapor Pressures. The experimental vapor pressures of the pure compounds measured in this work were compared with data reported in the literature. To calculate the vapor pressures of HFC-227ea at our temperatures, the dedicated equation proposed by Shi et al.[6] was used. As for HC-290, the data in the literature[7,8] were regressed with a Wagner equation[9] and the pure compounds' critical parameters given in Table 4: the results are shown in Table 5. There is very good consistency between our findings and data found in the literature, except for the data measured by Higashi et al.;[7] however, these authors declared an uncertainty in pressure measurement of up to ±5 kPa. In the case of HFC-227ea, a very good agreement was found with the data of Shi et al.[6]

VLE Data Reduction. For the VLE data reduction, the Carnahan Starling De Santis (CSD) equation of state (EoS) was first considered in the form proposed in ref 10, using the classic mixing rules and the pure fluid coefficients taken from ref 11. This is a typical approach for calculation of saturation properties, because of its simplicity. It requires only a single interaction parameter, and vapor−liquid equilibria are often well represented, though large deviations must be accepted in the calculation of other thermodynamic properties.

The interaction parameter k_{ij} was optimized by minimizing the following objective function:

$$\text{obf} = \sum_{i=1}^{N_p} \frac{\text{abs}(\Delta P)}{P_{\text{exp}}} \tag{1}$$

where N_p is the number of experimental data points, $\Delta P = P_{\text{cal}} - P_{\text{exp}}$, P_{cal} is the saturated pressure calculated by

Table 5. Vapor Pressures of Pure Compounds: Comparison between Experimental Data from This Study and Values Calculated from the Literature

		T/K = 278.15			T/K = 293.15			T/K = 308.15		
fluid	ref	P/kPa	$P - P_{tw}$/kPa	δP^a	P/kPa	$P - P_{tw}$/kPa	δP^a	P/kPa	$P - P_{tw}$/kPa	δP^a
HFC-227ea	*b*	234.6			389.1			610.5		
	6	234.8	0.2	0.08	389.0	0.1	0.02	610.5	0.0	0.00
HC-290	*b*	550.9			835.7			1216.1		
	7	558.7	7.8	1.39	845.0	9.3	1.11	1224.2	8.1	0.66
	8	550.5	−0.4	−0.07	836.3	0.6	0.07	1218.9	2.8	0.23

[a] $\delta P = 100\{(P_{exp} - P_{tw})\}/\{P_{exp}\}$. [b] This work.

Table 6. Results of VLE Data Reduction Using Different Models

	HC-290 + HFC-227ea								
	CSD EoS			LJ model			REFPROP 6.0		
T/K	278.15	293.15	308.15	278.15	293.15	308.15	278.15	293.15	308.15
δP^a	−0.25	−0.21	−0.22	0.71	0.35	-0.04	19.3	16.4	16.3
Abs$(\delta P)^b$	0.89	0.72	0.56	0.71	0.48	0.21	19.3	16.4	16.4
$10^2\delta y^c$	0.33	0.28	0.10	−0.34	-0.12	-0.15	1.0	0.21	-0.46
10^2Abs$(\delta y)^d$	0.37	0.36	0.20	0.39	0.28	0.19	8.0	6.6	5.1
δP_{azeo}	1.37	1.00	0.65	−0.66	-0.37	-0.11			
$10^2\delta y_{azeo}$	−2.13	−1.40	−0.74	1.13	1.05	0.53			
	k_{ij}	0.1177	K_T	0.8347					
			K_V	0.9446					
			F_{PQ}	0.0694					
			β	1.1044					
			γ	0.8970					

[a] $\delta P = \frac{100}{N_p}\sum_{i=1}^{N_p}[(P_{cal} - P_{exp})/P_{exp}]_i$. [b] $\text{Abs}(\delta P) = \frac{100}{N_p}\sum_{i=1}^{N_p}[|P_{cal} - P_{exp}|/P_{exp}]_i$. [c] $\delta y = \frac{1}{N_p - 2}\sum_{i=2}^{N_p-1}(y_{cal} - y_{exp})_i$. [d] $\text{Abs}(\delta y) = \frac{1}{N_p - 2}\sum_{i=2}^{N_p-1}(|y_{cal} - y_{exp}|)_i$

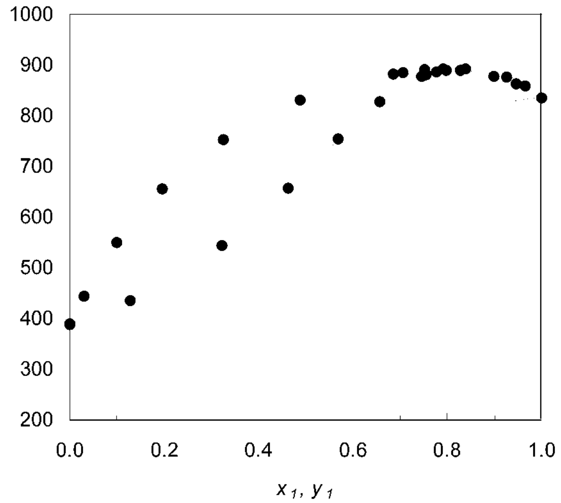

Figure 2. Vapor−liquid equilibrium experimental data for HC-290 (1) + HFC-227ea (2) at T = 293.15: (●) experimental data; (—) LJ model; (- - -) REFPROP 6.0 database fit.

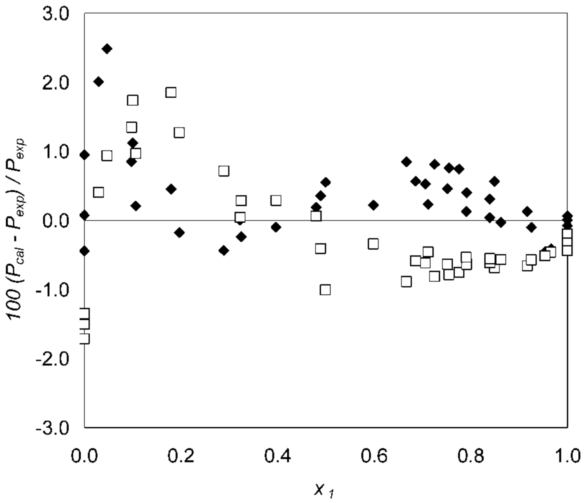

Figure 3. Percentage deviations of saturated pressure from experimental data for the CSD equation of state (□) and the LJ model (◆) for all isotherms.

the CSD EoS, and P_{exp} is the experimental pressure. The results of data regression show that the interaction parameter can be considered constant in the experimental range of temperatures. Values and deviations are shown in Table 6.

Next, the Lemmon−Jacobsen (LJ) free Helmholtz energy model[12,13] for mixtures was considered. The equations used for the pure compounds were taken from REFPROP 6.0.[14] This approach is rather complicated, and for systems with a markedly nonideal behavior, it requires up to five interaction parameters to produce acceptable results, though it achieves only a slightly better prediction of the vapor−liquid equilibrium than the CSD EoS. However, since it is based on a fundamental thermodynamic potential such as the Helmholtz energy, it enables the calculation of all the other thermodynamic properties with a greater accuracy than that of a classic EoS. The five interaction parameters were optimized by minimizing the same objective function (eq 1), as for the CSD EoS, and the results obtained are shown in Table 6. It is evident from the results of the regression that the parameters can be kept constant within the experimental range of temperatures. The calculated saturation boundaries are compared with the experimental data in Figure 1.

Finally, the experimental data were compared with those of REFPROP 6.0, where the same model is used with neutral interaction parameters. The database is clearly unable to satisfactorily predict the saturation boundaries (or the azeotropic behavior), as shown in Figure 2 for the isotherm at T = 293.15 K; the deviations are given in Table 6.

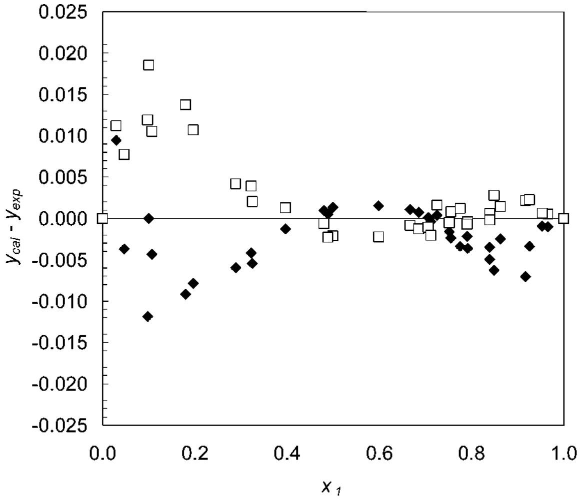

Figure 4. Absolute deviations of vapor-phase composition from experimental data for the CSD equation of state (□) and the LJ model (◆) for all isotherms.

Conclusions

The system considered in this paper shows a strong positive deviation from Raoult's law with the presence of an azeotrope at an HFC-290 mole fraction of about 0.8, as shown in Table 3. This behavior is very similar to that of the corresponding mixtures formed by HC + HFC.[4,15−17]

The vapor−liquid equilibria of the system are well represented by the CSD EoS with the classical mixing rules, but better results are obtained with the LJ model. This is an interesting result, since all the thermodynamic properties can be calculated through the Helmholtz energy by simple partial derivation and certainly with a greater accuracy than that with the classic cubic EoS. The deviations in pressure and vapor-phase compositions for the two models are shown in Figures 3 and 4.

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