Isothermal Vapor−Liquid Equilibrium Data for the Hexafluoroethane (R116) + Propane System at Temperatures from (263 to 323) K

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Isothermal vapor−liquid equilibrium data are presented for the system hexafluoroethane (R116) + propane. Measurements were performed for six isotherms (three isotherms below and three above the critical temperature of R116) ranging from (263.3 to 323.19) K, with pressure ranging from (0.344 to 3.851) MPa. The measurements were undertaken using a "static-analytic" type apparatus, with sampling of the equilibrium phases via pneumatic capillary samplers (Rolsi, Armine's patent). The apparatus as well as the samplers were developed in the CEP/TEP laboratory. The uncertainties in the measurements were within ± 0.01 K, ± 0.0003 MPa, and < 2.0 % for temperatures, pressures, and mole fractions, respectively. The full set of isothermal vapor−liquid equilibrium data was correlated with the Peng−Robinson equation of state, incorporating the Mathias−Copeman alpha function, with the Wong−Sandler mixing rule utilizing the NRTL activity coefficient model.

Introduction

There is a growing interest from Industry in the application of refrigerants as solvents for separation. To this effect, the suitability of hexafluoroethane (R116) as a separating agent for light hydrocarbons is being investigated. The critical temperatures of R116 and propane are significantly different (refer to Table 1), and therefore no azeotrope should be expected for this system. However, quasiazeotropic behavior is still useful for separation, especially for supercritical fluid extraction. Therefore, vapor−liquid equilibrium (VLE) measurements were undertaken at six isotherms for the system: three isotherms below and three above the critical temperature of R116. The system has not previously been studied, and the measurements represent new data. The data will also enable the improvement of the predictive Soave−Redlich−Kwong (PSRK) equation of state interaction parameters for certain functional groups, with the possibility of determining a separate functional group for R116 as a single molecule.

Measurements of binary VLE for systems containing R116 have been previously undertaken by Zhang et al.[1,2] with ethane, by Valtz et al.[3] with carbon dioxide, and by Madani et al.[4] with 1,1,1,2-tetrafluoroethane.

The measured VLE data were correlated with the Peng−Robinson equation of state, incorporating the Mathias−Copeman alpha function, with the Wong−Sandler mixing rule utilizing the NRTL activity coefficient model. The model parameters and the critical temperature and pressure locus for the system are also presented. This system corresponds to a type I system according to the classification of van Konynenburg and Scott.[5]

Table 1. Critical Parameters and Acentric Factor[17]

compound	T_c/K	P_c/MPa	ω
R116	293.04	3.042	0.229
Propane	369.95	4.246	0.152

Table 2. Mathias−Copeman Coefficients

coefficients	R116[a]	propane[14]
c_1	0.79629	0.600066
c_2	−0.55124	−0.006303
c_3	0.10316	0.173899

[a] Regressed from vapor pressure data from ref 3.

Table 3. *P*−*x*−*y* Data for the R116 (1) + Propane (2) System at (263.30, 283.25, and 291.22) K

T = 263.30 K			T = 283.25 K			T = 291.22 K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.344	0.000	0.000	0.639	0.000	0.000	0.795	0.000	0.000
0.453	0.019	0.218	0.784	0.020	0.168	0.958	0.020	0.149
0.651	0.063	0.450	0.944	0.045	0.296	1.155	0.048	0.281
0.849	0.135	0.581	1.117	0.079	0.401	1.350	0.083	0.377
1.053	0.286	0.677	1.332	0.136	0.491	1.551	0.130	0.455
1.198	0.490	0.743	1.501	0.197	0.556	1.758	0.190	0.520
1.298	0.652	0.802	1.705	0.302	0.620	1.956	0.269	0.574
1.373	0.844	0.878	1.914	0.451	0.682	2.161	0.377	0.624
1.406	0.961	0.963	2.103	0.616	0.747	2.361	0.502	0.676
1.392[a]	1.000	1.000	2.224	0.735	0.802	2.558	0.637	0.736
			2.298	0.814	0.851	2.727	0.763	0.807
			2.343	0.873	0.892	2.835	0.860	0.876
			2.378	0.946	0.949	2.880	0.917	0.924
			2.384[a]	1.000	1.000	2.893	0.941	0.945
						2.925[a]	1.000	1.000

[a] Vapor pressure of propane calculated from correlation.[14]

Experimental

Materials. R116 was purchased from Air Liquide and has a certified purity of greater than 99.999 vol %. Propane was obtained from Messer and has a certified minimum purity of 99.95 vol %. Both chemicals were used without further

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Table 4. $P-x-y$ Data for the R116 (1) + Propane (2) System at (296.23, 308.21, and 323.19) K

$T = 296.23$ K			$T = 308.21$ K			$T = 323.19$ K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.906	0.000	0.000	1.221	0.000	0.000	1.715	0.000	0.000
1.065	0.018	0.127	1.503	0.029	0.152	2.040	0.030	0.125
1.318	0.052	0.277	1.905	0.084	0.308	2.493	0.083	0.254
1.507	0.085	0.360	2.306	0.160	0.415	3.008	0.164	0.353
1.711	0.127	0.431	2.704	0.264	0.499	3.397	0.241	0.405
1.917	0.180	0.492	3.103	0.406	0.565	3.604	0.296	0.429
2.120	0.250	0.543	3.326	0.502	0.597	3.717	0.332	0.438
2.338	0.345	0.593	3.449	0.569	0.601	3.803	0.363	0.436
2.552	0.459	0.643				3.851	0.392	0.421
2.713	0.555	0.681						
2.890	0.661	0.731						
3.003	0.731	0.770						
3.087	0.784	0.804						
3.118	0.808	0.816						

Table 5. Model Parameters Regressed for the Peng−Robinson EoS with Mathias−Copeman Alpha Parameters and Wong−Sandler Mixing Rule Incorporating the NRTL Activity Coefficient Model

	temperature/K					
parameter	263.30	283.25	291.22	296.23	308.21	323.19
τ_{12}/J·mol^{-1}	2157	1773	1618	1058	1045	1139
τ_{21}/J·mol^{-1}	2946	2949	2911	3228	3352	3428
k_{12}	0.136	0.160	0.175	0.205	0.193	0.178

purification. The critical properties and parameters used in the data correlation are listed in Table 1.

Experimental Apparatus. The apparatus used for the VLE measurements in this work is based on a "static-analytic" method with sampling of both the liquid and vapor phases. The apparatus is similar to that described by Laugier and Richon[6] and Valtz et al.[7,8]

The equilibrium cell was immersed inside a temperature regulated liquid bath. The temperature of the equilibrium cell was measured with two platinum resistance thermometer probes (Pt-100) inserted into the walls of the equilibrium cell. Both Pt-100 probes were calibrated against a 25 Ω reference probe (TINSLEY Precision Instrument) certified by the Laboratoire National d'Essais (Paris) following the International Temperature Scale 1990 Protocol.

Pressures were measured using a pressure transducer (Druck, type PTX 611; range, (0 to 20) MPa). This sensor was calibrated against a dead weight pressure balance (model 5202S supplied by Desgranges and Huot).

Pressure and temperature data were recorded via a computer linked to an HP Data Acquisition Unit (HP34970A). The resulting uncertainties in the temperature and pressure measurement in this work are ± 0.01 K and ± 0.0003 MPa, respectively.

Analysis of samples of the equilibrium phases was performed using a gas chromatograph (VARIAN model CP-3800) equipped with a thermal conductivity detector (TCD) which was connected to a data acquisition system (BORWIN Ver 1.5, from JMBS). The analytical column used was Poropak Q model with 80/100 mesh (1/8" Silcosteel tube, 4 m length) supplied by Restek, France. The TCD was calibrated by repeated injections of known amounts of each pure component into the injector of the gas chromatograph using a gastight syringe. Taking into account the uncertainties due to calibrations and the deviations of analyses, the resulting uncertainties in vapor and liquid mole fractions are estimated to be less than < 2.0 %.

Experimental Procedure. The equilibrium cell and its associated loading lines are prior to any measurements evacuated to a pressure of approximately 0.1 Pa. This is undertaken at room temperature. The cell is then loaded with liquid propane (approximately 5 cm^3). The equilibrium temperature is assumed to be reached when the two Pt-100 probes (one located at the top of the equilibrium cell, the other in the bottom) give equivalent temperature values to within experimental uncertainty for a period of at least 10 min. After recording the vapor pressure of propane (the heavier component) at the equilibrium temperature, measurements of the equilibrium phases for various different compositions are undertaken. The composition is varied by the addition of R116 (the lighter component) and is introduced stepwise, leading to successive equilibrium mixtures of increasing overall R116 content. After each new R116 loading, equilibrium is assumed when the total pressure remains unchanged to within ± 1.0 kPa during a period of 10 min of rapid stirring.

For each equilibrium condition, at least five samples of both the vapor and liquid phases are withdrawn using the ROLSI pneumatic samplers[9] (www.rolsi.com) and analyzed to check for reproducibility of measurements.

Correlations

The critical temperatures (T_c), critical pressures (P_c), and acentric factors (ω) for each of the two pure components are provided in Table 1. The experimental VLE data were correlated using Thermosoft, in-house software developed by Armines/Ecole des Mines de Paris. The data were correlated using the PR EoS[10] incorporating the Mathias−Copeman alpha function[11] for accurate representation of the vapor pressures of each component. The Mathias−Copeman alpha function (eq 1) has three adjustable parameters (C_i) and was developed specifically for polar compounds. The Mathias−Copeman alpha function coefficients for both components are listed in Table 2.

$$\alpha(T) = \left[1 + c_1\left(1 - \sqrt{\frac{T}{T_c}}\right) + c_2\left(1 - \sqrt{\frac{T}{T_c}}\right)^2 + c_3\left(1 - \sqrt{\frac{T}{T_c}}\right)^3\right]^2 \quad (1)$$

If $T > T_c$

$$\alpha(T) = \left[1 + c_1\left(1 - \sqrt{\frac{T}{T_c}}\right)\right]^2 \quad (2)$$

The Wong−Sandler (WS)[12] mixing rule was used utilizing the NRTL activity coefficient model.[13]

$$b = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij}}{1 - \left(\frac{\sum_i x_i \frac{a_i}{b_i}}{RT} + \frac{g^E(T, P = \infty, x_i)}{CRT}\right)} \quad (3)$$

$$b - \frac{a}{RT} = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \quad (4)$$

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b - \frac{a}{RT}\right)_i + \left(b - \frac{a}{RT}\right)_j\right](1 - k_{ij}) \quad (5)$$

k_{ij} is an adjustable binary interaction parameter.

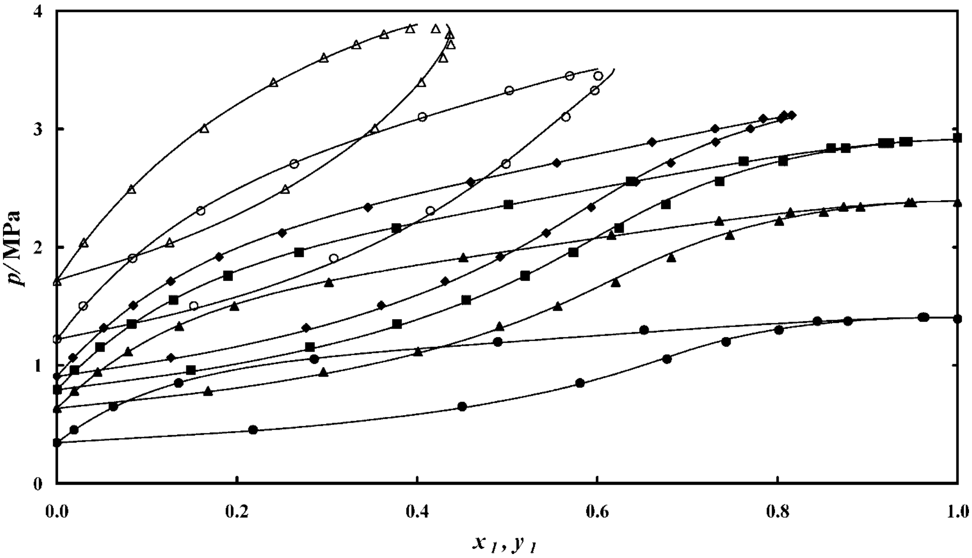

Figure 1. Plot of the $P-x-y$ data for the system R116 (1) + propane (2) (△, T = 323.19 K; ○, T = 308.21 K; ◆, T = 296.23 K; ■, T = 291.22 K; ▲, T = 283.25 K; ●, T = 263.30 K; —, model).

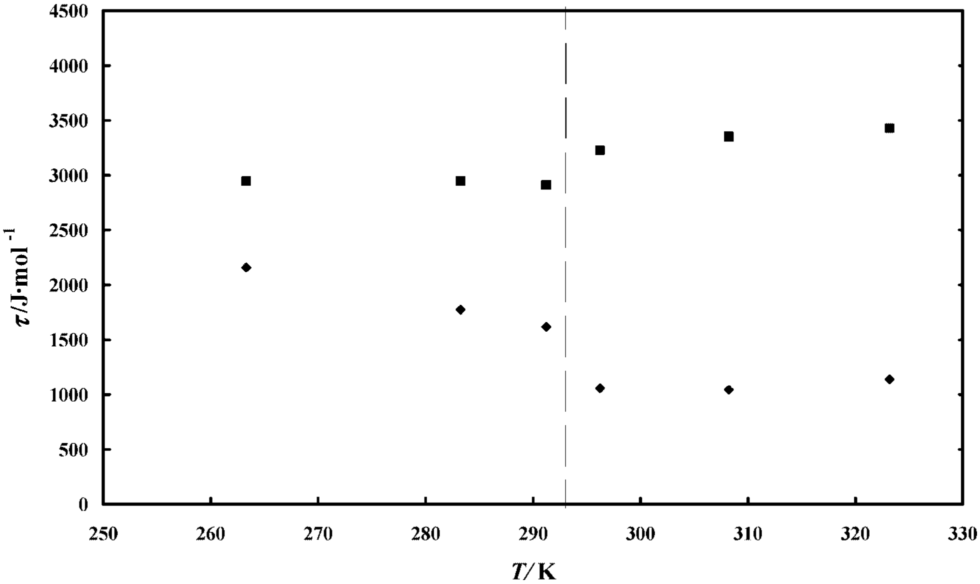

Figure 2. Plot of the NRTL model parameters versus the temperature for the six VLE isotherms measured (◆, τ_{12}; ■, τ_{21}; - - -, critical temperature of R116).

Table 6. Relative Deviation of MRDU and BIASU Obtained in Fitting Experimental VLE Data with PR EoS, Mathias−Copeman Alpha Function, and WS Mixing Rules Involving the NRTL Model

T/K	Bias x %	MRD x %	Bias y %	MRD y %
263.30	−1.19	2.11	−0.60	1.46
283.25	−0.46	1.63	−0.46	1.47
291.22	−0.53	1.62	−0.55	1.36
296.23	−0.38	1.41	−0.94	1.54
308.21	−0.22	1.43	−1.84	2.39
323.19	0.07	1.03	−0.46	1.28

The excess Gibbs energy model chosen is the NRTL local composition model.

$$\frac{g^{E}(T,P,x_i)}{RT} = \sum_i x_i \sum_j \frac{x_j \exp\left(-\alpha_{ji}\frac{\tau_{ji}}{RT}\right)}{\sum_k x_k \exp\left(-\alpha_{ki}\frac{\tau_{ki}}{RT}\right)}\tau_{ji} \qquad (6)$$

$\tau_{ii} = 0$ and $\alpha_{ii} = 0$.

α_{ji}, τ_{ji}, and τ_{ij} are adjustable parameters. It is recommended[14] to use $\alpha_{ji} = 0.3$ for systems like this one. τ_{ji} and τ_{ij} are adjusted directly onto VLE data through a modified Simplex algorithm using the following objective function

$$F = \frac{100}{N}\left[\sum_{1}^{N}\left(\frac{x_{\text{exp}} - x_{\text{cal}}}{x_{\text{exp}}}\right)^2 + \sum_{1}^{N}\left(\frac{y_{\text{exp}} - y_{\text{cal}}}{y_{\text{exp}}}\right)^2\right] \qquad (7)$$

where N is the number of data points; x_{exp} and x_{cal} are, respectively, the measured and calculated liquid phase mole fractions; and y_{exp} and y_{cal} are, respectively, the measured and calculated vapor phase mole fractions.

Discussion

The experimental VLE data are presented in Tables 3 and 4 for the isotherms below and above the critical temperature of R116, respectively. The model parameters for the Peng−Robinson EoS with the Mathias−Copeman alpha correlation with

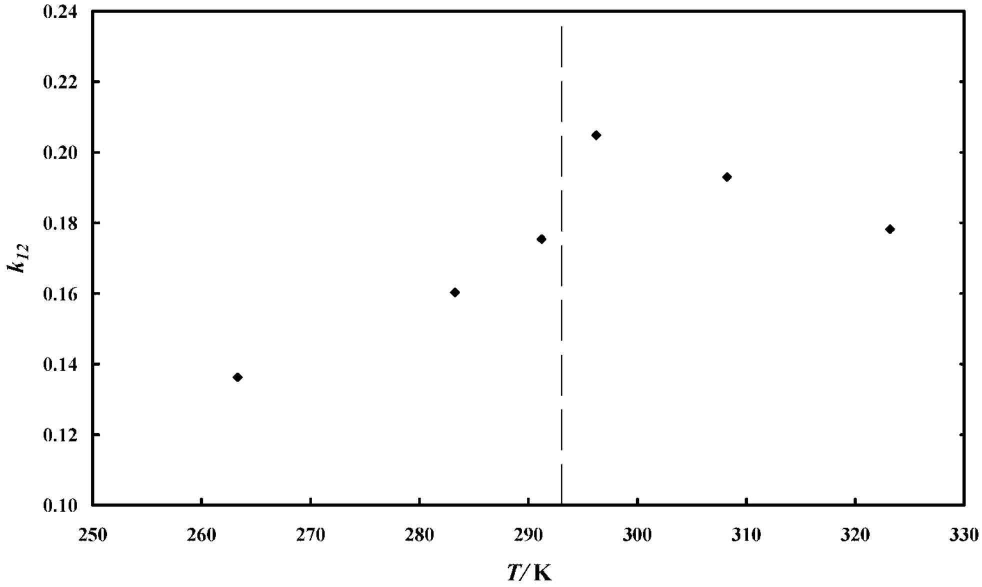

Figure 3. Plot of the EoS binary interaction parameter (k_{12}) versus temperature for the six isotherms measured (- - -, critical temperature of R116).

Wong−Sandler mixing rules incorporating the NRTL activity coefficient model are presented in Table 5. Graphical representation of the measured experimental data along with the fitted model is presented in Figure 1.

The deviation, MRDU, and the BIASU, applied on liquid and vapor phase mole fractions, are defined by

$$\mathrm{MRDU} = (100/N)\sum |(U_{\mathrm{cal}} - U_{\mathrm{exp}})/U_{\mathrm{exp}}| \qquad (8)$$

$$\mathrm{BIASU} = (100/N)\sum ((U_{\mathrm{exp}} - U_{\mathrm{cal}})/U_{\mathrm{exp}}) \qquad (9)$$

where N is the number of data points, and $U = x_1$ or y_1.

These indicators, which give information about the agreement between model and experimental results, are presented in Table 6.

There is a discontinuity of the correlated model parameters, as can be observed in Figures 2 and 3 for the NRTL and EoS binary interaction parameters, respectively. The discontinuity occurs at a temperature corresponding to the critical temperature for R116. This discontinuity phenomenon was observed in previous studies;[8,15,16] i.e., the parameters τ_{12}, τ_{21}, and k_{12} behave differently below and above the critical temperature of the light component.

Conclusions

In this paper, VLE data for the R116 + propane system are presented at six temperatures. Measurements were undertaken using a "static-analytic" method. The data were correlated with the Peng−Robinson EoS, with the Mathias−Copeman alpha function and the Wong−Sandler mixing rules incorporating the NRTL model. The experimental results are given with the following uncertainties: ± 0.01 K, ± 0.0003 MPa, and < 2.0 % for vapor and liquid mole fractions.

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