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Isothermal Vapour-Liquid Equilibrium Data for Binary Mixtures of Hexafluoroethane (R116) + n-Pentane or n-Hexane at Temperatures of 288 K and 297 K

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Abstract

The isothermal vapour-liquid equilibrium (VLE) data for two hexafluoroethane (R-116)/n-alkane systems were each measured at two temperatures of 288 K and 297 K. The two n-alkanes of interest are n-pentane and n-hexane. The pressures which were measured ranged from (0.017 to 7.040) MPa. A "static-analytic" VLE apparatus, equipped with pneumatic (Rapid Online Sampler-Injector) ROLSI® capillary samplers, was used to perform the measurements. The ROLSI® gives this apparatus the capability of sampling both the liquid and the vapour phases, without significant equilibrium perturbation with respect to the estimated analytical uncertainties. Vapour-liquid-liquid equilibria and liquid-liquid equilibria were experienced at R-116 compositions close to unity for the R-116 and n-hexane system.

Each of the four *P-x-y* VLE data sets was correlated with the Peng-Robinson Equation of State, modified by the inclusion of the Mathias Copeman alpha function in preference to the original Peng-Robinson configuration. The Wong-Sandler mixing rule, combined with the (Non-Random Two-Liquid) NRTL activity coefficient model, was used to account for the properties of the mixture.

Introduction

There has been little reported in open literature on studies related to the use of fluorinated refrigerants as solvents for hydrocarbon systems. A partial list of authors who have reported the vapour-liquid equilibrium (VLE) data of hexafluoroethane (R-116) with n-alkanes was supplied by Ramjugernath et al.[1] Authors who have reported VLE measurements of hexafluoroethane and alkanes include Ramjugernath et al.[1,2] and Zhang et al.[3,4] The system of R-116 and ethane was investigated by Zhang et al., whereas VLE data sets for the system of R-116 with both propane and n-butane were investigated by Ramjugernath et al.

The VLE measurements for the R-116 and n-pentane system, as well as R-116 and n-hexane system reported herein are a continuation of a previous study into the use of R-116 as a solvent for the separation of short-chained alkanes,[1,2] and have not been previously investigated. The separation of alkanes is of importance for the purification of fuels from natural gas reserves.

These systems would likely have their phase diagrams classified as either type I or type II by the classification of van Konynenburg and Scott.[5] In this classification scheme, a type I system is the simplest type, with only one critical locus curve between the two pure component critical points. This does not have a three-phase region. The type II system is more complex, and consists of two critical locus curves. One, between the two pure component critical points, and the other, starting at a fictitious 'critical point at infinite pressure', and ending at an upper

critical end point (UCEP). This type of system has a region in which there is liquid-liquid immiscibility, and the UCEP is the upper temperature limit of this three-phase region. Low temperature VLE data is often required to distinguish between type I and type II systems.

Each isothermal experimental data set reported herein was correlated with the Peng-Robinson Equation of State (PR-EOS).[6] The PR-EOS was modified by replacing the original alpha function with the Mathias-Copeman (M-C) alpha function.[7] This modification allowed a better representation of the vapour pressures of the n-pentane and the n-hexane due to the increase in the number of adjustable parameters that became available. The Wong-Sandler (W-S) mixing rules [8] were used in this correlation to represent the mixture properties with greater accuracy. These mixing rules utilised the NRTL excess Gibbs energy equation [9] to account for the liquid phase non-idealities.

These measurements will be useful in determining the behaviour of the solutes in supercritical R-116. The interaction parameter values for group contribution methods could also be updated by using the data sets that are reported here.

Experimental

Materials. The suppliers, the CAS numbers, the stated purities and the measured purities for the chemicals used in these measurements are given in Table 1. The n-pentane and n-hexane were degassed in the equilibrium cell, upon loading, but the R-116 was not further purified. The 'measured purities' of the pure components were estimated from the (gas chromatograph) GC peak area fractions, which were defined as the area under the peak for the given component, divided by the sum of all the peak areas. A VARIAN CP-3800 gas chromatograph fitted with a Porapack Q column with a mesh size of 80/100 was used. A thermal conductivity detector (TCD) was used to analyse these peaks.

The critical properties and acentric factors of R116, n-pentane and n-hexane are given in Table 2.

Experimental Apparatus. The "static-analytic type" apparatus, used for the VLE measurements of R-116 + propane and R-116 + n-butane by Ramjugernath et al., [1,2] was again used in this work. This apparatus was commissioned in the CTP laboratory (formerly CEP/TEP laboratory) at MINES ParisTech by Valtz et al., [10,11] based on the original static-analytic design of Laugier and Richon. [12]

The uncertainties for the measured data were estimated by the guidelines from NIST, outlined by Taylor and Kuyatt. [13] All of the combined expanded uncertainties were calculated with a coverage factor of $k = 2$. This value corresponds to a 95 % confidence interval.

The two Pt-100 temperature probes that were used to monitor the temperature of the cell were calibrated according to the 1990 International Temperature Scale Protocol. The reference probes that were used for this calibration were supplied by TINSLEY Precision Instruments and were certified by the Laboratoire National d'Essais (Paris). The combined expanded uncertainty in the measurement of temperature was estimated to be $U(T) = 0.03$ K. The constant temperature bath, inside of which the VLE cell was submerged, had a thermal stability of 0.01 K.

The pressure transducer employed for the monitoring of the pressure within the cell was a PTX 611 pressure transducer. This transducer had a range of 0 to 20 MPa and was supplied by Druck. The calibration of this transducer was performed against a 5202S dead weight pressure balance which was supplied by Desgranges and Huot in France. The expanded uncertainty in the pressure readings from this transducer was estimated to be $U(P) = 0.0006$ MPa.

Composition analysis of the vapour and the liquid phases was performed by means of a VARIAN CP-3800 gas chromatograph. The signal from the thermal conductivity detector was integrated with respect to time, to obtain the peak areas for the different components. A 4-m x 1/8'' Porapak Q column with a mesh size of 80/100 (supplied by Restek, France) was used to separate the components from each of the samples. The gas chromatograph calibration was performed by injecting many differing, but known volumes of each pure component into the column with a gas syringe. The relationship between the peak area and the amount of component that was injected to produce this peak could therefore be determined and used as the calibration of the detector. Upon taking all the possible uncertainty sources into account when performing the calibration, the combined expanded uncertainty in the measurement of the composition was estimated to be less than or equal to 0.005. However, as has been shown by Lasala et al., [14] for any data regression that considers the compositions in the fitting procedure, the combined expanded uncertainties for each composition must be estimated individually.

Experimental Procedure. The equilibrium cell and the associated loading lines were all subjected to a vacuum (0.1 Pa, absolute, at room temperature), prior to the measurement of each isotherm. The cell was thereafter loaded with roughly 5 cm^3 of the liquid component (n-pentane or n-hexane) and the cell was again subjected to a vacuum; for the degassing of the liquid. The pressure was thereafter allowed to equilibrate at the temperature of the particular isotherm being measured. This pressure was recorded as the vapour pressure of the pure component. It was assumed that the equilibrium vapour pressure had been attained when the equilibrium cell temperatures, reported by both Pt-100 temperature probes, were stable and equal for at least ten minutes. The standard uncertainties were considered during this operation.

The R-116 was thereafter added in step-wise amounts, with the equilibrium pressure and phase compositions being measured upon reaching equilibrium after each successive cell loading.

Equilibrium conditions were assumed to have been attained as soon as the changes in the cell pressure remained less than 0.1 kPa for a period of ten minutes. The contents of the cell were stirred vigorously throughout.

To ensure repeatability of the measurements, as well as to verify that the samples were representative of the equilibrium phase compositions, each phase was sampled at least five times. ROLSI® pneumatic samplers were used to perform the sampling of both the liquid and the vapour phases.

Correlations

The isothermal VLE data sets reported in this paper were correlated with a PR-EOS based model. [6] The PR-EOS, containing the M-C alpha function was fitted to the pure component vapour pressures to obtain the alpha function parameters.

A vapour pressure data set for R-116 was reported by Valtz et al. [15] For the n-pentane, vapour pressure measurements of Rice and El-Nikheli [16] and of Duce et al. [17] were used. For n-hexane, the vapour pressures reported by Rice and El-Nikheli, [16] Duce et al. [17], Marrufo et al. [18] and Fernández et al. [19] were used. The Mathias-Copeman alpha function coefficients regressed from the reported vapour pressures of the three components are listed in Table 3.

To determine the properties of the mixtures from pure component properties, the W-S mixing rule [8] with the NRTL local composition model was used. [9] A value of 0.3 was recommended for the alpha value in the NRTL model, for systems such as those investigated in this study. [19] Therefore, the only parameters that were adjusted to fit the model to the binary experimental data were τ_{ij} and τ_{ji}, from the NRTL local composition model, and the binary interaction parameter, k_{ij}, from the W-S mixing rule. These three parameters were adjusted to obtain a good fit of the model to the experimental data by using a modified Simplex algorithm. The

objective function that was used for this algorithm was a flash calculation function. This function is given by Equation 1.

$$F_{\text{obj}} = \frac{100}{N}\left[\sum_{1}^{N}\left(\frac{x_{\text{exp}} - x_{\text{calc}}}{x_{\text{exp}}}\right)^2 + \sum_{1}^{N}\left(\frac{y_{\text{exp}} - y_{\text{cal}}}{y_{\text{exp}}}\right)^2\right] \tag{1}$$

where N is the number of data points in the set; x_{exp} is the experimental liquid mole fraction, x_{cal} is the calculated liquid mole fraction, y_{exp} is the experimental vapour mole fraction and y_{cal} is the calculated vapour mole fraction.

The correlation of the experimental VLE data was performed using an 'in-house' data fitting software tool, developed by Armines and Mines ParisTech.

Results and Discussion

The measured vapour pressures for n-hexane [16-19] were plotted against predicted vapour pressures in Figure 1. The vapour pressures calculated using the PR-EOS with the original alpha function and with the M-C alpha function were both predicted and plotted in Figure 1. This comparison indicated that the use of the M-C alpha function provided a far better fit of the experimental data to the predicted data than when using the original PR-EOS alpha function. The PR-EOS with the M-C modification was therefore used for the VLE regression.

The VLE data set for the system of R-116 and n-pentane is reported in Table 4, with Figure 2 showing a plot of the experimental vapour-liquid equilibrium data alongside the data calculated from the regressed parameters. There was a good fit of the model to the measured data for this system. This system exhibits zeotropic behaviour. There are also no observable liquid immiscibilities, and thus, either the mixture is a type I system on the van Konynenburg and Scott [5] classification, or the mixture is a type II system that is above the UCEP.

The VLE data set for the system of R-116 and n-hexane is reported in Table 5. Also included in Table 5 are the vapour-liquid-liquid equilibrium (VLLE) and liquid-liquid equilibrium (LLE) data. The VLLE and LLE data points occurred at greater concentrations of R-116. These greater concentrations corresponded to the higher equilibrium pressures. A plot of the experimental VLE data against the data predicted with the model, using the regressed parameters, is given by Figure 3**.** This system exhibits zeotropic behaviour, with liquid miscibilities occurring at both measured temperatures. This system is therefore most likely to be a type II system. The VLLE and LLE data for the system were not included in the regression.

The regressed parameters that gave the best fit of the PR-EOS with the M-C alpha function and the W-S mixing rules, using the NRTL local composition model, to the experimental VLE data for both systems are given in Table 6.

Two summary statistics were used to indicate the degree of correlation between the experimental data and the models. These were the absolute mean relative deviation (MRD) of the regressed compositions and the bias of the regressed compositions. Equation 2 gives the calculation of the absolute mean relative deviation and the calculation of the bias is given by Equation 3.

$$\text{MRD}\ (u) = \frac{100}{N}\sum_{\mathrm{i}}^{\mathrm{N}}\left|\frac{\left(u_{exp}\text{-}u_{cal}\right)}{u_{exp}}\right| \tag{2}$$

$$\text{BIAS}\ (u) = \frac{100}{N}\sum_{\mathrm{i}}^{\mathrm{N}}\left(\frac{\left(u_{exp}\text{-}u_{cal}\right)}{u_{exp}}\right) \tag{3}$$

In both Equations 2 and 3, u is either the liquid or the vapour composition, and N is the number of experimental data points. '*exp*' and '*cal*' denote the experimental and calculated values respectively. The calculated values for the MRD and the bias are given in Table 7.

Conclusions

The vapour-liquid equilibrium measurements for the R-116 and n-pentane system and the R-116 and n-hexane system are reported herein. These measurements were performed using a "static-analytic" type VLE apparatus. Two isotherms were measured for each system, with one isotherm for each system being below the critical temperature of R-116 and the other above it. The measured VLE data was thereafter correlated with the Peng-Robinson EOS coupled with the Mathias-Copeman alpha function and the Wong-Sandler mixing rules. The Wong-Sandler mixing rules used the NRTL local composition model to describe the excess Gibbs energy of the system. Both systems exhibited zeotropic behaviour, with the R-116 + n-pentane system not exhibiting any liquid immiscibilities at the measured temperatures. The R-116 + n-hexane system, however, presented a large miscibility gap at the temperatures measured. This miscibility gap was not modelled with thermodynamic models, due to the limited data that was available.

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Table 1. Chemical Suppliers, CAS numbers, Stated Purities and Measured Purities

	Supplier	CAS Number	Stated Purity	Measured Purity [c]
R-116 [a]	Air Liquide	76-16-4	0.99999	-
n-pentane [b]	Riedel-de Haen	109-66-0	0.99	0.99
n-hexane [b]	Acros	110-54-3	0.99	0.99

[a] Further purification of the R-116 was not undertaken.

[b] Further purification of these components was performed by degassing in situ.

[c] Estimated from GC area fractions.

Table 2. Critical Properties (T_c, P_c) and Acentric Factors (ω) [a]

	T_c / K	P_c / MPa	ω
R-116	293.04	3.042	0.229
n-pentane	469.70	3.369	0.251
n-hexane	507.40	3.014	0.296

[a] The data values reported in this table were taken from Ref. 20.

Table 3. Mathias-Copeman Alpha Function coefficients, c_i.

	c_1	c_2	c_3
R-116 [a]	0.79629	-0.55124	0.10316
n-pentane [b]	0.73224	-0.09516	0.76161
n-hexane [c]	0.78670	0.01877	0.50091

[a] Obtained from regression of data found in reference 15

[b] Obtained from regression of data found in references 16 and 17

[c] Obtained from regression of data found in references 16-18

Table 4. Vapour-liquid equilibrium (*P*-*x*-*y*) data for the R-116 (1) + n-Pentane (2) system at temperatures, *T*, of 288.25 K and 296.24 K. [a]

T = 288.25 K					*T* = 296.24 K				
P/MPa	x_1	$U(x_1)$ [b]	y_1	$U(y_1)$ [c]	*P*/MPa	x_1	$U(x_1)$ [b]	y_1	$U(y_1)$ [c]
0.048	0.000	-	0.000	-	0.066	0.000	-	0.000	-
0.307	0.021	0.001	0.832	0.003	0.310	0.019	0.001	0.764	0.004
0.699	0.060	0.001	0.920	0.001	0.705	0.053	0.001	0.896	0.002
1.105	0.110	0.002	0.946	0.001	1.104	0.096	0.002	0.917	0.002
1.497	0.183	0.003	0.957	0.001	1.508	0.153	0.003	0.936	0.001
1.903	0.364	0.005	0.962	0.001	1.905	0.243	0.004	0.944	0.001
2.152	0.754	0.004	0.965	0.001	2.300	0.477	0.005	0.947	0.001
2.378	0.896	0.002	0.975	0.001	2.596	0.796	0.003	0.951	0.001
2.5178	0.952	0.001	0.985	0.001	2.900	0.916	0.002	0.965	0.001
					2.994	0.940	0.001	0.970	0.001

[a] Combined expanded uncertainties are $U(P)$ = 0.0006 MPa and $U(T)$ = 0.03 K (with k = 2)

[b] Combined expanded uncertainty in liquid phase composition (k = 2)

[c] Combined expanded uncertainty in vapour phase composition (k = 2)

Table 5. Vapour-liquid equilibrium (*P*-*x*-*y*) data for the R-116 (1) + n-hexane (2) system at temperatures, *T*, of 288.24 K and 296.23 K. [a]

T = 288.24 K					*T* = 296.23 K				
P/MPa	x_1	$U(x_1)$ [b]	y_1	$U(y_1)$ [c]	*P*/MPa	x_1	$U(x_1)$ [b]	y_1	$U(y_1)$ [c]
0.017	0.000	-	0.000	-	0.021	0.000	-	0.000	-
0.313	0.021	0.001	0.9506	0.0005	0.320	0.019	0.001	0.9316	0.0007
0.704	0.053	0.001	0.9746	0.0003	0.700	0.048	0.001	0.9626	0.0004
1.097	0.092	0.001	0.9815	0.0002	1.101	0.083	0.001	0.9731	0.0003
1.506	0.141	0.001	0.9834	0.0002	1.501	0.124	0.001	0.9768	0.0003
1.903	0.214	0.002	0.9839	0.0002	1.902	0.177	0.002	0.9784	0.0002
2.202	0.335	0.003	0.9832	0.0002	2.192	0.232	0.002	0.9785	0.0002
2.247 [d]	0.605	0.003	0.9829	0.0002	2.392	0.284	0.002	0.9775	0.0003
3.167 [e]	0.846	0.002	-	-	2.581	0.370	0.003	0.9764	0.0003
4.840 [e]	0.847	0.001	-	-	2.624 [d]	0.542	0.003	0.9765	0.0003
					7.040 [e]	0.847	0.001	-	-
					5.002 [e]	0.848	0.001	-	-

[a] Combined expanded uncertainties are $U(P)$ = 0.0006 MPa, $U(T)$ = 0.03 (with k = 2).

[b] Combined expanded uncertainty in liquid phase composition (k = 2)

[c] Combined expanded uncertainty in vapour phase composition (k = 2)

[d] Supposed vapour-liquid-liquid equilibrium.

[e] Supposed liquid-liquid equilibrium.

Table 6. Regressed temperature independent model parameters (τ_{ij} and k_{ij}) for the PR-EOS with the M-C alpha function and the W-S mixing rule using the NRTL local composition model at temperatures, *T*.

	R-116 (1) + n-pentane (2)		R-116 (1) + n-hexane (2)	
T / K	**288.25**	**296.24**	**288.24**	**296.23**
$\tau_{12}/J \cdot mol^{-1}$	**1323.2**	**1988.2**	**4016.5**	**3583.2**
$\tau_{21}/J \cdot mol^{-1}$	**3621.8**	**3213.0**	**2749.7**	**2692.9**
k_{12}	**0.356**	**0.319**	**0.305**	**0.332**

Table 7. Mean residual deviations and bias of compositions obtained in the fitting of the experimental VLE data to the PR-EOS with the M-C alpha function and the W-S mixing rule using the NRTL Model

	R-116 (1) + n-pentane (2)		R-116 (1) + n-hexane (2)	
T / K	**288.25**	**296.24**	**288.24**	**296.23**
MRD *x* %	**1.3**	**1.3**	**1.3**	**0.7**
bias *x* %	**-0.8**	**-0.8**	**-0.8**	**-0.2**
MRD *y* %	**0.2**	**0.2**	**0.2**	**0.5**
bias *y* %	**0.1**	**0.1**	**0.1**	**-0.4**

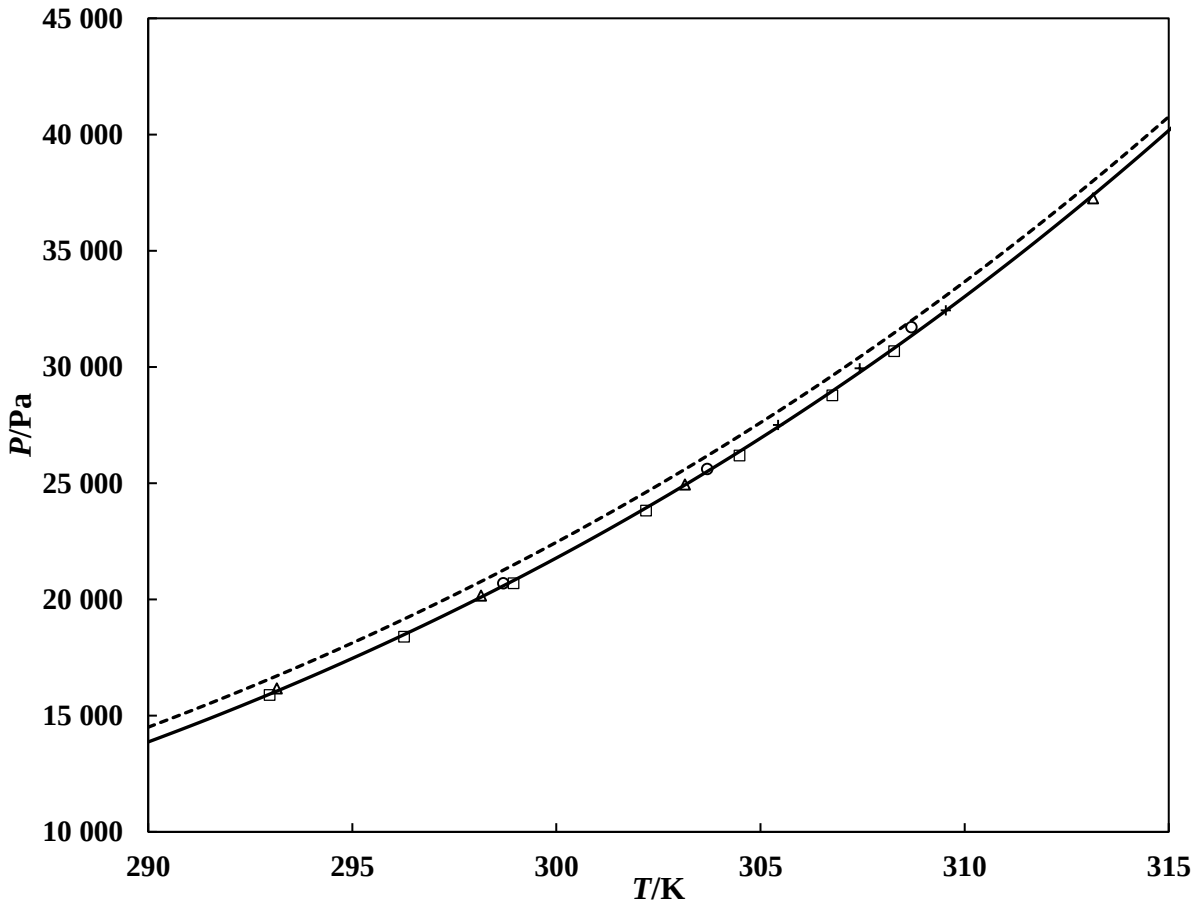


Figure 1. Vapour pressure of n-hexane. ○, Ref. 16; Δ, Ref. 17; +, Ref. 18; □, Ref. 19; ---, PR-EOS model with the original alpha function; ——, PR-EOS model with the M-C alpha function.

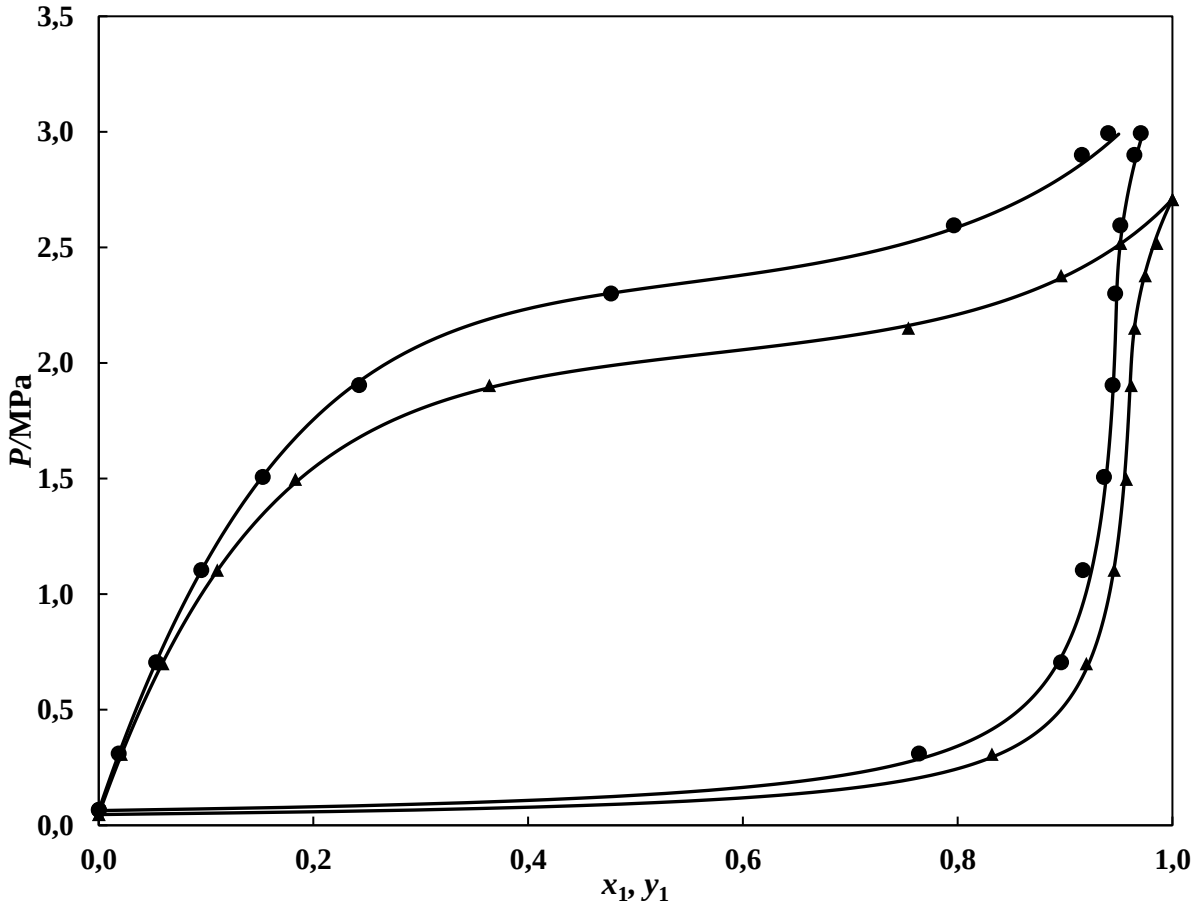


Figure 2. *P-x-y* data for the R116 (1) + n-pentane (2) system. ▲, T = 288.25 K; ●, *T* = 296.24 K; ——, PR-EOS based model.

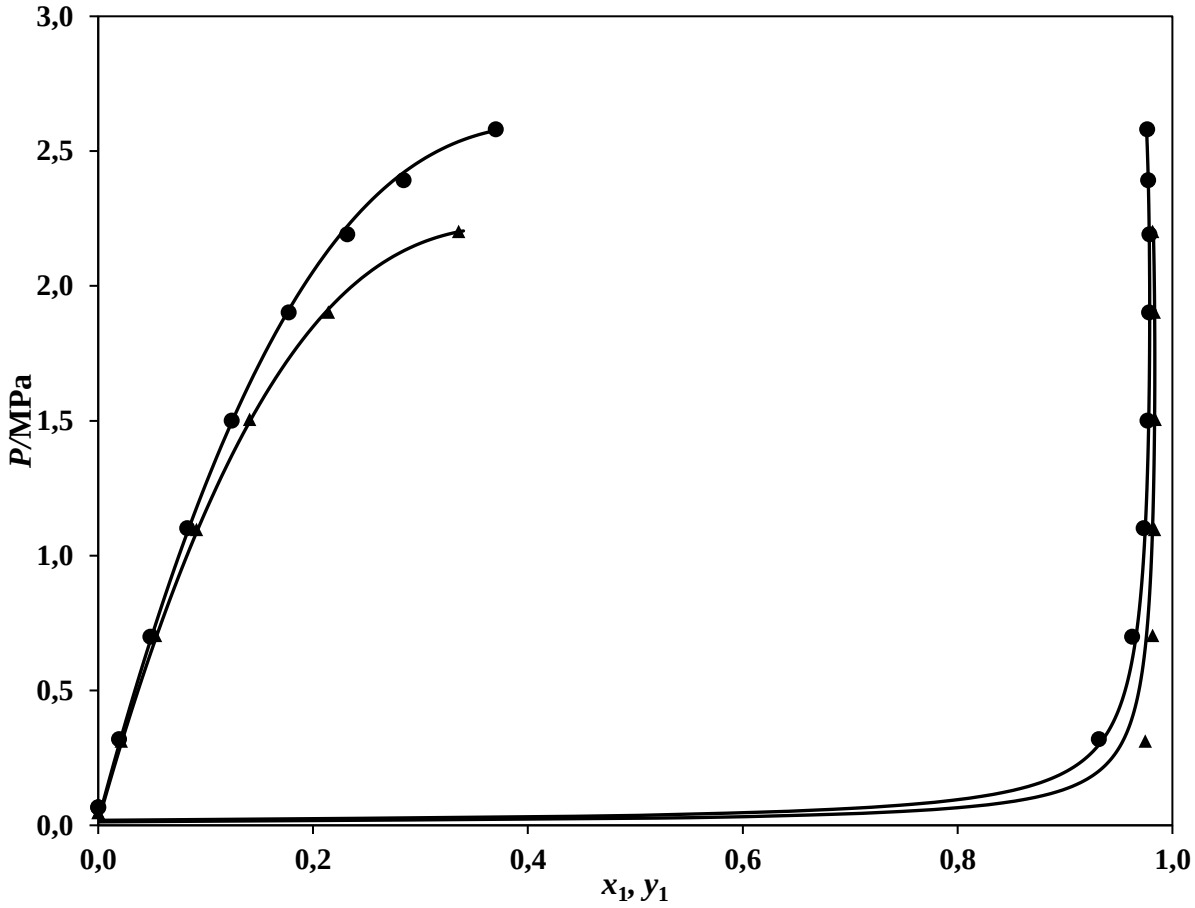
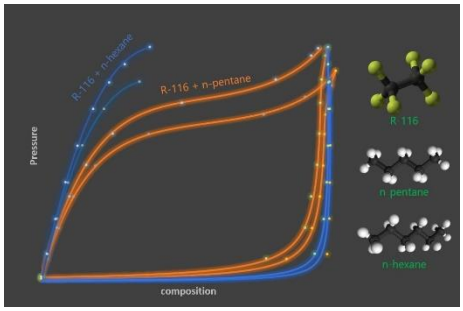


Figure 3. *P-x-y* data for the R116 (1) + n-hexane (2) system. ▲, T = 288.24 K; ●, *T* = 296.23 K; ——, PR-EOS based model.



TOC. For Table of Contents Use Only