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Isothermal Vapour-Liquid Equilibrium Data for the Hexafluoroethane (R116) + n-Butane System at Temperatures from (273 to 323) K

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Abstract

Isothermal vapour-liquid equilibrium data for the system of hexafluoroethane (R-116) + n-butane are reported in this paper. The measurements were undertaken at six different temperatures ranging from 273.27 to 323.19 K, with pressure ranging from 0.104 to 3.742 MPa. Two of the temperature sets were measured below, and the remaining four were measured above the critical temperature of R116. The measurements were performed in a “static-analytic” type VLE apparatus. The sampling of the equilibrium phases was performed via pneumatic ROLS[®] capillary samplers (Armine’s patent). The equipment was developed in the CEP/TEP laboratory at MINES ParisTech. Combined expanded uncertainties in the measurements were estimated to be 0.02 K for temperature, 0.0006 MPa for pressure, and 0.004 for composition, based on the NIST guidelines. Each set of isothermal vapour-liquid equilibrium data was correlated with the Peng-Robinson equation of state (PR-EOS). The

Mathias-Copeman alpha function and the Wong-Sandler mixing rule, utilizing the NRTL activity coefficient model, were incorporated into this equation of state.

Introduction

Although many fluorinated hydrocarbon refrigerants have critical temperatures that are close to ambient temperatures and low critical pressures, and could therefore rival carbon dioxide as a supercritical solvent, very few measurements of vapour-liquid equilibrium (VLE) data involving these refrigerants have been undertaken. Previous measurements of binary vapour-liquid equilibria with hexafluoroethane (R-116) have been undertaken by Zhang et al.^{1,2}, by Valtz et al.³, by Madani et al.⁴, and by Ramjugernath et al.⁵. Zhang et al. investigated the R-116 and ethane system, while Ramjugernath et al. reported their measurements of the R-116 and n-propane system.

In this study, the possibility of using R-116 as a solvent for the separation of short-chained alkanes is investigated. The R-116 + n-butane system is an entirely new system that has not been previously measured. According to van Konynenburg and Scott⁶, the R-116 + n-butane system can be classified as either a type I or a type II system. Low temperature VLE data would, however, be required to determine which of these two classes this system would fall within.

Measurements for this system were conducted both above and below the critical temperature of the R-116, to enable the estimation of the behaviour of the system in its supercritical state. The VLE measurements are also useful for updating the values of interaction parameters for group contribution methods. Due to the significant differences in the critical temperatures of the R-116 and of the n-butane, azeotropic behaviour was not expected⁵.

The Peng-Robinson equation of state (PR-EOS) was used to correlate the measured VLE data. The original alpha function of this EOS was replaced with the Mathias-Copeman alpha function. The Wong-Sandler mixing rule was used to determine the mixture parameters from the pure-species parameters, using the NRTL activity coefficient model to account for the liquid phase non-idealities.

Experimental

Materials. The suppliers, CAS numbers and stated purities of the R-116 and the n-butane are given in Table 1. The critical properties and acentric factors are given in Table 2.

Experimental Apparatus. A “static-synthetic type” apparatus was used for the VLE measurements detailed in this work. The principle of this technique was first described by Laugier and Richon ⁷. The equipment that was described by these authors has undergone continual improvement for various types of systems and nature of phase equilibria. The equipment that was commissioned by Valtz and co-workers ^{8,9} has a number of modifications which are useful for the study of the phase equilibria of systems containing fluorinated components. This equipment was used for these measurements, and includes ROLSI[®] pneumatic samplers for the sampling of both the liquid and the vapour phases.

For this equipment, the temperature of the equilibrium cell is kept constant by immersion of the cell in a temperature regulated bath with a thermal stability of within 0.01 K. Two Pt-100 platinum resistance thermometer probes are used to measure the cell temperature. One Pt-100 temperature probe is inserted into the cell wall at the top of the equilibrium cell and the other is inserted into the cell wall at its base. The Laboratoire National d’Essais (Paris) certified the 25 Ω reference probes (TINSLEY Precision Instruments) which were used to

calibrate the Pt-100 probes. This calibration was performed according to the 1990 International Temperature Scale Protocol.

The pressures inside of the equilibrium cell are measured with a PTX 611 pressure transducer supplied by Druck. This pressure transducer has a 0 to 20 MPa range. The pressure transducer was calibrated against a 5202S dead weight pressure balance supplied by Desgranges and Huot (France). Both the temperature and the pressure signals were converted to digital signal via the HP34970A Data Acquisition Unit. These digital signals are then recorded on a computer.

The analysis of the vapour and liquid phase compositions was performed with a VARIAN CP-3800 gas chromatograph fitted with a thermal conductivity detector. The gas chromatograph was connected to a BORWIN Ver. 1.5 data acquisition system, which was supplied by JMBS. For component separation, the gas chromatograph was fitted with a Porapak Q model analytical column (80/100 mesh, 4m x 1/8" Silcosteel tube). This column was supplied by Restek France.

The calibration of the gas chromatograph was undertaken by injecting a number of different volumes of each pure component, into the injection port of the gas chromatograph, with a gas syringe. The peak areas were then regressed against the volumes of pure component that were injected.

Experimental Procedure. Prior to these measurements, the equilibrium cell and the loading lines were evacuated to roughly 0.1 Pa at room temperature. Thereafter, the cell was loaded with a volume of approximately 5 cm³ of liquid n-butane. This was then allowed to reach equilibrium at the desired temperature and the vapour pressure of the pure n-butane was recorded. For the vapour pressure measurements, equilibrium was presumed to have been

attained when the temperatures being read by the two Pt-100 temperature probes were equal, to within the experimental uncertainty, for at least 10 minutes.

After the measurement of the vapour pressure of the n-butane at the equilibrium temperature, further measurements of the equilibrium phases at various compositions were undertaken by the stepwise addition of R-116 into the equilibrium cell. After every successive R-116 loading, the system was allowed to equilibrate and thereafter the pressure and temperature were recorded and the phases sampled. Equilibrium was presumed, for the binary system, as soon as the cell total pressure remained constant, to within ± 0.1 kPa for a period of 10 minutes, while the mixture was efficiently stirred.

For each equilibrium point, samples of both the liquid and the vapour phases were repeated at least five times, by means of the ROLSI™ pneumatic samplers, to ensure that the measurements were repeatable and were representative of the equilibrium compositions¹⁰.

Correlations

The VLE data measured in this study was correlated using an ‘in-house’ data fitting software tool, which was developed by Armines and Mines Paristech. The measured data was fitted to the Peng-Robinson equation of state,¹¹ which was modified by the inclusion of the Mathias-Copeman alpha function¹². The use of the Mathias-Copeman alpha function rather than the standard PR-EOS alpha function allowed for better representation of the vapour pressures of the individual components because there were more adjustable parameters available. This improved representation, by use of the Mathias-Copeman alpha function, has been found to occur for similar systems.

The Mathias-Copeman alpha function is given by Equation 1. This function has three adjustable parameters, c_1 , c_2 and c_3 . These parameters were obtained by fitting the PR-EOS,

with the Mathias-Copeman alpha function, to the pure component vapour pressures. The Mathias-Copeman alpha function coefficients for R-116 were regressed from the vapour pressures reported by Valtz et al.³. For n-butane, the coefficients were regressed from the vapour pressures measured in this study. The regressed Mathias-Copeman alpha function coefficients are listed in Table 3.

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

When the system temperature is greater than the critical point, a different expression can be applied for the Mathias-Copeman alpha function (see Equation 2).

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

The Wong-Sandler mixing rules¹³ were used as they combined the advantages of equations of state with those of excess Gibbs energy models in correlating the experimental data. These mixing rules utilised the NRTL local composition model to calculate the excess Gibbs energy, $g^E(T, P = \infty, x_i)$ ¹⁴.

For the NRTL local composition model, Renon and Prausnitz¹⁴ recommended a value of 0.3 for the value of α , for systems such as the one investigated herein. Consequently, only τ_{ij} and τ_{ji} from the NRTL local composition model and k_{ij} , the adjustable binary interaction parameter, were adjusted in order to obtain the best fit to the experimental values. A ‘modified simplex algorithm’ was used to perform these adjustments. A flash calculation algorithm was used for performing the correlation, with the objective function having the form given by Equation 3.

$$F_{\text{obj}} = \frac{100}{N} \left[\sum_1^N \left(\frac{x_{\text{exp}} - x_{\text{calc}}}{x_{\text{exp}}} \right)^2 + \sum_1^N \left(\frac{y_{\text{exp}} - y_{\text{calc}}}{y_{\text{exp}}} \right)^2 \right] \quad (3)$$

where N is the number of data points in the set; x_{exp} and x_{calc} are the experimental and calculated liquid mole fractions; and y_{exp} and y_{calc} are the experimental and calculated vapour mole fractions.

Critical Point Determination. The composition and pressure at the critical point can be determined from the experimental data using the method proposed by Ungerer et al.¹⁵. This method approximates the critical points and the near critical phase behaviour, for binary mixtures, by the use of extended scaling laws. In this method, the near-critical scaling law is extended with a linear term at positions near to the critical region of a pressure-composition diagram. The adjustable coefficients are regressed from a set of ‘coexistence points’ (P , x , y) from below the critical point. The equations representing the extended scaling laws are given by Equations 4 and 5.

$$y - x = \lambda_1 (P_c - P) + \mu (P_c - P)^\beta \quad (4)$$

$$\frac{y + x}{2} - x_c = \lambda_2 (P_c - P) \quad (5)$$

El Ahmar et al.¹⁶ discussed the procedures for the calculation of critical points using equations of state. In that investigation, the Stockfleth and Dohrn method¹⁷ was used to calculate the critical loci. This method was also used in this study, by using the PR-EOS combined with the Wong-Sandler mixing rules and the NRTL local composition model. The binary parameters which were used in the method were obtained by correlating the VLE data with R-116 as component 1.

Discussion

The VLE data and the accompanying combined expanded uncertainties measured at temperatures below the critical point are given in Table 4 while those which were measured at temperatures above the critical point are given in Table 5. All of these combined expanded uncertainties were calculated with a coverage factor of $k = 2$, according to the NIST guidelines, outlined by Taylor and Kuyatt.¹⁸ The combined expanded uncertainties for the temperature were all estimated to be less than 0.02 K; however, the combined expanded uncertainties in pressure and compositions are more variable, and are therefore included alongside the data in Tables 4 and 5.

Table 6 gives the regressed model parameters for the PR-EOS using the Mathias-Copeman alpha function and the Wong-Sandler mixing rule with the NRTL Gibbs excess energy model. The data that was calculated with these parameters is plotted alongside the experimental vapour-liquid equilibrium data in Figure 1. The fit of the PR-EOS was good, apart from the points that were in the regions near to the mixture critical points.

The critical points of the mixture for each of the isotherms above the critical temperature of R-116, calculated using the extended scaling laws, and the critical loci, calculated by the method of Stockfleth and Dohrn¹⁷, are also plotted on Figure 1. Table 7 gives the numerical values for the four critical points and the adjustable parameters obtained for Equations 4 and 5 during the extrapolation to these critical points. Table 8 lists the critical loci for the entire R-116 + n-butane composition range.

On Figure 2, which is a plot of the correlated NRTL model parameters against temperature, a clear discontinuity can be observed. The R-116 critical temperature, plotted on Figure 2, confirms that the discontinuity does, in fact, occur around the critical temperature. This discontinuity can also be observed to occur for the k_{ij} binary interaction parameter on Figure

3. These discontinuities have been observed to occur in a number of other studies of the vapour-liquid equilibria around the critical point ^{5, 9, 19, 20}.

The mean absolute relative deviation (MRD) of the compositions at the six different temperatures was calculated using Equation 6, where u is either x or y ⁵.

$$\text{MRD} (u) = \frac{100}{N} \sum_i^N \left| \frac{(u_{exp} - u_{cal})}{u_{exp}} \right| \quad (6)$$

The calculation of the bias of the regression; where, again, u can be either x , the liquid composition, or y , the vapour composition; was performed using Equation 7 ⁵.

$$\text{BIAS} (u) = \frac{100}{N} \sum_i^N \left(\frac{(u_{exp} - u_{cal})}{u_{exp}} \right) \quad (7)$$

In both equation 6 and equation 7, N is the number of experimental data points.

The calculated values for the MRD and the BIAS are given in Table 9. These values are useful as indicators of the resemblance of the data predicted by the model to the experimental results.

At 294.23 K, the absolute mean relative deviations were fairly high, with the bias of the correlation being almost as large as the MRD. This is only 1 K higher than the critical temperature of R-116 (see Table 2), and shows that the model used for these correlations has limitations at temperatures close to the critical temperature of one of the components.

Conclusions

This paper reports the measured vapour-liquid equilibrium data of the system consisting of R-116 and n-butane, which were undertaken in a “static-synthetic” cell at six different temperatures. The experimental data was thereafter used to determine parameters for the Peng-Robinson equation of state, utilizing the Mathias-Copeman alpha function and the Wong-Sandler mixing rules, which employ the NRTL model. The experimental uncertainties of the experimental data were estimated to be 0.02 K for temperature, 0.0006 MPa for pressure, and less than 0.004 for both the liquid and the vapour molar compositions.

The relationship between the critical temperature of R-116 and the adjustable parameters was examined. Thereafter, estimations of the critical points of the mixtures, using the extended scaling laws, and of the critical loci for the system, using the method of Stockfleth and Dohrn, were undertaken.

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Table 1. Chemical Suppliers, CAS numbers and Stated Purities ^a

	Supplier	CAS Number	Stated Purity
R-116	Air Liquide	76-16-4	0.99999
n-butane	Air Liquide	106-97-8	0.9995

^a Further purification of components was not undertaken.

Table 2. Critical Properties and Acentric Factors

	T _c /K	P _c /MPa	ω
R-116	293.04 ^a	3.042 ^a	0.229 ^a
n-butane	425.15 ^a	3.800 ^a	0.193 ^a

^a Ref. 21

Table 3. Mathias-Copeman Alpha Function Coefficients

	c_1	c_2	c_3
R-116 ^a	0.79629	-0.55124	0.10316
n-butane	0.68335	-0.23524	0.88966

^a Obtained from regression of data found in reference 3

Table 4. P-x-y Data for the R-116 (1) + n-Butane (2) System at Temperatures Below the Critical Temperature of R-116 ^a

$T = 273.27 \text{ K}$			$T = 288.25 \text{ K}$		
P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.104	0.000	0.000	0.177	0.000	0.000
0.300	0.021	0.615	0.357	0.017	0.470
0.501	0.048	0.770	0.697	0.053	0.713
0.703	0.084	0.831	1.098	0.115	0.795
0.903	0.132	0.863	1.488	0.224	0.850
1.103	0.213	0.885	1.891	0.502	0.870
1.301	0.385	0.904	2.207	0.757	0.908
1.503	0.703	0.925	2.491	0.914	0.955
1.851 ^b	1.000	1.000	2.708 ^b	1.000	1.000

^a Combined expanded uncertainties, U , are $U(P) = 0.0006 \text{ MPa}$, $U(x) = 0.002$ and $U(y) = 0.004$, with $k = 2$.

^b Vapour pressure of R-116 calculated from correlation given by Ref. 22.

Table 5. P-x-y Data for the R-116 (1) + n-Butane (2) System at Temperatures Above the Critical Temperature of R-116 ^a

$T = 294.23 \text{ K}$			$T = 296.23 \text{ K}$			$T = 308.21 \text{ K}$			$T = 323.19 \text{ K}$		
P/MPa	x_1	y_1									
0.215	0.000	0.000	0.231	0.000	0.000	0.332	0.000	0.000	0.498	0.000	0.000
0.357	0.012	0.323	0.366	0.011	0.340	0.499	0.013	0.304	0.712	0.015	0.260
0.744	0.050	0.673	0.751	0.048	0.660	0.905	0.049	0.588	1.104	0.045	0.492
1.144	0.102	0.775	1.149	0.101	0.764	1.300	0.092	0.698	1.601	0.094	0.624
1.564	0.199	0.817	1.700	0.230	0.827	1.704	0.152	0.756	2.101	0.155	0.690
1.942	0.372	0.850	2.251	0.534	0.862	2.103	0.242	0.789	2.602	0.246	0.729
2.252	0.595	0.874	2.655	0.782	0.893	2.503	0.385	0.810	3.102	0.378	0.748
2.548	0.779	0.900	2.805	0.848	0.913	2.902	0.584	0.828	3.510	0.524	0.755
2.858	0.912	0.945	2.979	0.912	0.938	3.308	0.769	0.840	3.742	0.631	0.738
2.910	0.932	0.954									

^a Combined expanded uncertainties, U , are $U(P) = 0.0006 \text{ MPa}$, $U(x) = 0.004$ and $U(y) = 0.004$, with $k = 2$.

Table 6. Regressed Model Parameters for the Peng-Robinson Equation of State with the Mathias-Copeman Alpha Function and the Wong-Sandler Mixing Rule, Combined with the NRTL Local Composition Model

	T/K					
	273.27	288.25	294.23	296.23	308.21	323.19
$\tau_{12}/J \cdot mol^{-1}$	1643	1300	1035	1146	947	1004
$\tau_{21}/J \cdot mol^{-1}$	3520	3703	3882	3790	3891	3824
k_{12}	0.252	0.264	0.278	0.266	0.260	0.248

Table 7. Extrapolated Critical Points (T_c , P_c , and x_{c1}) for the R-116 (1) + n-Butane (2) System, Determined from the Experimental Data with the Extended Scaling Laws (Equations 4 and 5) using the Adjustable Parameters (μ , λ_1 and λ_2) Provided.

T_c/K	P_c/MPa	x_{c1}	μ	λ_2	λ_2
294.23	2.949	0.955	0.0508	0.4918	-0.3254
296.23	3.006	0.932	0.1418	0.4093	-0.3053
308.21	3.324	0.808	0.2209	0.2301	-0.2315
323.19	3.787	0.693	0.3183	0.1052	-0.1680

Table 8. Predicted Critical Points using the PR-EOS for the R-116 (1) + n-Butane (2) System.

T/K	P_c/MPa	x_{c_1}	T/K	P_c/MPa	x_{c_1}
425.15	3.800	0.00	338.46	4.350	0.60
413.30	4.235	0.10	325.30	3.957	0.70
399.89	4.609	0.20	313.05	3.578	0.80
384.91	4.853	0.30	302.03	3.264	0.90
368.88	4.889	0.40	293.04	3.042	1.00
353.00	4.696	0.50			

Table 9. Absolute mean relative deviations (MRD) and bias of compositions obtained in the fitting of the experimental VLE data to the Peng-Robinson EOS with the Mathias-Copeman alpha function and the Wong-Sandler mixing rule using the NRTL local composition model.

	T/K					
	273.27	288.25	294.23	296.23	308.21	323.19
BIAS x %	-0.6	0.2	1.2	0.4	-0.4	-0.7
MRD x %	2.8	1.5	1.8	1.7	1.3	1.4
BIAS y %	-0.8	-1.0	-2.2	-0.6	-0.9	-1.0
MRD y %	0.8	1.1	2.3	0.6	0.9	1.1

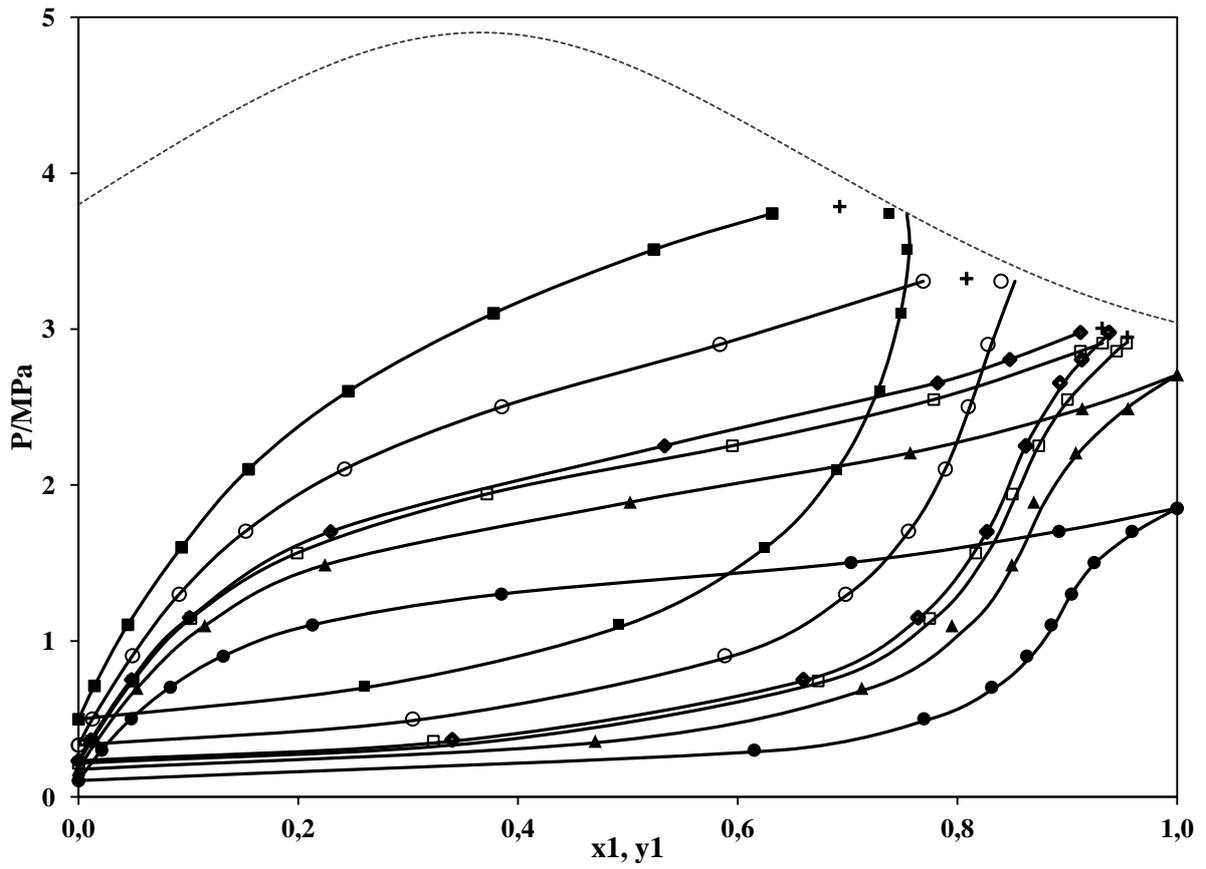


Figure 1. Plot of the P-x-y Data for the R116 (1) + n-Butane (2) System. ●, $T = 273.27$ K; ▲, $T = 288.25$ K; □, $T = 294.23$ K; ◇, $T = 296.23$ K; ○, $T = 308.21$ K; ■, $T = 323.19$ K; —, PR-EOS model; +, critical point value; ---, critical locus.

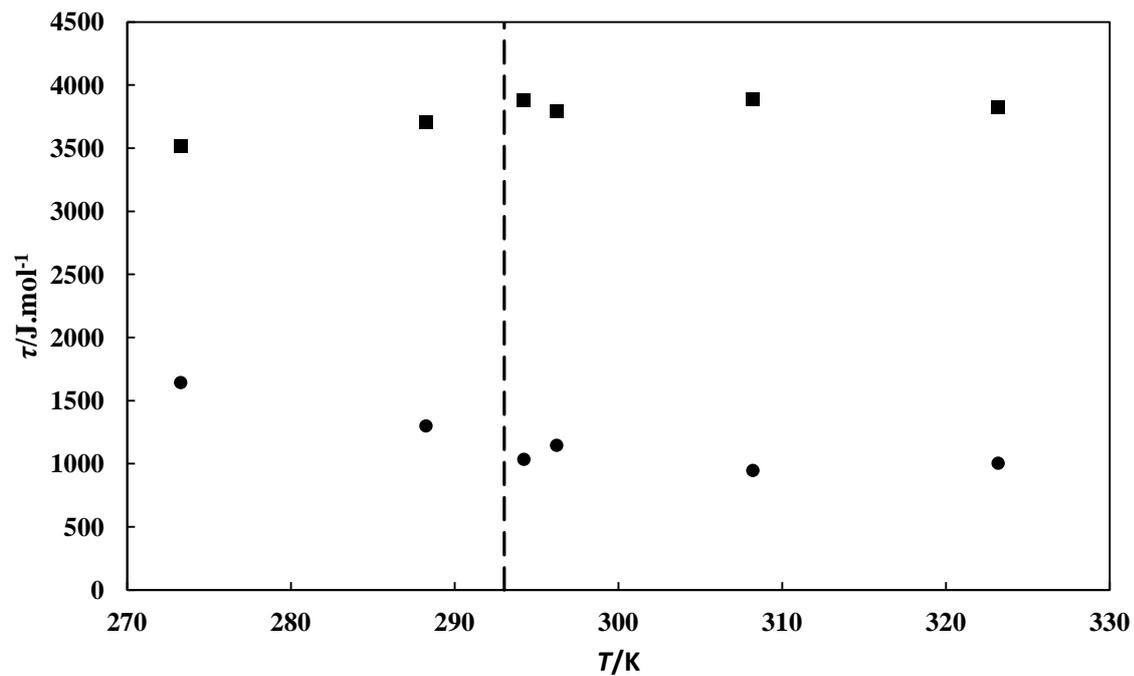


Figure 2. NRTL parameters versus temperature. ●, τ_{12} ; ■, τ_{21} ; - - -, R-116 critical temperature.

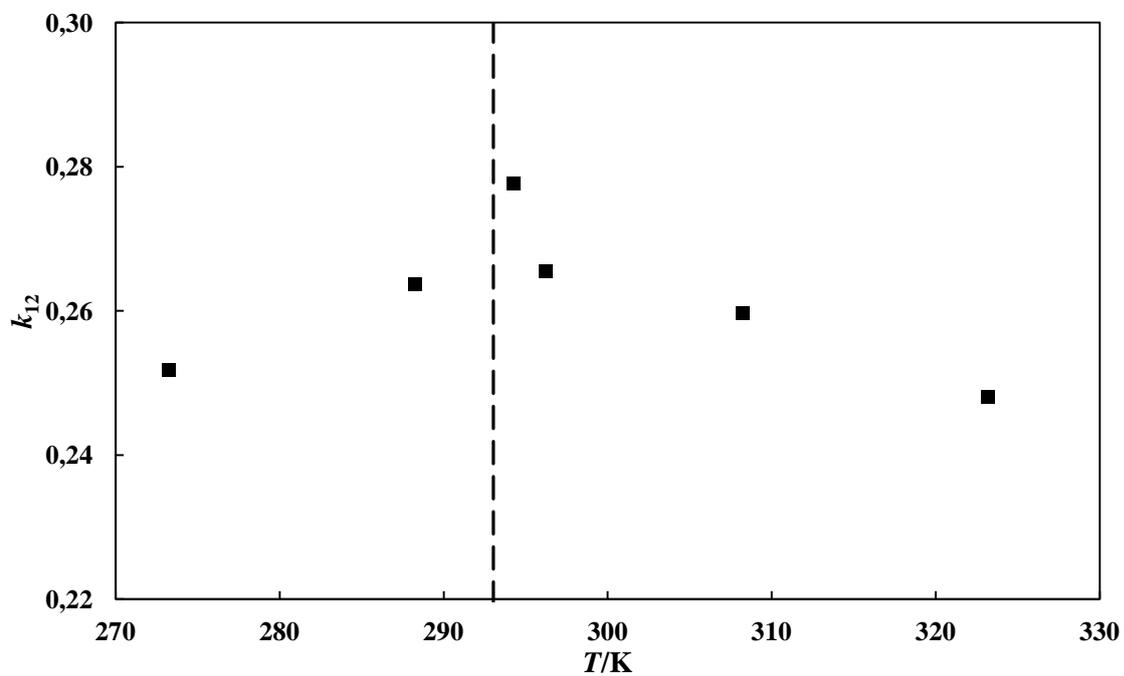


Figure 3. k_{12} versus temperature. - - -, R-116 critical temperature.

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