Vapor-liquid equilibrium data concerning refrigerant systems

Example (R116 + R143a)

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Abstract

Development of modern refrigeration systems is critical for the success of new global environmental protection efforts. The binary system of refrigerants: Hexafluoroethene (R116) + 1,1,1-trifluoroethane (R143a), has been studied with the aim of providing PTxy data. Isothermal vapor-liquid equilibrium data have generated using the "static analytic" method from 258 to 328 K at pressures from 0.39 to 3.89 MPa. The model composed of the Peng-Robinson of state, the Mathias-Copeman alpha function, the Wong-Sandler mixing rules and the NRTL cell theory is applied herein to correlate the data and calculate the critical line.

Keywords: VLE data ; refrigerants ; R-116, R-143a ; Supercritical gas solubility ; Critical points ; Phase diagrams

1. Introduction

In the awake of the global response for the protection of environment and sustainable development, the refrigeration industry is forced to find new fluids as acceptable refrigerants. The Montreal Protocol (1987) is one of the landmarks towards the replacement of ozone-destroying refrigerants like chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) by ozone friendly and non green house fluids. CFCs were prohibited in 1996 in signatory countries of the Montreal Protocol. The deadline for HCFCs which have low ozone depletion potential is 2030. Development of new refrigeration systems is critical for the success of new global environmental protection efforts. In our current research for good refrigerant candidates, we are providing phase equilibrium data (complete phase diagrams) for mixtures of various existing and/or new candidates for refrigeration industry [1-8]. The VLE cell used for these purposes relies on the "static-analytic" method [9] and Rolsi™ sampling [10]

Hexafluoroethane (R116), CAS no: 76-16-4, is a completely fluorinated haloalkane, which is derived from ethane. It is a non-flammable gas which is negligibly soluble in water and slightly soluble in alcohol. One of its main applications is the field of refrigeration. Due to the high C-F bond energy, R116 is very inert and unfortunately acts as an extremely stable greenhouse gas, with an atmospheric lifetime of 10000 years and a global warming potential (GWP) of 9000 [11]. However its ozone depletion potential (ODP) is 0 [12].

On the other hand, 1,1,1-trifluoroethane R143a, CAS no: 420-46-2, R143a has ozone depletion potential ODP = 0 and comparatively high Global Warming Potential (= 1000), non-toxic and fire-safe, it does not interact with structural and packing materials. Three hydrogen atoms in R143a molecule contribute to good solubility in mineral oils. Specific heat of vaporization is 19.88 kJ/mole at normal boiling point which is a bit higher than for R125 (18.82 kJ/mole). Discharge temperature is

lower than that of R12, R22 and R502. As energy analysis has showed, energy effectiveness of two-step cycle with R143a is close to the effectiveness of the cycle with R502, lower than that of R22, and higher than that of R125. R143a refrigerant belongs to composition of multi-component alternative blends suggested for substitution of R12, R22 and R502.

For the development of new refrigeration mixtures with minimal environmental impact (ozone depletion and global warming), it is to rely on reliable thermodynamic properties about a maximum of refrigerating fluid mixtures. In this work, we present VLE data points for the system (R116 + R143a) at three temperatures below the R116 critical temperature (258.45, 273.30, and 288.25 K) and five above (293.23, 298.17, 308.38, 318.34 and 328.18 K). The experimental results are fitted using using the Peng-Robinson [13] equation of state, using the Mathias-Copeman [14] alpha function and the Wong-Sandler [15] mixing rules involving NRTL [16] model. For the system R116 + R143a, no data were published in the literature.

2. Experimental Section

2.1 Materials

The R116 was purchased from DEHON (France) with 99.99 vol % certified purity. R143a was purchased from ARKEMA (France) with 99 vol% certified purity. Both chemicals were used as delivered.

2.2 Apparatus

The apparatus used in this work is based on the "static-analytic" method with liquid and vapor phase sampling. This apparatus is similar to that described by Laugier and Richon [9].

The equilibrium cell is immersed inside a temperature regulated liquid bath. Temperatures are measured by means of two platinum resistance thermometer probes (Pt100) inserted into the walls of the equilibrium cell. These Pt100 probes have been 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 are measured using a pressure transducer (Druck, type PTX611, range: 0 - 20 MPa). This sensor was calibrated against a dead weight pressure balance (5202S model from Desgranges & Huot).

Temperature and pressure data acquisition is performed with a computer linked to an HP unit (HP34970A). Resulting uncertainties on temperatures and pressures, after careful calibrations are ± 0.015 K and ± 0.0004 MPa, respectively.

The analyses of the equilibrium samples were carried out using a gas chromatograph equipped with a Thermal Conductivity Detector (TCD) connected to a Data Acquisition System. The analytical GC column used is a Porapak Q model, 80/100 Mesh (1/8" silcosteel tube, 4 m length, from Resteck, France). The TCD was repeatedly calibrated by introducing known amounts of each pure compound through a syringe into the injector of the gas chromatograph. Taking into account the uncertainties due to calibrations and dispersions of the analyses, resulting uncertainties about the equilibrium vapor and liquid mole numbers are estimated to be less than ± 2 %.

2.3 Experimental Procedure

At room temperature, the equilibrium cell and its loading lines are evacuated down to 0.1 Pa. The cell is first loaded with R143a as a liquid (about 5 cm^3). Equilibrium temperature is assumed to be reached when the two Pt100 probes (one located at top of equilibrium cell, the other in the bottom)

give equivalent temperature values within the experimental uncertainty for at least 10 minutes. The vapor pressure of R143a (the heavier component) is first recorded at equilibrium temperature. Then R116 (the lighter component) is introduced step by step, leading to successive equilibrium mixtures of increasing overall R116 content. After each new R116 introduction, equilibrium is assumed when the total pressure remains unchanged within $\pm$ 1.0 kPa during a period of 10 min under efficient stirring. For each equilibrium condition, at least five samples of both vapor and liquid phases are withdrawn using the pneumatic samplers ROLSI[TM] [10] and analyzed in order to check for measurements repeatability. Each isothermal two-phase envelope contains at least eight Pxy data points (for both liquid and vapor phases).

3. Correlations

The critical temperatures (T_C), critical pressures (P_C) for each of the two pure components are provided in Table 1. Our experimental VLE data are correlated by means of our homemade software TEP-ThermoSoft. We have used the PR EoS [11] with the Mathias-Copeman alpha function [12] for accurate representation of the pure component vapor pressures.

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

If $T > T_C$,

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

The Wong-Sandler (WS) mixing rules are chosen here [13],

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

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

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

k_{ij} is an adjustable binary interaction parameter.

The excess Gibbs energy model chosen is the NRTL [14] local composition model.

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

$\tau_{ii} = 0$ 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 [15] using the following objective function:

$$F = \frac{100}{N}\left[\sum_1^N \left(\frac{x_{\exp} - x_{cal}}{x_{\exp}}\right)^2 + \sum_1^N \left(\frac{y_{\exp} - y_{cal}}{y_{\exp}}\right)^2\right] \tag{7}$$

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

4. Results and discussion:

4.1 Vapor pressures

The critical temperatures (T_C), critical pressures (P_C) for each of the two components are provided in Table 1. R143a vapor pressures were measured at 15 temperatures from 258 to 338 K and used to adjust Mathias-Copeman parameters (see Table 2). Experimental and calculated vapor pressures values are reported in Table 3. The values calculated by the correlation are in good agreement with experimental values (mean relative absolute deviation (see eq. 2) is 0.53 % and bias (see eq. 3) is 0.01 %).

4.2 Vapor-liquid equilibrium data for the R116 + R143a mixture

The experimental and calculated VLE data are reported in Table 4 and plotted in Figure 1. The adjusted parameters corresponding to the WS mixing rules involving the NRTL model (ref. [16] recommends to use α_{ij} =0.3 for systems like the current ones), associated to the PR EoS, are given in Table 5, and plotted in Figures 2 and 3. This confirms what has been observed in previous studies [1-8], the parameters τ_{12}, τ_{21}, and k_{12} behave differently below and above the critical temperature of the lighter component (R116 in this work).

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

$$MRDU = (100/N)\sum \left|(U_{cal} - U_{\exp})/U_{\exp}\right| \tag{2}$$

$$BIASU = (100/N)\sum \left((U_{\exp} - U_{cal})/U_{\exp}\right) \tag{3}$$

Where N is the number of data points, and U = x_1 or y_1 or P for vapor pressures of pure compounds.

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

4.3 Critical line computation

The critical point of multicomponent mixtures can be calculated by the method of Heidemann and Khalil [18]. These authors developed an algorithm to calculate the critical point with a van der waals type EoS, combined with the classical mixing rules. In 1998, Stockfleth and Dohrn [19] improved this method by developping the algorithm of Heidemann and Khalil to apply it to a generalized equation of state. This last algorithm was chosen in this work to calculate the critical lines through our model. The temperature dependent binary parameters are those obtained by fitting VLE data in R116 supercritical domain. Results are plotted in figure 4. The predicted critical locus is in good agreement with the experimental phase envelopes as displayed in Figure 1.

5. Conclusion:

In this paper, we present VLE data for the system (R116 + R143a) at eight temperatures that are either below or above the R116. They were obtained using a "static-analytic" method. The experimental results are given with following uncertainties: $\pm$ 0.015 K, $\pm$ 0.0004 MPa and less than $\pm$ 4.0 % for vapor and liquid mole fractions.

The data are well correlated using our in-house thermodynamic software. This system can be classified as a diagram of type I or II according to van Konynenburg and Scott classification [20].

List of symbols:

c	Mathias-Copeman coefficient
F	Objective function
k_{ij}	Binary interaction parameter
P	Pressure [MPa]
T	Temperature [K]
x	Liquid mole fraction
y	Vapor mole fraction

Greek letters:

α_{ij}	non randomness NRTL model parameter (Eq 6)
τ_{ij}	NRTL model binary interaction parameter (Eq 6), [J. mol^{-1}]
ΔU	Deviation (U_{exp}-U_{cal})

Subscripts

c	Critical property
cal	Calculated property
exp	Experimental property

i,j	Molecular species
1	R116
2	R143a

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Table 1: Critical parameters (DDB, 97)

Compound	T_c/K	P_c/MPa
R116	293.035	3.042
R143a	346.25	3.759

Table 2: Mathias-Copeman coefficients.

Coefficients	R116*	R143a
c_1	0.8128	0.7191
c_2	-1.1603	0.2039
c_3	5.0299	-0.8472

* Values from ref. [8]

Table 3: Experimental and calculated vapor pressures for R143a.

T/K	P_{exp}/MPa	P_{cal}/MPa	ΔP/MPa
258.45	0.3884	0.3903	-0.0018
268.15	0.5446	0.5390	0.0056
273.30	0.6325	0.6338	-0.0013
283.06	0.8491	0.8472	0.0019
288.25	0.9767	0.9806	-0.0039
293.30	1.1143	1.1250	-0.0107
298.17	1.2967	1.2788	0.0179
303.24	1.4516	1.4549	-0.0033
308.38	1.6373	1.6512	-0.0139
313.10	1.8530	1.8482	0.0048
318.34	2.0796	2.0868	-0.0072
323.06	2.3304	2.3205	0.0099
328.18	2.5849	2.5952	-0.0103
333.06	2.8978	2.8787	0.0191
338.22	3.2048	3.2028	0.0020

Table 4: Vapor-liquid equilibrium pressures and phase compositions for the system R116 (1) + R143a (2), Δx and Δy are deviations in liquid and vapor mole fractions.

Experimental			Calculated		Deviations	
P_{exp}/MPa	x_1	y_1	x_{1cal}	$y_{1, cal}$	Δx	Δy
T = 258.45 K						
0.3884	0.0000	0.0000	0.0000	0.0000		
0.5234	0.0681	0.0723	0.2895	0.2802	-0.0042	0.0093

0.6311	0.1288	0.1381	0.4303	0.4248	-0.0093	0.0055
0.7050	0.1819	0.1883	0.5064	0.5007	-0.0064	0.0057
0.8287	0.2833	0.2862	0.6051	0.6020	-0.0029	0.0031
0.8943	0.3473	0.3482	0.6495	0.6474	-0.0009	0.0021
1.0063	0.4840	0.4795	0.7216	0.7186	0.0045	0.0030
1.0514	0.5514	0.5451	0.7510	0.7474	0.0063	0.0036
1.1004	0.6349	0.6269	0.7860	0.7809	0.0081	0.0051
1.1575	0.7454	0.7395	0.8335	0.8282	0.0059	0.0053
1.2058	0.8616	0.8627	0.8934	0.8911	-0.0011	0.0023
1.2149	0.8893	0.8954	0.9103	0.9118	-0.0061	-0.0015
1.2275	1.0000	1.0000	1.0000	1.0000		
T = 273.30 K						
0.6325	0.0000	0.0000	0.0000	0.0000		
0.8119	0.0650	0.0678	0.2392	0.2371	-0.0028	0.0021
0.9474	0.1222	0.1253	0.3647	0.3622	-0.0031	0.0025
1.0752	0.1839	0.1862	0.4568	0.4546	-0.0023	0.0022
1.2106	0.2606	0.2604	0.5364	0.5351	0.0002	0.0013
1.3572	0.3672	0.3567	0.6171	0.6100	0.0105	0.0071
1.4634	0.4540	0.4414	0.6678	0.6603	0.0126	0.0075
1.5729	0.5543	0.5457	0.7209	0.7130	0.0086	0.0079
1.7383	0.7406	0.7436	0.8153	0.8113	-0.0030	0.0040
1.7824	0.8043	0.8096	0.8507	0.8498	-0.0053	0.0009
1.8243	0.8754	0.8860	0.8966	0.9012	-0.0106	-0.0046
1.8380	0.9045	0.9107	0.9168	0.9189	-0.0061	-0.0021
1.8504	1.0000	1.0000	1.0000	1.0000		
T = 288.25 K						
0.9767	0.0000	0.0000	0.0000	0.0000		
1.2808	0.0892	0.0926	0.2551	0.2526	-0.0034	0.0025
1.4286	0.1393	0.1427	0.3434	0.3418	-0.0034	0.0016
1.6104	0.2081	0.2101	0.4330	0.4324	-0.0020	0.0006
1.8079	0.2938	0.2928	0.5143	0.5148	0.0010	-0.0005
1.9764	0.3777	0.3740	0.5776	0.5768	0.0037	0.0008
2.1786	0.4936	0.4889	0.6501	0.6472	0.0047	0.0029
2.3786	0.6246	0.6246	0.7258	0.7213	0.0000	0.0045
2.5777	0.7852	0.7871	0.8234	0.8202	-0.0019	0.0032
2.6251	0.8325	0.8351	0.8562	0.8548	-0.0026	0.0014
2.6575	0.8717	0.8738	0.8862	0.8852	-0.0021	0.0010
2.6976	1	1	1	1		
T = 293.23 K						
1.1143	0.0000	0.0000	0.0000	0.0000		
1.4030	0.0780	0.0800	0.2189	0.2135	-0.0020	0.0054

1.6200	0.1452	0.1478	0.3363	0.3337	-0.0026	0.0026
1.8319	0.2197	0.2206	0.4281	0.4276	-0.0009	0.0005
2.0212	0.2948	0.2933	0.4970	0.4988	0.0015	-0.0018
2.2462	0.3974	0.3924	0.5744	0.5738	0.0050	0.0006
2.4401	0.4974	0.4920	0.6361	0.6350	0.0054	0.0011
2.6536	0.6197	0.6189	0.7098	0.7063	0.0008	0.0035
2.8399	0.7438	0.7458	0.7856	0.7835	-0.0020	0.0021
2.9406	0.8233	0.8260	0.8420	0.8416	-0.0027	0.0004

			T = 298.17 K			
1.2967	0.0000	0.0000	0.0000	0.0000		
1.6269	0.0839	0.0883	0.2176	0.2298	-0.0044	-0.0122
1.8404	0.1449	0.1467	0.3194	0.3276	-0.0018	-0.0082
2.0221	0.2030	0.2015	0.3919	0.3974	0.0015	-0.0055
2.3629	0.3280	0.3216	0.5059	0.5071	0.0064	-0.0012
2.5413	0.4037	0.3965	0.5601	0.5584	0.0072	0.0017
2.7272	0.4893	0.4851	0.6143	0.6110	0.0042	0.0033
2.8449	0.5470	0.5472	0.6489	0.6457	-0.0002	0.0032
3.0705	0.6774	0.6786	0.7253	0.7220	-0.0012	0.0033
3.1163	0.7027	0.7076	0.7417	0.7404	-0.0049	0.0013
3.1764	0.7401	0.7476	0.7651	0.7673	-0.0075	-0.0022

			T = 308.38 K			
1.6373	0.0000	0.0000	0.0000	0.0000		
1.8906	0.0550	0.0556	0.1367	0.1303	-0.0006	0.0064
2.1216	0.1100	0.1120	0.2357	0.2312	-0.0020	0.0045
2.3118	0.1585	0.1611	0.3040	0.3010	-0.0026	0.0030
2.5354	0.2207	0.2224	0.3735	0.3717	-0.0017	0.0018
2.7337	0.2808	0.2809	0.4277	0.4266	-0.0001	0.0011
2.9653	0.3564	0.3554	0.4844	0.4838	0.0010	0.0006
3.1564	0.4241	0.4229	0.5275	0.5269	0.0012	0.0006
3.2979	0.4773	0.4773	0.5569	0.5569	0.0000	0.0000
3.4421	0.5378	0.5380	0.5818	0.5851	-0.0002	-0.0032

			T = 318.34 K			
2.0796	0.0000	0.0000	0.0000	0.0000		
2.3195	0.0463	0.0469	0.1013	0.0984	-0.0006	0.0029
2.4657	0.0757	0.0774	0.1651	0.1516	-0.0017	0.0135
2.6724	0.1215	0.1220	0.2241	0.2180	-0.0005	0.0061
2.8222	0.1537	0.1557	0.2628	0.2605	-0.0020	0.0023
3.0482	0.2074	0.2091	0.3187	0.3173	-0.0017	0.0014
3.2843	0.2689	0.2692	0.3699	0.3686	-0.0003	0.0013
3.4754	0.3226	0.3223	0.4036	0.4045	0.0003	-0.0008

3.5895	0.3647	0.3570	0.4193	0.4229	0.0077	-0.0036
			$T = 328.18$ K			
2.5849	0.0000	0.0000	0.0000	0.0000		
2.7608	0.0304	0.0305	0.0587	0.0559	-0.0001	0.0028
2.8533	0.0472	0.0477	0.0871	0.0843	-0.0005	0.0028
2.9367	0.0617	0.0634	0.1109	0.1085	-0.0017	0.0024
3.0807	0.0888	0.0908	0.1496	0.1469	-0.0020	0.0027
3.2252	0.1167	0.1188	0.1845	0.1818	-0.0021	0.0027
3.3619	0.1443	0.1461	0.2136	0.2116	-0.0018	0.0021
3.5280	0.1803	0.1807	0.2461	0.2435	-0.0004	0.0026
3.6324	0.2047	0.2036	0.2634	0.2611	0.0011	0.0023
3.7209	0.2268	0.2243	0.2712	0.2741	0.0025	-0.0029
3.8092	0.2468	0.2468	0.2844	0.2845	0.0000	-0.0001

Table 5: Values of the binary parameters at each temperature.

Data	T /K	τ_{12}/ J.mol^{-1}	τ_{21}/ J.mol^{-1}	k_{12}
	258.45	3952	-610	0.139
	273.30	3069	-372	0.172
This	288.25	3446	-793	0.181
work	293.23	3348	-903	0.191
	298.17	1946	-24	0.208
	308.38	3792	-1140	0.175
	318.34	4062	-1224	0.177
	328.18	4292	-1362	0.188

Table 6: Relative deviation MRDU and BIASU obtained in fitting experimental VLE data with PR EoS, Mathias-Copeman alpha function and WS mixing rules involving NRTL model.

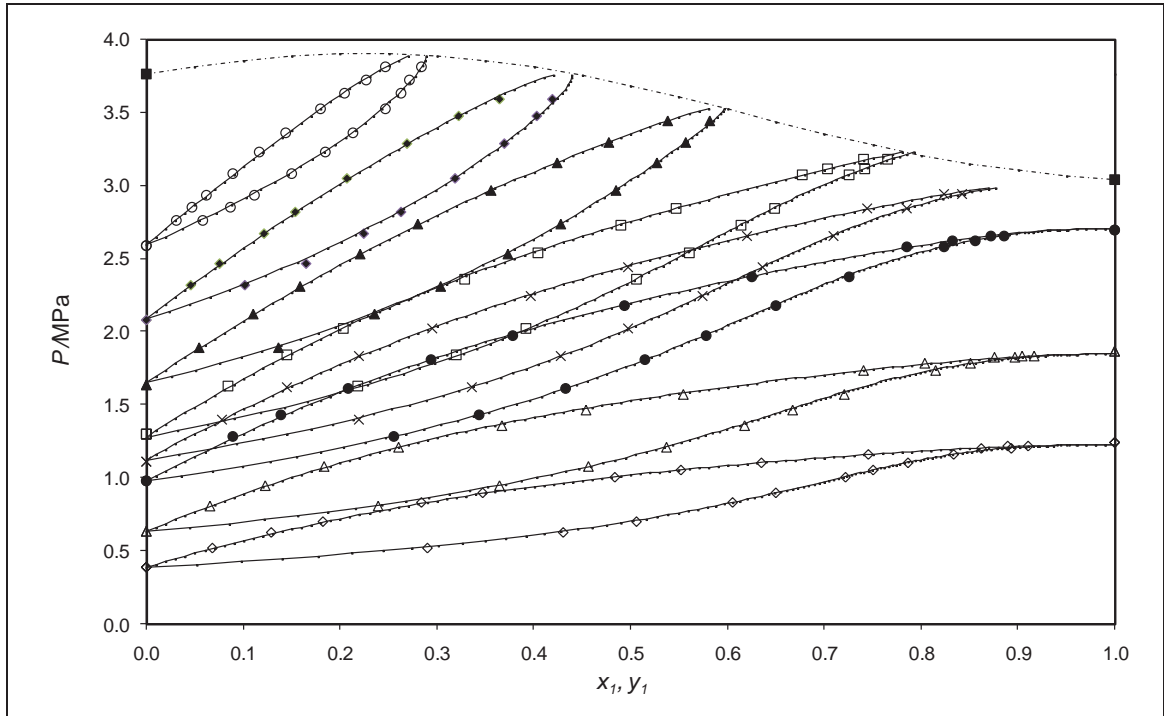| Data	T /K	Bias x %	MRD x %	Bias y %	MRD y %
	258.45	2.34	2.11	0.80	0.83
	273.30	1.08	1.67	0.50	0.64
This	288.25	0.63	1.03	0.34	0.35
work	293.23	1.06	0.93	0.45	0.53
	298.17	-2.12	1.38	-0.81	1.21
	308.38	2.07	0.66	0.89	1.02
	318.34	3.82	1.07	1.80	2.06
	328.18	2.71	1.15	1.52	1.74

Figure 1: Vapor-Liquid equilibrium diagrams of the R116 (1) + R143a (2) system at 8 temperatures

◇: 258.45 K, Δ: 273.30 K, ● : 288.25 K, × : 293.23 K, □: 298.17 K, ▲: 308.38 K, ♦:318.34 K, O : 328.18 K

---- : Predicted mixture critical line.

■ : Critical pressures of pure components.

Solid lines: Phase envelopes calculated with PR EoS, Mathias-Copemen alpha function, Wong-Sandler mixing rules and NRTL activity coefficient model with parameters from Table 5.
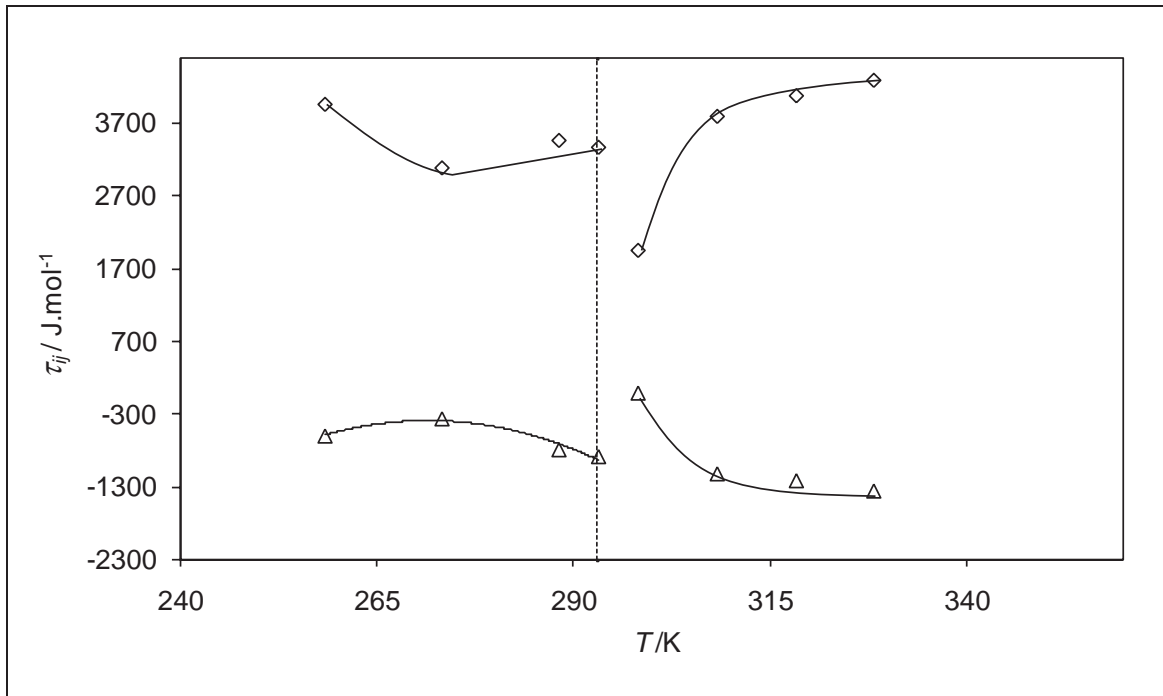
Figure 2: Binary NRTL Parameters τ_{12} ($\Diamond$) and τ_{21} (Δ) as a function of temperature.

Vertical dotted line represents the R116 critical temperature.
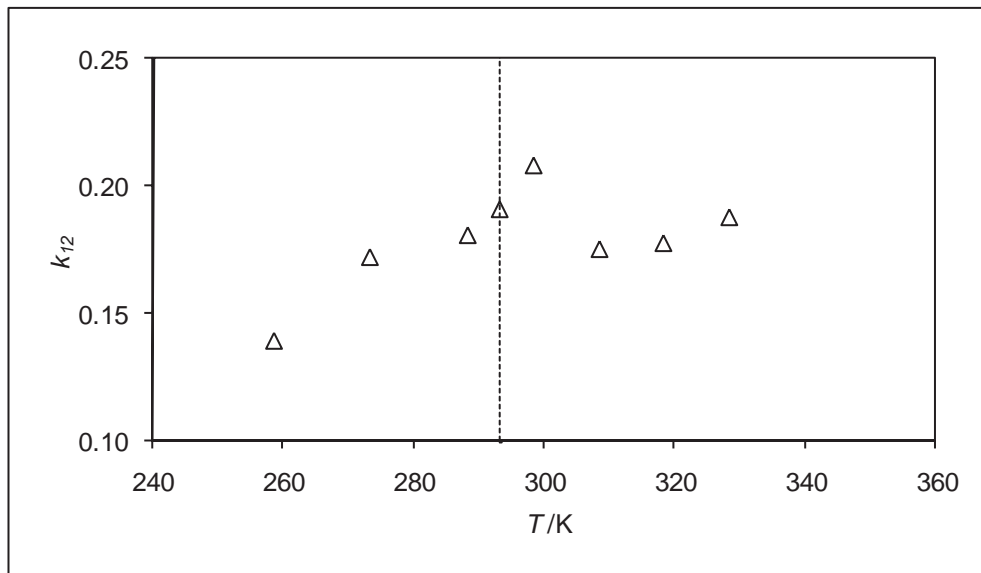

Figure 3: k_{12} binary parameter as a function of temperature.

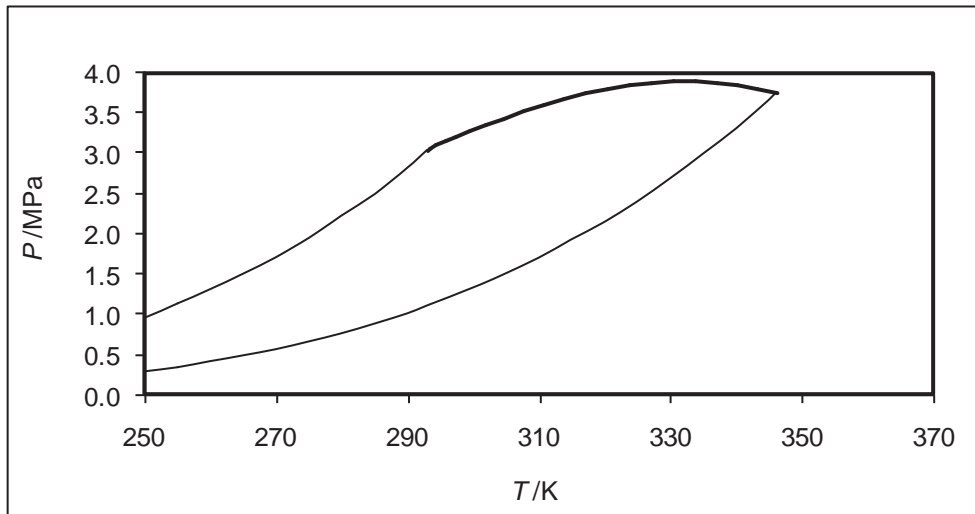Vertical dotted line represents the R116 critical temperature.

Figure 4: PT diagram of the R116 + R143a binary system. Solid lines: R116 and 143a vapor pressures. Bold solid line: mixture critical line.