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Vapor–liquid equilibria of the (hexafluoroethane + 1,1,1-trifluoroethane) binary system from 258 to 343 K up to 3.89 MPa

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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: Hexafluoroethane (R116) + 1,1,1-trifluoroethane (R143a), has been studied with the aim of providing PT_x data. Isothermal vapor–liquid equilibrium data have been 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 equation 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.

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Equilibres «liquide-vapeur» du système binaire hexafluoroéthane + 1,1,1-trifluoroéthane de 258 à 343 K jusqu'à 3,89 MPa

Mots-clés : Frigorigène ; Mélange binaire ; R116 ; R143a ; Expérimentation ; Calcul ; Pression ; Vapeur ; Équilibre ; Liquide–vapeur ; Équation

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1. Introduction

In the wake of the global response for the protection of the environment and sustainable development, the refrigeration industry is forced to find new fluids as acceptable refrigerants. The Montreal Protocol presented in 1987 is one of the landmarks towards the replacement of ozone-destroying refrigerants like chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) with 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 (Madani et al., 2008a,b; Valtz et al., 2002, 2007; Coquelet et al., 2005; Coquelet et al., 2003a,b; Rivollet et al., 2004; Coquelet et al., 2004) The VLE cell used for these purposes relies on the “static-analytic” method (Laugier and Richon, 1986) and Rolsi™ sampling (Guilbot et al., 2000).

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 in 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 10,000 years and a global warming potential (GWP) of 9000 (Marks et al., 2003). However its ozone depletion potential (ODP) is 0 (Bozin and Goodyear, 1968).

On the other hand, 1,1,1-trifluoroethane R143a, CAS no: 420-46-2, R143a has an ozone depletion potential ODP = 0 and comparatively high Global Warming Potential (=1000), is non-toxic and fir-safe, and it does not interact with structural and packing materials. Three hydrogen atoms in the 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 a 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 multicomponent 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), one has to rely on reliable thermodynamic properties for a number of refrigerating fluid mixtures. In this work, we present VLE data points for the system

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 ^a	R143a
c_1	0.8128	0.7191
c_2	-1.1603	0.2039
c_3	5.0299	-0.8472

^a Values from Valtz et al. (2007).

(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 the Peng–Robinson (Peng and Robinson, 1976) equation of state, using the Mathias–Copeman (Mathias and Copeman, 1983) alpha function and the Wong–Sandler (Wong and Sandler, 1992) mixing rules involving NRTL (Renon and Prausnitz, 1968) model. For the system R116 + R143a, no data were found previously 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 (1986).

The equilibrium cell is immersed inside a temperature regulated liquid bath. Temperatures are measured by means of two platinum resistance thermometer probes (Pt100)

Table 3 – Experimental and calculated vapor pressures for R143a. Calculated values are obtained with the PR EoS using the Mathias–Copeman alpha function and parameters of Table 2

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. Calculated values are from PR EoS + Mathias–Copeman alpha function + WS mixing rules involving the NRTL model

$P_{\text{exp}}/\text{MPa}$	x_1	$x_{1, \text{cal}}$	y_1	$y_{1, \text{cal}}$	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

Table 4 (continued)

$P_{\text{exp}}/\text{MPa}$	x_1	$x_{1, \text{cal}}$	y_1	$y_{1, \text{cal}}$	Δx	Δy
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

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 Poropak 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 $\pm 2\%$.

2.3. Experimental procedure and data correlation

The experimental procedure and the data correlation procedure are detailed in previous papers (Madani et al., 2008a,b). The adjustment of parameters is performed through a modified Simplex algorithm (Ab erg and Gustavsson, 1982) using the following objective function:

$$F = \frac{100}{N} \left[\sum_1^N \left(\frac{x_{\text{exp}} - x_{\text{cal}}}{x_{\text{exp}}} \right)^2 + \sum_1^N \left(\frac{y_{\text{exp}} - y_{\text{cal}}}{y_{\text{exp}}} \right)^2 \right] \quad (1)$$

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

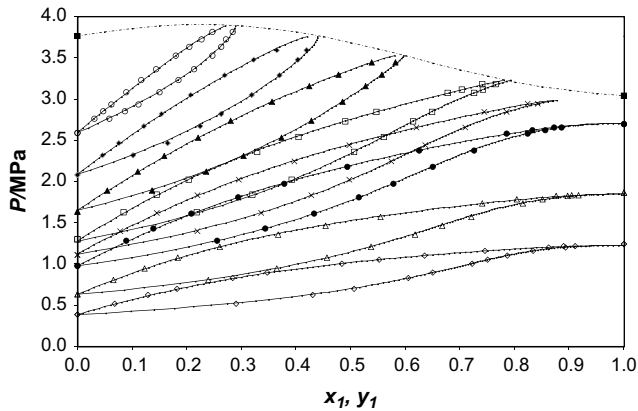


Fig. 1 – Vapor-liquid equilibrium diagrams of the R116 (1) + R143a (2) system at 8 temperatures. \diamond : 258.45 K, \triangle : 273.30 K, \bullet : 288.25 K, \times : 293.23 K, \square : 298.17 K, \blacktriangle : 308.38 K, \blacklozenge : 318.34 K, \circ : 328.18 K, —: Predicted mixture critical line. \blacksquare : Critical pressures of pure components. Solid lines: Phase envelopes calculated with PR EoS, Mathias–Copeman alpha function, Wong–Sandler mixing rules and NRTL activity coefficient model with parameters from Table 5.

fractions, y_{exp} and y_{cal} are respectively the measured and calculated vapor phase mole fractions. The objective function given in Eq. (1) allows convenient determination of binary interaction parameters for representation of T , P , vapor and liquid compositions in very good agreement with experimental ones.

3. Results and discussion

3.1. Vapor pressures

The critical temperature (T_c) and critical pressure (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. We have used the PR EoS (Peng and Robinson, 1976) equation of state, using the Mathias–Copeman (Mathias and Copeman, 1983) alpha function for accurate representation of the pure component vapor pressures.

Table 5 – Values of the binary parameters at each temperature

Data	T/K	$\tau_{12}/\text{J mol}^{-1}$	$\tau_{21}/\text{J mol}^{-1}$	k_{12}
This work	258.45	3952	–610	0.139
	273.30	3069	–372	0.172
	288.25	3446	–793	0.181
	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

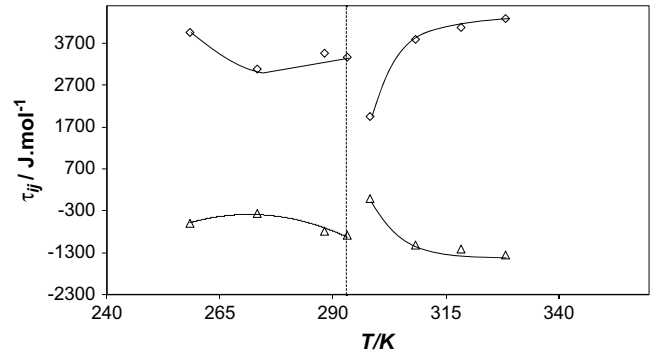


Fig. 2 – Binary NRTL Parameters τ_{12} (\diamond) and τ_{21} (\triangle) as a function of temperature. Vertical dotted line represents the R116 critical temperature.

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

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

Mathias–Copeman parameters adjusted on experimental data appear in 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%).

3.2. Vapor-liquid equilibrium data for the R116 + R143a mixture

The experimental and calculated VLE data are reported in Table 4 and plotted in Fig. 1. The adjusted parameters corresponding to the WS mixing rules involving the NRTL model (Renon and Prausnitz, 1968) recommend to use $\alpha_{ij} = 0.3$ for systems like the current ones, associated to the PR EoS, are given in Table 5, and plotted in Figs. 2 and 3. This confirms what has been observed in previous studies (Madani et al., 2008a,b; Valtz et al., 2002, 2007; Coquelet et al., 2005; Coquelet et al., 2003a,b; Rivollet et al., 2004;

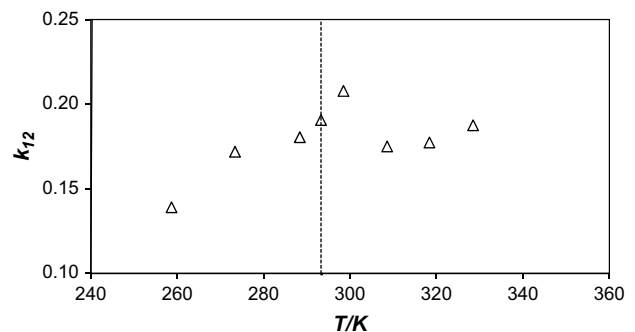


Fig. 3 – k_{12} Binary parameter as a function of temperature. Vertical dotted line represents the R116 critical temperature.

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 %
This work	258.45	2.34	2.11	0.80	0.83
	273.30	1.08	1.67	0.50	0.64
	288.25	0.63	1.03	0.34	0.35
	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

Coquelet et al., 2004), 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:

$$\text{MRDU} = (100/N) \sum |(U_{\text{cal}} - U_{\text{exp}})/U_{\text{exp}}| \quad (4)$$

$$\text{BIASU} = (100/N) \sum ((U_{\text{exp}} - U_{\text{cal}})/U_{\text{exp}}) \quad (5)$$

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.

3.3. Critical line computation

The critical point of multicomponent mixtures can be calculated by the method of Heidemann and Khalil (Heidemann

Table 7 – Calculated critical points for the R116 (1) + R143a (2) binary system

x_1	T_{cal}/K	$P_{\text{cal}}/\text{MPa}$
0.00	346.25 ^a	3.759 ^a
0.05	343.3	3.81
0.10	340.2	3.86
0.15	337.1	3.89
0.20	333.9	3.90
0.25	330.6	3.90
0.30	327.3	3.89
0.35	323.9	3.86
0.40	320.6	3.81
0.45	317.2	3.75
0.50	313.9	3.68
0.55	310.7	3.60
0.60	307.6	3.52
0.65	304.7	3.44
0.70	302.0	3.35
0.75	299.6	3.28
0.80	297.5	3.21
0.85	295.7	3.15
0.90	294.4	3.10
0.95	293.5	3.07
1.00	293.035 ^a	3.042 ^a

^a Values from DDB, 97.

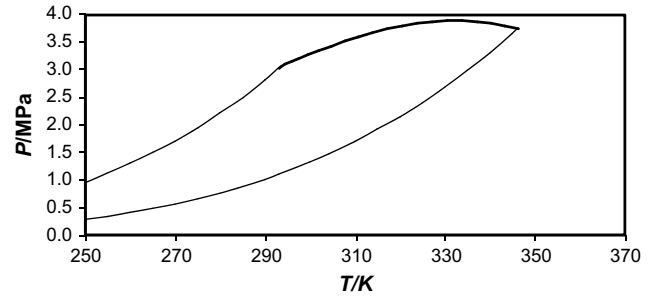


Fig. 4 – PT diagram of the R116 + R143a binary system. Solid lines: R116 and 143a vapor pressures. Bold solid line: mixture critical line.

and Khalil, 1980). 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 (1998) improved this method by developing 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 the R116 supercritical domain. Results are reported in Table 7 and plotted in Fig. 4. The predicted critical locus is in good agreement with the experimental phase envelopes as displayed in Fig. 1.

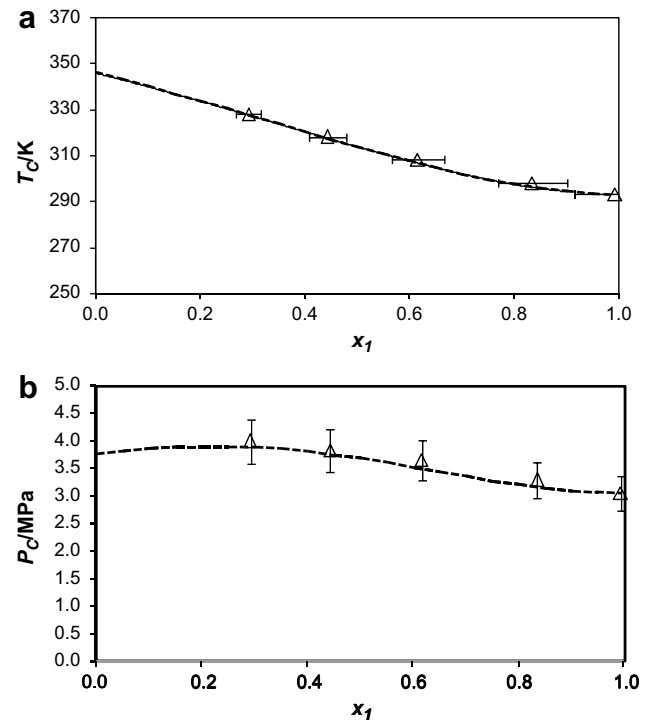


Fig. 5 – (a) Plot of critical temperature as a function of R116 mole fraction, calculated through relative volatility model. Error bar (8%) is the uncertainty estimated on relative volatility. (b) Plot of critical pressure as a function of R116 mole fraction, calculated through relative volatility model. Error bar (8%) is the uncertainty estimated on relative volatility.

Another method was also chosen to estimate the value of the critical point at the critical point where relative volatility is equal to one. So, using a correlation representing experimental relative volatility values allows estimation of the critical point. The liquid phase composition of the more volatile component is calculated at the equality of partition coefficients (relative volatility equals unity). At this composition, the calculated temperature and pressure are reported as critical data with uncertainties estimated to less than 8%. Calculated critical points appear in Fig. 5a and b.

4. Conclusion

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

This system can be classified as a diagram of type I or II according to van Konynenburg and Scott classification (van Konynenburg and Scott, 1980).

REFERENCES

- Abërg, E.R., Gustavsson, A.G., 1982. Design and evaluation of modified simplex method. *Anal. Chim. Acta* 144, 39–53.
- Bozin, S.E., Goodyear, C.C., 1968. Growth of ionization currents in carbon tetrafluoride and hexafluoroethane. *J. Phys. D: Appl. Phys.* 1, 327–334.
- Coquelet, C., Chareton, A., Valtz, A., Baba-Ahmed, A., Richon, D., 2003a. Vapor–liquid equilibrium data for the azeotropic difluoromethane + propane system at temperatures from 294.83 to 343.26 K and pressures up to 5.4 MPa. *J. Chem. Eng. Data* 48, 317–323.
- Coquelet, C., Nguyen Hong, D., Chareton, A., Baba-Ahmed, A., Richon, D., 2003b. Vapor–liquid equilibrium data for the difluoromethane + 1,1,1,2,3,3,3-heptafluoropropane system at temperatures from 283.20 to 343.38 K. *Int. J. Refrigeration* 26, 559–565.
- Coquelet, C., Chareton, A., Richon, D., 2004. Vapor–liquid equilibrium measurement and correlation of the difluoromethane (R32) + propane (R290) + 1,1,1,2,3,3,3-heptafluoropropane (R227ea) ternary mixture at temperatures from 269.85 to 328.35 K. *Fluid Phase Equilib.* 218, 209–214.
- Coquelet, C., Valtz, A., Richon, D., 2005. Vapor–liquid equilibrium data for the Difluoromethane (R32) + Dimethyl Ether (DME) system at temperatures from 283.03 to 363.21 K and pressures up to about 5.5 MPa. *Fluid Phase Equilib.* 232, 44–49.
- Dortmund Data Bank (DDB) Version 97. DDBST Software and Separation Technology GmbH, Oldenburg, Germany.
- Guilbot, P., Valtz, A., Legendre, H., Richon, D., 2000. Rapid on line sampler-injector, a reliable tool for HT-HP sampling and on line GC analysis. *Analusis* 28, 426–431.
- Heidemann, R.A., Khalil, A.M., 1980. The calculation of critical points. *AIChE J.* 26, 769–779.
- van Konynenburg, P.H., Scott, R.L., 1980. Critical lines and phase equilibria in binary van der Waals mixtures. *Philos. Trans. R. Soc. Lond.* 298, 495–540.
- Laugier, S., Richon, D., 1986. New apparatus to perform fast determinations of mixture vapor–liquid equilibria up to 10 MPa and 423 K. *Rev. Sci. Instrum.* 57, 469–472.
- Madani, H., Valtz, A., Coquelet, C., Meniai, A.H., Richon, D., 2008a. Vapor–liquid equilibrium data for the (hexafluoroethane + 1,1,1,2-tetrafluoroethane) system at temperatures from 263 to 353 K and pressures up to 4.16 MPa. *Fluid Phase Equilib.* 268, 68–73.
- Madani, H., Valtz, A., Coquelet, C., Meniai, A.H., Richon, D., 2008b. Vapor–liquid equilibrium data for the (carbon dioxide + 1,1-difluoroethane) system at temperatures from 258 to 343 K and pressures up to 7.57 MPa. *J. Chem. Thermodyn.* 40, 1490–1494.
- Marks, J., Kantamaneni, R., Pape, D., Rand, S., 2003. Protocol of measurement of tetrafluoromethane and hexafluoroethane from primary aluminum production. *Light Met.*, 221–226.
- Mathias, P.M., Copeman, T.W., 1983. Extension of the Peng–Robinson equation of state to complex mixtures: evaluation of various forms of the local composition concept. *Fluid Phase Equilib.* 13, 91–108.
- Peng, D.Y., Robinson, D.B., 1976. A new two parameters equation of state. *Ind. Eng. Chem. Fundam.* 15, 59–64.
- Renon, H., Prausnitz, J.M., 1968. Local composition in thermodynamic excess function for liquid mixtures. *AIChE J.* 14, 135–144.
- Rivollet, F., Chapoy, A., Coquelet, C., Richon, D., 2004. Vapor–liquid equilibrium data for the carbon dioxide (CO₂) + difluoromethane (R32) system at temperatures from 283.12 to 343.25 K and pressures up to 7.46 MPa. *Fluid Phase Equilib.* 218, 95–101.
- Stockfleth, R., Dohrn, R., 1998. An algorithm for calculating critical points in multicomponent mixtures which can easily be implemented in existing programs to calculate phase equilibria. *Fluid Phase Equilib.* 145, 43–52.
- Valtz, A., Coquelet, C., Baba-Ahmed, A., Richon, D., 2002. Vapor–liquid equilibrium data for the propane + 1,1,1,2,3,3,3-heptafluoropropane (R227ea) system at temperatures from 293.16 to 353.18 K and pressures up to 3.4 MPa. *Fluid Phase Equilib.* 202, 29–47.
- Valtz, A., Coquelet, C., Richon, D., 2007. Vapor–liquid equilibrium data for the hexafluoroethane + carbon dioxide at temperatures from 253 to 297 K and pressures up to 6.54 MPa. *Fluid Phase Equilib.* 258, 179–185.
- Wong, D.S.H., Sandler, S.I., 1992. A theoretically correct mixing rule for cubic equation of state. *AIChE J.* 38, 671–680.

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
 τ_{ij} : NRTL model binary interaction parameter [J mol^{-1}]
 ΔU : deviation ($U_{\text{exp}} - U_{\text{cal}}$)
 Subscripts
 c: critical property
 cal: calculated property
 exp: experimental property
 i, j: molecular species
 1: R116
 2: R143a