Vapour–liquid equilibrium data for the difluoromethane +1,1,1,2,3,3,3-heptafluoropropane system at temperatures from 283.20 to 343.38 K and pressures up to 4.5 MPa

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Isothermal vapour–liquid equilibrium data for the difluoromethane (R32)-1,1,1,2,3,3,3-Heptafluoropropane (R227ea) binary system are presented at 283.20, 303.21, 323.21 and 343.38 K and pressures up to 4.5 MPa. The experimental method, used for this work, is of the static-analytic type. It takes advantage of mobile pneumatic capillary samplers (Rolsi™, Armines' patent) developed in our laboratory. The four P, x, y isothermal data have been represented with the Soave–Redlich–Kwong (SRK) equation of state and the MHV1 rules involving the NRTL model.

1. Introduction

In 1987, the modification of the Montreal protocol has prohibited the use and the production of chlorofluorocarbons (CFC's) in industrialized nations. Accurate knowledge of the thermo-physical properties of mixtures containing HFC and hydrocarbons, which are proposed as alternative refrigerants, is of great importance to evaluate the performance of refrigeration cycles and to determine the optimum composition of new working fluids.

During the second Workshop on refrigerants held at Ecole des Mines in Paris, France, April 2001, under the auspices of IUPAC, Dr. J. Morley (DuPont Fluoro-

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products, Hemel Hempstead, UK) addressed the question "Are we near an industry standard for refrigerant properties?" He discussed the various important worldwide activities which were taking place to determine accurate thermophysical properties of candidate alternative refrigerant working fluids.

Knowledge of vapour–liquid equilibrium (VLE) data for new mixtures allows choosing those offering the best suitable thermodynamic properties. The development of models for representation and prediction of physical properties and phase equilibria as well as the improvement of current equations of state cannot be handled seriously without accurate VLE data.

Using an apparatus based on a static-analytic method, isothermal vapour–liquid equilibrium measurements on the difluoromethane (R32) + 1,1,1,2,3,3,3–heptafluoropropane (R227ea) binary mixture were performed at temperatures from 283.20 to 343.38 K. The

obtained data are fitted using the Soave–Redlich–Kwong (SRK) equation of state.

2. Experimental section

2.1. Materials

1,1,1,2,3,3,3-Heptafluoropropane (R227ea) is from DEHON (France) and has a certified purity higher than 99.99 vol.%. The difluoromethane (R32) is from DEHON (France) and has a certified purity higher than 99.99 vol.%. These chemicals were used as received without any further purification.

2.2. Apparatus and experimental procedures

The apparatus from which most of the data have been determined (Fig. 1) is based on a static-analytic method with liquid and vapour phase sampling. This apparatus is similar to that described by Laugier and Richon [1].

The equilibrium cell is immersed in a thermo-regulated liquid bath; the temperature is controlled within 0.01 K. For accurate temperature measurements in the equilibrium cell and to check for thermal gradients, two platinum resistance thermometers (Pt100) are inserted inside wells drilled into the body of the equilibrium cell at two different levels (see Fig. 1) and connected to an HP data acquisition unit (HP34970A). These two Pt100 are carefully and periodically calibrated against a 25 Ω reference platinum resistance thermometer (TINSLEY Precision Instruments). The resulting uncertainty is not higher than 0.02 K. The 25 Ω reference platinum resistance thermometer was calibrated by the Laboratoire National d'Essais (Paris) on the basis of the 1990 International Temperature Scale (ITS 90). Pressures are measured by means of a pressure transducer (Druck, type PTX611, range: 0–0.6 MPa) connected to the HP data acquisition unit (HP34970A) as are the two Pt100; the pressure transducer is maintained at constant temperature (temperature higher than the highest temperature of the study) thanks to a home-made air-thermostat thermally controlled by a PID regulator (WEST instrument, model 6100).

The pressure uncertainty is estimated to be within ±0.001 MPa, after a careful calibration against a dead weight balance (Desgranges & Huot 5202S, CP 0.3 to 40 MPa, Aubervilliers, France).

The HP on-line data acquisition unit is connected to a personal computer through a RS-232 interface. This complete data acquisition system allows real time readings and records of both temperatures and pressures during isothermal runs.

The analytical work was carried out using a gas chromatograph (VARIAN model CP-3800) equipped
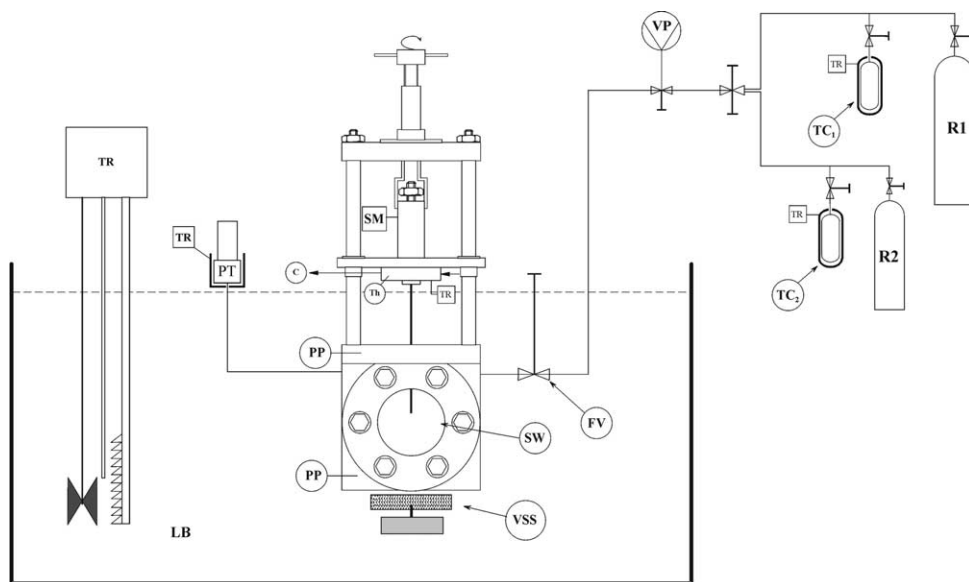
Fig. 1. Flow diagram of the equipment. C: carrier gas; EC: equilibrium cell; FV: feeding valve; LB: liquid bath; PP: platinum probe; R1C: refrigerant R32 cylinder; PT: pressure transducer; R2C: refrigerant R227ea cylinder; SM: sampler monitoring; SW: sapphire window; TC_1 and TC_2 thermal compressors; Th: thermocouple; TR: temperature regulator; VSS: variable speed stirring assembly; VP: vacuum pump.

with a thermal conductivity detector (TCD). Peak integrations are done on a computer containing a special card from Borwin through the software developed by Borwin (BORWIN ver 1.5, from JMBS, Le Fontanil, France). The analytical column is HaySep T 100/120 Mesh (silcosteel tube, length: 1.6 m, diameter: 1/8″ from Restek). The TCD was repeatedly calibrated by introducing known amounts of each pure compound through a syringe in the injector of the gas chromatograph. Taking into account the uncertainties due to calibrations and the dispersions of analyses, accuracy on vapour and liquid mole fractions is estimated to be within ±1.0% over the whole range of concentrations.

The experimental procedure is the following: at room temperature, the equilibrium cell and loading circuit are evacauated down to 0.1 Pa. One of the thermal compressors (TC_1) is loaded with liquid R32 while the other (TC_2) is loaded with liquid R227ea. At the required equilibrium temperature (equilibrium temperature is assumed to be reached when the two Pt100 thermometers give the same temperature value within their temperature uncertainty for at least 10 min), a volume of about 5 cm³ of R227ea is introduced into the equilibrium cell. The vapour pressure of R227ea (the heaviest component) is then recorded at this temperature. To describe the two-phase envelope with at least 8 *PTxy* data points, adequate amounts of the light component (R32) are introduced step by step, leading to successive new equilibrium mixtures. Equilibrium is assumed when

the total pressure remains unchanged within ±1.0 kPa during a period of 10 min under efficient stirring.

For each equilibrium condition, at least six samples of both vapour and liquid phases are withdrawn using the pneumatic samplers ROLSI™ as described by Guilbot et al. (2000) [2] and analyzed in order to check for measurement repeatability.

3. Correlations

Isothermal VLE measurements on the R32-R227ea system were performed in the temperature range from 283.20 to 343.38 K at pressures up to 4.5 MPa. The critical temperature (T_C), critical pressure (P_C), and acentric factor (ω) for each pure component [3] are respectively:

5.83 MPa, 351.55 K and 0.2710 for R32

2.98 MPa, 375.95 K and 0.3632 for R227ea.

Our experimental VLE data are correlated by means of home-made software (Thermopack from ARMINES-Ecole des Mines de Paris). The original Soave–Redlich–Kwong [4] equation of state (SRK EoS) gives good results for VLE of either non-polar or slightly polar mixtures. It is worthy to note that R32 is a polar compound and the use of the Soave alpha function would result in systematic deviations between experimental

and calculated vapour pressures. We have used the SRK EoS but with the Mathias–Copeman [5] alpha function with three adjustable parameters, which was especially developed for polar compounds.

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

c_1, c_2 and c_3 are the three adjustable parameters. Mathias–Copeman coefficients are evaluated in our whole temperature domain using a modified Simplex algorithm. The objective function is:

$$F = \frac{1}{N}\sum\left(\frac{P_{\exp} - P_{cal}}{P_{\exp}}\right)^2 \tag{2}$$

where N is the number of data points, $P_{\exp}$ is the measured pressure, and P_{cal} is the calculated pressure.

In our equation of state approach, we need mixing rules. The first mixing rules used to correlate the vapour–liquid equilibrium are the van der Waals mixing rules:

$$a = \sum_i\sum_j x_i x_j a_{ij} \tag{3}$$

$$b = \sum_i x_i b_i \tag{4}$$

where $a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right) \tag{5}$

k_{ij} is the binary interaction parameter found by a careful curve fitting involving our mixture data.

The second set of mixing rules involves an activity coefficient model. Among the different mixing rules available in literature we have selected the MHV1 (modified Huron–Vidal) mixing rules proposed by Michelsen [6] where the attractive parameter is calculated from Eq. (6) and molar covolume from Eq. (4):

$$a = b\left[\sum_i x_i \frac{a_i}{b_i} - \frac{RT}{q_1}\sum_i x_i Ln\left(\frac{b_i}{b}\right) + \frac{G_\gamma^E(T, P, x_i)}{q_1}\right] \tag{6}$$

The reference pressure is $P = 0$. Michelsen recommends $q_1 = -0.593$.

The excess Gibbs energy is calculated using the NRTL local composition model [7]:

$$\frac{G_{(T,P)}^E}{RT} = \sum_i x_i \sum_j \frac{x_j \mathrm{Exp}\left(-\alpha_{j,i}\frac{\tau_{j,i}}{RT}\right)}{\sum_k x_k \mathrm{Exp}\left(-\alpha_{k,i}\frac{\tau_{k,i}}{RT}\right)}\tau_{j,i} \tag{7}$$

$\tau_{i,i} = 0$ and $\alpha_{i,i} = 0$.

$\alpha_{j,i}$, $\tau_{j,i}$ and $\tau_{i,j}$ are adjustable parameters. For our system which belongs to a given polar mixture type it is recommended to use $\alpha_{j,i} = 0.3$.

$\tau_{j,i}$ and $\tau_{i,j}$ are adjusted directly to VLE data through a modified Simplex algorithm using the objective function:

$$F = \frac{1}{N}\left[\sum\left(\frac{P_{\exp} - P_{cal}}{P_{\exp}}\right)^2\right] \tag{8}$$

4. Results and discussion

4.1. Pure compound vapour pressures

We have measured the vapour pressures of the two components. The adjusted values of the SRK EoS Mathias–Copeman coefficients are:

$C_1 = 1.075$, $C_2 = -2.540$, $C_3 = 10.463$ for R32.

$C_1 = 1.104$, $C_2 = -1.296$, $C_3 = 4.923$ for R227ea.

Table 1 reports both our experimental data and pressures calculated through our model using just determined Mathias–Copeman coefficients. We have a good agreement (within 0.002 MPa) between experimental and calculated vapour pressures.

4.2. Vapour–liquid equilibrium

The VLE data obtained are listed in Table 2. At each temperature, we have adjusted the two ($\tau_{j,i}$ and $\tau_{i,j}$) NRTL parameters. They appear slightly temperature dependent as shown in Figs. 2 and 3.

Second order relationships are convenient for their representations:

$$\tau_{12} = 6.892 \times T + 1950 \tag{9}$$

$$\tau_{21} = -5.184 \times T - 775 \tag{10}$$

Table 1
Experimental and calculated vapour pressures of R32 and R227ea (SRK EoS + Mathias–Copeman coefficients)

R32			R227ea		
T (K)	$P_{\exp}$ (MPa)	P_{cal} (MPa)	T (K)	$P_{\exp}$ (MPa)	P_{cal} (MPa)
283.19	1.111	1.111	278.18	0.234	0.234
288.21	1.286	1.286	283.20	0.279	0.279
293.24	1.481	1.482	288.19	0.331	0.331
298.26	1.697	1.697	293.18	0.389	0.389
303.27	1.935	1.935	303.21	0.530	0.530
308.28	2.197	2.197	313.24	0.704	0.704
313.30	2.485	2.485	323.28	0.920	0.919
318.28	2.801	2.799	333.26	1.179	1.179
323.30	3.147	3.147	343.27	1.491	1.491
328.31	3.526	3.527	353.32	1.864	1.866
343.26	4.892	4.894			

Table 2
Vapour–liquid equilibrium pressures and phase compositions for R32(1)–R227ea(2) mixtures at different temperatures

| Experimental data				Calculated data: MHV1 mixing rules			
T (K)	P_{exp} (MPa)	x_1	y_{1exp}	P_{cal} (MPa)	y_{1cal}	ΔP	Δy
283.20	0.279	0.000	0.000	0.279	0.000	0.000	0.000
283.20	0.398	0.140	0.378	0.397	0.371	0.001	0.007
283.20	0.492	0.249	0.535	0.493	0.544	−0.001	−0.009
283.20	0.642	0.415	0.708	0.640	0.713	0.002	−0.005
283.20	0.747	0.539	0.789	0.748	0.798	−0.001	−0.009
283.20	0.887	0.705	0.873	0.886	0.881	0.001	−0.008
283.20	0.928	0.759	0.898	0.928	0.904	−0.001	−0.006
283.20	1.007	0.862	0.941	1.007	0.945	0.000	−0.004
303.21	0.530	0.000	0.000	0.530	0.000	0.000	0.000
303.21	0.717	0.137	0.328	0.715	0.324	0.002	0.004
303.21	0.909	0.275	0.528	0.913	0.531	−0.004	−0.003
303.21	1.126	0.416	0.671	1.121	0.674	0.005	−0.003
303.21	1.333	0.564	0.771	1.339	0.781	−0.007	−0.010
303.21	1.453	0.643	0.813	1.453	0.828	−0.001	−0.015
303.21	1.697	0.814	0.912	1.689	0.912	0.007	0.000
323.21	0.918	0.000	0.000	0.918	0.000	0.000	0.000
323.21	1.278	0.173	0.353	1.280	0.346	−0.002	0.007
323.21	1.534	0.289	0.497	1.535	0.499	−0.001	−0.002
323.21	1.813	0.411	0.621	1.810	0.622	0.003	−0.001
323.21	1.999	0.493	0.687	1.998	0.689	0.002	−0.002
323.21	2.217	0.588	0.759	2.216	0.758	0.002	0.001
323.21	2.474	0.704	0.825	2.481	0.831	−0.007	−0.006
323.21	2.701	0.800	0.884	2.699	0.886	0.002	−0.002
323.21	2.887	0.884	0.931	2.887	0.933	0.000	−0.002
343.38	1.488	0.000	0.000	1.495	0.000	−0.007	0.000
343.38	1.940	0.155	0.275	1.945	0.271	−0.004	0.004
343.38	2.087	0.203	0.342	2.092	0.337	−0.004	0.005
343.38	2.402	0.302	0.460	2.404	0.454	−0.002	0.006
343.38	2.783	0.419	0.570	2.790	0.569	−0.007	0.001
343.38	2.908	0.451	0.600	2.899	0.597	0.009	0.003
343.38	3.130	0.510	0.649	3.102	0.645	0.028	0.004
343.38	3.520	0.628	0.735	3.520	0.734	0.000	0.001
343.38	3.756	0.693	0.783	3.757	0.780	−0.001	0.003
343.38	4.194	0.816	0.866	4.217	0.866	−0.024	0.000
343.38	4.511	0.898	0.923	4.529	0.924	−0.017	−0.001
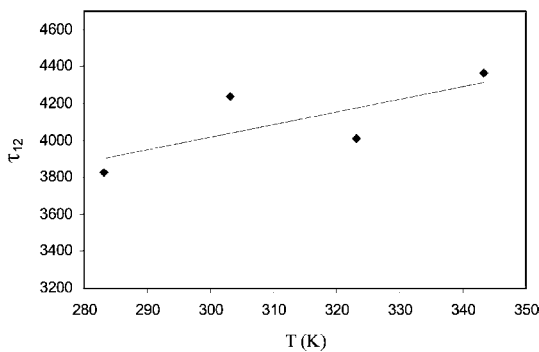
Fig. 2. τ_{12} NRTL binary parameter as a function of temperature. ◆: fitted on isothermal data (static-analytic method, this work); —: solid line calculated through Eq. (9).
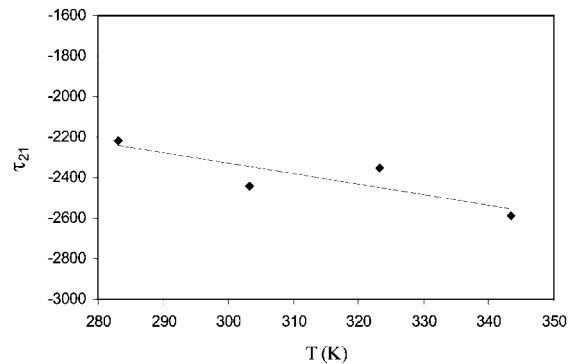

Fig. 3. τ_{21} NRTL Binary parameter as a function of temperature. ◆: Fitted on isothermal data (static-analytic method, this work); —: solid line calculated through Eq. (10).

Table 3
Mean relative absolute deviations on pressures and vapour phase compositions, using the Soave–Redlich–Kwong equation of state with MHV1 mixing rules

T (K)	BIASP (%)	MRDP (%)	BIASY (%)	MRDY (%)
283.20	0.00	0.13	0.01	0.12
303.21	0.04	0.31	−0.43	0.73
323.21	0.00	0.10	0.02	0.47
343.38	−0.09	0.32	0.51	0.54

Table 4
Vapour–liquid equilibrium pressures and liquid compositions for R32(1) – R227ea(2) mixtures at 293.73 K (PVT method, [9] and [10])

Experimental data		Calculated data: Van der Waals mixing rules		
P_{exp} (MPa)	x_1	P_{cal} (MPa)	y_{1cal}	ΔP
0.393	0.000	0.396	0.000	−0.003
0.643	0.221	0.644	0.487	−0.001
0.862	0.410	0.859	0.692	0.003
1.105	0.629	1.108	0.839	−0.003
1.493	1.000	1.501	1.000	−0.008

The results of modeling are reported in Table 2. The maximum deviations are 3×10^{-2} MPa on pressures and 1.5×10^{-2} on vapour phase compositions.

The mean relative absolute percentage deviations on pressure, MRDP, and the mean relative percentage deviations on vapour phase mole fraction, MRDY, listed in Table 3, are defined by Eq. (11):

$$\text{MRDU} = (100/N) \sum \left[\left| \left(U_{cal} - U_{exp} \right) / U_{exp} \right| \right] \quad (11)$$

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

We have also calculated the BIAS values which are listed in Table 3 and defined by Eq. (12):

$$\text{BIASU} = (100/N) \sum \left(\left(U_{exp} - U_{cal} \right) / U_{exp} \right) \quad (12)$$

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

4.3. Comparison with literature data

Park et al. [8] have studied this system at 283.15 and 303.15 K. We have adjusted these data with the SRK EoS and the Van der Waals mixing rules. It can be seen in Fig. 4 that these adjusted k_{ij} binary interaction parameters disagree with those adjusted on our own data. To point out which data are more reliable we have used another experimental method. This second experimental set-up is not based on a static-analytic method but on a static-synthetic one. The corresponding apparatus is a simplified version of the apparatus described by Fontalba et al. [9], and Valtz et al. [10]. It is based on the use of a variable volume cell allowing the simultaneous determi-
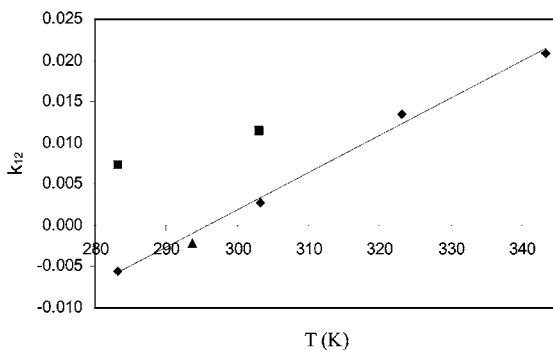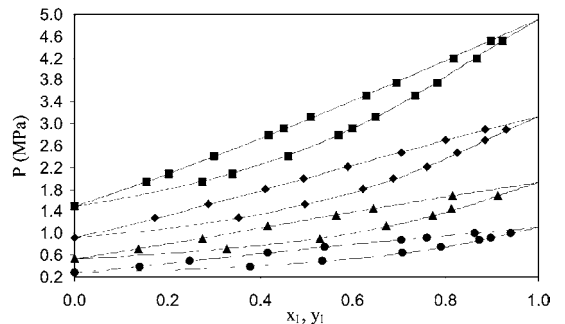

Fig. 4. Van der Waals mixing rules: Binary parameter k_{12} as a function of temperature. ◆: Static-analytic method (this work); —: Eq. (13); ▲: PVT method (this work); ■: Park et al.'s data [8].

Fig. 5. Vapour liquid equilibrium data for the R32(1) – R227ea(2) system at different temperatures. ●: 283.20 K, ▲: 303.21 K, ◆: 323.21 K, ■: 343.38 K, —: calculated with SRK EoS and MHV1 mixing rules (binary interaction parameters from Eqs. (9) and (10)).

nation of bubble pressures and saturated liquid molar volumes through pressure versus volume measurements. Herein, we measured only bubble pressures and compared them against the correlations. We have reported in Table 4 the experimental and calculated value with the Van der Waals mixing rules. Fig. 4 shows that the adjusted coefficient from data measured by the second method is in close relation with coefficients adjusted from data measured by the static-analytic method. So, there's a good agreement between static-analytic method and PVT method and unfortunately not with the data from Park et al. [8].

The binary parameter k_{ij} can be represented by a linear function of temperature [Eq.1 13].

$$k_{12} = -0.13307 + 0.00045 \times T \qquad (13)$$

Fig. 5 shows the vapour liquid equilibrium data for this system (data and modelisation) at each temperature.

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