

DENSITY OF HCFC 142b AND OF ITS MIXTURE WITH HCFC 22

Ana T. Sousa¹, Paulo Sousa Fialho¹, C. A. Nieto de Castro¹, R. Tufeu², B. Le Neindre²

¹*Departamento de Química, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Bloco C1, 1700 Lisboa, Portugal.*

²*LIMHP - CNRS, Université Paris Nord, 93430 Villetaneuse, France.*

Key words: binary mixture, densimeter, density, monochloro-difluoromethane, 1-chloro-1,1-difluoroethane, liquid, equation of state.

ABSTRACT

The density of the binary mixture 40/60 wt% of monochlorodifluoromethane (HCFC 22) and 1-chloro-1,1-difluoroethane (HCFC 142b) in the liquid phase, has been measured between 300 and 370 K and pressures up to 19 MPa, with an oscillating fork densimeter, operating in a relative mode. Toluene and vacuum have been used as calibrating fluids. The accuracy of the data is 0.08 %.

An equation for the dependence of density in temperature and pressure for HCFC 142b and for this mixture is also presented.

INTRODUCTION

Thermodynamic data on refrigerant mixtures are very important for the correct design of refrigerant equipment or heat pumps, both in industrial and domestic uses. Mixtures data are needed to allow an assessment of near azeotropic mixtures as

chlorinated fluorocarbons (CFC's) replacements and to aid in the identification of possible azeotropic mixtures (McLinden and Didion, 1989). However the data available restrain to mixtures that involve one fully halogenated compound which is not desirable as replacements because they have high ozone depletion potentials. The mixture of monochlorodifluoromethane and 1-chloro-1,1-difluoroethane involves two hydrochloro-fluorocarbons (HCFC 22 and HCFC 142b, respectively) which has a low ozone depletion potential of 0.06¹ and a low global warming potential of 0.39¹ is considered to be a good replacement of CFC 12, dichlorodifluoromethane (o.d.p. = 1.0 and g.w.p. = 2.9).

Recently we have measured the density of HCFC 142b in the liquid and gaseous states, for temperatures between 293 and 403 K and pressures up to 18 MPa, with an oscillating fork densimeter (Sousa et al 1990). It is the purpose of this paper to report on the density of the mixture of HCFC 22 + HCFC 142b with a composition 40/60 wt%, between 300 and 370 K and pressures up to 19 MPa, obtained with the same instrument.

EXPERIMENTAL

A densimeter (Anton Paar DMA 60) equipped with a high temperature-high pressure cell (DMA 512) was used for the present measurements. Details of the instrument and of the measuring principle were fully described in reference of (Sousa et al 1990). This type of densimeters operates in relative mode and the density of a sample at a given temperature and pressure, can be obtained from the measured period of vibration of the mechanical oscillator filled with the sample, τ , through the equation

$$\rho = \frac{(\rho_1 - \rho_2)(\tau^2 - \tau_2^2)}{\tau_1^2 - \tau_2^2} + \rho_2 \quad (1)$$

where ρ_1 , ρ_2 , τ_1 , τ_2 are the densities and the vibration periods of the samples of two calibrating fluids, at the same temperature and pressures, respectively.

In a recent work (Sousa et al 1990), the densimeter was calibrated with toluene and sulfurhexafluoride. This procedure was found to have some problems, introducing unnecessary uncertainty in the obtained density data, mainly caused by the fact that the critical point of SF_6 falls in to the temperature and pressure range of the measurements. Vacuum was chosen as the second calibrating environment, and eq. (1) can be then written

¹Relative to CFC 11 a per pound basis and for the 40/60 wt% mixture.

$$\rho = \frac{\rho_1(\tau^2 - \tau_0^2)}{\tau_1^2 - \tau_0^2} \quad (2)$$

where the τ_0 indicate the vibration period of the mechanical oscillator in vacuum. This period was expressed by the equation

$$\tau_0 = 3.49428 + 7.67 \times 10^{-4} T \quad (3)$$

with an error of 0.004 %. The vibration period of toluene was calculated using a Tait type equation, fitted to the experimental data,

$$\tau_1^2 = \frac{\tau_R^2}{1 - A \ln[(B + P) / (B + P_R)]} \quad (4)$$

with

$$\tau_R^2 = 14.386 + 3.36 \times 10^{-3} T + 2.03 \times 10^{-6} T^2 \quad (5)$$

$$B = 394.29 - 1.17 T + 8.89 \times 10^{-4} T^2 \quad (6)$$

and $A = 0.01546$, and τ_R is the value of τ at a reference state, chosen to have a pressure of 0.1 MPa. Equation (4) can reproduce the experimental values of τ_1^2 to within 0.005 %. The density of toluene was obtained from the work of Kashiwagi et al (1982), with an error of 0.06 %.

Pressure was measured with a Bourdon type gauge (Heise Co.) accurate to 5 kPa. The temperature of the densimeter cell was thermostated to within 0.01 K and measured to within 0.07 K with a Thermocoax type I thermocouple.

The mixture HCFC 22+HCFC 142b was obtained from ATOCHEM, France, with a composition of 40/60 wt% and with a purity of 99.85 %.

Prior to the measurements with the mixture, the calibration previously performed by Sousa et al (1990), was checked by introducing pure HCFC 142b in the cell and measuring its density at 330 K. The deviation from the previous measurements (Sousa et al 1990), did not exceed 0.02 %, which is within the uncertainty of the experimental data.

RESULTS

The densities of HCFC 142b measured by the authors, have been presented in a recent publication (Sousa et al 1990). As explained previously we have decided to change the calibration procedure, using vacuum and toluene. For the sake of the consistency with the present work, the densities of HCFC 142b have been recalculated, using eq. (2) to (6) and are presented in Table 1. The data has an estimated uncertainty of 0.02 % in the liquid phase and up to 1 % in the vapour phase.

TABLE 1

Density of 1-chloro-1,1-difluoroethane (HCFC 142b)

T/K	P / MPa	τ / s	ρ / kg.m ⁻³	σ_ρ / %
293.37	17.512	4.019449	1171.07	0.017
293.24	16.439	4.018711	1168.74	0.017
293.21	14.575	4.017515	1164.42	0.017
293.25	11.619	4.015514	1156.85	0.017
293.08	9.149	4.013731	1150.74	0.017
293.12	6.589	4.011806	1143.40	0.017
293.03	4.545	4.010181	1137.60	0.018
293.00	2.512	4.008536	1131.51	0.018
293.04	0.479	4.006784	1124.77	0.018
329.61	17.208	4.031209	1095.27	0.018
329.63	14.667	4.028970	1086.88	0.018
329.63	12.328	4.026759	1078.57	0.018
329.64	9.726	4.024128	1068.67	0.018
329.65	7.095	4.021223	1057.66	0.019
329.66	5.051	4.018767	1048.32	0.019
329.66	3.018	4.016086	1038.09	0.019
329.67	0.984	4.013138	1026.79	0.019
329.66	0.792	4.012820	1025.58	0.019
329.66	0.580	3.754025	25.41	0.68
368.20	15.932	4.041486	1002.40	0.019
368.24	12.976	4.037481	987.30	0.019
368.12	10.728	4.033818	973.95	0.019
368.12	8.229	4.029343	957.05	0.020
368.11	6.053	4.024783	939.78	0.020
368.18	4.019	4.019610	919.84	0.020
368.15	1.986	4.013155	895.20	0.020
368.11	1.783	3.799641	84.42	0.20
368.17	1.480	3.795826	70.19	0.24
368.18	1.166	3.790309	49.80	0.35
368.17	0.742	3.785458	31.98	0.55
368.18	0.377	3.781554	17.59	1.02
369.50	16.033	4.042161	1000.48	0.019
369.52	13.158	4.037879	984.34	0.019
369.48	13.153	4.037870	984.45	0.019

TABLE 1 (cont.)

Density of 1-chloro-1,1-difluoroethane (HCFC 142b)

T/K	P / MPa	τ / s	ρ / kg.m ⁻³	σ_p / %
369.53	10.728	4.034064	970.00	0.019
403.16	14.899	4.048581	907.37	0.020
403.09	12.409	4.042953	886.79	0.012
403.10	10.111	4.036675	863.37	0.020
403.13	8.471	4.030628	840.64	0.020
403.10	6.974	4.024115	816.34	0.020
403.09	5.345	4.014334	779.54	0.021
403.09	3.786	3.996039	710.57	0.021
403.17	3.422	3.866472	228.17	0.061
403.08	2.765	3.839767	131.07	0.12
403.10	2.097	3.828739	90.99	0.18
403.08	1.480	3.820708	61.95	0.28
403.08	0.873	3.814094	38.04	0.47

For the 40/60 wt% mixture of HCFC 22 and HCFC 142b the period of vibration of the densimeter cell filled with this mixture was measured at the approximate temperatures of 300, 310, 330, 349 and 369 K and pressures up to 19 MPa. The calculated densities, using again eq. (2) to (6), are presented in Table 2, and have an estimated uncertainty of 0.08 %.

TABLE 2

Density of mixture HCFC 22 + HCFC 142b (40/60 wt%), $\sigma_p = 0.08\%$

T/K	P/MPa	τ / s	ρ / kg.m ⁻³
300.01	18.687	4.032918	1203.0
300.04	17.704	4.032328	1200.7
300.04	15.547	4.030662	1194.5
299.68	13.249	4.028711	1188.3
299.99	12.227	4.027933	1184.4
299.92	11.457	4.026664	1179.6
300.05	10.799	4.026622	1179.2
299.92	9.585	4.025529	1175.5
299.91	7.166	4.023280	1167.0
299.96	5.577	4.021705	1160.8
299.91	4.434	4.020531	1156.5
300.02	3.018	4.019010	1150.3
299.92	2.188	4.018075	1147.1
299.91	1.409	4.017155	1143.6
299.91	0.731	4.016355	1140.5
309.84	17.633	4.034806	1177.4
309.86	17.198	4.034517	1176.3
309.89	16.661	4.034059	1174.5
309.88	15.061	4.032752	1169.6
309.92	14.221	4.031937	1166.4
309.91	13.249	4.031034	1163.0

TABLE 2 (cont.)

Density of mixture HCFC 22 + HCFC 142b (40/60 wt%), $\sigma_p = 0.08\%$

T/K	P/MPa	τ / s	ρ / kg.m ⁻³
309.90	12.227	4.030089	1159.4
309.92	11.113	4.029012	1155.3
309.91	10.162	4.028057	1151.7
309.92	9.149	4.027024	1147.7
309.91	8.127	4.025948	1143.7
309.91	7.075	4.024788	1139.2
309.91	6.053	4.023633	1134.8
309.89	5.517	4.023022	1132.6
309.89	3.625	4.020788	1124.0
309.88	2.046	4.018541	1115.4
309.89	0.964	4.017088	1109.7
329.77	16.874	4.039120	1126.5
329.76	15.203	4.037339	1119.8
329.77	15.193	4.037321	1119.7
329.75	14.221	4.036228	1115.6
329.75	14.211	4.036220	1115.6
329.75	12.611	4.034368	1108.5
329.74	11.761	4.033328	1104.6
329.75	10.101	4.031296	1096.9
329.76	7.621	4.027758	1083.3
329.77	6.640	4.026293	1077.6
329.76	5.021	4.023717	1067.7
329.76	3.827	4.021651	1059.8
329.74	2.825	4.019789	1052.7
329.74	1.996	4.018147	1046.3
329.73	1.470	4.017035	1042.0
349.47	16.226	4.042462	1071.6
349.49	15.173	4.041026	1066.1
349.48	14.160	4.039617	1060.7
349.49	13.117	4.038079	1054.9
349.48	12.146	4.036595	1049.3
349.48	10.688	4.034231	1040.3
349.49	9.129	4.031469	1029.7
349.49	7.611	4.028530	1018.4
349.48	6.053	4.025146	1005.4
349.48	5.031	4.022669	995.9
349.48	4.019	4.020002	985.6
349.49	3.018	4.017018	974.0
349.47	2.299	4.014621	964.8
369.38	19.325	4.050806	1033.9
369.38	19.132	4.050558	1033.0
369.24	18.008	4.048870	1027.2
369.48	16.216	4.046011	1015.6
369.51	15.011	4.043908	1007.5
369.51	13.148	4.040357	994.1
369.45	11.700	4.037306	982.7
369.48	10.111	4.033645	968.7

TABLE 2 (cont.)

Density of mixture HCFC 22 + HCFC 142b (40/60 wt%), $\sigma_\rho = 0.08\%$

T/K	P/MPa	τ / s	ρ / kg.m ⁻³
369.50	8.633	4.029591	953.1
369.52	7.075	4.024712	934.4
369.47	6.063	4.021074	920.6
369.51	4.039	4.011191	882.4
369.45	3.169	4.005072	859.0

The densities data obtained for HCFC 142b and for its mixture with HCFC 22 can be represented by an equation of the type

$$\rho = A_0 + A_1 T + A_2 T^2 + A_3 \frac{\tau^2}{\tau_0^2} + A_4 \frac{\tau^2}{\tau_0^2} T + A_5 \frac{\tau^2}{\tau_0^2} T^2 + A_6 P \quad (7)$$

with standard deviation of 0.1 kg.m⁻³ and 0.14 kg.m⁻³ respectively, which is commensurate with the experimental error. Equation (7) is an explicit form of equation (2), with temperature and pressure dependent coefficients. The values of the coefficients A_i obtained are presented in Table 3 and Fig. 1a) and b) show the departures of the experimental data from the eq. (7) for HCFC 142b and the mixture, respectively.

TABLE 3

Coefficients of equation (7)

	HCFC 142b	HCFC 22 + HCFC 142b (40/60 wt%)
A_0 / kg.m ⁻³	-5811.00	-6715.83
A_1 / kg.m ⁻³ .K ⁻¹	-8.028	-3.317
A_2 / kg.m ⁻³ .K ⁻²	0.01352	0.007368
A_3 / kg.m ⁻³	5807.8	6576.04
A_4 / kg.m ⁻³ .K ⁻¹	8.041	4.045
A_5 / kg.m ⁻³ .K ⁻²	-0.01353	-0.00831
A_6 / kg.m ⁻³ .MPa ⁻¹	-0.24846	-0.27176
σ / kg.m ⁻³	0.11	0.014

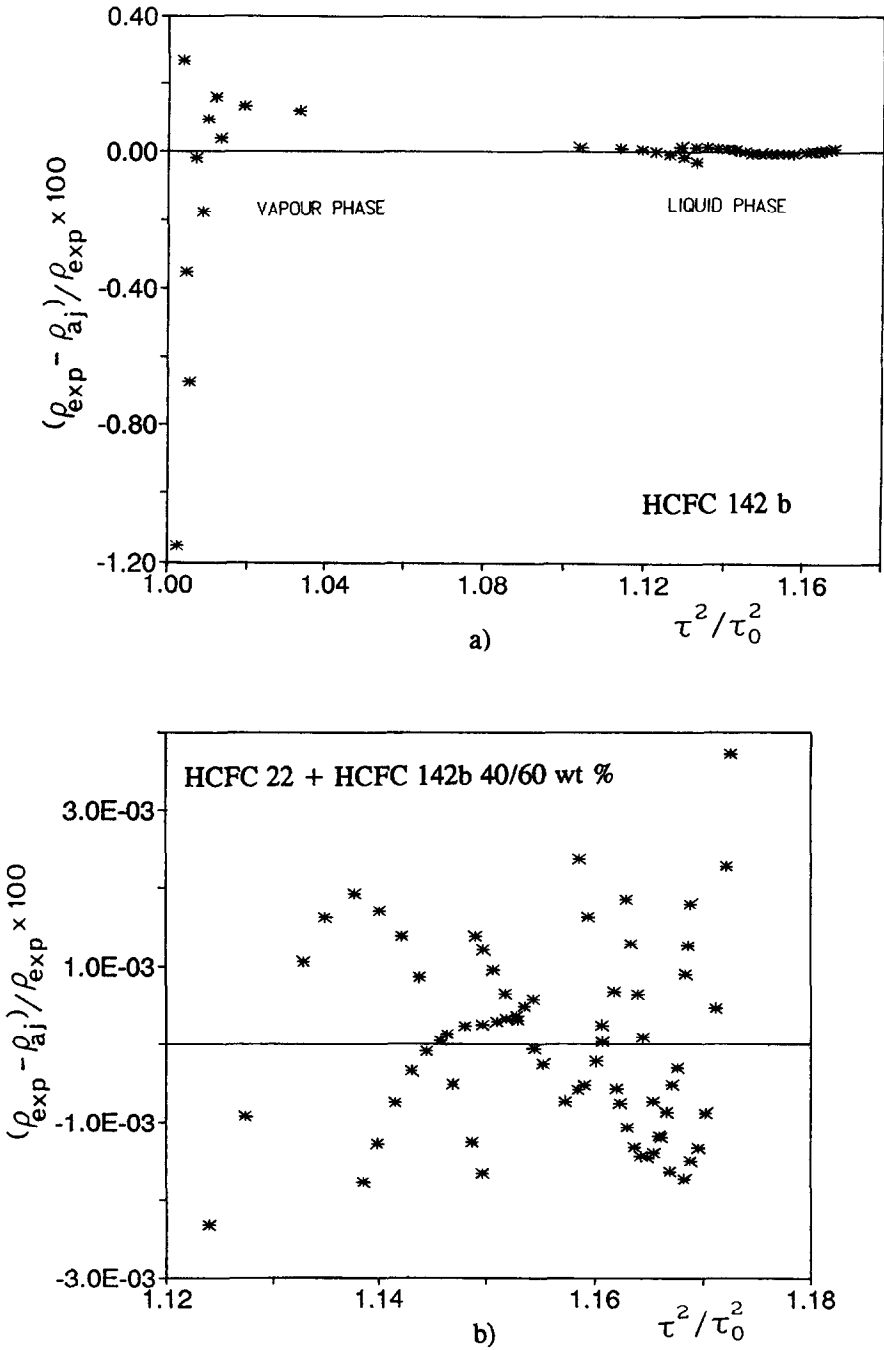


Fig. 1. The departure of experimental data from eq. (7); a) for HCFC 142 b; b) for the mixture HCFC 22 + HCFC 142b 40/60 wt %.

DATA CORRELATION

The experimental data (P, T, ρ) of HCFC 142b were fitted to an equation of state where the repulsive part is the tenth virial equation of state of hard spheres, with C_i representing the virial coefficients obtained for molecular dynamics simulation, and the attractive part is the DeSantis term, herein designated by HSDS:

$$\frac{PV}{RT} = \sum_{i=1}^{10} C_i \left(\frac{b}{V} \right)^{i-1} - \frac{a}{RT(V+b)} \quad (8)$$

where V is the molar volume. The coefficients a and b were assumed temperature dependent in the form

$$a = A_0 + A_1 T + A_2 T^2 \quad (9)$$

$$b = B_0 + B_1 T + B_2 T^2 \quad (10)$$

The saturation line data of the HCFC 142b (liquidus line) obtained by Maezawa et al (1989), and the critical point constants ($T_c = 410.25$ K, $P_c = 4.246$ MPa, $\rho_c = 435$ kg.m⁻³) were also included in the fit.

The equation of state for HCFC 142b reproduces the experimental data with a maximum deviation of 0.3 % for temperatures between 200 and 400 K and pressures up to 18 MPa, except near the critical point where density data in the saturation line are not available.

The equation used for the mixture is of the same form of eq. (8), but the parameters a and b are replaced by the mixture parameters a_{mix} and b_{mix} and V is replaced by the molar volume of the mixture. The temperature dependence of a_{mix} and b_{mix} was assumed to be given by eq. (9) and (10). Mixture parameters are also composition dependent and the dependences are assumed to be given by the quadratic van der Waals mixing rules

$$a_{\text{mix}} = x_1^2 a_{11} + 2x_1 x_2 a_{12} + x_2^2 a_{22} \quad (11)$$

$$b_{\text{mix}} = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22} \quad (12)$$

Also included in the fit of the mixture data was the saturation line of the this mixture obtained by Maezawa et al (1990).

Equation (8) reproduces the experimental data of the mixture studied with a maximum error of 1 % for the temperatures between 280 and 390 K and pressures up to 19 MPa.

Using eq. (11) and (12) the values of the interaction parameters a_{12} and b_{12} , and the temperature dependences can be obtained. The coefficients of eq. (9) and (10) for the interaction parameters are temperature and composition independent and, therefore, permit the estimation of the densities of the binary mixture of HCFC 22+HCFC 142b for any composition, temperature and pressure, through the eq. (8). For this calculations an estimate of the values of the parameters a_{22} and b_{22} is needed. With this purpose, density data of pure HCFC 22, obtained from the compilation of JSME Data Book, were adjusted to the eq. (8), and its temperature dependence was determined by eq. (9) and (10), with a maximum deviation of 0.3 % (except near the critical point), for temperatures between 170 and 360 K and pressures up to 15 MPa.

All the coefficients needed to use the equation of state for the pure components and for its binary mixture are presented in Table 4.

TABLE 4

Coefficients of equations (8), (9) and (10)

	HCFC 142b	HCFC 22	HCFC 22 + HCFC 142b	
			40/60 wt%	interaction Parameters
$A_0 / \text{J.m}^3.\text{mol}^{-2}$	16.12587	9.14762	11.64413	9.71321
$A_1 / \text{J.m}^3.\text{mol}^{-2}.\text{K}^{-1}$	-5.86×10^{-2}	-3.63×10^{-2}	-4.10×10^{-2}	-3.15×10^{-2}
$A_2 / \text{J.m}^3.\text{mol}^{-2}.\text{K}^{-2}$	5.69×10^{-5}	3.94×10^{-5}	3.82×10^{-5}	2.57×10^{-5}
$B_0 / \text{m}^3.\text{mol}^{-1}$	1.83×10^{-4}	1.38×10^{-4}	1.64×10^{-4}	1.62×10^{-4}
$B_1 / \text{m}^3.\text{mol}^{-1}.\text{K}^{-1}$	6.76×10^{-9}	-6.59×10^{-8}	-3.46×10^{-8}	-4.92×10^{-8}
$B_2 / \text{m}^3.\text{mol}^{-1}.\text{K}^{-2}$	-4.96×10^{-10}	-2.86×10^{-10}	-3.76×10^{-10}	-3.33×10^{-10}

Virial coefficients of the hard-spheres, taken from Ree and Hoover (1964) and Erpenbeck and Wood (1984):

C_1	1	C_6	0.0386 ± 0.0004
C_2	1	C_7	0.0137 ± 0.006
C_3	5/8	C_8	0.00421
C_4	0.28695	C_9	0.00131
C_5	0.1103 ± 0.0003	C_{10}	0.00040

Figures 2 and 3 show that, for the HCFC 142b and for its mixture 60/40 wt% with HCFC 22, a good fit was obtained for the zone where the high pressure data was hooked to the saturation boundary data. Figures 4a) and b) presented the corresponding scattering diagrams.

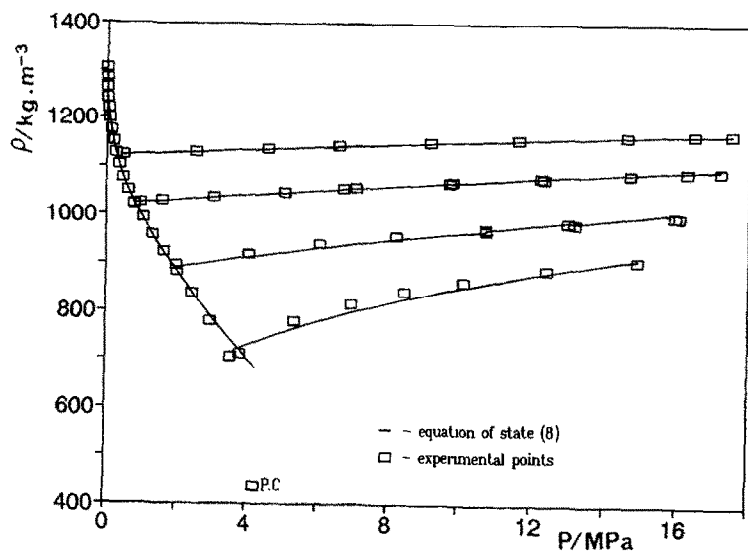


Fig. 2. The density of HCFC 142b as function of temperature and pressure.

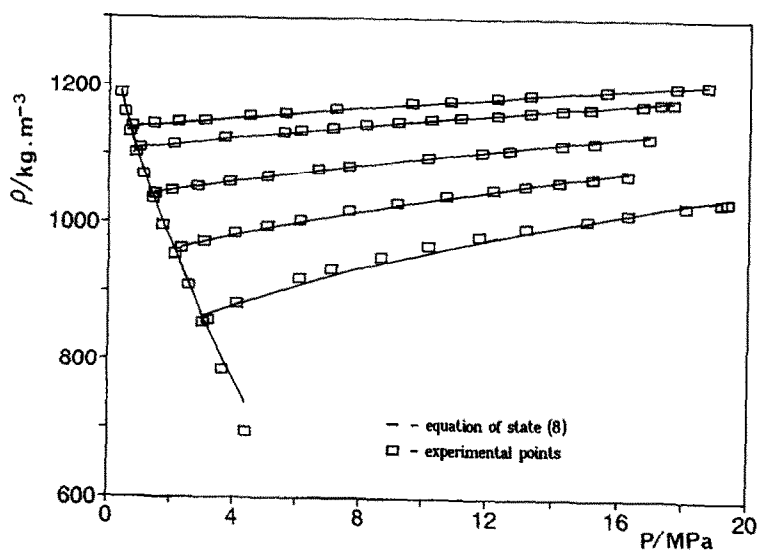


Fig. 3. The density of the mixture HCFC 22 + HCFC 142b 40/60 wt%, as function of temperature and pressure.

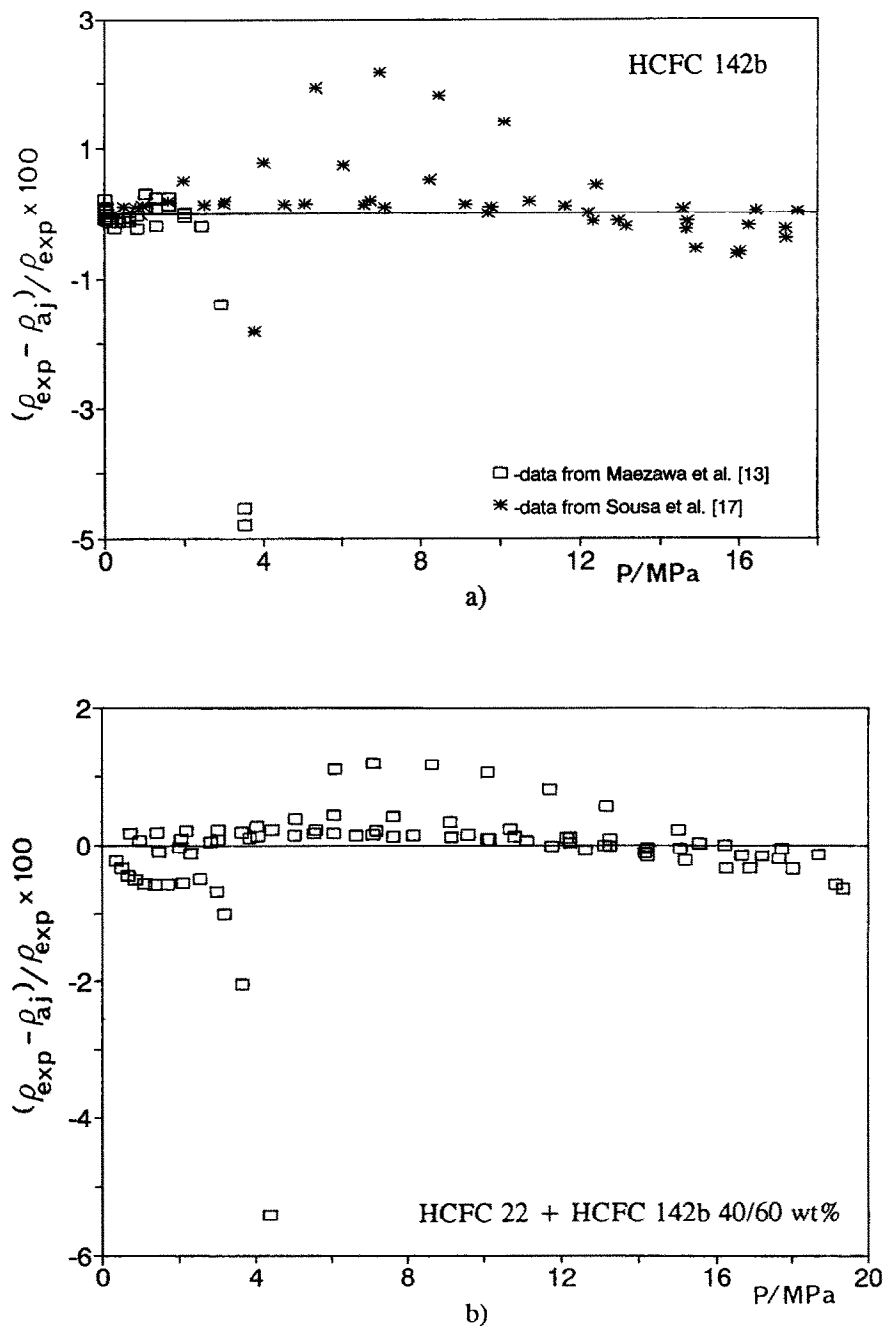


Fig. 4. The departures of experimental data from eq.(8): a) for HCFC 142b; b) for the mixture HCFC 22 + HCFC 142b 40/60 wt%.

CONCLUSION

This paper presents density data for HCFC 142b and its binary mixture 60/40 wt% with HCFC 22 obtained with a relative densimeter with an accuracy of 0.08 %.

The experimental data for the liquid phase of pure HCFC 142b and of its mixture with HCFC 22 were fitted to an equation of state, based on the exact hard spheres 10 virial repulsive term, added to a DeSantis attractive term, HSDS. This equation of state is capable of reproducing the data better than 1 %.

The work in progress will demonstrate the validity of known mixing rules and the predictability capacity of the equation of state herein presented.

ACKNOWLEDGMENTS

This work was partially funded by INIC/JNICT/CNRS agreement. The authors would like to thank ATOCHEM, France for supplying the mixture HCFC 142b+HCFC 22 sample.

REFERENCES

- DeSantis R, Gironi F, Marreli L, 1976, Ind. Eng. Chem. Fundam., 15:183
 Erpenbeck J, Wood W W, 1984, J. Stat. Phys., 35:321-340
Thermophysical Properties of Fluids, 1983, JSME Data Book
 Kashiwagi H, Hashimoto T, Tanaka Y, Kubota H, Makita T, 1982, Int. J. Thermophysics, 3:201-215
 McLinden M O, Didion D A, 1989, Int. J. Thermophys., 10:563-576
 Maezawa Y, Sato H, Watanabe K, 1989, Proc. 10 th Symp. Thermophys. Prop., (Ed JSME, Tokyo) , 71-74
 Ree F H, Hoover W G, 1964, J. Chem. Phys., 40: 939-950
 Sousa A T, Castro C A N, Tufeu R, Le Neindre B, 1991, High Temp.-High Pres., in press