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# Use of universal correlations to predict some thermophysical properties of alternative refrigerants

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**Abstract.** The necessary replacement of refrigerants with non-zero ozone depletion potential has generated in recent years a significant amount of theoretical and experimental work about the thermophysical properties of alternative refrigerants, pure compounds, mixtures or blends, with zero ozone depletion potential. However, the amount of data necessary for the engineering design for refrigeration and air-conditioning units requires the development of reliable procedures for the estimation of liquid phase properties, based on reliable and simple-to-use equations of state. An overall view is presented of work done in the use of universal reduced equations to predict the vapour pressure and the density of pure, binary, and ternary mixtures of hydrofluorocarbons, including methane, ethane, and propane derivatives. Some hints devised to extend the correlations obtained to fluoroethers are also discussed.

## 1 Introduction

The necessary replacement of refrigerants with non-zero ozone depletion potential and low global warming potential has generated in recent years a significant amount of theoretical and experimental work about the thermophysical properties of alternative refrigerants, pure compounds, mixtures or blends, with zero ozone depletion potential. Most of the fluids tested are methane, ethane, and propane derivatives, with low or zero chlorine content, including some ethers.

The amount of experimental data generated for the chlorine-free methane and ethane hydrofluorocarbons (HFCs) represents a coherent set of properties, in the temperature and pressure ranges usually encountered in the applications of these fluids, especially in the field of critical constants, vapour pressure, density and heat capacity in the saturation line, viscosity, and thermal conductivity. However, it is impossible, in the time frame required by legislators and industry, to obtain all the necessary data for all the pure fluids and mixtures, even for restricted ranges of temperature and pressure. In addition, some problems have been found with respect to the quoted purity of the samples used in the experimental determinations.

We present an overall view of our work in the use of universal reduced equations to predict the vapour pressure and the density of pure, binary, and ternary mixtures of hydrochlorofluorocarbons (HCFCs) and HFCs. The compounds studied include methane, ethane, and some propane derivatives (Fialho and Nieto de Castro 1995, 1996a, 1996b, 2000; Fialho et al 1995/1996). The need for the application of this type of equation to other compounds, candidates for refrigerant fluids, led us to initiate a study of the application of the same type of universal correlation to higher hydrocarbon derivatives and fluoroethers, presently in progress.

## 2 Universal reduced equations

### 2.1 *Density of pure fluids*

The increasing need for information on liquid density for the new refrigerants has led us to try to implement a new scheme to correlate and estimate this property from limited information, capable of being used in the temperature and pressure ranges commonly used in the refrigeration industry, both for pure fluids and their mixtures. This scheme is not a replacement for the use of individual experimental data or equations of state of the halocarbon refrigerants. However, the need for easy programmable techniques of general use and moderate accuracy justifies the corresponding-states approach. An option for a cubic equation of state, theoretically based, was chosen for easy computer applications. The hard sphere DeSantis (HSDS; Sousa et al 1992) equation of state was used to correlate the available experimental data of the density of liquid refrigerants (HCFC-114, HCFC-123, HCFC-142b, HFC-152a, R22), in order to obtain the parameters $a(T)$ and $b(T)$ needed to develop the model of the reduced equation of state.

The new model has been used to predict the data available for other fluids (HFC-32, HFC-125, HFC-134a, HFC-134, and HCFC-141b), with an error within $\pm 1.5\%$ for the reduced temperature, $T^* = T/T_c$, less or equal to 0.9 ($T_c$ is the critical temperature). To our best knowledge there is no other density estimation method applicable to the halocarbons with such a high accuracy. A brief description of the model equation of state is described below (further details from Fialho and Nieto de Castro 1995, 1996a; Fialho et al 1995/1996).

The Carnahan–Starling DeSantis (CSDS) equation of state (DeSantis et al 1976) was used with reasonable success by Morrison and McLinden (1986) in correlating the saturation lines and vapour phase of the refrigerants. In order to develop an equation of state to be applied to the liquid phase, including the saturation boundary (Sousa et al 1992) we decided to replace the repulsive form of the Carnahan–Starling term, a Padé approximant (3,3) to the six virial expansions of the hard-sphere virials (Carnahan and Starling 1969) by the first ten virial coefficients of the hard-sphere equation, calculated by several authors (Ree and Hoover 1964; Erpenbeck and Wood 1984), to obtain the best available theoretical description of the repulsive contribution:[1]

$$Z = \sum_{i=1}^{10} C_i (b\rho)^{i-1} - \frac{a\rho}{RT(1+b\rho)} \ , \tag{1}$$

where $y = b\rho/4$, $Z$ is the compressibility factor, $\rho$ is the density, $R$ is the gas constant, $T$ is the temperature, and $a$ and $b$ are van-der-Waals-type parameters, usually considered as adjustable. $C_i$ are the virial constants obtained from Monte Carlo and molecular dynamics simulations (Ree and Hoover 1964; Erpenbeck and Wood 1984). The values of $C_i$ are given in table 1. The parameters $a$ and $b$ were assumed as temperature dependent in the form:

$$a = a_0 + a_1 T + a_2 T^2 \ , \tag{2}$$

**Table 1.** Virial coefficients for the HSDS (Ree and Hoover 1964; Erpenbeck and Wood 1984).

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

[1] The constrained Padé approximant determined by Erpenbeck and Wood (1984) for the repulsive contribution can be used instead of this virial expression, which involves a greater number of coefficients. No significant effect would be found in the predictive results herein presented.

and

$$b = b_0 + b_1 T + b_2 T^2 \ . \tag{3}$$

The available data on the density of R114 (Wilson and Hules 1982; Fukuizumi and Uematsu 1991a), R123 (Maezawa et al 1990, 1991a; Piao et al 1991), R142b (Maezawa et al 1991a; Sousa et al 1992), R152a (Iso and Uematsu 1989), and R22 (Blanke et al 1988; Fukuizumi and Uematsu 1991b; Defibaugh and Morrison 1992) were used. The respective ranges of temperature and pressure, in reduced units, can be found in our original work (Fialho and Nieto de Castro 1995, 1996a; Fialho et al 1995/1996), covering ranges of $T/T_c$ from 0.46 to 1.00 and of $p/p_c$ from 0.0002 to 6.12 (where $p_c$ is critical pressure). The data were correlated with equation (2), for each fluid. With a nonlinear adjustment by the Levenberg–Marquadt method (Press et al 1986) it was possible to obtain the parameters $a_i$ and $b_i$ for each refrigerant.

Figure 1 shows the comparison of the correlation with the experimental data for $T^* = T/T_c$ less than or equal to 0.95. The deviations are less than $\pm 0.5\%$, comparable with the experimental uncertainty (less than $\pm 0.3\%$), and no systematic deviations are found for any fluid.

To obtain a general equation of state, we have chosen to represent the parameters obtained for the different refrigerants as a function of $T^*$ in order to observe their behaviour. It was found that in the case of $b$, the temperature dependence is so small that one can assume that it is negligible ($b \approx b_0$). As a second step, the parameters $a$ and $b$ were reduced with the critical constants according to the following expressions:

$$a^* = \frac{a\rho_c^2}{p_c} \ , \tag{4}$$

$$b^* = b\rho_c \ , \tag{5}$$

where $\rho_c$ is the critical density.

Because of the recent applications of these halocarbons, there are many independent measurement values for the critical constants in the literature. It was not possible to identify for some of the values their internal consistence and uncertainty. In order to select the best available set of data to be used in the general correlation, we have looked for similarity between the properties of liquid refrigerants. It appears that the dependence $Z_c = p_c/R\rho_c T_c$ on the molar mass is a good measure for the consistency of

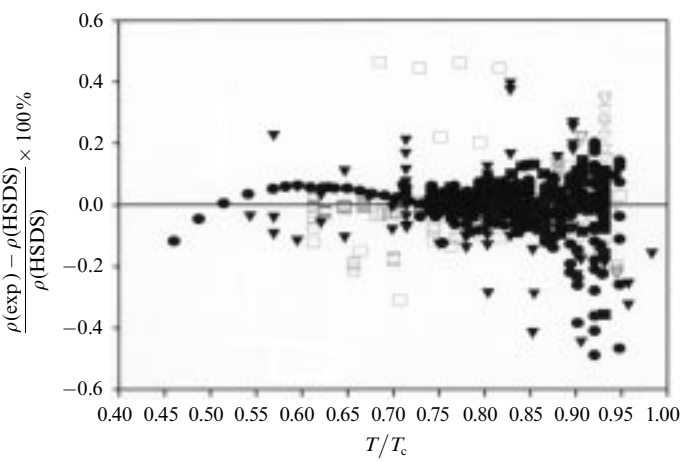


**Figure 1.** Deviations between the experimental density data and the estimation with the correlation expressed by equation (2), with the parameters of table 1: ■, HCFC-114; □, HCFC-123; ▼, HCFC-142b; ▽, HFC-152a; ●, HCFC-22.

the available data on the critical constants. This fact, associated with an analysis of the possible presence of impurities in the halocarbons studied by several authors, led us to choose the values of the critical constants displayed in table 2.

These values were used throughout the present study and are only shown as a consistent set for the correlation. For the case of HCFC-124 and HFC-125 the value of $p_c$ available in the literature was obtained by extrapolating the saturation line (McLinden 1990). The correlation obtained is shown in figure 2 and can be represented by:

$$Z_c = 0.317 - \frac{3.41 \times 10^{-3}}{M/\text{kg mol}^{-1}} - 0.138(M/\text{kg mol}^{-1}) \ ,$$

where $M$ is the molar mass. Most of the available critical compressibility factors can be represented by this equation within $\pm 2\%$. The values of $b^*$ were found to be temperature

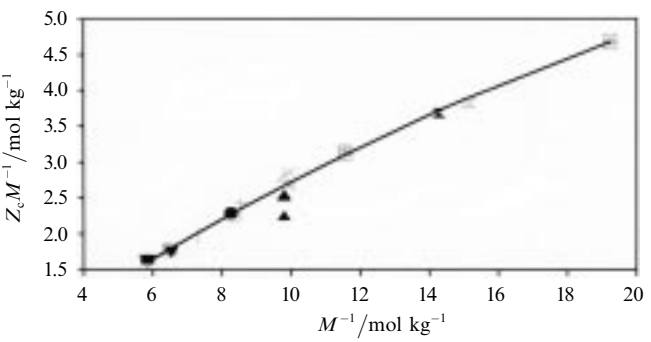


**Figure 2.** Ratio of the critical compressibility constant over the molar mass as a function of the inverse of the molar mass. The line was obtained by the use of equation (6). □, HCFC-115; ●, HCFC-12; ▼, HCFC-123; ▲, HFC-134a; ▽, HCFC-114; △, HFC-134; +, HCFC-141b; ×, HCFC-142b; |, HCFC-124; ○, HFC-125; ■, HCFC-114a; ⊠, R32; ⊞, R22; ⧖, HFC-152a; ⧗, R23; —, equation (7).

**Table 2.** Critical constants selected from the literature based on equation (6).

| Refrigerant | $\frac{M}{\text{kg mol}^{-1}}$ | $\frac{p_c}{\text{MPa}}$ | $\frac{T_c}{\text{K}}$ | $\frac{\rho_c}{\text{kg m}^{-3}}$ |
|---|---|---|---|---|
| HCFC-114a | 0.170922 | 3.303 [a] | 418.7 [a] | 578 [a] |
| HCFC-114 | 0.170922 | 3.252 [b] | 418.78 [b] | 576 [b] |
| HCFC-115 | 0.154470 | 3.118 [c] | 353.2 [d] | 604 [c] |
| HCFC-123 | 0.152930 | 3.674 [e] | 456.94 [e] | 550 [e] |
| HCFC-124 | 0.136475 | 3.634 [f] | 395.65 [g] | 560 [g] |
| CFC-12 | 0.120930 | 4.116 [h] | 385.15 [h] | 568 [i] |
| HFC-125 | 0.120020 | 3.631 [f] | 339.4 [j] | 572 [j] |
| HCFC-141b | 0.116950 | 4.46 [l] | 480 [l] | 460 [l] |
| HFC-134a | 0.102030 | 4.068 [e] | 373.69 [m] | 495.6 [m] |
| HFC-134 | 0.102030 | 4.64 [l] | 392 [l] | 510 [l] |
| HCFC-142b | 0.100495 | 4.041 [n] | 410.25 [a] | 446 [a] |
| HCFC-22 | 0.086468 | 4.98 [o] | 369.32 [i] | 515 [i] |
| HFC-23 | 0.070013 | 4.82 [p] | 298.98 [p] | 526 [p] |
| HFC-152a | 0.066050 | 4.52 [q] | 386.44 [q] | 368 [q] |
| HFC-32 | 0.052024 | 5.83 [r] | 351.56 [r] | 422.67 [r] |

[a] Mears et al 1955; [b] Higashi et al 1985; [c] Yada et al 1989b; [d] Asahi Glass Co. Ltd 1983; [e] Weber and Sengers 1990; [f] McLinden 1990; [g] Kubota et al 1988; [h] Sukornik 1989; [i] Higashi et al 1984; [j] Shankland et al 1989; McCain 1989; [l] Maezawa et al 1991a; [m] Du Pont 1979; [n] Tanikawa et al 1991; Yada et al 1991; [o] IIR 1982; [p] Shavandrin 1975; [q] Higashi et al 1987; [r] Holcomb et al 1993.

independent and a linear function of $M^{-1}$, as demonstrated in figure 3. The line is given by equation (7), and the values of the parameter $a^*$ depend on both temperature and molar mass through equation (8):

$$b^* = [2.0335 - 0.01039(M/\text{kg mol}^{-1})^{-1}] \pm 0.0044 \ , \tag{7}$$

$$a^* = \sum_{i=0}^{2} \left( \sum_{j=0}^{2} a_{ij}^* T^{*j} \right) (M/\text{kg mol}^{-1})^{i} \ . \tag{8}$$

Figures 3 and 4 show this behaviour and the parameters $a_{ij}^*$ are presented in table 3.

In order to test the consistency of the reduced equation we have calculated the densities of the refrigerants used in the development of the general correlating scheme.

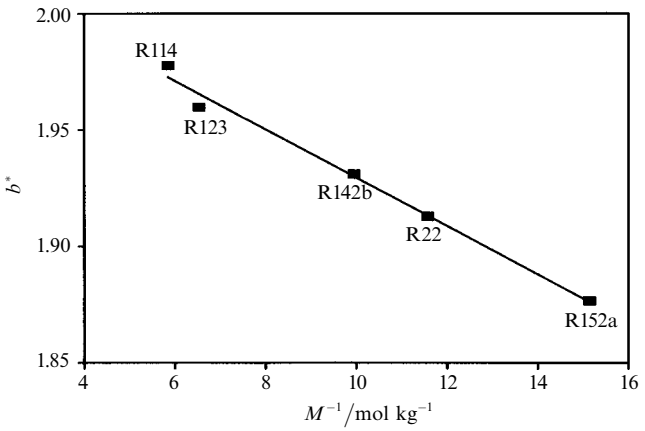


**Figure 3.** The reduced parameter $b^*$ as a function of the molar mass and reduced temperature, for several refrigerants. The line was calculated by correlation (9). ■, $T^* = 0.4$; □, $T^* = 0.5$; ▼, $T^* = 0.6$; ▽, $T^* = 0.7$; ●, $T^* = 0.8$; ○, $T^* = 0.9$.

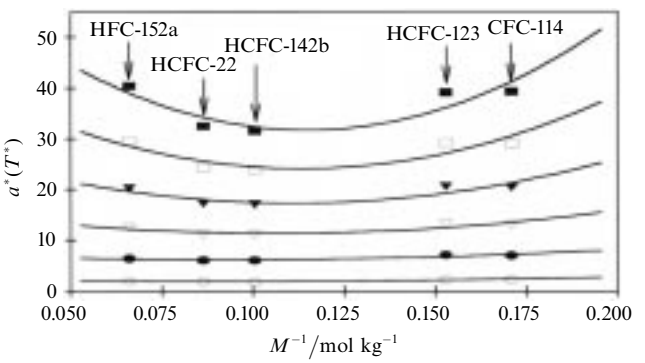


**Figure 4.** Behaviour of the reduced parameter $a^*$ as a function of the molar mass and reduced temperature, for several refrigerants. The line was calculated by correlation (9). ■, $T^* = 0.4$; □, $T^* = 0.5$; ▼, $T^* = 0.6$; ▽, $T^* = 0.7$; ●, $T^* = 0.8$; ○, $T^* = 0.9$.

**Table 3.** Parameters used in equation (8).

| | $a_{0j}$ | $a_{1j}$/mol kg$^{-1}$ | $a_{2j}$/mol$^2$ kg$^{-2}$ |
|---|---|---|---|
| $j = 0$ | $2.069249 \times 10^5$ | $-2.332869 \times 10^6$ | $9.949903 \times 10^6$ |
| $j = 1$ | $-4.245370 \times 10^5$ | $5.268112 \times 10^6$ | $-2.222515 \times 10^7$ |
| $j = 2$ | $2.194730 \times 10^5$ | $-2.991949 \times 10^6$ | $1.251112 \times 10^7$ |

Figure 5 shows the deviation between the experimental data of the refrigerants used in the scheme and the values obtained from equations (1) and (4)–(8). As can be seen no point deviates by more than 1.6% and most of the data deviate by no more than ±1% for $T^* \leqslant 0.9$, although some of the fluids show systematic trends, impossible to avoid with this type of averaged correlation.

The general equation was tested by calculating the densities of other refrigerants not used in its development, to test its ability to predict the density of the liquid phase, mainly by comparison with recently available data on HFC-32, HFC-125, HFC-134, HFC-134a, HFC-152a, and HCFC-141b.

Figure 6 shows the capability of our scheme for estimating the densities of refrigerants not included in the development scheme, over the ranges of pressure and temperature normally used in the refrigeration industries, from saturation line to compressed liquid, between vapour pressure and 20 MPa. It can be seen that the model can predict the data

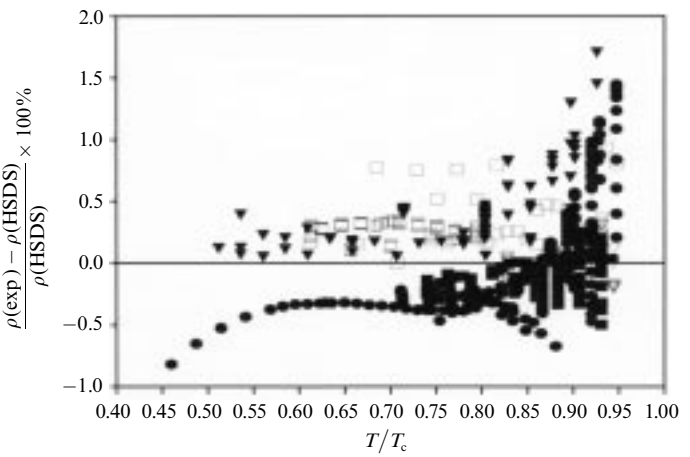


**Figure 5.** Deviation plot from the experimental data, used in the development of the reduced equation, and the calculations obtained by the model. □, HCFC-123; ●, R22; ▼, HCFC-142b; ▽, HFC-152a; ■, HCFC-114.

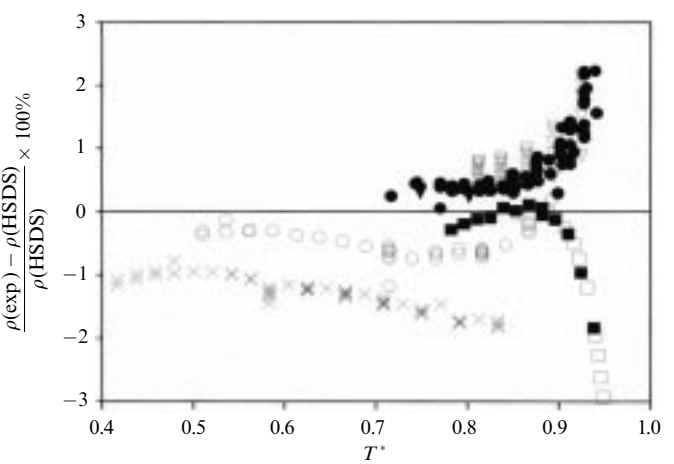


**Figure 6.** Deviation plot from the experimental data obtained for several refrigerants and the reduced equation of state developed. □, HFC-32 (Holcomb et al 1993); ■, HFC-32, (Widiatmo et al 1994); ●, HFC-134a (Morrison and Ward 1991); ▼, HFC-134a (Maezawa et al 1990); ▽, HFC-125 (Defibaugh and Morrison 1992); ×, HCFC-141b (Maezawa et al 1991a); ○, HFC-134 (Maezawa et al 1991a).

within ±1.5% for $T^* \leqslant 0.9$. Above this temperature, and as already stated, the modified HSDS equation is not capable of accommodating the curvature of the $\rho(p)$ isotherms well as the critical point is approached. More recent data on HFC-152a were compared also and the results are shown in figure 7. It can be also shown that the model is capable of predicting the density of HFC-152a within 1%.

A more stringent test was made with the data now available for HCFC-141b, which cover a wide range of temperatures and pressures (up to 380 MPa). Figure 8 shows that the deviations do not amount to more than 1.5%, and that the isothermal compressibility is rather well predicted in a wide pressure range, given the fact that the model was fitted with data up to 20 MPa. This corresponds to a factor of 1.25 in density, and means that the HSDS equation of state is capable of accommodating the effect of pressure very well.

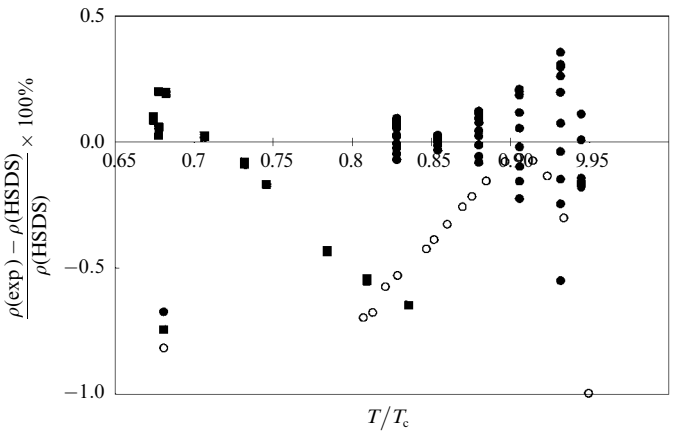


**Figure 7.** Deviation plot between the experimental density ($\rho_{exp}$) data and the predicted ($\rho_{HSDS}$) data taken from the HSDS model for HFC-152a. ■, Ström and Grén (1993); ●, Iso and Uematsu (1989); △, Holcomb et al (1993).

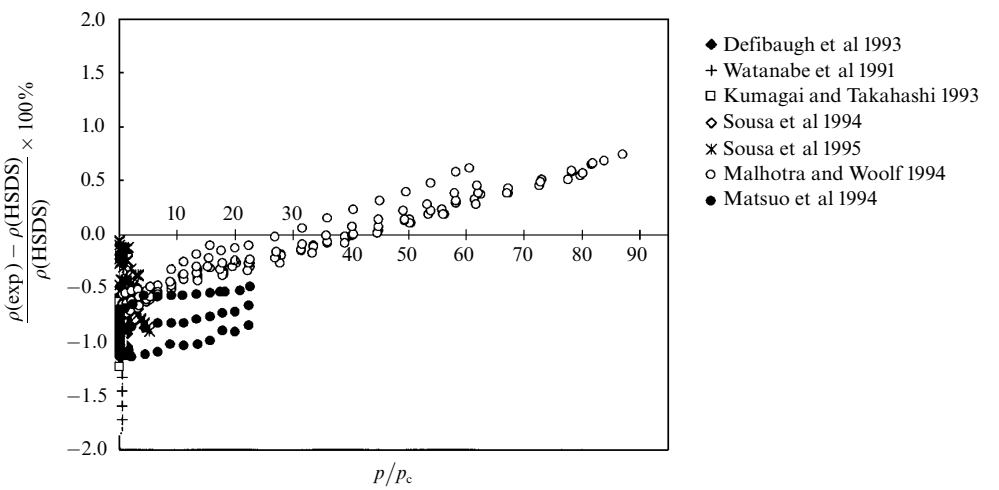


**Figure 8.** Deviation plot between the experimental density ($\rho_{exp}$) data and the predicted ($\rho_{HSDS}$) data taken from the HSDS model for HCFC-141b.

### 2.2 *Application to refrigerant mixtures*

The universal equation (HSDS) (Fialho and Nieto de Castro 1996b) has been applied to refrigerant mixtures. In order to be able to apply the HSDS model, it was necessary to introduce the mixing rules proposed by Reid et al (1987) for the combination of the

properties of the pure components of the mixture in order to obtain its properties. This rule can be expressed to a first approximation by the following:

$$Q_{\text{mix}} = \sum_i \sum_j x_i x_j Q_{ij} \ , \tag{9}$$

where $Q$ represents the property and $x$ the molar composition of the mixture. In the present case we have applied this rule to the critical temperature and critical molar volume. For the binary mixture,

$$T_{\text{c, mix}} = x_1^2 T_{\text{c,1}} + 2x_1 x_2 T_{c,12} + x_2^2 T_{\text{c,2}} \ , \tag{10}$$

$$V_{\text{c, mix}} = x_1^2 V_{\text{c,1}} + 2x_1 x_2 V_{\text{c,12}} + x_2^2 V_{\text{c,2}} \ , \tag{11}$$

where the subscripts 1 and 2 stand for components 1 and 2. The subscript 12 represents the cross term. To estimate this term we can use the usual geometric and arithmetic average combination rules (Reid et al 1987):

$$T_{\text{c,12}} = (T_{\text{c,1}} T_{\text{c,2}})^{1/2} \ , \tag{12}$$

$$V_{\text{c,12}} = \left( \frac{V_{\text{c,1}}^{1/3} + V_{\text{c,2}}^{1/3}}{2} \right)^3 \ . \tag{13}$$

To obtain the critical molar density for the mixture we invert the critical molar volume obtained from equation (11). The critical pressure for the mixture is calculated from the critical compressibility factor, obtained from the pure liquid data (Fialho and Nieto de Castro 1995), and is given by the combination of equation (6) and the following:

$$p_{\text{c, mix}} = R Z_{\text{c}} \rho_{\text{c, mix}} T_{\text{c, mix}} \ , \tag{14}$$

where $M$ for the mixtures is given by the linear mixing rule,

$$M = \sum_i x_i M_i \ . \tag{15}$$

We have applied the HSDS model for mixtures to binary mixtures of HCFC-142b + HCFC-22 (Kumagai et al 1991; Sousa et al 1992), HCFC-22 + HFC-152a (Maezawa et al 1991b), HFC-152a + HCFC-142b (Maezawa et al 1991c), and CFC-114 + HCFC-22 (Hazegawa et al 1985; Fukuizumi and Uematsu 1991c), and for the ternary mixture of HCFC-22 + HFC-152a + HCFC-142b (Maezawa et al 1991d). The mixtures can act as examples for the test of the model. Except for the binary mixture of CFC-114 + HCFC-22 for which we have compressed liquid data, all other mixtures cover only the liquid saturation line. Figure 9 shows the results obtained for the binary mixtures mentioned before.

The densities of the mixtures were predicted for $T^* \leqslant 0.9$ within 1.5%, and better than 2% for $0.90 \leqslant T^* \leqslant 0.95$. The calculations covered wide composition ranges, as the data compared for each mixture refer to several compositions. For instance, the mixture HFC-152a + HCFC-22 involves a composition range from (10/90) to (90/10).

No systematic deviations caused by composition ranges have been detected, although a systematic shift of about −1% is encountered for the ternary mixture. This is possibly caused by the need for more sophisticated mixing or combination rules. However, we preferred, for the sake of simplicity, to use a one-fluid model for the mixture, predicting its properties only from pure component data and the combination and mixing rules without the use of binary interaction parameters, normally obtained from mixture data. The deviations obtained from these mixtures to the model were better than 1.5% for $T^* = T/T_{\text{c}} \leqslant 0.9$, which is in good agreement with the values obtained for the pure fluids.

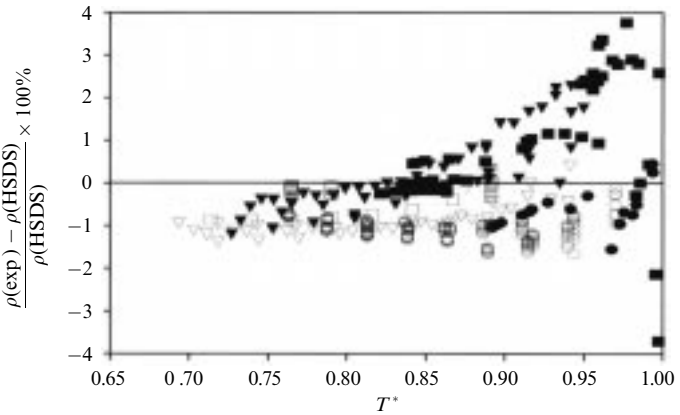


**Figure 9.** Deviations between the experimental density, obtained for different binary mixtures of refrigerants and the prediction by the reduced HSDS model with the combination and mixing rules. ■, HCFC-142b + HCFC-22 (Kumagai et al 1991); □, HCFC-142b + HCFC-22 (Sousa et al 1992); ▼, HCFC-22 + HFC-152a (Maezawa et al 1991b); ●, CFC-114 + HCFC-22 (Hazegawa et al 1985); ▽, HFC-152a + HCFC-142b (Maezawa et al 1991c); ○, CFC-114 + HCFC-22 (Fukuizumi and Uematsu 1991c).

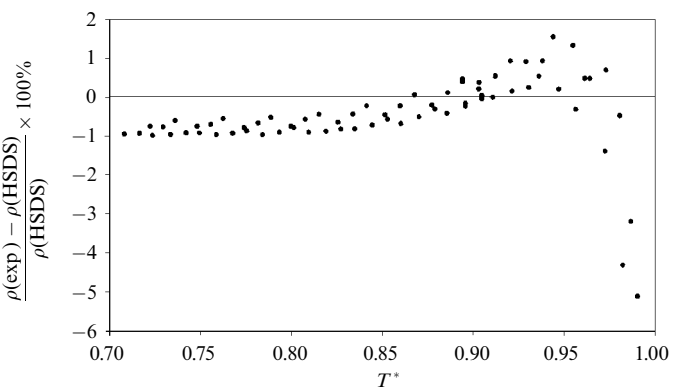


**Figure 10.** Deviations between the experimental density of the ternary mixture for HCFC-22 + HFC-152a + HCFC-142b (Maezawa et al 1991d) and that predicted by the reduced HSDS model with the combination and mixing rules.

## 3 Vapour pressure curve of halocarbons

### 3.1 *Universal correlation*

In order to develop a universal correlation scheme for interpolation and extrapolation purposes, possible regularities in the vapour pressure curves of several CFCs, HCFCs, and HFCs, namely CFC-114, HCFC-123, HCFC-141b, HCFC-142b, HCFC-143a, HFC-23, HFC-32, HFC-134, HFC-125, HFC-134a, and HFC-152a, have been studied (Fialho and Nieto de Castro 2000).

Values of the vapour pressures of the compounds studied were obtained from different sources (Hori et al 1982; Wilson and Hules 1982; Iso and Uematsu 1989; Weber 1989, 1990; Maezawa et al 1991a, 1991e; Monluc et al 1991; Morrison and Ward 1991; Piao et al 1991; Goodwin et al 1992; Tamatsu et al 1992; Defibaugh et al 1993; Holcomb et al 1993; Weber and Goodwin 1993; Bouchot and Richon 1994; Giuliani et al 1994).

The critical constants used, in addition to the values displayed in table 1, are displayed in table 4, together with the literature sources. About 600 data points were used, from 11 different refrigerants. The data for the logarithm of the reduced saturation

**Table 4.** Critical constants used for the correlation and the test.

| Refrigerant | $\frac{M}{\text{kg mol}^{-1}}$ | $\frac{p_c}{\text{MPa}}$ | $\frac{T_c}{\text{K}}$ | $\frac{\rho_c}{\text{kg m}^{-3}}$ |
|---|---|---|---|---|
| HFC-125 | 0.120020 | 3.633 [a] | 339.4 [a] | 572 [a] |
| HFC-143a | 0.084040 | 3.811 [b] | 346.25 [b] | 434 [b] |
| HCFC-225ca | 0.190928 | 2.974 [c] | 478 [d] | 578 [d] |
| HCFC-225cb | 0.190928 | 3.012 [c] | 484.85 [d] | 557 [d] |

[a] McLinden et al 1993; [b] McLinden 1990; [c] estimated with the technique proposed by Fialho and Nieto de Castro (1996a, 2000); [d] Matsuo et al 1994.

**Table 5.** Coefficients of equation (9).

| $a_1$ | $a_2$ | $a_3$ | $a_4$ | $a_5$ | $\sigma$ |
|---|---|---|---|---|---|
| −94.8179 | −135.342 | 13.1306 | 11.4013 | −29.4039 | 0.034 |

vapour pressure, $p_{sat}/p_c$, were fitted to a Padé approximant (2,2), where the independent term in the numerator was set to zero in order to constrain the correlation to the critical point (0,0):

$$\ln\left(\frac{p_{sat}}{p_c}\right) = \frac{a_1\tau + a_2\tau^2}{a_3 + a_4\tau + a_5\tau^2} \ , \tag{16}$$

where

$$\tau = \frac{T_c - T}{T_c} \ . \tag{17}$$

Table 5 shows the values of the coefficients $a_1$ to $a_5$ and the standard deviation of equation (9).

Figure 11 shows the representation of the function obtained for the different data points. The overlapping of the points and the adjusted function is remarkable, except for $p_{sat}/p_c < 0.002$, where some of the authors have used their instruments outside the range in which they were most accurate, thus increasing the dispersion, in the case of HCFC-141b and HFC-134 (Maezawa et al 1991..). Figure 12 shows the deviations of the different experimental points from the universal correlation of equations (16) and (17). It can be seen that those deviations do not amount to more than ±0.06 MPa.

3.2 *Predictions for other fluids*

In order to test the capability of the proposed universal correlation in predicting the vapour pressures of other halocarbons from their critical properties, we have calculated the vapour pressures of HCFC-124 (Niesen et al 1994; Weber and Silva 1994), a similar compound, and two C3 halocarbons, isomers HCFC-225ca and HCFC-225cb (Matsuo et al 1994), for which there are accurate experimental data. In the case of the C3 halocarbons it was necessary to estimate the critical pressure, for which was used the correlation between the critical compressibility factor dependence on the molar mass (Fialho and Nieto de Castro 1996a, 2000). Figure 13 shows the deviations for pressure, found to be less than 0.025 MPa, a result very encouraging for the use of such a corresponding-states approach in polar liquids.

In addition to this fact the universal behaviour predicts a value of the Pitzer acentric factor $\omega = 0.269 \pm 0.015$, a value very close to the individual values for the several compounds. This is another fact that must be explored in future investigations.

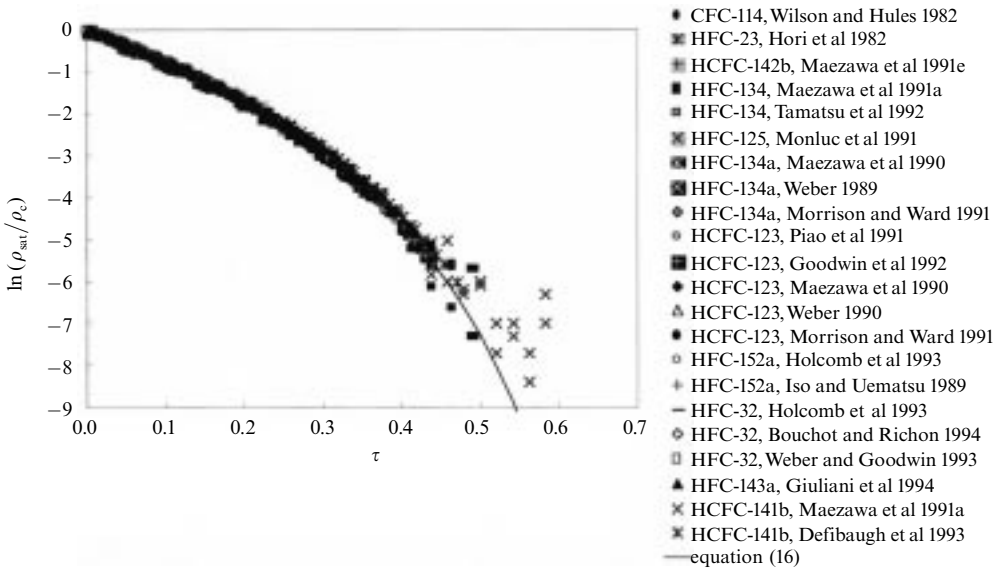


**Figure 11.** The universal curve for the variation of the reduced vapour pressure of halocarbons as a function of $\tau = T/T_c$.

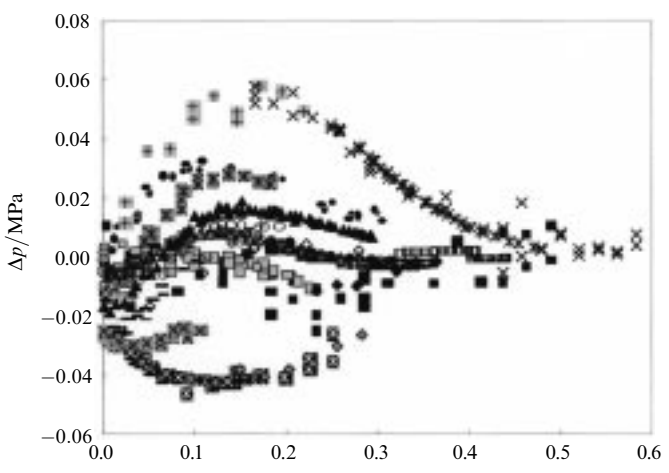


**Figure 12.** Deviations between experimental data of the reduced vapour pressure and the universal correlation as a function of $\tau = T/T_c$. Key as for figure 11.

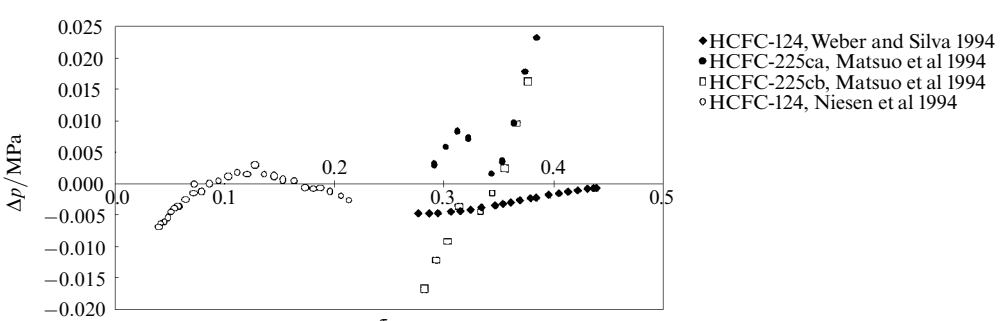


**Figure 13.** Deviations between the predicted and experimental values of the vapour pressure of HCFC-124, HCFC-225ca, and HCFC-225cb as a function of $\tau = T/T_c$.

## 4 Extensions of the present studies

Some recent measurements on the density of fluorinated ethanes can be used to test the applicability of the developed correlations to higher molecular weight compounds. Also, the recent interest in the use of fluorinated ethers as refrigerants opens a completely new field for property predictions, as most of these compounds have never been studied. Neglecting purity problems, already found to exist in round-robin tests of viscosity and thermal conductivity of refrigerants, we can try to apply the existing correlation to the prediction of the densities of HCFC-225ca ($CHCl_2CF_2CF_3$), HCFC-225cb ($CHClFCF_2CClF_2$), studied by Matsuo et al (1994), HFC-218 ($C_3F_8$), studied by Bouchot and Richon (1994), and E134 ($CH_2FOCH_2F$), studied by Defibaugh and Morrison (1992).

Figure 14 shows the results obtained for the propane derivatives, where no deviations greater than 0.5% are found for the HCFC-225, although the deviations are greater for the perfluoropropane. Figure 15 compares the correlation with the experimental density values for E134. Deviations of the order of 2.5%–3.5% are found, a signal that the expressions used are not totally correct, and must be modified for this type of compound.

The values of the critical compressibility factor, $Z_c$, $b^*(T)$ and $a^*(T, M)$ have probably to be modified to account for these deviations. A first possibility will be the Pitzer acentric factor, found to be similar for most of the methane and ethane derivatives, but possibly different for the propane derivatives and necessarily different for the compounds with the ether group. Another possibility is a dependence of the effective dipole moment,

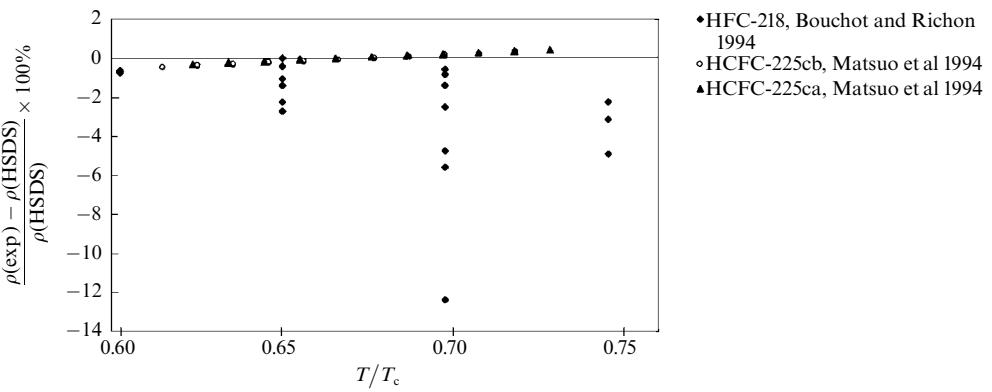


**Figure 14.** Deviations between the experimental density of refrigerants and the predicted values by the reduced HSDS model for HCFC-225ca, HCFC-225cb, and HFC-218.

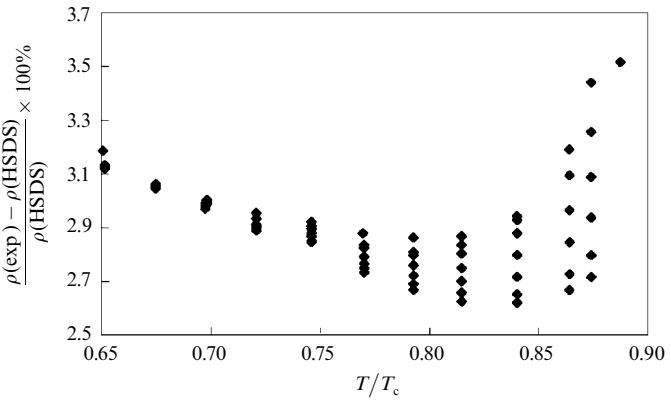


**Figure 15.** Deviations between the experimental density of refrigerants and the predicted values by the reduced HSDS model for E134 (◆, Defibaugh and Morrison 1992).

which varies significantly, in the liquid phase for all these compounds. Work currently under progress will demonstrate the validity of these hypotheses.

## 5 Conclusions

A new form of the Carnahan and Starling DeSantis equation of state, the HSDS equation of state, has been used to develop a general scheme for the estimation of the liquid densities of environmentally acceptable refrigerants. The scheme has an accuracy of $\pm 1.5\%$ for $T^* \leqslant 0.9$ and 3% for $0.9 \leqslant T^* \leqslant 0.95$, and pressures between vapour pressure and 20 MPa, based only on the knowledge of the critical constants, $p_c$ and $T_c$. As it now stands, it represents the most accurate and powerful general method of estimation of halocarbon liquid densities in the saturation line and in the compressed liquid region, based on a theoretical repulsive part and on an experimentally adjustable attractive part. It is very easy to use in a PC environment as it only needs 11 adjusted constants in addition to the fixed hard-sphere ten virial constants. It is also easily attached to phase equilibria and transport properties estimation packages.

The present model, together with mixing rules, can be applied to binary and ternary mixtures of refrigerants predicting the density with an uncertainty of 1.5% for $T^* \leqslant 0.9$, with only critical constants of the pure fluids. This is equivalent to a one-fluid model, without interaction parameters. As far as we can tell, there is no reason one cannot apply this model to a mixture of $n$ components with the same uncertainty. However, one should check these assumptions carefully, whenever possible.

A corresponding-states approach has been developed to correlate the vapour pressure dependence on temperature for halocarbons, CFCs, HCFCs, and HFCs, for a total of 11 compounds. The accuracy of the proposed scheme is better than $\pm 0.06$ MPa and it is simple and accurate. Tests of its predictability power with halocarbons of the C2 and C3 series show encouraging results, that will be extended in the near future, namely to fluorinated ethers.

Finally, the correlations developed for the density of pure fluids were applied to HCFCs and one HFC derived from propane and the results, once again, look encouraging. Its application to fluoroethers shows that there is a need for a different correlation, with an uncertainty commensurate with that of the experimental measurements.

This scheme is at present limited to halocarbons of the methane and ethane series with known critical constants. In absence of reliable critical density values, they should be estimated from known $T_c$ and $p_c$ through equation (6).

We hope to extend it in the future to propane derivatives and haloethers. If the results obtained are similar it could be transformed into a universal prediction scheme for refrigerants.

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