International Journal of Thermophysics, Vol. 21, No. 2, 2000

Prediction of the Vapor Pressure of Environmentally Acceptable Halocarbons[1]

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The vapor pressure and its dependence on temperature of halocarbons for $0.002 < p_R < 1$ have been analyzed in terms of universal behavior. Results for CFC-114, HCFC-123, HCFC-141b, HCFC-142b, HCFC-143a, HFC-23, HFC-32, HFC-134, HFC-125, HFC-134a, and HFC-152a for reduced temperatures between 0.55 and 1.0 show that the reduced vapor pressure can be expressed as a function of $1 - T_R$ by a Padé approximant. Deviations of the correlated data from the universal function do not amount to more than ± 0.06 MPa, with an average deviation of 0.025 MPa. Predictions of the saturation vapor pressures of HCFC-124, HCFC-225ca, and HCFC-225cb, which are the systems used to test the capability of this scheme, agree within 0.025 MPa, that is, within the accuracy of the corresponding states correlation. However, for HFC-236ea, the deviations are as large as -0.07 MPa. The present scheme can be used to calculate the Pitzer acentric factor, and an average value of $\omega = 0.269 \pm 0.015$ is obtained for all the fluids.

KEY WORDS: halocarbons; prediction; vapor pressure; universal correlation.

1. INTRODUCTION

Accurate thermophysical property data are very important in the development, design, planning, and operation of processes of several industries [1, 2], including modern processes in the chemical industry for environmentally important chemicals, including plant safety. One of the most important properties is vapor pressure over wide temperature ranges.

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[1] Paper presented at the Fifth Asian Thermophysical Properties Conference, August 30–September 2, 1998, Seoul, Korea.

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Although there have been many applications of corresponding-states-based equations, there has been none applied so far to such a wide number of polar substances as the halocarbons. In addition, for application purposes, a simple equation, based on the two-parameter corresponding states model, can be very useful.

As part of an overall program of measurement and estimation of the thermophysical properties of environmentally acceptable refrigerants developed in our laboratory in Lisbon [3], we have studied possible regular patterns in the vapor pressure curves of several CFCs, HCFCs, and HFCs. The compounds CFC-114, HCFC-123, HCFC-141b, HCFC-142b, HCFC-143a, HFC-23, HFC-32, HFC-134, HFC-125, HFC-134a, and HFC-152a were the refrigerants used in the development of a universal correlation model for interpolation and extrapolation of the vapor pressure.

In order to test the quality of the predictive scheme, the vapor pressures of HCFC-124, HCFC-225ca, HCFC-225cb, and HFC-236ea, which are important new refrigerants, were calculated and compared with experimental measurements. Possible extensions of the proposed equation to include a third parameter like the Pitzer acentric factor, or any other that reflects a macroscopic description of the molecular structure, are discussed.

2. RESULTS

Experimental values of the vapor pressures of the compounds covered by this study were obtained from various literature sources [4–21]. The critical constants used are displayed in Table I, together with the literature sources. About 600 data points were used for 11 different refrigerants. The logarithm of the reduced saturation vapor pressure, $p_{\mathrm{sat}}/p_{\mathrm{c}}$ was fitted to a Padé approximant (2, 2), where the constant term in the numerator was set to zero in order to constrain the correlation to the critical point (0, 0), as follows:

$$\ln\left(\frac{p_{\mathrm{sat}}}{p_{\mathrm{c}}}\right)=\frac{a_1\tau+a_2\tau^2}{a_3+a_4\tau+a_5\tau^2} \tag{1}$$

where

$$\tau=\frac{T_{\mathrm{c}}-T}{T_{\mathrm{c}}} \tag{2}$$

Table II shows the values of the coefficients a_1 to a_5 and the standard deviation σ of Eq. (1), and Fig. 1 shows the representation of the function for the different data points. The superposition of the points in the adjusted function is remarkable, except for the data for HCFC-141b and HFC-134

Table I. Critical Constants Used for the Correlation and the Test

Refrigerant	M (kg · mol^{-1})	p_c (MPa)	T_c (K)	ρ_c (kg · m^{-3})
CFC-114	0.170922	3.252 [22]	418.78 [22]	576 [22]
HCF-C123	0.152930	3.674 [23]	456.94 [23]	550 [23]
HCFC-124	0.136475	3.643 [24]	395.65 [24]	559.76 [24]
HCFC-141b	0.116950	4.46 [7]	477.3 [21]	461 [21]
HCFC-142b	0.100495	4.041 [25]	410.25 [26]	446 [25]
HFC-23	0.070013	4.82 [27]	298.98 [27]	526 [27]
HFC-32	0.052024	5.83 [28]	351.56 [28]	422.67 [28]
HFC-134	0.102030	4.615 [29]	391.74 [29]	536 [29]
HFC-125	0.120020	3.633 [29]	339.4 [29]	572 [29]
HFC-134a	0.102030	4.068 [30]	374.26 [30]	515.2 [30]
HFC-143a	0.084040	3.811 [31]	346.25 [31]	434 [31]
HFC-152a	0.066050	4.52 [32]	386.44 [32]	368 [32]
HFC-236ea	0.152039	3.4116 [37]	412.375 [37]	565 [37]
HCFC-225ca	0.190928	2.974[a]	478 [33]	578 [33]
HCFC-225cb	0.190928	3.012[a]	484.85 [33]	557 [33]

[a] These are estimated with the technique proposed by Fialho et al. [34, 35].

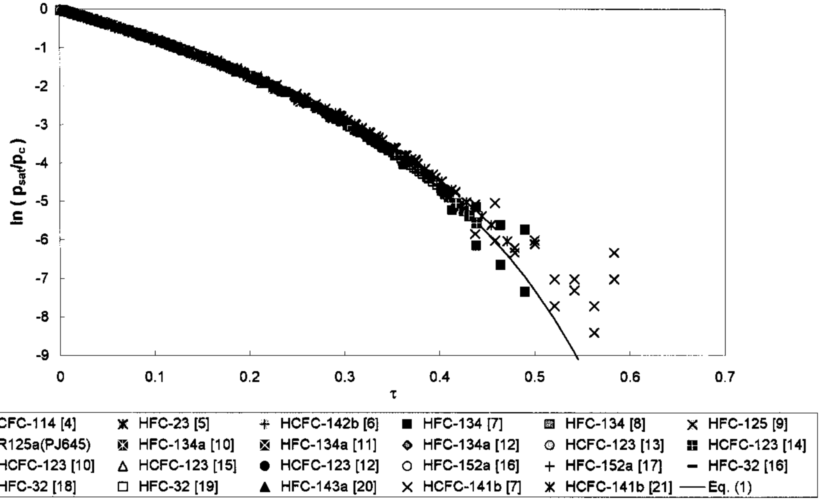

Fig. 1. The universal curve for the variation of the reduced vapor pressure of halocarbons as a function of $\tau = 1 - T/T_c$.

Table II. Coefficients of Eq. (1)

a_1	a_2	a_3	a_4	a_5	σ
−94.8179	−135.342	13.1306	11.4013	−29.4039	0.034

from Maezawa et al. [7] below $p_{\text{sat}}/p_{\text{c}} = 0.002$,[5] where they use their instrument outside the range for which it was most accurate, increasing the scatter in the data.

Figure 2 shows the deviations of the experimental points from the universal correlation of Eq. (1). It can be seen that the deviations are not larger than ±0.06 MPa, with an average deviation of ±0.025 MPa. From this equation, one can estimate the Pitzer acentric factor ω assumed by this model to be 0.269 ± 0.015. If we use the values calculated directly from the experimental vapor pressure data, it is found that ω varies from 0.225 for HCFC-141b to 0.323 for HFC-134a. This result seems to support that the present model is not very sensitive to the acentric factor value, and that its inclusion as a third parameter will not improve the correlation significantly.

In order to test the capability of the proposed universal correlation to predict the vapor pressures of other halocarbons not used in this scheme, only from their critical properties, the vapor pressures of HCFC-124 [24, 36], a similar compound, and three C_3 halocarbons, isomers HCFC-225ca, HCFC-225cb [33], and HFC-236ea [37], for which there are accurate experimental data, have been calculated.

In the case of HCFC-225ca and HCFC-225cb, it was necessary to estimate the critical pressure from the correlation between the critical compressibility factor and the relative molecular mass [34, 35]. This equation, found to give values of Z_c within 2% of the experimental values for 15 halocarbons derived from methane and ethane, is

$$Z_c = \frac{p_c}{R\rho_c T_c} = 0.317 - \frac{3.41 \times 10^{-3}}{M} - 0.138\, M \tag{3}$$

where M is the relative molecular mass in kg · mol^{-1}. Figure 3 shows deviations of the experimental vapor pressures from the predicted results. The deviations were found to be smaller than 0.025 MPa, a result consistent with the deviations obtained for the fluids used in the scheme, except for HFC-236ea, where the deviations can be as large as −0.07 MPa. Also shown in this figure are the most recent measurements on HFC-143a [38]

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[5] For most of the fluids, with critical pressures around 4 MPa, this means pressures smaller than 8 kPa.

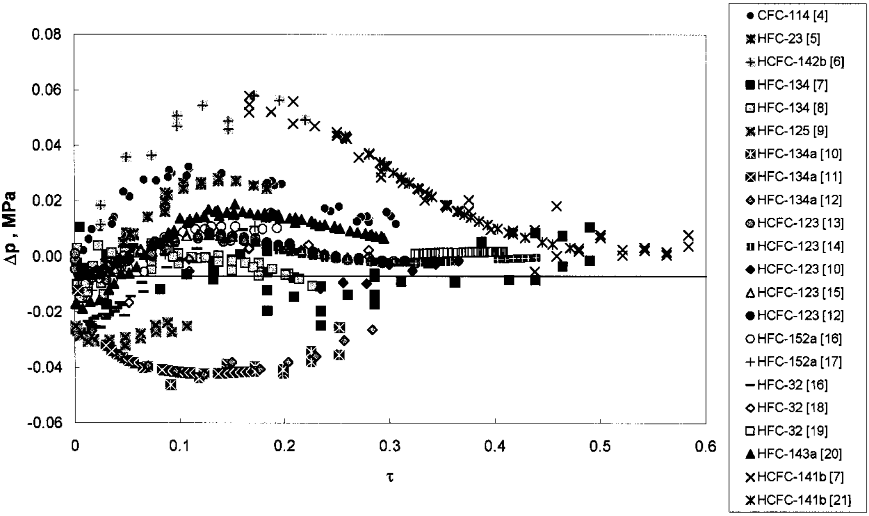

Fig. 2. Deviations of experimental data from the universal correlation as a function of $\tau = 1 - T/T_c$.

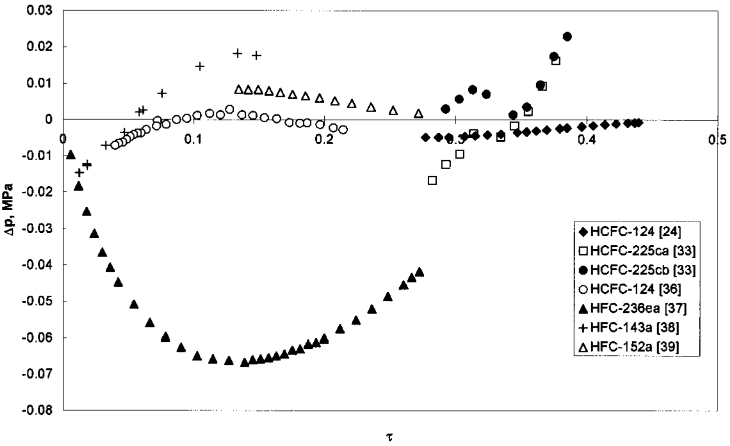

Fig. 3. Deviations of experimental data from the predicted values of the vapor pressure of HCFC-124, HCFC-225ca, HCFC-225cb, HFC-236ea, HFC-143a, and HFC-152a as a function of $\tau = 1 - T/T_c$.

and HFC-152a [39], where an accurate determination of T_c and p_c was made. Deviations of experimental values for these fluids from the universal equation are no more than 0.02 and 0.01 MPa, respectively. These results are very encouraging for the use of such a simple corresponding states approach in polar liquids.

Several equations have been developed in the past with polynomials or Padé approximants to correlate the vapor pressure of individual compounds that are more exact than the type of equation proposed here. One of the equations used to interpolate and extrapolate vapor pressures of organic compounds with high accuracy is the Wagner equation [40]. This equation uses a power series in τ, with constants different from fluid to fluid, but no universal form of it has been developed. In the monograph by Reid et al. [41], recommendations are made such that the available predictive schemes are not very accurate, and from the examples presented, they are less accurate than the universal equation proposed here.

3. CONCLUSIONS

A two-parameter corresponding states approach has been developed to correlate the vapor pressure dependence on temperature for halocarbons, CFCs, HCFCs, and HFCs, for a total of 11 compounds. This equation is very simple and can be used to interpolate or predict the vapor pressure of halocarbons from a knowledge of only their critical constants. As a consequence of the model developed, an average value of 0.269 ± 0.015 for the Pitzer acentric factor for all the fluids is obtained. The accuracy of the proposed scheme is better than ± 0.06 MPa, with an average deviation of 0.025 MPa.

Tests of its predictive power with halocarbons in the C_2 and C_3 series not used in its development show encouraging results, which will be extended in the near future, namely to fluorinated ethers. It will be also possible to introduce the Pitzer constant of the fluid in the model and improve the predictive model slightly, although this will restrict the applicability of the model to fluids with known Pitzer constants and therefore vapor pressure data. Further molecular parameters like dipole moments are presently under study and will be the subject of a future publication.

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