

APPLICATIONS OF THE HARD SPHERE DE SANTIS EQUATION OF STATE TO THE ESTIMATION OF THE DENSITY OF COMPRESSED ALTERNATIVE REFRIGERANTS

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INTRODUCTION

The density of liquid refrigerants is very important for the design of compression cycles in the refrigeration and air conditioning industries. The increasing concern with the environmental protection leads the governments to legislate in order to banish in the short term the use of the CFC's and in the long run the HCFC's. Considering those decisions, the industries need to find new replacements for those compounds, and suitable substitutes seem to be HFC's, fluorinated ethers, their mixtures and mixtures with small quantities of HCFC's. The only problem in using those alternative refrigerants is the lack of knowledge about their properties. Among them, the density is one of the most important.

It is the propose of this paper to show the use of a model that allows the user to estimate the liquid density for the refrigerants. The uncertainty of this model is of $\pm 2.0\%$ for reduced values of temperature less then 0.95 and reduced values of density less then 1.0. This model needs the information for the critical parameters and the pressure of the saturated liquid-vapour line. The Hard-Sphere DeSantis equation of state Ref. /1/ is use to give physical support to the model. The corrections to the attractive and repulsive part, a and b , have been calculated from a few experimental pure refrigerants Ref. /1/ (HCFC 152a, HCFC 22, HCFC 142b, HCFC 123, HCFC 114).

HARD-SPHERE DE SANTIS MODEL

The development of the Hard-Sphere DeSantis equation of state was present in a previous paper Ref. /1/. This equation of state is given by the expression,

$$\frac{P}{\rho RT} = \sum_{i=1}^{10} C_i (b(M, \rho_c) \rho)^{i-1} - \frac{a(T; M, T_c, \rho_c, p_c) \rho}{RT(1 + b(M, \rho_c) \rho)} \quad (1)$$

C_i are the hard-sphere virial constants, obtained from Monte Carlo Ref. /2/ and Molecular Dynamic Ref. /3/ simulations, given in Table 1. The functions, $b(M, \rho_c)$ and $a(T; M, T_c, \rho_c, p_c)$ are the repulsive and attractive van der Waals like terms, respectively. b is as a function of the relative molecular mass and the critical pressure, given by Eq. (2), and a depends on the temperature, relative molecular mass, critical temperature, critical density and critical pressure as described by Eq. (3).

$$b(M, \rho_c) = \frac{2.0335 + 0.01039 M}{\rho_c} \quad (2)$$

$$a(T; M, T_c, \rho_c, p_c) = \frac{p_c}{\rho_c^2} \sum_{i=0}^2 \left(\sum_{j=0}^2 a_{ij} T^{*j} \right) M^i \quad (3)$$

The parameters a_{ij} are given in Table 2.

| | | | |
|-------|---------------------|----------|---------------------|
| 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 |

Table 1: Virial coefficients for the hard-spheres Ref. /2/, Ref. /3/.

| a_{ij} | $i = 0$ | $i = 1$ | $i = 2$ |
|----------|-------------------------|-------------------------|-------------------------|
| $j = 0$ | 2.069249×10^5 | -2.332869×10^6 | 9.949903×10^6 |
| $j = 1$ | -4.245370×10^5 | 5.268112×10^6 | -2.222515×10^7 |
| $j = 2$ | 2.194730×10^5 | -2.991949×10^6 | 1.251112×10^7 |

Table 2: Parameters used in Eq. (3), Ref. /1/

APPLICATION TO THE ESTIMATION OF THE DENSITY OF SEVERAL HCFC's AND HFC's

In this work the model was use to compare with the experimental data available for the following refrigerants: HCFC 141b, HFC 125, HFC 134a, HFC 152a and HFC 32.

The deviations between the experimental liquid density data, for several authors, and the estimated densities from the model are present in figures 1 to 5, for each of the compounds.

The critical parameters used and the relative molecular mass for each of the compounds are present in table 3, the critical pressure was estimated from the relation /1/,

$$p_c = \rho_c RT_c \left(0.317 - \frac{3.41 \times 10^{-3}}{M} - 0.138M \right) \quad (4)$$

| Refrigerant | $\frac{M}{\text{kg mol}^{-1}}$ | $\frac{T_c}{\text{K}}$ | $\frac{\rho_c}{\text{kg m}^{-3}}$ |
|-------------|--------------------------------|------------------------|-----------------------------------|
| HCFC 141b | 0.116950 | 480 ^a | 460 ^a |
| HFC 125 | 0.120020 | 339.4 ^b | 572 ^b |
| HFC 134a | 0.102030 | 373.69 ^c | 495.6 ^c |
| HFC 152a | 0.066050 | 386.44 ^d | 368 ^d |
| HFC 32 | 0.052024 | 351.56 ^e | 422.67 ^e |

Table 3: Critical constants and relative molecular mass for the refrigerants. ^a Ref. /5/, ^b Ref. /21/, ^c Ref. /22/, ^d Ref. /23/, ^e Ref. /18/

DISCUSSION

As a result, from the analysis of the figures 1 to 5, the use of the HSDS model confirm the claimed uncertainty of $\pm 2.0\%$ for reduced temperature less then 0.95, both for saturation line and compressed liquid. This gives confidence to the applicability of the present model to fluids with the same molecular structure. The use of the model permits to conclude about the self-consistence of different author's sets of data. The positive or negative systematic behaviour for the deviations of each refrigerant is a result of the model being developed by adjusting only a few experimental fluids. The increasing deviation between 0.9 and 0.95 reduced temperatures is the result of the lack of flexibility of the model as the critical point is approached.

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SYMBOLS

$a(T; M, T_c, \rho_c, p_c)$ - attractive van der Waals like term

ρ - density

ρ_c - critical density

C_i - hard-sphere virial constants

R - ideal gas constant

p - pressure

p_c - critical pressure

M - relative molecular mass

T - temperature

T_c - critical temperature

$b(M, \rho_c)$ - repulsive van der Waals like term

a_{ij} - parameters of Eq. (3)