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Thermodynamic Properties for R-404A[1]

K. Fujiwara,[2,3] S. Nakamura,[2] and M. Noguchi[2]

An 18-coefficient modified Benedict–Webb–Rubin equation of state has been developed for R-404A, a ternary mixture of 44% by mass of pentafluoroethane (R-125), 52% by mass of 1,1,1-trifluoroethane (R-143a), and 4% by mass of 1,1,1,2-tetrafluoroethane (R-134a). Correlations of bubble point pressures, dew point pressures, saturated liquid densities, and saturated vapor densities are also presented. This equation of state has been developed based on the reported experimental data of *PVT* properties, saturation properties, and isochoric heat capacities by using least-squares fitting. These correlations are valid in the temperature range from 250 K to the critical temperature. This equation of state is valid at pressures up to 19 MPa, densities to 1300 kg · m^{-3}, and temperatures from 250 to 400 K. The thermodynamic properties except for the saturation pressures are calculated from this equation of state.

KEY WORDS: correlation; equation of state; R-125; R-134a; R-143a; R-404A; thermodynamic properties.

1. INTRODUCTION

R-502, an azeotropic mixture of 48.8% in mass of chlorodifluoroethane (R-22) and 51.2% in mass of chloropentafluoroethane (R-115), has been widely used as a refrigerant in low-temperature equipment. This substance has not been produced since 1996 according to the Montreal Protocol. R-507, an azeotropic mixture of 50% by mass of pentafluoroethane (R-125) and 50% by mass of 1,1,1-trifluoroethane (R-143a), has been considered as an alternative to R-502. R-404A, a ternary mixture of 44% by mass of R-125, 52% by mass of R-143a, and 4% by mass of 1,1,1,2-tetrafluoroethane (R-134a), has been also considered as an alternative to R-502.

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[2] Chemical Division, Daikin Industries, Ltd., 1-1 Nishi Hitotsuya, Settsu-shi, Osaka 566-8585, Japan.

[3] To whom correspondence should be addressed.

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We have correlated bubble point pressures, dew point pressures, saturated liquid densities, and saturated vapor densities for R-404A. We have also developed an equation of state for R-404A. The form is an 18-coefficient modified Benedict–Webb–Rubin equation of state proposed by Piao et al. [1]. The thermodynamic properties except for the saturation pressures are calculated from this equation of state.

2. EXPERIMENTAL DATA

The critical parameters were reported by Bouchot and Richon [2] and Nakamura et al. [3]. Bouchot and Richon [2] reported seven bubble point pressures, nine dew point pressures, nine saturated liquid densities, and nine saturated vapor densities at temperatures from 253 to 333 K.

Bouchot and Richon [2] also reported 214 *PVT* properties at pressures from 0.1 to 19 MPa, densities from 4 to 1279 $\mathrm{kg \cdot m^{-3}}$, and temperatures from 253 to 333 K. Nakamura et al. [3] reported 118 measurements at pressures from 1.5 to 15 MPa, densities from 47 to 1247 $\mathrm{kg \cdot m^{-3}}$, and temperatures from 263 to 403 K. Nakamura et al. [3] also reported 43 measurements along three isochores in a range of temperatures from 345 to 393 K, pressures from 3.7 to 7.8 MPa, and densities from 486 to 493 $\mathrm{kg \cdot m^{-3}}$.

One isochoric heat capacity datum was reported by Nakamura et al. [4] at a pressure of 3 MPa and temperature of 264 K.

3. CRITICAL PARAMETERS

The critical parameters of Nakamura et al. [3] were used in this study. The numerical values are given as follows:

$$P_c = 3.726 \pm 0.002\ \mathrm{MPa} \tag{1}$$

$$\rho_c = 490 \pm 2\ \mathrm{kg \cdot m^{-3}} \tag{2}$$

$$T_c = 345.15 \pm 0.01\ \mathrm{K} \tag{3}$$

4. CORRELATIONS

The following correlation for the bubble point pressure, P', was developed.

$$\ln\left(\frac{P'}{P_c}\right) = \frac{T_c}{T}\left[a'_1\left(1 - \frac{T}{T_r}\right) + a'_2\left(1 - \frac{T}{T_r}\right)^{1.5} + a'_3\left(1 - \frac{T}{T_r}\right)^3 + a'_4\left(1 - \frac{T}{T_r}\right)^6\right] \tag{4}$$

Table I. Coefficients in Eqs. (4)–(8)

I	a'_i	a''_i	b'_i	b''_i	c_i
1	−7.37917	−7.59385	0.963411	−2.13109	2.60716
2	1.26946	1.77079	5.68670	2.14542	9.41515
3	−1.64715	−3.71716	−10.2368	−4.61060	−0.325675
4	−7.12355	3.24320	7.23707	4.67897	−0.547398
5				−1.67211	
6				1.01657	

The numerical values of the coefficients are listed in Table I. Figure 1 shows a comparison of the bubble point pressure values calculated from Eq. (4) with the experimental data. Equation (4) represents the data of Bouchot and Richon [2] with a maximum deviation of −0.6% and a standard deviation of 0.3%.

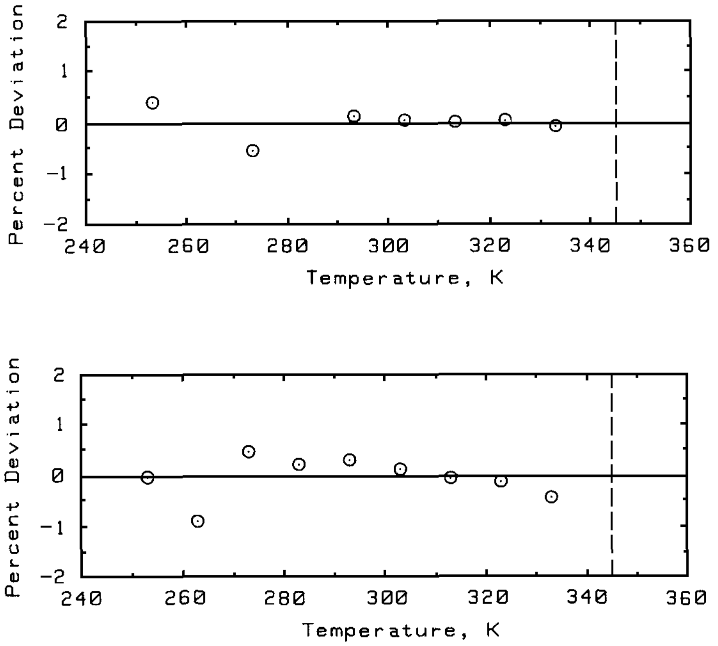

Fig. 1. Comparison of the bubble (top) and dew (bottom) point pressure values for R-404A calculated from Eqs. (4) (top) and (5) (bottom) with the experimental data: percentage deviation = $100(P_{\text{exp}} - P_{\text{calc}})/P_{\text{calc}}$; ○, Bouchot and Richon [2].

The dew point pressure, P'', correlation was developed as follows:

$$\ln\left(\frac{P''}{P_c}\right)=\frac{T_c}{T}\left[a_1''\left(1-\frac{T}{T_c}\right)+a_2''\left(1-\frac{T}{T_c}\right)^{1.5}+a_3''\left(1-\frac{T}{T_c}\right)^{3}+a_4''\left(1-\frac{T}{T_c}\right)^{6}\right] \tag{5}$$

The numerical values of the coefficients are listed in Table I. Figure 1 shows a comparison of the dew point pressure values calculated from Eq. (5) with the experimental data. Equation (5) represents the data of Bouchot and Richon [2] with a maximum deviation of −0.9% and a standard deviation of 0.4%.

The following correlation for saturated liquid density, ρ', was developed.

$$\frac{\rho'}{\rho_c}=1+b_1'\left(1-\frac{T}{T_c}\right)^{0.318}+b_2'\left(1-\frac{T}{T_c}\right)^{2/3}+b_3'\left(1-\frac{T}{T_c}\right)+b_4'\left(1-\frac{T}{T_c}\right)^{4/3} \tag{6}$$

The numerical values of the coefficients are listed in Table I. Figure 2 shows a comparison of the saturated liquid density values calculated from Eq. (6) with the experimental data. Equation (6) represents the data of Bouchot and Richon [2] within ±0.2%.

The correlation for saturated vapor density, ρ'', was developed as follows.

$$\frac{\rho''}{\rho_c}=1+b_1''\left(1-\frac{T}{T_c}\right)^{0.318}+b_2''\left(1-\frac{T}{T_c}\right)^{2/3}+b_3''\left(1-\frac{T}{T_c}\right)+b_4''\left(1-\frac{T}{T_c}\right)^{4/3}+b_5''\left(1-\frac{T}{T_c}\right)^{3}+b_6''\left(1-\frac{T}{T_c}\right)^{6} \tag{7}$$

The numerical values of the coefficients are listed in Table I. Figure 2 shows a comparison of the saturated vapor density values calculated from Eq. (7) with the experimental data. Equation (7) represents the data of Bouchot and Richon [2] with a maximum deviation of 1.3% and a standard deviation of 0.6%.

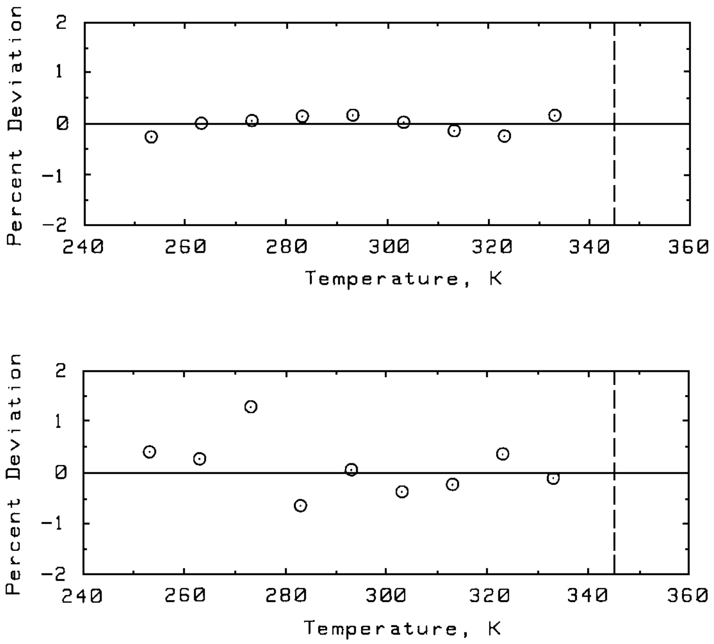

Fig. 2. Comparison of the saturated liquid (top) and vapor (bottom) density values for R-404A calculated from Eqs. (6) (top) and (7) (bottom) with the experimental data: percentage deviation = $100(\rho_{\mathrm{exp}} - \rho_{\mathrm{calc}})/\rho_{\mathrm{calc}}$; ○, Bouchot and Richon [2].

The coefficients of the following equation for ideal-gas heat capacity, C_{p}°, were determined using those of the equations for R-125, R-134a, and R-143a reported by McLinden et al. [5].

$$\frac{C_{\mathrm{p}}^{\circ}}{R} = c_1 + c_2 \frac{T}{T_{\mathrm{c}}} + c_3 \left(\frac{T}{T_{\mathrm{c}}}\right)^2 + c_4 \left(\frac{T}{T_{\mathrm{c}}}\right)^3 \tag{8}$$

where $R = 8.314471\ \mathrm{kJ \cdot kg^{-1} \cdot K^{-1}}$. The numerical values of the coefficients are given in Table I.

5. EQUATION OF STATE

Equations of state for mixtures are generally composed of equations of state for each component and mixing rules. Equations of state for each component with a large number of coefficients are used to meet the required accuracy of calculated properties. Mixing rules to apply these kinds of equations of state for mixtures are empirically developed. A large number of experimental data are required for each component as well as for the mixture. In some cases where an equation of state obtained for a mixture does not represent experimental data in the vapor–liquid equilibrium state accurately, a separate equation of state and mixing rules for the vapor–liquid equilibrium states have been developed.

We have developed an equation of state for R-404A by correlating measurements for the mixture as a pseudo-pure fluid because this equation of state is used primarily for the thermodynamic properties in the single phase. We have considered only data for the mixture at the composition given in Section 1. The saturation pressures are calculated from correlations which are given as functions of temperature. The saturated densities are obtained as points where the isotherms of this equation of state and these saturation pressure correlations intersect.

The form of the equation of state in this study is an 18-coefficient modified Benedict–Webb–Rubin (MBWR) equation of state proposed by Piao et al. [1]. The equation of state is given as follows:

$$P_r = \frac{T_r \cdot \rho_r}{Z_c} + \sum_{i=1}^{14} d_i \cdot \frac{\rho_r^{m_i}}{T_r^{n_i}} + \sum_{i=15}^{18} d_i \cdot \frac{\rho_r^{m_i+3}}{T_r^{n_i}} \cdot \exp(-\rho_r^2) \tag{9}$$

where $P_r = (P/P_c)$, $\rho_r = (\rho/\rho_c)$, $T_r = (T/T_c)$, $Z_c = (P_c M/R\rho_c T_c)$, $M = 97.604\ \mathrm{kg \cdot kmol^{-1}}$, and $R = 8.314471\ \mathrm{kJ \cdot kmol^{-1} \cdot K^{-1}}$. The coefficients are listed in Table II.

The present equation of state has been developed based on the reported experimental data of *PVT* properties, saturation properties, and isochoric heat capacities using least squares fitting.

The Helmholtz free energy function, A, derived from Eqs. (8) and (9) is given as follows:

$$A_r = \frac{A}{T_c R Z_c} = A_r^* + A_r^\circ \tag{10}$$

where A_r^* is given below:

$$\begin{aligned} A_r^* = {} & \sum_{i=1}^{14} d_i \cdot \frac{1}{m_i - 1} \cdot \frac{\rho_r^{m_i - 1}}{T_r^{n_i}} + \sum_{i=15}^{16} d_i \cdot \frac{1}{2} \cdot \frac{1}{T_r^{n_i}} \cdot [1 - \exp(-\rho_r^2)] \\ & + \sum_{i=17}^{18} d_i \cdot \frac{1}{2} \cdot \frac{1}{T_r^{n_i}} [1 - (1 + \rho_r^2)\exp(-\rho_r^2)] + \frac{T_r}{Z_c} \cdot \ln(\rho_r) \end{aligned} \tag{11}$$

Table II. Coefficients in Eq. (9) and Constants, c_u and c_s

i	m_i	n_i	d_i
1	2	−1	1.96433581401
2	2	0	−3.56987977471
3	2	2	−3.71200450596
4	2	3	−0.0926720977755
5	3	−1	2.45744505455
6	3	0	−4.50853991488
7	3	2	5.17635519994
8	4	0	−0.313494002253
9	4	2	−1.08476103077
10	5	0	1.61429976497
11	5	1	−0.848565739838
12	6	0	−0.516634795318
13	6	1	0.145585376781
14	7	0	0.109212328026
15	0	0	−0.504178247791
16	0	1	0.702360275972
17	2	0	−0.606504041978
18	2	1	1.25624780433
c_u			12.1997905929
c_s			16.4589008290

On the other hand, A_r° is expressed as follows:

$$A_r^\circ = U_r^\circ - T_r S_r^\circ \tag{12}$$

where

$$U_r^\circ = \frac{1}{Z_c}\left[(c_1-1)(T_r - T_r^\circ) + \frac{c_2}{2}(T_r^2 - T_r^{\circ 2}) + \frac{c_3}{3}(T_r^3 - T_r^{\circ 3}) + \frac{c_4}{4}(T_r^4 - T_r^{\circ 4}) + c_u\right] \tag{13}$$

$$S_r^\circ = \frac{1}{Z_c}\left[(c_1-1)\ln\frac{T_r}{T_r^\circ} + c_2(T_r - T_r^\circ) + \frac{c_3}{2}(T_r^2 - T_r^{\circ 2}) + \frac{c_4}{3}(T_r^3 - T_r^{\circ 3}) + c_s\right] \tag{14}$$

where $T_r^\circ = 273.15/T_c$. The two numerical constants, c_u and c_s, are given so that the specific enthalpy and entropy values at 273.15 K for the saturated liquid state are 200 kJ · kg^{-1} and 1 kJ · kg^{-1} · K^{-1}, respectively.

The enthalpy and entropy values are given in the following thermodynamic relations:

$$S_r = \frac{S}{RZ_c} = -\left(\frac{\partial A_r}{\partial T_r}\right)_{\rho_r} \tag{15}$$

$$H_r = \frac{H}{T_c R Z_c} = A_r - T_r\left(\frac{\partial A_r}{\partial T_r}\right)_{\rho_r} + \rho_r\left(\frac{\partial A_r}{\partial \rho_r}\right)_{T_r} \tag{16}$$

The isochoric heat capacity, isobaric heat capacity, and speed of sound values are also given in the following thermodynamic relations:

$$(C_v)_r = \frac{C_v}{RZ_c} = -T_r\left(\frac{\partial^2 A_r}{\partial T_r^2}\right)_{\rho_r} \tag{17}$$

$$(C_p)_r = \frac{C_p}{RZ_c} = T_r\left[-\left(\frac{\partial^2 A_r}{\partial T_r^2}\right)_{\rho_r} + \frac{\rho_r\left(\frac{\partial^2 A_r}{\partial T_r\,\partial \rho_r}\right)^2}{2\left(\frac{\partial A_r}{\partial \rho_r}\right)_{T_r} + \rho_r\left(\frac{\partial A_r}{\partial \rho_r^2}\right)_{T_r}}\right] \tag{18}$$

$$(W^2)_r = \frac{W^2}{T_c R Z_c} = \rho_r^2\left[\frac{2}{\rho_r}\left(\frac{\partial A_r}{\partial \rho_r}\right)_{T_r} + \left(\frac{\partial^2 A_r}{\partial \rho_r^2}\right)_{T_r} - \frac{\left(\frac{\partial^2 A_r}{\partial T_r\,\partial \rho_r}\right)^2}{\left(\frac{\partial^2 A_r}{\partial T_r^2}\right)_{\rho_r}}\right] \tag{19}$$

6. DISCUSSION

Figure 3 shows a comparison of the single-phase density values calculated from Eq. (9) with experimental data. The present equation of

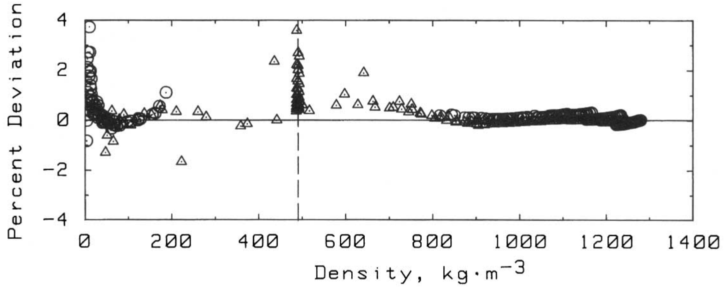

Fig. 3. Comparison of the single-phase density values for R-404A calculated from Eq. (9) with the experimental data: percentage deviation = $100(\rho_{\text{exp}} - \rho_{\text{calc}})/\rho_{\text{calc}}$; ○, Bouchot and Richon [2]; △, Nakamura et al. [3].

state represents the data of Bouchot and Richon [2] in the liquid state within ±0.3%; in the vapor, the data are represented with a maximum deviation of 4.3% and a standard deviation of 1.2%. The data at densities up to 150 $\mathrm{kg \cdot m^{-3}}$ are represented within ±0.5 $\mathrm{kg \cdot m^{-3}}$. This equation of state represents the data of Nakamura et al. [3] with a maximum deviation of 2.3% and a standard deviation of 0.4% except for the 43 measurements along three isochores: 487, 490, and 493 $\mathrm{kg \cdot m^{-3}}$. These 43 data are represented by the present equation of state within ±0.5% in pressure.

Figure 4 shows a comparison of the saturated liquid density values calculated from Eqs. (4) and (9) with the experimental data. The present equation of state represents the data of Bouchot and Richon [2] within ±0.2%.

Figure 4 shows a comparison of the saturated vapor density values calculated from Eqs. (5) and (9) with the experimental data. The present

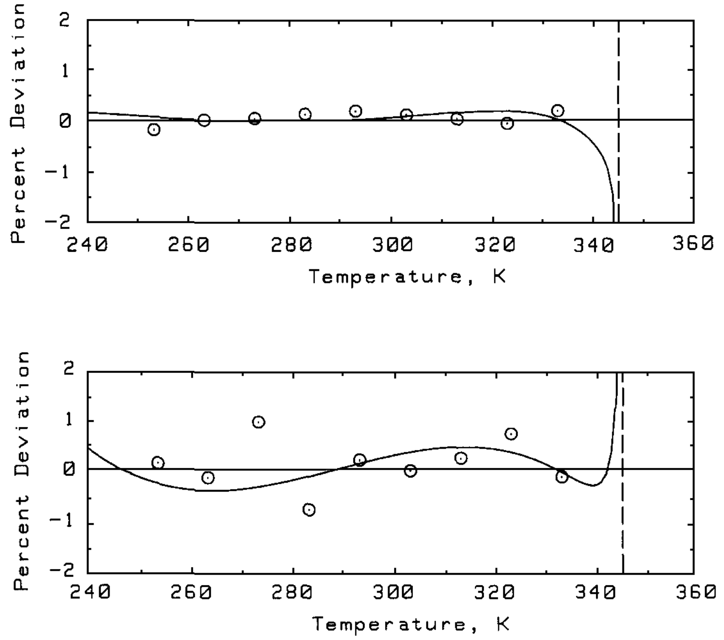

Fig. 4. Comparison of the saturated liquid (top) and vapor (bottom) density values for R-404A calculated from Eqs. (4) and (9) (top) and Eqs. (5) and (9) (bottom) with experimental data: percentage deviation $= 100(\rho_{\mathrm{exp}} - \rho_{\mathrm{calc}})/\rho_{\mathrm{calc}}$; ○, Bouchot and Richon [2];—, Eqs. (6) (top) and (7) (bottom).

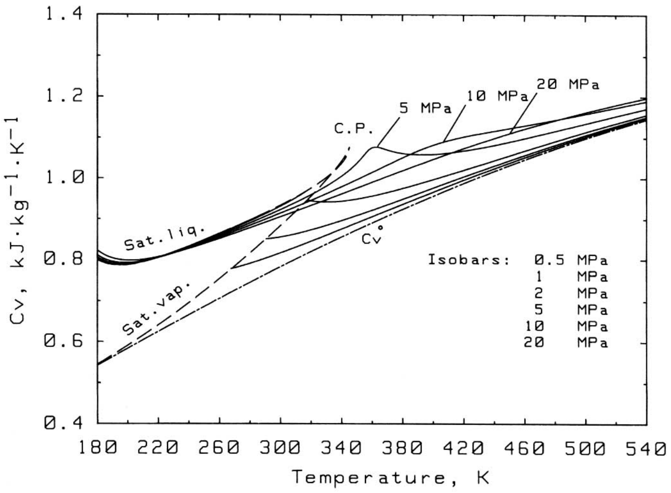

Fig. 5. Isochoric heat capacity values for R-404A calculated from Eq. (17).

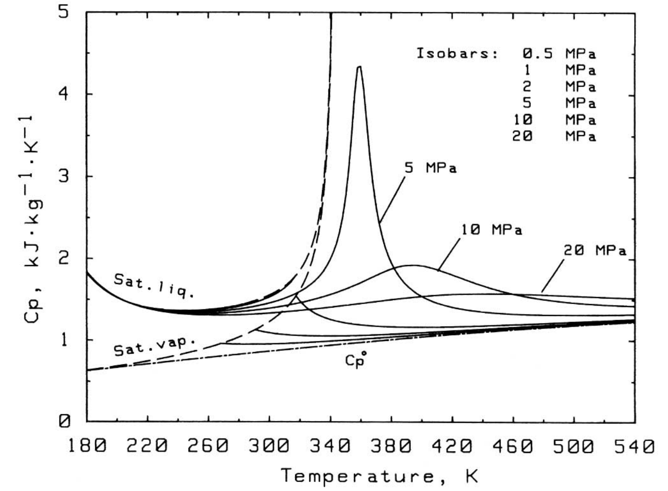

Fig. 6. Isochoric heat capacity values for R-404A calculated from Eq. (18).

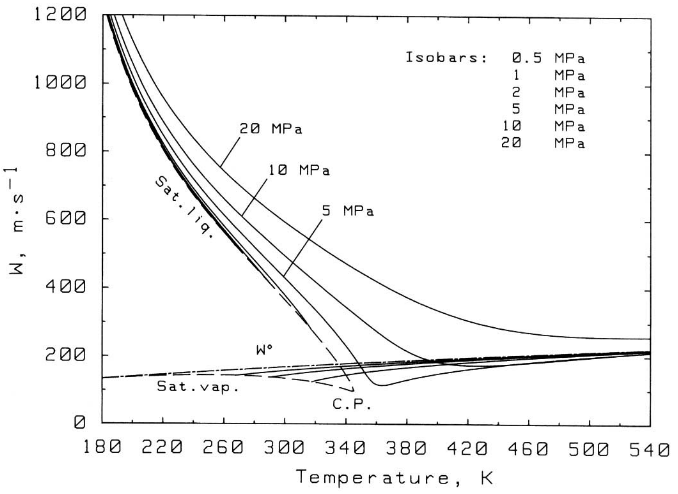

Fig. 7. Speed of sound values for R-404A calculated from Eq. (19).

equation of state represents the data of Bouchot and Richon [2] with a maximum deviation of 1% and a standard deviation of 0.5%.

The isochoric heat capacity value of Nakamura et al. [4] in the liquid state is represented by Eq. (17) with a deviation of −2.8%.

Figures 5–7 show the isochoric heat capacity, isobaric heat capacity, and speed-of-sound values calculated from Eqs. (17), (18), and (19), respectively. These isobars show consistent behavior from the thermodynamic point of view between 220 and 540 K.

7. CONCLUSION

An 18-coefficient MBWR equation of state for R-404A has been developed. Correlations of bubble point and dew point pressures and of saturated liquid and vapor densities are also presented. These correlations are considered to be valid at temperatures from 250 K to the critical temperature. This equation is considered to be valid in the range of temperatures from 250 to 400 K, densities up to 1300 kg · m^{-3}, and pressures up to 19 MPa. This equation of state gives the thermodynamic properties except for the saturation pressures.

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