Thermodynamic Properties of HFC-32, HFC-125, and HFC-134a Mixtures

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ABSTRACT

This study presents an equation of state for these mixtures which are developed based on the available *PVT*x, VLE, heat capacity and speed of sound measurements. The present equations of state are expected to be effective for VLE and superheated gaseous and compressed liquid phases, where the range of temperatures is from 200 K to 470 K, and pressures up to 20 MPa. The present equations are effective not only for the ternary mixture at different compositions but also for HFC-32/125, and HFC-32/134a , and even HFC-125/134a binary mixtures.

Keywords: binary mixture, critical parameter, equation of state, *PVT*x, ternary mixture, VLE.

INTRODUCTION

HCFC-22, which is one of the most widely used working fluids in air-conditioning systems, is scheduled to be phased out before 2030 by the international agreement. HFC-32/134a and HFC-32/125 binary mixtures, and HFC-32/125/134a ternary mixture are considered as the candidates to replace HCFC-22. There is a strong demand for the reliable thermodynamic properties for these alternative working fluids.

Many experimental studies have been reported for these important mixtures in an extensive range of pressure, temperature and composition. This study presents an equation of state for these mixtures which are developed based on these available *PVT*x, VLE, heat capacity and speed of sound measurements. The presented equation of state covers whole

compositions of ternary mixture and the entire fluid phase

EQUATIONS OF STATE FOR PURE FLUIDS

We have developed equations of state for HFC-32[1], HFC-125[2], and HFC-134a[3] based on the reported measurements, with the same functional form. The developed 18-coefficient modified BWR equation of state is given below:

$$P_r = T_r \cdot \rho_r / Z_c + B_1 \cdot \rho_r^2 + B_2 \cdot \rho_r^3 + B_3 \cdot \rho_r^4 + B_4 \cdot \rho_r^5 + B_5 \cdot \rho_r^6 + B_6 \cdot \rho_r^7 + (B_7 \cdot \rho_r^3 + B_8 \cdot \rho_r^5) \cdot \exp(-\rho_r^2) \quad (1)$$

$B_1 = a_1 T_r + a_2 + a_3/T_r^2 + a_4/T_r^3$ $\qquad$ $B_5 = a_{12} + a_{13}/T_r$

$B_2 = a_5 T_r + a_6 + a_7/T_r^2$ $\qquad$ $B_6 = a_{14}$

$B_3 = a_8 + a_9/T_r^2$ $\qquad$ $B_7 = a_{15} + a_{16}/T_r$

$B_4 = a_{10} + a_{11}/T_r$ $\qquad$ $B_8 = a_{17} + a_{18}/T_r$

where $P_r = P/P_c$, $\rho_r = \rho/\rho_c$, $T_r = T/T_c$, $Z_c = P_c/(R_x \cdot T_c \cdot \rho_c)$, $R_x = R/m$; $R = 8.314471$ J/(mol·K).

These equations represent almost all of the *PVT* data within ±0.5 % for HFC-32, HFC-125, and HFC-134a, respectively. These equations of state also represent the vapor pressures, saturated vapor/ liquid densities, and heat capacities with high accuracy. The coefficients of Eq.(1) and other details of these equations are presented in references [1-3].

CRITICAL PARAMETERS OF MIXTURE

There are two sets of measurements of the critical parameters available from Higashi et al.[4], and Nagel and Bier[5]. Among them only Nagel and Bier[5] reported the critical pressures. From these measurements, the following correlations were developed to represent the critical locus for this ternary mixture.

$$P_{cm} = x_1^2 \cdot P_{c1} + x_2^2 \cdot P_{c2} + x_3^2 \cdot P_{c3} + P_c^E \quad (2)$$

$$\rho_{cm} = x_1^2 \cdot \rho_{c1} + x_2^2 \cdot \rho_{c2} + x_3^2 \cdot \rho_{c3} + \rho_c^E \quad (3)$$

$$T_{cm} = x_1^2 \cdot T_{c1} + x_2^2 \cdot T_{c2} + x_3^2 \cdot T_{c3} + T_c^E \quad (4)$$

where

$$P_c^E = 8845 \cdot x_1 \cdot x_2^{1.040} + 7825 \cdot x_2 \cdot x_3^{0.994} + 10035 \cdot x_3 \cdot x_1^{1.009} + 700 \cdot x_1 \cdot x_2 \cdot x_3 \quad (5)$$

$$r_c^E = 11.25 \cdot x_1 \cdot x_2^{1.030} + 9.73 \cdot x_2 \cdot x_3^{0.992} + 11.25 \cdot x_3 \cdot x_1^{0.980} + 0.8 \cdot x_1 \cdot x_2 \cdot x_3 \quad (6)$$

$$T_c^E = 682 \cdot x_1 \cdot x_2^{1.007} + 712.5 \cdot x_2 \cdot x_3^{0.999} + 729 \cdot x_3 \cdot x_1 + 5 \cdot x_1 \cdot x_2 \cdot x_3 \quad (7)$$

The subscripts, 2 and 3 indicate HFC-32, HFC-125 and HFC-134a, and x_i indicates the mole fraction of i component. These correlations represent the critical pressures of Nagel and Bier[5] with a standard deviation of 0.12%, and a maximum deviation of -0.31%; critical densities of Higashi et al.[4] and Nagel and Bier[5] with standard deviations of 2.00% and 0.23%, and maximum deviations of 2.83% and -0.41%; critical temperatures of Higashi et al.[4] and Nagel and Bier[5] with standard deviations of 0.058% and 0.033%, and maximum deviations of 0.13% and -0.069%, respectively.

EQUATION OF STATE FOR MIXTURE

There are 15 reports[6-20] reporting more than 5000 *PVT*x measurements, which covers comprehensive compositions, pressures and temperatures range. Figure 1 shows the distribution of the available *PVT*x measurements for all of different compositions.

There are 10 reports[7,9,12-13,16,18-22] available which reported more than 1400 points VLE data. Regarding the derived properties, Magee[23] reported 131 points of *C*v data for HFC-32/134a@30/70 wt%, and Nakamura[24] reported 6 points of *C*v for different compositions, in compressed liquid phase. Hozumi et al.[25] reported 530 points of speed of sound in superheated gaseous phase, for various compositions.

Based on these reported thermodynamic properties, an equation of state for this mixture was developed. The thermodynamic properties of the mixture is given by the following equation of state:

$$P_r = x_1 \cdot P_{r1} + x_2 \cdot P_{r2} + x_3 \cdot P_{r3} + k_{mix} \cdot P_r^E \quad (8)$$

where $P_r = P/P_{cm}$, $\rho_r = \rho/\rho_{cm}$, $T_r = T/T_{cm}$. P_{r1}, P_{r2} and P_{r3} are the equation of state for pure fluids, Eq.(1), and $k_{mix} \cdot P_r^E$ is the residual part from the ideal mixing. P_r^E is an equation for the residual part. A new mixing rule k_{mix} for this mixture was proposed as follows:

$$k_{mix} = d_{12} \cdot x_1 \cdot x_2^{1.10} + d_{23} \cdot x_2 \cdot x_3 + d_{31} \cdot x_3 \cdot x_1^{1.10} + d_{123} \cdot x_1^{0.9} \cdot x_2^{1.2} \cdot x_3^{0.6} \quad (9)$$

$$d_{12} = 0.247470 + 1.47647\rho_r - 2.16869\rho_r^2 + 1.77969\rho_r^3 - 0.465584\rho_r^4$$

$$d_{23} = 0.107712 + 0.271327\rho_r - 0.593654\rho_r^2 + 0.418627\rho_r^3 - 0.0383766\rho_r^4$$

$$d_{31} = 0.286548 + 1.95888\rho_r - 2.19654\rho_r^2 + 2.08583\rho_r^3 - 0.635465\rho_r^4$$

$$d_{123} = -0.05$$

The equation of state for the residual part is given as:

$$P_r^E = E_1 \cdot \rho_r^2 + E_2 \cdot \rho_r^3 + E_3 \cdot \rho_r^4 + E_4 \cdot \rho_r^5 + E_5 \cdot \rho_r^6 + E_6 \cdot \rho_r^7 + E_7 \cdot \rho_r^8 \quad (10)$$

where

$E_1 = e_1 \cdot T_r^2 + e_2 + e_3/T_r^2 + e_4/T_r^3$

$E_2 = e_5 \cdot T_r^2 + e_6 + e_7/T_r^3$

$E_3 = e_8 \cdot T_r^2 + e_9/T_r + e_{10}/T_r^2$

$E_4 = e_{11} \cdot T_r^2 + e_{12}/T_r + e_{13}/T_r^2$

$E_5 = e_{14} + e_{15}/T_r + e_{16}/T_r^2$

$E_6 = e_{17} + e_{18}/T_r + e_{19}/T_r^2$

$E_7 = e_{20}/T_r^2$

$P_r^E = P^E/P_{cm}$, $\rho_r = \rho/\rho_{cm}$, $T_r = T/T_{cm}$

Table 1. Coefficients of Eq.(10)

i	e_i	i	e_i
1	-8.38590513903	11	-0.925158415527
2	22.6414027058	12	12.1455193420
3	-10.9061853330	13	-28.8129287538
4	2.68881393381	14	3.20170773648
5	10.8254585604	15	-8.69391897029
6	-25.9383399640	16	12.7401947550
7	-2.01463864000	17	-0.659998176269
8	-1.33726095393	18	1.42317484331
9	-2.22827937095	19	-2.28049865531
10	27.0080950488	20	0.123216354628

The coefficients of Eq.(10) are listed in Table 1. Figure 2 shows the behavior of the mixing rule k_{mix} at $\rho_r = 1$. HFC-32/134a pair shows a major mixing effect, and HFC-

125/134a shows a minor one. The mixing effect over all composition performs a smooth surface.

To avoid complexity, for the two phase region, we selected the Peng-Robinson equation of state[26] to represent the VLE, just to give the *P*-*T*-x-y relationship. The mixing rule for the Peng-Robinson equation[26] is given as:

$$(a\acute{a})_m = x_1^2\cdot(a\acute{a})_1 + x_2^2\cdot(a\acute{a})_2 + x_3^2\cdot(a\acute{a})_3 + 2\cdot(1 - k_{12})\cdot x_1\cdot x_2\cdot[(a\acute{a})_1\cdot(a\acute{a})_2]^{0.5} + 2\cdot(1 - k_{13})\cdot x_1\cdot x_3\cdot[(a\acute{a})_1\cdot(a\acute{a})_3]^{0.5} + 2\cdot(1 - k_{23})\cdot x_1\cdot x_2\cdot[(a\acute{a})_2\,(a\acute{a})_3]^{0.5} + 3\cdot k_{123}\cdot x_1\cdot x_2\cdot x_3\cdot[(a\acute{a})_1\cdot(a\acute{a})_2\cdot(a\acute{a})_3]^{1/3} \quad (11)$$

and

$$k_{12} = 1.00000 - 0.00004\cdot(T - 273.15) \quad (12)$$

$$k_{13} = 1.00000 + 0.00003\cdot(T - 273.15) \quad (13)$$

$$k_{23} = 0.99750 - 0.00009\cdot(T - 273.15) \quad (14)$$

$$k_{123} = 0.00000 - 0.00013\cdot(T - 273.15) \quad (15)$$

k_{12}, k_{13}, k_{23}, and k_{123} are the mixing parameters for HFC-32/125, -32/134a, -125/134a binary mixtures, and HFC-32/125/134a ternary mixture. These parameters, which depend on the temperature, though their influence is very small, were determined from the available VLE data[7,9,12-13,16,18-22].

The adopted ideal gas heat capacities are the correlations reported by McLinden et al.[27] for HFC-134a, Hozumi et al.[28] for HFC-32 and HFC-125, respectively. By using the above equations and correlations, we can calculate the thermodynamic properties of HFC-32/125, HFC-32/HFC-134a binary, and HFC-32/125/134a ternary mixtures.

DISCUSSION

Figures 3-6 show the comparisons of the *PVT*x data and the present equation of state for HFC-32/125, HFC-32/134a and HFC-125/134a binary mixtures, and HFC-32/125/134a ternary mixture. The present equation of state represents most of the *PVT*x ±0.5-1.0% in pressure/density deviations for superheated gaseous and compressed liquid phases, respectively. Some of the measurements exceed ±1.0%, and it is considered to be the

uncertainty of the measurements itself.

On the other hand, as shown in Figs. 7-8, the bubble/dew-point pressure measurements show a rather large scattering compared to the case of *PVT*x measurements.

The present mixing rule for Peng-Robinson equation[26] represents almost all of the measurements within ±1.0-2.0%. But still some of the measurements exceed ±2.0 %.

Figure 9 shows the comparison of the present equation of state with *C*v data. The presents equation of state for mixture represents the *C*v data by Magee[23] with a standard deviation of 0.74% and a maximum deviation of 1.78%, and by Nakamura et al.[24] with a standard deviation of 1.14% and a maximum deviation of -3.25%. Meanwhile, as shown in Fig. 10, the present equation of state also represents the speed of sound data by Hozumi et al.[25] with a standard deviation of 0.036%, and a maximum deviation of -0.18%.

CONCLUSIONS

In this study, we have developed equations of state for the ternary mixture from the equations of state for the constituent refrigerants. The present equations of state are effective for VLE and superheated gaseous and compressed liquid phases, where the range of temperatures is from 200 K to 470 K, and pressures up to 20 MPa. The present equations are effective not only for the ternary mixture at different compositions but also for HFC-32/125, and HFC-32/134a , and even HFC-125/134a binary mixtures.

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