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THERMODYNAMIC PROPERTIES OF HFC-32/HFC-134a BINARY SYSTEM

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ABSTRACT

In this paper, we discussed the development of equation of state for a binary mixture refrigerant from the equations of state for both constituent refrigerants. We have developed 18-coefficient modified Benedict-Webb-Rubin equations of state for HFC-134a (1,1,1,2-tetrafluoroethane), HCFC-123 (1,1-dichloro-2,2,2-trifluoroethane), and HFC-32 (difluoromethane), respectively. The van der Waals mixing rule has been applied on the 2nd virial coefficients of the equations of state for HFC-32 and HFC-134a, and a linear mixing rule on the other coefficients. The equation of state for the refrigerant mixture represents all of the available *PVT*x measurements of HFC-32/HFC-134a at 20, 40, 60, and 80 wt% within ±0.5 % in pressure. For two phase region, the Peng-Robinson equation of state and the Hankinson-Brobst-Thomson equation optimized by Widiatmo et al.[1] are adopted in this study. The thermodynamic properties of HFC-32/HFC-134a in superheated vapor phase and two phase region at any composition could be calculated from the developed equations.

The thermodynamic property tables and pressure-enthalpy diagram for HFC-32/HFC-134a binary system with 30/70 wt% are also included in the present paper.

INTRODUCTION

HCFC-22 (chlorodifluoromethane) is one of the most important working fluids in the air-conditioning systems. But it is scheduled to be phased out before 2030 due to the possibility of ozone depletion and global warming effect, and the time limit for the phaseout seems to be forwarded. There is no single-component refrigerant to replace HCFC-22 at the moment, and some of the binary and/or ternary mixtures were proposed. HFC-32/HFC-134a binary system is considered as one of the most probable substances to replace HCFC-22. Both of HFC-32 and HFC-134a do not have chlorine atoms, so that the

ozone depletion potentials are being zero, and the global warming impact is also very small. The thermodynamic behaviors of HFC-32/HFC-134a (30/70 wt%) are very close to that of HCFC-22. These enchanting facts attracted us to focus on the present binary system.

EQUATIONS OF STATE FOR HFC-32 AND HFC-134a

The thermodynamic properties of HFC-32 and HFC-134a have been studied very much world widely. There exist more than 1000 and 3000 points of measured thermodynamic properties. The measurements include almost all of the thermodynamic properties and cover the entire fluid phase. Based on these reported measured data, the equations of state for HFC-32[2] and HFC-134a[3] have been developed by the present authors. These equations of state were developed in the same functional form, because then it becomes much easier to apply mixing rule on these equations. We do not repeat here the details of the developed equations[2,3] but those for HFC-32 and HFC-134a do have the same functional form as given below:

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

$$B_1 = a_1T_r + a_2 + a_3/T_r^2 + a_4/T_r^3 \qquad B_2 = a_5T_r + a_6 + a_7/T_r^2$$
$$B_3 = a_8 + a_9/T_r^2 \qquad B_4 = a_{10} + a_{11}/T_r$$
$$B_5 = a_{12} + a_{13}/T_r \qquad B_6 = a_{14}$$
$$B_7 = a_{15} + a_{16}/T_r \qquad B_8 = a_{17} + a_{18}/T_r$$

where $P_r = P/P_c$, $\varrho_r = \varrho/\varrho_c$, $T_r = T/T_c$, $Z_c = P_c/(R_xT_c\varrho_c)$, $R_x = R/m$; $R = 8.31451$ J/(mol·K). P_c, ϱ_c, T_c, and m are the critical parameters and the molar mass of each component. All of these coefficients and constants are given in Table 1.

Table 1. Coefficients and constants of Eq. (1)

j	d_j	e_j	HFC-32 a_{1j}	HFC-134a a_{2j}
1	2	-1	2.33772608838	1.7564525
2	2	0	-4.64281719812	-3.3927644
3	2	2	-4.21137704721	-3.3451825
4	2	3	-.00836050789868	-0.095376281
5	3	-1	0.954934626378	2.2228031
6	3	0	-1.60710890397	-5.3843708
7	3	2	6.6770586947	5.0859126
8	4	0	0.806243035324	3.3749875
9	4	2	-1.78495674349	-1.1563581
10	5	0	-0.488971055693	-1.4894909
11	5	1	-1.68915187685	-1.2820563
12	6	0	0.721720083656	0.69982128
13	6	1	0.546443281958	0.34208486
14	7	0	-0.179145208567	-0.098455731
15	3	0	0.0517502791964	2.1316985
16	3	1	-1.32319847945	-2.2697938
17	5	0	-0.436652505917	-2.3042055
18	5	1	0.218255184003	2.3040808
P_c [kPa]			5784	4063.5
ϱ_c [kg/m^3]			424	508
T_c [K]			351.255	374.27
m [kg/kmol]			52.024	102.032

The equation of state for HFC-32 represents almost all of the *PVT* data within ±0.5 % in pressure, and for HFC-134a also represents the *PVT* data within ±0.5 %. These equations of state also represent the vapor pressures, saturated vapor/ liquid densities, and heat capacities.

We compared the coefficients of two equations of state in Fig. 1. The numerical magnitude of each coefficient appeared in both equations is much the same as shown in Fig. 1. This fact suggests

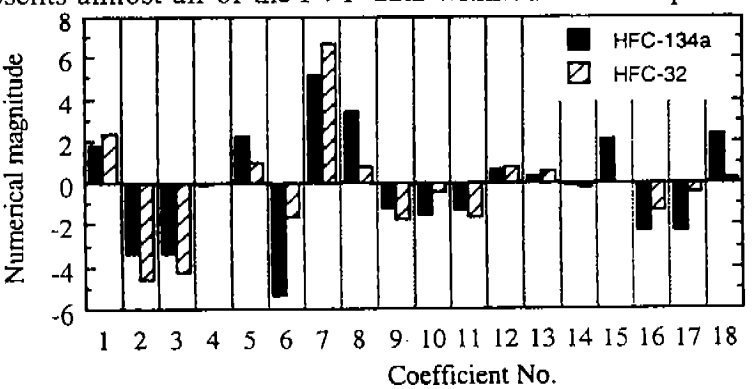

Fig. 1. Coefficients of equations for HFC-32 and HFC-134a

an applicability of the principle of corresponding states for the mixtures, since the results in Fig.1 imply the similarity in contribution of each corresponding term. By applying some kind of mixing rule, these equations of state could be used as the fundamental equations of state for binary mixture.

EQUATION OF STATE FOR MIXTURE

The available thermodynamic properties for HFC-32/HFC-134a binary mixture are very limited at the present. There is no equation of state for this binary system except some of the predicted ones. The experimental measurements are also very limited. Sato et al.[4] reported a very valuable set of *PVTx* data in the superheated vapor phase for four different compositions. Widiatmo et al.[1] reported 24 bubble point data at 20, 40, 60, and 80 wt% of HFC-32 with a Peng-Robinson equation of state for vapor-liquid-equilibrium (VLE) and a modified Hankinson-Brobst-Thomson equation of state for liquid densities. Fujiwara et al.[5] reported some VLE data. Defibaugh and Morrison[6] measured compressed liquid and saturated densities at 50 wt% of HFC-32, but their data are not available.

The critical locus of the binary mixture is essential so as to formulate the equation of state in dimensionless form. This is, however, not the case for the present mixture and therefore we have applied a following normalization to each coefficient, b_{ij}, with dimension in the present study:

$$b_{ij} = a_{ij} \cdot (T_c^{ej} / \varrho_c^{dj}) \cdot P_c; \quad i = 1, 2; \quad j = 1, 2, 3, \ldots \ldots, 18 \qquad (2)$$

where a_{ij} is the coefficient in Eq.(1), i denotes the pure refrigerant, j is the term number, d_j and e_j are the exponents of density and temperature in Eq.(1), as summarized in Table.1.

The following mixing rule was then applied to the second virial coefficients in accord with Eq.(1):

$$b_{mj} = x_1^2 \cdot b_{1j} + 2 \cdot (1-k_{12}) \cdot x_1 \cdot x_2 \cdot (b_{1j} \cdot b_{2j})^{0.5} + x_2^2 \cdot b_{2j}; \quad j = 1, 2, 3, 4 \qquad (3)$$

where x is the molar fraction, a subscript m indicates mixture, 1 and 2 indicate HFC-32 and HFC-134a, j = 1 to 4 indicate the number of coefficients, respectively. k_{12} in Eq.(3) is the mixing parameter for HFC-32/HFC-134a binary mixture, which was determined from the *PVT*x measurements[4] in superheated vapor phase by using the least square fittings:

$$k_{12} = 0.00148123 + 0.000332455 \cdot \varrho^{2.4} \qquad (4)$$

For the other coefficients when $j \geq 5$, the mixing rule is simply given as follows:

$$b_{mj} = x_1 \cdot b_{1j} + x_2 \cdot b_{2j}; \quad j = 5, 6, \ldots \ldots, 18 \qquad (5)$$

On the other hand, the Peng-Robinson equation of state[7], and the modified Hankinson-Brobst-Thomson equation[8, 9] by Widiatmo et al.[1] were selected to represent the VLE, and the saturated liquid densities which could not be reproduced by P-R equation[7].

Table 2. Constants for Eqs. (6)-(9)

	HFC-32	HFC-134a
ω_i	0.271	0.344
V^*_i [cm³/mol]	117.3	119.1

The P-R equation[7] is given in Eq.(6) associated with the mixing rules given in Eq. (7).

$$P = R \cdot T/(V - b) - a \cdot \alpha/(V^2 + 2 \cdot b \cdot V - b^2) \qquad (6)$$

$$a = 0.45724 \cdot R \cdot T_c^2 / P_c, \qquad b = 0.07780 \cdot R \cdot T_c / P_c,$$
$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2$$

The mixing rule for Peng-Robinson equation is given as:

$$(a \cdot \alpha)_m = x_1^2 \cdot (a \cdot \alpha)_1 + 2 \cdot (1 - k_{12}) \cdot x_1 \cdot x_2 \cdot [(a \cdot \alpha)_1 \cdot (a \cdot \alpha)_2]^{0.5} + x_2^2 \cdot (a \cdot \alpha)_2 \qquad (7)$$
$$b_m = x_1 \cdot b_1 + x_2 \cdot b_2 \qquad \omega_m = x_1 \cdot \omega_1 + x_2 \cdot \omega_2$$

where $k_{12} = 0.002$ which was optimized by Widiatmo et al.[1] for this binary system.

The saturated liquid density was calculated from the following modified H-B-T equation[8, 9]:

$$V = V^* \cdot V_r^0 \cdot (1 - \omega_m \cdot V_r^\delta) \qquad (8)$$

$$V_r^0 = 1 + a \cdot \tau^{1/3} + b \cdot \tau^{2/3} + c \cdot \tau + d \cdot \tau^{4/3} \qquad V_r^\delta = (e + f \cdot T_r + g \cdot T_r^2 + h \cdot T_r^3)/(T_r - 1.00001)$$
$$a = -1.52816, \quad b = 1.43907, \quad c = -0.81446, \quad d = 0.190454,$$
$$e = -0.296123, \quad f = 0.386914, \quad g = -0.0427258, \quad h = -0.0480645$$
$$T_r = T/T_c, \qquad \tau = 1 - T_r$$

The mixing rule for H-B-T equation[1, 9] is given below:

$$T_{cm} = \{ x_1^2 \cdot (V^*_1 \cdot T_{c1}) + 2 \cdot (1 - k_{12}) \cdot x_1 \cdot x_2 \cdot [(V^*_1 \cdot T_{c1}) \cdot (V^*_2 \cdot T_{c2})]^{0.5} + x_2^2 \cdot (V^*_2 \cdot T_{c2}) \} / V^*_m \qquad (9)$$
$$V^*_m = \sum x_i \cdot V^*_i + 3 \cdot (\sum x_i \cdot V^{*2/3}_i) \cdot (\sum x_i \cdot V^{*1/3}_i)$$
$$\omega_m = x_1^2 \cdot \omega_1 + 2 \cdot (1 - l_{12}) \cdot x_1 \cdot x_2 \cdot (\omega_1 \cdot \omega_2)^{0.5} + x_2^2 \cdot \omega_2$$

where $k_{12} = 0.005$, and $l_{12} = 0$ were proposed by Widiatmo et al.[1] for this binary system. The other constants for Eqs.(6)-(9) are given in Table 2.

The adopted ideal gas heat capacity, which is needed when we calculate the derived properties, are the correlations reported by McLinden et al.[10]. By using the above equations and correlations, the thermodynamic properties of HFC-32/HFC-134a binary system could be calculated.

DISCUSSION

Figure 2 shows the comparison of the *PVT*x data by Sato et al.[4] and the present equation of state for mixture in superheated vapor phase. The present equation of state represents these measurements within ±0.5 % in pressure.

On the other hand, as shown in Fig. 3,

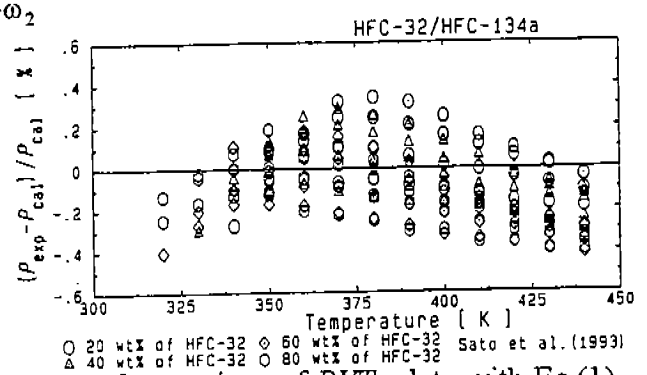

Fig. 2. Comparison of *PVT*x data with Eq.(1)

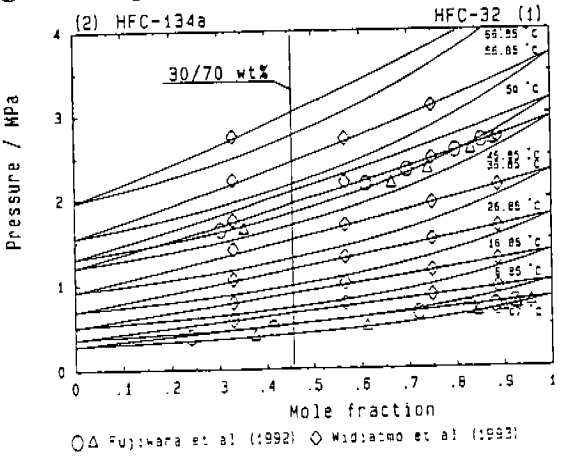

Fig. 3. Comparison of VLE data with E.(6)

Eq.(6) shows a good agreement with the VLE data by Widiatmo et al.[1], and Fujiwara et al.[5]. For the saturated liquid densities[1], as shown in Fig.4, Eq.(8) represents all of the measurements within ±0.5 %.

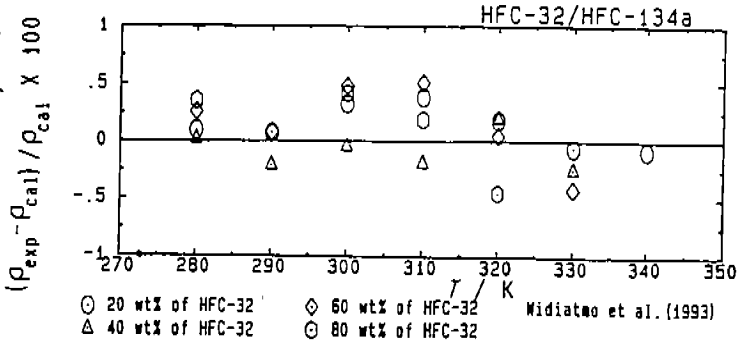

Fig. 4. Comparison of sat. liq. densities with Eq.(8)

THERMODYNAMIC PROPERTY TABLES AND CHARTS

The thermodynamic properties of HFC-32/134a binary mixture was calculated from above equations and correlations.

The saturated thermodynamic properties of 30 wt% of HFC-32 are given in Table 3. The pressure-enthalpy diagram for the blend with 30 wt% of HFC-32, the most important information for the engineering applications, is given in Fig. 5.

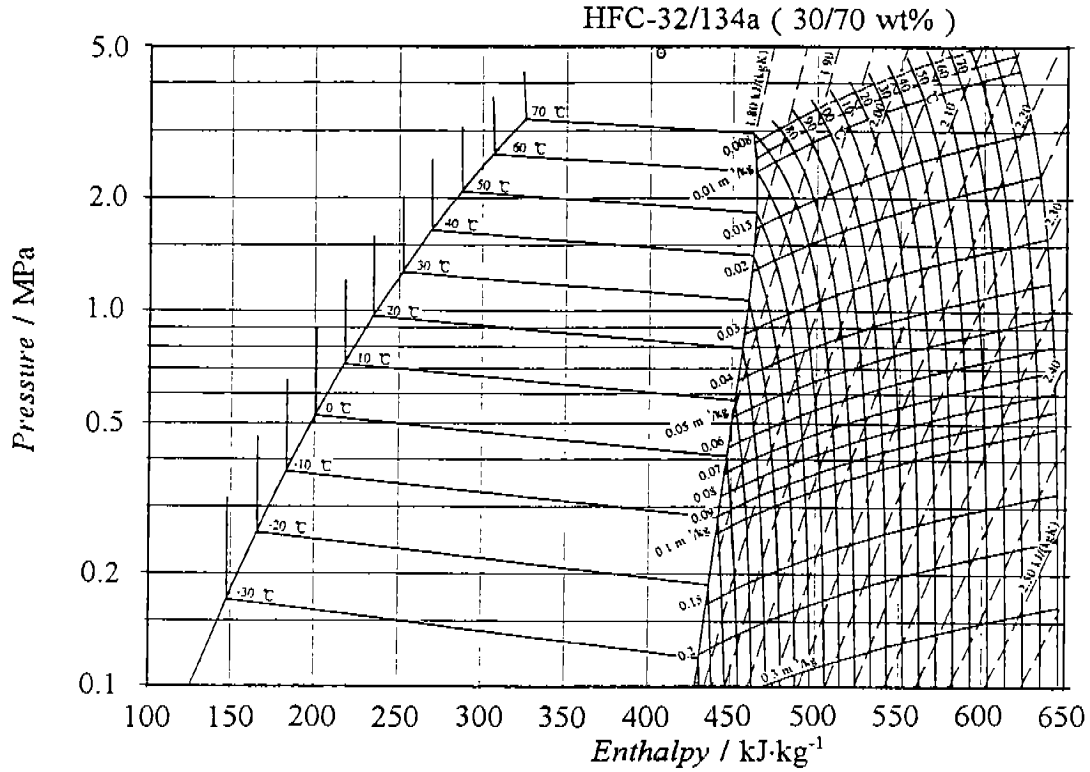

Fig. 5 Pressure-enthalpy diagram of HFC-32/134a (30/70 wt%) system

CONCLUSIONS

In this study, we discussed the development of equation of state for binary mixture from those for constituent refrigerants. We presented a promising possibility if the equations of state for pure fluids were developed purposely, although we still need to challenge to overcome existing difficulty in applying the equation to VLE. We do need much ample measured data, and some new mixing rules which will reproduce thermodynamic properties in the entire fluid phase.

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Table. 3 Saturation properties of HFC-32/134a (30/70 wt%) system

t °C	P kPa	ϱ kg/m³	C_p kJ/(kg·K)	C_v kJ/(kg·K)	w m/s	h kJ/kg	s kJ/(kg·K)	liquid vapor
-30	171.54	1305.03	1.4674	0.7435	1035.67	147.09	0.7959	l
	120.24	4.917	0.7841	0.6528	167.60	429.97	1.9660	v
-20	257.61	1274.40	1.4839	0.7726	950.06	165.07	0.8681	l
	187.80	7.497	0.8191	0.6770	168.78	435.78	1.9449	v
-10	373.93	1242.58	1.5041	0.7982	872.16	182.66	0.9358	l
	282.20	11.054	0.8589	0.7025	169.37	441.30	1.9264	v
0	526.87	1209.33	1.5286	0.8212	799.83	200.00	1.0000	l
	410.07	15.854	0.9045	0.7293	169.32	446.48	1.9099	v
10	723.29	1174.38	1.5582	0.8422	731.51	217.22	1.0613	l
	578.80	22.226	0.9576	0.7575	168.54	451.23	1.8948	v
20	970.42	1137.31	1.5945	0.8618	666.02	234.43	1.1202	l
	796.51	30.594	1.0209	0.7872	166.96	455.45	1.8806	v
30	1275.84	1097.58	1.6399	0.8804	602.43	251.75	1.1774	l
	1072.12	41.528	1.0987	0.8185	164.46	459.02	1.8667	v
40	1647.41	1054.37	1.6985	0.8986	539.95	269.30	1.2332	l
	1415.45	55.839	1.1986	0.8515	160.92	461.75	1.8524	v
50	2093.11	1006.40	1.7778	0.9169	477.85	287.23	1.2881	l
	1837.43	74.759	1.3358	0.8866	156.20	463.37	1.8371	v
60	2620.86	951.44	1.8924	0.9357	415.40	305.73	1.3428	l
	2350.48	100.330	1.5427	0.9241	150.17	463.47	1.8193	v
70	3237.77	884.91	2.0771	0.9558	351.71	325.10	1.3980	l
	2969.41	136.341	1.9020	0.9648	142.84	461.28	1.7972	v