HIGH PRESSURE VAPOR-LIQUID EQUILIBRIA FOR THE HFC125-HFC152a SYSTEM

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Abstract – We measured vapor-liquid equilibria (VLE) for the system of pentafluoroethane (HFC125)-difluoroethane (HFC152a) over the temperature range from 268.15 K to 373.15 K. Fitting VLE data obtained to an extended BWR equation of state, binary interaction parameters were correlated as a linear function of temperature. Applying the equation of state including the binary interaction parameters to refrigeration cycle, estimation of coefficient of performance (COP) revealed about 13.3 % energy-saving against chlorodifluoromethane (HCFC22), when the mole fraction of HFC125 is 0.44. As the condition of COP estimation, we assumed that temperature changes of out-side fluids were from 285.15 down to 280.15 K and 305.15 up to 310.15 K with 3 K in minimum temperature difference, respectively.

Key words: Fluorocarbon, HFC125, HFC152a, VLE, Equation of State, BWR Equation of State, Binary Interaction Parameter, Refrigeration, Coefficient of Performance, COP

INTRODUCTION

Although HCFC22 is popular as a refrigerant, it depletes the ozone-layer. As alternative refrigerants, fluorocarbon mixtures are expected to be excellent energy-saving ones. Our final goal is to find clean and energy-saving mixture refrigerants composed of fluorocarbons. We selected HFC152a as one of the alternatives that doesn't deplete the ozone-layer and is an excellent energy-saving refrigerant. However, it explodes. We expected that explosion will be to prevented by mixing HFC125 with it. We measured vapor-liquid equilibria for the HFC125-HFC152a system over the temperature range from 268.15 K to 373.15 K. Using the binary interaction parameters obtained from correlating VLE measurements, we tried to compare coefficient of performance (COP) between the system in this work and HCFC22.

EQUATION OF STATE

1. BWR Equation of State

Vapor-liquid equilibrium data were correlated with a following extended BWR equation of state with five polar parameters for polar contribution in addition to non-polar ones [Nishiumi et al., 1984],

$$P = \rho RT + \left\{ B_0 RT - (A_0 + \Psi_A) - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0 + \Psi_E}{T^4} \right\} \rho^2$$

$$+ \left(bRT - a - \frac{d}{T} - \frac{e}{T^4} - \frac{f}{T^{23}} \right) \rho^3$$

$$+ \alpha \left(a + \frac{d}{T} + \frac{e}{T^4} + \frac{f}{T^{23}} \right) \rho^6$$

$$+ \left(\frac{c}{T^2} + \frac{g}{T^8} + \frac{h}{T^{17}} + T\Psi_S \right) \rho^3 (1 + \gamma \rho^2) \exp(-\gamma \rho^2) \quad (1)$$

where

$$\Psi_S = S_3 + \frac{S_1}{T^{S_2}} \quad (2)$$

Fifteen generalized coefficients for non-polar contribution such as B_0, A_0 and C_0 are function of T_c, V_c and ω. Parameters for polar substances Ψ_E, Ψ_A, S_3 and S_1 are related to five reduced quantities Ψ_E^*, Ψ_A^*, s_3^*, s_1^* and s_2, as follows:

$$\Psi_E = \Psi_E^* RT_c^5 V_c$$

$$\Psi_A = \Psi_A^* RT_c \, V_c$$

$$s_3 = s_3^* RT_c^2$$

$$s_1 = s_1^* RT_c^{S_2} \, V_c^2 \quad (3)$$

Values of Ψ_E^* and Ψ_A^* are obtained from the second virial coefficient data. The other three polar parameters are obtained by fitting to vapor pressure data.

2. Mixing Rules

We employ the following mixing rules to systems containing polar substances [Nishiumi et al., 1984]. Comparison of the statistical mechanics with the second virial coefficient terms in Eq. (1) gives the following results, for example,

$$C_0 = \sum_{j=1}^{N} \sum_{i=1}^{N} x_i x_j C_{0ij} \quad (4)$$

where C_0 is a value for a mixture in Eq. (1), and x_i and x_j are mole fractions of components i and j, respectively. Assuming that the corresponding state principle can apply to binary interaction, we obtain,

$$C_{0ij} = (0.356306 + 1.7087\omega_{ij})RT_{cij} \, V_{cij} \quad (5)$$

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Similarly, B_{0ij}, A_{0ij}, D_{0ij} and E_{0ij} are function of T_{cij}, V_{cij} and ω_{ij}.
where

$$T_{cij} = m_{ij}\sqrt{T_{ci}T_{cj}} \qquad (6)$$

m_{ij} is called a binary interaction parameter between i and j. Usually, a value is obtained by fitting to VLE data, because

it is much sensitive to the choice of m_{ij} for systems composed of fluorocarbons.

EXPERIMENTAL APPARATUS
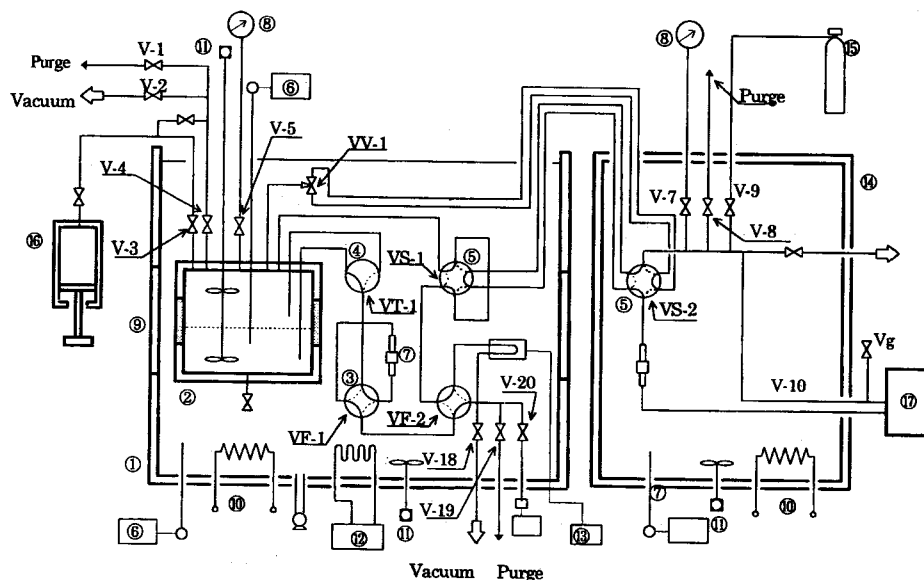
Figs. 1 and 2 show apparatuses for vapor-liquid equilibria

Fig. 1. Schematic diagram of experimental apparatus for low temperature.

① Constant temperture liquid bath
② Equilibrium cell
③ 4-way valve
④ 3-way valve
⑤ 6-way valve
⑥ Thermometer
⑦ Recirculation pump (Magnetic pump)
⑧ Pressure gage
⑨ Glass window
⑩ Heater
⑪ Fan
⑫ Handy cooler
⑬ Density meter
⑭ Constant temperature air bath
⑮ Helium bomb
⑯ Sample charging pump (Liquid injector)
⑰ GC

Fig. 2. Schematic diagram of experimental apparatus for high temperature.

① Glass window
② Block heaters
③ Insulated jacket
④ Platinum resistance element
⑤ Pressure gauge
⑥ Equilibrium cell
⑦ Liquid sample valve
⑧ Magnetic stirrer
⑨,⑩ Rotating magnet
⑪ Temperature controller
⑫ Sampling manifold
⑬ 6-way valve
⑭ Magnetic pump
⑮ 6-way valve
⑯ Heater
⑰ Propeller
⑱ Pressure gauge
⑲ Liquid injector
⑳ Sample cylinder

measurement in this work [Nishiumi et al., 1993], where the former is for low temperature measurement, and the latter for high. The analysis of the composition was carried out with gas-chromatograph. Accuracies of temperature are within 0.02 K for the lower temperature apparatus, and 0.05 K for the higher one. Both accuracies of pressure are within 0.2 %.

VAPOR PRESSURES OF COMPONENTS

Table 1 shows experimental vapor pressure data on both HFC125 and HFC152a, where open circles and squares are obtained by low temperature apparatus, and solid by high temperature one. Fitting to experimental data in Table 1, optimum polar parameters were determined and shown in Table 2 together with the critical properties for fluorocarbons.

Fig. 3 compares saturated vapor pressures of HFC125, HFC 152a and HCFC22. Using the obtained parameters and critical properties in extended BWR equation of state, we obtained excellent agreement about deviations between experimental vapor pressure data and estimated ones within 3 absolute average deviations.

VAPOR-LIQUID EQUILIBRIA

Fig. 4 shows VLE for the HFC125-HFC152a system ranging from 268.15 to 373.15 K in this work together with Table 3 of experimental data. We measured VLE at low tempera-

Table 1. Experimental vapor pressure data in this work

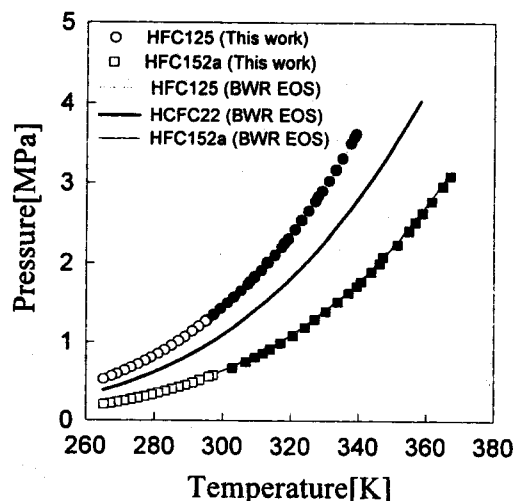| Temperature [K]	Vapor pressure [MPa]	Temperature [K]	Vapor pressure [MPa]
HFC125		HFC152a	
265.13	0.5207	265.18	0.1991
271.30	0.6325	267.13	0.2128
275.21	0.7159	271.17	0.2452
281.12	0.8532	275.10	0.2824
284.95	0.9571	277.11	0.3020
287.04	1.0170	281.10	0.3525
291.06	1.1386	285.13	0.3962
295.41	1.2778	287.13	0.4237
297.39	1.3449	291.11	0.4786
301.38	1.4934	295.84	0.5551
303.38	1.5704	297.16	0.5756
305.37	1.6497	302.86	0.6678
307.99	1.7670	306.76	0.7473
309.41	1.8541	311.77	0.8581
313.13	2.0070	317.04	0.9885
315.37	2.1021	320.63	1.0836
318.13	2.2570	324.19	1.1866
319.30	2.3021	330.34	1.4065
323.14	2.5360	337.02	1.6460
325.23	2.6494	340.70	1.7652
328.06	2.8330	346.23	1.9986
331.24	3.0241	351.48	2.2379
333.24	3.1654	356.73	2.5427
335.14	3.3110	361.54	2.8030
339.14	3.6120	367.02	3.1309

Fig. 3. Saturated vapor pressures of HFC125, HFC152a and HCFC22.

Table 2. Critical properties and polar parameters for fluorocarbons

Component	P_c [MPa]	T_c [K]	V_c [l/mol]	ω [-]
HFC125	3.16	339.40	0.2100	0.2770
HFC152^a	4.50	386.60	386.60	0.2660
Ψ_A^*	Ψ_E^*	s_3^*	s_1^*	s_2^*
-0.13	-0.0110	-0.0689	-0.0896	3.175
0.02	0.0317	-0.0051	0.0437	5.289

tures (268.15, 273.15, 293.15 K) with the apparatus in Fig. 1 and that at high temperatures (313.15, 323.15, 333.02, 348.15, 353.15, 363.15, 373.15 K) in Fig. 2. Interaction parameter m_{ij} obtained by fitting to these experimental VLE data shown in Fig. 5. The binary interaction parameters for the HFC125-HFC152a system, m_{ij}, were correlated as a linear function dependent on temperature in K, as follows.

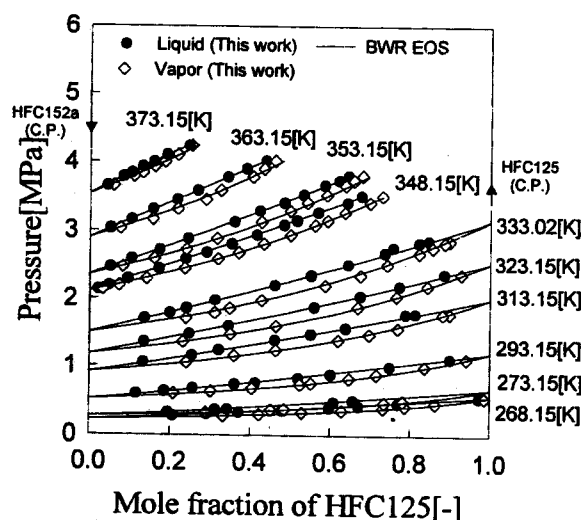$$m_{ij} = 1.030 - 0.8364 \times 10^{-4} \times T \tag{7}$$

Fig. 4. Comparison of VLE data on HFC125-HFC152a in this work with calculated values using a correlated function.

Table 3. Vapor-liquid equilibrium data for the system of HFC 125-HFC152a in this work

Mole fraction of HFC125 [-]		Pressure [MPa]
x	y	
T=268.15 [K]		
0.207	0.333	0.276
0.292	0.422	0.299
0.372	0.529	0.329
0.481	0.630	0.358
0.597	0.733	0.397
0.671	0.788	0.427
0.770	0.863	0.466
0.973	0.987	0.554
T=273.15 [K]		
0.195	0.289	0.324
0.313	0.452	0.368
0.343	0.486	0.378
0.609	0.735	0.476
0.658	0.781	0.500
T=293.15 [K]		
0.116	0.209	0.598
0.187	0.302	0.633
0.257	0.405	0.676
0.361	0.525	0.736
0.413	0.552	0.755
0.520	0.647	0.825
0.601	0.716	0.883
0.749	0.836	0.998
0.900	0.941	1.118
T=313.15 [K]		
0.133	0.240	1.052
0.254	0.359	1.155
0.321	0.463	1.239
0.461	0.619	1.388
0.551	0.697	1.476
0.638	0.768	1.569
0.788	0.881	1.775
0.812	0.898	1.785
T=323.15 [k]		
0.135	0.232	1.357
0.247	0.350	1.476
0.345	0.464	1.597
0.559	0.668	1.882
0.674	0.765	2.045
0.773	0.843	2.195
0.886	0.927	2.372
T=333.02 [K]		
0.136	0.239	1.710
0.199	0.310	1.790
0.240	0.348	1.860
0.311	0.427	1.980
0.460	0.586	2.200
0.551	0.674	2.350
0.643	0.741	2.510
0.735	0.821	2.680
0.756	0.855	2.760
0.821	0.886	2.830
0.845	0.898	2.860

Table 3. Continued

Mole fraction of HFC125 [-]		Pressure [MPa]
x	y	
T=348.15 [K]		
0.021	0.032	2.137
0.048	0.072	2.195
0.095	0.140	2.293
0.172	0.236	2.442
0.238	0.318	2.587
0.290	0.370	2.679
0.353	0.432	2.810
0.415	0.499	2.940
0.483	0.560	3.083
0.515	0.592	3.153
0.568	0.635	3.274
0.641	0.698	3.417
0.676	0.729	3.514
T=353.15 [K]		
0.051	0.081	2.469
0.103	0.159	2.590
0.173	0.239	2.725
0.243	0.315	2.884
0.359	0.426	3.127
0.422	0.498	3.292
0.483	0.541	3.414
0.531	0.589	3.529
0.584	0.636	3.667
0.621	0.657	3.737
0.643	0.679	3.807
T=363.15 [K]		
0.051	0.075	3.033
0.103	0.155	3.160
0.156	0.217	3.314
0.216	0.287	3.454
0.267	0.324	3.590
0.342	0.404	3.786
0.388	0.432	3.904
0.437	0.460	4.021
T=373.15 [K]		
0.043	0.058	3.657
0.083	0.108	3.788
0.103	0.130	3.842
0.130	0.160	3.933
0.158	0.185	4.002
0.190	0.217	4.102
0.245	0.252	4.237

The back-calculated values from the above correlation give excellent agreement with experimental data as shown in Fig. 4.

COP COMPARISON

As conditions of COP prediction, we assumed that temperature changes of out-side fluids were from 285.15 down to 280.15 K and 305.15 up to 310.15 K with each minimum 3 K difference for heat transfer. The values of COP are obtained from PVT, enthalpy and entropy calculations using the equation of state in this work.
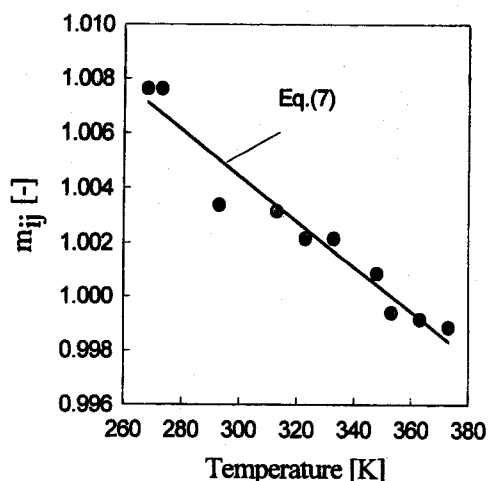
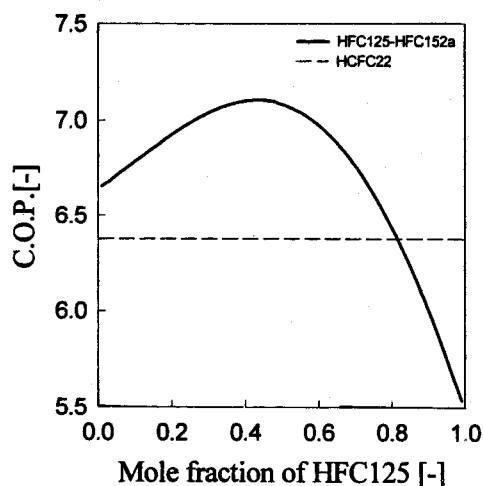Fig. 5. Binary interaction parameter for HFC125-HFC152a system.

Fig. 6. Comparison of COP for the HFC125-HFC152a system with one for HCFC22 from extended BWR equation of state with correlated binary interaction parameter.
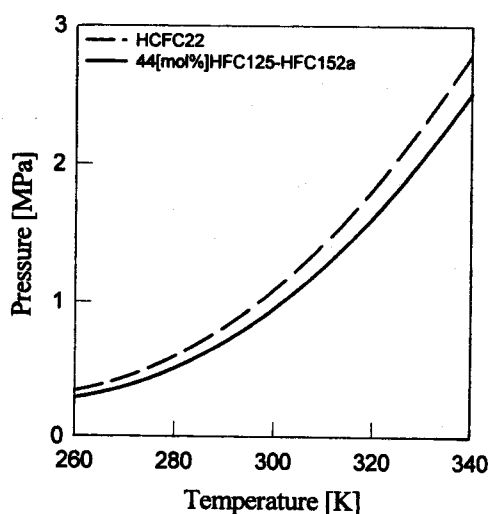

Fig. 7. Comparison of vapor pressure of HFC125-HFC152a system (mole fraction of HFC125 is 0.44) with that of HCFC22.

Fig. 6 shows that COP for the HFC125-HFC152a system using the equation of state using the correlated binary interaction parameters, Eq. (7).

We can find that COP for the HFC125-HFC152a system for mole fraction 0.44 of HFC125 will be about 13.3 % energy-saving against HCFC22 which is popular and effective as a refrigerant at present at the conditions mentioned. In addition, vapor pressure of the HFC125-HFC152a system is lower than that of HCFC22 shown in Fig. 7. In other words, the present heat pump apparatus is available for withstanding pressure.

Following are advantage points of the HFC125-HFC152a system against HCFC22, when mole fraction of HFC125 is 0.44.

(1) This mixture doesn't deplete the ozone-layer.
(2) This mixture isn't harmful.
(3) COP of this mixture is higher than that of HCFC22, revealed about 13.3 % energy-saving against HCFC22 under the mentioned above condition.
(4) The present heat pump apparatus is available for withstanding pressure.

However, we need further explosion experiments, because it is not certain whether this mixture is not flammable or not explosive.

CONCLUSIONS

Measuring vapor pressure of components, and VLE for the HFC125-HFC152a system, we can predict thermodynamic properties quantitatively using an extended BWR equation of state. From the standpoint of energy saving of heat pump system under the above mentioned, the equation of state predicts that the HFC125-HFC152a system will be an excellent mixture refrigerant which save energy 13.3 % in comparison with HCFC22, although we need further experiments whether it is flammable or explosive.

ACKNOWLEDGMENT

NOMENCLATURE

A_0, B_0, C_0, D_0, E_0, a, b, c, d, e, f, g, h, α, γ : fifteen reduced
    constants for non-polar parameters contribution in Eq. (1) [-]
Ψ_A, Ψ_E : polar parameters in second virial coefficient contribution
    in Eq. (1) [-]
Ψ_s : quantity related to polar contribution defined by Eq. (2)
    [-]
s_1, s_2, s_3 : polar parameters defined by Eq. (2) [-]
s_1^*, s_3^* : reduced polar parameters defined by Eq. (3) [-]
B   : second virial coefficient [cm^3/mol]
m_{ij} : binary interaction parameter [-]
P   : pressure [MPa]
P_c : critical pressure [MPa]
v_c : volume [mol/l]
T   : temperature [K]

T_c : critical temperature [K]
ρ : density [mol/cm^3]
R   : gas constant [J/molK]
ω : Pitzer's acentric factor [-]
x   : liquid mole fraction [-]

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