PVTx Properties in the Gas Phase for Binary R-125/143a System

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Abstract

The mixture of pentafluoroethane (R-125) and 1,1,1-trifluoroethane (R-143a) is a promising alternative for the conventional refrigerant R-502. In this paper, we present 220 *PVTx* property measurements of this binary system along four isoplethes in the gas phase which were performed by an established Burnett apparatus. The uncertainties in the present measurement were estimated to be within ±8 mK for temperature, ±0.8 kPa for pressure, ±0.15% for density, and ±0.1 mol % for composition, respectively. On the basis of the present *PVTx* property measurements, which lie in the range of temperatures from 310 K to 380 K, pressures up to 4.8 MPa, densities from 0.04 mol·dm^{-3} to 2.5 mol·dm^{-3}, and compositions from 0.27 to 0.74 mole fraction of R-125, a truncated virial equations of state with an accuracy of ±0.2% in pressure was developed for the binary R-125/143a system using the well-known mixing rule for the virial coefficients in terms of the statistical thermodynamics. The temperature dependence of the second virial coefficients including the cross-second virial coefficients for this system is also discussed.

Keywords: Burnnet measurement; Equation of state; Mixture; PVTx properties; R-125/143a.

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1. Introduction

The mixture of pentafluoroethane (R-125) and 1,1,1-trifluoroethane (R-143a) is an azeotropic refrigerant with refrigeration characteristics similar to R-502. Concerning its thermodynamic properties, however, few measurements [1] have been reported. More experimental data are needed in an extensive range to reveal the *PVTx* properties of R-125/143a system.

In this paper, the authors present new gas-phase *PVTx* measurements along four isoplethes of R-125/143a system which were performed by the Burnett method. On the basis of the present measurements, a truncated virial equations of state for this binary system is then developed by applying the conventional mixing rules in terms of the statistical thermodynamics. The temperature dependence of the second virial coefficients for R-125/143a system will also be discussed.

2. Experimentation and Results

The *PVTx* measurements for R-125/143a system were performed by a Burnett apparatus, which has already been described in details in our previous paper [2].The Burnett isothermal expansions were only done at 380 K and the measurements at other temperatures were obtained by combining the isochoric method. By using this procedure, the *PVTx* properties were able to be obtained over a wide range in the gas phase with a single filling of the sample. A total of 220 *PVTx* measurements (including some data in the two-phase region) were obtained along four independent isoplethes 0.2733 (34.94 mass %), 0.4118 (50.00 mass %), 0.5652 (64.99 mass %), and 0.7370 (80.01 mass %) mole fractions of R-125. They are given in Table 1.

The uncertainty in temperature measurements was estimated to be ±8 mK: the

sum of ±2 mK for the uncertainty of the platinum resistance thermometer, ±1 mK for the uncertainty of the thermometer bridge, and ±5 mK for the possible temperature fluctuation of the thermostated bath. The experimental uncertainty in pressure measurements was estimated to be ±0.8 kPa, which consists of the reproducibility of the differential pressure measurements, ±0.6 kPa, and the accuracy of the pressure gauge, ±0.2 kPa. The uncertainty in density values was estimated to be ±0.15%. Considering all the possible effects on the composition determination, the uncertainty of the sample compositions determined in the present measurements was estimated to be ±0.1 mol %. According to the analysis performed by the chemical manufacturers, the purities of R-125 and R-143a samples used to blend the R-125/143a mixtures were 99.99 mol % and 99.999 mol %, respectively.

3. Development of Virial Equation of State for R-125/143a System

To represent the experimental *PVTx* data in the gas phase of R-125/143a system, a truncated virial equation of state was developed in terms of the statistical thermodynamics. The developed virial equation of state consists of three virial terms:

$$Z = 1 + B_{\mathrm{m}}\rho + C_{\mathrm{m}}\rho^{2} + D_{\mathrm{m}}\rho^{3} \tag{1}$$

B_{m} and C_{m} in Eq. (1) are calculated with the conventional mixing rules:

$$B_{\mathrm{m}} = \sum_{i=1}^{2}\sum_{j=1}^{2} x_i x_j B_{ij} \tag{2}$$

$$C_{\mathrm{m}} = \sum_{i=1}^{2}\sum_{j=1}^{2}\sum_{k=1}^{2} x_i x_j x_k C_{ijk} \tag{3}$$

Since the contribution of D_{m} to the results is quite small, the simple mole-fraction average method is applied for D_{m}:

$$D_{\mathrm{m}} = \sum_{i=1}^{2} x_i D_i \tag{4}$$

B_{ij} in Eq. (2), C_{ijk} in Eq. (3), and D_i in Eq. (4) are expressed as follows:

$$B_{11} = B_1 = b_1 + b_2 T_{\mathrm{r},1}^{-1} + b_3 \exp(T_{\mathrm{r},1}^{-1}) \tag{5}$$

$$B_{22} = B_2 = b_4 + b_5 T_{\mathrm{r},1}^{-1} + b_6 \exp(T_{\mathrm{r},2}^{-1}) \tag{6}$$

$$B_{12} = B_{21} = b_7 + b_8 T_{\mathrm{r},12}^{-1} + b_9 \exp(T_{\mathrm{r},12}^{-1}) \tag{7}$$

$$C_{111} = C_1 = c_1 + c_2 T_{\mathrm{r},1}^{-3} + c_3 T_{\mathrm{r},1}^{-13} \tag{8}$$

$$C_{222} = C_2 = c_4 + c_5 T_{\mathrm{r},2}^{-5} + c_6 T_{\mathrm{r},2}^{-12} \tag{9}$$

$$C_{112} = C_{211} = C_{121} = c_7 + c_8 T_{\mathrm{r},112}^{-5} + c_9 T_{\mathrm{r},112}^{-7} \tag{10}$$

$$C_{221} = C_{122} = C_{212} = c_{10} + c_{11} T_{\mathrm{r},221}^{-5} + c_{12} T_{\mathrm{r},221}^{-6} \tag{11}$$

$$D_1 = d_1 T_{\mathrm{r},1}^{-3} \tag{12}$$

$$D_2 = d_2 T_{\mathrm{r},2}^{-3} \tag{13}$$

and

$$T_{\mathrm{r},i} = T / T_{\mathrm{c},i} \tag{14}$$

$$T_{\mathrm{r},ij} = T / T_{\mathrm{c},ij} \tag{15}$$

$$T_{\mathrm{r},ijk} = T / T_{\mathrm{c},ijk} \tag{16}$$

with

$$T_{\mathrm{c},ij} = (T_{\mathrm{c},i} T_{\mathrm{c},j})^{\frac{1}{2}} \tag{17}$$

$$T_{\mathrm{c},ijk} = (T_{\mathrm{c},i} T_{\mathrm{c},j} T_{\mathrm{c},k})^{\frac{1}{3}} \tag{18}$$

where the critical temperatures, $T_{\mathrm{c},1}$ =339.165 K for R-125 and $T_{\mathrm{c},2}$ = 345.88 K for R-143a, were reported by Kuwabara et al. [3] and Higashi and Ikeda [4], respectively.

Note that $T_{c,ij}$ and $T_{c,ijk}$ are not real critical temperatures but parameters used in the present model. On the basis of the developed virial equations of state for pure R-125 and R-143a [5], the numerical coefficients in the present model were found by fitting the *PVTx* data given in Table 1. The numerical coefficients including those for pure components in the present model are tabulated in Table 2.

4. Discussion

For the pure R-143a and R-125, experimental *PVT* data in the gas phase were reproduced by the present model within ±0.15% in pressure [5]. For R-125/143a mixtures, deviations of the experimental *PVTx* data from the present model are shown in Fig. 1. It is apparent that the present model represents accurately the data by the present study within ±0.2% in pressure. Although the data by Weber and Defibaugh [1] and those by Magee [6] were not used as input data, their deviations from the present model are also illustrated in Fig. 1. The data by Weber and Defibaugh show increasing positive deviation with increasing density and the maximum deviation is about +0.42%. The data by Magee are in good agreement within ±0.2% in pressure with the present model. Although the data by Weber and Defibaugh [1] and those by Magee [6] are almost at the same composition (0.5 mole fraction of R-125), the data by Weber and Defibaugh exhibit a slightly different behavior from those by Magee as well as by the present study.

According to the above discussion, it can be said that the present measurements are self-consistent and in good agreement with the reported measurements. The present model reproduces the experimental data by the present study and Magee [6] within ±0.2% in pressure for temperatures from 300 to 400 K and at pressures up to 5 MPa.

The temperature dependence of the second virial coefficients for pure components and of the cross-second virial coefficients for R-125/143a system described by the present model is shown in Fig. 2. It is apparent that the second virial coefficients of R-125 and R-143a by Zhang et al. [7] are represented very well by the present model. In addition, it is interesting to note that the curve of the second virial coefficients calculated at 0.5 mole fraction of R-125 is very close to the curve of the cross-virial coefficients B_{12} at higher temperatures.

5. Conclusion

The *PVTx* properties in the gas phase for the binary R-125/R-143a system have been measured using the Burnett apparatus. A total of 220 *PVTx* properties were obtained along four isoplethes 0.2733, 0.4118, 0.5652, and 0.7370 mole fractions of R-125.

By using these experimental values, a virial equation of state for R-125/143a system has been developed. The developed model represents the experimental gas-phase *PVTx* data within ±0.2% in pressure for the range of temperatures from 300 to 400 K and pressures up to about 5.0 MPa. The present model for R-125/143a system is valid for the entire range of compositions.

6. List of Symbols

B	Second virial coefficient
C	Third virial coefficient
D	Forth virial coefficient
R	Universal gas constant

T	Temperature
T_r	Reduced temperature
x	Mole fraction
Z	Compressed factor
r	Density

Subscripts

c	Critical point
i	i-th component in a mixture
j	j-th component in a mixture
k	k-th component in a mixture
m	Mixture

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Table 1. Experimental *PVTx* properties of R-125 /143a system

T/K	*P*/kPa	ρ /mol·dm^{-3}	x_1*	*T*/K	*P*/kPa	ρ /mol·dm^{-3}	x_1*
380.000	4763.4	2.5254	0.2733	320.000	369.9	0.1462	0.2733
365.000	4237.8	2.5273	0.2733	305.000	350.2	0.1463	0.2733
350.000	3691.4	2.5292	0.2733	380.000	300.0	0.09699	0.2733
340.000	3313.7	2.5304	0.2733	380.000	201.0	0.06453	0.2733
330.000	2718.7	2.5317[a]	0.2733	380.000	134.4	0.04293	0.2733
320.000	2171.9	2.5329[a]	0.2733				
310.000	1716.6	2.5341[a]	0.2733	390.000	4691.6	2.1813	0.4118
380.000	3722.6	1.6803	0.2733	380.000	4408.8	2.1824	0.4118
365.000	3410.9	1.6816	0.2733	365.000	3969.7	2.1840	0.4118
350.000	3089.2	1.6828	0.2733	350.000	3515.9	2.1857	0.4118
335.000	2753.8	1.6840	0.2733	340.000	3199.9	2.1867	0.4118
325.000	2235.9	1.6848[a]	0.2733	330.000	2743.7	2.1878[a]	0.4118
380.000	2780.0	1.1180	0.2733	320.000	2192.8	2.1888[a]	0.4118
365.000	2593.8	1.1188	0.2733	310.000	1728.7	2.1899[a]	0.4118
350.000	2401.1	1.1196	0.2733	300.000	1339.0	2.1909[a]	0.4118
335.000	2202.9	1.1205	0.2733	380.000	3381.0	1.4521	0.4118
320.000	1995.1	1.1213	0.2733	365.000	3119.7	1.4532	0.4118
380.000	2002.0	0.7439	0.2733	350.000	2852.9	1.4542	0.4118
365.000	1888.5	0.7445	0.2733	335.000	2575.2	1.4553	0.4118
350.000	1771.6	0.7450	0.2733	325.000	2378.5	1.4560	0.4118
335.000	1651.5	0.7455	0.2733	380.000	2488.5	0.9662	0.4118
320.000	1528.6	0.7461	0.2733	365.000	2331.7	0.9669	0.4118
305.000	1398.6	0.7466	0.2733	350.000	2170.3	0.9676	0.4118
380.000	1404.9	0.4949	0.2733	335.000	2005.4	0.9683	0.4118
365.000	1334.2	0.4953	0.2733	320.000	1832.8	0.9690	0.4118
350.000	1261.8	0.4956	0.2733	310.000	1711.1	0.9695	0.4118
335.000	1188.0	0.4960	0.2733	380.000	1771.9	0.6428	0.4118
320.000	1112.7	0.4963	0.2733	365.000	1674.7	0.6433	0.4118
305.000	1034.6	0.4967	0.2733	350.000	1577.3	0.6437	0.4118
380.000	968.7	0.3293	0.2733	335.000	1476.5	0.6442	0.4118
365.000	924.1	0.3295	0.2733	320.000	1373.1	0.6447	0.4118
350.000	878.5	0.3298	0.2733	305.000	1265.6	0.6451	0.4118
335.000	832.2	0.3300	0.2733	380.000	1233.7	0.4277	0.4118
320.000	784.5	0.3303	0.2733	365.000	1173.7	0.4280	0.4118
305.000	736.9	0.3305	0.2733	350.000	1112.8	0.4283	0.4118
380.000	660.1	0.2191	0.2733	335.000	1050.4	0.4286	0.4118
365.000	630.8	0.2193	0.2733	320.000	986.6	0.4289	0.4118
350.000	602.3	0.2194	0.2733	305.000	920.9	0.4292	0.4118
335.000	572.3	0.2196	0.2733	380.000	846.2	0.2846	0.4118
320.000	542.8	0.2197	0.2733	365.000	807.8	0.2848	0.4118
305.000	511.5	0.2199	0.2733	350.000	769.3	0.2850	0.4118
380.000	446.2	0.1458	0.2733	335.000	730.2	0.2852	0.4118
365.000	427.8	0.1459	0.2733	320.000	690.0	0.2854	0.4118
350.000	408.9	0.1460	0.2733	305.000	649.2	0.2856	0.4118
335.000	389.7	0.1461	0.2733	380.000	574.6	0.1893	0.4118

Table 1. (continued)

T/K	P/kPa	r /mol·dm^{-3}	x_1*	T/K	P/kPa	r /mol·dm^{-3}	x_1*
365.000	549.8	0.1894	0.4118	320.000	1364.9	0.6372	0.5652
350.000	524.9	0.1896	0.4118	305.000	1258.7	0.6377	0.5652
365.000	549.8	0.1894	0.4118	380.000	1222.7	0.4227	0.5652
350.000	524.9	0.1896	0.4118	365.000	1163.6	0.4230	0.5652
335.000	499.9	0.1897	0.4118	350.000	1103.1	0.4233	0.5652
320.000	474.1	0.1898	0.4118	335.000	1041.5	0.4236	0.5652
305.000	448.4	0.1900	0.4118	320.000	978.7	0.4239	0.5652
380.000	387.5	0.1260	0.4118	305.000	914.1	0.4242	0.5652
365.000	371.8	0.1261	0.4118	380.000	837.9	0.2813	0.5652
350.000	355.4	0.1262	0.4118	365.000	800.2	0.2815	0.5652
335.000	339.1	0.1263	0.4118	350.000	761.8	0.2817	0.5652
320.000	322.3	0.1264	0.4118	335.000	722.9	0.2819	0.5652
305.000	305.7	0.1265	0.4118	320.000	683.4	0.2821	0.5652
380.000	260.1	0.08382	0.4118	305.000	643.3	0.2823	0.5652
365.000	249.6	0.08388	0.4118	380.000	568.6	0.1871	0.5652
350.000	239.2	0.08394	0.4118	365.000	544.3	0.1872	0.5652
335.000	228.5	0.08400	0.4118	350.000	519.5	0.1874	0.5652
320.000	217.7	0.08406	0.4118	335.000	494.5	0.1875	0.5652
305.000	206.6	0.08412	0.4118	320.000	469.2	0.1876	0.5652
380.000	174.1	0.05577	0.4118	305.000	443.7	0.1878	0.5652
380.000	116.3	0.03710	0.4118	380.000	383.3	0.1245	0.5652
				365.000	367.3	0.1246	0.5652
380.000	4406.1	2.1571	0.5652	350.000	351.3	0.1247	0.5652
365.000	3973.5	2.1587	0.5652	335.000	335.0	0.1248	0.5652
350.000	3522.6	2.1603	0.5652	320.000	318.7	0.1249	0.5652
340.000	3211.6	2.1614	0.5652	305.000	302.3	0.1249	0.5652
330.000	2779.9	2.1624[a]	0.5652	380.000	257.3	0.08284	0.5652
320.000	2217.5	2.1635[a]	0.5652	365.000	247.2	0.08290	0.5652
310.000	1747.5	2.1645[a]	0.5652	350.000	236.4	0.08296	0.5652
300.000	1354.9	2.1655[a]	0.5652	335.000	225.6	0.08302	0.5652
380.000	3371.7	1.4352	0.5652	320.000	214.9	0.08308	0.5652
365.000	3114.6	1.4363	0.5652	305.000	204.6	0.08314	0.5652
350.000	2849.6	1.4373	0.5652	380.000	172.2	0.05512	0.5652
335.000	2573.5	1.4384	0.5652	380.000	115.0	0.03667	0.5652
325.000	2380.6	1.4391	0.5652				
380.000	2472.9	0.9549	0.5652	380.000	4185.5	1.9614	0.7370
365.000	2318.6	0.9556	0.5652	365.000	3797.6	1.9629	0.7370
350.000	2160.2	0.9563	0.5652	350.000	3404.3	1.9643	0.7370
335.000	1996.3	0.9570	0.5652	335.000	2983.4	1.9657	0.7370
320.000	1826.3	0.9577	0.5652	325.000	2540.6	1.9667[a]	0.7370
310.000	1707.5	0.9581	0.5652	315.000	2015.1	1.9677[a]	0.7370
380.000	1757.9	0.6354	0.5652	380.000	3160.8	1.3050	0.7370
365.000	1663.0	0.6359	0.5652	365.000	2932.6	1.3060	0.7370
350.000	1566.0	0.6363	0.5652	350.000	2698.0	1.3069	0.7370
335.000	1466.8	0.6368	0.5652	335.000	2455.4	1.3079	0.7370

Table 1. (continued)

T/K	P/kPa	r /mol·dm^{-3}	x_1*	T/K	P/kPa	r /mol·dm^{-3}	x_1*
320.000	2198.2	1.3088	0.7370	380.000	519.0	0.1702	0.7370
380.000	2293.1	0.8683	0.7370	365.000	496.9	0.1703	0.7370
365.000	2157.1	0.8689	0.7370	350.000	474.8	0.1704	0.7370
350.000	2016.7	0.8696	0.7370	335.000	452.7	0.1706	0.7370
335.000	1870.0	0.8702	0.7370	320.000	429.7	0.1707	0.7370
320.000	1721.3	0.8708	0.7370	305.000	406.1	0.1708	0.7370
305.000	1565.2	0.8714	0.7370	380.000	349.3	0.1132	0.7370
380.000	1618.0	0.5777	0.7370	365.000	334.9	0.1133	0.7370
365.000	1533.9	0.5781	0.7370	350.000	320.7	0.1134	0.7370
350.000	1446.5	0.5785	0.7370	335.000	306.3	0.1134	0.7370
335.000	1361.5	0.5790	0.7370	320.000	291.4	0.1135	0.7370
320.000	1270.8	0.5794	0.7370	380.000	234.2	0.07533	0.7370
380.000	1120.0	0.3844	0.7370	365.000	224.8	0.07539	0.7370
365.000	1068.6	0.3847	0.7370	350.000	215.5	0.07544	0.7370
350.000	1014.6	0.3850	0.7370	335.000	206.2	0.07549	0.7370
335.000	958.4	0.3852	0.7370	320.000	196.3	0.07555	0.7370
320.000	903.5	0.3855	0.7370	305.000	186.4	0.07560	0.7370
305.000	846.0	0.3858	0.7370	380.000	156.7	0.05012	0.7370
380.000	766.4	0.2558	0.7370	365.000	150.5	0.05016	0.7370
365.000	732.2	0.2560	0.7370	350.000	144.4	0.05019	0.7370
350.000	697.8	0.2562	0.7370	335.000	137.8	0.05023	0.7370
335.000	663.2	0.2564	0.7370	320.000	131.7	0.05026	0.7370
320.000	627.4	0.2565	0.7370				

[a] data in the two-phase region; * x_1 denotes the mole fraction of R-125.

Table 2. Numerical coefficients in Eqs. (5) through (13) for R-125/143a

i	b_i / dm^3·mol^{-1}	c_i / dm^6·mol^{-2}	d_i / dm^9·mol^{-3}
1	0.4229178	0.8218857×10^{-3}	-0.2287655×10^{-3}
2	0.1170954	0.2697741×10^{-1}	-0.1609560×10^{-2}
3	–0.2979276	-0.1737623×10^{-2}	
4	0.4313633	0.1172257×10^{-1}	
5	0.4302782	0.2601947×10^{-1}	
6	–0.4208974	-0.2750444×10^{-2}	
7	0.4264145	0.1079943×10^{-3}	
8	-0.2315745×10^{-2}	0.7503169×10^{-1}	
9	–0.2586190	-0.4617602×10^{-1}	
10		0.4594123×10^{-2}	
11		0.8836004×10^{-1}	
12		-0.6117517×10^{-1}	

Figure Captions

Fig. 1. Deviations of experimental *PVTx* data of R-125/143a system from the present model: , 0.2733 (mole fraction of R-125), this work; , 0.4188, this work; , 0.5652, this work; , 0.7370, this work; , 0.5090, Weber and Defibaugh [1]; , 0.5000, Magee [6].

Fig. 2. Temperature dependence of the second virial coefficients for R-125/143a system: —, present model; , R-125, Zhang et al. [7]; , R-143a, Zhang et al. [7].

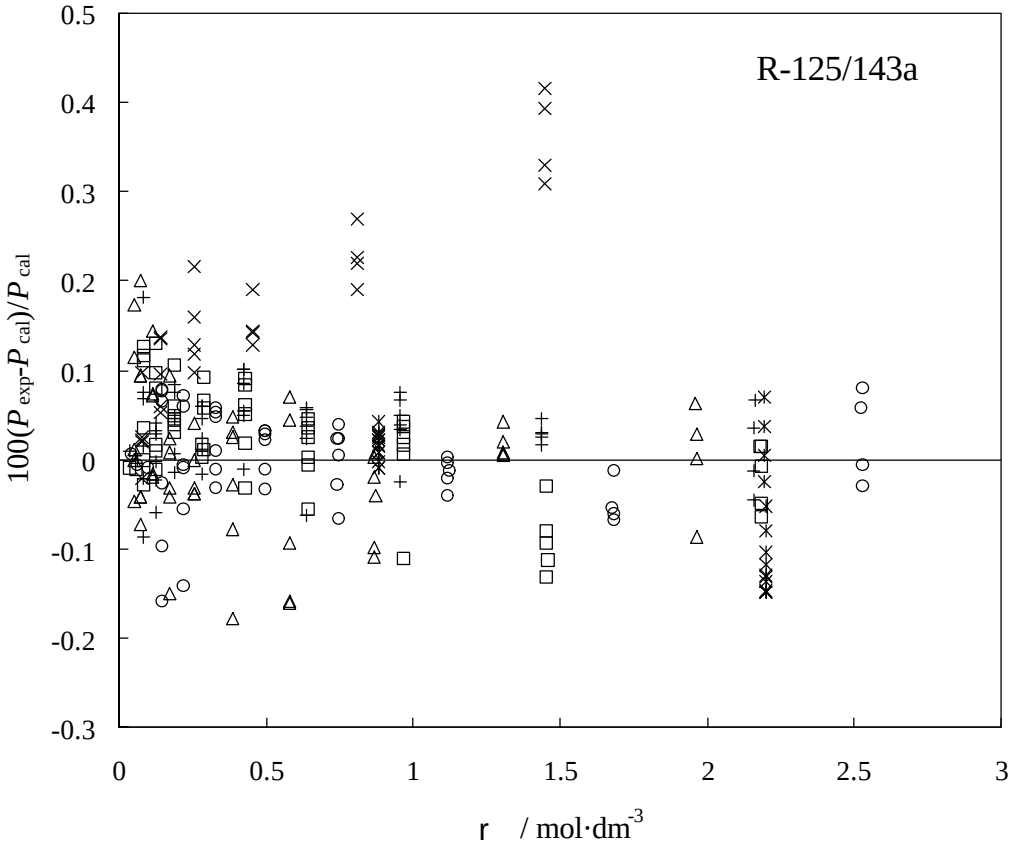
R-125/143a
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
100(P exp-P cal)/P cal
0
0.5
1
1.5
2
2.5
3
r / mol·dm-3

Fig. 1

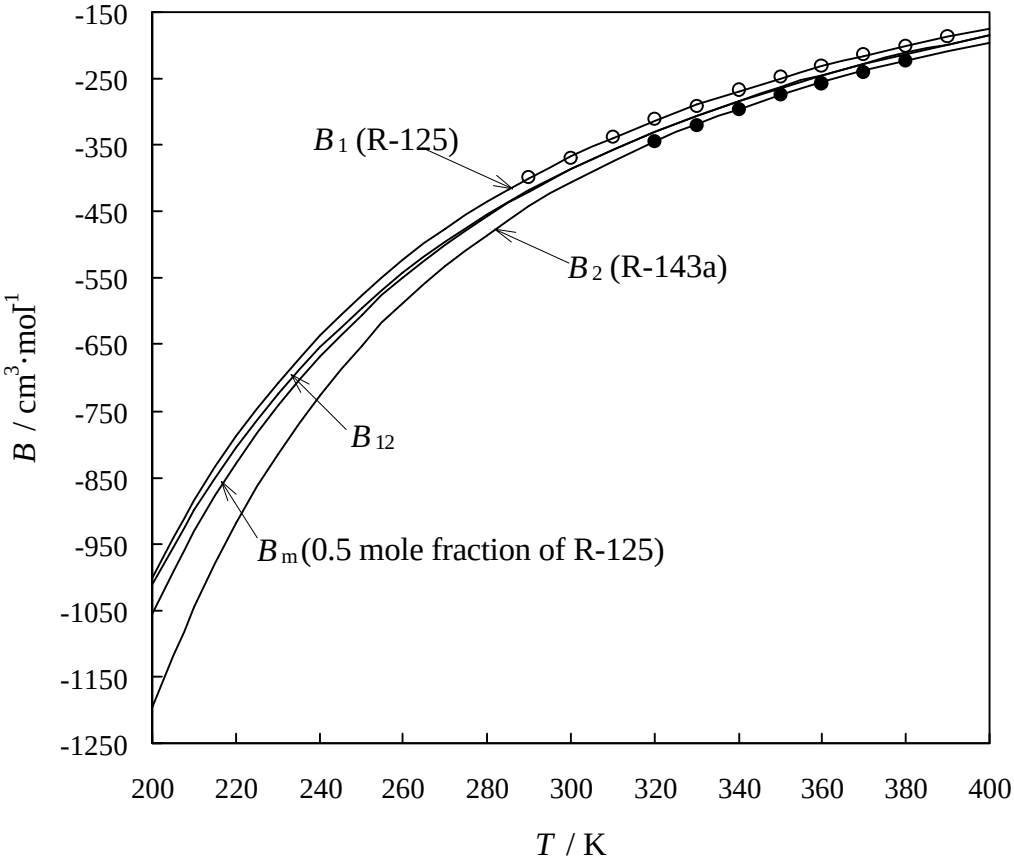
-150
-250
-350
-450
-550
-650
-750
-850
-950
-1050
-1150
-1250
200
220
240
260
280
300
320
340
360
380
400
B / cm3·mol-1
T / K
B1 (R-125)
B2 (R-143a)
B12
Bm (0.5 mole fraction of R-125)

Fig. 2