International Journal of Thermophysics, Vol. 20, No. 5, 1999

Thermal Conductivity of Binary Refrigerant Mixtures of HFC-32/125 and HFC-32/134a in the Liquid Phase

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Received March 15, 1999

The liquid thermal conductivity of mixtures of HFC-32/125 and HFC-32/134a was measured using the transient hot-wire apparatus in the temperature ranges from 213 to 293 K and from 193 to 313 K, respectively, in the pressure range from 2 to 30 MPa and with HFC-32 mass fractions of 0.249, 0.500, and 0.750 for each system. The uncertainty of the thermal conductivity was estimated to be ±0.7%. For practical applications, the thermal conductivity data for the two mixtures were represented by a polynomial in temperature, pressure, and mass fraction of HFC-32 with a standard deviation of 1.0%.

KEY WORDS: HFC-32/125; HFC-32/134a; binary mixture; refrigerant; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

The refrigerant HCFC-22 has been widely used in large-scale refrigerators and air-conditioning systems. However, because of its damage to the ozone layer, the production and the use of HCFC-22 will be prohibited after 2020 according to the Montreal Protocol and its amendments. Therefore, it is urgent to find suitable alternative refrigerants to HCFC-22. Considering the system performance and flammability, it is very difficult to find a pure refrigerant which can substitute for HCFC-22. At present, binary and ternary mixtures consisting of HFC-32, HFC-125, and HFC-134a, such as HFC-32/125, HFC-32/134a, and HFC-32/125/134a, are proposed as

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0195-928X/99/0900-1403$16.00/0

promising alternatives to HCFC-22 in refrigeration and air-conditioning systems.

For practical applications of these mixtures as working fluids, numerous experimental measurements of the thermodynamic properties for these HFC refrigerant mixtures have been completed in recent years. However, research on the transport properties of HFC mixtures has fallen comparatively behind. The lack of thermal conductivity data with a high accuracy motivated us to make the present measurements of thermal conductivity of mixtures of HFC-32/125 and HFC-32/134a in the liquid phase over wide temperature and pressure ranges.

2. EXPERIMENTAL

Measurements of the liquid thermal conductivity for the binary HFC refrigerant mixtures were carried out using the transient hot-wire method. The apparatus and experimental procedures have been previously described in detail [1]. The hot wire used in the present work was made of platinum with a diameter of $10\,\mu$m and an effective length of about 50 mm. In order to compensate for the end effects of the wire, two electrical voltage potential leads of the same platinum wire were spot-welded at positions about 10 mm from each end of the wire. The temperature of the sample was measured with a platinum resistance thermometer calibrated on ITS-90 to within an expanded uncertainty of ± 0.12 K. The pressure was measured with a precise digital pressure gauge to within an expanded uncertainty of ± 0.142 MPa. The NIST Database REFPROP Version 6.0 [2] was employed to calculate the densities of the binary mixtures of HFC-32/125 and HFC-32/134a to within an estimated uncertainty of ± 0.1 %.

The sample of HFC-32 was supplied by Showa Denko Co, Ltd., with a stated purity of better than 99.98 wt%. The samples of HFC-125 and HFC-134a were provided by Du Pont-Mitsui Fluorochemicals Co, Ltd.; their purities were confirmed to be 99.6 and 99.9 wt%, respectively. Both mixtures of HFC-32/125 and HFC-32/134a were prepared gravimetrically to yield the samples with HFC-32 mass fractions of 0.249, 0.500, and 0.750. The mixture samples were prepared and loaded into the measurement cell in the liquid phase. After the measurement, the samples in the measurement cell were removed, and their composition was checked using gas chromatography. The expanded uncertainties of the mass fraction of HFC-32 for the mixtures of HFC-32/125 and the mixtures of HFC-32/134a were estimated to be ± 0.30 and ± 0.42 wt%, respectively. At the same state point, three or four measurements were repeated, and the reproducibility of the experimental results was within ± 0.5 %. The reported thermal conductivity was the arithmetic average of three or four measurements. The ISO guide for the expression of uncertainty in measurement [3] was used to evaluate the uncertainties of temperature, pressure, mass fractions of the mixtures, and thermal conductivity in the present study. The expanded uncertainty of the measured thermal conductivity was estimated to be $\pm 0.7\%$.

To check the performance of the present transient hot-wire instrument, the thermal conductivity of liquid toluene was measured before and after measuring the HFC refrigerant mixtures. The experimental results for toluene agreed very well within $\pm 0.5\%$ with our previous work [4] and the IUPAC recommended correlation [5].

3. RESULTS AND DISCUSSION

3.1. HFC-32/125

The measurements of thermal conductivity for three mixtures of HFC-32/125 were performed in the temperature range from 213 to 293 K and in the pressure range from 2 to 30 MPa with HFC-32 mass fractions of 0.249, 0.500, and 0.750. The experimental data for the mixtures with three mass fractions of HFC-32 are listed in Tables I, II, and III, respectively. The experimental values of thermal conductivity of the mixtures of HFC-32/125 are less than the mass fraction and mole fraction averages of the pure components, although the deviations from the mass fraction average are very small; but the maximum deviation from the mole fraction average is as large as 21%. For engineering use, the reported thermal conductivity data were correlated by a polynomial equation in temperature, pressure, and mass fraction of HFC-32 as follows:

$$\lambda(T, P, w) = \lambda^0(T, P)[(1 + \phi(T, P)\, w + \varphi(T, P)\, w^2] \quad (1)$$

where

$$\lambda^0(T, P) = \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} T^i P^j \quad (2)$$

$$\phi(T, P) = \sum_{i=0}^{2} \sum_{j=0}^{2} b_{ij} T^i P^j \quad (3)$$

$$\varphi(T, P) = \sum_{i=0}^{2} \sum_{j=0}^{2} c_{ij} T^i P^j \quad (4)$$

$\lambda^0(T, P)$ indicates the liquid thermal conductivity of HFC-125. The functions $\phi(T, P)$ and $\varphi(T, P)$ indicate the correlation of the linear and quadratic

Table I. Thermal Conductivity of the Mixture of HFC-32/125 (24.9 wt%/75.1 wt%)

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
213.2	2	1468	0.1145
213.2	10	1485	0.1176
213.1	20	1504	0.1212
213.1	30	1522	0.1253
233.1	2	1401	0.1039
233.2	10	1423	0.1081
233.1	20	1447	0.1125
233.1	30	1468	0.1170
253.0	2	1330	0.0939
253.0	10	1359	0.0985
253.0	20	1389	0.1041
252.9	30	1414	0.1082
272.9	2	1251	0.0847
272.9	10	1291	0.0897
272.8	20	1329	0.0957
272.8	30	1359	0.1014
292.8	2.5	1161	0.0814
292.9	10	1215	0.0856
292.8	20	1265	0.0901
292.8	30	1303	0.0947

Table II. Thermal Conductivity of the Mixture of HFC-32/125 (50.0 wt%/50.0 wt%)

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
213.1	2	1381	0.1386
213.1	10	1397	0.1428
213.1	20	1414	0.1468
213.0	30	1429	0.1499
233.0	2	1319	0.1262
233.0	10	1338	0.1314
233.0	20	1360	0.1359
233.0	30	1378	0.1405
253.0	2	1252	0.1155
253.0	10	1277	0.1207
253.0	20	1304	0.1258
253.0	30	1326	0.1300
273.0	2	1178	0.1056
273.0	10	1212	0.1108
273.0	20	1246	0.1162
273.0	30	1273	0.1215
293.0	2.5	1094	0.0954
293.0	10	1141	0.1027
293.0	20	1185	0.1080
292.9	30	1219	0.1126

Table III. Thermal Conductivity of the Mixture of HFC-32/125 (75.0 wt%/25.0 wt%)

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
213.0	2	1306	0.1651
213.0	10	1319	0.1693
213.0	20	1335	0.1739
213.0	30	1349	0.1785
233.0	2	1247	0.1513
233.0	10	1264	0.1563
233.0	20	1283	0.1614
233.0	30	1300	0.1662
253.0	2	1185	0.1375
253.0	10	1207	0.1431
253.0	20	1230	0.1489
253.0	30	1250	0.1548
273.0	2	1115	0.1250
272.9	10	1145	0.1309
272.9	20	1175	0.1382
272.9	30	1200	0.1435
292.9	2.5	1038	0.1161
292.9	10	1078	0.1199
292.9	20	1117	0.1275
292.9	30	1147	0.1348

Table IV. Optimum Values of the Coefficients a_{ij} in Eq. (2) for HFC-32/125

a_{ij}	$i=0$	$i=1$	$i=2$
$j=0$	2.0347×10^{-1}	-5.5302×10^{-4}	2.1755×10^{-7}
$j=1$	1.7779×10^{-3}	-1.5417×10^{-5}	4.3340×10^{-8}
$j=2$	-2.4433×10^{-5}	2.5675×10^{-7}	-7.0531×10^{-10}

Table V. Optimum Values of the Coefficients b_{ij} in Eq. (3) for HFC-32/125

b_{ij}	$i=0$	$i=1$	$i=2$
$j=0$	1.1336×10^{1}	-9.0530×10^{-2}	1.9214×10^{-4}
$j=1$	-6.4381×10^{-1}	5.4823×10^{-3}	-1.1748×10^{-5}
$j=2$	9.3713×10^{-3}	-8.0950×10^{-5}	1.7621×10^{-7}

Table VI. Optimum Values of the Coefficients c_{ij} in Eq. (4) for HFC-32/125

c_{ij}	$i=0$	$i=1$	$i=2$
$j=0$	-1.1514×10^{1}	9.8982×10^{-2}	-2.0555×10^{-4}
$j=1$	6.1609×10^{-1}	-5.1849×10^{-3}	1.0889×10^{-5}
$j=2$	-8.2966×10^{-3}	7.0019×10^{-5}	-1.4867×10^{-7}

coefficients of the thermal conductivity of the mixtures as a function of mass fraction. Tables IV, V, and VI list the coefficients a_{ij}, b_{ij}, and c_{ij}, respectively. These equations can represent all of the experimental results for the mixtures of HFC-32/125 with a standard deviation of 1.0% and a maximum deviation of -3.2% as shown in Fig. 1.

Two other studies of the thermal conductivity for mixtures of HFC-32/125 were made using the transient hot-wire method. Ro et al. [6]

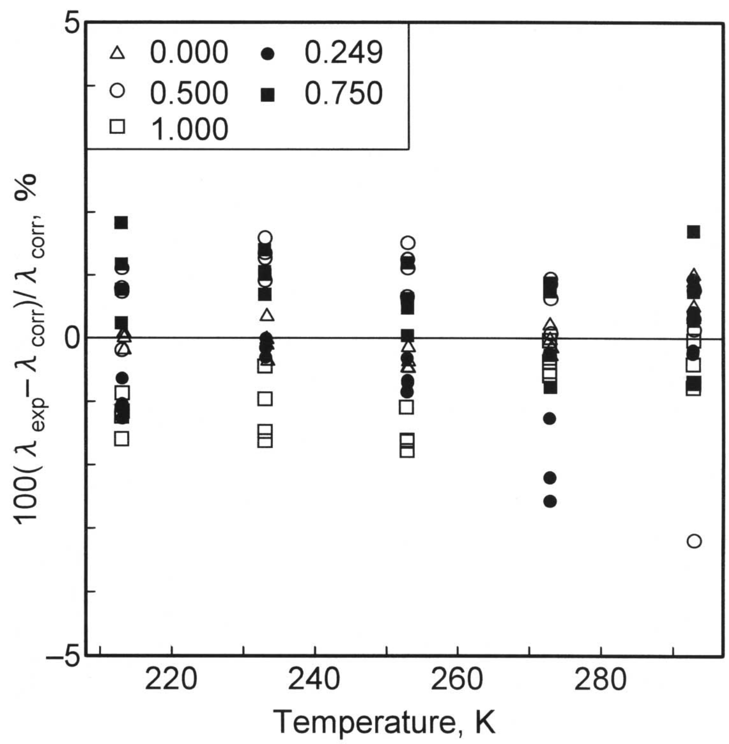

Fig. 1. Percentage deviations of the present experimental data from Eq. (1) for the mixtures of HFC-32/125.

measured the liquid thermal conductivity of HFC-32/125 in the temperature range from 233 to 323 K and in the pressure range from 2 to 20 MPa with HFC-32 mass fractions of 0.2522, 0.4131, 0.4956, 0.5939, and 0.7595. The uncertainty of their experimental results was estimated to be less than $\pm 2\%$. Spindler et al. [7] measured the saturated liquid thermal conductivity of HFC-32/125 (50 wt%/50 wt%) in the temperature range from 223 to 333 K with an uncertainty of $\pm 2\%$. The experimental results of Spindler et al. were presented only by a correlation. Figure 2 shows the percentage deviations of the experimental results of Ro et al. and Spindler et al. based on Eq. (1) for the mixtures of HFC-32/125. The experimental data of Ro et al. are all higher than the present results by about 4 to 5%. However, the experimental results of Spindler et al. are lower than the present equation by about 2 to 7%. Since Ro's thermal conductivity data showed reasonable agreement with ours for pure HFC-32 and pure HFC-125, it is hard to explain the marked differences in the thermal conductivity data between Ro's results and ours for HFC-32/125 and to relate these

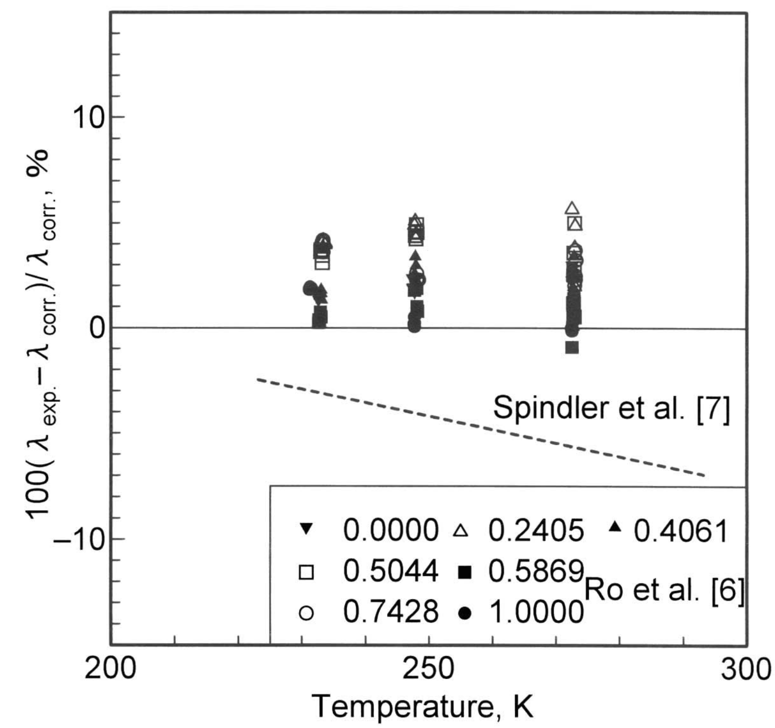

Fig. 2. Comparisons of Eq. (1) for the mixtures of HFC-32/125 with other measurements.

with the thermal conductivity data of pure HFC-32 and pure HFC-125. While measuring the thermal conductivity of the mixtures, the possibility of sample composition change and sample contamination during the experiment should be taken into account. It is necessary to check the composition change of the sample inside the measurement cell after finishing all measurements using gas chromatography. The present experimental results of thermal conductivity for HFC-32/125 system were also compared with the thermal conductivity predictions of REFPROP 6.0. The present experimental results are significantly lower than the predicted values, with an average absolute deviation of 7.3% and a maximum deviation of −9.6%.

Table VII. Thermal Conductivity of the Mixture of HFC-32/134a (24.9 wt%/75.1 wt%)

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
193.3	2	1464	0.1432
193.3	10	1476	0.1464
193.3	20	1488	0.1493
193.3	30	1500	0.1530
213.0	2	1411	0.1340
213.0	10	1424	0.1379
213.1	20	1440	0.1416
213.1	30	1454	0.1452
233.0	2	1354	0.1235
232.9	10	1371	0.1272
232.9	20	1390	0.1319
232.9	30	1406	0.1356
252.9	2	1294	0.1130
252.9	10	1316	0.1173
252.9	20	1339	0.1222
252.9	30	1358	0.1265
272.9	2	1230	0.1022
272.9	10	1258	0.1078
272.8	20	1286	0.1133
272.8	30	1310	0.1180
292.9	2.5	1161	0.0936
292.9	10	1196	0.0988
292.8	20	1231	0.1049
292.8	30	1260	0.1091
314.8	3	1073	0.0846
314.6	10	1122	0.0897
314.4	20	1170	0.0959
314.2	30	1206	0.1002

3.2. HFC-32/134a

The measurements of thermal conductivity for three mixtures of HFC-32/134a were carried out in the temperature range from 193 to 313 K and in the pressure range from 2 to 30 MPa with HFC-32 mass fractions of 0.249, 0.500, and 0.750. The experimental results for the three mixtures of HFC-32/134a with different mass fractions of HFC-32 are listed in Tables VII, VIII, and IX, respectively. The thermal conductivity of the mixtures of HFC-32/134a shows mass fraction and mole fraction dependences similar to those for the mixtures of HFC-32/125.

For engineering applications, the measured thermal conductivity data were correlated by the same polynomials as in the case of HFC-32/125.

Table VIII. Thermal Conductivity of the Mixture of HFC-32/134a (50.0 wt%/50.0 wt%)

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
193.2	2	1401	0.1627
193.2	10	1412	0.1650
193.2	20	1425	0.1688
193.2	30	1436	0.1716
213.2	2	1347	0.1522
213.2	10	1361	0.1554
213.2	20	1376	0.1587
213.2	30	1390	0.1629
233.1	2	1291	0.1414
233.1	10	1308	0.1450
233.0	20	1326	0.1499
233.0	30	1342	0.1545
253.1	2	1231	0.1295
253.0	10	1252	0.1342
253.0	20	1275	0.1392
253.0	30	1294	0.1441
273.0	2	1166	0.1178
273.0	10	1194	0.1227
273.0	20	1222	0.1293
272.9	30	1245	0.1343
292.9	2.5	1095	0.1055
292.8	10	1131	0.1124
292.8	20	1167	0.1187
292.8	30	1196	0.1241
314.7	3	1003	0.0907
314.3	10	1056	0.0976
314.1	20	1104	0.1075
313.9	30	1141	0.1121

Table IX. Thermal Conductivity of the Mixture of HFC-32/134a (75.0 wt%/25.0 wt%)

Temperature (K)	Pressure (MPa)	Density ($kg \cdot m^{-3}$)	Thermal conductivity, λ ($W \cdot m^{-1} \cdot K^{-1}$)
193.3	2	1344	0.1847
193.3	10	1354	0.1884
193.2	20	1366	0.1921
193.3	30	1377	0.1953
213.1	2	1291	0.1717
213.1	10	1303	0.1763
213.1	20	1318	0.1802
213.1	30	1331	0.1836
233.1	2	1235	0.1603
233.0	10	1251	0.1653
233.0	20	1269	0.1697
233.0	30	1284	0.1743
253.0	2	1176	0.1468
253.0	10	1196	0.1518
252.9	20	1218	0.1575
252.9	30	1237	0.1625
272.9	2	1110	0.1329
272.8	10	1138	0.1393
272.8	20	1165	0.1458
272.8	30	1188	0.1513
292.9	2.5	1038	0.1187
292.9	10	1074	0.1253
292.8	20	1109	0.1333
292.8	30	1138	0.1398
316.1	3	934.9	0.1060
315.8	10	991.2	0.1125
315.6	20	1042	0.1203
315.5	30	1079	0.1275

Table X. Optimum Values of the Coefficients a_{ij} in Eq. (2) for HFC-32/134a

a_{ij}	$i=0$	$i=1$	$i=2$
$j=0$	2.0877×10^{-1}	-4.1438×10^{-4}	-3.4532×10^{-8}
$j=1$	8.5903×10^{-4}	-5.9203×10^{-6}	1.7278×10^{-8}
$j=2$	-2.9022×10^{-5}	2.2909×10^{-7}	-4.6320×10^{-10}

Table XI. Optimum Values of the Coefficients b_{ij} in Eq. (3) for HFC-32/134a

b_{ij}	$i=0$	$i=1$	$i=2$
$j=0$	9.3451×10^{-1}	-2.9927×10^{-3}	2.7811×10^{-6}
$j=1$	-3.0582×10^{-2}	1.9520×10^{-4}	-2.2182×10^{-7}
$j=2$	3.2198×10^{-4}	-2.2222×10^{-7}	-6.1733×10^{-9}

Table XII. Optimum Values of the Coefficients c_{ij} in Eq. (4) for HFC-32/134a

c_{ij}	$i=0$	$i=1$	$i=2$
$j=0$	-7.4805×10^{-1}	7.0684×10^{-3}	-1.2229×10^{-5}
$j=1$	3.2193×10^{-2}	-2.2541×10^{-4}	2.9357×10^{-7}
$j=2$	-2.3574×10^{-4}	-5.3992×10^{-5}	7.9882×10^{-9}

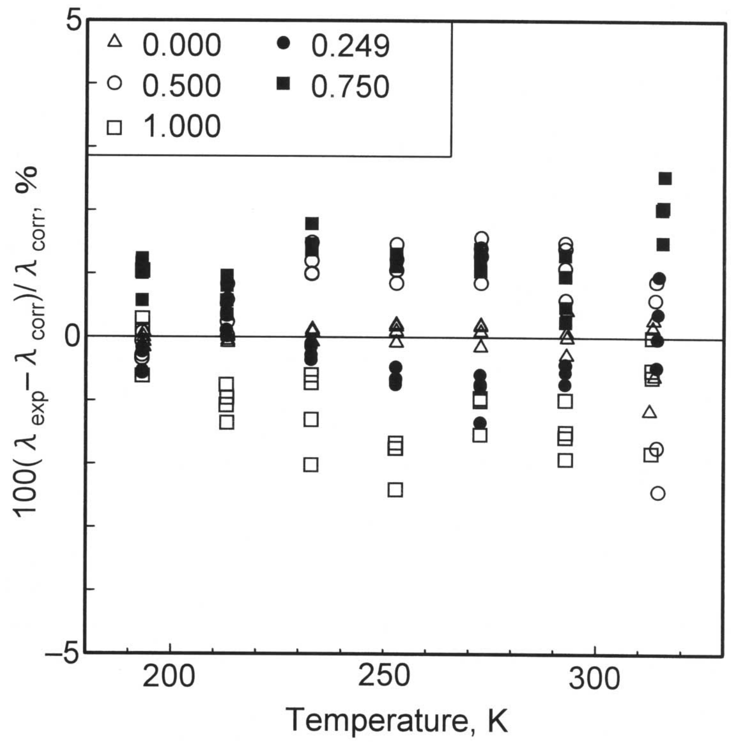

Fig. 3. Percentage deviations of the present experimental data from Eq. (1) for the mixtures of HFC-32/134a.

This time, $\lambda^0(T, P)$ indicates the liquid thermal conductivity of HFC-134a. Tables X, XI, and XII list the coefficients of the correlations a_{ij}, b_{ij}, and c_{ij}, respectively. The deviations of the present experimental data from the correlation are shown in Fig. 3. The correlation can represent all of the experimental results with a standard deviation of 1.0% and a maximum deviation of 2.5%.

There is only one other study of the liquid thermal conductivity of mixtures of HFC-32/134a, by Ro et al. [8]. The transient hot-wire method with one bare platinum wire 25 μm in diameter was used in their work to measure the liquid thermal conductivity of mixtures of HFC-32/134a in the temperature range from 223 to 323 K and in the pressure range from 2 to 20 MPa, with HFC-32 mass fractions of 0.3057, 0.5107, and 0.7496. The uncertainty of their experimental results was estimated to be less than ± 2.0%. Figure 4 illustrates the deviations of their experimental data based on the present correlation. It is found that the agreement with the present

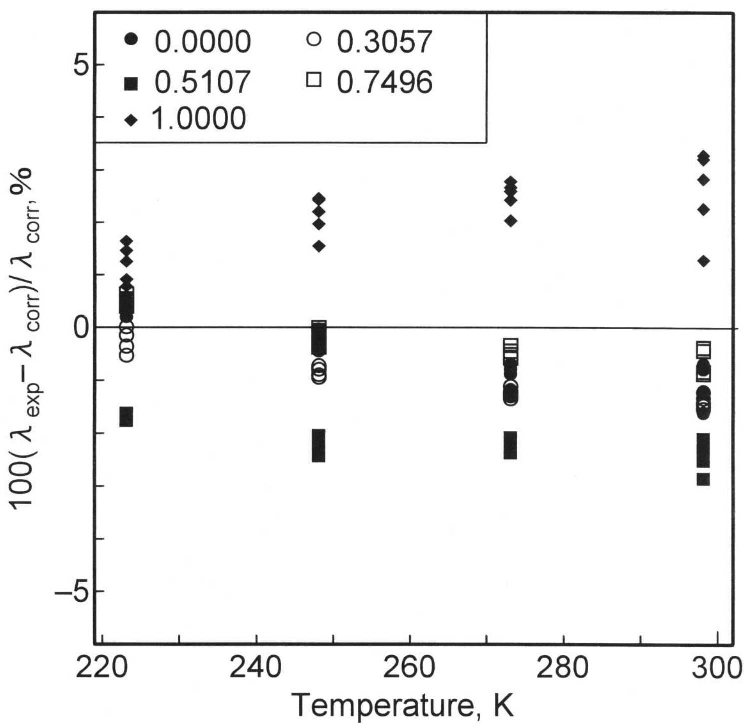

Fig. 4. Comparisons of Eq. (1) for the mixtures of HFC-32/134a with the data of Ro et al. [8].

data is satisfactory. The present experimental results of thermal conductivity are also compared with the predicted values of REFPROP 6.0. The average absolute deviation and maximum deviation of the present experimental results based on the thermal conductivity predictions are 3.9 and −7.8%, respectively.

ACKNOWLEDGMENTS

The authors wish to thank Showa Denko Co., Ltd., and Du Pont-Mitsui Fluorochemicals Co., Ltd., for their supply of the samples and K. Nomura and N. Muro for their assistance with the experiments.

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