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Liquid Thermal Conductivity of Ternary Mixtures of Difluoromethane (R32), Pentafluoroethane (R125), and 1,1,1,2-Tetrafluoroethane (R134a)[1]

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The thermal conductivities of ternary refrigerant mixtures of difluoromethane (R32), pentafluoroethane (R125), and 1,1,1,2-tetrafluoroethane (R134a) in the liquid phase have been measured by the transient hot-wire method with one bare platinum wire. The experiments were performed in the temperature range of 233 to 323 K and in the pressure range of 2 to 20 MPa at various compositions. The measured data are correlated as a function of temperature, pressure, and composition. From the correlation, we can calculate the thermal conductivity of pure refrigerants and their binary or ternary refrigerant mixtures. The uncertainty of the measurements is estimated to be ±2%.

KEY WORDS: correlation; R125; R134a; R32; refrigerant; ternary mixture; thermal conductivity; transient hot-wire method.

1. INTRODUCTION

In recent years, HFC refrigerant mixtures have been proposed as promising working fluids in refrigeration and heat pump systems because environmental impacts can be reduced. Therefore, many studies of the thermodynamic and transport properties of HFC refrigerant mixtures have been conducted. In particular, binary or ternary refrigerant mixtures of R32, R125, and R134a, or pure HFC refrigerants in some cases, are expected to be suitable alternatives to CFC or HCFC refrigerants. Much experimental data for the thermal conductivities of pure refrigerants, R32, R125, and

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R134a, have been reported [1–14]. However, there are some discrepancies between the various results that exceed the mutual uncertainties of experiments. Moreover, although binary and ternary refrigerant mixtures such as R410A (R32 : R125 = 0.50 : 0.50 by mass fraction), R407C (R32 : R125 : R134a = 0.23 : 0.25 : 0.52 by mass fraction), etc. are being used in many refrigeration and heat pump systems, there are few published data for their thermodynamic and transport properties. We have reported the thermal conductivities for several binary refrigerant mixtures of R32/134a, R32/125, and R125/134a in previous papers [15–17]. This paper reports experimental data for the thermal conductivity of ternary refrigerant mixtures, R32/125/134a, in the liquid phase. It is expected that the thermal conductivities for binary or ternary refrigerant mixtures of R32, R125, and R134a over a wide range of temperature and pressure will be useful in designing and analyzing thermal systems.

2. EXPERIMENTS

A transient hot-wire method has been adopted in numerous studies because it is highly accurate in the measurement of thermal conductivity. In this study, the same method with one bare platinum wire was used, even though the refrigerants in this study are polar. The basic principle, the apparatus, and the procedures of our experiment have been described in detail in previous studies [15, 16]. According to the fundamental working equation describing the transient hot-wire method, the measured temperature rise versus the logarithm of time should be linear. Therefore, the measurement time is chosen to be 100–300 ms after applying electric current to the wire in order to maintain the linearity and minimize other sources of errors. The errors due to polarization, natural convection, etc., are negligible since there is no distortion of the linearity during the measurement period.

As a heat source, one platinum wire of 25 μm in diameter and 128.40 mm in length was used. The temperature was measured by a platinum resistance thermometer to within an uncertainty of 0.01 K. The temperature of the thermostatted bath in which the pressure vessel containing the hot-wire cell is submerged is kept constant within a variation of ± 0.02 K. To avoid freezing at low temperatures, ethylene glycol was used as the fluid in the bath. The pressure was measured by a Bourdon-type pressure gauge with an uncertainty of 0.5 %. The refrigerants were supplied by DuPont Company, and their purities are better than 99.8 %. In measuring the thermal conductivity of refrigerant mixtures, it is important and difficult to determine accurate compositions of the mixtures. The composition of the refrigerant mixtures was measured by weighing the mass of each component of the mixture with a precise balance. Before and after the measurement, the composition of the refrigerant mixture was checked with a gas chromatograph. The uncertainty in the composition measurement was less than 0.005 in mole fraction. The uncertainty in the thermal conductivity measurement is estimated to be ±2%. The measured thermal conductivity data are averages of five measurements under the same conditions. The reproducibility is within ±0.5%.

3. RESULTS

Experiments for measuring the thermal conductivities of R32/125/134a mixtures were performed in the temperature range of 233 to 323 K at intervals of approximately 25 K and in the pressure range of 2 to 20 MPa. The mass fractions of R32, R125, and R134a of the mixtures are 0.180/0.612/0.208, 0.217/0.197/0.586, 0.230/0.250/0.520, 0.253/0.381/0.366, 0.384/0.200/0.416, 0.422/0.390/0.188, and 0.610/0.201/0.189. The thermal conductivities of the refrigerant mixtures are presented in Table I as a fuction of temperature and pressure.

The temperature dependence of the thermal conductivity of a R32/125/134a mixture with a composition of 0.230 : 0.250 : 0.520 by mass fraction is plotted in Fig. 1 along isobars, and the pressure dependence along isotherms is shown in Fig. 2. As is shown in Table I for most cases, the thermal conductivities of R32/125/134a mixtures in the liquid phase increase almost linearly with decreasing temperature and with increasing pressure. The composition dependence of the thermal conductivity of R32/125/134a mixtures for $T = 0°\text{C}$ and $P = 10$ MPa is plotted in Fig. 3, where the graph forms a slightly concave surface. It is known that the thermal conductivity of a mixture in the liquid phase is generally smaller than that of the mass fraction average of the thermal conductivities of the pure components [18]. In our previous studies, we reported that the composition dependence of the thermal conductivity for three binary mixtures of R32, R125, and R134a shows similar tendencies, although the deviations from the mass fraction average are minor.

The measured thermal conductivities for R32/125/134a mixtures have been correlated, using a least-squares regression method, with the following equations:

$$\lambda_{\text{pure}} = a_1 + a_2 T_r + a_3 T_r^2 + a_4 P_r + a_5 P_r^2 + a_6 T_r^2 P_r + a_7 T_r P_r^2 \tag{1}$$

$$\begin{aligned} \lambda = {} & w_1\lambda_1 + w_2\lambda_2 + w_3\lambda_3 + c_1 w_1 w_2 \sqrt{\lambda_1\lambda_2} + c_2 w_2 w_3 \sqrt{\lambda_2\lambda_3} \\ & + c_3 w_3 w_1 \sqrt{\lambda_3\lambda_1} + (d_1 w_1 w_2 w_3 + d_2 w_1^2 w_2^2 w_3^2 + d_3 w_1^3 w_2^3 w_3^3) \sqrt[3]{\lambda_1\lambda_2\lambda_3} \end{aligned} \tag{2}$$

Table I. Measured Thermal Conductivities of R32/125/134a Mixtures[a]

T (°C)	P (MPa)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)	T (°C)	P (MPa)	λ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)
R32 : R125 : R134a = 0.180 : 0.612 : 0.208			R32 : R125 : R134a = 0.217 : 0.197 : 0.586		
−40.2	2.0	0.1040	−40.3	2.0	0.1132
−40.3	5.0	0.1057	−40.3	5.0	0.1150
−40.3	10.0	0.1089	−40.0	10.0	0.1177
−40.2	15.0	0.1101	−39.9	15.0	0.1199
−40.2	20.0	0.1123	−40.4	20.0	0.1221
−25.1	2.0	0.0969	−25.2	2.0	0.1067
−25.1	5.0	0.0986	−25.2	5.0	0.1082
−24.6	10.0	0.1010	−25.2	10.0	0.1105
−24.6	15.0	0.1036	−25.1	15.0	0.1137
−24.7	20.0	0.1062	−25.1	20.0	0.1150
−0.1	2.0	0.0853	−0.6	2.0	0.0931
−0.1	5.0	0.0873	−0.6	5.0	0.0952
−0.1	10.0	0.0904	−0.4	10.0	0.0989
−0.1	15.0	0.0933	−0.3	15.0	0.1023
0.0	20.0	0.0961	−0.3	20.0	0.1050
24.9	2.0	0.0729	24.5	2.0	0.0841
24.9	5.0	0.0759	24.5	5.0	0.0862
24.9	10.0	0.0803	24.5	10.0	0.0893
25.0	15.0	0.0843	24.6	15.0	0.0924
25.1	20.0	0.0874	24.7	20.0	0.0954
50.4	5.0	0.0641	50.8	5.0	0.0738
50.3	10.0	0.0702	51.0	10.0	0.0780
50.4	15.0	0.0743	50.8	15.0	0.0821
50.3	20.0	0.0786	50.8	20.0	0.0852
R32 : R125 : R134a = 0.230 : 0.250 : 0.520			R32 : R125 : R134a = 0.253 : 0.381 : 0.366		
−40.4	2.0	0.1169	−40.5	2.0	0.1136
−40.4	5.0	0.1182	−40.4	5.0	0.1153
−40.4	10.0	0.1201	−40.3	10.0	0.1173
−40.3	15.0	0.1222	−40.2	15.0	0.1196
−40.4	20.0	0.1242	−40.4	20.0	0.1214
−25.1	2.0	0.1085	−25.4	2.0	0.1058
−25.1	5.0	0.1104	−25.4	5.0	0.1075
−25.2	10.0	0.1133	−25.3	10.0	0.1102
−25.2	15.0	0.1157	−25.3	15.0	0.1125
−25.3	20.0	0.1173	−25.3	20.0	0.1148
−0.2	2.0	0.0957	−0.5	2.0	0.0938
−0.4	5.0	0.0979	−0.3	5.0	0.0958
−0.4	10.0	0.1014	−0.3	10.0	0.0989
−0.3	15.0	0.1042	−0.2	15.0	0.1018
−0.4	20.0	0.1071	−0.1	20.0	0.1046
24.8	2.0	0.0837	25.0	2.0	0.0814
25.0	5.0	0.0861	24.8	5.0	0.0835
25.1	10.0	0.0897	24.7	10.0	0.0881
25.0	15.0	0.0931	24.8	15.0	0.0912
25.0	20.0	0.0966	24.7	20.0	0.0948
50.2	5.0	0.0757	50.5	5.0	0.0722
50.2	10.0	0.0799	50.5	10.0	0.0768
50.3	15.0	0.0843	50.6	15.0	0.0811
50.3	20.0	0.0873	50.5	20.0	0.0851

Table I. *(Continued)*

T (°C)	P (MPa)	λ ($W \cdot m^{-1} \cdot K^{-1}$)	T (°C)	P (MPa)	λ ($W \cdot m^{-1} \cdot K^{-1}$)
R32 : R125 : R134a = 0.384 : 0.200 : 0.416			R32 : R125 : R134a = 0.422 : 0.390 : 0.188		
−40.3	2.0	0.1306	−40.3	2.0	0.1225
−40.3	5.0	0.1323	−40.3	5.0	0.1243
−40.1	10.0	0.1350	−40.5	10.0	0.1270
−40.1	15.0	0.1376	−40.3	15.0	0.1293
−40.4	20.0	0.1399	−40.3	20.0	0.1315
−25.2	2.0	0.1217	−25.2	2.0	0.1135
−25.2	5.0	0.1232	−25.2	5.0	0.1156
−25.3	10.0	0.1257	−25.1	10.0	0.1183
−25.2	15.0	0.1282	−25.1	15.0	0.1213
−25.1	20.0	0.1307	−25.2	20.0	0.1236
−0.3	2.0	0.1070	−0.4	2.0	0.1004
−0.3	5.0	0.1094	−0.2	5.0	0.1024
−0.2	10.0	0.1126	−0.2	10.0	0.1058
−0.2	15.0	0.1163	−0.1	15.0	0.1086
−0.2	20.0	0.1196	−0.1	20.0	0.1116
25.0	2.0	0.0935	24.8	2.0	0.0868
25.0	5.0	0.0966	24.9	5.0	0.0889
24.8	10.0	0.0997	24.9	10.0	0.0932
25.0	15.0	0.1043	25.1	15.0	0.0966
25.0	20.0	0.1085	25.2	20.0	0.1003
50.0	5.0	0.0818	50.0	5.0	0.0761
50.1	10.0	0.0874	50.0	10.0	0.0801
50.3	15.0	0.0921	50.1	15.0	0.0855
50.2	20.0	0.0970	50.1	20.0	0.0904
R32 : R125 : R134a = 0.610 : 0.201 : 0.189					
−40.5	2.0	0.1408			
−40.5	5.0	0.1423			
−40.6	10.0	0.1446			
−40.5	15.0	0.1473			
−40.6	20.0	0.1505			
−25.2	2.0	0.1314			
−25.1	5.0	0.1331			
−25.2	10.0	0.1361			
−25.1	15.0	0.1386			
−25.2	20.0	0.1412			
−0.2	2.0	0.1156			
−0.1	5.0	0.1184			
−0.2	10.0	0.1217			
−0.2	15.0	0.1248			
0.0	20.0	0.1282			
24.9	2.0	0.1007			
24.8	5.0	0.1034			
25.0	10.0	0.1071			
24.9	15.0	0.1110			
24.8	20.0	0.1150			
50.0	5.0	0.0880			
50.0	10.0	0.0919			
50.0	15.0	0.0970			
50.1	20.0	0.1019			

[a] Compositions in mass fractions.

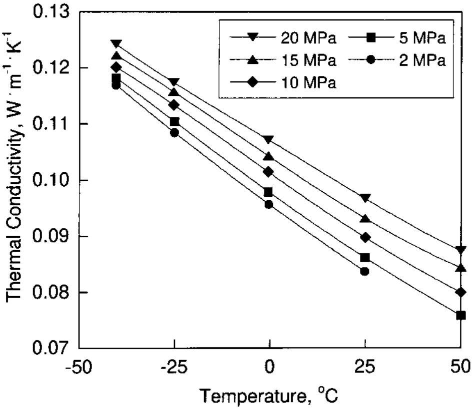

Fig. 1. Measured thermal conductivities of R32/125/134a mixtures; temperature dependence along isobars for a mass fraction of 0.230 for R32 and 0.250 for R125.

where λ is the thermal conductivity of a mixture in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, and λ_1, λ_2, and λ_3 represent the thermal conductivities of pure R32, R125, and R134a, respectively. In Eq. (1), T_r is a reduced temperature and P_r is a reduced pressure; w_1, w_2, and w_3 in Eq. (2) are the mixture mass fractions of R32, R125, and R134a, respectively. The critical values are reported in Table II, and the coefficients a_i in Eq. (1) for pure refrigerants are given in

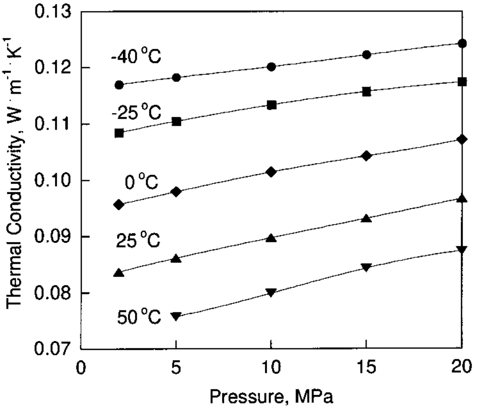

Fig. 2. Measured thermal conductivities of R32/125/134a mixtures; pressure dependence along isotherms for a mass fraction of 0.230 for R32 and 0.250 for R125.

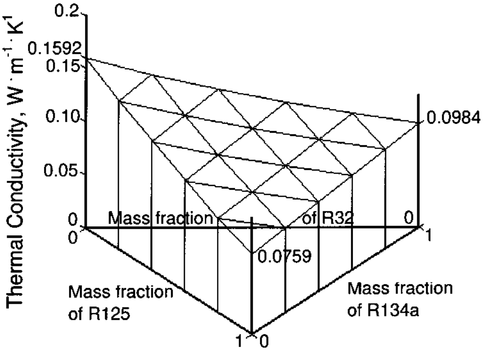

Fig. 3. Measured thermal conductivities of R32/125/134a mixtures; composition dependence for $T = 0°C$ and $P = 10$ MPa.

Table II. Critical Values of R32, R125, and R134a [19]

	T_c (°C)	P_c (MPa)
R32	351.26	5.777
R125	339.17	3.618
R134a	374.27	4.065

Table III. Coefficients of Eq. (1) for R32, R125, and R134a

	R32	R125	R134a
a_1	3.03507×10^{-1}	2.45548×10^{-1}	2.13818×10^{-1}
a_2	-1.07280×10^{-1}	-2.84034×10^{-1}	-1.70805×10^{-1}
a_3	-1.16167×10^{-1}	7.94960×10^{-2}	5.71644×10^{-3}
a_4	-2.54523×10^{-3}	-1.35757×10^{-3}	2.74879×10^{-4}
a_5	9.69901×10^{-4}	5.13034×10^{-4}	8.46768×10^{-5}
a_6	1.37438×10^{-2}	6.57088×10^{-3}	4.51171×10^{-3}
a_7	-1.56977×10^{-3}	-7.46366×10^{-4}	-2.39855×10^{-4}

Table IV. Coefficients of Eq. (2) for R32/125/134a Mixtures

Coefficient	Value
c_1	-2.19410×10^{-1}
c_2	-5.16430×10^{-1}
c_3	-2.57272×10^{-1}
d_1	-1.07011×10^{1}
d_2	6.68897×10^{2}
d_3	-1.03961×10^{4}

Table III. Table IV gives the coefficients c_i and d_i in Eq. (2). Thermal conductivity data for R32/125, R32/125, and R125/134a binary mixtures are taken from our previous reports [15–17]. The thermal conductivities of pure R32, R125, and R134a as well as their binary refrigerant mixtures in the liquid phase can be predicted from Eqs. (1) and (2). The root-mean-

Table V. Root-Mean-Square Deviations from Eqs. (1) and (2)[a]

	w_1	w_2	w_3	RMS (%)
Pure	1.000	0.000	0.000	0.19
	0.000	1.000	0.000	0.41
	0.000	0.000	1.000	0.19
Binary	0.000	0.785	0.215	0.11
	0.000	0.571	0.429	1.04
	0.000	0.374	0.626	0.65
	0.000	0.191	0.809	0.37
	0.252	0.748	0.000	1.55
	0.413	0.587	0.000	1.49
	0.496	0.504	0.000	1.29
	0.594	0.406	0.000	1.27
	0.760	0.240	0.000	1.77
	0.306	0.000	0.694	0.98
	0.511	0.000	0.489	1.30
	0.750	0.000	0.250	1.02
Ternary	0.180	0.612	0.208	1.20
	0.217	0.197	0.586	1.64
	0.230	0.250	0.520	0.62
	0.253	0.381	0.366	0.65
	0.384	0.200	0.416	2.91
	0.422	0.390	0.188	2.67
	0.610	0.201	0.189	0.72

[a] w_1, mass fraction of R32; w_2, mass fraction of R125; w_3, mass fraction of R134a.

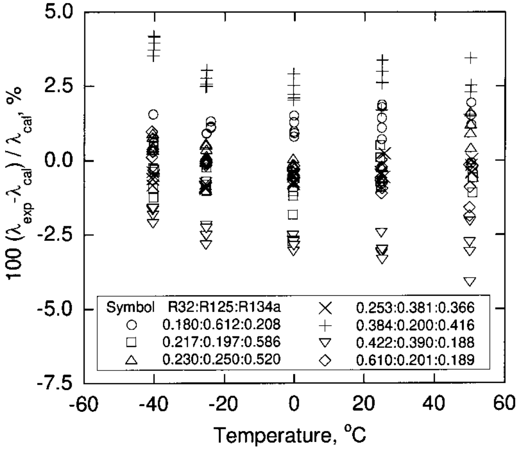

Fig. 4. Percentage deviations of the experimental thermal conductivity data from Eqs. (1) and (2) for R32/125/134a mixtures.

square deviations in applying Eqs. (1) and (2) to predict thermal conductivities are shown in Table V.

Figure 4 shows deviations of measured thermal conductivity data for ternary mixtures from those calculated from Eqs. (1) and (2). The root-mean-square deviation of all experimental data from Eqs. (1) and (2) is about 1.2%, and the maximum deviation of the thermal conductivity from Eqs. (1) and (2) is 4.2%.

4. CONCLUSION

Measurements of the thermal conductivity of R32/125/134a mixtures in the liquid phase are reported. The experiments were performed with a transient hot-wire method in the temperature range of 233–323 K and in the pressure range of 2–20 MPa for various compositions of the mixture. A correlation has been proposed, based on the experimental data, to predict the thermal conductivity of pure components and binary and ternary mixtures. The root-mean-square deviation is about 1.2%. The uncertainty of the measurement is estimated to be ±2%.

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