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The Thermal Conductivity of Binary Mixtures of Liquid R22 with R142b and R152a at Low Temperatures[1]

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The paper presents the thermal conductivity of mixtures of liquid refrigerants. The group of systems studied consists of two binary mixtures of R22/R142b and R22/R152a. The measurements have been carried out in the temperature range 160–300 K for pressures from 0.2 to 8.0 MPa in a transient coaxial-cylinder instrument. The uncertainty of the thermal conductivity data is estimated to be ±2%. The experimental method and apparatus were validated by using the measurements of refrigerant R22. The results presented have been used to develop a correlation for the description of the thermal conductivity of refrigerants.

KEY WORDS: binary mixtures; low temperatures; refrigerants; R22; R142b; R152a; thermal conductivity; transient method.

1. INTRODUCTION

Halogenated halocarbon mixtures have, in recent years, attracted wide attention as working fluids for cooling systems and heat pump applications. With respect to the current debate about the stratospheric ozone layer depletion, refrigerants R22, R142b, and R152a are often considered as acceptable working fluids. The nonazeotropic refrigerant mixtures of R22 with flammable refrigerants such as R142b and R152a will reduce the flammability of these substances.

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However, knowledge of the thermophysical properties of binary mixtures is rather limited, so experimental and theoretical investigations are very important. Application of refrigerant mixtures such as R22 + R142b and R22 + R152a requires detailed information about thermophysical properties such as density, viscosity, and thermal conductivity.

In this paper, absolute measurements of the thermal conductivity of two binary mixtures are reported in the range of 160–300 K at pressures to 8 MPa. To date, results were obtained for mixtures containing 37.7/62.3 mass% R22/R142b, 76.5/23.5 mass% R22/R142b, 26.9/73.1 mass% R22/R152a, and 71.7/28.3 mass% R22/R152a.

2. EXPERIMENTS

The measurements were performed with a transient coaxial-cylinder cell. The basic principle of the design and the apparatus were described in a previous paper [1]. The characteristics of this apparatus are listed in Table I.

The width of the test fluid layer is 0.265 mm. Heat is generated in the inner cylinder from a wire with a high electrical resistance. The temperature drop across the fluid layer between the inner and the outer cylinders is measured with thermocouples placed in bores drilled in the cylinders. The cell is placed into the vacuum chamber and the vacuum chamber is immersed in a Dewar filled with liquid nitrogen. Vacuum is created by means of a mechanical pump and a diffusion pump.

The cell was cooled to the temperature of the liquid nitrogen, and after high vacuum was obtained in the vacuum chamber, the cell was filled with the liquid refrigerant under study. The inner cylinder heater was switched on and the cell assembly began warming up slowly. During the heating period, the following measurements were taken: the amount of heat transferred through the fluid layer, Q; the temperature difference between the cylinders, ΔT; the heating rate, b; the pressure; and the temperature.

Table I. Characteristics of the Coaxial Cylinder Apparatus

	Outer cylinder	Inner cylinder
Material	Copper	Copper
Radius (mm)	$R = 14.323$	$R_0 = 13.793$
Length (mm)	$L = 130.00$	$L_0 = 95.01$

The thermal conductivity is calculated from the equation

$$\lambda = \frac{Q}{B \Delta T}(1 - \delta - \delta_0) \tag{1}$$

where B is the geometric constant defined by

$$B = \frac{2\pi L}{\ln(R/R_0)} \tag{2}$$

and where δ and δ_0 are heat capacity corrections of the liquid layer and of the inner cylinder, depending on the rate of heating. The heating rate did not exceed 0.01 $\mathrm{K \cdot s^{-1}}$. The power of the heater was less than 10 W, and the temperature difference between cyclinders was no more then 2–3 K. The uncertainty in Q, ΔT, and B was, respectively, within 0.1, 1.3, and 0.5% in the worst case. The possible error in determining the heat capacity corrections did not exeed 0.2%. The total uncertainty in λ was estimated to be 1.7–2.0%.

3. RESULTS

The thermal conductivity measurements were made with toluene at atmospheric pressure as a function of temperature and with liquid refrigerant R22 to check the performance of the instrument described. Toluene has been recommended by IUPAC as a liquid thermal-conductivity standard [2] and refrigerant R22 was chosen because a large number of accurate experimental data are available [3].

The measurements of the thermal conductivity of toluene at atmospheric pressure were 0.1589 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ at 180 K, 0.1581 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ at 190 K, 0.1575 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ at 200 K, and 0.1557 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ at 220 K, while the recommended values [4] are 0.1590, 0.1580, 0.1570, and 0.1530 $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$, respectively. The experimental values were corrected to nominal temperatures, with the corrections smaller than ±0.1%. The measurements of the thermal conductivity of R22 are listed in Table II and were performed near its saturation pressure.

The measured values are in agreement with previously published data, especially with those recommended by Vargaftik et al. [4]. The deviations between the values recommended in [4, 5] and the experimental data for R22 are well with the uncertainty of recommended data of ±(2–4)%.

The measurements were made on commercially available reserarch-grade toluene and refrigerants R22, R142b, and R152a. The R22 ($CHClF_2$) was specified 99.96% pure by the supplier. The R142b ($C_2H_3F_2Cl$) sample purity was certified to be 99.75%. The R152a ($C_2H_4F_2$) used was a

Table II. Experimental Data for the Thermal Conductivity of Refrigerant R22 at 0.9 MPa

T (K)	$10^4 \lambda$ ($\mathrm{W \cdot m^{-1} \cdot K^{-1}}$)
208.56	1222
212.43	1205
216.48	1187
220.23	1170
227.38	1138
235.31	1103
245.52	1058
255.38	1025
258.50	985
265.17	971
270.59	963
274.47	930
280.17	912
283.25	898
286.23	885
289.60	875

research-grade sample which has, according to the manufacturer, the State Institute of Applied Chemistry (GIPCh), a purity of at least 99.90%. The mixtures were made gravimetrically from the pure components R22, R142b, and R152a.

The thermal conductivity of the refrigerant R22 and the mixture of R22 + R142b at two different compositions, $\xi_{R22} = 37.7$ and 76.5%, was measured. ξ_{R22} represents the percentage mass fraction of the refrigerant R22.

The mixtures of R22 + R152a were measured at mass fractions $\xi_{R22} = 26.9$ and 71.7%. The experimental results of the thermal conductivity as a function of temperature for four refrigerant mixtures and for pure R142b and R152a are tabulated in Tables III–VIII.

The temperature dependence of the thermal conductivity near saturation pressure in the range 160–300 K is represented by

$$\lambda_s = a + bT + cT^2 + dT^3 \tag{3}$$

here λ_s is the thermal conductivity of the saturated liquid, and a, b, c, and d are fitting constants given in Table IX; λ_s is expressed in $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ and T in K. Figures 1 and 2 show plots of the deviation of the experimental

Table III. Experimental Data for the Thermal Conductivity of Mixtures of R22 and R142b (Mass Fraction $\xi_{R22} = 0.377$)

T (K)	P (MPa)	$10^4 \lambda$ $(W \cdot m^{-1} \cdot K^{-1})$
179.19	2.70	1276
202.70	2.91	1168
219.13	7.00	1124
228.19	6.98	1091
240.89	7.19	1063
261.05	2.87	964
274.52	6.57	938
284.32	6.76	901

Table IV. Experimental Data for the Thermal Conductivity of Mixtures of R22 and R142b (Mass Fraction $\xi_{R22} = 0.765$)

T (K)	P (MPa)	$10^4 \lambda$ $(W \cdot m^{-1} \cdot K^{-1})$
164.77	6.25	1422
189.41	8.14	1310
210.90	8.09	1179
230.31	8.14	1135
251.68	8.12	1059
261.02	3.88	984
280.43	4.04	911
295.76	4.22	854

Table V. Experimental Data for the Thermal Conductivity of Mixtures of R22 and R152a (Mass Fraction $\xi_{R22} = 0.269$)

T (K)	P (MPa)	$10^4 \lambda$ $(W \cdot m^{-1} \cdot K^{-1})$
176.60	5.22	1512
190.72	3.62	1445
209.11	3.11	1351
222.70	2.70	1302
259.05	2.44	1163
281.63	2.84	1025
289.91	2.82	990

Table VI. Experimental Data for the Thermal Conductivity of Mixtures of R22 and R152a (Mass Fraction $\xi_{R22} = 0.717$)

T (K)	P (MPa)	$10^4 \lambda$ ($W \cdot m^{-1} \cdot K^{-1}$)
218.08	7.80	1257
230.96	8.02	1211
259.11	7.96	1106
274.44	7.08	1009
289.50	7.58	939
297.45	7.76	916

Table VII. The Thermal Conductivity of R142b

T (K)	P (MPa)	$10^4 \lambda$ ($W \cdot m^{-1} \cdot K^{-1}$)
210.40	4.31	1164
223.14	6.46	1121
235.43	7.22	1083
243.74	7.30	1046
259.29	7.59	995
270.83	7.24	944
289.55	7.51	872

Table VIII. The Thermal Conductivity of R152a

T (K)	P (MPa)	$10^4 \lambda$ ($W \cdot m^{-1} \cdot K^{-1}$)
189.61	7.71	1590
203.45	8.19	1526
212.50	8.19	1484
221.12	7.72	1446
231.04	7.88	1396
241.71	8.55	1349
253.08	8.08	1290
260.28	8.07	1264
270.72	8.09	1216
280.84	7.87	1162
299.83	7.89	1076

Table IX. Constants for Eq. (3)

Refrigerant	Constant			
	a	$10^4 b$	$10^9 c$	$10^9 d$
R22	0.254060	−9.856998	2338.213	−3.1935423
R142b	0.196987	−3.923461	7.169691	—
R152a	0.210057	−1.514409	−712.0839	—

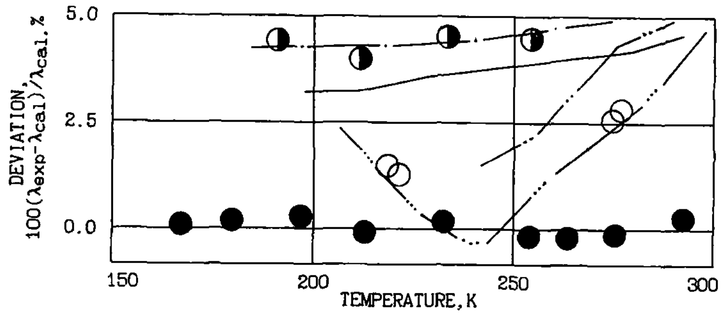

Fig. 1. Deviations of calculated data [Eq. (3)] from the experimental and recommended thermal conductivity values of R142b near the saturation pressure. (●) Present work; (○) Ref. 7; (◑) Ref. 8; (——) Ref. 9; (—·—) Ref. 4; (—··—) Ref. 10; (—···—) Ref. 11.

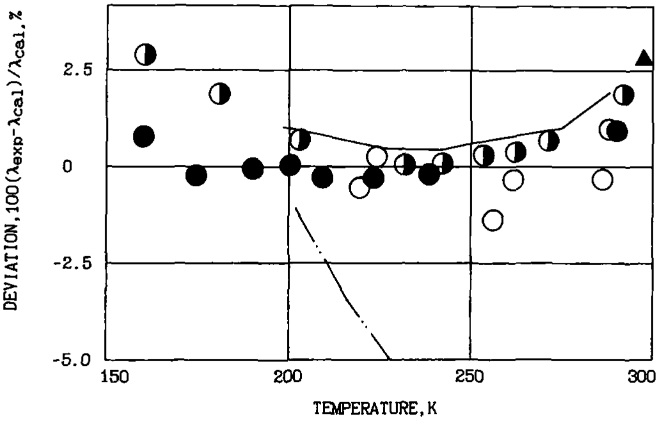

Fig. 2. Deviations of the experimental thermal conductivity values of R152a near the saturation pressure from Eq. (3). (●) Present work; (○) Ref. 7; (▲) Ref. 12; (◑) Ref. 13; (——) Ref. 9; (—··—) Ref. 11.

results and values proposed by the compilations from the values obtained by Eq. (3).

The isothermal thermal conductivity for liquid refrigerants up to elevated pressures is represented by the following equation [3]:

$$\lambda = \lambda_s + K_p(P - P_s) \tag{4}$$

with P in MPa and λ in $W \cdot m^{-1} \cdot K^{-1}$, where the subscript s refers to the saturation pressure, and K_p is a parameter whose value is derived from the fit. K_p values obtained from our measurements are represented by the relation

$$10^4 K_p = \alpha_0 + \alpha_1 \tau + \alpha_2 \tau^2 \tag{5}$$

with $\alpha_0 = 6.025$, $\alpha_1 = -13.398$, and $\alpha_2 = 17.771$. Here τ is the temperature divided by the critical temperature. By using Eqs. (3)–(5) the experimental results for R22, R142b, and R152a can be corrected with an average deviation of 0.6% and a maximum deviation of almost 2.5%, the latter only for one point for refrigerant R152a at 299.83 K and 7.89 MPa. The values used for the critical-point temperature are $T_c = 369.28$ K for R22 [14], $T_c = 410.25$ K for R142b [10], and $T_c = 386.33$ for R152a [15].

For estimating the thermal conductivity of liquid mixtures, a number of correlations are reported in the literature. Several empirical equations have been proposed for binary solutions [3]. Some of them are of a purely empirical nature, whereas others are based on theoretical assumptions. The thermal conductivity of binary mixtures can be estimated by an equation proposed by Filippov [16] for aqueous solutions,

$$\lambda = \lambda_1 \xi_1 + \lambda_2 \xi_2 - \alpha \, |\lambda_1 - \lambda_2| \, \xi_1 \xi_2 \tag{6}$$

where λ is the thermal conductivity of binary mixture, λ_1 and λ_2 are the thermal conductivities, and ξ_1 and ξ_2 are the mass fractions of the components. According to Eq. (6), α is a coefficient which is assumed to be a constant.

A modified Filippov-type equation was proposed by Yata et al. [6]:

$$\lambda = \lambda_1 \xi_1 + \lambda_2 \xi_2 - \alpha(\lambda_1 - \lambda_2) \, \xi_1 \xi_2 (\xi_2 - \varkappa) \tag{7}$$

where α is a function of temperature and $\varkappa$ is a constant. This type gave better results over a wide temperature range for aqueous solution.

An empirical equation we proposed earlier for R22 + R13B1 and R22 + R115 liquid mixtures [3] is

$$\lambda = (\lambda_1 \xi_1 + \lambda_2 \xi_2)(1 - \beta \xi_1 \xi_2) \tag{8}$$

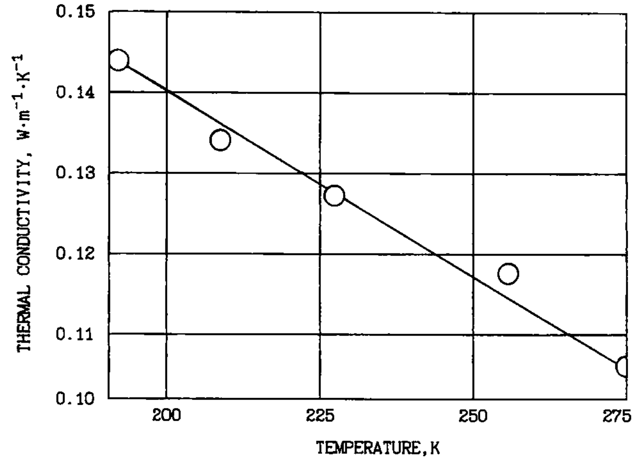

Fig. 3. Measured temperature dependence of the thermal coductivity of the mixture R22/R152a for a concentration $\xi_{R22} = 0.269$ and a pressure 3.0 MPa. (O) Present work; (——) Eq. (8).

The thermal conductivities of R22 + R142b and R22 + R152a have been fitted by Eq. (8). Just as for R22 + R13B1 and R22 + R115 mixtures, we obtained $\beta = 0.20$. A deviation plot of experimental values for binary mixtures of R22 + R152a from Eq. (8) is shown in Fig. 3. It is shown in Fig. 3 that the present results are in agreement with Eq. (8). Equation (8) can by used for the mixtures in this study with an uncertainty of the order of 3%.

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