THERMAL CONDUCTIVITY AND DENSITY OF ETHERS

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The results of experimental investigation of the thermal conductivity and density of liquid ethers (diethyl-, diallyl-, dipropyl-, dibutyl-, diheptyl-, and dioctyl-) in the ranges of temperatures from 290.6 to 723.2 K and pressures (0.98-981) $\cdot 10^5$ Pa are given as well as equations establishing the relationship between the thermal conductivity of liquid ethers and their density at different temperatures and pressures.

Previously, the thermal conductivity and density of liquid ethers were studied only at atmospheric pressures [1, 2]. Our data coincide with the data of [1, 2] within the accuracy of the experiment.

The densities of liquid ethers were measured by the method of hydrostatic weighing [3], whereas their thermal conductivities were found using the cylindrical regular thermal regime bicalorimeter method [4]. The densities of liquid ethers were investigated within the ranges of temperatures from 293.2 to 583.4 K and pressures (0.98-981) $\cdot 10^5$ Pa and were measured from isotherms with a temperature step of 25 K and a pressure step of (49-98) $\cdot 10^5$ Pa. At given pressures and temperatures, the density measurements were conducted 2 or 3 times, with reproducibility not exceeding 0.02%. The deviation of test points from the fitted curves is also not over 0.02%. The general relative error of the density measurements is not in excess of 0.1%.

In Fig. 1 the density isotherms of liquid diethyl ether are given, from which it is seen that the density increases with pressure and decreases with the rise in temperature.

The thermal conductivity of liquid ethers was measured by the regular thermal regime cylindrical bicalorimeter method from isotherms within the ranges of temperatures 292-723.2 K and pressures (0.98-490) $\cdot 10^5$ Pa. In the thermal conductivity measurements the studied layer thickness was 0.55 mm. The temperature drop at the boundary of the studied layer varied from 1.31 to 0.65 K.

The thickness of the layer studied and the magnitude of the temperature difference at its boundary were selected in such a way as to exclude convective heat transfer in experiments. Within the entire region of temperatures and pressures, the product GrPr was smaller than 1000. The absence of convection was also checked by measuring the thermal conductivity coefficient at various temperature differences at the boundaries of the studied layer. The identical results obtained confirmed the absence of convection in the experiments. The general relative error of thermal conductivity measurements amounted to 4.2%.

Experimental data on the thermal conductivity of liquid diamyl ether are listed in Table 1. According to the table, the thermal conductivity of liquid ethers increases with pressure linearly, whereas it decreases with rise in temperature.

As the temperature grows, the influence of pressure on the thermal conductivity of liquid ethers increases. For example, when a pressure change from $0.98 \cdot 10^5$ to $490 \cdot 10^5$ Pa at a temperature of 293 K increases the thermal conductivity of dipropyl ether by 20%, then at a temperature of 669.2 K this change comprises 53.7%.

In order to establish the interrelation between the thermal conductivity and density of liquid ethers at atmospheric pressure and different temperatures, we used the following functional relation

$$\frac{\lambda}{\lambda_1} = f\left(\frac{\rho}{\rho_1}\right), \tag{1}$$

where λ and λ_1 are the thermal conductivities of liquid ethers at temperatures T and T_1; ρ and ρ_1 are the densities of these ethers at temperatures T and T_1; $T_1 = 293$ K.

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TABLE 1. Thermal Conductivity ($\lambda \cdot 10^3$, W/(m·K)) of Diamyl Ether at Various Temperatures and Pressures

T, K	P, 10^5 Pa					
	0,98	98	196	294	392	490
291,5	130	134	142	147	150	152
331,2	124	131	137	140	145	150
375,6	112	118	131	138	141	144
414,5	103	108	123	129	132	136
454,5	98	103	116	123	126	134
494,2		93	109	116	120	129
538,2		86	102	108	112	125
574,9		80	98	104	108	114
588,2		79	96	99	104	109
608,2		78	94	97	102	107
620,5		76	92	95	100	105
648,3		74	90	92	98	103
668,2		72	88	90	96	101

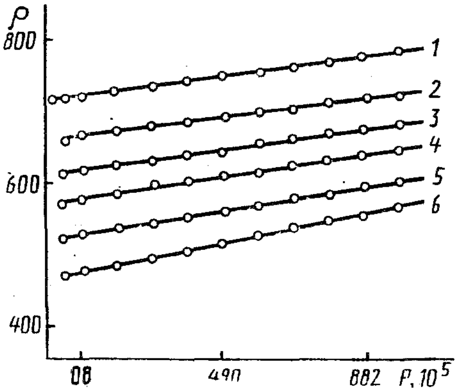

Fig. 1

Fig. 1. Diethyl ether density vs pressure at temperature T, K: 1) 296.7; 2) 368.4; 3) 416.2; 4) 462.2; 5) 516.4; 6) 561.3. ρ, kg/m^3; P, 10^5 Pa.

The validity of Eq. (1) is demonstrated in Fig. 2 from which it is seen that experimental data fall well along a common straight line. The equation of this straight line has the form

$$\lambda = \left(1{,}5\frac{\rho}{\rho_1} - 0{,}5\right)\lambda_1. \tag{2}$$

Given experimental values for the density of ethers as a function of temperature, we can calculate the temperature dependence of the thermal conductivity of liquid ethers at atmospheric pressure from Eq. (2) with an error of 2-3% if the value of λ_1 is known.

It would be of interest to relate λ_1 in Eq. (2) to the molecular mass μ and to the number of atoms of carbon in an ether molecule n. For the liquid ethers studied the dependence of λ_1 on μ and n is described by the equations

$$\lambda_1 = [2{,}22\cdot 10^{-2}(\ln\mu)^2 + 0{,}102\ln\mu + 0{,}243],\ \mathrm{W/(m\cdot K)}, \tag{3}$$

$$\lambda_1 = -3{,}63\cdot 10^{-5}\,n^2 - 8{,}83\cdot 10^{-2}n + 0{,}133,\ \mathrm{W/(m\cdot K)}. \tag{4}$$

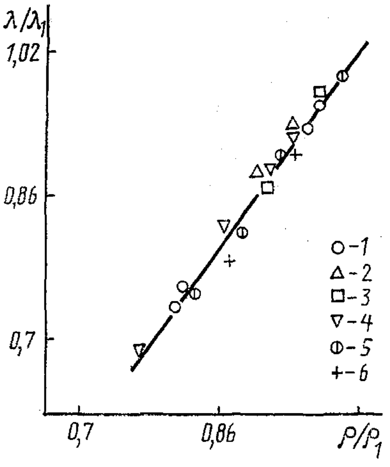

Fig. 2

Fig. 2. Relation $\lambda/\lambda_1 = f(\rho/\rho_1)$ for liquid ethers at atmospheric pressure: 1) diethyl; 2) dipropyl; 3) diamyl; 4) dioctyl; 5) dihexyl; 6) dibutyl.

Equations (2)-(4) yield

$$\lambda = (1{,}5\rho/\rho_1 - 0{,}5)\,[2{,}22\cdot 10^{-2}(\ln\mu)^2 + 0{,}102\ln\mu + 0{,}243],\ \mathrm{W/(m\cdot K)}, \tag{5}$$

$$\lambda = (1{,}5\,\rho/\rho_1 - 0{,}5)\,(-3{,}63\cdot 10^{-5}n^2 - 8{,}83\cdot 10^{-2}n + 0{,}133),\ \mathrm{W/(m\cdot K)}. \tag{6}$$

Knowing the molar mass μ, the number of carbon atoms n and the temperature dependence of density, it is possible to calculate the thermal conductivity at atmospheric pressure for ethers not investigated experimentally from Eqs. (5) and (6) with an error of 2-4%.

To establish the interrelation between the thermal conductivity and density of liquid ethers at high state parameters on the basis of the thermodynamic similarity theory, the following functional relation was used:

$$\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\Big/\left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1 = f\left[\frac{\rho_{P,T}}{\rho_{P_1,T_1}}\Big/\left(\frac{\rho_{P,T}}{\rho_{P_1,T_1}}\right)_1\right], \tag{7}$$

where $\lambda_{P,T}$ is the thermal conductivity at pressure P and temperature T; λ_{P_1,T_1} is the thermal conductivity at pressure P_1 and temperature T_1; $(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ the values of $\lambda_{P,T}/\lambda_{P_1,T_1}$ for $(\rho_{P,T}\rho_{P_1,T_1})$; $(\rho_{P,T}/\rho_{P_1,T_1}) = 1.15$; $P_1 = 98\cdot 10^5$ Pa and $T_1 = 473$ K.

The validity of Eq. (7) for all of the studied ethers is shown in Fig. 3, from which it is seen that experimental points lie well along the common curve. The equation of this curve has the form

$$\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\Big/\left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1 = 2{,}7\left\{\frac{\left(\dfrac{\rho_{P,T}}{\rho_{P_1,T_1}}\right)}{\left(\dfrac{\rho_{P,T}}{\rho_{P_1,T_1}}\right)_1}\right\} - 4{,}5\left\{\frac{\left(\dfrac{\rho_{P,T}}{\rho_{P_1,T_1}}\right)}{\left(\dfrac{\rho_{P,T}}{\rho_{P_1,T_1}}\right)_1}\right\} + 2{,}58. \tag{8}$$

Using Eq. (8) one can calculate the thermal conductivity $\lambda_{P,T}$ of liquid ethers as a function of density $\rho_{P,T}$, if the values of λ_{P_1,T_1}, ρ_{P_1,T_1}, and $(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ are known.

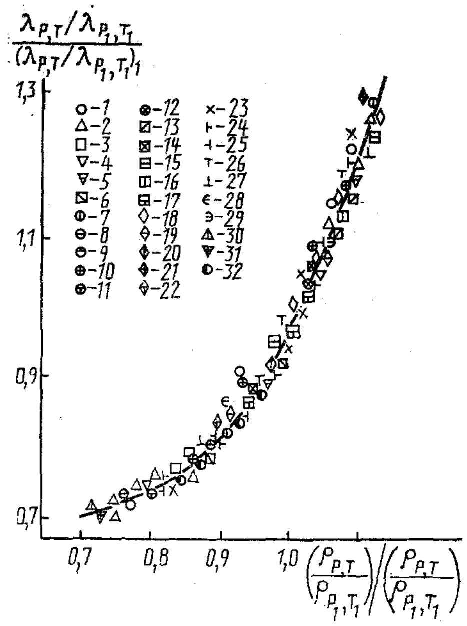

Fig. 3. The relation $(\lambda_{P,T}/\lambda_{P_1,T_1})/(\lambda_{P,T}/\lambda_{P_1,T_1})_1 = f[(\rho_{P,T}/\rho_{P_1,T_1})/(\rho_{P,T}/\rho_{P_1,T_1})_1]$ for liquid ethers: diethyl (1-6), dipropyl (7-12), diallyl (13-17), dihexyl (18-22), dioctyl (23-27), dibuthyl (28-32).

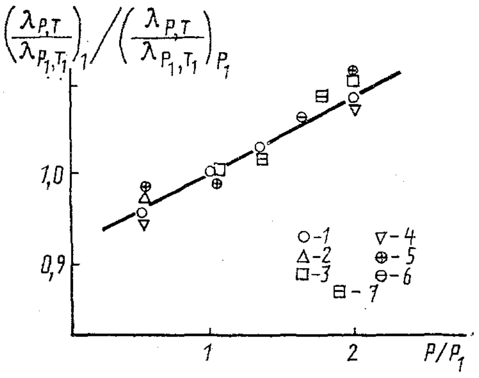

Fig. 4. Dependence of $(\lambda_{P,T}/\lambda_{P_1,T_1})_1/(\lambda_{P,T}/\lambda_{P_1,T_1})_{P_1}$ on P/P_1 for liquid ethers: 1) diethyl; 2) dipropyl; 3) dibuthyl; 4) diamyl; 5) dihexyl; 6) diheptyl; 7) dioctyl.

Examination of the dependence of $(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ on pressure has shown that experimental data for some ethers fall on different straight lines. To obtain a single straight line for all ethers, the experimental data were processed in the form of the following functional relation

$$\left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1 \Bigg/ \left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_{P_1} = f\left(\frac{P}{P_1}\right), \tag{9}$$

where $(\lambda_{P,T}/\lambda_{P_1,T_1})_1$ are the values of $(\lambda_{P,T}/\lambda_{P_1,T_1})_{P_1}$ at a pressure P_1; $P_1 = 196 \cdot 10^5$ Pa.

The validity of functional relation (9) is shown in Fig. 4 which shows experimental data for seven ethers lying, with minor deviations, along a common straight line which is described by the equation

$$\frac{\left(\dfrac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1}{\left(\dfrac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_{P_1}} = 0{,}036\,\frac{P}{P_1} + 0{,}95. \tag{10}$$

TABLE 2. Calculated Values of the Thermal Conductivity ($\lambda \cdot 10^3$ W/(m·K)) of Ethers at Different Temperatures and Pressures

Diethyl		Diallyl		Dipropyl		Dibuthyl		Diamyl		Dioctyl	
T, K	λ	T, K	λ	T, K	λ	T, K	λ	T, K	λ	T, K	λ
$P=58,86$ MPa		$P=58,86$ MPa		$P=58,86$ MPa		$P=58,86$ MPa		$P=58,86$ MPa		$P=58,86$ MPa	
296,7	154	291,7	164	294,3	166	294,6	167	296,6	169	293,2	170
416,2	115	365,02	134	401,8	130	400,9	135	392,2	142	364,7	144
516,4	91	475,2	107	501,3	109	497,2	117	466,3	119	471,2	127
		552,3	95			594,7	93	561,8	100	583,4	119
$P=78,48$ MPa		$P=78,48$ MPa		$P=78,48$ MPa		$P=78,48$ MPa		$P=78,48$ MPa		$P=78,48$ MPa	
296,7	164	291,7	176	294,3	177	294,6	178	296,6	179	293,2	175
416,2	117	365,02	149	401,8	141	400,9	146	392,2	149	364,7	164
516,4	93	475,2	118	501,3	115	497,2	126	456,3	136	471,2	136
		552,3	99			594,7	109	561,8	113	583,4	126
$P=98,1$ MPa		$P=98,1$ MPa		$P=98,1$ MPa		$P=98,1$ MPa		$P=98,1$ MPa		$P=98,1$ MPa	
296,7	175	291,7	181	294,3	180	294,6	186	236,6	189	293,2	180
416,2	128	365,02	153	401,8	145	400,9	157	392,2	162	364,7	167
516,4	100	475,2	122	501,4	120	497,2	134	456,3	144	471,2	154
		552,3	116			594,6	119	561,8	127	583,4	135

We shall write down the dependence of $(\lambda_{P,T}/\lambda_{P_1,T_1})_{P_1}$ of the studied ethers on the molar mass as

$$\left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_{P_1} = 0{,}4\mu + 1{,}3. \tag{11}$$

Equations (10) and (11) yield

$$\left(\frac{\lambda_{P,T}}{\lambda_{P_1,T_1}}\right)_1 = (1{,}82 \cdot 10^{-9}P + 0{,}95)(0{,}4\mu + 1{,}3). \tag{12}$$

For the ethers studied the dependence of λ_{P_1,T_1} and ρ_{P_1,T_1} on the molar mass μ is described by the equations:

$$\lambda_{P_1,T_1} = 0{,}173\mu^2 + 9{,}3 \cdot 10^{-2}\mu + 7{,}37 \cdot 10^{-2}, \quad \mathrm{W/(m{\cdot}K)}, \tag{13}$$

$$\rho_{P_1,T_1} = 803{,}6\mu + 511{,}6, \quad \mathrm{kg/m^3}. \tag{14}$$

Substituting Eqs. (12)-(14) into Eq. (8) to calculate the thermal conductivity of liquid ethers as a function of temperature and pressure, we obtain

$$\begin{aligned}\lambda_{P,T} = \Bigg\{\Bigg[2{,}7\left(\frac{\rho_{P,T}}{803{,}6\mu + 511{,}6}\right)^2 - 4{,}5\left(\frac{\rho_{P,T}}{803{,}6\mu + 511{,}6}\right) + 2{,}58\Bigg] \times \\ \times (1{,}82 \cdot 10^{-9}P + 0{,}95)(0{,}4\mu + 1{,}3)(0{,}173\mu^2 + 9{,}3 \cdot 10^{-2}\mu + 7{,}73 \times \\ \times 10^{-2}), \quad \mathrm{W/(m{\cdot}K)}.\end{aligned} \tag{15}$$

Equation (15) establishes the relation of the thermal conductivity to the density of liquid ethers at different temperatures and pressures and also to the molar mass of the studied ethers. With the available experimental values for the density of liquid ethers at different temperatures and pressures, this equation can be used to calculate their thermal conductivity as a function of temperature and pressure. The checking of the equation has shown that the error in the calculated values of the thermal conductivity within the ranges of temperatures 293-723 K and pressures (0.98-981)·10^5 Pa does not exceed 6%.

Using the experimental data on density and Eq. (15), we have calculated the thermal conductivity of diethyl-, diallyl-, dipropyl-, dibuthyl-, diamyl-, dehexyl-, dioctyl ethers in the temperature range 293-723 K up to the pressure of $981 \cdot 10^5$ Pa (Table 2).

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