AN EXPERIMENTAL INVESTIGATION OF THE THERMAL CONDUCTIVITIES OF ESTERS OF CARBOXYLIC ACIDS

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Inzhenerno-Fizicheskii Zhurnal, Vol. 13, No. 2, pp. 177–183, 1967

UDC 536.2

This paper gives the results of an experimental investigation of the thermal conductivities of a homologous series of esters of saturated monobasic acids. Equations for calculating the thermal conductivity of liquids in relation to temperature and composition are presented.

The esters of carboxylic acids can be regarded as products of replacement of hydrogen in the carboxyl group $\mathrm{R-C}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OH}\end{smallmatrix}$ by a hydrocarbon radical R'. Hence, the chemical formula of the esters can be put in the form $\mathrm{R-C}\begin{smallmatrix}\nearrow \mathrm{O}\\ \searrow \mathrm{OR'}\end{smallmatrix}$.

It was found in [1–2] that in homologous series of saturated hydrocarbons nC_nH_{2n+2} and normal alcohols $nC_nH_{2n+1}OH$ the thermal conductivity is affected by the number of CH_2 groups in the hydrocarbon radical R.

As distinct from them, in a homologous series of esters the composition of the substance depends not only on the change in R, but also in the hydrocarbon radical R'. As a result, esters $C_nH_{2n+1}COOC_nH_{2n+1}$ with the same number of carbon atoms in the molecule may be derivatives of different saturated monobasic acids.

Hence, it is of definite interest to investigate the effect of the composition of R and R' on the thermal conductivity of the corresponding esters and to determine how these coefficients vary with the composition and temperature.

The thermal conductivities of some representatives of a homologous series of carboxylic acid esters have been investigated by several authors [3–6]. The measurements, however, were restricted to compounds of low molecular weight (mainly esters of formic and acetic acids) and covered a small range of temperatures. In addition, the measurements were made by different methods and differed in accuracy.

We measured the thermal conductivities of esters of various saturated acids in a wide temperature range, including regions close to the melting and boiling points. For this purpose we selected chemically pure reagents with the number of carbon atoms in the molecule n = 2–22. Measurements were made by the hot-wire method with a maximum error of 1.5%. A full description of the apparatus was given in [1].

The results of experiments on 21 esters are given in Table 1 and those for esters of formic acid and methyl esters of carboxylic acids are given in Fig. 1a, b.

Measurements made for various temperature drops (4–10° C) in the layer of investigated liquid showed good agreement. The deviation of the experimental results from the averaging straight lines was less than 1%, which lies with the limits of experimental error.

To compare the results of our measurements with the data of other authors (Table 2) we took the values of the thermal conductivities (λ_{30}) given in [3]. These values were obtained by averaging the experimental data of various authors with allowance for the error of measurement. For comparison we took substances for which there were data of at least two authors.

As Table 2 shows, the deviations of our measurements from the corresponding mean values of the thermal conductivities did not exceed 2%. The results of our measurements of the thermal conductivities of a homologous series of esters enabled us to determine the nature of the variation of λ with temperature. As Fig. 1a, b and Table 1 show, the thermal conductivities of all the considered esters decreased with increase of temperature.

It was found in [1, 2] that for a homologous series of saturated hydrocarbons, individual representatives of aromatic, halide-substituted, and other normal liquids the temperature coefficient α decreases with increase in molecular weight.

A similar picture was observed in the case of esters (Fig. 2). The temperature coefficient α depended only on the number of carbon atoms in the molecule of the substance. In other words, among the investigated compounds different esters of different monobasic acids with the same molecular weight have the same value of α. For substances with n = 2–10 carbon atoms in the molecule, α can be determined from the following relationship:

$$\alpha \cdot 10^3 = 2.12 - 0.127(n-2). \qquad (1)$$

For esters with n = 11–22 the value of α can be assumed constant and $\approx 1 \cdot 10^{-3}$ 1/deg.

Figure 2 also gives the values of α from [3] for calculation of the temperature dependence of the thermal conductivities of some esters. It is easy to see that the temperature coefficients of the propyl and butyl esters of formic acid, and of the ethyl, butyl, and amyl esters of acetic acid are close to the results which we obtained. For the methyl and ethyl esters of formic acid, however, α differs considerably. The value of α for the methyl ester of formic acid is about 1/3 of the corresponding value of the temperature coefficient for the ethyl ester of the same acid, which is unlikely. This can probably be attributed to the fact that measurement of λ of these substances in [3] were carried out in a narrow temperature range, which does not allow an accurate determination of α.

Table 1

Experimental Values of Thermal Conductivities of Carboxylic Acid Esters

t, °C	λ, $\frac{\text{W}}{\text{m}\cdot\text{deg}}$	t, °C	λ, $\frac{\text{W}}{\text{m}\cdot\text{deg}}$	t, °C	λ, $\frac{\text{W}}{\text{m}\cdot\text{deg}}$	t, °C	λ, $\frac{\text{W}}{\text{m}\cdot\text{deg}}$
1. Methyl ester of formic acid		2. Methyl ester of acetic acid		3. Methyl ester of propionic acid		4. Methyl ester of valeric acid	
2.7	0.1926	3.9	0.1635	4.3	0.1509	4.7	0.1423
5.7	0.1923	6.1	0.1628	5.5	0.1506	7.4	0.1418
7.5	0.1914	8.2	0.1622	9.0	0.1503	9.9	0.1413
24.2	0.1845	29.5	0.1546	26.2	0.1451	27.1	0.1372
27.4	0.1832	32.3	0.1535	29.0	0.1442	28.6	0.1371
28.8	0.1822	34.5	0.1533	31.7	0.1431	67.6	0.1286
		43.4	0.1505	63.7	0.1343	68.6	0.1280
				65.5	0.1331	100.9	0.1207
				67.8	0.1323		
5. Methyl ester of caproic acid		6. Methyl ester of stearic acid		7. Ethyl ester of formic acid		8. n-Propyl ester of formic acid	
4.7	0.1402	55.5	0.1512	4.2	0.1661	5.2	0.1506
6.0	0.1393	58.0	0.1505	6.2	0.1652	7.7	0.1502
7.3	0.1396	60.3	0.1497	8.6	0.1640	9.6	0.1493
27.0	0.1367	107.4	0.1433	26.6	0.1584	25.2	0.1456
28.3	0.1361	110.3	0.1430	28.1	0.1579	28.3	0.1440
29.8	0.1358	173.9	0.1336	32.1	0.1568	31.1	0.1433
112.6	0.1186	175.8	0.1325	47.9	0.1519	73.8	0.1313
114.4	0.1177	177.6	0.1315			74.9	0.1312
9. n-Butyl ester of formic acid		10. n-Amyl ester of formic acid		11. n-Heptyl ester of formic acid		12. n-Octyl ester of formic acid	
5.2	0.1454	5.1	0.1421	4.4	0.1409	5.5	0.1433
7.6	0.1444	7.6	0.1413	7.1	0.1407	8.9	0.1423
10.1	0.1437	10.3	0.1414	9.6	0.1402	11.0	0.1421
25.8	0.1402	32.0	0.1367	26.7	0.1367	105.7	0.1265
28.7	0.1400	33.3	0.1363	28.0	0.1366	108.8	0.1252
80.4	0.1286	104.9	0.1220	112.7	0.1221	165.3	0.1172
84.1	0.1268	106.7	0.1212	114.2	0.1209	167.4	0.1169
93.4	0.1262	108.5	0.1203	116.1	0.1204		
93.9	0.1256			145.5	0.1164		
				147.7	0.1151		
13. Ethyl ester of acetic acid		14. Ethyl ester of butyric acid		15. Ethyl ester of caproic acid		16. n-Hexyl ester of acetic acid	
6.2	0.1500	4.3	0.1412	4.8	0.1412	4.6	0.1414
7.4	0.1495	6.7	0.1405	7.4	0.1411	5.8	0.1406
26.9	0.1444	24.9	0.1366	9.9	0.1408	7.2	0.1403
28.1	0.1440	27.8	0.1358	34.6	0.1351	42.1	0.1337
29.4	0.1437	79.3	0.1244	37.4	0.1354	44.8	0.1328
57.0	0.1349	80.6	0.1238	40.2	0.1337	124.3	0.1184
60.1	0.1340			112.9	0.1208	125.6	0.1183
				115.8	0.1199	126.9	0.1178
				140.7	0.1152		

Table 1 (cont'd)

t, °C	λ, $\frac{W}{m \cdot deg}$	t, °C	λ, $\frac{W}{m \cdot deg}$	t, °C	λ, $\frac{W}{m \cdot deg}$	t, °C	λ, $\frac{W}{m \cdot deg}$
17 n-Butyl ester of propionic acid		18. n-Butyl ester of palmitic acid		19. n-Butyl ester of stearic acid		20. n-Hexyl ester of propionic acid	
4.6	0.1397	23.3	0.1523	43.4	0.1535	5.1	0.1396
7.2	0.1388	26.1	0.1514	43.9	0.1540	6.5	0.1392
9.6	0.1387	66.5	0.1451	44.9	0.1537	7.9	0.1390
41.6	0.1319	70.5	0.1443	90.6	0.1467	10.6	0.1389
43.9	0.1314	116.2	0.1377	91.3	0.1461	37.3	0.1347
67.5	0.1270	117.7	0.1370	120.0	0.1426	38.5	0.1342
70.9	0.1261	119.3	0.1361	121.5	0.1419	39.5	0.1339
114.5	0.1170	168.5	0.1291	123.9	0.1412	116.2	0.1209
116.2	0.1163	171.3	0.1291	167.3	0.1349	117.7	0.1212
				169.2	0.1337	119.5	0.1207
				171.4	0.1332	157.4	0.1146
				178.1	0.1326	159.2	0.1143
				179.9	0.1316		

21. n-Amyl ester of butyric acid

t, °C	λ, $\frac{W}{m \cdot deg}$	t, °C	λ, $\frac{W}{m \cdot deg}$
4.4	0.1430	24.6	0.1391
6.1	0.1425	25.9	0.1386
7.5	0.1426	114.4	0.1228
10.0	0.1416	115.9	0.1222
23.3	0.1395	117.7	0.1221

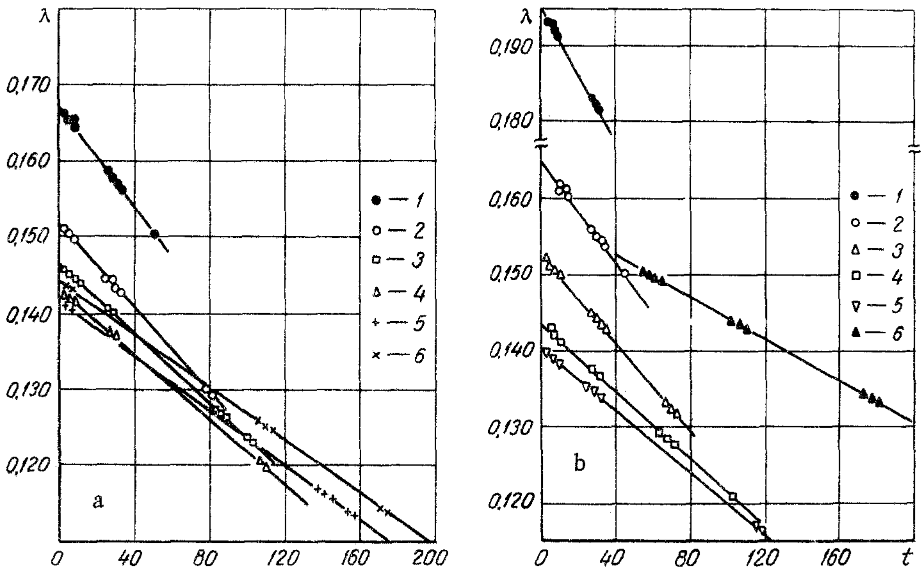

Fig. 1. Results of measurements of thermal conductivity (λ, W/m · deg; t, °C). a) Esters of formic acid: 1) ethyl; 2) propyl; 3) n-butyl; 4) n-amyl; 5) n-heptyl; 6) n-octyl. b) methyl esters of: 1) formic; 2) acetic; 3) propionic; 4) valeric; 5) caproic; 6) stearic acids.

Table 2

Comparison of Our Measurements with Data of Other Authors

Esters	Reference	Thermal conductivity λ^*_{30}, W/m · deg at t = 30° C	Reliability of λ^*_{30}, according to [3], % at t = 30° C	Our measurements of λ^*_{30}, W/m · deg at t = 30° C	$\frac{\lambda^*_{30}-\lambda_{30}}{\lambda_{30}}$, %
Ethyl ester of formic acid	[3.5]	0.1606	1.7	0.1572	+2.1
Propyl ester of formic acid	[3.5]	0.1454	1.7	0.1436	+1.2
Methyl ester of acetic acid	[5.6]	0.1570	1.6	0.1545	+1.6
Ethyl ester of acetic acid	[3,4,5,6]	0.1436	1.5	0.1432	+0.3

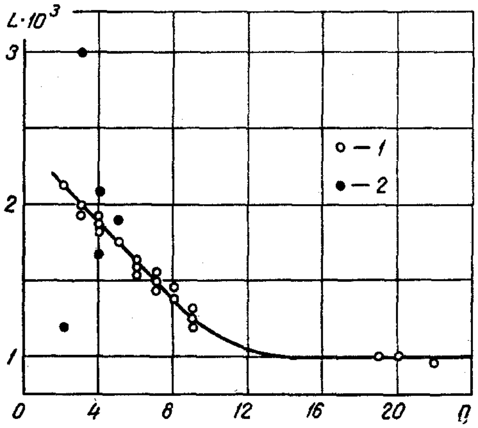

Fig. 2. Change in temperature coefficient α in relation to number n of carbon atoms in molecule of esters: 1) This work; 2) data of [3].

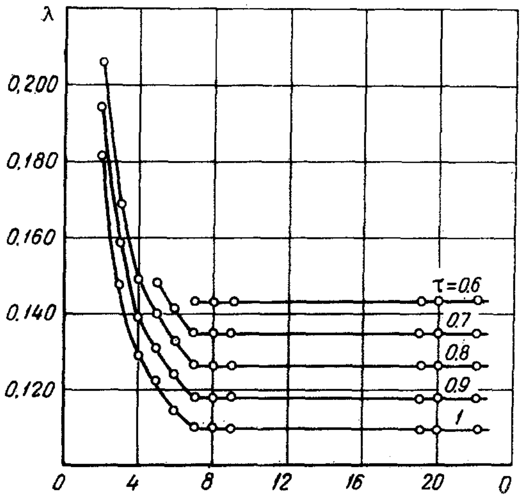

Fig. 3. Thermal conductivities at reduced temperatures τ in relation to number n of carbon atoms in molecule of esters.

Table 3

Comparison of Experimental and Calculated Data

Equations	Ethyl ester of acetic acid				Methyl ester of acetic acid			
	t, °C	λ_{exp}	λ_{calc}	$\frac{\lambda_{calc}-\lambda_{exp}}{\lambda_{exp}}$, %	t, °C	λ_{exp}	λ_{calc}	$\frac{\lambda_{calc}-\lambda_{exp}}{\lambda_{exp}}$, %
Weber [5]	40	0.1402	0.1312	—6.4	20	0.1582	0.1523	—3.7
	60	0.1346	0.1288	—4.3				
Smith [7]	40	0.1402	0.1565	+11.6	20	0.1582	0.1816	+14.8
	60	0.1346	0.1540	+5.8				
Palmer [8]	40	0.1402	0.1544	+10.7	20	0.1582	0.1739	+9.9
	60	0.1346	0.1529	+13.2				
Sakiadis and Coates [9]	40	0.1402	0.1489	+6.1	20	0.1582	0.1733	+9.6
	60	0.1346	0.1472	+9.0				

Table 4

Comparison of Experimental and Calculated Data

Equation	t, °C	λ_{exp}	λ_{calc}	$\frac{\lambda_{calc}-\lambda_{exp}}{\lambda_{exp}}$, %
$\lambda=\lambda_{S_1}\left[1.75-0.75\frac{S}{S_1}\right]$	20	0.1462	0.1462	—
	40	0.1402	0.1408	+0.4
	60	0.1346	0.1356	+0.7

Several equations have been proposed for calculation of the thermal conductivities of liquids [5, 7–9]. It is difficult to use them, however, since they require a knowledge of various thermophysical properties which are not available for most substances. In addition, these equations often give results which differ considerably from the experimental values. As was shown in [10], the average deviations are usually 15%, and for individual substances 50%. We found that the least deviations from the equations were obtained in the determination of the thermal conductivities of esters.

For comparison Table 3 gives our experimental data for methyl and ethyl esters of acetic acid and those calculated with the equations from [5, 7–9].

The table shows that for esters the deviations reach 10–15%. This is probably due to the fact that the indicated methods do not have a reliable theoretical basis and, as was shown in [11], in the case of liquids it is impossible to predict the region of their application. Of practical interest for the calculation of thermal conductivities is the equation proposed in [2]. For nonassociated liquids it has the form

$$\lambda = \lambda_{S_1}\left[1.75 - 0.75\,\frac{S}{S_1}\right]. \qquad (2)$$

This equation can be used to calculate $\lambda = f(t)$ when entropy data are available. Table 4 compares the experimental and calculated values for the thermal conductivity of the ethyl ester of acetic acid.

As the table shows, Eq. (2) leads to good agreement between the calculated and experimental values. It should be noted that it was obtained by generalization of numerous experimental data for various nonassociated liquids and mixtures in wide temperature ranges [2].

We could not use Eq. (2), however, for generalization of the experimental values of the thermal conductivity of higher members in the homologous series of esters in view of the absence of entropy data. Hence, we used the method based on the theory of corresponding states.

From the obtained experimental values of λ for 21 carboxylic acid esters we found λ_τ at the corresponding reduced temperatures $\tau = T/T_{\text{boil}}$ with n = 2–22 carbon atoms in the molecule (Fig. 3).

The figure shows that irrespective of the change in the number of carbon atoms in the radicals R and R' all esters with the same molecular weight have the same λ_τ. At first there is a reduction in the value of λ_τ with increase in n, and then for all esters of different saturated monobasic acids with $n \geq 7$, λ_τ at the corresponding values of τ has the same values. The deviation of the mean values in most cases is less than 1%.

The obtained laws of variation of λ_τ enable us to calculate the thermal conductivities of different esters with $n \geq 7$ from the equation

$$\lambda = 0.1102 + 0.083(1 - \tau), \qquad (3)$$

which can be used in the whole range of the liquid state. Our comparisons of the calculated and experimental results showed that the deviations were within the limits of experimental error.

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10 November 1966

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