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THERMAL CONDUCTIVITY OF LIQUID PROPIONATES AT HIGH TEMPERATURE AND PRESSURE

R. A. Mustafaev and T. P. Musaev

UDC 536.222

Experimental data on thermal conductivity of octyl- and heptylpropionate over a wide range of temperature and pressure are presented.

Special and complex apparatus is required to perform experiments at high pressure and temperature. In recent years nonstationary methods have been employed widely, in particular, the technique of the spherical and cylindrical regular regime bicalorimeter [1-3]. These methods do not consider the temperature dependence of thermophysical properties, which differ little from stationary values over the duration of the experiment (at high temperature), and moreover, do not permit determination of the temperature dependence of thermal conductivity from a single experiment. In this connection, monotonic heating techniques are more promising for studies over a wide temperature and pressure range. They are convenient because measurements over a wide temperature range do not require multiple reestablishments of a stationary state, and because they do permit determination of the thermal conductivity temperature dependence $\lambda = F(T)$ in a single experiment over a temperature range which is infinite in principle.

The present study, which is a continuation of previous investigations [4-11], is dedicated to experimental determination of the thermal conductivity of liquid propionates (octyl- and heptylpropionate). The specimens studied were chemically pure, with chromatographic analysis revealing a content of not less than 99.20% of the desired substance.

The temperature range studied extended from room temperature to 600°K at pressures up to 147 MPa. Measurements were performed by the continuous heating method in a newly developed variant of the cylindrical bicalorimeter. The theory behind the method, the experimental technique used, and the construction of the device were described in detail in [9, 11, 12].

The main component of the experimental equipment is a cylindrical bicalorimeter consisting of two coaxially arranged cylinders. The gap between the cylinders is filled with the liquid to be studied.

The experimental thermal conductivity determination reduces to measurement of the time delay of the core temperature relative to the temperature of the block. Measurements were performed at various heating rates, which permitted variation of the temperature differential across the liquid layer over the range 3-8°K. The absence of convection was verified by measurements performed at different heating rates. In calculating the thermal conductivity, all the corrections intrinsic to this technique [11] were applied. No correction for radiation was provided in view of the absence of data on absorption spectra of the materials studied. Maximum relative measurement error is estimated to be ±2%. Reproducibility of

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TABLE 1. Experimental Values of Thermal Conductivity λ, W/m•deg K, for Propionates at Various Temperatures and Pressures

T, °K	P, MPa							
	0,098	19,6	39,2	58,8	78,4	98,0	117,6	147,0
				Octylpropionate				
312,4	0,1325	0,1397	0,1474	0,1557	0,1621	0,1697	0,1747	0,1858
330,0	0,1284	0,1375	0,1454	0,1548	0,1605	0,1674	0,1731	0,1825
344,7	0,1254	0,1364	0,1447	0,1524	0,1586	0,1650	0,1726	0,1820
352,6	—	0,1326	0,1421	0,1510	—	0,1649	0,1709	—
374,5	0,1200	0,1301	0,1387	—	0,1557	0,1617	0,1688	0,1771
390,7	0,1155	0,1274	0,1370	0,1451	0,1547	—	0,1673	0,1765
405,3	0,1127	—	0,1347	0,1431	0,1509	0,1581	0,1667	0,1750
427,6	—	0,1221	0,1330	0,1400	0,1490	0,1562	—	0,1742
442,8	—	0,1181	0,1295	0,1362	0,1474	0,1556	0,1624	0,1720
457,2	—	0,1152	0,1274	0,1358	—	0,1531	0,1609	0,1711
465,7	—	0,1149	0,1259	0,1344	0,1451	0,1528	0,1600	0,1707
480,7	—	0,1109	0,1232	0,1337	0,1449	0,1517	—	0,1700
495,7	—	0,1098	0,1211	0,1324	0,1426	0,1500	0,1581	0,1672
513,4	—	0,1076	0,1195	0,1299	0,1400	0,1475	—	0,1664
525,7	—	0,1054	0,1168	0,1288	0,1394	0,1467	0,1533	0,1651
547,8	—	—	0,1145	0,1250	0,1351	0,1431	0,1530	0,1641
577,4	—	0,0987	0,1112	0,1231	0,1337	—	0,1504	0,1622
592,9	—	0,0975	0,1081	0,1209	0,1318	0,1411	0,1500	0,1602
603,4	—	0,0951	0,1076	0,1200	0,1304	0,1400	0,1482	0,1591
615,8	—	—	0,1075	0,1189	0,1291	0,1400	0,1490	0,1600
				Heptylpropionate				
312,4	0,1350	0,1431	0,1500	0,1570	—	0,1696	0,1758	0,1851
322,3	0,1300	0,1420	0,1474	—	0,1632	0,1690	0,1764	—
337,9	0,1277	0,1399	—	0,1547	0,1617	0,1681	0,1742	0,1850
352,6	0,1243	0,1368	0,1430	0,1500	0,1577	0,1675	0,1731	0,1841
367,7	0,1205	—	0,1425	0,1475	0,1570	0,1660	—	0,1812
382,3	0,1184	0,1304	0,1399	—	0,1565	0,1637	0,1724	0,1810
390,7	0,1154	0,1300	0,1386	0,1449	—	0,1631	0,1720	0,1809
405,3	—	—	0,1372	0,1441	0,1538	0,1612	0,1681	—
412,8	—	0,1261	0,1340	—	0,1513	0,1599	0,1676	0,1787
435,7	—	0,1230	0,1325	0,1409	0,1486	0,1575	0,1672	0,1776
442,8	—	0,1220	0,1290	0,1375	0,1481	0,1560	0,1670	0,1761
457,2	—	0,1161	0,1287	0,1354	0,1475	—	0,1651	0,1760
465,7	—	0,1150	0,1255	0,1350	0,1449	0,1552	0,1632	0,1741
480,7	—	0,1144	0,1250	0,1331	—	0,1534	0,1620	0,1730
495,8	—	0,1125	—	0,1326	0,1420	0,1529	—	0,1721
525,7	—	0,1075	0,1183	0,1290	0,1394	—	0,1599	0,1708
555,8	—	0,1011	0,1144	0,1245	0,1367	0,1471	—	0,1684
585,3	—	—	0,1123	0,1214	0,1340	0,1430	0,1555	0,1671
600,3	—	0,0965	0,1090	—	0,1335	0,1424	0,1531	0,1668
615,8	—	0,0945	0,1075	0,1184	0,1305	0,1420	0,1525	0,1655

experimental data obtained at identical state parameters was within 1%. The experimental results are presented in Table 1.

There are no experimental data available on the thermal conductivity of these substances at high values of the state parameter. Only a single study [13] offers thermal conductivity values of propionates at atmospheric pressure, but does not include data for octyl- and heptyl propionates.

The contemporary theory of the liquid state does not permit establishment of a temperature dependence for calculation of thermal conductivity as a function of temperature and pressure. Therefore semiempirical and empirical methods must be used to calculate thermal conductivity. Recently, a number of formulas for such calculations have been proposed [14]. A general shortcoming of these formulas is the fact that they are either approximate in nature, covering only a limited state parameter range, or else are complex and contain quantities the determination of which requires performance of special experiments.

In a generalization of thermal conductivity data for paraffin hydrocarbons [4], the present authors established that at atmospheric pressure there exists a unique functional dependence of thermal conductivity upon reduced temperature $\tau = T/T_b$. Analysis of the results for the propionates at high temperatures and pressures reveals that at identical pressures and reduced temperatures it is true that $\lambda n_C^{1/5} = \text{const}$. This fact permitted formulation of the generalized equation

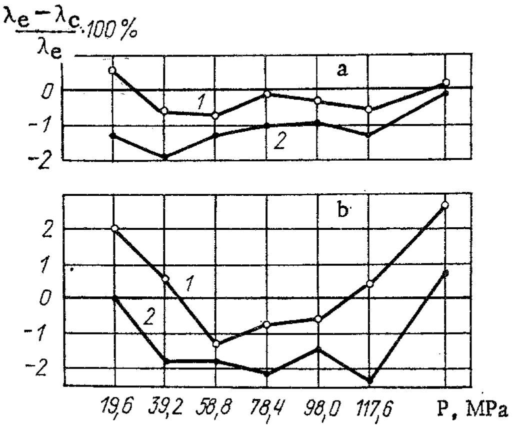

Fig. 1. Comparison of experimental data on thermal conductivity of octylpropionate (1) and heptylpropionate (2) with calculated values at temperatures of 330°K (a) and 570°K (b).

$$\lambda = \frac{1}{n_C^{1/5}} [(2.12 \cdot 10^{-5} P + 0.2975) - (0.12 - 4.8 \cdot 10^{-5} P) \tau]$$

for thermal conductivity calculation over a wide temperature and pressure range.

Comparison of the experimental data obtained with calculations by this formula at T = 330 and 570°K over a wide pressure range (Fig. 1) showed that the proposed formula describes the function $\lambda = F(P, T)$ with satisfactory accuracy, the mean deviation of the calculated values from experiment comprising about 2%.

NOTATION

T_b, boiling point at atmospheric pressure; n_C, number of carbon atoms per molecule.

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THERMAL CONDUCTIVITY OF AMYL AND ISOAMYL PROPIONATES

K. D. Guseinov and T. F. Klimova

UDC 536.2

Results of an experimental study of thermal conductivity of amyl and isoamyl propionate over the temperature range 300-600°K at pressures of 0.1-50 MPa are presented.

Complex ethers of propionic acid are used in the cellulose industry as high-boiling-point solvents for nitrocellulose and as plasticizers for cellulose acetate, although their transfer properties have not been studied over a wide range of state parameters.

The coaxial cylinder method with stationary regime [1] was used to study the thermal conductivity coefficient. The measurement cell consisted of two coaxially arranged cylinders of refined copper. The inner diameter of the outer cylinder was 13.13 mm, with outer diameter of 80 mm. A set of internal cylinders 140 mm long with diameters of 11.01, 12.03, and 12.40 mm was used. The thickness of the propionate layer studied was 0.55 mm in the liquid phase and 0.36 mm in the gaseous phase. Working surfaces of the cylinders were polished and chromium-plated. All other components of the device were made of type 1Kh18N9T stainless steel.

The temperature differential across the liquid layer was measured by a six-junction Chromel—Copel differential thermocouple, calibrated to a 10-Ω standard platinum resistance thermometer to an accuracy of 0.02°K. Three holes were drilled to a depth of 30, 60, and 98 mm in the outer and inner cylinders to hold the thermocouple junctions, which were held in place by copper inserts.

Use of a material with high thermal conductivity (red copper) for the measurement cylinder reduced axial temperature gradients to values less than the sensitivity of the thermocouples [2].

A heater made of 0.15-mm-diameter Constantan wire was located along the axis of the inner cylinder. The power dissipated by this heater was measured by a potentiometric circuit using the voltage drop across the heater and a 10-Ω reference winding connected in series with the heater. Temperature was measured by a 10-Ω resistance thermometer (No. 2000, constructed at VNIIFTRI). Pressure was generated and controlled by a piston manometer, type MP-600, class 0.05.

The equation used to calculate the thermal conductivity coefficient from the experimental data included all the characteristic corrections for this method [1, 3].

TABLE 1. Thermal Conductivity of Air at Atmospheric Pressure

T, °K	308,2	341,1	386,3	438,1	486,0	527,1	569,0
$\lambda \cdot 10^4$, W/m·degK	263	292	325	360	387	426	549

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