Journal of Engineering Physics and Thermophysics, Vol. 72, No. 3, 1999

THERMAL CONDUCTIVITY OF CAPROIC ACID ESTERS AT HIGH PRESSURES AS A FUNCTION OF THE TEMPERATURE

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UDC 536.6

We present results of an investigation of the thermal conductivity of octylcaproate and nonylcaproate. We obtained generalized formulas to calculate the thermal conductivity of caproates as a function of temperature and pressure.

Caproate esters ($C_5H_{11}COOC_nH_{2n+1}$) are derivatives of monobasic caproic acid in which a hydrogen atom is replaced by a hydrocarbon radical. They are slightly polar liquids that differ from normal liquids (*n*-alkanes etc.) in many properties.

Caproates have found wide application in contemporary chemical technology. First of all, they are used as high-temperature solvents of cellulose acetate and nitrate, oils, fats, rubbers, polymerizing resins, polyamides, polystyrene, and so on.

The thermophysical properties of caproates at high pressures and temperatures have received practically no study. An analysis of published works shows that to date the thermal conductivity of just the first two members (methylcaproate, ethylcaproate) of the homologous series of caproates have been investigated experimentally at atmospheric pressure [1].

In our previous works we presented results of investigation of the thermal conductivity λ of caproates (methyl-, ethyl-, propyl-, butyl-, hexyl-, and heptylcaproate) at high pressures and temperatures [2-7].

Below we present results of a study of octylcaproate and nonylcaproate in the range of temperatures from room to 640 K and pressures of (0.1–98) MPa.

Measurements of thermal conductivity were made by the method of monotonic heating. The theory of the method, measurement procedure, design of the device, and characteristic corrections entering the computational equation are presented in detail in [8, 9].

The main unit of the device is a cylindrical bicalorimeter the gap in which is filled with the test liquid. The inner cylinder (a rod) is made of copper M1. The working surfaces of the rod were carefully ground, chrome-plated, and polished. The outer cylinder is a massive copper block into which a tube made of 1Kh18N9T stainless steel was molded.

Experimental determination of thermal conductivity is reduced to measurement of the lag in time of the temperature of the rod relative to that of the block. For this we used an R-345 potentiometer of class 0.001 and a 51-SD stopwatch; to create and measure the pressure, we used an MP-2500 load-piston pressure gauge of class 0.05 and a set of standard pressure gauges. In calculating thermal conductivity, we introduced all corrections characteristic of this method [10].

Prior to investigation, the liquid was subjected to distillation in vacuum, after which its purity was evaluated on a Tsvet-4 chromatograph. Analysis showed that the content of the main product was not lower than 98%.

The main characteristics of the caproates are presented in Table 1.

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Azerbaidzhan Technical University, Baku. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 72, No. 3, pp. 412-419, May-June, 1999. Original article submitted April 6, 1995; revision submitted April 24, 1996.

 1062-0125/99/7203-0384$22.00

TABLE 1. Basic Physicochemical Characteristics of the Caproates Investigated

Substance	Chemical formula	Content of main component, %	M, kg/kmole	ρ_4^{20}, kg/m^3	T_{boil}, K
Methylcaproate	$C_5H_{11}COOCH_3$	99.98	130.2	884.6	424
Ethylcaproate	$C_5H_{11}COOC_2H_5$	99.96	144.2	871.0	441
Propylcaproate	$C_5H_{11}COOC_3H_7$	99.81	158.2	870.2	460
Butylcaproate	$C_5H_{11}COOC_4H_9$	98.11	172.3	868.4	480
Amylcaproate	$C_5H_{11}COOC_5H_{11}$	99.61	186.2	865.3	499
Hexylcaproate	$C_5H_{11}COOC_6H_{13}$	99.12	200.3	864.0	519
Heptylcaproate	$C_5H_{11}COOC_7H_{15}$	99.21	214.2	862.1	539
Octylcaproate	$C_5H_{11}COOC_8H_{17}$	99.21	228.2	858.4	559
Nonylcaproate	$C_5H_{11}COOC_9H_{19}$	99.32	242.1	856.2	579

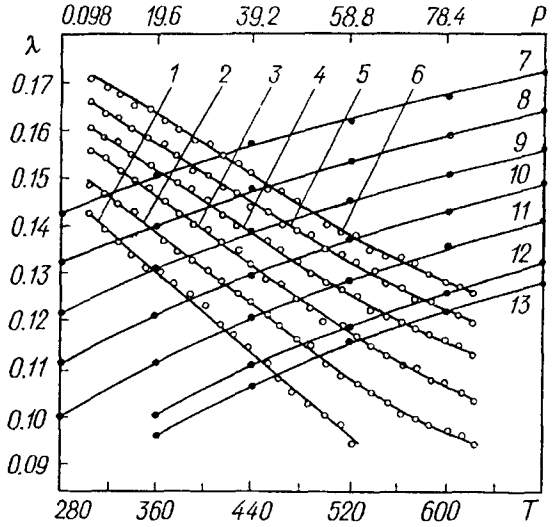

Fig. 1. Isobars and isotherms of the thermal-conductivity coefficient of octylcaproate: 1) 0.098 MPa; 2) 19.6; 3) 39.24; 4) 58.5; 5) 78.4; 6) 98.0; 7) 300 K; 8) 350; 9) 400; 10) 450; 11) 500; 12) 550; 13) 600. λ, W/(m·K); P, MPa; T, K.

The calculated maximum error is 2.2%. The reproducibility of experimental data obtained for the same parameters of state lies within ±1%. Absence of the effect of convection is confirmed by a series of experiments at different rates of heating (temperature head).

Measurements in the region of high temperatures did not reveal thermal decomposition of the substance, which was confirmed by repeated chromatographic analysis of the product after the experiments and the reproducibility of results of repeated measurements at relatively low temperatures carried out subsequent to investigations in the region of high temperatures. Because of the absence of information on absorption spectra, the correction for radiation was not taken into account. The results obtained are presented in Table 2. They were used as a basis for constructing isobars; isotherms of corresponding cross sections were constructed for internal consistency. Isobars and isotherms of the thermal conductivity of octylcaproate are shown in Fig. 1. The isobars and isotherms of the thermal conductivity of the other investigated caproates have a similar form.

Because of the difficulty in formulating experiments for determining the thermal conductivity of liquids, especially at high pressures and temperatures, it seems justifiable to devise computational methods that would allow one to calculate λ with a sufficient degree of accuracy in a wide range of state parameters. In recent times such works have been carried out by a number of authors, and relations have been proposed that connect λ of liquids

TABLE 2. Experimental Values of the Thermal Conductivity $\lambda \cdot 10^3$ W/(m·K) of Caproates as a Function of the Temperature and Pressure

T, K	P, MPa					
	0.098	19.6	39.2	58.8	78.4	98.0
			Octylcaproate			
304.4	142	149	156	161	166	171
316.2	139	147	154	159	164	169
340.2	134	143	150	155	160	165
353.4	131	140	148	153	159	164
377.4	128	135	143	149	155	160
389.2	125	133	140	148	152	158
402.5	123	131	139	145	151	157
414.3	119	129	137	143	148	155
438.1	114	124	132	139	144	151
451.2	111	121	129	137	143	148
463.8	108	119	128	135	140	147
476.6	105	111	125	133	139	145
500.7	100	111	120	128	135	140
513.5	98.2	109	119	127	134	139
525.9	94.8	107	117	125	132	138
537.3		105	115	122	130	135
550.2		103	113	121	128	134
562.1		101	111	120	127	133
574.4		99.6	110	119	125	132
599.2		96.5	107	116	122	128
611.3		95.6	105	115	121	127
624.5		94.5	104	113	120	126
			Nonylcaproate			
308.1	144	153	159	166	171	176
320.4	142	150	158	164	169	174
345.8	137	146	153	159	165	170
357.3	134	144	156	157	163	168
369.6	131	142	148	155	161	167
394.7	127	136	145	151	157	163
406.5	124	135	142	148	155	161
418.2	121	133	140	147	153	158
430.1	119	129	137	145	152	157
453.2	114	125	133	141	147	153
465.7	112	123	131	139	146	151
490.5	106	118	126	134	142	148
502.7	104	116	124	133	138	146
515.2	100	113	122	130	137	144
527.4	98.5	110	120	128	135	142
540.1	96.1	109	117	126	134	140
552.7	94.2	107	115	125	132	137
564.8		105	114	123	129	137
576.3		103	113	121	128	135
589.3		101	111	119	127	134
614.7		94.8	108	117	123	131
626.3		96.7	107	115	122	129
639.9		95.1	106	114	121	128

TABLE 3. Comparison of Calculated Values of $\lambda \cdot 10^3$, W/(m·K), by Formula (3) with Experimental Data of [1]

T, K	Methylcaproate			Ethylcaproate		
	λ_{calc}	λ [1]	δ, %	λ_{calc}	λ [1]	δ, %
213	156	153	1.9	155	153	1.3
233	153	151	1.3	150	150	0
253	146	145	0.7	145	146	−0.7
273	141	141	0	140	142	−1.4
293	137	136	0.7	136	138	−1.5
313	133	133	0	131	134	−2.2

with other physical parameters [11, 12]. However, a common deficiency of these relations is their approximate nature and their validity mainly at room temperature. These facts in large measure justify searches for new ways of determining λ of liquids by applying generalized relations.

At Azerbaidzhan Technical University, on the basis of systematic experimental investigations of the thermophysical properties of individual hydrocarbons of various homologous series, it was possible to discover a number of important dependences [13-15]. They may serve as a basis for developing a method to calculate λ of caproates.

Analysis of the results obtained shows that the temperature dependence of λ of different homologs of the given series is different, and with an increase in the molar mass the temperature coefficients λ do not remain constant. However, at temperatures that are equidistant from the normal boiling point, i.e., at the same values of $T_{boil} - T$, the following relation holds for the entire homologous series of caproates:

$$M^k \lambda = \text{idem}. \tag{1}$$

Here k depends on the number of carbon atoms in the molecule n_C: when $n_C \leq 10$, $k = 1/3$, and when $n_C > 10$, $k = 0$.

It follows from Eq. (1) that for two representatives of the studied homologous series at $T'_{boil} - T_1 = T''_{boil} - T_2$ the following approximate relations are valid:

$$\frac{\lambda_1}{\lambda_2} = \sqrt[3]{\left(\frac{M_2}{M_1}\right)} \quad \text{when} \quad n_C \leq 10, \quad \lambda_1 = \lambda_2 \quad \text{when} \quad n_C > 10. \tag{2}$$

Here λ_1 and λ_2 are the thermal conductivities of homologs 1 and 2 at the temperatures T_1 and T_2, respectively.

Formulas (2) allow one to calculate the thermal conductivity of all members of the homologous series of caproates from the thermal conductivity of one homolog and its molecular weight.

Analysis of functions (1) for different values of the difference $T_{boil} - T$ shows that the indicated dependence has a universal character for caproates and can be approximated by a equation of the form

$$M^k \lambda = \sum_{i=0}^{2} a_i (T_{boil} - T)^i. \tag{3}$$

The coefficient a_i in Eq. (3) has the following values:

$$\text{when} \quad n_C \leq 10: \quad a_0 = 0.544; \quad a_1 = 0.102 \cdot 10^{-2}; \quad a_2 = 0.7 \cdot 10^{-6};$$

$$\text{when} \quad n_C > 10: \quad a_0 = 0.09089; \quad a_1 = 0.1589 \cdot 10^{-3}; \quad a_2 = 0.173 \cdot 10^{-6}.$$

A merit of the above formula is that it does not involve physical quantities that require additional experimental determination and it makes it possible to calculate the thermal conductivity of caproates directly in the entire region of the liquid state at atmospheric pressure.

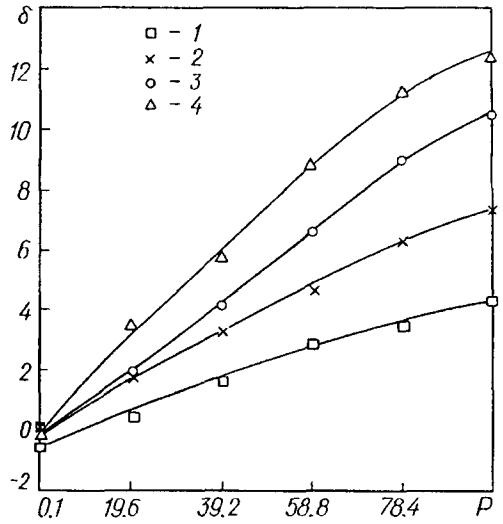

Fig. 2. Dependence of the error of calculation of the thermal conductivity of nonylcaproate on the pressure by Misnar's formula: 1) $T = 306.1$ K; 2) 406.5; 3) 478; 4) 540.1. δ, %.

The proposed formula was obtained by generalizing results of our experiments carried out at temperatures $T \geq 300$ K. However, it also applies for calculations in the region of negative temperatures. To be sure, the legitimacy of this extrapolation can be proved only by measuring the thermal conductivity at low temperatures. In the literature there are experimental data on the thermal conductivity of methylcaproates and ethylcaproates in the region of negative temperatures [1]. Using these data, experimental results on determination of values of λ are compared in Table 3 with results calculated by formula (3) in a region of temperatures not encompassed by our investigations. Satisfactory agreement of them is observed (the discrepancy does not exceed the errors of the measurements, evaluated to be ±2.2%). The results of the comparison confirm additionally that the formula proposed is quite reliable and is suited for description of the temperature dependence of λ in a wide temperature range.

To determine the thermal conductivity of liquids at high parameters of state use is often made of the well-known Misnar formula [16]

$$\lambda_{P,T} = \lambda_T \left[1 + \frac{1}{\sqrt{\rho_0 T_{\text{boil}}}} \left(\frac{P}{144 - 0.3t}\right)^{2/3}\right], \tag{4}$$

where λ_T is the thermal conductivity at atmospheric pressure and temperature T; ρ_0 is the density at 0 °C; t is the temperature, °C.

On the basis of our experimental data we checked the possibility of using Misnar's formula to calculate λ of caproates. The results of a comparison showed that the error of calculation increases with increase in pressure and attains 12%. This is confirmed by Fig. 2, which shows the dependence of the error of calculation δ on the pressure for nonylcaproate. A similar result is observed for the other caproates. Moreover, it should be noted that Misnar's formula is limited by the boiling temperature of the liquid, it is inapplicable above this temperature. Different forms of Tate's equation are widely used to generalize the transport properties of liquids [17, 18].

To generalize the experimental results obtained by us, we used the equation

$$\lambda = \lambda_0 \left(1 + A \ln \frac{B + P}{B + P_0}\right), \tag{5}$$

Here P_0 is atmospheric pressure; λ_0 is the thermal conductivity of the liquid at the pressure P_0; A and B are coefficients associated with the temperature.

TABLE 4. Values of the Coefficients of Eqs. (6)

i	$n_C \leq 10$		$n_C > 10$	
	a_i	b_i	a_i	b_i
0	−1.411	287.0	−0.64438	86.37584
1	−1.082	133.055	−2.21751	8.07856
2	0.189	−71.84	0.09685	−11.86219
3	0.220	−30.825	0.09698	−11.53108
4	−0.021	8.594	0.01925	−2.49993

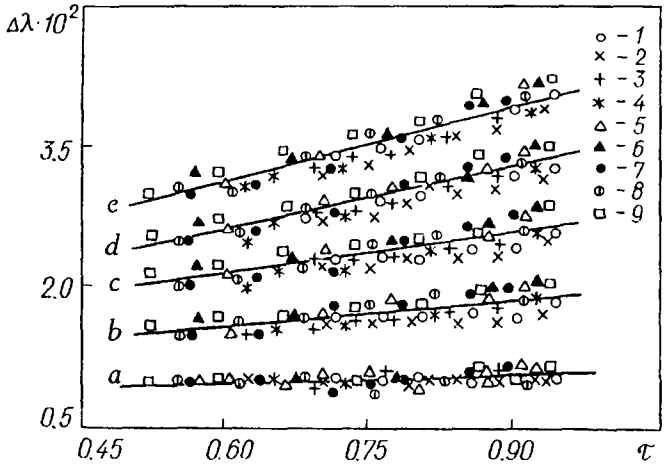

Fig. 3. Dependence $\Delta\lambda = f(\tau)$ for caproates [a) $P = 19.6$ MPa; b) 39.2; c) 58.8; d) 78.4; e) 98.0]: 1) methylcaproate; 2) ethylcaproate; 3) propylcaproate; 4) butylcaproate; 5) amylcaproate; 6) hexylcaproate; 7) heptylcaproate; 8) octylcaproate; 9) nonylcaproate.

Processing of experimental data shows that the dependences of the coefficients A and B on the temperature for the substances investigated by us are smooth curves and are described by polynomials of the form

$$A = \sum_{i=0}^{4} a_i \left(\frac{T - T_{boil}}{100}\right)^i ; \quad B = \sum_{i=0}^{4} b_i \left(\frac{T - T_{boil}}{100}\right)^i , \tag{6}$$

Values of the coefficients a_i and b_i are presented in Table 4. To determine the temperature dependence of λ_0, formula (3) is suited. Thus, Eqs. (3) and (5), with (6) taken into account, allow one to calculate λ in a wide range of temperatures and pressures.

Relations (2) and (5) describe experimental data with an arithmetic-mean error of 3%; the maximum error at some points attains 5%.

To obtain a single formula for calculation of the thermal-conductivity coefficient of caproates in a wide range of temperatures and pressures we plotted dependences of the excess thermal conductivity $\Delta\lambda = \lambda_{P,T} - \lambda_T$ on the reduced temperature $\tau = T/T_{boil}$. Results of this processing are presented in Fig. 3, from which it follows that the dependence $\Delta\lambda = f(\tau)$ constructed for isobars is represented by straight lines with different inclinations to the abscissa. Thus, the indicated relationship can be represented by the linear function

$$\lambda_{P,T} - \lambda_T = C + D\tau . \tag{7}$$

Here the coefficients C and D for all the substances investigated are linear functions of pressure; they are approximated by the equations

$$C = c_1 + c_2 P , \quad D = d_1 + d_2 P . \tag{8}$$

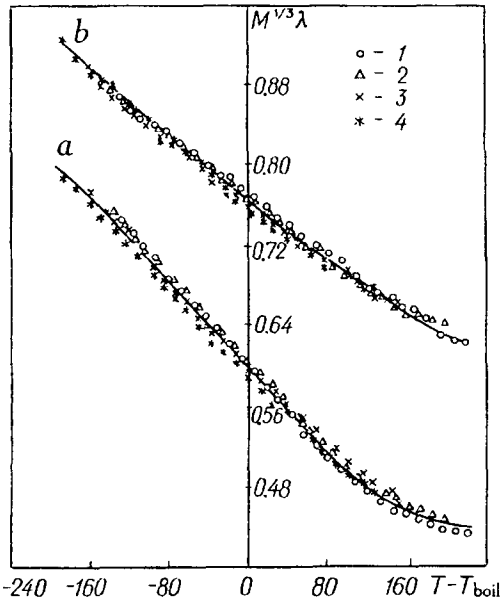

Fig. 4. Dependence $M^{1/3}\lambda = f(T - T_{boil})$ for caproates [a) $P = 19.6$ MPa; b) 98.0]: 1) methylcaproate; 2) ethylcaproate; 3) propylcaproate; 4) butylcaproate.

Using relations (8), the computational formula (7) is represented in the form

$$\lambda_{P,T} - \lambda_T = c_1 + c_2 P + (d_1 + d_2 P)\,\tau\,, \tag{9}$$

where $c_1 = 6.71 \cdot 10^{-3}$; $c_2 = 9.78 \cdot 10^{-5}$; $d_1 = -3.325 \cdot 10^{-3}$; $d_2 = 3.022 \cdot 10^{-4}$.

As seen from formula (9), determination of the thermal conductivity of caproates as a function of temperature and pressure can be carried out if the relationship between the thermal conductivity λ_T and the temperature at atmospheric pressure is known. Simultaneous use of Eqs. (3) and (9) allows this to be done. The average deviation of computed values of λ from experimental values does not exceed 2%.

Analyzing the obtained voluminous experimental information on the thermal conductivity of caproates at high pressures, we found that isobars in the coordinates $M^k\lambda = f(T - T_{boil})$ for all the substances investigated have a universal character. Figure 4 presents results of such processing of experimental data for the two isobars 19.6 and 98.0 MPa for caproates with $n_C \leq 10$. The remaining isobars occupy an intermediate position. Such a dependence is also observed for caproates with the number of carbon atoms in a molecule $n_C > 10$. As seen from the figure, for each isobar at temperatures that are equidistant from the normal temperature of boiling T_{boil} of the liquid, i.e., at equal values of $T - T_{boil}$, relation (1) is satisfied. An isobar is described by the nonlinear equation

$$M^k\lambda = A_0 + A_1 (T - T_{boil}) + A_2 (T - T_{boil})^2\,. \tag{10}$$

Here the coefficients A_0, A_1, and A_2 for all the caproates are universal pressure-dependent ones.

Having established the form of the functional relationship of the coefficients of Eq. (10), we obtained a generalized formula to calculate caproates in a wide range of temperatures and pressures in the form

$$M^k\lambda = \sum_{i=0}^{2} \sum_{j=0}^{2} a_{ij} P^i (T - T_{boil})^i\,, \tag{11}$$

where $k = 1/3$ when $n_C \leq 10$ and $k = 0$ when $n_C > 10$. From formulas (10) and (11) it follows that $A = \sum_{i=0}^{2} a_2 P^i$; the coefficients are presented in Table 5. The coefficients of Eq. (11) were found with the aid of a computer on the basis of experimental data by the least-squares method.

TABLE 5. Coefficients $a_{ij} \cdot 10^8$ of Eq. (11)

j	i		
	0	1	2
For $n_C \leq 10$			
0	54,388,200	260,938	−367.02
1	−102,274	134.605	1.47789
2	69.9816	0.505394	−0.0104252
For $n_C > 10$			
0	9,089,100	64,855	−226.51
1	−15,899	78.62	−0.38565
2	17.317	0.058893	0.00016932

The proposed formula is a generalized one, it does not contain quantities that require additional experimental determination, and it makes it possible to calculate directly the thermal conductivity of caproates in a wide range of temperatures and pressures. A comparison of obtained experimental data with data calculated by Eq. (11) showed good agreement in the entire investigated range of temperatures and pressures with an average discrepancy of 1.2% and a maximum discrepancy of 2.6%. Thus, the proposed procedure provides rather high accuracy of calculation of λ of caproates at high pressures as a function of the temperature.

Using this equation, it is possible to carry out a calculation of $\lambda = f(P, T)$ for caproates not studied as yet, bypassing laborious and expensive experimental investigations.

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