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# THERMAL CONDUCTIVITY OF SUCCINIC ACID ESTERS IN WIDE TEMPERATURE AND PRESSURE RANGES

**R. A. Mustafaev and R. S. Ragimov** UDC 536.2

*Results of experimental investigation of the thermal conductivity of succinic acid esters in a wide range of the parameters of state are reported. Equations are derived which describe well the experimental results.*

Succinic acid esters find wide application in the chemical and petrochemical industries, power generation, medicine, etc. Some of these esters, having a high boiling point (about 500 K), can be successfully used as heat carriers and cooling liquids. Nevertheless, data on their thermophysical properties are almost absent in the literature.

The present work, being a continuation of previous investigations [1-7], is devoted to experimental investigation of the thermal conductivity $\lambda$ of succinic acid esters (diethyl, dipropyl, and dinonyl); the substances were chemically pure, and chromatographic analysis showed no less than 99.30% of the basic substance. Characteristics of the investigated esters are given in Table 1.

Investigations were carried out at temperatures from room temperature to 575 K and at pressures to 60 MPa. The method, measurement procedure, and design of the device are described in detail in [8-10].

The basic unit of the device is a cylindrical bicalorimeter consisting of two coaxial cylinders. The gap between the cylinders is filled with the investigated liquid. Experimental determination of thermal conductivity involves measurement of the time lag of the core temperature relative to the temperature of the unit. Measurements were made at different heating rates, which allowed the temperature drop in the liquid to be varied within the limits of 3-8 K. The absence of convection was checked by measurements at different heating rates. In calculating thermal conductivity, all corrections inherent in the method were made [10]. A correction for radiation was not introduced, because of the absence of data on absorption spectra of the investigated substances. The maximum relative error of measurement was estimated as ±2.2%. The reproducibility of the experimental data obtained at the same parameters of state was within ±1%.

Table 2 gives smoothed values of thermal conductivity of the investigated esters.

For each liquid we recorded seven isobars between atmospheric pressure and 60 MPa. Measurements were made at approximately 12 K intervals.

Experimental values were obtained by averaging several measurements in the same regime. The internal consistency of the results obtained was checked by constructing isobars and isotherms of the thermal conductivities of the substances.

Figure 1 shows isobars and isotherms of the thermal conductivity of diethyl ester. Other esters have isobars and isotherms of thermal conductivity of a similar form.

Unfortunately, at present, despite substantial development of the theory of liquids, we have no reliable methods for calculation and prediction of the thermophysical properties of substances, especially of complex substances, polar compounds, and our investigated esters.

Therefore, the development of methods of calculation of thermophysical properties of poorly known substances is still urgent, since the amount of applied liquid organic compounds is still ahead of the volume of experimental studies, and this trend will apparently not change in the future. Moreover, the ranges of temperatures

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TABLE 1. Characteristics of the Investigated Esters

| Ester | Formula | $M$ | $T_b$, K | $\rho$, kg/m$^3$ | Purity with respect to mass, % |
|---|---|---|---|---|---|
| Diethyl | $C_{18}H_{14}O_4$ | 174.20 | 490.85 | 1037.0 | 99.53 |
| Dipropyl | $C_{10}H_{18}O_4$ | 202.25 | 523.95 | 999.3 | 99.62 |
| Dinonyl | $C_{22}H_{42}O_4$ | 370.58 | 723.15 | 910.0 | 99.37 |

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

| $T$, K | $P$, MPa | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.1 | 10 | 20 | 30 | 40 | 50 | 60 |
| | | | | Diethyl ester | | | |
| 298.15 | 159 | 164 | 170 | 175 | 183 | 187 | 192 |
| 323.15 | 155 | 150 | 166 | 171 | 177 | 183 | 188 |
| 348.15 | 151 | 156 | 162 | 168 | 173 | 178 | 184 |
| 373.15 | 147 | 153 | 159 | 154 | 169 | 175 | 180 |
| 398.15 | 143 | 149 | 154 | 160 | 165 | 171 | 176 |
| 423.15 | 139 | 144 | 150 | 156 | 161 | 167 | 173 |
| 448.15 | 136 | 141 | 147 | 152 | 157 | 163 | 169 |
| 473.15 | 132 | 138 | 143 | 148 | 154 | 159 | 166 |
| 498.15 | – | 134 | 140 | 145 | 150 | 157 | 162 |
| 523.15 | – | 131 | 136 | 142 | 147 | 153 | 159 |
| 548.15 | – | 126 | 133 | 139 | 145 | 151 | 157 |
| 573.15 | – | 124 | 130 | 137 | 143 | 149 | 155 |
| | | | | Dipropyl ester | | | |
| 298.15 | 155 | 162 | 167 | 173 | 178 | 183 | 190 |
| 323.15 | 151 | 158 | 164 | 170 | 175 | 180 | 185 |
| 348.15 | 148 | 154 | 160 | 166 | 172 | 176 | 182 |
| 373.15 | 144 | 151 | 157 | 162 | 168 | 173 | 179 |
| 398.15 | 141 | 147 | 153 | 159 | 164 | 170 | 175 |
| 423.15 | 137 | 143 | 149 | 155 | 160 | 166 | 172 |
| 448.15 | 133 | 140 | 146 | 150 | 157 | 163 | 168 |
| 473.15 | 130 | 136 | 142 | 148 | 153 | 159 | 165 |
| 498.15 | 125 | 132 | 138 | 145 | 150 | 156 | 162 |
| 523.15 | – | 129 | 136 | 140 | 147 | 153 | 159 |
| 573.15 | – | 124 | 132 | 138 | 144 | 151 | 157 |
| 548.15 | – | 120 | 128 | 135 | 142 | 148 | 155 |
| | | | | Dinonyl ester | | | |
| 298.15 | 157 | 161 | 165 | 169 | 174 | 177 | 182 |
| 323.15 | 153 | 157 | 161 | 165 | 170 | 174 | 179 |
| 348.15 | 149 | 153 | 158 | 162 | 166 | 171 | 176 |
| 373.15 | 145 | 150 | 154 | 159 | 163 | 168 | 173 |
| 398.15 | 141 | 146 | 151 | 156 | 161 | 165 | 170 |
| 423.15 | 138 | 143 | 148 | 153 | 158 | 163 | 167 |
| 448.15 | 135 | 139 | 144 | 150 | 155 | 161 | 165 |
| 473.15 | 132 | 136 | 141 | 147 | 152 | 157 | 163 |
| 498.15 | 129 | 134 | 138 | 144 | 149 | 155 | 160 |
| 523.15 | 126 | 131 | 136 | 141 | 147 | 152 | 158 |
| 548.15 | 123 | 128 | 134 | 139 | 145 | 151 | 156 |
| 573.15 | 120 | 126 | 132 | 138 | 143 | 150 | 154 |

TABLE 3. $\lambda\Phi^{0.0625}$ of the Investigated Esters as a Function of Temperature

| $T$, K | $\lambda\Phi^{0.0625}\cdot 10^3$ for Esters | | |
|---|---|---|---|
| | diethyl | dipropyl | dinonyl |
| 298.15 | 134 | 134 | – |
| 323.15 | 130 | 130 | 128 |
| 348.15 | 126 | 126 | 125 |
| 373.15 | 122 | 122 | 122 |
| 398.15 | 118 | 117 | 119 |
| 423.15 | 115 | 115 | 116 |
| 448.15 | 112 | 113 | 113 |
| 473.15 | 110 | 109 | 110 |
| 498.15 | – | 106 | 107 |
| 523.15 | – | – | 104 |
| 548.15 | – | – | 102 |
| 573.15 | – | – | 100 |

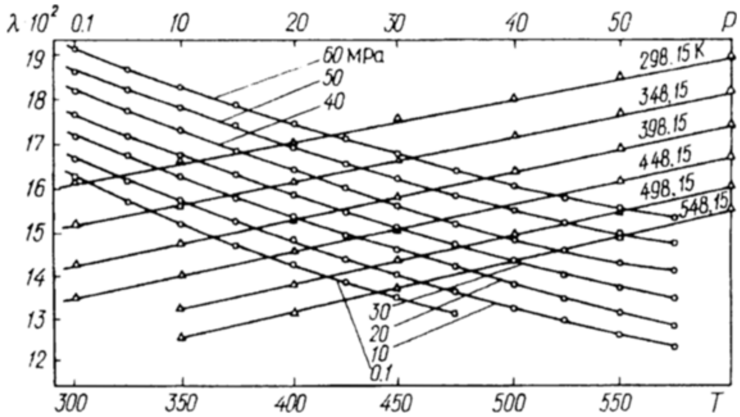


Fig. 1. Isobars and isotherms of the thermal conductivity of diethyl ester. $\lambda$, W/m·K; $P$, MPa; $T$, K.

and pressures in which substances are used broaden steadily. These factors stimulate interest in prediction of the thermophysical properties of substances that are either almost uninvestigated or investigated in a limited range of the parameter of state.

An analysis of experimental results for the temperature dependence $\lambda = f(T)$ at atmospheric pressure has revealed that at the same temperatures for all the investigated esters the following condition is fulfilled:

$$\lambda\Phi^{0.0625} = \text{idem}\,, \tag{1}$$

where $\Phi = n_C/M$; $n_C$ = is the number of carbon atoms in a molecule; $M$ is the molecular mass.

Table 3 illustrates to what extent condition (1) is satisfied.

From (1) it follows that for two representatives of the given homologous series the relation

$$\frac{\lambda_1}{\lambda_2} = \left(\frac{\Phi_2}{\Phi_1}\right)^{0.0625}, \tag{2}$$

holds where $\lambda_1$ is the thermal conductivity of homolog 1 and $\lambda_2$ is that of homolog 2.

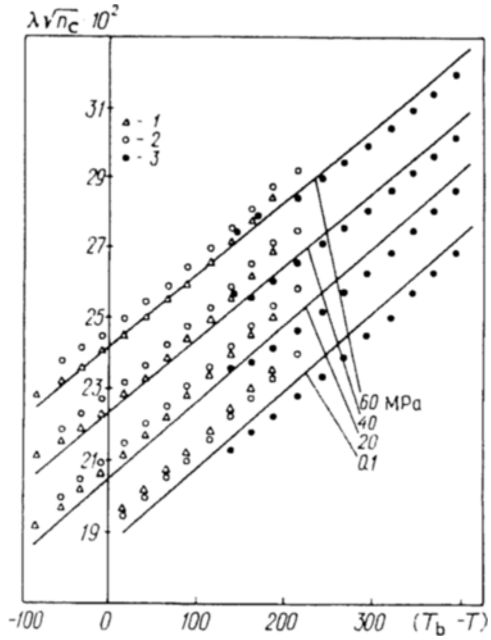


Fig. 2. Temperature dependence of $\lambda \sqrt[5]{n_C}$ for succinic acid esters at different pressures: 1) diethyl ester; 2) dipropyl ester; 3) dinonyl ester.

For a given liquid $\Phi$ is a constant and formula (2) allows calculation of thermal conductivity of all terms in the given homologous series by using the thermal conductivity of one homolog.

Condition (1) made it possible to establish the following generalized relation for $\lambda = f(T)$:

$$\lambda = \frac{(1675 - 1.2T)}{\left(\frac{n_C}{M}\right)^{0.0625}} \cdot 10^{-4} . \tag{3}$$

Relating $\lambda$ to the molecular mass $M$ and the number of carbon atoms $n_C$, the formula obtained describes the temperature dependence of $\lambda$ sufficiently exactly at temperatures of from 298.15 K to the boiling point $T_b$ of the liquid. A comparison of the experimental data with those calculated by formula (3) has shown that their deviation does not exceed $\pm 2\%$.

Analyzing the experimental data obtained at high parameters of state, we have found that the isobars in the coordinates $\lambda \sqrt[5]{n_C} = f(T_b - T)$ are of a universal character and represent straight lines. Thus, for each isobar at temperatures equidistant from the normal boiling point $T_b$ of the liquid, i.e., at equal $T_b - T$, the following relation holds:

$$\lambda \sqrt[5]{n_C} = \text{idem} . \tag{4}$$

From (4) it follows that for two representatives of the homologous series $T_b' - T_1 = T_b'' - T_2$ the relation

$$\frac{\lambda_1}{\lambda_2} = \sqrt[5]{\left(\frac{n_C''}{n_C'}\right)} . \tag{5}$$

is valid.

Formula (5) allows calculation of the thermal conductivity of all terms entering this homologous series by the thermal conductivity of one of the homologs and the number of carbon atoms in a molecule.

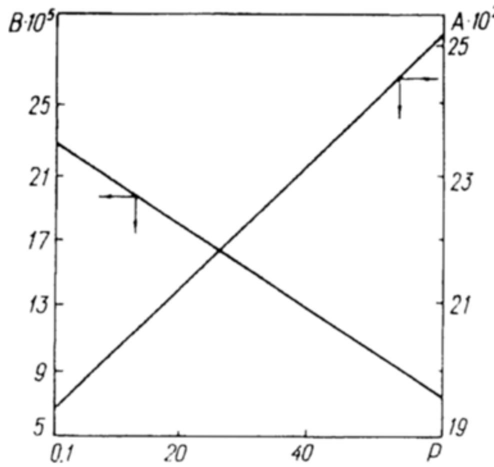


Fig. 3. Coefficients $A$ and $B$ vs pressure.

Figure 2 shows the results of processing of experimental data for the investigated esters in the coordinates $\lambda\sqrt[5]{n_C} = f(T_b - T)$. As is seen, the experimental points for all the investigated esters in the above coordinates fall on a straight line that can be described by the equation

$$\lambda (P, T) = \frac{1}{\sqrt[5]{n_C}} [A + B (T_b - T)], \tag{6}$$

where the coefficients $A$ and $B$ are universal, depending on the pressure.

The dependences $A(P)$ and $B(P)$ are also linear and respesented in Fig. 3.

Computer-aided processing of the plots by the least-squares method has allowed us to determine $A(P)$ and $B(P)$ and represent Eq. (6) finally in the following form

$$\lambda = \frac{1}{\sqrt[5]{n_C}} [1920 + 10P + (2.3 - 0.007P) (T_b - T)] \cdot 10^{-4}. \tag{7}$$

Formula (7) is a generalized relation that contains no quantities to be determined in additional experiments and allows direct calculation of the thermal conductivity of the esters of the investigated homologous series in wide ranges of temperatures and pressures. Deviation of the calculated from experimental $\lambda$ values does not exceed $\pm 2\%$.

Using this equation, one can calculate $\lambda = f(P, T)$ of unstudied esters from the given homologous series without performing laborious and expensive experiments.

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