THE TEMPERATURE DEPENDENCE OF THE THERMAL CONDUCTIVITY OF NARROW FRACTIONS OF OZEKSUAT OIL

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The theory of corresponding states can be used to investigate the thermal conductivity of narrow fractions of oil.

This paper gives the results of an experimental investigation of the thermal conductivity λ and density ρ of thirty-seven narrow (10 and 25°) fractions of high-paraffin Ozeksuat oil.

The thermal conductivity of the fractions was measured by the hot-wire method at temperatures of 20°–220° C and pressures of 0.10–1.96 MN/m^2. The error in measuring λ did not exceed ±1.5%.

The density of the fractions at 20° C was determined by a pycnometer and in the temperature range 20°–100° C on a special apparatus by hydrostatic weighing on a ADV-200 balance. The accuracy of determining ρ was ±0.02%.

In the investigated temperature range λ and ρ vary linearly

$$\lambda_t = \lambda_{30}[1 - \alpha(t - 30)], \quad (1)$$

$$\rho_t = \rho_{20}[1 - \beta(t - 20)]. \quad (2)$$

Figure 1 compares the values of λ, ρ, α, and β of the fractions and the paraffins comprising more than 50% of the investigated fractions. The data for paraffins of normal structure were taken from [1–3].

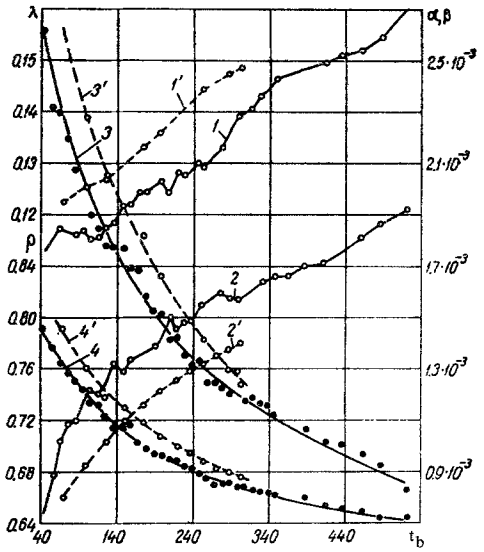

Fig. 1. Dependence of λ, ρ, α, and β of fractions and paraffins on mean boiling point t_b, ° C of fractions: 1 and 1') for λ_{30}^f and λ_{30}^p; 2 and 2') ρ_{20}^f and ρ_{20}^p; 3 and 3') α^f and α^p; 4 and 4') β^f and β^p.

The graphs in Fig. 1 show that λ, ρ, α, and β of paraffins and the investigated fractions vary in a similar manner. The presence of naphthenic and aromatic hydrocarbons in the fractions reduces the thermal conductivity and increases the density of the fractions in comparison with paraffins.

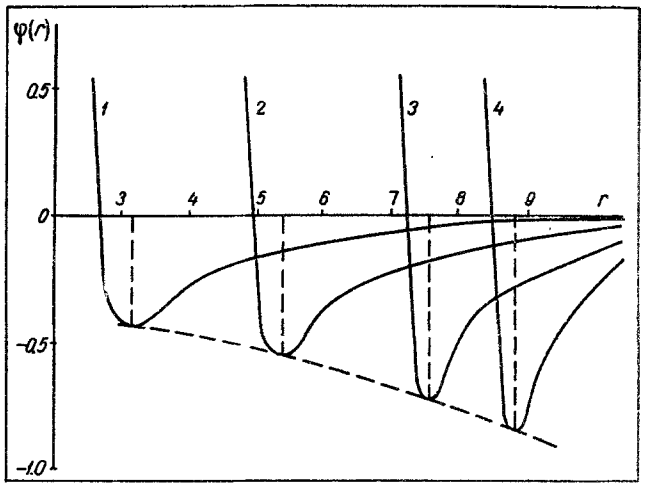

Fig. 2. Potential energy of interaction $\varphi(r)$ between molecules as a function of the distance r, in Å, between them, for normal paraffins: C_5H_{12} (1), C_6H_{14} (2), C_7H_{16} (3), and C_8H_{18} (4).

Below we will attempt to find a qualitative relationship between the thermal conductivity and the molecular structure of the paraffins and investigated fractions and to determine the temperature dependence of their thermal conductivities from the law of corresponding states.

For thermodynamically similar substances, such as paraffins, the potential energy $\varphi(r)$ of interaction between the molecules can be put in the form [4]

$$\varphi(r) = \varepsilon f(r/\sigma). \quad (3)$$

For nonpolar paraffin molecules this universal function can be regarded as approximately equal to the Lennard-Jones potential

$$\varphi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6]. \quad (4)$$

The curves [5] from Eq. (4) are plotted in Fig. 2.

A comparison of the experimental thermal conductivity data with the potential energy curves shows that the higher the boiling point (critical temperature) of paraffins, the greater the binding energy between the molecules, the higher the lines of the temperature dependence of the thermal conductivity and the lower the temperature coefficient α. By comparing experimental data for the viscosity and compressibility of paraffins

with the potential energy curves Golik [5] found that the deeper the potential well (the greater ε), the higher the curves of the temperature dependence of the viscosity and the lower the compressibility.

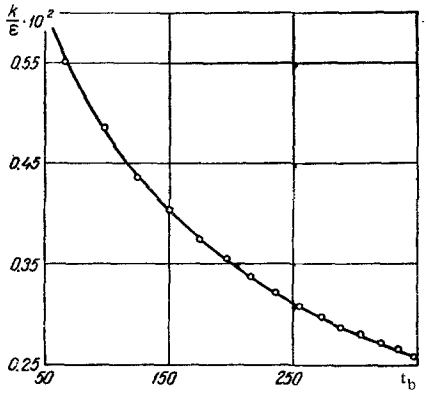

Fig. 3. Relationship between k/ε (first approximation) of normal paraffins and boiling point t_b, °C.

The above relationships will obviously be valid for the narrow fractions too, since the variation of the physical properties of paraffins and the investigated fractions in relation to the boiling point is qualitatively the same (i.e., similar).

In the investigation and generalization of experimental data for homogeneous pure substances by the similarity method T_{cr}, P_{cr}, and V_{cr} or other parameters which determine the properties of the molecules of the substance [ε and σ from formula (3)] are usually chosen as characteristic parameters [4]. In the generalization of experimental data for mixtures great difficulties arise in the choice of the characteristic and, hence, reduced parameters, which satisfy the generalized relationships.

As our calculations showed, the mean boiling point of the fractions, which might have been a very convenient parameter in the generalization of the experimental thermal conductivity data for mixtures, did not give satisfactory results. The boiling point cannot be a characteristic parameter even for liquids of the same homologous series, as is also shown in [6].

According to the law of corresponding states, for the range of parameters in which the effect of pressure on the thermal conductivity of a liquid can be neglected, a valid expression is [4]

$$\lambda^* = \lambda^*(T^*). \quad (5)$$

The form of this function depends only on the form of the potential function f. For spherical nonpolar molecules the reduced temperature can be represented as

$$T^* = kT/\varepsilon. \quad (6)$$

Expression (6) shows that the reduced temperature is inversely proportional to the depth of the potential well (i.e., to ε), the value of which for chemically similar molecules varies in accordance with a definite law.

Comparing the variation of k/ε (Fig. 3), β, and α (Fig. 1) we conclude that the variation of k/ε and β is qualitatively the same. Hence, the universal function (5) can be put in the form

$$\lambda^* = \lambda^*(\beta T) = \lambda^*(\tau). \quad (7)$$

In addition, the qualitatively similar variation of β and α is confirmed by Vargaftik's well-known rule

$$\lambda_1/\lambda_2 = (\rho_1/\rho_2)^{4/3}, \quad (8)$$

which can be regarded as a special case of (7).

The value of β when the density varies linearly with the temperature can be calculated from Eq. (2).

It should be noted, however, that the value of the temperature coefficient β depends on the temperature at which the initial density is taken (ρ_{20}, for instance). The value of β changes when this temperature changes, but its variation is qualitatively the same for similar substances.

For the generalization of the experimental data it is much more convenient to take the initial density at

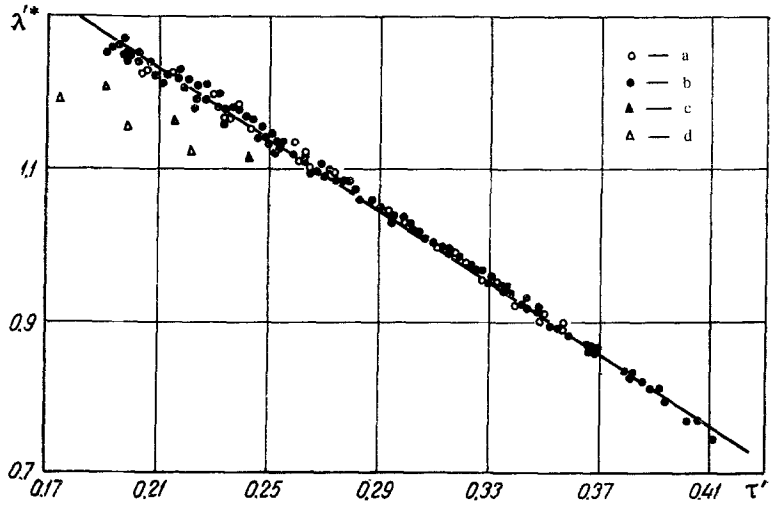

Fig. 4. Generalized thermal conductivity relationship for: a) Paraffins; b) fractions of Ozeksuat oil; c) fraction (260°–270° C) of Anastas'ev oil; d) fraction (340°–350° C) of Anastas'ev oil.

T = 0° K [7]. In this case the temperature coefficient is determined from the expression

$$\beta' = (\rho_1 - \rho_2)/(\rho_1 T_2 - \rho_2 T_1).$$

It should be borne in mind in the calculation of β' that the accuracy of determining it depends on the selected temperature difference between T_1 and T_2. The accuracy increases with increase in the temperature difference.

On the graph (Fig. 4) 160 experimental values of the thermal conductivity of narrow fractions of Ozeksuat oil in the temperature range 20°–220° and 29 values of the thermal conductivity of some paraffins in the temperature range 20°–220° C from [3] are plotted in the reduced coordinates $\lambda'^* = \lambda_T/\lambda_{T'=0.31}$ and $\tau' = \beta' T$; the value $\lambda_{T'=0.31}$ is taken at the reference value of the reduced temperature $\tau' = 0.31$. The number 0.31 is chosen to include all the experimental data in the investigated temperature range.

The graph shows that the experimental values of the thermal conductivity of narrow fractions and paraffins deviate from the general line, given by the equation

$$\lambda_T/\lambda_{\tau'=0.31} = 1.728 - 2.559\,\tau',$$

by not more than 2.4%. The mean square deviation does not exceed 1.0%.

To confirm this we determined the thermal conductivity and density of two fractions (with boiling point 260°–270° and 340°–350° C) of Anastas'ev oil. Anastas'ev oil has a paraffin-naphthene-aromatic base and differs considerably in its properties from Ozeksuat oil [11]. The graph in Fig. 4 shows that the experimental points for the investigated fractions of Anastas'ev oil deviated considerably (by as much as 10%) from the general line.

We also tested experimental data for commercial oil products [8–10]. The experimental points for B-70 benzine and T-1 fuel [8], samples No. 3 and No. 4 [9], DL diesel fuel and tractor kerosene [10] fitted the general line fairly well. The data for T-5 fuel [8], T-1 and TS-1 fuels [10], and B-70 benzine [9], deviated considerably from it. In view of this, Zenkevich's conclusion [7] that low-viscosity oil products (fuels), form a group of similar substances is not correct.

The thermal conductivity of oil products and its variation evidently depend on the nature of the oil, on its group hydrocarbon composition. Hence, the relationships obtained above are not valid for all oil products, but only for products obtained from oils of the same origin. In this case, as the graph in Fig. 4 shows, not only low-viscosity, but also high-viscosity fractions with a boiling point up to 550° C, fit the general line quite well.

These investigations have shown that there is a definite relationship between the thermal conductivity and molecular structure of the investigated liquids and that the theory of similarity can be applied not only to homogeneous pure liquids, but also to complex mixtures, such as fractions of high-paraffin Ozeksuat oil.

NOTATION

ε and σ are constants characterizing the chemical nature of the interacting molecules (σ has the dimensions of length and ε the dimension of energy); r is the distance between molecules; λ^* is the reduced thermal conductivity; T* is the reduced temperature: $f(r/\sigma)$, $\lambda^*(T^*)$ are universal functions for similar substances: k is the Boltzmann constant; T is the absolute temperature. The superscripts p and f refer to paraffins and fractions, respectively.

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