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ON PREDICTION OF THE THERMAL CONDUCTIVITY OF LIQUIDS

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Based on the Predvoditelev-Vargaftik formula, which relates uniquely thermal conductivity with density, a method is developed to predict the thermal conductivity of organic liquids, their mixtures, as well as petroleum products over a wide range of state parameters. The method employs a three-constant equation of state of a cellular model. The method is distinguished by the small amount of initial information required and an acceptable prediction accuracy.

At present, the prediction of liquid properties is an urgent problem, since the possibilities of experimental studies are limited and a rigorous theoretical approach is almost impossible, because the theory of the liquid state of a substance is insufficiently developed. Since liquids find wide application as working media and heat agents, in chemical engineering, petroleum chemistry, power engineering, and cooling technology, one faces the problem of determining the thermal conductivity λ of liquids when investigating thermal processes and calculating and designing heat-exchange equipment. Having no way of analyzing the available methods of predicting λ of liquids, we point out some drawbacks typical of these methods: the methods are applicable for a narrow assortment of substances and a rather limited range of state parameters, they are often complicated and cumbersome and need extensive experimental data, since the initial data do not always ensure the required level of accuracy. The existing methods of λ investigation in binary liquid systems mainly come down to a study of the properties of the systems as functions of only the concentration of their component at atmospheric pressure. In this connection, we suggest a new method for predicting λ of liquids and liquid mixtures over a wide range of state parameters.

The method is based on the Predvoditelev-Vargaftik formula, which uniquely relates the thermal conductivity of a liquid to its density:

$$\lambda = B\rho^{4/3} . \tag{1}$$

Liquid density is reliably predicted by the equation of state of the cellular model of a liquid derived by P. M. Kesselman and I. V. Onufriev [1]:

$$z = 1 - 1.744 \frac{\varepsilon_{\text{liq}}}{kT} \left[(b_{0\text{liq}} \rho)^2 - 0.4654 \, (b_{0\text{liq}} \rho)^4 \right] , \tag{2}$$

where

$$\frac{\varepsilon_{\text{liq}}}{k} = 0.795 T_{\text{cr}} \exp \left[c \left(1 - T/T_{\text{cr}}\right) \right] ,$$

$$b_{0\text{liq}} = \frac{2}{3} \pi N \sigma_{\text{liq}}^{3} , \quad \sigma_{\text{liq}}^{-3} = a - bT ,$$

a, b, c are constants. The theoretical and physical validity and the high accuracy of prediction of thermodynamic properties over a wide range of state parameters make it possible to employ Eq. (2) to describe the properties of

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TABLE 1. Quality of Thermal Conductivity Prediction of Organic Liquids

Liquid	Ref.	T, K	P, MPa	Mean error, %	
				method 1	method 2
Hexane	[3]	290–450	0.1–50	2.42	3.43
Pentadecane	[4], [5]	290–620	0.1–49	2.13	3.50
Octene-1	[3]	290–500	0.1–50	2.07	2.00
Hexadecene-1	[4], [5]	290–550	0.1–49	2.48	2.81
Benzene	[3]	290–550	0.1–150	2.04	4.11
n-Xylene	[3]	290–550	0.1–150	2.22	2.87
Heptanol	[4], [5]	290–500	0.1–221	2.29	3.10
Decanol	[3]	290–450	0.1–100	1.86	3.53
Gas condensates:					
Stavropol deposit	[6]	273–313	0.1	1.05	0.83
Bukhara deposit	[6]	273–313	0.1	3.85	4.40
Shatlyk deposit (fraction 275–250°C)	[9]	293–530	0.1–40	1.16	1.35
Petroleum:					
Ozeksuatskaya (fraction 210–220°C)	[7]	293; 473	0.1–49	–	2.53
Malgobenskaya (fraction fraction 150–160°C)	[7]	293; 473	0.1–49	–	3.28
Technical-grade oils:					
PMS-10	[8]	293–573	0.1	0.40	0.38
PFMS-4	[8]	293–573	0.1	0.23	0.36
PÉS-1	[8]	293–573	0.1	0.30	0.36
Diesel fuel	[8]	293–333	0.1	0.13	0.15

liquid mixtures using the data on the pure components and the theory of conformal solutions [1]. In [2], different methods of density prediction are described in detail which can be varied depending on the amount of initial information.

An extensive study of the coefficient B from formula (1) for different classes of organic liquids, i.e., saturated and unsaturated hydrocarbons, aliphatic alcohols, aromatic hydrocarbons, and liquid petroleum products, has revealed that in general the coefficient B changes with temperature and pressure. However, with sufficiently high accuracy of density prediction in the range $(0.4 \pm 0.8)T_{cr}$, the parameter B can be used in the form

$$B \cdot 10^4 = B_0 \cdot 10^4 + 0.0002\, P \; (P\,,\ \text{MPa})\,, \tag{3}$$

where B_0 is a constant. Here, the error in λ calculation is, on the average, 4–5%. Depending on the volume of initial information and the required accuracy, two basic approaches to B_0 determination are adopted for pure liquids:

1) Given experimental data on the thermal conductivity of a liquid on the saturation line or on the constant-pressure line $P = 0.1$ MPa, the coefficient B_0 is selected to fit the condition of the best description of the file of experimental data by formula (1);

2) If λ is known only at one experimental point (usually λ and ρ at $T = 293.15$ K, $P = 0.1$ MPa are most available), it is recommended to let B_0 be equal to

TABLE 2. Mean Error in Prediction of the Thermal Conductivity of Mixtures $\delta\lambda_m$, %

Mixture	Ref.	T, K	P, MPa	Weight fraction x	Method	
					1	2
Cyclohexane–benzene	[5]	293–393	0.1	0.25; 0.50; 0.75	1.50	0.86
Cyclohexane–toluene	[5]	293–353	0.1	0.25; 0.50	1.01	0.80
Heptane–hexanol	[10]	293–393	0.1	0.25; 0.50; 0.75	1.91	2.25
Octane–decanol	[10]	293–393	0.1	0.50	0.95	2.38
Heptane–hexadecane	[10]	293–393	0.1	0.50	1.25	1.35
Octane–heptadecane	[10]	293–393	0.1	0.25; 0.50; 0.75	1.97	1.73
Octane–octene-1	[11]	280–420	0.1–50	0.25; 0.50; 0.75	3.56	4.18
Hexane–heptane	[12]	208–473	0.1–50	0.25; 0.50; 0.75	2.21	2.30
Hexane–pentane	[12]	208–473	0.1–50	0.25; 0.50; 0.75	3.61	3.80
Hexane–nonene	[12]	320–473	0.1–50	0.25; 0.50; 0.75	2.54	–
Hexane–decene	[12]	220–473	0.1–50	0.25; 0.50; 0.75	2.00	2.25
Hexane–toluene	[13]	198–473	0.1–50	0.25; 0.50; 0.75	1.03	2.25

$$B_0 = \lambda_0/\rho_0^{4/3},$$

where λ_0, ρ_0 are the thermal conductivity and the density of the liquid at the known experimental point.

Both approaches have been verified for several classes of organic liquids, namely, saturated ($C_5 - C_{24}$) and unsaturated ($C_7 - C_{18}$) hydrocarbons, aliphatic alcohols ($C_7 - C_{18}$), and aromatic hydrocarbons (benzene toluene, μ-xylene, n-xylene, o-xylene). Table 1 illustrates the quality of λ prediction for several selected representatives of the investigated classes of liquids, which shows the reliability of the suggested prediction method.

An analysis of the errors in thermal conductivity calculations gives grounds to extend the described method of λ prediction to liquid mixtures. To predict the thermal conductivity of mixtures λ_m, it is recommended to use Eqs. (1) and (3). Since the density of liquid solutions is calculated with an experimental accuracy [1], the problem of λ_m prediction is reduced to development of a method for calculation of the coefficient B_0 for mixtures (B_{0m}). By analogy with pure liquids, several methods are adopted for B_{0m} determination.

If λ is known for a mixture of fixed composition on the constant-pressure line $P = 0.1$ MPa or at one experimental point, then methods 1) and 2) for pure liquids can be used to predict the thermal conductivity of a mixture. This approach has been used to predict the thermal conductivity of petroleum products, and multicomponent liquid mixtures, whose composition is usually unknown. Determination was made of the thermal conductivity of liquid petroleum fractions (the Oseksuatsk and Malgobensk deposits) and gaseous condensates of the Shatlyk, Stavropol, Maikop, and Bukhara deposits as well as some commercial oils and liquid fuels. The density of these mixtures was calculated by the equation of state (2). The calculation error was, on the average, 2–3% (see Table 1).

Since data on the thermal conductivity of mixtures are limited in number, whereas λ of many components of these mixtures is known, it is necessary to develop methods of B_{0m} prediction that employ data on the thermal conductivity of the individual components. By analogy with pure liquids, two basic approaches to B_{0m} prediction have been developed.

1. The availability of data on the thermal conductivity of individual mixture components makes it possible to calculate B_{0i} for each component. It is suggested that B_{0m} be calculated by an additive scheme

$$B_{0\mathrm{m}} = \sum_{i=1}^{n} B_{0i} x_i , \tag{4}$$

where n is the number of mixture components.

2. If the λ of the individual components is known for the same T and P (usually λ at $T = 293.15$ K, $P = 0.1$ MPa are most available), it is recommended that B_{0i} be determined for each component at the given parameters and $B_{0\mathrm{m}}$ calculated by formula (4).

Both methods suggested for $B_{0\mathrm{m}}$ determination were implemented in λ prediction for 17 binary liquid mixtures, of which eight were predicted at high pressures. Table 2 shows the quality of λ prediction for mixtures. It is seen that the prediction error increases with a decrease in the amount of initial information and is 3–4%, on the average, not exceeding 10%.

In conclusion, the main features of the suggested prediction method are a small amount of initial information, the possibility of λ prediction over a wide range of state parameters, its applicability for an extensive and much-used class of organic liquids, reliability, and simplicity of implementation.

NOTATION

λ, thermal conductivity; z, compressibility; $P/RT\rho$; P, pressure; R, universal gas constant; T, temperature; ρ, density; k, Boltzmann constant; N, Avogadro number; M, molecular weight; x, weight concentration. Subscripts: liq, liquid; cr, critical; m, mixture.

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