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A new temperature–thermal conductivity relationship for predicting saturated liquid thermal conductivity

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Abstract

A new temperature–thermal conductivity relationship similar to the Rackett equation for saturated liquid densities is proposed. The first-order group contribution values proposed earlier for predicting the thermal conductivity at the normal boiling point [S.R.S. Sastri, K.K. Rao, Chem. Eng. 100(8) (1993) 106–107] are revised. Combining these two, the thermal conductivities of organic liquids are predicted over the entire saturated liquid region using the normal boiling point, critical temperature and chemical structure as inputs. Below the normal boiling point, the average absolute deviation and the maximum absolute deviation between the predicted data and the literature data are 5.6% and 28.9%, respectively. These figures compare favourably with those of the Nagvekar method [M. Nagvekar, T.E. Daubert, Ind. Eng. Chem. Res. 26 (1987) 1562–1565], claimed to be the best available one applicable to all types of liquids. The deviations between the predicted and literature values are of the same order as the variations in the experimental data, even at temperatures upto 0.98 T_r, where T_r is the reduced temperature. The proposed correlation is in agreement with the observation of B.C. Sakiadis and J. Coates [AIChE J. 1 (1955) 275–288] regarding the near constancy of the pseudo critical thermal conductivity for members of the homologous series, but it does not support their other expectations regarding the regularity in the variation in the thermal conductivity and temperature coefficient of thermal conductivity for these liquids. The periodic variation in the temperature coefficient with the number of carbon atoms observed by J.D. Raal and R.L. Rijisdijk [J. Chem. Eng. Data 26 (1981) 351–359] for *n*-alcohols is also not supported. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Thermal conductivity; Method of calculation; Organic liquids; Normal boiling point; Critical temperature

1. Introduction

Liquid thermal conductivity is an important transport property required in heat transfer calculations. An accurate determination of this property is very difficult due to the development of convective currents and heat losses during the experiment. As a result, data on liquid thermal conductivity are not as readily available as those for other properties of liquids. Even in cases where data are available, it is difficult to evaluate the accuracy of the same [1–5]. Deviations upto 20% in the thermal conductivity values and still larger deviations for the temperature coefficients reported by different investigators are common [1–4]. In view of this, it often becomes necessary to use estimated data. Most of the available methods for estimating liquid thermal conductivity depend on the prediction of the data at a selected reference temperature and subsequent extension to other temperatures, using one of the established temperature–thermal conductivity relationships. For example, the Sato–Riedel [5,6] and Sastri et al. [7] methods predict the data at the normal boiling point, while the Missenard [8] and API Technical Data Book methods [9] use 293.15 K as the reference temperature. The application of these methods is recommended generally for temperatures below or near the normal boiling point only [5]. Birkett [6], Nagvekar [10], Reid et al. [5] and Sastri et al. [7] discussed the other limitations of these methods. Other correlations, including the theoretical and semi-theoretical ones proposed for the estimation of liquid thermal conductivity, involve one or more additional parameters like liquid density and hence their utility is restricted to those cases where reliable data on these parameters are readily available.

In this paper, the authors propose a new temperature–thermal conductivity relationship to correlate the data in the saturated liquid region ranging from the triple point to temperatures very close to the critical point. This relationship is combined with the data on the thermal conductivity at the normal boiling point (estimated by a group contribution

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method proposed earlier by Sastri et al. [7]) to predict the data over the entire saturated liquid region.

2. Existing temperature–thermal conductivity relationships

Except for some liquids, like those containing multihydroxy and multi-amine groups, the thermal conductivity of organic liquids decreases with temperature. Below or near the normal boiling point over small temperature ranges, the variation in thermal conductivity with temperature can be represented by

$$k = A - BT \tag{1}$$

where k is the liquid thermal conductivity (W m^{-1} K^{-1}) at temperature T (K) and A and B are constants that depend on the liquid. The relationship proposed by Riedel [11–13] is found to be better over a wider temperature range [5,14]. According to this

$$k = C\left[1 + \frac{20}{3}(1 - T_r)^{2/3}\right] \tag{2}$$

where C is a material dependant constant and T_r the reduced temperature.

Teja et al. [15] and Nagvekar [10,16] used a more generalised form of Eq. (2), which is written as

$$k = D + E(1 - T_r)^{2/3} \tag{3}$$

Eq. (3) reduces to Eq. (2) when $E = 20/3\ D$. Nagvekar [10,16] also gave values for D and E in terms of group contributions. Baroncini et al. [17] used $(1 - T_r)^{0.38}/T_r^{1/6}$ as the temperature parameter. Pachaiyappan [18], Narasimhan et al. [19], and Sastri et al. [7] used T_{ref}/T as the parameter. Sastri et al. [7] showed that the use of the normal boiling point as T_{ref} would lead to a generalised relationship.

As pointed out earlier, all these temperature functions are unreliable above a reduced temperature of 0.8.

3. Proposed method

Over a wide range of conditions, the variation in fluid thermal conductivity depends on its density and temperature. It is generally accepted that the former can be correlated in terms of the latter two parameters. The density and temperature of a saturated fluid being interrelated, it should follow that the thermal conductivity of a saturated liquid can be expressed as a function of either of these variables. Since the Rackett equation and its modifications [20–25] successfully correlate the saturated liquid densities, an attempt is made to test the applicability of such equations to the thermal conductivities of saturated liquids.

According to these equations

$$k = MN^{(1-T_r)^n} \tag{4}$$

where M and N are constants specific to the liquid and n is the index which may be common for all liquids. The constants M and N being material dependant, Eq. (4) will serve only the limited purpose of correlating the data for interpolation unless generalised relationships are found for these constants. For this purpose, the methodology adopted by Sastri et al. [25] for predicting saturated liquid densities using a generalised form of Rackett equation was used as described below.

Using the critical temperature T_C and normal boiling point T_B as two reference points, Eq. (4) can be written as

$$k = k_C^*\left[\left(\frac{k_B}{k_C^*}\right)^{[(1-T_r)/(1-T_{Br})]^n}\right] \tag{5}$$

where k_B is the thermal conductivity at T_B, k_C^*, the pseudo thermal conductivity at T_C and $T_{Br} = T_B/T_C$. Extending the similarity with liquid densities further, it was assumed that

$$\frac{k_C^*}{k_B} = a \tag{6}$$

where a is a constant. k_C^* in Eqs. (5) and (6) is a characteristic value of the liquid that may or may not have any relationship with the actual thermal conductivity at the critical point. Eq. (5) is not applicable in the vicinity of the critical point since it neither indicates the large enhancement in k in the vicinity of the critical point nor the infinite value at the critical point predicted by modern theories. Eq. (5) can now be written as

$$k = k_B a^{[1-[(1-T_r)/(1-T_{Br})]^n]} \tag{7}$$

Application of Eq. (6) still requires data on k_B for a given liquid. Experimental k_B values are available for a few compounds only. For the others, these can be estimated easily by a first-order group contribution method proposed by Sastri et al. [7] according to the equation

$$k_B = \sum \Delta k_B + \sum \Delta k_{cor} \tag{8}$$

where $\sum \Delta k_B$ is the sum of the incremental values of the constituent groups and Δk_{cor} the correction factor required for some specific cases. The original Δk_B and Δk_{cor} values were based on the data of liquids with low and medium molecular weights and needed some revision when applied to the liquids with higher molecular weights. The following procedure was adopted for revising these values. Initially, the Δk_B values for CH_3 and CH_2 groups were optimised for Eq. (7) from the data of n-paraffins, using Newton's forward interpolation method for minimising the percentage average absolute deviation between the calculated and literature thermal conductivity data for this group. The values for other groups were subsequently optimised by selecting a group of liquids which contained one additional group compared to the earlier one, assuming no change in the values for the former group. A similar procedure was adopted for revising the correction factors. The revised

Table 1
Group contributions for calculating liquid thermal conductivity at the normal boiling point

Group	Δk_B (W m^{-1} K^{-1})	Remarks
Hydrocarbon		
$-CH_3$	0.0545	–
$-CH_2-$	−0.0008	–
$-\overset{\vert}{C}H-$	−0.0600	–
$-\overset{\vert}{\underset{\vert}{C}}-$	−0.1230	–
$=CH_2$	0.0545	–
$=CH-$	0.0020	–
$=\underset{\vert}{C}-$	−0.0630	–
$=C=$	0.1200	–
Ring	0.1130	in polycyclic compounds all rings are treated as separate rings
Non-hydrocarbon		
$-O-$	0.0100	–
$-OH$	0.0830	in aliphatic primary alcohols and phenols having no branch chains
	0.0680	others
$>CO$	0.0175	–
$>CHO$	0.0730	–
$-COO-$	0.0070	–
$-COOH$	0.0650	–
$-NH_2$	0.0880	–
$-NH-$	0.0065	–
$-NH-$ (ring)	0.0450	–
$-\overset{\vert}{N}-$	−0.0605	–
N (ring)	0.0135	–
$-CN$	0.0645	–
$-NO_2$	0.0700	–
S	0.0100	–
$-F$	0.0568	in perfluoro carbons
	0.0510	in others
$-Cl$	0.0550	–
$-Br$	0.0415	–
$-I$	0.0245	–
$-H$	0.0675	in methane, formic acid, formates etc.
Ring (three member)	0.1500	–
Ring (other)	0.1100	in polycyclic compounds all rings are considered as non-hydrocarbon rings

values for Δk_B and Δk_{cor} are given in Tables 1 and 2, respectively.

As a next step, the values of a and n were optimised using data from the literature [1–5,10,26–58], according to the method mentioned earlier.

4. Results and discussion

During the optimisation studies, it was found that the liquids studied need to be divided into two groups: (i) alcohols and phenols and (ii) others. The values of a and n for these two groups are

$$a = 0.856,\ n = 1.23 \text{ for alcohols and phenols} \tag{9a}$$

Table 2
Correction factors for calculating liquid thermal conductivity at the normal boiling point

Type of correction	Δk_{cor} (W m^{-1} K^{-1})
Hydrocarbons	
Compounds containing four or less carbon atoms	(5-C) × 0.0150, where C is number of carbon atoms
Non-hydrocarbons	
Compounds containing single CH_3 group with non-hydrocarbon groups other than COOH, Br, I[a]	0.0600
Compounds containing two hydrocarbon groups – two CH_3 or CH_3CH_2 or CH_2=CH with non-hydrocarbon groups other than COOH, Br, I[a]	0.0285
Unsaturated aliphatic compounds having three hydrocarbon groups	0.0285
Special groups $Cl(CH_2)_nCl$	0.0350
Compounds having more than one non-hydrocarbon group with hydrocarbon groups[a]	0.0095
Compounds having non-hydrocarbon groups only	0.1165

[a] Aliphatic non-hydrocarbon liquids like methylformate, aceticanhydride and ethylformate, having more than one type of non-hydrocarbon group and (i) one or two methyl groups or (ii) one ethyl group only, require two correction factors (one due to the hydrocarbon groups and the other due to the presence of more than one type of non-hydrocarbon group: see Appendix, example 2).

and

$$a = 0.160,\ n = 0.20 \text{ for other liquids} \tag{9b}$$

Sastri et al. [59] found it necessary to treat alcohols as a separate group of liquids for predicting surface tension.

Detailed evaluation of the proposed correlation was carried out on the basis of the average and maximum percentage deviations between the predicted and literature thermal conductivity values. Liquids containing multi-hydroxy and multi-amine groups for which thermal conductivity increases with temperature are excluded from the present evaluation. Table 3 gives a summary of the results for temperatures below the normal boiling point. Table 4 gives the corresponding data for the higher temperature range. Table 3 also gives comparative data for the methods of Sastri et al. [7] and Nagvekar [10,16]. Since a substantial amount of data is common to the present study and that of Nagvekar [10], the results of the latter study are utilised in the present evaluation.

The average absolute deviation (AAD) and maximum absolute deviation (MAD) between the data predicted by Eq. (7) and the literature data below the normal boiling point are 5.6% and 28.9%, respectively, for the 208 liquids (748 points) tested (Table 3). For the data above the normal boiling point, the AAD and MAD are 8.3% and 30.7%, respectively for 186 points tested (Table 4).

It can be seen that the AAD for the data predicted by Eq. (7) at temperatures below the normal boiling point compares favourably with that of Nagvekar which was

Table 3
Evaluation of the proposed method for predicting the saturated liquid thermal conductivity below the normal boiling point

Liquid			Proposed method (see Eq. (7))		Sastri et al. [7]		Nagvekar [10]	
Type	No.	Points (NP)	AAD	MAD	AAD	MAD	AAD	MAD
Hydrocarbons	65	261	6.0	28.9	5.9	24.0	3.7	23.2
Oxygen derivatives								
Ethers	9	29	8.6	17.1	7.4	18.8	7.3	20.4
Aldehydes	6	18	3.4	8.7	3.0	8.0	8.3	21.9
Ketones	8	26	5.0	10.7	4.1	11.9	6.3	34.6
Acids	7	30	7.0	22.0	7.3	22.7	6.5	68.0
Esters	18	57	6.7	18.3	7.1	18.6	9.7	35.0
Alcohols and Phenols	24	135	3.3	12.1	4.3	15.8	6.2	23.2
Nitrogen derivatives								
Amines	15	56	5.5	20.6	4.2	19.4	4.2	26.3
N-ring	3	6	3.0	8.9	5.5	8.8	NA	NA
Nitriles	3	9	2.5	6.3	3.2	6.7	1.2	4.0
Nitro	4	9	5.3	11.9	4.7	9.6	1.6	10.6
Sulphur derivatives	2	3	2.8	3.3	3.2	3.3	NA	NA
Halogen derivatives								
Fluorine	7	11	7.5	14.6	8.9	18.4	3.3	6.8
Chlorine	18	44	6.1	24.8	5.9	24.3	6.6	16.2
Bromine	3	11	4.4	8.4	4.9	9.0	2.1	12.8
Iodine	2	7	2.3	4.9	2.2	4.4	3.8	11.9
Mixed	10	22	9.9	27.8	9.6	25.0	3.5	7.0
Multi group derivatives	4	14	10.3	18.6	10.3	19.0	1.0	4.4
All liquids	208	748	5.6 (5.5)	28.9 (29.0)	5.8	25.0	5.9	68.0

NA: Method not applicable.
AAD% $= (1/\mathrm{NP})\sum 100|[(k_{\mathrm{cal}} - k_{\mathrm{lit}})/k_{\mathrm{lit}}]|$.
Figures in parenthesis indicate deviations with T_C estimated by the method of Somayajulu [57].

found to be superior to the other recommended methods [10,16]. The maximum deviation for the present method (28.9%) is also significantly lower compared to that of the latter method (68%). The Nagvekar method gave lower AAD for hydrocarbons compared to Eq. (7). The apparently lower AADs obtained with the former method in the case of some other groups of liquids, such as those containing fluorine and nitrogen, are due to the relatively large number of group values used compared to the number of liquids tested, and in a few cases, the group values are based on the single compound tested [10]. The use of the temperature function proposed earlier by Sastri et al. [7] also gave deviations of the same order as the present one for temperatures below the normal boiling point (Table 3) and has the additional advantage of being simpler and not requiring data on T_C. A further limited comparison of the thermal conductivities predicted by the different methods for the liquids selected by Reid et al. [5] and given in Table 5 supports the above conclusions.

Table 4
Evaluation of proposed correlation for predicting liquid thermal conductivity at temperatures above the normal boiling point

T range (K)	Points (NP)	AAD	MAD
$T_B - 0.95\ T_r$	163	7.9	30.7
$0.95\ T_r - 0.98\ T_r$	23	9.9	24.9
$T_B - 0.98\ T_r$	186	8.3	30.7
	–	10.0[a]	53.8[a]
	–	(8.3)	(32.3)

[a] Figures correspond to the method of Sastri et al. [7].
AAD% $= (1/\mathrm{NP})\sum 100|[(k_{\mathrm{cal}} - k_{\mathrm{lit}})/k_{\mathrm{lit}}]|$.
Figures in parenthesis indicate deviations with T_C estimated by the method of Somayajulu [57].

At temperatures above the normal boiling point, Eq. (7) gave significantly lower AAD and MAD of 8.3% and 30.9%, respectively, compared to the corresponding values of 10.0% and 53.8%, respectively, for the method of Sastri et al. [7]. Predicted data in the T_r range 0.98–1.0 using Eq. (7) were, in general, found to be lower than the literature data. The observed increase in liquid thermal conductivity in the region close to the critical temperature [5], which is not indicated by Eq. (7), may be the reason for this. In view of this, the data above 0.98 T_r are not included in the evaluation of the proposed correlation.

It can be seen from Tables 3–5 that the proposed method is applicable to all types of organic liquids (except those

Table 5
Comparison of different methods for predicting the thermal conductivity of liquids selected by Reid et al. [5]

Liquid	T (K)	k_{lit} (W m^{-1} K^{-1})	% Deviation in predicted thermal conductivity by the method of				
			Eq. (7)	Sastri et al. [7]	Nagvekar [10]	Baroncini et al.[a]	Miscenard and Riedel[a]
Propane	323	0.0783	23.4	20.1	−25.0	−19.0	18.0
n-Pentane	293	0.114	−3.4	−4.3	2.4	−5.7	17.0
	303	0.111	−2.6	−3.0	1.4	−5.9	17.0
n-Decane	314	0.121	1.1	−3.6	5.5	−3.2	9.5
	349	0.119	2.7	−2.4	5.0	−2.9	9.8
Cyclohexane	293	0.124	−3.6	−4.1	5.1	−1.2	3.7
Methylcyclopentane	293	0.121	−5.5	−6.5	−3.5	−3.2	3.8
	311	0.115	−3.5	−4.5	−2.5	−2.2	4.7
Benzene	293	0.148	−7.1	−7.3	−4.1	0.0	−5.1
	323	0.100	−4.1	−4.6	−2.9	1.9	−4.0
	389	0.114	2.5	−1.9	−2.0	15.1	−1.8
Ethylbenzene	293	0.132	2.0	1.7	−5.5	2.0	4.4
	353	0.118	5.4	3.8	−5.7	2.9	5.3
Ethanol	293	0.165	7.5	9.7	−7.1	3.3	24.0
	313	0.152	13.9	15.2	−2.6	0.0	28.0
	347	0.35	23.0	23.2	2.9	3.5	32.0
n-Octanol	293	0.166	−3.1	0.5	−2.2	−11.0	5.6
t-Butyl alcohol	311	0.116	0.9	0.0	2.1	4.5	77.0
m-Cresol	293	0.150	1.6	10.0	1.3	10.0	28.0
	353	0.145	−0.6	3.7	−0.5	3.8	21.0
Aniline	290	0.178	−0.1	2.3	−2.5	NA	10.0
Propionic acid	285	0.173	−16.0	−17.3	−11.5	−8.9	15.0
Methylene chloride	253	0.159	−0.5	0.2	NA	−17.0	−6.3
	293	0.148	0.3	0.0	NA	−19.0	−7.9
Carbon tetrachloride	253	0.110	−7.2	−5.7	NA	−6.4	15.0
	293	0.103	−6.2	−6.4	NA	−7.3	14.0
Ethyl bromide	293	0.103	−4.4	−4.7	−3.7	2.0	−6.9
Chlorobenzene	2.33	0.141	−1.2	4.7	3.6	−0.5	2.6
	353	0.111	9.0	8.1	7.9	2.4	7.1
Iodobenzene	253	0.106	−3.3	3.9	−3.9	−15.0	5.1
	353	0.0938	−0.8	−0.6	4.1	−17.0	4.5
Ethyl acetate	293	0.147	−12.7	−14.3	−9.5	2.9	3.1
	333	0.141	−15.4	−16.2	−15.4	2.4	−2.7
Butyl acetate	293	0.137	−0.8	−3.1	2.7	2.5	9.2
Acetone	273	0.171	0.5	−0.5	−6.6	−9.8	3.7
	313	0.151	6.0	5.3	−3.1	−6.9	6.6
Diethylether	293	0.129	−6.0	−6.8	−6.3	3.9	22.0
Acetaldehyde	293	0.190	−1.1	−1.2	−22.4	NA	−11.0
AAD	–		5.5	6.1	5.7	6.3	14.8

[a] As cited in Reid et al. [5].
% Deviation $= 100[k_{\mathrm{cal}} - k_{\mathrm{lit}}]/k_{\mathrm{lit}}$.
NA: Method not applicable.
AAD% $= (1/\mathrm{NP})\sum 100|([k_{\mathrm{cal}} - k_{\mathrm{lit}})/k_{\mathrm{lit}}]|$.

containing multi-hydroxy and multi-amine groups) over the entire saturated liquid region, the only inputs required being the data on T_B and T_C, besides the chemical structure. This is in contrast to the earlier methods which have limitations over the types of liquids and range of temperatures. For example, the method of Baroncini et al. is not applicable to compounds containing nitrogen and sulphur, while the methods of Nagvekar and Sato et al. are not applicable to the lower members of the series. The need to assign separate values for the contribution of individual compounds like cyclohexanol, 1,2-propylene oxide and dioxane even after providing for a large number of groups (84 nos.) and the anomalous change in the contribution of certain groups with temperature (for example, the basic ketone group at a T_r of 0.4807) are some of the other drawbacks of the Nagvekar method. Besides, these methods are recommended for use upto a T_r of 0.8 only. On the other hand, even at temperatures close to T_C – in the reduced temperature range 0.95–0.98 T_r – the MAD for the data predicted by Eq. (7) is of the same order as that for the lower temperature range (Tables 3 and 4).

In order to extend the application of the proposed method to liquids for which the data on T_C are not available, the use of T_C as predicted by group contribution methods is examined. The use of T_C as predicted by the method of Somayajulu [57] gave AAD and MAD of 5.5% and 29.0%, respectively, for the data below the normal boiling point. The corresponding AAD and MAD for the data above the normal boiling point are 8.3% and 32.3%, respectively. Comparison of these figures with the data in Tables 3 and 4 shows that the use of the predicted T_C does not significantly affect the over all reliability of the proposed method.

The generalised nature of the present correlation makes it possible to examine some of the observations of earlier investigators [4,60].

According to the proposed method, k_C/k_B is a constant (see Eq. (6)). Since the contribution of the CH_2 group is relatively small (Table 1), k_B and hence k_C may be considered to be nearly constant for a given series of compounds except the lower members. This observation is close to the expectation of Sakiadis et al. [60] that the thermal conductivities obtained by the extrapolation of data at lower temperatures to the critical temperature should be a constant for the members of a homologous series.

Another observation that follows from the theory of Sakiadis et al. [60] relates to the regularity in the variation in k at a given reduced temperature for the members of a homologous series. The thermal conductivity data at 0.6 T_r, calculated from Eq. (7) for n-paraffins and n-aliphatic primary alcohols given in Table 6, do not support the conclusion that the thermal conductivity at the same reduced temperature should show a decreasing trend with chain length for the members of a homologous series [60].

Table 6
Variation in thermal conductivity with chain length for n-alkanes and n-alcohols at $T_r = 0.6$ K

No. of C atoms	n-Alkanes		n-Alcohols	
	k_{cal} (see Eq. (7))	k_{lit}	k_{cal} (see Eq. (7))	k_{lit}
1	0.1797	0.1820[a]	0.2043	0.2021[b]
2	0.1546	0.1510[b]	0.1740	0.1655[b]
3	0.1415	0.1397[b]	0.1439	0.1507[b]
4	0.1274	0.1255[b]	0.1436	0.1451[b]
5	0.1130	0.1194[b]	0.1433	0.1426[b]
6	0.1142	0.1183[b]	0.1433	0.1423[b]
7	0.1152	0.1174[b]	0.1432	0.1435[b]
8	0.1163	0.1156[b]	0.1433	0.1469[b]
9	0.1173	0.1132[b]	0.1436	0.1484[b]
10	0.1182	0.1127[b]	0.1447	0.1466[b]
11	0.1190	0.1214[b]	–	–
12	0.1198	0.1066[b]	0.1437	0.1502[b]
13	0.1205	0.1152[b]	–	–
14	0.1209	0.1094[b]	–	–
15	0.1221	0.1147[b]	–	–
16	0.1224	0.1101[b]	–	–
17	0.1235	0.1199[b]	–	–
18	0.1243	0.1224[b]	0.1580	0.1494[b]
19	0.1247	0.1241[b]	–	–
20	0.1252	0.1153[b]	–	

[a] Green [26].

[b] Nagvekar [10].

Table 7
Variation in the temperature coefficient of thermal conductivity for n-alcohols

Alcohols	$dk/dT \times 10^3$ (see Eq. (10))		$dk/dT \times 10^3$ literature[a]
	$T = 273.15$ K	$T = 0.6$ T_r	
Methanol	−0.250	−0.232	−0.260
Ethanol	−0.234	−0.216	−0.251
1-Propanol	−0.195	−0.175	−0.234
1-Butanol	−0.194	−0.170	−0.208
1-Pentanol	−0.194	−0.165	−0.178
1-Hexanol	−0.196	−0.163	−0.176
1-Heptanol	−0.198	−0.161	−0.247
1-Octanol	−0.202	−0.161	−0.270
1-Nonanol	−0.207	−0.163	−0.260
1-Decanol	−0.219	−0.168	−0.232

[a] Raal et al. [4].

Lastly, there is a divergence in the observations of Sakiadis et al. [60] and Raal et al. [4] regarding the variation in the temperature coefficient of the liquid thermal conductivity for the members of a homologous series. Differentiating Eq. (7) with respect to T, the temperature coefficient of thermal conductivity can be derived as

$$\frac{dk}{dT} = \frac{\left[kn(1-T_r)^{n-1}\ln a\right]}{T_C(1-T_{Br})^n} \tag{10}$$

The temperature coefficients for n-aliphatic primary alcohols, calculated from Eqs. (7), (9a) and (10) at $T = 273$ K and $T_r = 0.6$ are given in Table 7. The data reported by Raal et al. at 273 K are also given in Table 7 for comparison. It can be seen that the calculated data (Table 7) do not indicate any regularity in the variation observed by Sakiadis et al. [60] or the periodicity in the variation observed by Raal et al. [4]. The results of the present study are considered to be more reliable compared to the data of Sakiadis et al. [60] or Raal et al. [4] since the former are derived from generalised equations which are applicable over the entire saturated liquid region and the latter from data over small temperature ranges only. In this context, it may also be noted that Eq. (7) represents all the data on phenols and alcohols with AAD and MAD of 3.9% and 19.0%, respectively. The corresponding figures for the data of Raal et al. are 2.1% and 6.5%, respectively, which are within the range of the variation in the experimental data reported [61].

Some examples of the estimation of the saturated liquid thermal conductivity by the proposed method are given in the Appendix A.

5. Conclusions

A new temperature thermal–conductivity correlation similar to the Rackett equation for saturated liquid densities is proposed. In combination with a first-order group contribution method for predicting the thermal conductivity at the normal boiling point, the proposed method can be used to predict the liquid thermal conductivity at any point on the saturated liquid curve. The proposed correlation is applicable to all liquids except those showing an increasing trend with temperature. The correlation compares favourably with those of Nagvekar and Sastri et al. for temperatures below the normal boiling point. At higher temperatures, the deviations are within the range of the variation in the experimental data. Data derived from the proposed correlation do not support the observations of Sakiadis et al. and Raal et al. regarding the relative variation in the thermal conductivity and temperature coefficient within the members of a homologous series.

6. Nomenclature

A	constant in Eq. (1) ($\mathrm{W\,m^{-1}\,K^{-1}}$)
a	constant in Eq. (6)
B	constant in Eq. (1) ($\mathrm{W\,m^{-1}\,K^{-2}}$)
C	constant in Eq. (2) ($\mathrm{W\,m^{-1}\,K^{-1}}$)
D	constant in Eq. (3) ($\mathrm{W\,m^{-1}\,K^{-1}}$)
E	constant in Eq. (4) ($\mathrm{W\,m^{-1}\,K^{-1}}$)
k	thermal conductivity of a saturated liquid at temperature T ($\mathrm{W\,m^{-1}\,K^{-1}}$)
k_B	thermal conductivity of a saturated liquid at the normal boiling point ($\mathrm{W\,m^{-1}\,K^{-1}}$)
Δk_B	contribution of the group/structure to thermal conductivity at the normal boiling point ($\mathrm{W\,m^{-1}\,K^{-1}}$)
k_C^*	pseudo thermal conductivity at the critical point ($\mathrm{W\,m^{-1}\,K^{-1}}$)
Δk_{cor}	correction factor to thermal conductivity at the normal boiling point ($\mathrm{W\,m^{-1}\,K^{-1}}$)
M	constant in Eq. (4) ($\mathrm{W\,m^{-1}\,K^{-1}}$)
N	constant in Eq. (4)
n	index in Eq. (5)
T	temperature of a saturated liquid (K)
T_B	normal boiling point of the liquid (K)
T_{Br}	reduced boiling point of the liquid, T_B/T_C (K)
T_C	critical temperature of the liquid (K)
T_r	reduced temperature, T/T_C
T_{ref}	reference temperature (K)

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Appendix A

Some examples of saturated liquid thermal conductivity estimation by the proposed method

1. Benzene at 389 K

$T_B =$	$T_C =$	$1 - T_r =$	$1 - T_{Br} =$
353.24 K	562.16 K	0.3080	0.3716

Estimation of k_B (Table 1)

Constituent	Number	Δk_B ($\mathrm{W\,m^{-1}\,K^{-1}}$)
=CH–	6	0.002×6
Aromatic hydrocarbon ring	1	0.113×1

$$k_B = \sum \Delta k_B = 0.125\,\mathrm{W\,m^{-1}\,K^{-1}}$$

For hydrocarbons, $a = 0.16$ $n = 0.20$

$$k = k_B a^{[1-(1-T_r/1-T_{Br})^n]} = 0.1168\,\mathrm{W\,m^{-1}\,K^{-1}}$$

$k_{lit} = 0.114\ \mathrm{W\,m^{-1}\,k^{-1}}$ [5]
Deviation $= 100 \times (0.1168 - 0.114)/0.114 = 2.5\%$

2. Methyl formate at 323 K

$T_B =$	$T_C =$	$1 - T_r =$	$1 - T_{Br} =$
304.85 K	487.2 K	0.337	0.3743

Estimation of k_B (Tables 1 and 2)

Constituent	Number	Δk_B ($\mathrm{W\,m^{-1}\,K^{-1}}$)
–H	1	0.0545×1
–COO–	1	0.007×1
$-CH_3$	1	0.0545×1

Corrections

Type	Δk_{cor} ($\mathrm{W\,m^{-1}\,K^{-1}}$)
Non-hydrocarbon with single methyl group	0.060
Presence of two non-hydrocarbon groups	0.095

$$k_B = \sum \Delta k_B + \sum \Delta k_{cor} = 0.1985\,\mathrm{W\,m^{-1}\,K^{-1}}$$

For esters, $a = 0.16$ $n = 0.2$

$$k = k_B a^{[1-(1-T_r/1-T_{Br})^n]} = 0.1911\,\mathrm{W\,m^{-1}\,K^{-1}}$$

$k_{lit} = 0.179\ \mathrm{W\,m^{-1}\,K^{-1}}$ [5]
Deviation $= 100 \times (0.1911 - 0.179)/0.179 = 6.8\%$

3. 2-Methyl-2-propanol at 311 K

$T_B =$	$T_C =$	$1 - T_r =$	$1 - T_{Br} =$
355.5 K	506.21 K	0.3856	0.2977

Estimation of k_B (Table 1)

Constituent	Number	Δk_B ($\mathrm{W\,m^{-1}\,K^{-1}}$)
$-CH_3$	3	0.0545×3
$-\overset{\mid}{C}H-$	1	-0.123×1
–OH tertiary	1	0.068×1

$$k_B = \sum \Delta k_B = 0.1085\ \mathrm{W\,m^{-1}\,K^{-1}}$$

For alcohols, $a = 0.856 \qquad n = 1.23$

$$k = k_{\mathrm{B}} a^{[1-(1-T_{\mathrm{r}}/1-T_{\mathrm{Br}})^n]} = 0.115\,\mathrm{W\,m^{-1}\,K^{-1}}$$

$$k_{\mathrm{lit}} = 0.116\,\mathrm{W\,m^{-1}\,K^{-1}}\ [5]$$

$$\mathrm{Deviation} = 100 \times (0.115 - 0.116)/0.116 = -0.9\%$$

References

[1] D.K.H. Briggs, Thermal conductivity of liquids, Ind. Eng. Chem. 49 (1957) 418–421.

[2] G.M. Mallan, M.S. Michaelian, F.J. Lockhart, Liquid thermal conductivities of organic compounds and petroleum fractions, J. Chem. Eng. Data 17 (1972) 412–415.

[3] R.W. Powell, H. Groot, Use of thermal comparator method for thermal conductivity measurements on liquids, values for three organic series: normal alcohols, acids and saturated hydrocarbons, Int. J. Heat Mass Transfer 15 (1972) 360–366.

[4] J.D. Raal, R.L. Rijsdijk, Measurement of alcohol thermal conductivities using a relative strain compensated hot wire method, J. Chem. Eng. Data 26 (1981) 351–359.

[5] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th ed., McGraw-Hill, New York, 1987.

[6] J.D. Birkett, Thermal conductivity, in: W.J. Lyman, W.F. Reehl, D.H. Rosenblatt (Eds.), Handbook of Chemical Property Estimation Methods, McGraw-Hill, New York, 1982.

[7] S.R.S. Sastri, K.K. Rao, Quick estimating for thermal conductivity, Chem. Eng. 100(8) (1993) 106–107.

[8] A. Missenard, Conducitivit é thermique des solides, liquides, gaz et de leurs melanges, Eyrolles Editions, Paris, 1965.

[9] American Petroleum Institute, Technical Data Book – Petroleum Refining, ch. 12, 4th ed., Washington, DC, revisions extant 1984.

[10] M. Nagvekar, A group contribution method for liquid thermal conductivities, M.S. Thesis, The Pennsylvania State University, University Park, 1984.

[11] L. Riedel, The thermal conductivity of aqueous solutions and strong electrolytes, Chem. Ing. Tech. 23 (1951) 59–64.

[12] L. Reidel, New thermal conductivity measurements for organic liquids, Chem. Ing. Tech. 23 (1951) 321–324.

[13] L. Reidel, Thermal conductivity measurements on mixtures of various organic compounds with water, Chem. Ing. Tech. 23 (1951) 465–469.

[14] A.K. Rahalkar, D.S. Viswanath, N.R. Kuloor, Prediction of thermal conductivity of organic liquids – a corresponding states approach, Ind. J. Technol. 7(3) (1969) 67–74.

[15] A.S. Teja, P. Rice, A generalised corresponding states method for the prediction of the thermal conductivity of liquids and liquid mixtures, Chem. Eng. Sci. 36 (1981) 417–422.

[16] M. Nagvekar, T.E. Daubert, A group contribution method for liquid thermal conductivity, Ind. Eng. Chem. Res. 26 (1987) 1362–1365.

[17] C. Baroncini, P. Di Filippo, G. Latini, M. Pacetti, Organic liquid thermal conductivity: a prediction method in the reduced temperature range 0.3 to 0.8, Int. J. Thermophys. 2(1) (1981) 21–38.

[18] V. Pachiayappan, Thermal conductivity of organic liquids, Br. Chem. Eng. 16 (1971) 382–384.

[19] K.S. Narasimhan, K.M. Swamy, K.L. Narayana, New correlation for thermal conductivity, Chem. Eng. 82(8) (1975) 83–84.

[20] H.G. Rackett, Equation of state for saturated liquids, J. Chem. Eng. Data 15 (1970) 514–517.

[21] C.F. Spencer, R.P. Danner, Improved equation for prediction of saturated liquid density, J. Chem. Eng. Data 17 (1972) 234–240.

[22] H.E. Rea, C.F. Spencer, R.P. Danner, Effect of pressure and temperature on the liquid densities of pure hydrocarbons, J. Chem. Eng. Data 18 (1973) 227–230.

[23] T. Yamada, R.D. Gunn, Saturated liquid molar volumes, the Rackett equation, J. Chem. Eng. Data 18 (1973) 234–236.

[24] C.F. Spencer, S.B. Adler, A critical review of equations for predicting saturated liquid density, J. Chem. Eng. Data 23 (1978) 82–89.

[25] S.R.S. Sastri, S. Mohanty, K.K. Rao, Prediction of saturated liquid volumes of organic compounds, Fluid Phase Equilibria 132 (1997) 33–46.

[26] D.W. Green (Ed.), Perry's Chemical Engineer's Handbook, Section 3, 6th ed., McGraw-Hill, New York, 1984.

[27] R.W. Gallant, Physical properties of hydrocarbons Part 9, Thermal conductivity of C1 to C4 hydrocarbons, Hydrocarbon Processing 45(12) (1966) 113–122.

[28] V.P. Sokolova, I.F. Golubev, Thermal conductivity of methane at different temperatures and pressures, Thermal Eng. 14(3) (1967) 123–127.

[29] D.E. Leng, E.W. Comings, Thermal conductivity of propane, Ind. Eng. Chem. 49 (1957) 2042–2045.

[30] L.T. Carmichael, J. Jacobs, B.H. Sage, Thermal conductivity of fluids, propane, J. Chem. Eng. Data 13 (1968) 40–46.

[31] H.M. Roder, C.A. Nieto de Castro, Thermal conductivity of liquid propane, J. Chem. Eng. Data 27 (1982) 12–15.

[32] R.C. Reid. J.M. Prausnitz, T.K. Sherwood, The Properties of Gases and Liquids, 3rd ed., McGraw-Hill, New York, 1977.

[33] R.C. Reid, T.K. Sherwood, The Properties of Gases and Liquids, Their Estimation and Correlation, McGraw-Hill Book Co., New York, l958.

[34] R.W. Powell, A.R. Challoner, Measurement of thermal conductivity of *n*-octadecane, Ind. Eng. Chem. 53 (1961) 581–582.

[35] B.J. Gudzinowicz, R.H. Campbell, J.S. Adams, Thermal conductivity measurements of complex saturated hydrocarbons, J. Chem. Eng. Data 9 (1964) 79–82.

[36] E.G. Hancock (Ed.), Propylene and Its Industrial Derivatives, Earnest Benn Ltd., London, 1973, p. 74.

[37] G.W. Swift, A. Migliox, Measurements of thermal conductivity and viscosity of liquid propylene, J. Chem. Eng. Data 29 (1984) 56–59.

[38] V. Pachaiyappan, S.H. Ibrahim, N.R. Kuloor, A new correlation for thermal conductivity, Chem. Eng. 74(4) (1967) 140–144.

[39] A.K. Abas-zade, Heat conductivity of some organic compounds in the critical region, Doklady Akad. Nauk, S.S.S.R. 68 (1949) 665–668; CA 44: 921C.

[40] R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics, 60th ed., CRC Press, Boca Raton, FL, 1979.

[41] J.A. Dean (Ed.), Lange's Handbook of Chemistry, 13th ed., McGraw-Hill, New York, 1985.

[42] W.H. Hedley, M.V. Milnes, W.H. Yanko, Thermal conductivity and viscosity of biphenyl and the terphenyls, J. Chem. Eng. Data 15 (1970) 122–127.

[43] D.E. Gray (coordinating Ed.), American Institute of Physics Handbook, 2nd ed., McGraw-Hill, New York, 1963, 4-85–4-87.

[44] D.T. Jamieson, G. Cartwright, Thermal conductivity of associated fluids, J. Chem. Eng. Data 25 (1980) 199–201.

[45] I.F. Golubev, T.N. Vasil Kovaskaya, The thermal conductivity of methanol and ethyl alcohol at different temperatures and pressures, Thermal Eng. 16(5) (1969) 126–133.

[46] V.N. Popov, B.A. Melov, Thermal conductivity of the ethanol–water system in the temperature range 20–300°C and at pressure up to 30 M N/m^2, Thermal Eng. 18(8) (1981) 125–129.

[47] T.N. Vasil Kovaskaya, I.F. Golubev, Thermal conductivity of *n*-propyl and iso-propyl alcohols at various temperatures and pressures, Thermal Eng. 16(6) (1969) 128–132.

[48] J.E.S. Venart, R.C. Prasad, Thermal conductivity of phenol, J. Chem. Eng. Data 25 (1980) 198–199.

[49] C.C. Li, Thermal conductivity of liquid mixtures, AIChE J. 22 (1976) 927–930.

[50] D.Q. Kern, Process Heat Transfer, McGraw-Hill, New York, 1950, p. 800.

[51] V. Pachiayappan, S.H. Ibrahim, N.R. Kuloor, Thermal conductivities of organic liquids – a new correlation, J. Chem. Eng. Data 11 (1966) 73–76.

[52] O.B. Cecil, R.H. Munch, Thermal conductivity of organic liquids, Ind. Eng. Chem. 48 (1956) 437–440.

[53] M. Grayson (Ed.), Kirk–Othmer Encyclopaedia of Chemical Technology, vol. 1, 5, 11 and 15, 3rd ed., Wiley, New York, 1978–81.

[54] J.E.S. Venart, Fluid thermal conductivity measurements, J. Scient. Inst. 411(12) (1964) 727–731.

[55] J.E.S. Venart, Liquid thermal conductivity measurements, J. Chem. Eng. Data 10 (1965) 239–241.

[56] R.M.Di. Guillo, W.L. Mc Gregor, A.S. Teja, Thermal conductivities of the ethanolamines, J. Chem. Eng. Data 37 (1992) 242–245.

[57] G.R. Somayajulu, Estimation procedures for critical constants, J. Chem. Eng. Data 34 (1989) 106–120.

[58] T.E. Daubert, R.P. Danner, Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation, vol. 1–4, Design Institute for Physical Property Data, AIChE, Hemisphere, New York, 1989.

[59] S.R.S. Sastri, K.K. Rao, A simple method to predict surface tension of organic liquids, Chem. Eng. J. 59(2) (1995) 181–186.

[60] B.C. Sakiadis, J. Coates, Thermal conductivity of liquids, AIChE J. 1 (1995) 275–288.

[61] D.T. Jamieson, J.B. Irving, J.S. Tudhope, Liquid Thermal Conductivity – a Data Survey to 1973, H.M. Stationary office, Edinburgh, UK, 1975.