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Correlation of Liquid Thermal Conductivity Using Molecular Connectivity Indices

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Correlations for the thermal conductivity of liquids at 0.1 MPa and saturated liquids were proposed for hydrocarbons and non-hydrocarbon compounds separately in this work. The proposed correlations require only structural descriptors, that is, molecular connectivity indices and the number of heteroatoms, as input parameters. Since molecular connectivity indices can be calculated once the molecular structure of the substance concerned is known, the correlations based on them are predictive in nature. The new correlations were compared with existing correlations, and for the 65 hydrocarbons and the 192 non-hydrocarbon compounds adopted in this work, the average absolute deviations are 4.02 and 4.31%, respectively.

KEY WORDS: thermal conductivity; liquid; correlation; prediction; molecular connectivity index.

1. INTRODUCTION

Thermal conductivity is an important property in process design and development, since most processes involve heat transfer. Although abundant experimental data exist, it is still necessary to develop estimation methods with known accuracy. A number of models [1–6] have been proposed to correlate or predict the thermal conductivity of liquids, and the predictive models can be divided into two groups in general. The first group is those models that correlate thermal conductivity with other physical properties, for example, the method of Sato and Riedel [3], who correlated thermal conductivity with the critical temperature and normal boiling point temperature for a substance. Klaas and Viswanath [5], on

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the other hand, correlated the two input parameters in their model with molar polarization. This kind of model cannot be applied to substances whose required properties are not available. The other kind of predictive models are those models that correlate thermal conductivity with the molecular structure of the substance concerned. These can be subdivided into two groups, those based on the group-contribution concept, and those based on molecular structural descriptors, such as topological indices. The models of Nagvekar and Daubert [4] and Rodenbush et al. [6] are two representative group-contribution models. Although group-contribution models are predictive, they cannot be applied to substances whose group parameters are not available, and these models usually cannot distinguish isomers, ortho, meta, and para placement in rings, etc.

Molecular connectivity indices, the commonly used molecular structural descriptors, have been widely used in the correlation of the physiochemical properties of organic substances [7, 8], and some predictive correlations based on them have been developed in our previous work [9, 10]. Since molecular connectivity indices can be easily calculated as long as the molecular structure of the substance is known, correlations based on them are predictive and easy to apply. Furthermore, they can distinguish isomers without difficulty. Therefore, correlations based on molecular connectivity indices are more attractive and useful, which is the motivation of this work.

2. THE CONNECTIVITY INDEX

Connectivity indices have been widely used as molecular structural descriptors, which contain a large amount of information about the molecule, including the numbers of hydrogen and non-hydrogen atoms bonded to each non-hydrogen atom, the details of the electronic structure of each atom, and the molecular structural features [7, 8, 11]. The definitions for the connectivity indices used in this work are given below.

The general expression for the m-th order simple connectivity index is as follows:

$$^{m}\chi_{k} = \sum_{j=1}^{n_m} \prod_{i=1}^{m+1} (\delta_i)_j^{-0.5} \tag{1}$$

where m is the order of the connectivity index, k denotes a contiguous path type of a fragment, which is divided into paths (P), clusters (C), path/clusters (PC), and chains (cycles) (CH). n_m is the number of the relevant paths, and δ_i is the simple connectivity index, equal to the number of non-hydrogen atoms to which the ith non-hydrogen atom is bonded.

If δ_i is replaced by δ_i^V, the valence connectivity index, we can obtain the expression for the mth order valence connectivity index, ${}^m\chi_k^V$, as follows:

$$ {}^m\chi_k^V = \sum_{j=1}^{n_m} \prod_{i=1}^{m+1} (\delta_i^V)_j^{-0.5} \tag{2}$$

where the valence connectivity index, δ^V, is defined by

$$\delta^V = \frac{Z^V - h}{Z - Z^V - 1} \tag{3}$$

In Eq. (3), Z is the atomic number, Z^v is the number of valence electrons, and h is the number of hydrogen atoms suppressed.

The calculation method for the total structure valence connectivity index, χ_t^V, is as follows:

$$\chi_t^V = \frac{1}{(\prod_{i=1}^{n} \delta_i^V)^{1/2}} \tag{4}$$

The above molecular connectivity indices can be calculated easily by hand as long as the molecular structure of the substance concerned is known, and the values of the connectivity indices for the hydrocarbons and the non-hydrocarbon compounds used in this work are listed in Tables I and II, respectively. A review of the development of the connectivity index was recently published by Randić [12].

3. DEVELOPMENT OF NEW CORRELATIONS FOR THERMAL CONDUCTIVITY OF LIQUIDS USING CONNECTIVITY INDICES

The temperature dependence of the thermal conductivity can be written as [13, 14]

$$\lambda = 2pvmlC_v \tag{5}$$

where p is the probability of energy transfer on collision, v is the vibrational frequency, m is the number of molecules per unit area, l is the distance between adjacent planes, and C_v is the specific heat. Based on Eq. (5), Viswanath and Rao [1] proposed the following expression:

$$(\lambda/\lambda_0) = A(T/T_0)^{-b} \tag{6}$$

where λ_0 is the value of thermal conductivity at T_0 and A and b are constants for a given substance. Furthermore, Klaas [15] found that the value

Table I. Calculated Results for Hydrocarbons and the Connectivity Indices Used

Substance	Temp. range (K)	NDP	${}^0\chi^V$	${}^1\chi$	χ_c^3	AAD[a] (%)
propane	213.15–223.15	2	2.707	1.414	0.000	1.32
butane	252.15–252.65	2	3.414	1.914	0.000	2.75
isobutane	193.15–257.15	2	3.577	1.732	0.577	4.95
pentane	273.15–323.15	6	4.121	2.414	0.000	3.55
isopentane	273.15–323.15	6	4.284	2.270	0.408	0.66
hexane	273.15–333.15	4	4.828	2.914	0.000	2.28
2-methylpentane	310.95	1	4.992	2.770	0.408	5.89
3-methylpentane	310.95	1	4.992	2.808	0.289	4.86
2,2-dimethylbutane	310.95	1	5.207	2.561	1.561	6.35
2,3-dimethylbutane	310.95	1	5.155	2.643	0.667	6.13
heptane	293.15–453.15	9	5.536	3.414	0.000	3.17
octane	233.15–393.15	9	6.243	3.914	0.000	1.81
3-methyheptane	293.15	1	6.406	3.808	0.289	1.91
nonane	233.15–413.15	10	6.950	4.414	0.000	1.56
decane	253.15–433.15	10	7.657	4.914	0.000	1.36
undecane	253.15–453.15	11	8.364	5.414	0.000	1.59
dodecane	273.15–473.15	11	9.071	5.914	0.000	2.10
tridecane	273.15–493.15	12	9.778	6.414	0.000	2.09
tetradecane	293.15–513.15	12	10.485	6.914	0.000	2.14
pentadecane	293.15–533.15	12	11.192	7.414	0.000	1.87
hexadecane	313.15–553.15	13	11.899	7.914	0.000	1.90
heptadecane	313.15–573.15	14	12.607	8.414	0.000	1.80
octadecane	313.15–573.16	14	13.314	8.914	0.000	1.63
nonadecane	313.15–593.15	15	14.021	9.414	0.000	1.56
cosane	313.15–613.15	16	14.728	9.914	0.000	1.67
uncosane	333.15	1	15.435	10.414	0.000	6.21
docosane	333.15	2	16.142	10.914	0.000	4.57
tricosane	333.15	1	16.849	11.414	0.000	6.83
tetracosane	333.15	1	17.556	11.914	0.000	7.11
ethylene	112.15–244.35	3	1.414	1.000	0.000	6.80
propylene	293.15–323.15	2	2.284	1.414	0.000	9.93
isobutylene	191.95–255.95	2	3.207	1.732	0.577	3.11
hex-1-ene	273.15–323.15	3	4.406	2.914	0.000	2.82
hex-2-ene	293.15	1	4.569	2.914	0.408	1.42
hep-1-ene	273.15–348.15	4	5.113	3.414	0.000	1.49
oct-1-ene	273.15–373.15	5	5.820	3.914	0.000	2.03
dec-1-ene	273.15	1	6.527	4.914	0.000	6.36
dodecene	273.15	1	7.941	5.914	0.000	7.11
tetradec-1-ene	273.15	1	9.356	6.914	0.000	8.14
2-methyl-1,3-butadiene	133.15–303.15	18	3.492	2.270	0.408	3.68
benzene	283.15–433.15	16	3.464	3.000	0.000	5.37
toluene	193.15–513.15	20	4.387	3.394	0.289	3.60
ethylbenzene	293.15–413.15	7	5.094	3.932	0.204	3.19
o-xylene	293.15–413.15	7	5.309	3.805	0.471	1.88

Table I. *(Continued)*

Substance	Temp. range (K)	NDP	$^0\chi^V$	$^1\chi$	χ_c^3	AAD[a] (%)
m-xylene	293.15–413.15	7	5.309	3.788	0.577	1.58
p-xylene	293.15–413.15	7	5.309	3.388	0.577	4.99
n-propylbenzene	273.15	1	5.801	4.432	0.204	5.33
isopropylbenzene	293.15–413.15	7	5.964	4.305	0.500	3.78
1,2,3-trimethylbenzene	273.15	1	6.232	4.215	0.664	0.69
1,3,5-trimethylbenzene	293.15–413.15	7	6.232	4.182	0.866	7.35
1,2,4-trimethylbenzene	293.15–413.15	7	6.232	4.198	0.760	2.68
n-butylbenzene	293.15–413.15	7	6.508	4.932	0.204	8.94
naphthalene	358.15–373.15	2	5.619	4.966	0.333	8.53
1,2,3,4-tetrahydronaphthalene	293.15	1	6.138	4.966	0.333	7.27
diphenyl	349.15–373.15	4	6.774	5.966	0.333	4.60
tertbutylbenzene	293.15–413.15	7	6.887	4.605	1.510	3.89
1,2,4,5-tetramethylbenzene	283.15–353.15	2	7.155	4.609	0.943	7.04
m-terphenyl	355.35–372.95	3	10.083	8.933	0.667	6.83
p-cymene	293.15	1	6.887	4.698	0.789	6.27
p-terphenyl	486.45–493.15	3	10.083	8.933	0.667	8.18
phenanthrene	378.15–393.15	2	7.774	6.949	0.606	2.97
cyclohexane	283.15–353.15	6	4.243	3.000	0.000	2.44
cyclohexene	293.15–310.95	2	3.983	3.000	0.000	2.98
methylcyclopentane	293.15–311.15	2	4.406	2.894	0.289	2.91
cyclopentane	310.95	1	3.536	2.500	0.000	3.52
system average error		371				4.02

[a] $\mathrm{AAD} = \frac{1}{\mathrm{NDP}} \sum_i \left| \frac{\lambda_i^{\exp} - \lambda_i^{\mathrm{cal}}}{\lambda_i^{\exp}} \right| \times 100$, where NDP is the number of data points.

of A varies from 0.98 to 1.10 and the value of b varies from 0.60 to 0.68 for common substances.

In this work, the values of A and b are taken as 1.0 and 0.6, respectively, and Eq. (6) becomes

$$(\lambda/\lambda_0) = (T/T_0)^{-0.6} \tag{7}$$

Equation (7) can be rewritten as

$$\lambda = aT^{-0.6} \tag{8}$$

where $a = \lambda_0 T_0^{0.6}$.

The parameter a in Eq. (8) was taken as an adjustable parameter in this work, and it is correlated with the connectivity indices for a substance in the following section.

Table II. Calculated Results for Non-Hydrocarbon Compounds and the Connectivity Indices Used

Substance	Temp. range (K)	NDP	$^0\chi$	$^1\chi$	$^0\chi^V$	χ_t^V	N_{at}	AAD (%)
methanol	293–330	6	2.000	1.000	1.447	0.4470	0	4.35
ethanol	213.15–333.15	13	2.707	1.414	2.154	0.3162	0	3.69
propanol	300–370	6	3.414	1.914	2.861	0.2236	0	2.90
isopropanol	300–350	4	3.577	1.732	3.025	0.2582	0	2.56
butanol	213–390	11	4.121	2.414	3.569	0.1581	0	5.95
isobutanol	285–303.15	4	4.284	2.270	3.732	0.1826	0	2.09
secbutanol	273.15–338.15	3	4.284	2.270	3.732	0.1826	0	4.24
terbutanol	310.8	1	4.500	2.000	3.947	0.2236	0	10.74
pentanol	273.15–310.15	3	4.828	2.914	4.276	0.1118	0	8.01
isoamyl alcohol	298.15–303.15	2	4.992	2.770	4.439	0.1291	0	1.06
tertamyl alcohol	273–293	2	5.207	2.561	4.654	0.1581	0	12.30
hexanol	294.05–310.95	5	5.536	3.414	4.983	0.0791	−1	3.06
heptanol	273.15–308.65	3	6.243	3.914	5.690	0.0559	−1	2.27
heptan-3-ol	310.95	1	6.406	3.808	5.853	0.0646	−1	4.31
octanol	293.15–485.15	4	6.950	4.414	6.397	0.0395	−1	5.11
octan-2-ol	293.15–303.15	2	7.113	4.270	6.560	0.0456	−1	6.39
nonanol	273.15–303.15	3	7.657	4.914	7.104	0.0280	−1	1.36
decanol	293.15–298.15	2	8.364	5.414	7.811	0.0198	−1	3.59
undecanol	303.15	1	9.071	5.914	8.518	0.0140	−1	0.04
dodecanol	303.15–308.15	2	9.778	6.414	9.226	0.0099	−1	3.73
tetradecanol	323	1	11.192	7.414	10.640	0.0049	−1	3.32
octadecanol	337–347	2	14.021	9.414	13.468	0.0012	−1	–1.90
allyl alcohol	298.15	1	3.414	1.914	2.439	0.1291	0	6.97
cyclohexanol	293.15–298.15	2	5.113	3.394	4.560	0.0456	−1	11.28
m-cresol	293.15–353.15	3	5.983	3.788	4.757	0.0124	−1	4.24
benzyl alcohol	293.15–303.15	2	5.820	3.932	4.541	0.0101	−1	2.59
diethyl ether	193.15–293.15	6	4.121	2.414	3.822	0.2041	0	2.82
di-*n*-propyl ether	273.15–293.15	2	5.536	3.414	5.237	0.1021	0	4.95
ethyl *n*-butyl ether	310.95	1	5.536	3.414	5.237	0.1021	0	1.33
di-*n*-butyl ether	273.15–310.95	2	6.950	4.414	6.651	0.0510	0	1.54
methyl phenyl ether	303.15	1	5.820	3.932	4.795	0.0131	0	3.69
phenetole	293.15	1	6.527	4.432	5.502	0.0093	0	1.81
diphenyl ether	318.15–329.89	2	8.933	6.449	7.182	0.0004	0	3.13
ethylene glycol mono-*n*-butyl ether	293.15–310.95	2	6.243	3.914	5.391	0.0323	0	13.57
ethylene glycol mono-*n*-hexyl ether	293.15	1	7.657	4.914	6.805	0.0161	0	12.00
ethylene glycol mono-2-ethylbutyl ether	293.15	1	7.820	4.846	6.968	0.0186	0	9.19
ethylene glycol mono-phenyl ether	293.15	1	7.234	4.932	5.656	0.0029	0	12.72
ethylene glycol diethyl ether	293.15	1	6.243	3.914	5.645	0.0417	0	9.70

Table II. *(Continued)*

Substance	Temp. range (K)	NDP	$^0\chi$	$^1\chi$	$^0\chi^V$	χ_t^V	N_{at}	AAD (%)
ethylene glycol dibutyl ether	293.15	1	9.071	5.914	8.473	0.0104	0	1.69
diethylene glycol monomethyl ether	293.15	1	6.243	3.914	5.092	0.0186	0	10.53
diethylene glycol mono-*n*-butyl ether	310.95	1	8.364	5.414	7.213	0.0066	0	13.55
diethylene glycol diethyl ether	293.15	1	8.364	5.414	7.467	0.0085	0	9.33
diethylene glycol dibutyl ether	293.15	1	11.192	7.414	10.296	0.0021	0	3.82
dipropylene glycol	273	1	7.276	4.126	5.872	0.0136	0	5.42
acetaldehyde	273.15–303.15	3	2.707	1.414	1.986	0.2357	0	6.61
propionaldehyde	293.15–310.95	2	3.414	1.914	2.693	0.1667	0	1.40
n-butyraldehyde	273.15–310.95	3	4.121	2.414	3.400	0.1179	0	3.09
isobutyraldehyde	310.95	1	4.284	2.270	3.563	0.1361	0	11.76
valeraldehyde	273.15	1	4.828	2.914	4.107	0.0833	0	4.23
benzaldehyde	293.15–303.15	2	5.820	3.932	4.372	0.0076	0	1.54
furfuraldehyde	303.15–313.65	3	5.113	3.432	3.626	0.0093	0	7.70
heptanal	273.15	1	6.243	3.914	5.521	0.0417	0	0.39
decanal	273.15	1	8.364	5.414	7.642	0.0147	0	1.79
paraldehyde	303.15	1	6.853	4.182	5.957	0.0131	0	11.01
acetone	273–356	5	3.577	1.732	2.908	0.2041	0	6.43
methyl ethyl ketone	273.15–310.95	3	4.284	2.270	3.615	0.1443	0	3.41
diethyl ketone	273.15–310.95	2	4.992	2.808	4.322	0.1021	0	3.78
methyl *n*-propyl ketone	273.15–310.95	3	4.992	2.770	4.322	0.1021	0	2.49
cyclohexanone	293.15–303.15	2	5.113	3.394	4.444	0.0361	0	0.56
methyl butyl ketone	273.15	1	5.699	3.270	5.029	0.0722	0	1.53
acetylacetone	303.15	1	5.862	3.126	4.524	0.0295	0	5.45
acetophenone	303.15	1	6.690	4.305	5.295	0.0066	0	1.23
methyl *n*-amyl ketone	273.15–310.95	2	6.406	3.770	5.737	0.0510	0	2.46
di-*n*-propyl ketone	273.15–310.95	2	6.406	3.808	5.736	0.0510	0	2.47
ethyl *n*-butyl ketone	273.15–310.65	2	6.406	3.808	5.737	0.0510	0	1.98
methyl hexyl ketone	273.15–310.95	2	7.113	4.270	6.443	0.0361	0	2.64
diamyl ketone	293.15	1	9.234	5.808	8.565	0.0128	0	2.27
dihexyl ketone	313.15	1	10.648	6.808	9.979	0.0064	0	3.17
formic acid	298.15	1	2.707	1.414	1.433	0.1054	0	5.50
acetic acid	285.15–348.15	4	3.577	1.732	2.355	0.0913	0	3.88
propionic acid	285.15–303.15	3	4.284	2.270	3.063	0.0646	0	5.78
n-butyric acid	285.15–303.15	3	4.992	2.770	3.770	0.0456	0	3.29
isobutyric acid	285.15–303.15	2	5.155	2.643	3.933	0.0527	0	5.46
n-valeric acid	285.15–303.15	2	5.699	3.270	4.477	0.0323	0	3.92
isovaleric acid	303.15	1	5.862	3.126	4.640	0.0373	0	0.44
n-caproic acid	273.15–303.15	2	6.406	3.770	5.184	0.0228	0	2.11
oenanthic acid	303.15–323.15	2	7.113	4.270	5.891	0.0161	0	2.05

Table II. *(Continued)*

Substance	Temp. range (K)	NDP	$^0\chi$	$^1\chi$	$^0\chi^V$	χ_t^V	N_{at}	AAD (%)
n-caprylic acid	293.15–323.15	5	7.820	4.770	6.599	0.0114	0	1.99
n-capric acid	313.15–373.15	2	9.234	5.770	8.013	0.0057	0	4.73
myristic acid	338.15–373.15	2	12.063	7.770	10.841	0.0014	0	3.58
palmitic acid	343.15–373.15	2	13.477	8.770	12.255	0.0007	0	2.78
lauric acid	323.15	1	10.648	6.770	9.427	0.0029	0	1.04
methyl formate	293–297.2	2	3.414	1.914	2.394	0.0962	0	6.21
ethyl formate	277.15–303.15	3	4.121	2.414	3.101	0.0680	0	2.00
n-propyl formate	278.15–303.15	3	4.828	2.914	3.808	0.0481	0	3.94
n-butyl formate	278.15–303.15	2	5.536	3.414	4.515	0.0340	0	2.59
n-amyl formate	278.25	1	6.243	3.914	5.222	0.0241	0	4.40
heptyl formate	277.55	1	7.657	4.914	6.637	0.0120	0	4.07
octyl formate	278.68	1	8.364	5.414	7.344	0.0085	0	2.79
methyl acetate	277.05–303.15	3	4.284	2.270	3.317	0.0833	0	3.56
ethyl acetate	293.15–333.15	4	4.992	2.770	4.024	0.0589	0	1.42
n-propyl acetate	285.15–310.95	3	5.699	3.270	4.731	0.0417	0	2.27
isopropyl acetate	293.15	1	5.862	3.126	4.894	0.0481	0	3.00
n-butyl acetate	273.15–303.15	3	6.406	3.770	5.438	0.0295	0	2.03
n-amyl acetate	293.15–303.15	2	7.113	4.270	6.145	0.0208	0	0.85
hexyl acetate	277.75	1	7.820	4.770	6.852	0.0147	0	1.87
phenyl acetate	293.15	1	7.397	4.788	5.703	0.0027	0	1.03
n-octyl acetate	310.95	1	9.234	5.770	8.266	0.0074	0	1.88
secoctyl acetate	303.15	1	9.397	5.664	8.429	0.0085	0	10.50
n-decyl acetate	310.95	1	10.648	6.770	9.680	0.0037	0	3.06
octadecyl acetate	313.65	1	16.305	10.77	15.337	0.0002	0	9.50
methyl propionate	310.95	1	4.992	2.808	4.024	0.0589	0	3.33
ethyl propionate	303.15–310.95	2	5.699	3.308	4.731	0.0417	0	1.52
n-propyl propionate	310.95	1	6.406	3.808	5.438	0.0295	0	1.52
butyl propionate	277.75	1	7.113	4.308	6.145	0.0208	0	3.24
n-amyl propionate	310.95	1	7.820	4.808	6.852	0.0147	0	1.24
hexyl propionate	278.25	1	8.527	5.308	7.559	0.0104	0	4.64
methyl butyrate	285.15–303.15	2	5.699	3.308	4.731	0.0417	0	1.97
ethyl *n*-butyrate	277.45–310.95	3	6.406	3.808	5.438	0.0295	0	1.46
n-amyl butyrate	277.55–291.15	2	8.527	5.308	7.559	0.0104	0	1.20
methyl *n*-valerate	285.15–303.15	2	6.406	3.808	5.438	0.0295	0	1.50
ethyl *n*-valerate	293.15–303.15	2	7.113	4.308	6.145	0.0208	0	6.68
isobutyl valerate	294.15	1	8.690	5.164	7.722	0.0120	0	2.20
amyl valerate	294.15	1	9.234	5.808	8.266	0.0074	0	4.05
methyl methacrylate	290.15	1	5.862	3.181	4.524	0.0295	0	0.16
methyl caproate	300.15	1	7.113	4.308	6.145	0.0208	0	0.71
ethyl caproate	277.95	1	7.820	4.808	6.852	0.0147	0	2.42
diethyl oxalate	293.15	1	7.983	4.719	6.047	0.0035	0	2.39
methyl benzoate	293.15	1	7.397	4.843	5.703	0.0027	0	1.09
ethyl benzoate	293.15–294.85	2	8.104	5.343	6.410	0.0019	0	2.23
aniline	273.15–373.15	5	5.113	3.394	3.964	0.0185	−1	10.56

Table II. *(Continued)*

Substance	Temp. range (K)	NDP	$^{0}\chi$	$^{1}\chi$	$^{0}\chi^{V}$	χ_{t}^{V}	N_{at}	AAD (%)
nitrobenzene	273.15–398.15	6	6.690	4.305	4.651	0.0024	−1	11.29
adiponitrile	296.45	1	6.243	3.914	4.723	0.0125	−2	3.96
1-nitropropane	310.95	1	4.992	2.770	3.678	0.0373	−1	9.28
m-toluidine	293.15	1	5.983	3.788	4.887	0.0160	−1	2.29
o-toluidine	293.15	1	5.983	3.805	4.887	0.0160	−1	0.79
ethyl nitrate	303.15	1	4.992	2.770	3.379	0.0215	−1	12.15
n-propyl nitrate	303.15	1	5.699	3.270	4.086	0.0152	−1	9.21
n-butyl nitrate	303.15	1	6.406	3.770	4.793	0.0108	−1	4.85
quinoline	293.15–303.15	2	6.812	4.966	5.489	0.0024	−1	4.80
NN-diethylaniline	293.15–303.15	2	8.104	5.381	7.248	0.0072	−1	9.66
NN-dimethylaniline	293.15	1	6.690	4.305	5.834	0.0143	−1	4.50
NN-dimethylacetamide	293.15–298.15	2	5.155	2.643	4.355	0.0913	−1	11.20
NN-dimethylformamide	293.15–313.15	3	4.284	2.270	3.433	0.1054	−1	11.28
refrig11	213.15–373.15	17	4.500	2.000	4.280	0.2755	2.63	6.98
refrig21	233.15–373.15	15	3.577	1.732	3.223	0.2810	2.51	7.19
refrig142	193.15–313.15	15	4.284	2.270	3.174	0.0661	4.66	6.92
carbon tetrachloride	253.15–473.15	23	4.500	2.000	5.036	0.8265	0.48	5.21
chlorobenzene	273.15–393.15	5	5.113	3.394	4.521	0.0364	0.12	2.50
fluorobenzene	273.15–293.15	2	5.113	3.394	3.765	0.0121	2.27	3.19
chloroethane	273.15	1	2.707	1.414	2.841	0.8018	0.12	13.53
1-chloropropane	273.15–285.15	2	3.414	1.914	3.548	0.5669	0.12	12.27
1-chloro-2-methylpropane	285.15	1	4.284	2.270	4.418	0.4629	0.12	6.99
1-chloropentane	273.15–310.95	2	4.828	2.914	4.962	0.2835	0.12	3.35
1-chlorohexane	293.15	1	5.536	3.414	5.669	0.2004	0.12	0.60
1-chloroheptane	273.15	1	6.243	3.914	6.377	0.1417	0.12	1.01
1-chlorononane	273.15	1	7.657	4.914	7.791	0.0709	0.12	0.69
1-chlorodecane	310.95	1	8.364	5.414	8.498	0.0501	0.12	4.21
m-chlorotoluene	293.15	1	5.983	3.788	5.443	0.0315	0.12	1.41
o-chlorotoluene	293.15	1	5.983	3.805	5.443	0.0315	0.12	0.71
p-chlorotoluene	293.15–313.15	2	5.983	3.788	5.443	0.0315	0.12	2.35
m-dichlorobenzene	293.15	1	5.983	3.788	5.577	0.0357	0.24	4.79
o-dichlorobenzene	293.15	1	5.983	3.805	5.577	0.0357	0.24	1.35
p-dichlorobenzene	333.15	1	5.983	3.788	5.577	0.0357	0.24	4.26
dichloromethane	273.15–293.15	4	2.707	1.414	2.975	0.9091	0.24	7.36
1,1-dichloroethane	273.15	1	3.577	1.732	3.845	0.7423	0.24	5.45
1,2-dichloroethane	273.15–293.15	3	3.414	1.914	3.682	0.6429	0.24	7.34
1,2-dichloropropane	293.15	1	4.284	2.270	4.552	0.5249	0.24	7.23
dichloroethylene	293.15	1	3.414	1.914	3.422	0.4286	0.24	5.83
1,5-dichloropentane	310.95	1	5.536	3.414	5.803	0.2273	0.24	7.14
chloroform	273.15–313.15	4	3.577	1.732	3.979	0.8417	0.36	6.12
1,2,3-trichlorobenzene	333.15	1	6.853	4.215	6.634	0.0351	0.36	1.55
1,3,5-trichlorobenzene	343.15	1	6.853	4.182	6.634	0.0351	0.36	5.08
1,1,1-trichloroethane	273.15	1	4.500	2.000	4.902	0.7289	0.36	1.72

Table II. *(Continued)*

Substance	Temp. range (K)	NDP	$^0\chi$	$^1\chi$	$^0\chi^V$	χ_t^V	N_{at}	AAD (%)
1,2,4-trichlorobenzene	293.15–301.15	2	6.853	4.198	6.634	0.0351	0.36	4.29
trichloroethylene	293.15	1	4.284	2.270	4.479	0.4208	0.36	1.07
ally bromide	293.15	1	3.414	1.914	3.956	0.5669	0	5.33
benzyl chloride	298.15	1	5.820	3.932	5.228	0.0257	0.12	2.98
bromobenzene	290.15–303.15	3	5.113	3.394	5.351	0.0630	0	4.72
bromomethane	298.65	1	2.000	1.000	2.964	1.9640	0	12.32
bromoethane	273.15–303.15	4	2.707	1.414	3.671	1.3887	0	1.63
1-bromopropane	273.15–310.95	2	3.414	1.914	4.378	0.9820	0	0.86
2-bromopropane	293.15	1	3.577	1.732	4.541	1.1339	0	1.69
1-bromobutane	273.15–310.95	3	4.121	2.414	5.085	0.6944	0	1.27
1-bromo-2-methyl-propane	285.15—298.15	2	4.284	2.270	5.248	0.8018	0	9.11
1-bromopentane	273.15–310.95	2	4.828	2.914	5.792	0.4910	0	2.82
1-bromohexane	273.15–310.95	2	5.536	3.414	6.500	0.3472	0	3.61
1-bromoheptane	303.15	1	6.243	3.914	7.207	0.2455	0	3.90
1-bromooctane	293.15	1	6.950	4.414	7.914	0.1736	0	2.80
1-bromononane	273.15–293.15	2	7.657	4.914	8.621	0.1227	0	1.64
1-bromodecane	303.15	1	8.364	5.414	9.328	0.0868	0	0.99
iodobenzene	273.15–293.15	2	5.113	3.394	5.978	0.0831	−0.42	1.27
iodomethane	293.15	1	2.000	1.000	3.591	2.5912	−0.42	6.42
iodoethane	273.15–303.15	3	2.707	1.414	4.298	1.8323	−0.42	3.59
1-iodopropane	273.15–310.95	2	3.414	1.914	5.005	1.2956	−0.42	1.49
1-iodobutane	273.15–292.55	2	4.121	2.414	5.713	0.9161	−0.42	0.64
1-iodo-2-methyl-propane	293.15	1	4.284	2.270	5.876	1.0579	−0.42	3.09
1-iodopentane	273.15–293.15	2	4.828	2.914	6.420	0.6478	−0.42	2.18
1-iodohexane	273.15	1	5.536	3.414	7.127	0.4581	−0.42	1.30
1-iodoheptane	273.15	1	6.243	3.914	7.834	0.3239	−0.42	2.43
1-iodooctane	273.15	1	6.950	4.414	8.541	0.2290	−0.42	3.50
1-iodononane	273.15	1	7.657	4.914	9.248	0.1619	−0.42	5.08
system average error		444						4.31

4. RESULTS AND DISCUSSION

The experimental thermal conductivity data, at either 0.1 MPa pressure or at saturation pressure if the temperature is above the normal boiling point, were collected mainly from two sources [16, 17]. These data, most of them are accurate to ±5%, were adopted as the database to develop the new correlations. Since a unique correlation cannot give satisfactory correlative accuracy for both hydrocarbons and non-hydrocarbon compounds, two separate correlations were proposed. Based on the experimental data for 65 hydrocarbons with 371 data points, the following expression for a was obtained:

$$a = 11.43 - 8.482({}^0\chi^V)^{0.1} + 1.156({}^1\chi)^{0.6} - 0.1423\,{}^3\chi_c \tag{9}$$

where ${}^0\chi^V$, ${}^1\chi$, and ${}^3\chi_c$ are zero-order valence, first-order and third-order cluster connectivity indices, respectively, and λ calculated with Eq. (9) is in $W \cdot m^{-1} \cdot K^{-1}$. The average absolute deviations (AADs) for the 65 hydrocarbons calculated with Eqs. (8) and (9) are reported in Table I. The AAD varies from 0.66% to 9.93% for the substances concerned, with the system average AAD being 4.02%, which is within the experimental uncertainty in the data ($\pm 5\%$).

Equations (8) and (9) are applicable to the liquids at either 0.1 MPa pressure or at saturation pressure if the temperature is above the normal boiling point. Most reliable results can be obtained in the temperature range of $T_r = 0.5$ to 0.8, and the application to a temperature outside this range should be made with caution.

For non-hydrocarbon compounds, the experimental data for 192 compounds with 444 data points were collected to develop the expression for a, and the following expression was obtained:

$$a = 4.451 + 0.7978\,{}^0\chi - 11.99({}^0\chi^V)^{0.3} + 4.959({}^1\chi)^{0.3} + 8.590\chi_t^{V\,0.05} - 0.4371 N_{at} \tag{10}$$

and

$$N_{at} = 2.27N_F + 0.12N_{Cl} - 0.42N_I - N_{OH} - N_N \tag{11}$$

where ${}^0\chi$ and χ_t^V are zero-order and total structure valence connectivity indices, respectively. N_{at} is an atomic correction term, and N_F, N_{Cl}, N_I, and N_N represent the number of atoms of fluorine, chloride, iodine, and nitrogen in the compound, and N_{OH} represents the number of hydroxyls in the alcohol whose carbon atoms are larger than five. The calculated results are given in Table II, which shows that the overall AAD for the 192 compounds is 4.31%, covering a range of 0.04 to 13.57% for the compounds concerned.

Similar to the correlation proposed for hydrocarbon compounds, Eqs. (8), (10), and (11) are applicable to non-hydrocarbon liquids at either 0.1 MPa pressure or at saturation pressure if the temperature is above the

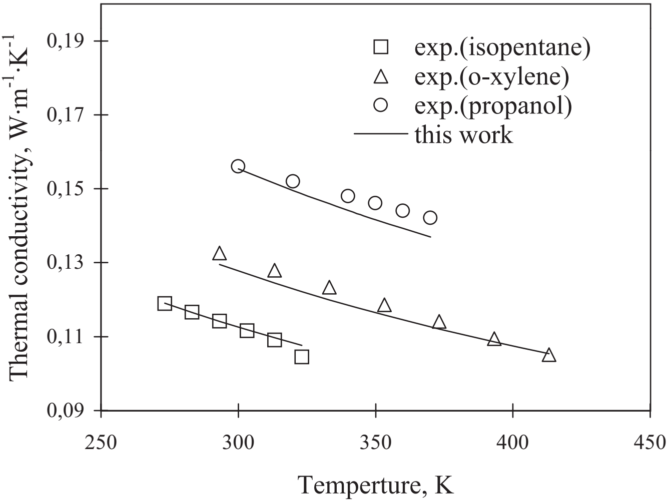

Fig. 1. Experimental and calculated thermal conductivities for some compounds.

normal boiling point, and reliable results can be obtained in the temperature range of $T_r = 0.5–0.7$.

The experimental and calculated thermal conductivities for some compounds are depicted in Fig. 1, which shows that the new correlations give good representation of the temperature dependence of the thermal conductivity of liquids.

Comparisons of the new correlations with some existing correlations are shown in Tables III and IV for hydrocarbons and non-hydrocarbon compounds, respectively. The methods of Nagvekar and Daubert [4] and Rodenbush et al. [6] are predictive methods based on the group-contribution concept, while the Sato and Riedel method [3] is a correlation of thermal conductivity with other physical properties. From the tables, it is evident that the method of Rodenbush et al. shows the best accuracy, however, the division of groups in their method is very detailed. The new correlations show worse accuracy than the method of Rodenbush et al., but better accuracy than the other two methods; however, the new correlations are easier to apply. Of course, the present work adopts two correlations for hydrocarbons and non-hydrocarbon compounds separately, which may bring slight inconvenience for application; however, the distinction of hydrocarbons and non-hydrocarbons is so easy, this should bring very little problem in practical applications.

Table III. Comparison of the New Correlation with Existing Models (Hydrocarbons)

Substance	Temp. range (K)	NDP	AAD (%) Nagvekar, Daubert [4]	Rodenbush et al. [6]	Sato, Riedel [3]	This work
propane	223–323	3	15.63	9.89	26.46	13.79
n-pentane	273–323	8	2.22	3.43	18.45	3.99
n-octane	233–393	9	1.92	1.46	3.71	1.81
n-decane	253–433	12	2.82	1.26	3.60	1.29
cyclohexane	283–353	6	3.43	1.83	10.75	2.44
methylcyclopentane	293–311	2	2.99	0.56	14.12	2.91
benzene	283–433	19	4.07	2.39	2.40	5.44
ethylbenzene	293–413	9	5.11	1.82	3.96	2.80
o-xylene	293–413	7	1.25	1.50	3.89	1.88
hexene	273–323	3	4.47	0.24	11.24	2.82
system average error		78	4.39	2.44	9.86	3.92

Table IV. Comparison of the New Correlation with Existing Models (Non-Hydrocarbon Compounds)

Substance	Temp. range (K)	NDP	AAD (%) Nagvekar, Daubert [4]	Rodenbush et al. [6]	Sato, Riedel [3]	This work
ethanol	213–347	16	11.94	4.40	18.28	3.69
n-octanol	293–485	4	5.57	5.04	15.00	5.11
tert-butyl alcohol	311	1	2.10	1.20	26.00	10.74
m-cresol	293–353	3	0.92	4.52	4.99	4.24
diethyl ether	193–293	7	9.24	2.69	1.40	3.55
propionic acid	285–303	3	4.70	6.11	6.69	5.78
ethyl acetate	293–333	4	11.33	1.64	8.23	1.42
butyl acetate	273–303	3	2.56	0.76	4.39	2.03
acetaldehyde	273–303	3	22.43	5.31	11.82	6.61
acetone	273–356	5	5.28	2.25	2.88	6.43
methyl *n*-propyl ketone	273–310	3	2.55	3.43	0.80	2.49
methyl butyl ketone	273	1	6.45	3.14	0.60	1.53
methylene chloride	273–293	6	–	1.81	10.90	8.70
carbon tetrachloride	253–473	25	–	3.84	6.55	5.06
chlorobenzene	273–393	7	3.00	3.69	1.97	4.30
ethyl bromide	273–303	4	2.83	1.64	9.33	1.63
idobenzene	273–353	4	2.21	3.28	1.53	2.51
aniline	290	1	2.50	2.00	14.52	5.76
system average error		100	5.98	3.15	8.10	4.53

5. CONCLUSION

Two new correlations for the estimation of the thermal conductivity of organic liquids at 0.1 MPa and saturated liquids were proposed for hydrocarbons and non-hydrocarbon compounds, respectively. Since only molecular connectivity indices and the number of heteroatoms are required in the calculations, they are predictive models, and are very easy to apply. Comparing with those existing correlations, which require either other physical properties or group parameters, the new correlations can be applied to predict the thermal conductivity for a substance as long as its molecular structure is known. Therefore, the new correlations provide an alternative estimation method for the thermal conductivity of liquids, which requires only molecular structural information. The calculated results show that the new correlations give good accuracy, which are useful for molecular and process design and development.

NOMENCLATURE

A, a	Parameters
AAD	Average absolute deviation defined in the footnote of Table I
b	Parameter
C_v	Specific heat
h	Number of hydrogen atoms suppressed
l	Distance between adjacent planes
m	Number of molecules per unit area
NDP	Number of data points
N_{at}	Atomic correction term
N_{Cl}	Number of chloride atoms in the compound
N_{F}	Number of fluorine atoms in the compound
N_{I}	Number of iodine atoms in the compound
N_{N}	Number of nitrogen atoms in the compound
N_{OH}	Number of hydroxyl in the alcohol
p	Probability of energy transfer on collision
T, T_0	Temperature
T_{r}	Reduced temperature
v	vibrational frequency
Z	Atomic number
Z^v	Number of valence electrons

Greek Letters

${}^m\chi$	mth-order connectivity index
${}^m\chi^V$	mth-order valence connectivity index
χ_t^V	Total structure valence connectivity index
δ_i	Simple connectivity index
δ_i^v	Valence connectivity index
λ, λ_0	Thermal conductivity

Subscripts

c	Cluster

Superscripts

cal.	Calculated value
exp.	Experimental value

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