Organic Liquid Thermal Conductivity: A Prediction Method in the Reduced Temperature Range 0.3 to 0.8

C. Baroncini,[1] P. Di Filippo,[2] G. Latini,[1] and M. Pacetti[2]

A general correlation for organic liquid thermal conductivity, λ, estimation is proposed of the following type:

$$\lambda = A \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}}$$

where T_r is the reduced temperature and the factor A is practically temperature independent and characteristic of the particular compound investigated. The values of the factor A for 144 organic liquids are calculated (through selected experimental λ data) and are listed. The proposed correlation is tested, and the mean general deviation between calculated and selected experimental λ values is found to be smaller than 2% over wide temperature ranges (generally from $T_r = 0.3$ to $T_r = 0.8$); the maximum deviations are normally smaller than 6%. Successively, the compounds are investigated as members of the respective families in order to provide an expression for A by means of the best available physical properties of the liquids. Correlations are proposed (for alcohols, aromatics, esters, refrigerant fluids, paraffins, cycloparaffins, ketones, organic acids, ethers, and olefins) that contain the same reduced temperature dependence evidenced in the above equation and that differ in the expression suggested for the factor A. In this way, the thermal conductivity of the organic liquids can be evaluated, with a mean deviation generally less than 5%, in absence of experimental λ data.

KEY WORDS: liquids; property correlations; thermal conductivity; transport properties.

---

[1] Istituto de Fisica Sperimentale, Universita di Ancona, Ancona, Italy.
[2] Istituto di Fisica Tecnica, Universita di Ancona, Ancona, Italy

1. INTRODUCTION

The knowledge of the values of the thermal conductivity, λ, of liquids is needed in several engineering problems, but the experimental data generally cover a limited temperature range (often a small range near room temperature), and sometimes they are by various authors, using different techniques that may not always be comparable to each other. Moreover, for some liquids, the experimental λ values are not available.

If the experimental situation is subject to these difficulties, theoretical studies do not offer a better solution because the equations based on rigorous statistical mechanics [1, 2] are very difficult to solve and, moreover, produce thermal conductivity values affected with unacceptable errors. For these reasons, it appears convenient, in order to predict the thermal conductivity, to consider estimation methods empirically obtained or based on simple theories.

Actually, several correlations of this type exist in the literature, so that a critical study [3, 4] was developed by the authors of the present paper according to the following plan:

1. About 30 empirical or semiempirical equations existing in the literature were collected and represented in S.I. units.
2. Twenty liquids, belonging to the most important organic families, were chosen for which selected experimental thermal conductivity values exist in wide temperature ranges (generally from the melting point to the normal boiling point).
3. The thermal conductivity of the indicated 20 liquids was estimated through the collected correlations at various temperatures.

This investigation evidenced some general results:

1. The correlations based on a simplified theory are generally less accurate than the merely empirical ones.
2. The thermal conductivity of almost all organic liquids decreases when the temperature increases, and this experimental evidence is seldom satisfied by correlations that do not expressly contain the temperature.
3. Some equations give very satisfactory results at room temperature, i.e., about 20°C, but the errors become considerable when the temperature differs appreciably from this.
4. The best correlations (for example, those due to Reid et al. [5], to Scheffy and Johnson [6, 7], to Pachaiyappan and Vaidyanathan [8], and to Vaidyanathan and Velayutham [9]) normally exhibit mean general deviations between experimental and estimated thermal conductivity values slightly higher than 10%, and maximum deviations generally less than 30% over all the investigated temperature ranges.

The above-summarized general results, whose details are contained in ref. [4], pointed out the need for a new formula able to predict the values of λ for the organic liquids with deviations more acceptable than those indicated above.

The starting point was the Viswanath's equation [10]:

$$\lambda = \frac{3.6 \times 10^{-7}}{C} \cdot \frac{M^{1/2} \cdot \Delta H_{vb}}{V_b^{2/3} \cdot T^{1/2}} \cdot \frac{(1 - T_r)^{0.38}}{(1 - T_{br})^{0.38}} \tag{1}$$

where M is the molecular weight, V_b and ΔH_{vb} are the molal volume and the latent heat of vaporization at the normal boiling point, T is the absolute temperature, T_r is the reduced temperature, T_{br} is the reduced normal boiling point, and C is a particular "packing factor" depending on the liquid molecular structure.

The results of the calculations using Eq. (1) were not satisfactory (mean deviation between experimental and calculated λ values for 20 liquids was equal to 39%), but the following advantages were evidenced:

1. Equation (1) is very simple and does not contain parameters that are, in general, temperature dependent, an exception being the factor C as specified below.
2. The dependence of the estimated λ values on the temperature is generally of the same kind as the experimental one.

The "packing factor" C, which is assumed by Viswanath to be constant and equal to 2, really depends on the temperature and on the molecular structure of each compound, so that Eq. (1) was modified and the following correlation was proposed [4]:

$$\lambda = A_r \cdot \frac{M^{1/2} \cdot \Delta H_{vb}}{V_b^{2/3} \cdot T_r^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{(1 - T_{br})^{0.38}} \tag{2}$$

The factor A_r (whose S.I. units are $kg^{1/2} \cdot kmol^{-1/6} \cdot m \cdot s^{-1} \cdot K^{-1}$), characteristic of each liquid, is practically temperature independent, and its evaluation needs only a few selected experimental thermal conductivity data or even only one datum. Equation (2) was checked, and the result was satisfactory: the mean general deviation and the maximum deviation between experimental and calculated λ values for 20 organic liquids are less than 2 and 7%, respectively, for large temperature ranges.

The next step in the research concerned the factor A_r and its dependence on the physical properties of the liquids; this problem was solved for 30 refrigerant fluids [11, 12], and the following equation was proposed:

$$A_r = h \cdot T_c^{-1/3} \tag{3}$$

1. INTRODUCTION

The knowledge of the values of the thermal conductivity, λ, of liquids is needed in several engineering problems, but the experimental data generally cover a limited temperature range (often a small range near room temperature), and sometimes they are by various authors, using different techniques that may not always be comparable to each other. Moreover, for some liquids, the experimental λ values are not available.

If the experimental situation is subject to these difficulties, theoretical studies do not offer a better solution because the equations based on rigorous statistical mechanics [1, 2] are very difficult to solve and, moreover, produce thermal conductivity values affected with unacceptable errors. For these reasons, it appears convenient, in order to predict the thermal conductivity, to consider estimation methods empirically obtained or based on simple theories.

Actually, several correlations of this type exist in the literature, so that a critical study [3, 4] was developed by the authors of the present paper according to the following plan:

1. About 30 empirical or semiempirical equations existing in the literature were collected and represented in S.I. units.
2. Twenty liquids, belonging to the most important organic families, were chosen for which selected experimental thermal conductivity values exist in wide temperature ranges (generally from the melting point to the normal boiling point).
3. The thermal conductivity of the indicated 20 liquids was estimated through the collected correlations at various temperatures.

This investigation evidenced some general results:

1. The correlations based on a simplified theory are generally less accurate than the merely empirical ones.
2. The thermal conductivity of almost all organic liquids decreases when the temperature increases, and this experimental evidence is seldom satisfied by correlations that do not expressly contain the temperature.
3. Some equations give very satisfactory results at room temperature, i.e., about 20°C, but the errors become considerable when the temperature differs appreciably from this.
4. The best correlations (for example, those due to Reid et al. [5], to Scheffy and Johnson [6, 7], to Pachaiyappan and Vaidyanathan [8], and to Vaidyanathan and Velayutham [9]) normally exhibit mean general deviations between experimental and estimated thermal conductivity values slightly higher than 10%, and maximum deviations generally less than 30% over all the investigated temperature ranges.

Table I. General Table of the Liquids Investigated with Values of the Factor A, the Mean Deviations $\Delta\%$, and the Maximum Deviations $\Delta_{max}\%$ Between the Experimental λ Data and Those Predicted According to Eq. (4).

Liquids investigated	M	T_b	T_c	Red. temp. range	A	$\Delta\%$	$\Delta_{max}\%$
Paraffins							
Methane	16.04	111.7	190.6	0.57–0.92	0.264	0.9	1.4
Propane	44.10	231.1	369.8	0.41–0.63	0.185	2.9	4.6
n-Butane	58.12	272.7	425.2	0.36–0.64	0.168	3.0	5.2
n-Pentane	72.15	309.2	469.8	0.33–0.58	0.149	2.5	4.5
n-Hexane	86.18	342.1	507.4	0.44–0.68	0.152	0.3	0.8
3-Methylpentane	86.18	336.4	504.4	0.60–0.64	0.145	0.3	0.9
2-Methylpentane	86.18	333.4	497.5	0.61–0.65	0.143	0.0	0.0
2,3-Dimethylbutane	86.18	331.2	499.9	0.61–0.65	0.138	0.3	1.0
2,2-Dimethylbutane	86.18	322.9	488.7	0.62–0.65	0.133	0.3	1.0
n-Heptane	100.20	371.6	540.3	0.38–0.70	0.156	1.0	1.9
n-Octane	114.23	398.8	569.2	0.39–0.66	0.149	1.6	3.5
3-Methylheptane	114.23	392.1	563.6	0.52	0.145	0.0	0.0
2,2,4-Trimethylpentane	114.23	372.4	543.9	0.56–0.67	0.125	0.3	1.2
n-Nonane	128.26	424.0	594.6	0.38–0.70	0.149	1.1	1.9
n-Decane	142.29	447.3	617.6	0.39–0.70	0.153	1.0	2.8
n-Undecane	156.31	469.1	638.8	0.47–0.71	0.152	0.3	0.9
n-Dodecane	170.34	489.5	658.3	0.46–0.71	0.153	0.6	1.0
n-Tridecane	184.37	508.6	675.8	0.45–0.67	0.151	0.4	0.9
n-Tetradecane	198.39	526.7	694.0	0.42–0.65	0.151	0.1	0.8
n-Pentadecane	212.42	543.8	707.0	0.43–0.67	0.151	0.2	0.8
n-Hexadecane	226.45	560.0	717.0	0.42–0.66	0.153	0.5	1.9
n-Heptadecane	240.47	575.2	733.0	0.43–0.62	0.153	0.0	0.0
n-Octadecane	254.50	589.5	745.0	0.42–0.61	0.151	1.3	2.7
n-Nonadecane	268.53	603.1	756.0	0.41–0.61	0.155	0.1	0.7
n-Eicosane	282.56	617.0	767.0	0.42–0.60	0.150	1.3	2.7
n-Docosane	310.61	641.7	789.0	0.41–0.60	0.153	1.0	1.7
n-Tricosane	324.64	653.3	801.3	0.42–0.57	0.155	0.7	1.4
n-Tetracosane	338.67	664.5	813.7	0.40–0.58	0.155	1.5	2.5
Organic acids							
Formic acid	46.03	373.8	580.0	0.51–0.63	0.342	3.8	6.6
Acetic acid	60.05	391.1	594.4	0.48–0.60	0.185	1.6	3.4
Propionic acid	74.08	414.0	612.0	0.48–0.63	0.175	3.3	5.1
n-Butyric acid	88.10	436.4	628.0	0.47–0.70	0.173	4.8	7.7
Isobutyric acid	88.10	427.9	609.0	0.47–0.50	0.162	1.8	1.9
n-Valeric acid	102.13	458.7	651.0	0.46–0.68	0.164	3.7	6.6
Isovaleric acid	102.13	426.4	633.6	0.44–0.57	0.147	0.6	0.7
n-Caproic acid	116.16	475.2	661.8	0.41–0.64	0.164	2.8	4.7
n-Caprylic acid	144.21	510.7	689.1	0.43–0.64	0.164	2.7	4.1
Pelargonic acid	158.23	526.6	700.3	0.43–0.63	0.166	1.9	4.0
n-Capric acid	172.26	542.2	691.1	0.45–0.65	0.165	2.5	3.9
Mystiric acid	228.36	523.7	660.3	0.50–0.69	0.191	2.4	3.7
Oleic acid	282.45	558.6	726.5	0.41	0.243	0.0	0.0

Table I. Continued.

Liquids investigated	M	T_b	T_c	Red. temp. range	A	$\Delta\%$	$\Delta_{max}\%$
Alcohols							
Methyl alcohol	32.04	338.1	513.2	0.40–0.65	0.250	2.6	4.6
Ethyl alcohol	46.07	351.7	516.2	0.39–0.65	0.206	1.0	2.1
Allyl alcohol	58.08	370.0	545.0	0.55	0.198	0.0	0.0
n-Propyl alcohol	60.09	370.4	536.7	0.47–0.62	0.188	2.4	4.3
Isopropyl alcohol	60.09	355.4	508.3	0.54–0.66	0.177	2.2	3.1
n-Butyl alcohol	74.12	390.8	563.0	0.38–0.65	0.181	3.0	6.0
sec-Butyl alcohol	74.12	372.7	536.0	0.52–0.73	0.171	2.2	3.6
tert-Butyl alcohol	74.12	355.6	506.2	0.58–0.64	0.147	0.5	0.9
Isobutyl alcohol	74.12	381.0	547.7	0.50–0.61	0.166	2.4	4.4
n-Amyl alcohol	88.15	411.0	586.0	0.47–0.65	0.177	2.3	3.3
tert-Amyl alcohol	88.15	375.2	545.0	0.54–0.65	0.148	0.6	0.9
Phenol	94.11	455.0	694.2	0.45–0.51	0.175	1.1	1.3
n-Hexyl alcohol	102.18	430.2	610.0	0.45–0.65	0.178	3.0	7.0
o-Cresol	108.14	464.2	697.6	0.43	0.166	0.0	0.0
m-Cresol	108.14	475.4	705.8	0.42–0.50	0.162	1.2	2.0
p-Cresol	108.14	475.1	704.6	0.42	0.153	0.0	0.0
Benzyl alcohol	108.14	478.6	677.0	0.45–0.63	0.189	4.4	7.2
1-Heptyl alcohol	116.20	449.5	633.0	0.43–0.62	0.169	1.9	3.1
1-Octyl alcohol	130.23	468.4	658.0	0.45–0.58	0.175	1.0	2.1
2-Octyl alcohol	130.23	452.9	637.0	0.44–0.60	0.158	2.3	3.6
Ketones							
Acetone	58.08	329.4	508.7	0.38–0.70	0.203	0.6	1.3
Ethylmethyl ketone	72.11	352.8	535.6	0.40–0.66	0.178	1.7	3.1
Diethyl ketone	86.13	375.1	561.1	0.42–0.63	0.173	1.1	2.3
Methyl-n-propyl ketone	86.13	375.5	564.0	0.45–0.66	0.171	1.1	2.0
Methyl isobutyl ketone	100.16	389.6	571.0	0.48–0.70	0.167	0.9	1.7
Esters							
Methyl formate	60.05	304.9	487.2	0.56–0.64	0.243	0.5	1.0
Ethyl formate	74.08	327.4	508.4	0.54–0.70	0.205	1.1	1.8
Methyl acetate	74.08	330.1	506.8	0.54–0.66	0.202	0.6	0.7
n-Propyl formate	88.11	353.7	538.7	0.50–0.66	0.180	0.7	1.5
Ethyl acetate	88.11	350.3	523.2	0.50–0.65	0.181	0.4	0.7
Methyl propionate	88.11	353.0	530.6	0.50–0.65	0.181	0.6	0.8
Ethyl propionate[a]	102.13	372.0	546.0	0.57–0.65	0.169	1.9	3.4
n-Propyl acetate	102.13	374.8	549.4	0.55–0.64	0.172	0.1	0.8
n-Butyl formate	102.13	380.1	560.7	0.49–0.65	0.171	1.3	2.5
Methyl butyrate	102.13	375.5	554.5	0.55	0.170	0.0	0.0
n-Amyl formate	116.16	403.6	575.8	0.47–0.67	0.166	1.5	2.8
n-Butyl acetate	116.16	399.2	579.0	0.47–0.64	0.162	1.4	2.5
n-Propyl propionate[a]	116.16	395.7	578.0	0.54–0.61	0.162	1.8	2.9
Ethyl n-butyrate	116.16	394.0	566.0	0.48–0.65	0.164	1.0	1.7
Methyl n-valerate	116.16	400.5	566.9	0.48–0.66	0.166	1.5	2.1
n-Amyl acetate	130.18	421.6	597.1	0.46–0.60	0.159	0.3	0.8

Table I. Continued.

Liquids investigated	M	T_b	T_c	Red. temp. range	A	$\Delta\%$	$\Delta_{max}\%$
Esters *(continued)*							
Isoamyl acetate	130.18	412.0	599.3	0.46–0.61	0.150	0.2	0.7
Ethyl n-valerate	130.18	419.0	570.2	0.53	0.154	0.0	0.0
Butyl propionate	130.18	419.1	593.7	0.46–0.66	0.159	1.2	1.7
n-Amyl propionate[a]	144.21	441.9	614.5	0.51–0.57	0.154	2.1	3.4
n-Amyl butyrate	158.23	459.5	628.7	0.43–0.63	0.159	1.7	2.8
n-Butyl stearate	340.57	495.7	607.4	0.52–0.75	0.195	4.6	8.3
Ethers							
Diethyl ether	74.12	307.8	465.8	0.41–0.65	0.179	1.6	4.0
Di-n-propyl ether	102.18	364.2	531.0	0.34–0.55	0.151	1.8	3.6
Ethyl phenyl ether	122.17	443.0	647.0	0.39–0.52	0.156	0.4	0.7
Di-n-butyl ether	130.23	415.6	580.0	0.36–0.63	0.140	2.7	4.6
Diphenyl ether	170.20	531.1	767.2	0.43–0.67	0.152	1.4	3.6
Aromatics							
Benzene	78.12	353.3	562.1	0.50–0.75	0.172	1.7	4.5
Toluene	92.15	383.8	594.0	0.31–0.83	0.153	3.2	8.0
o-Xylene	106.17	417.6	630.2	0.40–0.85	0.149	1.8	6.3
m-Xylene	106.17	412.3	617.0	0.38–0.83	0.150	0.5	1.3
p-Xylene	106.17	411.5	616.2	0.44–0.85	0.150	2.7	7.4
Ethylbenzene	106.17	409.4	617.1	0.31–0.67	0.149	0.5	1.9
1,2,3-Trimethylbenzene	120.19	449.2	664.5	0.41–0.53	0.142	1.0	1.7
1,2,4-Trimethylbenzene	120.19	442.5	649.1	0.42–0.67	0.143	0.5	0.9
1,3,5-Trimethylbenzene	120.19	437.9	637.3	0.35–0.68	0.152	0.7	1.9
n-Propylbenzene	120.19	432.4	638.3	0.29–0.65	0.141	1.9	4.1
Isopropylbenzene	120.19	425.6	631.0	0.43–0.65	0.139	0.2	0.8
1,2,4,5-Tetramethylbenzene	134.22	470.0	675.0	0.52–0.63	0.140	1.5	1.8
Cymene	134.22	450.3	653.0	0.45	0.135	0.0	0.0
n-Butylbenzene	134.22	456.4	660.5	0.31–0.70	0.140	1.1	1.6
tert-Butylbenzene	134.22	442.3	660.0	0.44–0.63	0.132	1.4	3.4
Pentamethylbenzene	148.24	505.0	691.2	0.48–0.61	0.145	2.3	3.5
Hexamethylbenzene	162.27	538.0	767.2	0.58–0.67	0.143	2.8	5.2
Cycloparaffins							
Cyclopentane	70.13	322.4	511.6	0.60–0.63	0.165	0.3	0.8
Methylcyclopentane	84.16	345.0	532.7	0.58–0.62	0.146	0.3	0.9
Cyclohexane	84.16	353.9	553.4	0.54–0.63	0.144	0.0	0.0
Methylcyclohexane	98.19	374.1	572.1	0.53–0.70	0.130	1.3	3.8
Olefins							
Ethylene	28.05	169.4	282.4	0.40–0.90	0.256	4.4	10.1
Propylene	42.08	225.4	365.0	0.80–0.88	0.213	5.6	6.2
Isobutylene	56.11	266.3	417.9	0.46–0.60	0.174	5.2	9.0
Hex-1-ene	84.16	336.6	504.0	0.34–0.82	0.156	2.3	8.7
Hex-2-ene	84.16	342.0	518.0	0.566	0.155	0.0	0.0

Table I. Continued.

Liquids investigated	M	T_b	T_c	Red. temp. range	A	$\Delta\%$	$\Delta_{max}\%$
Olefins *(continued)*							
Hept-1-ene	98.19	366.8	537.2	0.35–0.80	0.157	1.9	5.0
Oct-1-ene	112.22	394.4	566.6	0.48–0.75	0.152	1.7	2.6
Oct-2-ene[a]	112.22	398.1	580.0	0.52–0.60	0.158	1.8	2.9
Refrigerant fluids belonging to the fmaily of the ORGANIC HALIDES							
Methyl chloride R40	50.49	248.9	416.3	0.48–0.90	0.244	6.0	10.8
Ethyl chloride R160	64.52	285.4	460.4	0.59–0.62	0.164	0.4	0.6
1,1-Difluoroethane R152a	66.05	248.4	386.6	0.42–0.91	0.179	1.5	2.8
Fluoroform R23	70.02	191.1	299.1	0.59–0.93	0.185	2.1	5.2
Methylene chloride R30	84.93	313.0	510.0	0.36–0.61	0.178	0.6	1.5
Chlorodifluoromethane R22	86.46	232.4	369.2	0.41–0.90	0.162	1.5	3.4
Carbon tetrafluoride R14	88.01	145.2	227.5	0.65–0.93	0.130	2.8	5.5
1,1-Dichloroethane R150a	98.97	330.4	523.0	0.52–0.60	0.140	1.1	1.5
Chlorodifluoroethane R142b	100.50	263.4	410.2	0.47–0.92	0.134	3.0	5.6
Dichlorofluoromethane R21	102.92	282.0	451.6	0.34–0.96	0.148	3.3	6.8
Chlorotrifluoromethane R13	104.46	191.7	302.0	0.50–0.90	0.126	2.9	4.5
Chloroform R20	119.38	334.3	536.4	0.40–0.64	0.142	0.2	1.2
Dichlorodifluoromethane R12	120.91	243.4	385.0	0.32–0.92	0.122	2.3	4.5
Trichlorofluoromethane R11	137.37	297.0	471.1	0.37–0.92	0.120	1.9	5.1
Hexafluoroethane R116	138.01	194.9	292.8	0.59–0.90	0.113	2.2	7.0
Bromotrifluoromethane R13B1	148.92	215.4	340.1	0.55–0.82	0.100	3.1	8.4
Carbon Tetrachloride R10	153.82	349.7	556.3	0.45–0.65	0.123	0.5	1.4
Chloropentafluoroethane R115	154.47	234.0	353.2	0.49–0.94	0.104	1.4	2.3
1,2-Dichl. tetr. fl. ethane R114	170.92	276.9	418.9	0.44–0.93	0.099	1.3	4.8
Trichl. trifl. ethane R113	187.38	320.7	487.3	0.50–0.90	0.100	1.6	4.7
Tetrachl. difl. ethane R112	203.83	364.7	551.0	0.44–0.68	0.099	0.3	0.6
Dibr. tetrafl. ethane R114B2	259.83	320.4	487.6	0.35–0.66	0.083	0.5	1.2
Mean general deviation 1.5							

[a]Experimental λ data not within $\pm 5\%$.

the variable T_r and the corresponding selected experimental values of λ; the calculations confirm our preceding results: that is, A is practically temperature independent.

At this point, the value of A corresponding to each compound is inserted in Eq. (4), which can be tested. Table I presents the A values, the mean deviations, $\Delta\%$, in the explored temperature ranges between experimental and estimated thermal conductivity data and the maximum deviations, $\Delta_{max}\%$. The calculations were developed in steps of 10°C and the results can be summarized as follows:

1. Equation (4), where the factor A assumes the proper value characteristic of each compound, can be advantageously used in order to evaluate the thermal conductivity λ from the melting point ($T_r \simeq 0.3$) to the normal boiling point ($T_r \simeq 0.7$) and higher.
2. The mean deviations, $\Delta\%$, between experimental and estimated λ values are generally smaller than 2%.
3. The maximum deviations, $\Delta_{max}\%$, are generally smaller than 6%.

The situation can be clarified by Fig. 1, where the dotted line represents the experimental results for a generic organic liquid, and the full line represents the curve corresponding to Eq. (4): the intersection points between the two lines generally occur at $T_r \simeq 0.3$, at $T_r \simeq 0.8$, and close to $T_r = 0.5488$ [which is the inflexion point of Eq. (4)]. For $T_r < 0.3$ and for $T_r > 0.9$, Eq. (4) does not give correct values of λ.

In conclusion, it must pointed out that the calculation of the factor A for a single compound can be developed by using only a few accurate experimental values of λ close to $T_r = 0.55$ (even only one value at $T_r \simeq 0.55$); in this way, it is possible to predict the thermal conductivity at different temperatures with a mean deviation generally smaller than 2%. Unfortunately, this method cannot be employed when selected experimental data of λ are not available. This difficulty nevertheless can be overcome if suitable expressions, relating the factor A to the physical properties of the liquids, are found.

3. THE FACTOR A AND ITS DEPENDENCE ON THE PHYSICAL PROPERTIES OF ORGANIC LIQUIDS

The factor A, practically temperature independent and characteristic of each liquid as pointed out above, depends on the molecular structure, and it appears reasonable to suppose the existence of a mathematical relation between A and the physical properties of the compounds. In the present paper, an empirical approach to this problem is pursued and, based on the hypothesis by Missenard [19], "the thermal conductivities of liquids belonging to the same family are strictly connected," the different series will be separately investigated.

Another hypothesis, expressed in order to limit the investigation to the most available physical properties of the liquids, can be summarized as follows:

$$A = f(M, T_b, T_c) \tag{5}$$

It is supposed that the factor A can be expressed by appropriate relations (different from family to family) that contain only the molecular weight M, the normal boiling point T_b, and the critical temperature T_c.
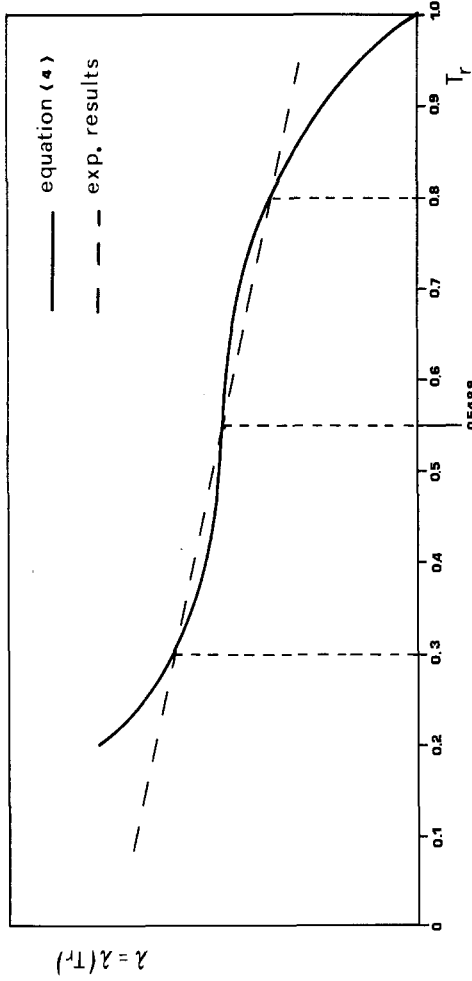
Fig. 1. Thermal conductivity, λ, versus reduced temperature, T_r, according to Eq. (4), compared with experimental results.

3.1. Paraffins

In order to find the particular mathematical form of the function $f(M,T_b,T_c)$, the values of M, T_b and T_c (Table I) must be analyzed. The values of the factor A for the group of the paraffins from n-nonane to n-tetracosane are very close to the mean value 0.152, with deviations generally smaller than 2%; this evidence shows that the function $f(M,T_b,T_c)$ must assume the same value for the cited 15 compounds. The most simple functions that take into account this requirement contain T_b/T_c or T_c/T_b: the first ratio increases slowly and the second decreases slowly when M increases, so that the following expressions can be investigated:

$$A \propto \frac{T_b}{M \cdot T_c} \tag{6}$$

$$A \propto \frac{M \cdot T_c}{T_b} \tag{7}$$

Expression (6) must be preferred as soon as the subgroups of paraffins with the same molecular weight M are analyzed: the values of the factor A of the five liquids corresponding to $M = 86.18$ decrease when T_b decreases, and the same evidence is verified for the paraffins with $M = 114.23$. This result, nevertheless, is not conclusive, and the quantities M, T_b, and T_c in expression (6) must be raised to suitable powers, so that the formula proposed is

$$A = h \cdot \frac{T_b^b}{M^a \cdot T_c^c} \tag{8}$$

where the exponents a, b, c and the proportionality factor h remain to be fixed. In conclusion, if methane, propane, and n-butane are excluded from the calculations, the following results are obtained: $a = 1/2$, $b = 6/5$, $c = 1/6$, and $h = 0.00350$. Then Eq. (4), in the case of the paraffins, becomes

$$\lambda = 0.00350 \cdot \frac{T_b^{6/5}}{M^{1/2}T_c^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{9}$$

Table II contains the mean and the maximum deviations between the experimental thermal conductivity values and those estimated through Eq. (9). Several attempts that were developed to take into account methane, propane, and n-butane with acceptable deviations were unsuccessful. Similar behavior was observed for some organic liquids with $M < 50$ or $M > 250$. A

Table II. Mean and Maximum Deviations Between Experimental λ Data and Those Predicted According to Eqs. (9)–(19)

Liquids investigated	Δ%	$\Delta_{max}\%$	Liquids investigated	Δ%	$\Delta_{max}\%$
Paraffins; Eq. (9)			Paraffins; Eq. (9)		
Methane[a]			n-Decane	1.3	3.7
Propane[a]			n-Undecane	0.9	1.9
n-Butane[a]			n-Dodecane	0.7	1.8
n-Pentane	4.0	6.9	n-Tridecane	1.4	2.3
n-Hexane	3.9	4.4	n-Tetradecane	2.0	2.8
3-Methylpentane	0.6	0.9	n-Pentadecane	2.0	2.7
2-Methylpentane	0.3	0.9	n-Hexadecane	1.3	2.8
2,3-Dimethylbutane	2.3	2.9	n-Heptadecane	0.3	0.9
2,2-Dimethylbutane	3.7	4.1	n-Octadecane	2.3	4.5
n-Heptane	4.8	5.8	n-Nonadecane	0.6	0.8
n-Octane	1.4	2.1	n-Eicosane	2.5	5.4
3-Methylheptane	1.6	1.6	n-Docosane	0.8	1.4
2,2,4-Trimethylpentane	15.4	16.7	n-Tricosane	2.6	3.4
n-Nonane	1.1	3.8	n-Tetracosane	2.1	3.9

Mean general deviation is 2.4%

Organic acids; Eq. (10)			Organic acids; Eq. (10)		
Formic acid[a]			n-Caproic acid	2.8	4.8
Acetic acid	1.8	4.0	n-Caprylic acid	3.3	7.2
Propionic acid	3.3	5.4	Pelargonic acid	5.3	8.7
n-Butyric acid	4.7	7.1	n-Capric acid	4.5	7.5
Isobutyric acid	3.6	5.6	Mystiric acid[a]		
n-Valeric acid	4.2	7.9	Oleic acid[a]		
Isovaleric acid	4.5	5.1			

Mean general deviation is 2.9%

Alcohols; Eq. (11)			Alcohols; Eq. (11)		
Methyl alcohol	8.2	12.9	tert-Amyl alcohol	4.2	4.7
Ethyl alcohol	3.3	5.3	Phenol	2.8	4.5
Allyl alcohol	6.2	6.2	n-Hexyl alcohol	4.8	9.1
n-Propyl alcohol	3.3	5.5	o-Cresol	3.2	3.2
Isopropyl alcohol	2.4	3.8	m-Cresol	8.6	10.6
n-Butyl alcohol	4.2	8.7	p-Cresol	15.3	15.3
sec-Butyl alcohol	2.4	5.3	Benzyl alcohol	3.8	7.8
tert-Butyl alcohol	8.4	9.6	1-Heptyl alcohol	3.3	6.1
Isobutyl alcohol	4.6	6.7	1-Octyl alcohol	8.3	9.3
n-Amyl alcohol	3.7	6.6	2-Octyl alcohol	3.0	6.3

Mean general deviation is 5.1%

Table II. Continued.

Liquids investigated	$\Delta\%$	$\Delta_{max}\%$	Liquids investigated	$\Delta\%$	$\Delta_{max}\%$
Ketones; Eq. (12)			Ketones; Eq. (12)		
Acetone	8.8	9.6	Methyl-n-propyl ketone	3.8	5.2
Ethylmethyl ketone	2.4	4.8	Methyl isobutyl ketone	2.5	4.1
Diethyl ketone	2.4	3.7			

Mean general deviation is 4.0%

Esters; Eq. (13)			Esters; Eq. (13)		
Methyl formate	3.0	3.9	n-Butyl acetate	1.3	2.8
Ethyl formate	0.6	1.2	n-Propyl propionate	2.1	2.9
Methyl acetate	2.9	3.6	Ethyl n-butyrate	1.6	2.9
n-Propyl formate	4.4	5.3	Methyl n-valerate	1.4	2.1
Ethyl acetate	2.8	3.0	n-Amyl acetate	2.3	3.3
Methyl propionate	3.7	4.5	Isoamyl acetate	0.8	1.5
Ethyl propionate	2.7	5.1	Ethyl n-valerate	0.9	0.9
n-Propyl acetate	1.4	1.8	Butyl propionate	2.9	4.3
n-Butyl formate	3.2	5.0	n-Amyl propionate	4.3	7.3
Methyl butyrate	2.2	2.2	n-Amyl butyrate	11.6	14.0
n-Amyl formate	1.7	3.3	Butyl stearate[a]		

Mean general deviation is 2.8%

Ethers; Eq. (14)			Ethers; Eq. (14)		
Diethyl ether	1.6	4.6	Di-n-Butyl ether	3.1	6.5
Di-n-Propyl ether	4.5	7.8	Diphenyl ether	8.3	10.9
Ethyl Phenyl ether	2.7	3.3			

Mean general deviation is 4.0%

Aromatics; Eq. (15)			Aromatics; Eq. (15)		
Benzene	2.2	3.4	n-Propylbenzene	2.5	5.1
Toluene	5.5	8.2	Isopropylbenzene	1.3	1.6
o-Xylene	4.5	6.6	1,2,4,5-Tetramethylbenzene	6.5	10.3
m-Xylene	2.9	8.5	Cymene	0.8	0.8
p-Xylene	4.5	6.1	n-Butylbenzene	3.1	4.7
Ethylbenzene	2.5	3.9	tert-Butylbenzene	1.5	3.0
1,2,3-Trimethylbenzene	4.5	6.0	Pentamethylbenzene	4.9	7.9
1,2,4-Trimethylbenzene	2.8	3.4	Hexamethylbenzene	7.0	12.1
1,3,5-Trimethylbenzene	4.3	5.1			

Mean general deviation is 3.7%

Cycloparaffins; Eq. (16)			Cycloparaffins; Eq. (16)		
Cyclopentane	3.7	4.1	Cyclohexane	1.9	2.7
Methylcyclopentane	1.2	1.7	Methylcyclohexane	2.8	4.2

Mean general deviation is 2.4%

Table II. Continued.

Liquids investigated	$\Delta\%$	$\Delta_{max}\%$	Liquids investigated	$\Delta\%$	$\Delta_{max}\%$
Olefins; Eq. (17)			Olefins; Eq. (17)		
Ethylene	6.5	9.8	Hex-2-ene	7.4	7.4
Isobutylene	10.1	20.5	Hept-1-ene	2.1	6.9
Propylene	5.8	6.8	Oct-1-ene	3.9	5.7
Hex-1-ene	6.1	7.1	Oct-2-ene	6.9	9.5

Mean general deviation is 6.1%

Liquids investigated	$\Delta\%$	$\Delta_{max}\%$	Liquids investigated	$\Delta\%$	$\Delta_{max}\%$
First group of refrig; Eq. (18)			First group of refrig; Eq. (18)		
Carbon tetrachloride R10	6.7	8.3	1,2-Dichlorotetrafluoroethane R114	4.3	6.5
Trichlorofluoromethane R11	3.4	6.5	Chloropentafluoroethane R115	2.4	4.7
Dichlorodifluoromethane R12	2.6	4.1	Hexafluoroethane R116	3.8	7.8
Chlorotrifluoromethane R13	3.0	4.2	Chlorodifluoroethane R142b	2.8	5.6
Bromotrifluoromethane R13B1	7.5	10.1	1,1-Dichloroethane R150a	1.2	1.8
Carbon tetrafluoride R14	2.8	5.1	1,1-Difluoroethane R152a	8.3	10.3
Tetrachlorodifluoroethane R112	0.6	1.1	Ethyl chloride R160	4.1	4.6
Dibromotetrafluoroethane R114B2	3.4	4.6	Trichlorotrifluoroethane R113	1.9	3.6

Liquids investigated	$\Delta\%$	$\Delta_{max}\%$			
Second group of refrig; Eq. (19)					
Chloroform R20	3.0	4.4			
Dichlorofluoromethane R21	5.3	10.5			
Chlorodifluoromethane R22	1.7	5.3			
Fluoroform R23	6.1	11.0			

Mean general deviation of the two groups is 3.7%

[a]Mean deviation between experimental and estimated λ values greater than 20%.

similar procedure is carried out also for the other organic families, which are investigated in order to obtain relations similar to Eq. (9).

3.2. Organic Acids

The values obtained for the organic acids are $a = 1/2$, $b = 6/5$, $c = 1/6$, and $h = 0.00319$. Thus

$$\lambda = 0.00319 \cdot \frac{T_b^{6/5}}{M^{1/2}T_c^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{10}$$

The results are summarized in Table II. Formic acid ($M = 46.03$), mystiric acid ($M = 228.38$), and oleic acid ($M = 282.45$) must be excluded from the use of Eq. (10).

3.3. Alcohols

The values obtained for the alcohols are $a = 1/2, b = 6/5, c = 1/6$, and $h = 0.00339$. Thus

$$\lambda = 0.00339 \cdot \frac{T_b^{6/5}}{M^{1/2}T_c^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{11}$$

The results are summarized in Table II.

3.4. Ketones

The ketones investigated are only five in number, but the results, summarized in Table II, are satisfactory enough so that the following values are proposed with the corresponding equation: $a = 1/2, b = 6/5, c = 1/6$, and $h = 0.00383$. Thus

$$\lambda = 0.00383 \cdot \frac{T_b^{6/5}}{M^{1/2}T_c^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{12}$$

The results are summarized in Table II.

3.5. Esters

The values for the esters are $a = 1, b = 6/5, c = 1/6$, and $h = 0.0415$. Thus

$$\lambda = 0.0415 \cdot \frac{T_b^{6/5}}{M \cdot T_c^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{13}$$

The results are summarized in Table II; butyl stearate ($M = 340.57$) must be excluded from the use of eq. (13).

3.6. Ethers

On the basis of the five investigated compounds, the following values and the corresponding equation are proposed: $a = 1, b = 6/5, c = 1/6$, and $h = 0.0385$. Thus

$$\lambda = 0.0385 \cdot \frac{T_b^{6/5}}{M \cdot T_c^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{14}$$

The results are given in Table II.

3.7. Aromatics

The values for the aromatics are $a = 1$, $b = 6/5$, $c = 1/6$, and $h = 0.0346$. Thus

$$\lambda = 0.0346 \cdot \frac{T_b^{6/5}}{M \cdot T_c^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{15}$$

The results are given in Table II.

3.8. Cycloparaffins

On the basis of the four investigated compounds, the following values and the corresponding equation are proposed: $a = 1$, $b = 6/5$, $c = 1/6$, and $h = 0.0310$. Thus

$$\lambda = 0.0310 \cdot \frac{T_b^{6/5}}{M \cdot T_c^{1/6}} \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{16}$$

The results are given in Table II.

3.9. Olefins

The values for the olefins are $a = 1$, $b = 6/5$, $c = 1/6$, and $h = 0.0361$. Thus

$$\lambda = 0.0361 \cdot \frac{T_b^{6/5}}{M \cdot T_c^{1/6}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{17}$$

The results are given in Table II.

3.10. Refrigerant Fluids Belonging to the Family of Organic Halides

In addition to the prediction method mentioned earlier in this paper and involving ΔH_{vb} and V_b, satisfactory results are obtained if the refrigerant fluids belonging to the family of the organic halides are divided into different

subgroups, for which the following values of a, b, c, and h are suggested: $a = 1/2$, $b = 0$, and $c = -1/6$ for all the investigated refrigerant fluids; $h = 0.494$ for the subgroup from R10 to R14; and $h = 0.494$ for the subgroup from R110 to R160. The equation proposed for these subgroups is

$$\lambda = 0.494 \cdot \frac{T_c^{1/6}}{M^{1/2}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{18}$$

Finally, $h = 0.562$ for the subgroup from R20 to R23, and the equation proposed for this subgroup is

$$\lambda = 0.562 \cdot \frac{T_c^{1/6}}{M^{1/2}} \cdot \frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \tag{19}$$

The results are given in Table II.

4. CONCLUSIONS

The results of this work may be summarized as follows. First, Eq. (4) can be successfully used if a few selected experimental thermal conductivity data are available; the factor A can be evaluated and Eq. (4) can be used to compute λ values, in the reduced temperature range 0.3 to 0.8 and over, with mean deviations generally smaller than 2%. It is interesting to note that even only one experimental value of λ at $T_r \cong 0.55$ can be used in the calculation of A; this was the approach adopted in our laboratory with satisfactory results [20].

Second, if selected experimental thermal conductivity data are not available, Eqs. (9)–(19) are proposed for the substances of the respective families. In this case, the mean deviations are greater than 2%, but they are generally smaller than 5%. Attention must be paid to the compounds with $M < 50$ or $M > 250$. Moreover, as a natural generalization of the research on liquid thermal conductivity, it should be possible to obtain correlations for groups of series [21], and in this case, it appears interesting to take into consideration the suggestion of Liley [22], which proposes that the thermal conductivity difference $\lambda(\text{liq.}) - \lambda(\text{sat. vapor})$ is a function of the enthalpy difference, in order to give a more general and physically sound correlation.

ACKNOWLEDGMENT

REFERENCES

1. R. P. Tye, *Thermal Conductivity*, Vol. 2 (Academic Press, London, 1969).
2. E. McLaughlin, *Chem. Rev.* **64**:390 (1964).
3. G. Latini and M. Pacetti, *Bull. I.I.F./I.I.R.* **6**:1 (1977).
4. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, *Int. J. Thermophys.* **1**:159 (1980).
5. R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd ed. (McGraw-Hill, New York, 1977), pp. 518–525.
6. W. J. Scheffy, Tech. Rept. PR-85-R, Princeton University, Princeton, N.J., pp. 1–99, 1958 (AD 204 891).
7. W. J. Scheffy and E. F. Johnson, *J. Chem. Eng. Data* **6**:245 (1961).
8. V. Pachaiyappan and K. R. Vaidyanathan, in *Proc. Sixth Symp. Thermophys. Prop.*, P. E. Liley, ed. (Am. Soc. Mech. Eng., New York, 1973) pp. 15–21.
9. K. R. Vaidyanathan and M. Velayutham, *Chem. Eng. World*, **IX**:69 (1974).
10. D. S. Viswanath, *Am. Inst. Chem. Eng. J.* **13**:850 (1967).
11. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, *Progress in Refrigeration Science and Technology*, Vol. II (I.I.F./I.I.R., Padua, Italy, 1980), pp. 279–284.
12. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, *Memorie presentate al XXXIV Congresso Nazionale A.T.I.*, Vol. 1 (CO. GRA. S. Centro Stampa Facoltà di Ingegneria, Palermo, Italy, 1979).
13. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, 7th European Thermophysical Properties Conference, Antwerpen (Belgium), June 30–July 4, 1980.
14. D. T. Jamieson, J. B. Irving, and J. S. Tudhope, *Liquid Thermal Conductivity, A Data Survey to 1973* (Her Majesty's Stationery Office, Edinburgh, 1975).
15. Y. S. Touloukian, P. E. Liley, and S. C. Saxena, *Thermal Conductivity of Nonmetallic Liquids and Gases* (Plenum Press, New York, 1970).
16. N. B. Vargaftik, *Tables on the Thermophysical Properties of Liquids and Gases* (John Wiley & Sons, New York, 1975).
17. *ASHRAE Handbook & Product Directory, 1977 Fundamentals* (American Society of Heating, Refrigeration, and Air-Conditioning Engineers, New York, 1978).
18. R. H. Perry and C. H. Chilton, *Chemical Engineer's Handbook*, 5th ed. (McGraw-Hill, New York 1973).
19. F. A. Missenard, *Rev. Gên. Therm., Fr.* **141**:751–759 (1973).
20. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, *Memorie del XXXV Congresso Nazionale A.T.I.* (CELID, La Grafica Nuova, Turin, Italy, 1980), pp. 217–228.
21. J. C. Bishop and P. E. Liley, in *Proc. Sixth Symp. Thermophys. Prop.*, P. E. Liley, ed. (Am. Soc. Mech. Eng., New York, 1973).
22. P. E. Liley, in *Proc. Fifth Symp. Thermophys. Prop.*, C. F. Bonilla, ed. (Am. Soc. Mech. Eng., New York, 1970), pp. 197–199.