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Thermal Conductivity of Organic Liquid Binary Mixtures: Measurements and Prediction Method

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A correlation presented in previous papers for the prediction of organic liquid thermal conductivity, λ, is generalized in order to estimate the thermal conductivity of the binary mixtures of organic liquids. The proposed equation contains the reduced temperature, the molar fractions, and two factors characteristic of the components. The comparison between predicted and experimental λ values is developed at atmospheric pressure, taking into account data present in the literature and experimental values obtained at the Department of Energy of Ancona University, using the steady-state hot-wire method. Fifty binary mixtures are considered (28 of them are investigated by the authors at 25 and 50°C), and the mean general deviation between predicted and experimental thermal conductivity values (621 data points) is 2.5%.

KEY WORDS: liquid binary mixtures; property correlations; thermal conductivity, transport properties.

1. INTRODUCTION

The values of the thermal conductivity, λ, of liquids are often unknown at certain temperatures; however, several correlations [1, 2] exist which are able to predict λ. In spite of the great demand for a knowledge of the thermal conductivity of binary mixtures, only a limited amount of data exists in the literature; and the existing correlations require λ values of the components at each investigated temperature. As an example of these correlations, the equation of Filippov and Novoselova [3] can be presented:

$$\frac{\lambda_m - \lambda_1}{\lambda_2 - \lambda_1} = Cw_2^2 + w_2(1 - C) \tag{1}$$

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where λ_m, λ_1, and λ_2 are the thermal conductivities of the mixture and of the components, w_2 is the weight fraction of the second component, and C is a constant for the mixture, usually assumed equal to 0.72. Other correlations proposed in the literature [4] present the same disadvantages: it is necessary to know λ_1 and λ_2 at different temperatures, and a mixture parameter also normally appears, which only with a rough approximation can be assumed constant for all the mixtures.

These considerations have led to the investigation of binary mixtures along the following two directions: (i) new experimental thermal conductivity values are necessary; and (ii) a new predictive method is needed that is simpler and more accurate than those which exist in the literature. The above two directions are followed in this paper: the experimental data obtained by the authors (together with several other values obtained by other investigators) are critically examined, and a new correlation is proposed.

2. EXPERIMENTAL APPARATUS AND RESULTS

A relative method, employing the hot-wire technique, was used [5]. The conductivity cell consists of a thin platinum wire (0.1 mm in diameter and 81 mm in length), placed axially along a Pyrex glass tube (9 mm in internal diameter) and welded to thicker platinum leads (0.6 mm in diameter). The apparatus was used in the four leads arrangement so that the electrical resistance of the wire could be measured with a Kelvin bridge. The cell was immersed in a constant temperature bath, whose temperature could be controlled to better than ± 0.001°C.

The thermal conductivity of 28 binary mixtures was measured at two temperatures: 25 and 50°C. The binary mixtures were chosen among those for which experimental data did not exist in the literature and among those for which experimental results existed at temperatures different from 25 and 50°C. By this procedure it was possible to reach the following three goals:

1. New measurements are presented at temperature ranges which are either unexplored or partially explored;
2. The trend of the thermal conductivity of the binary mixture as a function of the temperature can be investigated by comparing the new measurements with those existing in literatue;
3. It is possible to improve a correlation previously proposed by the authors [6].

The experimental results are presented in Table I.

Table I. Experimental Data of Thermal Conductivity at 25 and 50°C for the Binary Mixtures Investigated[a]

w	λ_m (25°C)	λ_m (50°C)	w	λ_m (25°C)	λ_m (50°C)
Acetone/n-butyl alcohol			Acetone/sec-butyl alcohol		
0.00	0.1480	0.1400	0.00	0.1350	0.1303
0.25	0.1457	0.1403	0.25	0.1400	0.1361
0.50	0.1584	0.1468	0.50	0.1523	0.1421
0.75	0.1626	0.1508	0.75	0.1584	0.1500
1.00	0.1600	0.1510	1.00	0.1600	0.1510
Acetone/carbon tetrachloride			Acetone/chloroform		
0.00	0.0982[b]	0.1002	0.00	0.1180	0.1100
0.25	0.1122[b]	0.1062	0.25	0.1194	0.1160
0.50	0.1303[b]	0.1201	0.50	0.1302	0.1280
0.75	0.1416[b]	0.1316	0.75	0.1426	0.1377
1.00	0.1600[b]	0.1510	1.00	0.1600	0.1510
Acetone/n-ethyl alcohol			Acetone/n-hexyl alcohol		
0.00	0.1603[b]	0.1513	0.00	0.1500	0.1480
0.25	0.1617[b]	0.1526	0.25	0.1490	0.1460
0.50	0.1602[b]	0.1514	0.50	0.1540	0.1480
0.75	0.1622[b]	0.1533	0.75	0.1580	0.1501
1.00	0.1600[b]	0.1510	1.00	0.1600	0.1510
Acetone/methyl formate			Benzene/chloroform		
0.00	0.1840	0.1786	0.00	0.1180	0.1100
0.25	0.1667	0.1640	0.25	0.1172	0.1164
0.50	0.1668	0.1620	0.50	0.1232	0.1232
0.75	0.1609	0.1583	0.75	0.1340	0.1302
1.00	0.1600	0.1510	1.00	0.1433	0.1376
Benzene/methyl formate			n-Bytyl acetate/sec-butyl alcohol		
0.00	0.1840	0.1786	0.00	0.1350	0.1303
0.25	0.1682	0.1576	0.25	0.1272	0.1236
0.50	0.1562	0.1508	0.50	0.1306	0.1276
0.75	0.1482	0.1403	0.75	0.1138	0.1296
1.00	0.1433	0.1376	1.00	0.1368	0.1309

[a] w is the weight fraction of the first component, and λ_m is the thermal conductivity of the mixture in $W \cdot m^{-1} \cdot K^{-1}$.

[b] Also published in the literature [6] by the authors of the present paper.

Table I. *(Continued)*

w	λ_m (25°C)	λ_m (50°C)	w	λ_m (25°C)	λ_m (50°C)
n-Butyl acetate/diethyl ether			n-Butyl acetate/ethyl methyl ketone		
0.00	0.1278	0.1180	0.00	0.1428	0.1374
0.25	0.1430	0.1333	0.25	0.1472	0.1351
0.50	0.1445	0.1345	0.50	0.1382	0.1326
0.75	0.1375	0.1306	0.75	0.1314	0.1322
1.00	0.1368	0.1309	1.00	0.1368	0.1309
n-Butyl acetate/toluene			n-Butyl alcohol/diethyl ketone		
0.00	0.1296	0.1252	0.00	0.1507	0.1454
0.25	0.1358	0.1273	0.25	0.1399	0.1372
0.50	0.1366	0.1306	0.50	0.1407	0.1351
0.75	0.1379	0.1289	0.75	0.1387	0.1364
1.00	0.1368	0.1309	1.00	0.1480	0.1400
n-Butyl alcohol/toluene			sec-Butyl alcohol/toluene		
0.00	0.1296[b]	0.1252	0.00	0.1296	0.1252
0.25	0.1338[b]	0.1272	0.25	0.1387	0.1298
0.50	0.1376[b]	0.1310	0.50	0.1362	0.1325
0.75	0.1414[b]	0.1340	0.75	0.1330	0.1333
1.00	0.1480[b]	0.1400	1.00	0.1350	0.1302
di-n-Butyl ether/chloroform			di-n-Butyl ether/methyl alcohol		
0.00	0.1180	0.1100	0.00	0.2013	0.1940
0.25	0.1172	0.1115	0.25	0.1722	0.1679
0.50	0.1200	0.1159	0.50	0.1560	0.1496
0.75	0.1219	0.1158	0.75	0.1425	0.1329
1.00	0.1257	0.1249	1.00	0.1257	0.1249
Carbon tetrachloride/cyclohexane			Carbon tetrachloride/ethyl alcohol		
0.00	0.1176	0.1119	0.00	0.1603	0.1513
0.25	0.1132	0.1067	0.25	0.1400	0.1299
0.50	0.1058	0.1014	0.50	0.1252	0.1105
0.75	0.1025	0.0993	0.75	0.1086	0.1010
1.00	0.0982	0.1002	1.00	0.0982	0.1002
Carbon tetrachloride/n-propyl alcohol			Chloroform/diethyl ketone		
0.00	0.1426	0.1395	0.00	0.1507	0.1454
0.25	0.1349	0.1250	0.25	0.1433	0.1374
0.50	0.1248	0.1151	0.50	0.1283	0.1262
0.75	0.1102	0.1073	0.75	0.1238	0.1176
1.00	0.0982	0.1002	1.00	0.1180	0.1100

Table I. *(Continued)*

w	λ_m (25°C)	λ_m (50°C)	w	λ_m (25°C)	λ_m (50°C)
Chloroform/methyl alcohol			Cyclohexane/ethyl alcohol		
0.00	0.2013	0.1940	0.00	0.1603	0.1513
0.25	0.1646	0.1638	0.25	0.1408	0.1374
0.50	0.1467	0.1464	0.50	0.1335	0.1295
0.75	0.1303	0.1262	0.75	0.1214	0.1184
1.00	0.1180	0.1100	1.00	0.1176	0.1119
Cyclohexane/n-propyl alcohol			Ethyl alcohol/methyl alcohol		
0.00	0.1426	0.1395	0.00	0.2012	0.1940
0.25	0.1305	0.1281	0.25	0.1886	0.1858
0.50	0.1251	0.1214	0.50	0.1691	0.1660
0.75	0.1226	0.1208	0.75	0.1646	0.1603
1.00	0.1176	0.1119	1.00	0.1603	0.1513
Ethyl alcohol/n-propyl alcohol			n-Hexyl alcohol/toluene		
0.00	0.1426	0.1395	0.00	0.1296	0.1252
0.25	0.1516	0.1409	0.25	0.1340	0.1305
0.50	0.1524	0.1449	0.50	0.1360	0.1260
0.75	0.1577	0.1523	0.75	0.1403	0.1320
1.00	0.1603	0.1513	1.00	0.1500	0.1480

3. DISCUSSION OF THE λ_m FUNCTION AND THE EXISTING CORRELATIONS

Table I shows that in general the thermal conductivity of the mixtures is not a simple function of the conductivities and concentrations of the components; moreover, additivity rules cannot generally be applied. Deviations from linearity are evident in several cases, and in some cases the thermal conductivity of the mixture exhibits a minimum. Also, the thermal conductivity of a mixture usually has a value rather lower than that calculated from the simple additivity rule [7]:

$$\lambda_m = \lambda_1 m_1 + \lambda_2 m_2 \tag{2}$$

where λ_m, λ_1, and λ_2 are the thermal conductivities of the mixture and of the components, and m_1 and m_2 are the mass fractions.

These considerations, which have been noted in the past by some investigators [4, 8, 9], led to correlations [4] which contain the weight fractions of the thermal conductivities of the components of the mixture

raised to some powers. These correlations generally give acceptable results unless the system exhibits a minimum in the relation of λ_m versus composition. Furthermore, as pointed out above, Eqs. (1) and (2) do not contain the temperature explicitly and require a knowledge of λ_1 and λ_2, which is not always possible to have. For these reasons, in a previous paper [6] a new prediction method was proposed based on the following equations:

$$\lambda = A\left(\frac{(1-T_r)^{0.38}}{T_r^{1/6}}\right) \tag{3}$$

$$\lambda_m = \lambda_1 x_1^2 + \lambda_2 x_2^2 + 2\lambda_{12} x_1 x_2 \tag{4}$$

In Eq. (3), λ is the thermal conductivity of a pure liquid, T_r is the reduced temperature, and A is a parameter characteristic of each substance and is temperature independent. Equation (3) was tested [10] for 144 liquids in the reduced temperature range 0.3–0.8 with mean deviations between predicted and experimental thermal conductivity values generally less than 2%. Equation (4) is the "quadratic mixing law" proposed by McLaughlin [11] and is considered to have the most logical form for the thermal conductivity λ_m of a binary mixture. In Eq. (4), λ_1, λ_2, x_1, x_2 are the thermal conductivities and the mole fractions of the components, and λ_{12} is the "cross-term coefficient," which generally is a characteristic quantity for each mixture.

Combination of Eqs. (3) and (4) leads to the following correlation:

$$\lambda_m = (A_1 x_1^2 + A_2 x_2^2 + n\sqrt{A_1 A_2}\, x_1 x_2)\frac{(1-T_r)^{0.38}}{T_r^{1/6}} \tag{5}$$

In Eq. (5), A_1 and A_2 are parameters characteristic of the mixture components, T_r is the "reduced" temperature of the mixture, and n is a pure number (characteristic of each mixture), whose value ranges from 1.0 to 2.0. The critical temperature of a mixture usually is not experimentally known, so that a linear mole-fraction average of the pure component critical temperatures is used, that is, a "pseudocritical temperature"; more sophisticated methods do not produce appreciable advantages in the term $(1-T_r)^{0.38}/T_r^{1/6}$. Equation (5) was checked in the case of 30 binary mixtures: the mean deviations between predicated and experimental thermal conductivity values are generally less than 2%, and the maximum deviations are generally less than 5%.

The correlation (5) is essentially empirical, nevertheless some of its advantages have to be emphasized. First, Eq. (5) does not require a knowledge of λ_1 and λ_2, which depend on the temperature, but it contains simply A_1 and A_2, which are temperature independent and are related to the molecular weight M, the normal boiling point T_b, and the critical

temperature T_c by suitable mathematical expressions [10]. Second, according to Eq. (3), A and the critical temperature T_c characterize completely, with respect to the thermal conductivity, the behavior of each pure liquid. According to Eq. (5), A_1, A_2, T_{c_1}, T_{c_2}, x_1, x_2, and n characterize completely, still with respect to the thermal conductivity, the behavior of each binary mixture.

The last problem to be solved is concerned with the pure number n, because T_{c_1} and T_{c_2} are generally well known, and the values of factor A are given in the literature [10–13] or can be calculated, as pointed out above [10]. At this point the goal is to free Eq. (5) from any arbitrary factor, particularly from n, which may be possible on the basis of the experimental data presented in Table I and in the literature.

4. THE PROPOSED CORRELATION

The thermal conductivity data for 50 organic liquid binary mixtures (including the 28 mictures experimentally investigated by the authors and presented in Table I) were taken into consideration, and for each mixture the respective factor n was calculated through Eq. (5). The results are shown in Table II, which contains, for each mixture, the values of the molecular weights M, of the critical temperatures T_c, of the parameters A, of the parameter n, and the mean and maximum deviations between the thermal conductivity values predicted according to Eq. (5) and the experimental data. Table II also shows the investigated temperatures and the sources of the experimental data. The results are satisfactory, but the aim, as pointed out above, is to propose a simple prediction method useful for engineering purpose. This means that the factor n must be expressed in such a way that, in the absence of experimental thermal conductivity data, correlation (5) can be used.

Table II reveals the trend that as the molecular weight values of the mixture components approach each other, the values of n approaches 2. Also, when the molecular weights become further apart, the value of n approaches 1. In the first case the correlation (5) becomes

$$\lambda = (\sqrt{A_1}\, x_1 + \sqrt{A_2}\, x_2)^2 \left(\frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \right) \tag{6}$$

and in the second case,

$$\lambda = (A_1 x_1^2 + A_2 x_2^2 + \sqrt{A_1 A_2}\, x_1 x_2) \left(\frac{(1 - T_r)^{0.38}}{T_r^{1/6}} \right) \tag{7}$$

Table II. Parameters for the Investigated Binary Mixtures[a]

Binary mixture	M_1	M_2	T_{c1} (K)	T_{c2} (K)	A_1 ($W \cdot m^{-1} \cdot K^{-1}$)	A_2 ($W \cdot m^{-1} \cdot K^{-1}$)	n	$\bar{\Delta}$ (%)	Δ_{max} (%)	Temp. and ref., exp λ_m data
Acetone/aniline	58.08	93.15	508.7	766.4	0.203	0.173	2.0	1.2	2.1	0°C [14]
Acetone/n-butyl alcohol	58.08	74.12	508.7	563.0	0.203	0.181	2.0	1.9	5.5	0°C, 25°C, 50°C [14] [b] [b]
Acetone/sec-butyl alcohol	58.08	74.12	508.7	536.0	0.203	0.171	2.0	2.0	5.3	0°C, 25°C, 50°C [14] [b] [b]
Acetone/carbon tetra-chloride	58.08	153.82	508.7	556.3	0.203	0.123	1.5	1.8	4.4	0°C, 25°C, 50°C [14] [6] [b]
Acetone/chloroform	58.08	119.38	508.7	536.4	0.203	0.142	1.6	1.6	3.1	25°C, 50°C [b] [b]
Acetone/ethyl alcohol	58.08	46.07	508.7	516.2	0.203	0.206	2.0	0.9	1.9	25°C, 50°C [6] [b]
Acetone/n-hexyl alcohol	58.08	102.18	508.7	610.0	0.203	0.178	1.8	2.2	6.4	0°C, 25°C, 50°C [14] [b] [b]
Acetone/methyl alcohol	58.08	32.04	508.7	513.2	0.203	0.250	2.0	1.4	2.3	0°C, 50°C [14] [15]
Acetone/methyl formate	58.08	60.05	508.7	487.2	0.203	0.243	1.9	2.0	4.8	15°C, 25°C, 50°C [16] [b] [b]
Acetone/toluene	58.08	92.15	508.7	594.0	0.203	0.153	2.0	1.4	1.8	0°C [14]
Aniline/nitrobenzene	93.15	123.11	766.4	782.0	0.173	0.151	2.0	2.3	4.4	0°C, 75°C, 150°C [14] [15] [15]
Benzene/chloroform	78.12	119.38	562.1	536.4	0.172	0.142	1.8	1.5	4.1	15°C, 20°C, 25°C, 40°C [3] [17] [b] [b]

Benzene/diethyl ether	78.12	74.12	562.1	465.8	0.172	0.179	2.0	1.2	2.9	15°C, 25°C [3] [6]
Benzene/methyl alcohol	78.12	32.04	562.1	513.2	0.172	0.250	1.6	1.5	4.7	0°C [14]
Benzene/methyl formate	78.12	60.05	562.1	487.2	0.172	0.243	1.8	1.2	3.7	15°C, 25°C, 50°C [3] [b] [b]
Benzene/toluene	78.12	92.15	562.1	594.0	0.172	0.153	1.9	1.1	3.2	0°C, 50°C [14] [15]
n-Butyl acetate/sec-butyl alcohol	116.16	74.12	579.0	536.0	0.162	0.171	1.8	2.0	5.7	25°C, 50°C [b] [b]
n-Butyl acetate/diethyl ether	116.16	74.12	579.0	465.0	0.162	0.179	2.0	2.7	7.0	0°C, 25°C, 50°C [14] [b] [b]
n-Butyl acetate/ethyl methyl ketone	116.26	72.11	579.0	535.6	0.162	0.178	2.0	1.6	6.5	25°C, 50°C [b] [b]
n-Butyl acetate/toluene	116.16	92.15	579.0	594.0	0.162	0.153	2.0	1.6	4.7	0°C, 25°C, 50°C [14] [b] [b]
n-Butyl alcohol/carbon tetrachloride	74.12	153.82	563.0	556.3	0.181	0.123	1.5	1.2	3.2	0°C, 50°C, 65°C [14] [15] [15]
n-Butyl alcohol/diethyl ketone	74.12	86.13	563.0	561.1	0.181	0.173	1.8	2.4	5.8	25°C, 50°C [b] [b]
n-Butyl alcohol/toluene	74.12	92.15	563.0	594.0	0.181	0.153	1.9	1.5	2.7	0°C, 25°C, 50°C [14] [6] [b]
sec-Butyl alcohol/toluene	74.12	92.15	563.0	594.0	0.171	0.153	2.0	2.0	4.5	0°C, 25°C, 50°C [14] [b] [b]
di-n-Butyl ether/carbon tetrachloride	130.23	153.82	580.0	55.63	0.145	0.123	1.9	2.2	4.7	0°C [14]
di-n-Butyl ether/ chloroform	130.23	119.38	580.0	536.4	0.145	0.142	2.0	2.3	6.1	0°C, 25°C, 50°C [14] [b] [b]

[a] Parameters are the molecular weights M_1 and M_2, the critical temperatures T_{c1} and T_{c2}, A and n as defined, the mean $\bar{\Delta}$ and the maximum Δ_{max} deviations between predicted and experimental thermal conductivity data, and the temperatures and sources of the experimental data.

Table II. *(Continued)*

Binary mixture	M_1	M_2	T_{c1} (K)	T_{c2} (K)	A_1 ($W \cdot m^{-1} \cdot K^{-1}$)	A_2 ($W \cdot m^{-1} \cdot K^{-1}$)	n	$\bar{\Delta}$ (%)	Δ_{max} (%)	temp. and ref., exp λ_m data
di-n-Butyl ether/methyl alcohol	130.23	32.04	580.0	513.2	0.145	0.250	1.0	4.0	11.1	0°C, 25°C, 50°C [14] [b] [b]
Carbon tetrachloride/ cyclohexane	153.82	84.16	556.3	553.4	0.123	0.144	1.7	1.3	4.0	25°C, 40°C, 50°C, 60°C [b] [18 [b] [18]
Carbon tetrachloride/ dichloromethane	153.82	84.93	556.3	510.0	0.123	0.178	1.7	1.1	3.3	0°C [14]
Carbon tetrachloride/ diethyl ether	153.82	74.12	556.3	465.3	0.123	0.179	1.5	1.6	2.4	0°C [14]
Carbon tetrachloride/ ethyl alcohol	153.82	46.07	556.3	516.2	0.123	0.206	1.0	4.7	12.9	25°C, 36.5°C, 50°C [b] [19] (b)
Carbon tetrachloride/ n-heptyl alcohol	153.82	116.20	556.3	633.0	0.123	0.169	1.7	1.6	4.3	0°C,50°C, 65°C [14] [5] [15]
Carbon tetrachloride/ n-hexyl alcohol	153.82	102.18	556.3	610.0	0.123	0.178	1.5	1.8	6.4	0°C, 50°C [14] [15]
Carbon tetrachloride/ n-propyl alcohol	153.82	60.09	55.63	536.7	0.123	0.188	1.4	3.1	6.8	25°C, 36.5°C, 50°C [b] [19] [b]
Carbon tetrachloride/ toluene	153.82	92.15	556.3	594.0	0.123	0.153	1.7	0.9	2.3	0°C, 50°C, 65°C [14] [15] [15]
Chloroform/diethyl ether	119.38	74.12	536.4	465.8	0.142	0.179	1.6	1.8	3.9	−50°C, 0°C [15] [14]
Chloroform/diethyl ketone	119.38	86.13	536.4	561.1	0.142	0.173	2.0	2.8	5.9	25′C, 30.6°C, 50°C [b] [20] [b]
Chloroform/methyl alcohol	119.38	32.04	536.4	513.2	0.142	0.250	1.0	4.4	9.7	25°C, 50°C [b] [b]

Chloroform/ethyl methyl ketone	119.38	72.11	536.4	535.6	0.142	0.178	1.7	1.9	3.0	30.6°C [20]
Cyclohexane/ethyl alcohol	84.16	46.07	553.4	516.2	0.144	0.206	1.6	2.1	5.5	25°C, 36.7°C, 50°C [b] [19] [b]
Cyclohexabe/n-propyl alcohol	84.16	60.09	553.4	536.7	0.144	0.188	1.7	3.1	6.9	25°C, 37.6°C, 50°C [b] [19] [b]
Diethyl ether/1,2-dichloroethane	74.12	98.96	465.8	561.0	0.179	0.161	2.0	1.7	4.1	0°C [14]
Diethyl ether/ nitrobenzene	74.12	123.11	465.8	782.0	0.179	0.151	2.0	1.4	4.2	0°C [14]
Diethyl ether/toluene	74.12	92.15	465.8	594.0	0.179	0.153	2.0	0.9	1.6	0°C [14]
Ethyl alcohol/methyl alcohol	46.07	32.04	516.2	513.2	0.206	0.250	1.9	2.4	5.3	25°C, 50°C [b] [b]
Ethyl alchol/n-propyl alcohol	46.07	60.09	516.2	536.7	0.206	0.188	1.9	2.2	6.8	25°C, 50°C [b] [b]
n-Heptyl alcohol/toluene	116.20	92.15	633.0	594.0	0.169	0.153	2.0	1.2	2.3	0°C [14]
n-Hexyl alcohol/toluene	102.18	92.15	610.0	594.0	0.178	0.153	1.8	2.2	6.4	0°C, 25°C, 50°C [14] [b] [b]
Methyl alcohol/toluene	32.04	92.15	513.2	594.0	0.250	0.153	1.4	2.5	5.6	0°C,50°C [14] [15]
Nitrobenzene/toluene	123.11	92.15	782.0	594.0	0.151	0.153	2.0	1.5	1.7	0°C [14]

Mean general deviation on 621 experimental values at different temperatures and concentrations is $\Delta = 2.0\%$

Between these two extreme cases, corresponding, for example, to the system benzene/diethyl ether ($n = 2.0$) and to the system chloroform/methyl alcohol ($n = 1.0$), all the investigated binary mixtures are placed.

It may be possible to develop a correlation between n and the molecular weights of the components of the mixture. However, it is interesting to remember [10] that, for some organic liquid families, A is inversely proportional to the square root of M and, for other organic liquid families, to M. This result can be utilized and n can be related directely to A_1 and A_2 so that Eq. (5) does not become complicated because of the introduction of further physical parameters.

A rough relation between n and the ratio A_1/A_2 may be of the following type:

$$1.00 \leqslant \frac{A_1}{A_2} < 1.35 \qquad n = 2.0$$

$$1.35 \leqslant \frac{A_1}{A_2} < 1.50 \qquad n = 1.7$$

$$1.50 \leqslant \frac{A_1}{A_2} < 1.70 \qquad n = 1.4$$

$$1.70 \leqslant \frac{A_1}{A_2} \qquad n = 1.0$$

The above indications, used in Eq. (5), lead to a mean general deviation between predicted and experimental thermal conductivity data (621 data points) equal to 2.6%; this is satisfactory for engineering purposes and allows the use of the correlation (5) also when experimental data are not available to calculate n, but the method is rough and not very practical.

It is preferable to attempt a mathematical expression of the type

$$n = f(A_1/A_2) \tag{8}$$

and the analysis of the experimental thermal conductivity values leads to the simple formula:

$$n = 2.20 \frac{A_1}{A_2} \qquad (A_1 \leqslant A_2) \tag{9}$$

so that the proposed general correlation for the binary organic liquid mixtures is

$$\lambda = \left(A_1 x_1^2 + A_2 x_2^2 + 2.20 \sqrt{\frac{A_1^3}{A_2}}\, x_1 x_2\right)\left(\frac{(1 - T_r)^{0.38}}{T_r^{1/6}}\right) \tag{10}$$

where $A \leqslant A_2$.

5. RESULTS AND DISCUSSION

Table III lists the mean and the maximum deviations between the thermal conductivity values predicted according to Eq. (10) and the experimental data. The mean general deviation is 2.5% for 621 data points concerned with the 50 investigated binary mixtures at different temperatures and concentrations. The goals reached are the following:

1. The correlation (10) is simple and contains only the temperature of the mixture, the critical temperatures of the components, and their respective A parameters. The critical temperatures are generally wellknown. The A parameters are presented in the literature [10–13] for nearly 170 pure liquids, or, in any case, may easily be calculated through simple expression [10].
2. The correlation (10), valid for the binary mixtures, is the generalization of Eq. (3), valid for pure liquids.
3. The reliability of the thermal conductivity values predicted according to the correlation (10) is comparable to the reliability of the best experimental data.
4. In the correlation (10), λ_1 and λ_2 do not appear, while the temperature appears explicitly.
5. All the investigated systems obey Eq. (10), including the systems which exhibit a minimum in the relation for thermal conductivity versus composition.

In Eq. (5) the two components of the mixture appear symmetrically, and the factor n is a measure of the difference between them. In the correlation (10), this fact is evidenced in the cross-term $2.20\sqrt{A_1^3/A_2}\,x_1x_2$, which becomes $2.20\sqrt{A_1A_2}\,x_1x_2$ when $A_1 \simeq A_2$.

Table III. The Mean $\bar{\Delta}$ and the Maximum Δ_{max} Deviations Between the Thermal Conductivity Values Predicted According to Eq. (10) and the Experimental Data

Micture	$\bar{\Delta}$ (%)	Δ_{max} (%)
Acetone/aniline	1.6	3.5
Acetone/n-butyl alcohol	2.2	4.6
Acetone/sec-butyl alcohol	2.4	5.2
Acetone/carbon tetrachloride	2.8	5.2
Acetone/chloroform	1.9	4.7
Acetone/ethyl alcohol	2.3	4.6
Acetone/n-hexyl alcohol	2.4	7.2
Acetone/methyl alcohol	2.4	4.9

Table III. *(Continued)*

Mixture	$\bar{\Delta}$ (%)	Δ_{max} (%)
Acetone/methyl formate	2.2	5.2
Acetone/toluene	4.1	7.3
Aniline/nitrobenzene	2.2	6.0
Benzene/chloroform	1.5	3.7
Benzene/diethyl ether	2.6	4.7
Benzene/methyl alcohol	2.1	6.9
Benzene/methyl formate	3.0	6.5
Benzene/toluene	0.8	2.0
n-Butyl acetate/sec-butyl alcohol	4.2	10.1
ñButyl acetate/diethyl ether	2.7	7.1
n-Butyl acetate/ethyl methyl ketone	1.7	6.6
n-Butyl acetate/toluene	0.9	2.0
n-Butyl alcohol/carbon tetrachloride	1.1	3.1
n-Butyl alcohol/diethyl ketone	5.8	9.7
n-Butyl alcohol/toluene	1.3	2.7
sec-Butyl alcohol/toluene	2.1	4.5
di-n-Butyl ether/carbon tetrachloride	2.0	4.7
di-n-Butyl ether/chloroform	3.8	9.2
di-n-Butyl ether/methyl alcohol	4.0	7.5
Carbon tetrachloride/cyclohexane	2.5	5.2
Carbon tetrachloride/dichloromethane	3.4	5.2
Carbon tetrachloride/diethyl ether	1.4	2.2
Carbon tetrachloride/ethyl alcohol	4.4	13.1
Carbon tetrachloride/n-heptyl alcohol	2.4	5.7
Carbon tetrachloride/n-hexyl alcohol	1.8	6.4
Carbon tetrachloride/n-propyl alcohol	3.4	6.8
Carbon tetrachloride/toluene	0.9	1.8
Chloroform/ether	2.7	7.0
Chloroform/diethyl ketone	3.2	7.2
Chloroform/methyl alcohol	5.1	10.4
Chloroform/methyl ketone	1.3	2.9
Cyclohexane/ethyl alcohol	2.4	5.5
Cyclohexane/n-propyl alcohol	3.1	6.8
Kethyl ether/1,2-dichloroethane	1.4	3.5
Diethyl ether/nitrobenzene	1.4	2.2
Diethyl ether/toluene	2.3	3.4
Ethyl alcohol/methyl alcohol	2.6	6.5
Ethyl alcohol/n-propyl alcohol	3.3	6.8
n-Heptyl alcohol/toluene	1.0	2.3
n-Hexyl alcohol/toluene	2.5	6.4
Methyl alcohol/toluene	2.7	6.5
Nitrobenzene/toluene	3.1	5.4
Mean general deviation	2.5%	

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REFERENCES

1. G. Latini and M. Pacetti, *Bull. I.I.F./I.I.R.* **6**:1 (1977).
2. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, *Int. J. Thermophys.* **1**:159 (1980).
3. L. P. Filippov and N. S. Novoselova, *Vestnik Moskov. Gas. Univ.* **10**(3):37 (1955).
4. R. C. Reid, J. M. Prausnitz, and T. K. Sherwoord, *The Properties of Gases and Liquids*, 3rd ed. (McGraw-Hill, New York, 1977), pp. 531–537.
5. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, *Memoire del XXXV Congresso Nazionale A.T.I.* (CELID, La Grafica Nuova, Turin, Italy, 1980), pp. 217–228.
6. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, *Thermal Conductivity 17*, J. G. Hust, ed. (Plenum, New York, 1983), pp. 285–291.
7. N. V. Tsederberg, *Teploenergetika* **3**(9):42 (1956).
8. S. Bretsznajder, *Prediction of Transport and Other Physical Properties of Fluids* (Pergamon Press, Elmsford, N. Y., 1971), pp. 313–328.
9. N. V. Tsederberg, *Thermal Conductivity of Gases and Liquids* (Edward Arnold, London, 1965), pp. 211–222.
10. C. Baroncini, P. Di Filippo, G. Latini, and M. Pacetti, *Int. J. Thermophys.* **2**:21 (1981).
11. E. McLaughlin, *Chem. Rev.* **64**:390 (1964).
12. C. Baroncini, P. Di Filippo, and G. Latini, *Int. J. Refrigeration* **6**(1):60 (1983).
13. C. Baroncini and G. Latini, Symposium on Transport Properties of Fluids—Lisbon 1982; published in Quaderno FT/TC-2, Instituto di Fisica Generale e Fisica Tecnica, February 1982, Ancona University, Italy.
14. D. T. Jamieson and E. H. Hastings, *Thermal Conductivity 8* (Purdue Univ., 1968), pp. 631–641.
15. 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), 00. 102–132.
16. L. P. Filippov, *Vestnik Moskov. Gas. Univ.* **10**(8):67 (1955).
17. L. Riedel, Mitt. Kaltetech. Inst., Karlsruhe (1948), no. 2.
18. J. E. S. Venart, Fourth Symposium on Thermophysical Properties, Univ. Delaware, 1968.
19. W. J. Barnette, Ph.D. thesis, Lousiana State University, 1967.
20. C. P. Kerr, Ph.D. thesis, Louisiana University, 1968.