J. Chem. Eng. Data **1997,** *42,* 971−974

Thermal Conductivities of Some Organic Solvents and Their Binary Mixtures

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The thermal conductivity of 12 pure organic solvents, acetone, acetonitrile, acrylonitrile, carbon tetrachloride, chloroform, 1,2-dichloroethane, ethanol, ethyl acetate, heptane, tetrahydrofuran, toluene, and water, and eight binary mixtures, acetone + ethanol, acetone + ethyl acetate, ethanol + heptane, ethanol + carbon tetrachloride, ethyl acetate + ethanol, heptane + acetone, heptane + toluene, and water + ethanol, were measured by an absolute transient hot-wire method at some selected temperatures from 253.15 K to 303.15 K. A correlation previously developed was used to calculate the thermal conductivity. The agreement between the experimental and the calculated thermal conductivities is satisfactory.

Introduction

Thermal conductivity data are indispensable in engineering work involving heat transfer applications and design. Yet, reliable data on this important transport property are not abundant, though there exist considerable thermal conductivity values of liquids and liquid mixtures in the literature (Beaton and Hewitt, 1989; Daubert and Danner, 1996; Jamieson et al., 1975; Vargaftik, 1975). Further, high-quality measurements of the thermal conductivity of liquids and liquid mixtures are required to test new correlations and prediction methods for thermal conductivity.

The experimental methods used for the measurement of thermal conductivity can be divided in two groups: steady state and transient. The transient hot-wire technique has now become the most widely used method for determining the thermal conductivity of liquids. It is generally considered to be the most accurate method (Wakeham, 1989; Ramires et al., 1995). It involves the electrical heating of a thin wire immersed in the liquid and the determination of the temperature rise of the wire, which is usually determined from its resistance. For an overall discussion of the experimental techniques for the measurement of the thermal conductivity of liquids, the reader is refered to recent monographs on the subject (Assael et al., 1991).

In the present work, the thermal conductivity of some organic solvents, acetone, acetonitrile, acrylonitrile, carbon tetrachloride, chloroform, 1,2-dichloroethane, ethanol, ethyl acetate, heptane, tetrahydrofuran, toluene, and water, and some binary mixtures, acetone + ethanol, acetone + ethyl acetate, ethanol + heptane, ethanol + carbon tetrachloride, ethyl acetate + ethanol, heptane + acetone, heptane + toluene, and water + ethanol, have been measured by an absolute transient hot-wire method over a range of temperature from 253.15 K to 303.15 K at atmospheric pressure.

Experimental Section

Materials. All pure organic solvents used were obtained from Shanghai Chemical Corporation China. Absolute ethanol with a purity better than 99.8% as claimed by the supplier was used without further purification. The other solvents were all analytical reagent grade. Acetone, acetonitrile, carbon tetrachloride, chloroform, 1,2-dichloroethane, ethyl acetate, heptane, toluene (≥99.5%, respectively), acrylonitrile, and tetrahydrofuran (≥99.0%, respectively) were treated by appropriate procedures (Riddick et al., 1986). They were further purified by fractional distillation in a 1.5 m long column and dehydrated by standing over 0.4 nm activated molecular sieves. Deionized water was further doubly distilled and degassed before its use. All the binary mixtures were prepared by mass. A Mettler balance, Switzerland, with a precision of ±0.0001g was used. Precautions were taken in order to minimize evaporation losses during storage and preparation of the solutions.

Table 1. Densities, ρ, and Refractive Indices, n_D, of the Pure Solvents at 20 °C and Comparison with Literature Data

	ρ/g·cm^{-3}		n_D	
solvent	exptl	lit.[a]	exptl	lit.[a]
acetone	0.7897	0.79117	1.3591	1.35868
acetonitrile	0.7855	0.7822	1.3440	1.3441
acrylonitrile	0.8063	0.8060[b]	1.3913	
carbon tetrachloride	1.5942	1.59417	1.4600	1.4602
chloroform	1.4830	1.48911	1.4461	1.4459
1,2-dichloroethane	1.2350	1.25209	1.4449	1.4448
ethanol	0.7893	0.78937	1.3611	1.36143
ethyl acetate	0.9004	0.9003	1.3722	1.3723
heptane	0.6836	0.68369	1.3877	1.38764
tetrahydrofuran	0.8890	0.8867	1.4053	1.4071
toluene	0.8671	0.86684	1.4960	1.49694
water	0.9984	0.9982058	1.3330	1.332988

[a] TRC Databases (1996). [b] Riddick et al. (1986).

Densities, ρ, of pure solvents were measured to ±0.0001 g·cm^{-3} with an Anton Paar, DMA-45 digital densimeter. Refractive indices, n_D^{20}, were measured using an Abbe's refractometer. The measured values are included in Table 1 along with literature values (TRC databases, 1996).

Apparatus. The liquid thermal conductivity was measured by an absolute transient hot-wire method. The principle and the working equations for the technique have

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S0021-9568(96)00351-2 CCC: $14.00

Table 2. Experimental Thermal Conductivity, λ, of Pure Solvents and Comparison with Literature Data

	λ/W·K^{-1}·m^{-1}							
T/K	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
	acetone		acetonitrile		acrylonitrile		carbon tetrachloride	
253.15	0.1687	0.1773	0.2307	0.2254	0.1837	0.1804	0.1078	0.1117
263.15	0.1644	0.1731	0.2238	0.2217	0.1792	0.1767	0.1057	0.1094
273.15	0.1623	0.1689	0.2168	0.2181	0.1748	0.1730	0.1039	0.1072
283.15	0.1601	0.1648	0.2100	0.2146	0.1699	0.1693	0.1017	0.1049
293.15	0.1567	0.1607	0.2034	0.2112	0.1648	0.1657	0.0995	0.1027
303.15	0.1525	0.1567			0.1592	0.1622	0.0972	0.1005
	chloroform		1,2-dichloroethane		ethanol		ethyl acetate	
253.15	0.1315	0.1272	0.1407	0.1457	0.1755	0.1746	0.1584	0.1544
263.15	0.1279	0.1245	0.1390	0.1430	0.1723	0.1720	0.1555	0.1515
273.15	0.1240	0.1218	0.1371	0.1404	0.1695	0.1695	0.1526	0.1486
283.15	0.1206	0.1191	0.1353	0.1377	0.1665	0.1670	0.1496	0.1457
293.15	0.1169	0.1165	0.1335	0.1351	0.1635	0.1645	0.1465	0.1429
303.15	0.1134	0.1139	0.1317	0.1325	0.1615	0.1622	0.1429	0.1400
	heptane		tetrahydrofuran		toluene		water	
253.15	0.1353	0.1364[a] 0.1364[b]	0.1680		0.1434	0.1414[a] 0.1445[b]		
263.15	0.1323	0.1331[a] 0.1334[b]	0.1647		0.1407	0.1387[a] 0.1415[b]		
273.15	0.1294	0.1298[a] 0.1304[b]	0.1611		0.1385	0.1360[a] 0.1385[b]		
283.15	0.1262	0.1265[a] 0.1274[b]	0.1578		0.1343	0.1333[a] 0.1355[b]	0.5803	0.5781[c] 0.5800[b]
293.15	0.1233	0.1233[a] 0.1244[b]	0.1544		0.1318	0.1306[a] 0.1325[b]	0.5981	0.5975[c] 0.5984[b]
303.15	0.1207	0.1201[a] 0.1214[b]	0.1509		0.1302	0.1279[a] 0.1295[b]	0.6157	0.6157[c] 0.6154[b]

[a] Data from ESDU. [b] Nieto de Castro et al. (1986). [c] Ramires et al. (1995).

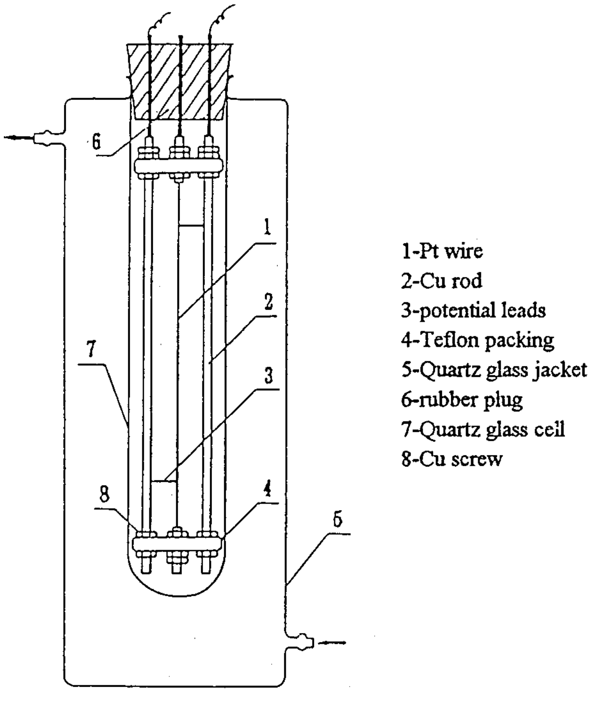

Figure 1. Hot-wire cell.

Table 3. Experimental Thermal Conductivity, λ, of Binary Mixtures

	λ/W·K^{-1}·m^{-1}				λ/W·K^{-1}·m^{-1}		
w_1[a]	253.15 K	273.15 K	293.15 K	w_1	253.15 K	273.15 K	293.15 K
acetone (1) + ethanol (2)				acetone (1) + ethyl acetate (2)			
0.0000	0.1755	0.1695	0.1635	0.0000	0.1584	0.1526	0.1465
0.1009	0.1750	0.1685	0.1620	0.0996	0.1597	0.1542	0.1484
0.3005	0.1729	0.1663	0.1603	0.3046	0.1622	0.1569	0.1509
0.4905	0.1717	0.1654	0.1583	0.4005	0.1637	0.1576	0.1517
0.6905	0.1709	0.1635	0.1575	0.7368	0.1663	0.1603	0.1543
0.8970	0.1696	0.1629	0.1570	0.8990	0.1680	0.1616	0.1559
1.000	0.1687	0.1623	0.1567	1.0000	0.1687	0.1623	0.1567
ethanol (1) + heptane (2)				ethanol (1) + carbon tetrachloride (2)			
0.0000	0.1353	0.1294	0.1233	0.0000	0.1078	0.1039	0.1017[b]
0.1089	0.1369	0.1316	0.1253	0.1145	0.1131	0.1081	0.1057[b]
0.3013	0.1429	0.1377	0.1303	0.3114	0.1250	0.1185	0.1154[b]
0.4870	0.1502	0.1454	0.1380	0.4653	0.1353	0.1299	0.1259[b]
0.6899	0.1611	0.1543	0.1471	0.6828	0.1500	0.1446	0.1417[b]
0.8991	0.1708	0.1654	0.1580	0.8928	0.1680	0.1642	0.1590[b]
1.0000	0.1755	0.1695	0.1635	1.0000	0.1755	0.1695	0.1665[b]
ethyl acetate (1) + ethanol (2)				heptane (1) + acetone (2)			
0.0000	0.1755	0.1695	0.1635	0.0000	0.1687	0.1623	0.1567
0.1150	0.1734	0.1676	0.1613	0.0996	0.1643	0.1581	0.1519
0.3017	0.1699	0.1640	0.1576	0.2978	0.1559	0.1489	0.1420
0.4818	0.1670	0.1610	0.1539	0.4679	0.1494	0.1416	0.1337
0.7007	0.1635	0.1569	0.1507	0.6634	0.1416	0.1357	0.1284
0.8825	0.1602	0.1543	0.1481	0.8395	0.1369	0.1313	0.1242
1.0000	0.1584	0.1526	0.1465	1.0000	0.1353	0.1294	0.1233
heptane (1) + toluene (2)				water (1) + ethanol (2)			
0.0000	0.1434	0.1385	0.1343[b]	0.0000			0.1635
0.0986	0.1419	0.1372	0.1323[b]	0.1000			0.1890
0.2996	0.1400	0.1352	0.1304[b]	0.2998			0.2428
0.4921	0.1384	0.1334	0.1286[b]	0.5004			0.3155
0.6716	0.1369	0.1317	0.1272[b]	0.7012			0.4169
0.9041	0.1353	0.1299	0.1262[b]	0.8967			0.5291
1.000	0.1353	0.1294	0.1262[b]	1.0000			0.5981

[a] w_1 is the weight fraction of species 1. [b] Experimental data at 283.15 K.

been fully discussed by Assael et al. (1991). The experimental apparatus and the procedure of its performance have been described previously in detail (Cai et al., 1993). The hot-wire cell used in this work is shown in Figure 1. The measurements on the thermal conductivity were all under atmospheric pressure. The hot wire, a platinum wire, was of the same specification as that in our previous work (Cai et al., 1993). For the thermal conductivity measurements of polar liquids, an insulated hot wire should be applied. This modification was carried out with the procedure described by Ramires et al. (1993). The cell was housed in a temperature-controlled environment where temperature fluctuations were kept within ±0.1 K. The hot-wire cell was connected to a Haake F3-C liquid thermostatic bath with a claimed temperature stability of $\pm 5 \times 10^{-4}$ K. It can secure a stabilization of ±0.02 K during the period of measurement. The total uncertainty

Table 4. Values of Parameters, *D* and *C*, of Eq 4 and the Standard Deviations, σ, for the Thermal Conductivity of the Pure Solvents

solvent	D	$C \times 10^4$	σ
acetone	6.8034	−1.9502	0.0074
acetonitrile	7.9901	0.0387	0.0061
acrylonitrile	4.9299	−1.9474	0.0008
carbon tetrachloride	2.4599	−1.3266	0.0026
chloroform	3.6528	−0.6703	0.0063
1,2-dichloroethane	3.4813	0.5591	0.0002
ethanol	9.0339	−3.6309	0.0064
ethyl acetate	4.7625	−3.9617	0.0057
heptane	3.2029	−6.1832	0.0035
tetrahydrofuran	5.1043	1.2090	0.0112
toluene	4.1933	−6.2030	0.0078
water	31.2798	9.4816	0.0102

in the measured thermal conductivity of the apparatus is estimated to be ±0.7%.

Results and Discussion

Heptane, toluene, and water have been suggested as the standard reference materials of liquid thermal conductivity (Nieto de Castro et al., 1986; Ramires et al., 1995). Table 2 gives the experimental thermal conductivities at 253.15 K, 263.15 K, 273.15 K, 283.15 K, 293.15 K, and 303.15 K and the reference values of the three compounds (Data from ESDU, Nieto de Catro et al., 1986; Ramires et al., 1995). They are in reasonable agreement. Table 2 also lists the experimental data for other pure solvents compared with those found in the literature (TRC Databases, 1996).

The thermal conductivities of eight binary mixtures, acetone + ethanol, acetone + ethyl acetate, ethanol + heptane, ethanol + carbon tetrachloride, ethyl acetate + ethanol, heptane + acetone, heptane + toluene, and water + ethanol, were measured with respect to compositions at the three seleced temperatures of 253.15 K, 273.15 K, and 283.15 K, or 293.15 K, respectively, and the experimental data are given in Table 3. Only the thermal conductivity values for acetone + ethanol binary mixtures at 298.15 K and for the ethanol + carbon tetrachloride system at 298.15 K and 323.13 K are found in the literature (DIPMIX Database, 1992); no experimental data below 298.15 K for these two systems and no reference data for other binary mixtures are found in the literature.

In our previous work (Lei, 1995; Lei et al, 1997), a liquid was assumed to be a mixture of microcrystallites and vacancies, and a correlation of liquid thermal conductivity was developed. The correlation was proposed on the basis of the significant structure theory, the theory of solid physics, and the kinetic theory of gases.

The thermal conductivity of a liquid can be expressed as eq 1 according to the significant structure theory (Eyring, 1967)

$$\lambda = \frac{V_S}{V}\lambda_S + \frac{V - V_S}{V}\lambda_g \tag{1}$$

where λ, λ_S, and λ_g are the thermal conductivities of the liquid, the solid-, and the gaslike molecules, respectively, and V, V_S are the volumes of the liquid and the solid-like molecules, respectively.

According to our supposition, the thermal conductivity of a liquid is the sum of the contributions of those microcrystallites and vacancies. Equation 1 may then, by analogy, be used to express the liquid thermal conductivity where λ_S and λ_g now represent the thermal conductivities of the microcrystallites and vacancies, respectively.

The thermal conductivity of the microcrystallites may be estimated as follows from the theory of solid physics (Lei, 1995)

$$\lambda_S = D\frac{T^{4/7}V_S}{(V - V_S)^{2/7}} \tag{2}$$

where D is a parameter to be determined and T is the temperature.

The thermal conductivity of the vacancies are calculated from the kinetic theory of gases (Reid et al., 1987)

$$\lambda_g = C\frac{\sqrt{T/M}}{V_C^{2/3}\Omega_g} \tag{3}$$

where C is another parameter to be determined and M, V_C, and Ω_g are the molecular weight, the critical volume, and the collision integral, respectively.

Then, the thermal conductivity of liquids can be expressed as

Table 5. Binary Interaction Coefficients, k_{ij}, the Standard Deviations, σ, and the Maximum Average Absolute Deviations, $[(\lambda_c - \lambda)/\lambda]_{max}$, for the Binary Mixtures of the Correlation by Eqs 4−13

system	T/K	exptl data	k_{ij}	σ	$[(\lambda_c - \lambda)/\lambda]_{max}$
acetone (1) + ethanol (2)	253.15	7	−0.028	0.0021	0.0187
	273.15	7	0.015	0.0003	−0.0022
	293.15	7	0.053	0.0015	−0.0138
acetone (1) + ethyl acetate (2)	253.15	7	−0.084	0.0017	0.0187
	273.15	7	−0.073	0.0004	−0.0038
	293.15	7	−0.072	0.0012	−0.0126
ethanol (1) + carbon tetrachloride (2)	253.15	7	−0.175	0.0017	0.0180
	273.15	7	−0.123	0.0015	0.0207
	283.15	7	−0.091	0.0008	−0.0077
ethanol (1) + heptane (2)	253.15	7	−0.079	0.0027	0.0229
	273.15	7	−0.102	0.0016	−0.0219
	293.15	7	−0.074	0.0017	0.0138
ethyl acetate (1)+ ethanol (2)	253.15	7	−0.116	0.0017	0.0152
	273.15	7	−0.110	0.0008	−0.0076
	293.15	7	−0.098	0.0027	−0.0138
heptane (1) + acetone (2)	253.15	7	−0.092	0.0024	−0.0216
	273.15	7	−0.057	0.0010	−0.0102
	293.15	7	−0.027	0.0012	−0.0126
heptane (1) + toluene (2)	253.15	7	0.016	0.0005	−0.0064
	273.15	7	0.018	0.0007	−0.0096
	283.15	7	0.050	0.0014	−0.0188
water (1) + ethanol (2)	293.15	7	−0.014	0.0130	−0.0476

$$\lambda = D\frac{T^{4/7}V_{\mathrm{S}}^{2}}{(V - V_{\mathrm{S}})^{2/7}V} + C\frac{V - V_{\mathrm{S}}}{V}\frac{\sqrt{T/M}}{V_{\mathrm{C}}^{2/3}\Omega_{\mathrm{g}}} \tag{4}$$

where D and C are two parameters characteristic of a liquid, which should be determined from experimental data by a least-error fit (Lei, 1995). Equation 4 has been used for 98 compounds including inorganic, organic, polar, and nonpolar substances over wide ranges of temperature. The values of D and C and the standard deviations, σ, of the correlation for the investigated compounds in this work are listed in Table 4.

The mixing rules are selected as follows to make eq 4 be extended for mixtures.

$$D_{\mathrm{m}} = \sum_{i}\sum_{j} x_i x_j D_{ij} \tag{5}$$

$$D_{ij} = \sqrt{D_i D_j} \tag{6}$$

$$C_{\mathrm{m}} = \sum_{i} x_i C_i \tag{7}$$

$$V_{\mathrm{Sm}} = \sum_{i}\sum_{j} x_i x_j V_{\mathrm{S}ij} \tag{8}$$

$$V_{\mathrm{S}ij} = (1 - k_{ij})(V_{\mathrm{S}i}^{1/3} + V_{\mathrm{S}j}^{1/3})^3 / 8 \tag{9}$$

$$M_{\mathrm{m}} = \sum_{i} x_i M_i \tag{10}$$

$$V_{\mathrm{Cm}} = \sum_{i}\sum_{j} x_i x_j V_{\mathrm{C}ij} \tag{11}$$

$$V_{\mathrm{C}ij} = (V_{\mathrm{C}i}^{1/3} + V_{\mathrm{C}j}^{1/3})^3 / 8 \tag{12}$$

$$T_{\mathrm{Cm}} = \sum_{i} x_i T_{\mathrm{C}i} \tag{13}$$

where x_i is the molar fraction of component i, and k_{ij} is a binary interaction coefficient that must be determined from experimental data. The data of T_{C}, V_{C}, and M used in the correlation are from Reid et al. (1987).

Table 5 presents the binary interaction coefficients, k_{ij}, the standard deviations σ, and the maximum average absolute deviations $[(\lambda_{\mathrm{c}} - \lambda)/\lambda]_{\max}$, for the thermal conductivity correlation. The values in Table 5 show that the correlation results are generally satisfactory. The larger discrepancy between the experimental and the correlated data for the water + ethanol system may be ascribed to the drawback of the correlation because the strong intermolecular actions in this kind of system were not considered especially.

In conclusion, the developed correlation, eq 4, is valid for pure liquids. Equation 4, combining the appropriate mixing rules, eqs 5−13, is also valid for binary mixtures. The comparison of the observed values, the correlation results, and the literature data gives satisfactory agreement.

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Received for review November 8, 1996. Accepted June 13, 1997.⊗

JE960351M

⊗ Abstract published in *Advance ACS Abstracts*, August 1, 1997.