

Liquid Thermal Conductivities of Hydrocarbon—Alcohol Mixtures

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The author previously measured the thermal conductivities of liquid hydrocarbons and alcohols and their mixtures under atmospheric pressure by use of a relative horizontal parallel-plate method (steady-state type).

A correlation method previously proposed was found to be successful for the binary mixtures. To give a more generalized correlation, potential parameters were reevaluated by selecting benzene as a reference substance. To apply this model to various binary mixtures, the local mole fraction concept was introduced for the calculation of mixture parameter because the interactions between hydrocarbon and alcohol molecules are complex.

Introduction

The thermal conductivity of liquids is an important transport property required in the design and analysis of various heat transfer process. Therefore, the thermal conductivities of many substances have been measured by several workers and were compiled by Touloukian et al.¹⁾ But, there are few data for liquid mixtures although a number of thermal conductivity data have been reported for pure liquids. The discrepancies among the data reported by different workers are not negligible.

The purposes of the author's work are to measure the thermal conductivities of hydrocarbons, alcohols, and their mixtures and also to establish the correlation method. The author measured previously the thermal conductivities of seven hydrocarbons (benzene, toluene, *p*-xylene, *n*-heptane, *n*-octane, *n*-nonane, and *n*-decane) and ten alcohols (ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 1-pentanol, 2-methyl-1-butanol, 1-hexanol, and 1-heptanol) at temperatures from 20 to 70°C under atmospheric pressure by use of a relative horizontal parallel-plate method (steady-state type). Then, the thermal conductivities of binary hydrocarbon mixtures (*n*-decane—*n*-heptane, benzene—*p*-xylene, and benzene—*n*-

heptane), and binary alcohol mixtures (1-butanol—2-butanol, 1-propanol—2-butanol, ethanol—2-butanol, and ethanol—1-pentanol) were measured.^{5,7)} Further, additional thermal conductivity data were reported at 25.0 and 40.0°C for four binary hydrocarbon—alcohol mixtures (toluene—ethanol, *n*-heptane—1-heptanol, benzene—2-butanol, and toluene—1-heptanol).⁸⁾

The author has proposed the correlation model to represent the thermal conductivities of nonpolar and polar pure liquid on the basis of the hole theory concept and the lattice model of Horrocks and McLaughlin.³⁾ To apply these model to binary mixtures, the local mole fraction concept is introduced for the calculation of mixture parameters. Based on the two-fluid model, the present model is applied to binary mixtures by introducing two binary characteristic parameters.

1. Experimental Apparatus

The experimental apparatus and procedure used in the present study were almost the same as described in the previous papers.^{5,7)} A brief description of the apparatus and procedure is given below. As shown in Fig. 1, the apparatus is of a relative horizontal parallel-plate, steady-state type. A glass plate (260×260×10 mm), G,

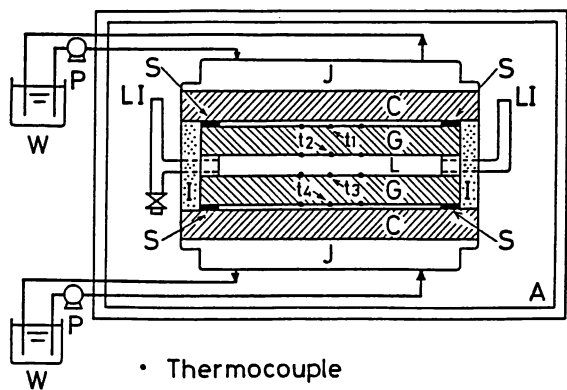


Fig. 1 Schematic diagram of the experimental apparatus: A, constant-temperature air bath; C, copper plate; I, insulating material; J, jacket; L, liquid layer; LI, liquid inlet; P, circulating pump; S, silicone rubber; W, constant-temperature water bath.

was used as a standard material. The thermal conductivity of the standard glass plate was calibrated with distilled water. The value of the thermal conductivity of distilled water recommended by Touloukian et al.¹¹⁾ was adopted in this study. A liquid sample, L, was held between standard glass plates and the dimension of liquid layer was $220 \times 220 \times 4.84$ mm. Copper-constantan thermocouples (0.07 mm in diameter) were provided to measure the temperature gradients across the liquid layer and the standard glass plates. These thermocouples were fastened to both sides of the glass plates with a small quantity of epoxy adhesive. These thermocouples were used in order to ascertain whether the temperature on each surface of the glass plates was uniform.

By circulating water of a constant temperature (controlled within $\pm 0.01^\circ\text{C}$) through jackets, J, a temperature gradient was established in the test fluid around the desired experimental temperature. High-temperature water was circulated through the upper jacket, and heat flux was directed downward in order to minimize heat transfer by convection. The thermal conductivity of liquid sample, λ , was obtained as

$$\lambda = \lambda_0 (d/d_0) (\Delta T_0/\Delta T) \quad (1)$$

where ΔT_0 and ΔT are the temperature differences of the standard glass plate and liquid

sample, and λ_0 and d_0 are the thermal conductivity and thickness of the standard glass plate, respectively. d is the thickness of the liquid sample.

The reproducibility of the thermal conductivity by this method was within 1%, and the maximum uncertainty of the present thermal conductivity finally obtained was estimated to be within 2%.

Hydrocarbons and alcohols used in this study were guaranteed reagents. Their purities, determined by gas chromatography, were more than 98.6%.

2. Correlation of Thermal Conductivities

2.1 Correlation of Thermal Conductivities of Pure Liquids⁹⁾

The structure of liquid is approximately assumed to be a face-centered cubic lattice. As heat conduction in liquid can be considered to be caused mainly by the vibrations of molecules, the following equation has been proposed to predict the thermal conductivity of liquid.^{3,5)}

$$\lambda = \sqrt{2} (V_0/V) C_V \nu / a N_A \quad (2)$$

where V_0 denotes solid molar volume at the melting point, V is liquid molar volume, a is the distance between a molecule and its neighbor, C_V is the constant-volume heat capacity, ν is the frequency of molecular vibration, and N_A is Avogadro's number.

Assuming harmonic oscillation of central molecule in the cell, the frequency ν can be derived as⁷⁾

$$\nu = \frac{1}{2\pi\sqrt{M/N_A}} \left[\frac{2z\varepsilon(T)}{r^2 v^{*2}} \left\{ \frac{l(y)}{v^{*2}} - 2m(y) \right\} \right]^{1/2} \quad (3)$$

where

$$l(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1 - y)^{-10} - 1 \quad (4)$$

$$m(y) = (1 + y)(1 - y)^{-4} - 1 \quad (5)$$

and

$$y = (r/a)^2 \quad (6)$$

$$v^* = V_0 / \{\sigma(T)\}^3 N_A \quad (7)$$

$$r = \{a - C\sigma(T)\} / 2 \quad (8)$$

$$a = 2^{1/6} (V_0/N_A)^{1/3} \quad (9)$$

$$z = 12 (V_0/V) \quad (10)$$

$$V_0 = 1.48 V_w \quad (11)$$

In the present study, the solid molar volume at melting point V_0 is correlated with van der Waals volume V_w in Eq. (11). The van der Waals volume V_w can be obtained by Bondi's method.¹⁾ The value of C_v are given by the group contribution method proposed in the previous work.⁶⁾ To calculate the frequency, the temperature dependent potential parameters $\epsilon(T)$ and $\sigma(T)$ contained in the Lennard-Jones (12-6) potential are needed. They have been approximated as following equations.⁷⁾

$$\epsilon(T) = \epsilon^0(1 + \beta/T)^2 \quad (12)$$

$$\sigma(T) = \sigma^0(1 + \beta/T)^{-1/6} \quad (13)$$

Further, a proportionality constant C in Eq. (8) introduced in the previous works^{5,7)} to estimate the molecular contact length required for energy transfer should be evaluated as

$$C = C^0(1 + \gamma) \quad (14)$$

where β and γ are the empirical parameters for polar effect. Values of β and γ are zero for nonpolar liquids. In the present study, the author has attempted to obtain a generalized correlation for parameters (ϵ^0 , σ^0 and C^0) selecting benzene as reference substance because benzene molecule seems relatively spherical and nonpolar. These parameters were determined to give the best fit with the thermal conductivity obtained previously for nonpolar hydrocarbons⁵⁾ using the Simplex method. They could be correlated with Pitzer's acentric factor ω ,⁹⁾ and the following expressions were obtained.⁸⁾

$$\epsilon^0/kT_c = 0.7260 + 0.2415(\omega - 0.212) \quad (15)$$

$$(\sigma^0)^3 N_A / V_c = 0.2205 - 0.2316(\omega - 0.212) + 0.2907(\omega - 0.212)^2 \quad (16)$$

$$C^0 = 1.00 - 0.8755(\omega - 0.212) \quad (17)$$

The value of ω of benzene is 0.212. Further, parameters β and γ are given as follows on the basis of thermal conductivity data of alcohols.⁷⁾ The author correlated β and γ with the Stiel's polar factor χ ,²⁾ and had to separate normal alcohols from branched alcohols to perform the correlation.

Normal alcohol :

$$\beta/T_c = 0.05703 + 0.5116\chi + 3.2373\chi^2 \quad (18)$$

$$(1 + \gamma)RT_c/\Delta H^{vap} = 0.1129 + 0.02398\chi - 0.5049\chi^2 \quad (19)$$

Branched alcohol :

$$\beta/T_c = 0.05768 + 0.5364\chi + 5.0973\chi^2 \quad (20)$$

$$(1 + \gamma)RT_c/\Delta H^{vap} = 0.1856 + 2.1983\chi + 14.949\chi^2 \quad (21)$$

By using the above correlation, the thermal conductivities of hydrocarbons and alcohols can be calculated within average deviation of 2.6%.

2.2 Correlation of Thermal Conductivities of Liquid Mixtures

Equation (2) can be readily extended to a mixture by adopting the mixing rules. Namely, Eq. (2) becomes

$$\tilde{\lambda} = \sqrt{2}(\tilde{V}_0/\tilde{V})\tilde{C}_v\tilde{\nu}/\tilde{a}N_A \quad (22)$$

where \tilde{V}_0 , \tilde{V} , \tilde{C}_v , $\tilde{\nu}$, and \tilde{a} are average values for a liquid mixture with a given composition. On the basis of the concept of the two-fluid model,¹⁰⁾ the frequency of a liquid mixture is given as

$$\tilde{\nu} = \sum_i x_i \nu_{(i)} \quad (23)$$

where

$$\nu_{(i)} = \frac{1}{2\pi\sqrt{M_i/N_A}} \left[\frac{2\tilde{z}\epsilon(T)_{(i)}}{\tilde{r}^2\tilde{\nu}^{*2}} \left\{ \frac{l(\tilde{y})}{\tilde{r}^{*2}} - 2m(\tilde{y}) \right\} \right]^{1/2} \quad (24)$$

The functions $l(\tilde{y})$ and $m(\tilde{y})$ are the same as Eqs. (4) and (5), respectively. The values of \tilde{y} are obtained by

$$\tilde{y} = (\tilde{r}/\tilde{a})^2 \quad (25)$$

$$\tilde{a} = 2^{1/6}(\tilde{V}/N_A)^{1/3} \quad (26)$$

$$\tilde{z} = 12(\tilde{V}_0/\tilde{V}) \quad (27)$$

$$\tilde{r} = \left[\tilde{a} - \sum_i \sum_j x_i x_j \{ C\sigma(T) \}_{ij} \right] / 2 \quad (28)$$

$$\tilde{V}_0 = \sum_i \sum_j x_i x_j \{ V_0 \}_{ij} \quad (29)$$

$$\tilde{\nu}^* = \tilde{V}_0 / \left[\sum_i \sum_j x_i x_j \{ \sigma(T) \}_{ij} \right]^3 N_A \quad (30)$$

$$\tilde{V} = \left(\sum_i M_i x_i \right) / \bar{\rho} \quad (31)$$

In Eqs. (25) to (30), the cross-terms are given as

$$\{ C\sigma(T) \}_{ij} = (1 - l_{ij}) \sqrt{C_i \sigma(T)_{ii} C_j \sigma(T)_{jj}} \quad (32)$$

$$\{ V_0 \}_{ij} = (1 - l_{ij}) \sqrt{V_{0ii} V_{0jj}} \quad (33)$$

$$\{ \sigma(T) \}_{ij} = (1 - l_{ij}) \sqrt{\sigma(T)_{ii} \sigma(T)_{jj}} \quad (34)$$

where l_{ij} is the binary characteristic parameter between molecule i and j . The values of l_{ij} in Eqs. (32) to (34) are assumed to be equal.

The values of $\epsilon(T)_{(i)}$ are approximated by

$$\epsilon(T)_{(i)} = \sum_j x_{j(i)} \epsilon(T)_{ij} \quad (35)$$

where $x_{j(i)}$ denotes the local mole fraction of

molecule j surrounding a molecule i . According to Wilson,¹²⁾ the author adopted the following expressions.

$$x_{j(i)} = x_j \exp(\tau_{ji}) / [x_i + x_j \exp(\tau_{ji})] \quad (36)$$

where

$$\tau_{ji} = \{\epsilon(T)_{ji} - \epsilon(T)_{ii}\} / kT \quad (37)$$

$$\epsilon(T)_{ij} = (1 - k_{ij}) \sqrt{\epsilon(T)_{ii} \epsilon(T)_{jj}} \quad (38)$$

k_{ij} is the binary characteristic parameter.

The average constant-volume heat capacity is approximated by

$$\bar{C}_V = \sum_i x_i C_{V_i} \quad (39)$$

The thermal conductivities of mixtures can be calculated when k_{ij} and l_{ij} are known. The optimum values of k_{ij} and l_{ij} for binary mixtures of hydrocarbon—hydrocarbon systems, alcohol—alcohol systems, and hydrocarbon—alcohol systems were evaluated by fitting the model to the experimental results by the Simplex method. The average deviations between experimental and calculated values of thermal conductivity from Eq. (22) by the optimum k_{ij} and l_{ij} are within 1.0%.

3. Correlation of the Binary Characteristic Parameters

Adequate correlation between the binary characteristic parameters (k_{ij} and l_{ij}) and $(T_{C1}/V_{C1})/(T_{C2}/V_{C2})$ are obtained. In binary hydrocarbon mixtures and binary alcohol mixtures, the liquid with higher thermal conductivity is selected as component 1; and in hydrocarbon—alcohol mixtures, hydrocarbon is component 1.

The characteristic parameter k_{ij} can be correlated by the following equation for binary mixtures.

$$k_{12} = -0.4728 + 0.9371\theta - 0.195\theta^2 \quad (40)$$

Further, the characteristic parameter l_{ij} can be expressed as follows.

Hydrocarbon—hydrocarbon systems:

$$l_{12} = -0.0564 + 0.0789\theta - 0.037\theta^2 \quad (41)$$

Alcohol—alcohol systems:

$$l_{12} = -0.0315 + 0.0508\theta - 0.0280\theta^2 \quad (42)$$

Hydrocarbon—alcohol systems:

$$l_{12} = -0.1354 + 0.2696\theta - 0.1398\theta^2 \quad (43)$$

where

$$\theta = (T_{C1}/V_{C1}) / (T_{C2}/V_{C2}) \quad (44)$$

The typical examples of calculated thermal conductivities from Eq. (22) with correlated val-

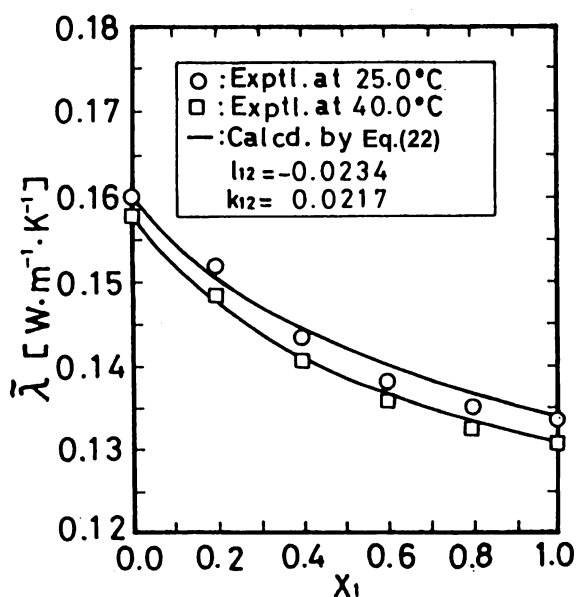


Fig. 2 Experimental and calculated thermal conductivities by Eq. (22) using correlated values of k_{12} and l_{12} by Eqs. (40) and (43) for toluene-ethanol binary mixture.

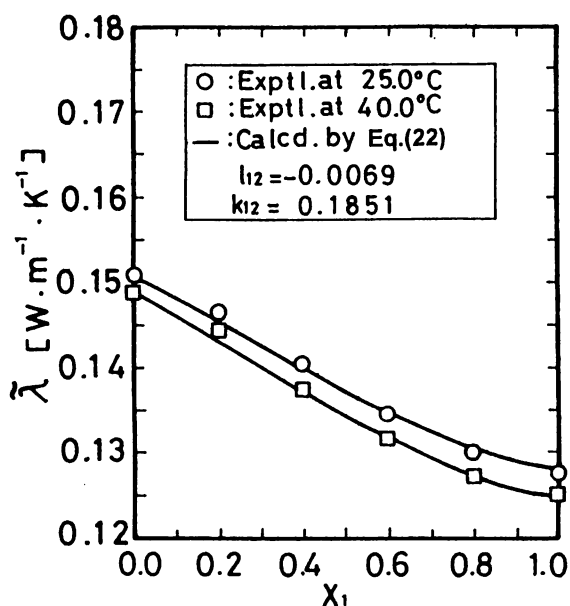


Fig. 3 Experimental and calculated thermal conductivities by Eq. (22) using correlated values of k_{12} and l_{12} by Eqs. (40) and (43) for *n*-heptane-1-heptanol binary mixture.

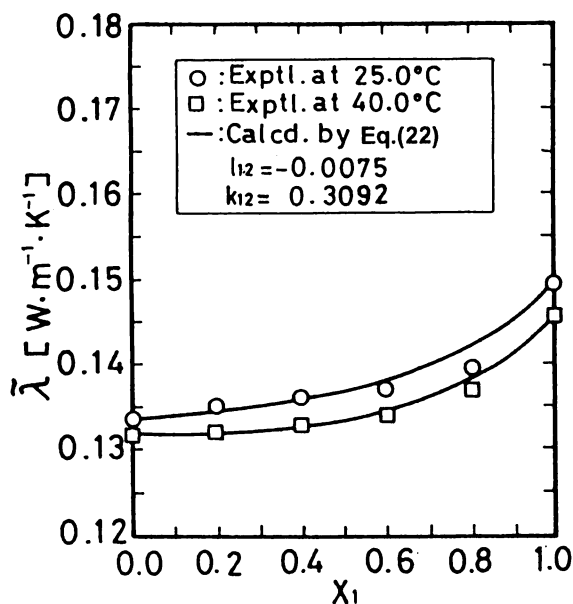


Fig. 4 Experimental and calculated thermal conductivities by Eq. (22) using correlated values of k_{12} and l_{12} by Eqs. (40) and (43) for benzene-2-butanol binary mixture.

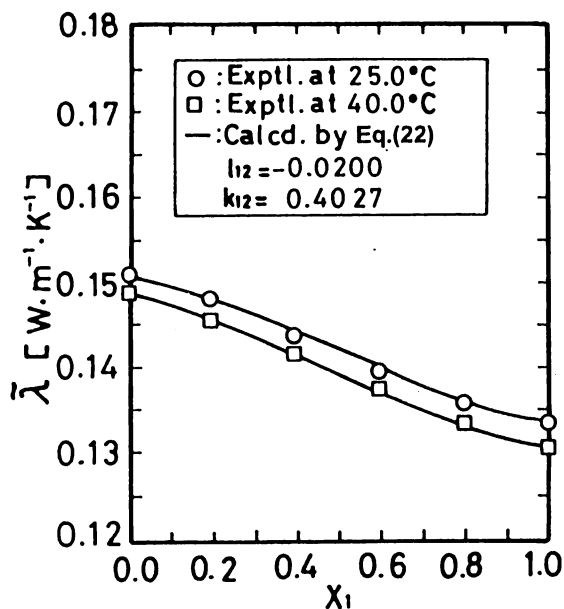


Fig. 5 Experimental and calculated thermal conductivities by Eq. (22) using correlated values of k_{12} and l_{12} by Eqs. (40) and (43) for toluene-1-heptanol binary mixture.

ues of k_{12} and l_{12} are shown in Figs. 2 to 5 by solid lines. Relatively good agreement can be obtained for the thermal conductivities of binary mixtures.

The comparisons of the literature values with the present correlation are shown in Fig. 6. This is the thermal conductivity of benzene-toluene binary mixture at 50°C measured by Jamieson et al.⁴⁾ The solid line is the calculated result by the present correlation method. The average deviation between experimental and calculated results is within 3.4%.

Conclusions

A generalized correlation method for calculating thermal conductivity of nonpolar and polar liquid is proposed. Based on the two-fluid model, the present correlation model can be applied to binary mixtures by introducing the binary characteristic parameters k_{12} and l_{12} . These parameters can be estimated by the T_c and V_c of pure components.

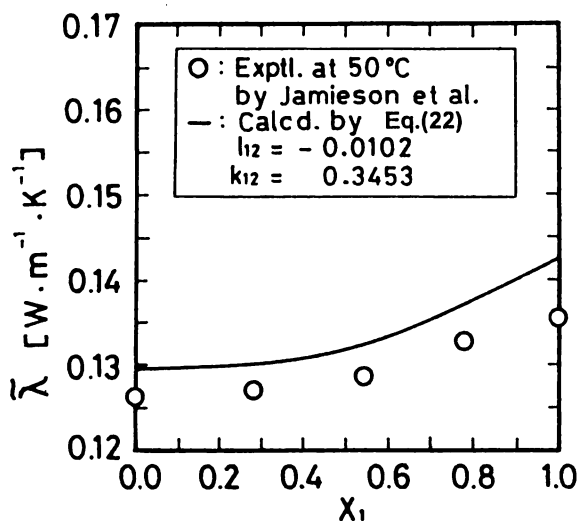


Fig. 6 Thermal conductivity of benzene-toluene binary mixture measured by Jamieson et al.⁴⁾ at 50°C.

Nomenclature

- a = distance between a molecule and its neighbor [m]
- C = proportionality constant in Eq. (8) [—]
- C_v = constant-volume heat capacity [J·K⁻¹·mol⁻¹]
- ΔH^{vap} = heat of vaporization at normal boiling

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point	[J·mol ⁻¹]
k = Boltzmann's constant	[J·K ⁻¹]
k_{ij} = binary characteristic parameter between molecules i and j ; see Eq. (38)	[—]
l_{ij} = binary characteristic parameter between molecules i and j ; see Eqs. (32) to (34)	[—]
M = molar mass	[kg·mol ⁻¹]
N_A = Avogadro number	[mol ⁻¹]
r = displacement of a molecule from its equilibrium position in a crystal lattice	[m]
T = absolute temperature	[K]
V = liquid molar volume	[m ³ ·mol ⁻¹]
V_0 = solid molar volume at melting point	[m ³ ·mol ⁻¹]
V_W = van der Waals volume	[m ³ ·mol ⁻¹]
v^* = reduced solid molar volume at melting point; see Eq. (3)	[—]
x = mole fraction	[—]
$x_{j(i)}$ = local mole fraction of molecule j surrounding a molecule of component i	[—]
$y = (r/a)^2$, defined by Eq. (6)	[—]
z = coordination number	[—]
β = empirical parameter for polar effect; see Eqs. (12) and (13)	[K]
γ = empirical parameter for polar effect; see Eq. (14)	[K]
ϵ^0 = energy parameter of potential function	[J]
λ = thermal conductivity	[W·m ⁻¹ ·K ⁻¹]
ν = frequency of molecular vibration	[s ⁻¹]
ρ = density	[kg·m ⁻³]
σ^0 = collision diameter of molecule	[m]
$\tau_{ji} = \{\epsilon(T)_{ji} - \epsilon(T)_{ii}\}/kT$, defined by Eq. (37)	[—]
χ = Stiel's polar factor	[—]
ω = Pitzer's ascetric factor	[—]

<Subscripts and Superscripts>

c = critical value
i, j = components i and j
\sim = mixture property
1, 2 = components 1 and 2

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