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THERMAL CONDUCTIVITIES OF LIQUIDS AND THEIR MIXTURES FOR HYDROCARBONS AND ALCOHOLS

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Key Words: Physical Property, Thermal Conductivity, Relative Horizontal Parallel-Plate Method, Alcohol, Hydrocarbon, Binary Mixture, Binary Characteristic Parameter, Correlation

Introduction

The authors previously measured the thermal conductivities of liquid hydrocarbons and alcohols and also of binary hydrocarbon mixtures and alcohol mixtures under atmospheric pressure by use of a relative horizontal parallel-plate method (steady-state type).[4,6]

In the present study, additional thermal conductivity data are 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.

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

1. Experiments and Results

The experimental apparatus and procedure used in the present study were almost the same as described in the previous works.[4,6] The thermal conductivities of the four binary hydrocarbon–alcohol mixtures are listed with their densities in **Tables 1** to **4**. Hydrocarbons and alcohols used in the present study were guaranteed reagents supplied by Nakarai Chemicals, Ltd. Their purities, determined by gas chro-

Table 1. Thermal conductivity and density of toluene–ethanol binary mixtures

Toluene mole fraction	$\tilde{\lambda}$ [W·m^{-1}·K^{-1}] 25.0°C	40.0°C	$\tilde{\rho}$ [kg·m^{-3}] 25.0°C	40.0°C
0.0	0.160_2	0.157_8	785.3	772.4
0.2	0.152_0	0.148_4	810.9	797.5
0.4	0.143_4	0.140_6	828.4	814.6
0.6	0.138_2	0.135_7	841.8	827.8
0.8	0.135_2	0.132_3	852.5	838.5
1.0	0.133_5	0.130_5	862.4	848.5

Table 2. Thermal conductivity and density of *n*-heptane–1-heptanol binary mixtures

n-Heptane mole fraction	$\tilde{\lambda}$ [W·m^{-1}·K^{-1}] 25.0°C	40.0°C	$\tilde{\rho}$ [kg·m^{-3}] 25.0°C	40.0°C
0.0	0.151_0	0.148_8	818.0	807.4
0.2	0.146_6	0.144_4	790.3	779.4
0.4	0.140_6	0.137_5	762.3	750.9
0.6	0.134_6	0.131_5	734.2	722.3
0.8	0.129_8	0.127_0	706.4	693.9
1.0	0.127_5	0.125_0	679.5	666.4

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Table 3. Thermal conductivity and density of benzene–2-butanol binary mixtures

Benzene mole fraction	$\tilde{\lambda}$ [W·m^{-1}·K^{-1}] 25.0°C	40.0°C	$\tilde{\rho}$ [kg·m^{-3}] 25.0°C	40.0°C
0.0	0.133_5	0.131_7	802.5	790.0
0.2	0.135_2	0.132_1	814.3	800.5
0.4	0.136_1	0.132_8	826.5	811.9
0.6	0.137_2	0.134_0	840.1	824.8
0.8	0.139_7	0.137_0	855.3	839.5
1.0	0.149_5	0.145_7	873.9	858.0

Table 4. Thermal conductivity and density of toluene–1-heptanol binary mixtures

Toluene mole fraction	$\tilde{\lambda}$ [W·m^{-1}·K^{-1}] 25.0°C	40.0°C	$\tilde{\rho}$ [kg·m^{-3}] 25.0°C	40.0°C
0.0	0.151_0	0.148_8	818.0	807.4
0.2	0.148_2	0.145_6	824.9	813.8
0.4	0.143_7	0.141_6	832.3	820.5
0.6	0.139_6	0.137_5	840.5	828.1
0.8	0.135_9	0.133_4	850.2	837.0
1.0	0.133_5	0.130_5	862.4	848.5

matography, were more than 98.6%. The maximum uncertainty of the thermal conductivity values is estimated to be within 2%.

2. Correlation of Thermal Conductivities of Liquids

As previously proposed,[4,6] the thermal conductivities of pure liquids can be correlated by the following equation.

$$\lambda=\sqrt{2}(V_0/V)C_v v/aN_A \tag{1}$$

Assuming harmonic oscillation of the central molecule in the cell, the frequency v can be derived as[6]

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

where

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

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

and

$$y=(r/a)^2 \tag{5}$$

$$v^*=V_0/\sigma(T)^3N_A \tag{6}$$

$$r=\{a-C\sigma(T)\}/2 \tag{7}$$

The solid molar volume at melting point V_0 can be estimated by an empirical equation previously proposed:[6]

$$V_0=1.48V_w \tag{8}$$

where V_w is the van der Waals volume, which can be obtained from the group contribution method of Bondi.[1] The values of the constant-volume heat capacity C_v are given by the group contribution method proposed in the previous work.[5] To calculate the frequency v, the temperature-dependent parameters $\varepsilon(T)$ and $\sigma(T)$ contained in the Lennard-Jones (12–6) potential are needed. They have been approximated as following equations.[6]

$$\varepsilon(T)=\varepsilon^\circ(1+\beta/T)^2 \tag{9}$$

$$\sigma(T)=\sigma^\circ(1+\beta/T)^{-1/6} \tag{10}$$

Further, a proportionality constant C in Eq. (7) introduced in the previous works[4,6] to estimate the molecular contact length required for energy transfer should be evaluated as

$$C=C^\circ(1+\gamma) \tag{11}$$

where β and γ are the empirical parameters for polar effect. For nonpolar liquids, values of β and γ are zero. In the present study, we have attempted to obtain a generalized correlation for these parameters, selecting benzene as a reference substance because the benzene molecule seems relatively spherical and nonpolar. Using the thermal conductivity data obtained previously for nonpolar hydrocarbons,[4] the following expressions were finally found:

$$\varepsilon^\circ/kT_c=0.7260+0.2415(\omega-0.212) \tag{12}$$

$$(\sigma^\circ)^3N_A/V_c=0.2205-0.2316(\omega-0.212)+0.2907(\omega-0.212)^2 \tag{13}$$

$$C^\circ=1.00-0.8755(\omega-0.212) \tag{14}$$

where ω denotes Pitzer's acentric factor[7] and the value of ω of benzene is 0.212. Further, parameters β and γ for polar liquids are given as follows on the basis of thermal conductivity data of alcohols.

Normal alcohol:

$$\beta/T_c=0.05703+0.5116\chi+3.2373\chi^2 \tag{15}$$

$$(1+\gamma)RT_c/\Delta H^{vap}=0.1129+0.02398\chi-0.5049\chi^2 \tag{16}$$

Branched alcohol:

$$\beta/T_c=0.05768+0.5364\chi+5.0973\chi^2 \tag{17}$$

$$(1+\gamma)RT_c/\Delta H^{vap}=0.1856+2.1983\chi+14.949\chi^2 \tag{18}$$

Where χ is Stiel's polar factor.[2] The values of ω and χ for alcohols were recalculated here on the basis of the original definitions.[6] By using the above correlations, the thermal conductivities of pure hydrocarbons and alcohols can be calculated within 2.6%.

3. Correlation of Thermal Conductivities of Liquid Mixtures

Equation (1) can readily be extended to a mixture by adopting the mixing rules. Namely, Eq. (1) becomes

$$\tilde{\lambda}=\sqrt{2}\,(\tilde{V}_\circ/\tilde{V})\tilde{C}_v\tilde{v}/\tilde{a}N_A \tag{19}$$

where $\tilde{V}_\circ$, $\tilde{V}$, $\tilde{C}_v$, $\tilde{v}$, 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,[8] the frequency of a liquid mixture is given as

$$\tilde{v}=\sum_i x_i v_{(i)} \tag{20}$$

where

$$v_{(i)}=\frac{1}{2\pi\sqrt{M_i/N_A}}\left[\frac{2\tilde{z}\varepsilon(T)_{(i)}}{\tilde{r}^2\tilde{v}^{*2}}\left\{\frac{l(\tilde{y})}{\tilde{v}^{*2}}-2m(\tilde{y})\right\}\right]^{1/2} \tag{21}$$

The functions $l(\tilde{y})$ and $m(\tilde{y})$ are as follows.

$$l(\tilde{y})=(1+12\tilde{y}+25.2\tilde{y}^2+12\tilde{y}^3+\tilde{y}^4)(1-\tilde{y})^{-10}-1 \tag{22}$$

$$m(\tilde{y})=(1+\tilde{y})(1-\tilde{y})^{-4}-1 \tag{23}$$

The values of $\tilde{y}$ are obtained by

$$\tilde{y}=(\tilde{r}/\tilde{a})^2 \tag{24}$$

$$\tilde{a}=2^{1/6}(\tilde{V}_\circ/N_A)^{1/3} \tag{25}$$

$$\tilde{r}=\left[\tilde{a}-\sum_i\sum_j x_i x_j\{C\sigma(T)\}_{ij}\right]\Big/2 \tag{26}$$

and

$$\tilde{V}_\circ=\sum_i\sum_j x_i x_j\{V_\circ\}_{ij} \tag{27}$$

The following averaging rules are further adopted in order to evaluate $\tilde{v}^*$ and $\tilde{z}^*$.

$$\tilde{v}^*=\frac{\tilde{V}_\circ}{N_A\left[\sum_i\sum_j x_i x_j\{\sigma(T)\}_{ij}\right]^3} \tag{28}$$

$$\tilde{z}=12(\tilde{V}_\circ/\tilde{V}) \tag{29}$$

The molar volume of a mixture $\tilde{V}$ can be obtained from

$$\tilde{V}=\left(\sum_i M_i x_i\right)\Big/\tilde{\rho} \tag{30}$$

where $\tilde{\rho}$ is the density of the mixture. The density data of the hydrocarbon–alcohol mixtures are available from Tables 1 to 4, and those of binary hydrocarbon mixtures and binary alcohol mixtures were presented in the previous works.[4,6]

In Eqs. (26) to (28), the cross-terms are given as

$$\{C\sigma(T)\}_{ij}=(1-l_{ij})\sqrt{C_i\sigma(T)_{ii}C_j\sigma(T)_{jj}} \tag{31}$$

$$\{V_\circ\}_{ij}=(1-l_{ij})\sqrt{V_{\circ ii}V_{\circ jj}} \tag{32}$$

$$\{\sigma(T)\}_{ij}=(1-l_{ij})\sqrt{\sigma(T)_{ii}\sigma(T)_{jj}} \tag{33}$$

where l_{ij} is the binary characteristic parameter between molecules i and j. The values of l_{ij} contained in Eqs. (31) to (33) are assumed to be equal.

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

$$\varepsilon(T)_{(i)}=\sum_j x_{j(i)}\varepsilon(T)_{ij} \tag{34}$$

where $x_{j(i)}$ denotes the local mole fraction of molecule j surrounding a molecule i. According to Wilson,[9] we adopted the expression

$$x_{j(i)}=x_j\exp(\tau_{ji})/\{x_i+x_j\exp(\tau_{ji})\} \tag{35}$$

where

$$\tau_{ji}=\{\varepsilon(T)_{ji}-\varepsilon(T)_{ii}\}/kT \tag{36}$$

In the present study, $\varepsilon(T)_{ji}$ and $\varepsilon(T)_{ij}$ are equal and are given as

$$\varepsilon(T)_{ij}=(1-k_{ij})\sqrt{\varepsilon(T)_{ii}\varepsilon(T)_{jj}} \tag{37}$$

where k_{ij} is the binary characteristic parameter.

The average constant-volume heat capacity is approximated by

$$\tilde{C}_v=\sum_i x_i C_{vi} \tag{38}$$

The thermal conductivities of mixtures can be calculated when the values of the characteristic parameters k_{ij} and l_{ij} are known. It is very difficult to predict theoretically the values of k_{ij} and l_{ij} for complex mixtures. Therefore, 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[3] and are presented in **Table 5**. The average errors between experimental results and the calculated values of thermal conductivity from Eq. (19) by using the optimum values of k_{ij} and l_{ij} are also shown in Table 5. The average errors are within 0.8% as shown in Table 5, and they are as small as the present experimental errors.

4. Correlation of the Binary Characteristic Parameters

Adequate correlations between the binary characteristic parameters and $(T_{c1}/V_{c1})/(T_{c2}/V_{c2})$ are obtained as shown in **Figs. 1** and **2**. In binary hydrocarbon mixtures and binary alcohol mixtures, the liquid with the higher thermal conductivity is selected as component 1; and in hydrocarbon–alcohol mixtures, the hydrocarbon is component 1. They are well expressed by the following quadratic equations.

The characteristic parameter k_{12} can be correlated

Table 5. Optimum values of k_{12} and l_{12} and average error between experimental results and calculated values of thermal conductivity by Eq. (19) for liquid binary mixtures

No.	System	k_{12}	l_{12}	Avg. error [%]*		Source
1	*n*-Decane(1)–*n*-Heptane(2)	0.1522	−0.0144	0.8 (25.2°C)**	0.6 (50.4°C)**	4)
2	Benzene(1)–*p*-Xylene(2)	0.4201	−0.0111	0.6 (25.1°C)	0.3 (45.1°C)	4)
3	Benzene(1)–*n*-Heptane(2)	0.5479	−0.0209	0.6 (25.1°C)	0.8 (45.1°C)	4)
4	1-Butanol(1)–2-Butanol(2)	0.2555	−0.0083	0.1 (25.0°C)	0.2 (50.0°C)	6)
5	1-Propanol(1)–2-Butanol(2)	0.3936	−0.0124	0.2 (25.0°C)	0.3 (50.0°C)	6)
6	Ethanol(1)–2-Butanol(2)	0.5193	−0.0185	0.3 (25.0°C)	0.3 (50.0°C)	6)
7	Ethanol(1)–1-Pentanol(2)	0.5367	−0.0274	0.3 (25.0°C)	0.2 (50.0°C)	6)
8	Toluene(1)–Ethanol(2)	0.0393	−0.0234	0.6 (25.0°C)	0.4 (40.0°C)	Present work
9	*n*-Heptane(1)–1-Heptanol(2)	0.1662	−0.0068	0.5 (25.0°C)	0.3 (40.0°C)	Present work
10	Benzene(1)–2-Butanol(2)	0.3246	−0.0076	0.5 (25.0°C)	0.3 (40.0°C)	Present work
11	Toluene(1)–1-Heptanol(2)	0.4039	−0.0199	0.3 (25.0°C)	0.2 (40.0°C)	Present work

* Avg. error $=\{\sum |\lambda_{exptl.}-\lambda_{calcd.}| \times 100/\lambda_{exptl.}\}/N$; N = number of data.
** Values in parentheses denote experimental temperatures.

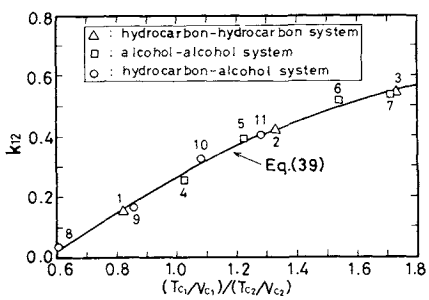

Fig. 1. Correlation of binary characteristic parameter k_{12} for liquid binary mixture. (Numbers are the same as in Table 5.)

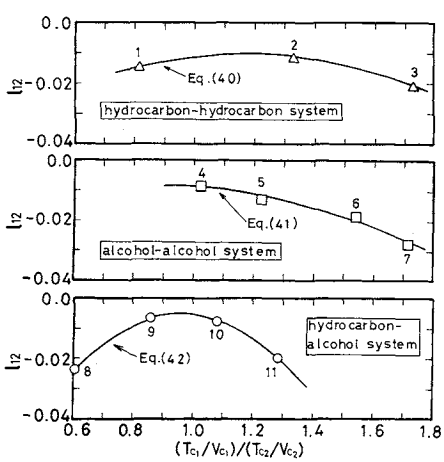

Fig. 2. Correlation of binary characteristic parameter l_{12} for liquid binary mixture. (Numbers are the same as in Table 5.)

by the following equation for various mixtures.

$$k_{12}=-0.4728+0.9371\theta-0.1995\theta^2 \qquad (39)$$

Further, the characteristic parameter l_{12} can be expressed as follows.

hydrocarbon–hydrocarbon systems:

$$l_{12}=-0.0564+0.0789\theta-0.0337\theta^2 \qquad (40)$$

alcohol–alcohol systems:

$$l_{12}=-0.0315+0.0508\theta-0.0280\theta^2 \qquad (41)$$

hydrocarbon–alcohol systems:

$$l_{12}=-0.1354+0.2696\theta-0.1398\theta^2 \qquad (42)$$

where

$$\theta=(T_{c1}/V_{c1})/(T_{c2}/V_{c2}) \qquad (43)$$

The average errors between experimental results and calculated values of the thermal conductivity from Eqs. (39) to (42) for liquid binary mixtures are less than 1%. Relatively good agreement can be obtained for the thermal conductivities of binary mixtures by use of Eqs. (39) to (42).

Conclusions

The thermal conductivities of four binary hydrocarbon–alcohol mixtures were measured at 25.0 and 40.0°C under atmospheric pressure by use of a relative horizontal parallel-plate method.

A generalized correlation method for calculating thermal conductivity of nonpolar and polar liquids is proposed. They can be calculated by use of pure substance properties T_c, V_c, ΔH^{vap}, ω, and χ. Further, 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 critical temperatures and critical molar volumes of pure components.

Nomenclature

a	=	distance between a molecule and its neighbor	[m]
C	=	proportionality constant	[—]
C_v	=	constant-volume heat capacity	[J·K^{-1}·mol^{-1}]
ΔH^{vap}	=	heat of vaporization at normal boiling point	[J·mol^{-1}]
k	=	Boltzmann's constant	[J·K^{-1}]
k_{ij}	=	binary characteristic parameter between molecules i and j; see Eq. (37)	[—]

l_{ij} = binary characteristic parameter between molecules i and j; see Eqs. (31)–(33) [—]
M = molar mass [kg·mol^{-1}]
N = number of data [—]
N_A = Avogadro's 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_o = 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. (6) [—]
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. (5) [—]
z = coordination number [—]

β = empirical parameter for polar effect; see Eqs. (9) and (10) [—]
γ = empirical parameter for polar effect; see Eq. (11) [—]
ε° = energy parameter of potential function [J]
θ = $(T_{c1}/V_{c1})/(T_{c2}/V_{c2})$, defined by Eq. (43) [—]
λ = thermal conductivity of liquid [W·m^{-1}·K^{-1}]
ν = frequency of molecular vibration [s^{-1}]
ρ = density [kg·m^{-3}]
σ° = collision diameter of molecule [m]
τ_{ij} = $\{\varepsilon(T)_{ji}-\varepsilon(T)_{ii}\}/kT$, defined by Eq. (36) [—]
χ = Stiel's polar factor [—]
ω = Pitzer's acentric factor [—]

⟨Subscripts and Superscripts⟩
c = critical value
calcd. = calculated
exptl. = experimental
i, j = components i and j
~ = mixture property
1, 2 = components 1 and 2

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HIGH-PRESSURE VAPOR-LIQUID EQUILIBRIUM CALCULATIONS BY USE OF THE CORRESPONDING-STATES PRINCIPLE

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Key Words: Vapor-Liquid Equilibrium, Hydrocarbon, Corresponding-States Principle

Prediction of vapor-liquid equilibria of asymmetric mixtures by use of the corresponding-states principle has recently been developed by a number of investigators.[1,3,6] Joffe[3] and Plöcker *et al.*[6] have used the Lee-Kesler correlations[4] with the pseudocritical method. Arai *et al.*[1] presented mixing rules combining functionally different equations of state on the basis of the three-parameter corresponding-states principle.

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In this work we use a one-fluid theory with new mixing rules on the basis of the corresponding-states principle to calculate the vapor-liquid equilibria for asymmetric mixtures of hydrocarbons. Data used in evaluating this calculation are taken from the literature.

1. Corresponding-States Principle with Mixing Rules

Following Van Ness,[10] the fugacity coefficient of component i at constant T and P is related to the mixture fugacity coefficient by