The Thermal Conductivity of *n*-Hexadecane + Ethanol and *n*-Decane + Butanol Mixtures

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New absolute measurements, by the transient hot-wire technique, of the thermal conductivity of *n*-hexadecane and binary mixtures of *n*-hexadecane with ethanol and *n*-decane with butanol are presented. The temperature range examined was 295–345 K and the pressure atmospheric. The concentrations of the mixtures studied were 92% (by weight) of *n*-hexadecane and 30 and 70% (by weight) of *n*-decane. The overall uncertainty in the reported thermal conductivity data is estimated to be $\pm 0.5\%$, an estimate confirmed by the measurement of the thermal conductivity of water. A recently extended semiempirical scheme for the prediction of the thermal conductivity of mixtures from the pure components is used to correlate and predict the thermal conductivity of these mixtures, as a function of both composition and temperature.

1. INTRODUCTION

In recent years, the sharp reduction of lead in gasolines led to the development of a growing number of processes in which alcohols and alkanes coexist to produce oxygenated additives for gasoline. These oxygenated products usually include methanol, ethanol, or mixtures of higher alcohols [1]. Depending on the process, the hydrocarbons coexisting with the alcohols play the role of an azeotropic agent, a selective extraction solvent, or a heat-transfer fluid. Data on the vapor–liquid equilibrium and the thermal conductivity of such mixtures are still very scarce.

For the specific study of the vapor–liquid equilibrium of these mixtures, the Subcommittee on Thermodynamic Data of the International Union of Pure and Applied Chemistry, in its Third Workshop Meeting in

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Budapest in 1987, decided to concentrate on five "key mixtures." These key mixtures were *n*-hexane with methanol, ethanol, and hexanol, *n*-hexadecane with ethanol, and *n*-decane with butanol, which were selected because they display different hydrogen bonding and different size of molecules. The measurement of the thermal conductivity of these mixtures will also contribute to the very few accurate mixture data existing today. Such measurements are required for the development and testing of the few semiempirical schemes available for the prediction of this property.

In a companion paper [2], the thermal conductivity of the mixtures of *n*-hexane with methanol, ethanol, and hexanol was investigated. In this paper, concluding the study of the thermal conductivity of the aforementioned key mixtures, accurate absolute measurements of the thermal conductivity of mixtures of *n*-hexadecane with ethanol and *n*-decane with butanol are presented. The temperature range studied was 295–345 K and the pressure atmospheric.

2. EXPERIMENTAL

The technique employed in these measurements was the transient hot-wire technique, with two anodized tantalum wires as the heat source. The instrument employed in these measurements has been described in detail elsewhere [3, 4]. The instrument was used unchanged for the present series of measurements, which extend over the temperature range 295–345 K at atmospheric pressure. The usual experimental procedures [4] have been adopted, and measurements of the thermal conductivity of water have been carried out to confirm the continued good operation of the equipment by Comparison with our earlier results [4]. The samples of the pure liquids used were all supplied by B.D.H. Chemicals Ltd., with a nominal purity 99.0% for *n*-hexadecane, 99.0% for *n*-decane, 99.7% for ethanol, and 99.8% for butanol. The mixtures were prepared gravimetrically and the uncertainty in the composition was less than 0.005%. The compositions studied, expressed as weight percentage of the alkane in the alkane–alcohol mixtures, were 92% of *n*-hexadecane (mole fraction, 0.700) and 30 and 70% of *n*-decane (mole fractions, 0.183 and 0.549). The study of the *n*-hexadecane + ethanol mixture was restricted to only one concentration due to the immiscibility of this mixture at lower concentrations in the temperature range examined.

3. RESULTS

The overall uncertainty in the reported thermal-conductivity measurements is estimated to be better than ±0.5%, an estimate which is

confirmed by measuring water after every mixture [4]. Tables I and II show the experimental thermal-conductivity values of each mixture at atmospheric pressure as a function of temperature. In addition, in Table I, the experimental thermal-conductivity values of n-hexadecane are also presented. Our previously reported thermal-conductivity values of n-decane [6], ethanol, and butanol [5] are also included for comparison purposes. The thermal conductivity values for each system studied have been represented by a linear function of the absolute temperature T, as

$$\lambda = \lambda_0[1 + \alpha(T - 198.15)] \tag{1}$$

where λ_0 is the extrapolated (or interpolated) thermal conductivity at 298.15 K, and α the linear thermal-conductivity gradient for the temperature range studied. The values of λ_0 and α for the pure liquids and each mixture are shown in Table III. In the same table, the absolute standard deviations of the fits are also displayed. It can be seen that the maximum standard deviation of the present measurements is $\pm 0.2\%$.

Figure 1 shows the deviations of the present measurements of n-hexadecane from Eq. (1). The maximum deviation of the present measurements from Eq. (1) is less than $\pm 0.17\%$. In the same figure, measurements of other investigators are also shown. The only other accurate absolute set of measurements performed in a transient hot-wire instrument is the measurements of Wada et al. [7]. The quoted uncertainty of these measurements is $\pm 1.5\%$ It can be seen that the deviations of these measurements from Eq. (1) are below $\pm 1\%$, which is well within the

Table I. The Thermal Conductivity of n-Hexadecane + Ethanol Mixtures as
a Function of Temperatuee at Atmospheric Pressure
(Concentrations in Weight Percentage of n-Hexadecane)

0%		92%		100%	
T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})	T (K)	λ (mW·m^{-1}·K^{-1})
305.74	160.7	297.70	144.2	297.22	142.2
311.13	160.0	300.63	143.4	302.55	141.7
316.15	159.6	303.87	142.9	304.32	141.2
319.87	159.1	308.77	142.1	309.97	140.7
323.96	159.0	313.80	141.7	316.92	139.8
325.82	158.7	319.91	140.7	317.62	139.8
328.95	159.0	320.49	140.8	326.13	138.8
331.43	158.3	324.40	140.6	329.95	138.4
335.06	158.0			332.87	137.8
				337.94	137.7

Table II. The Thermal Conductivity of n-Decane + Butanol Mixtures as a Function of Temperature at Atmospheric Pressure (Concentrations in Weight Percentage of n-Decane)

0%		30%		70%		100%	
T (K)	λ (mW·m⁻¹·K⁻¹)	T (K)	λ (mW·m⁻¹·K⁻¹)	T (K)	λ (mW·m⁻¹·K⁻¹)	T (K)	λ (mW·m⁻¹·K⁻¹)
301.64	147.1	294.91	138.5	295.50	134.4	300.08	132.4
307.24	146.6	297.32	137.9	302.77	133.2	305.60	131.1
312.57	145.9	305.04	136.8	304.89	132.6	310.82	129.7
317.59	145.3	305.80	136.9	307.09	132.9	315.05	128.4
323.85	144.3	311.05	135.8	312.38	131.6	320.31	127.2
329.48	144.2	311.91	136.0	324.04	129.6	325.00	125.9
333.81	144.1	319.29	134.8	327.09	129.3	332.12	124.4
335.44	143.3	321.84	134.3	330.70	129.1	339.59	122.2
345.12	143.0	329.66	132.9	340.88	127.6	344.07	121.5

Table III. Coefficients of the Least-Squares Straight-Line Fit of
the Thermal Conductivity of the Mixtures as a Function
of Temperature, Eq. (1) (Concentrations in Weight Percentage of n-Alkane)

	λ_0 $(mW \cdot m^{-1} \cdot K^{-1})$	α $(10^{-3} K^{-1})$	σ $(\%)$
n-Hexadecane + ethanol			
0% n-hexadecane	161.21	-0.525 ± 0.043	± 0.11
92% n-hexadecane	143.78	-0.936 ± 0.058	± 0.20
100% n-hexadecane	142.05	-0.813 ± 0.023	± 0.12
n-Decane + butanol			
0% n-decane	147.57	-0.718 ± 0.053	± 0.17
30% n-decane	137.93	-1.115 ± 0.040	± 0.16
70% n-decane	133.88	-1.140 ± 0.041	± 0.20
100% n-decane	132.89	-1.906 ± 0.015	± 0.11

mutual uncertainty of the two instruments. The measurements of Powell
and Groot [8] were also performed in a transient operated instrument.
The measurements of Bogatov et al. [9], Gollis et al. [10], Mukhamed-
zyanov et al. [11], and Sakiadis and Coates [12] were all performed in
steady state-type of instruments. The scatter of the above measurements,
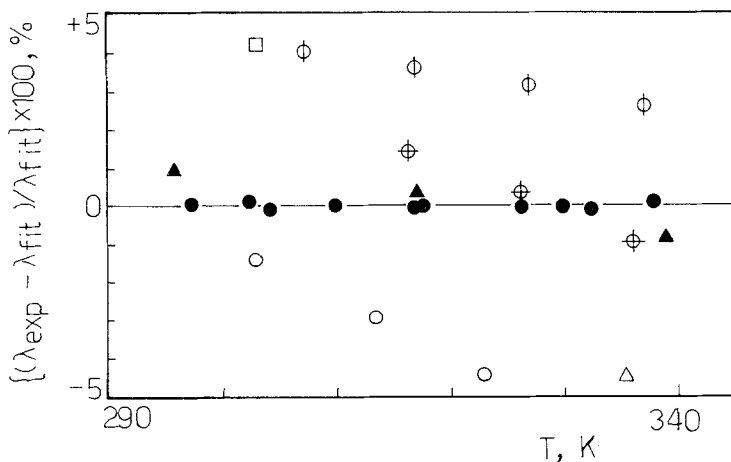about $\pm 5\%$, is probably attributed to convective effects or incomplete
theory.

Fig. 1. Deviations of the experimental thermal conductivity values of n-hexa-
decane from Eq. (1). ($\bullet$) Present work; ($\blacktriangle$) Ref. 7; ($\square$) Ref. 8; ($\bigcirc$) Ref. 9;
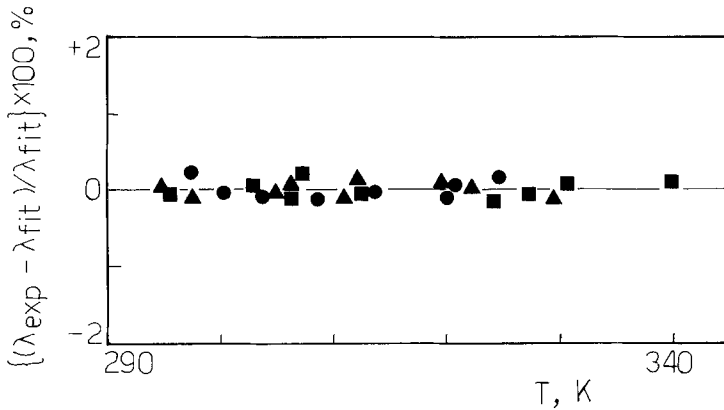($\triangle$) Ref. 10; (φ) Ref. 11; ($\oplus$) Ref. 12.

Fig. 2. Deviations of the experimental thermal conductivity values of the mixtures from Eq. (1). n-Hexadecane + ethanol: (●) 92%. n-Decane + butanol: (▲) 30%; (■) 70%.

Figure 2 shows the deviations of the present experimental measurements of the thermal conductivity of the mixtures from Eq. (1). The maximum deviation is less than ±0.25%. Comparison of the present experimental measurements with those of other investigators cannot be performed, as to our knowledge the thermal conductivity of these mixtures has not been measured by other investigators.

4. DISCUSSION

4.1. The Pure Liquids

The correlation of Eq. (1) is suitable only for interpolation and cannot be used for extrapolation or prediction. For such purposes, it has been shown [13] that a correlation in terms of the density or molar volume is much more suitable. The hard-sphere model of the dense fluid state [14] suggests the form of such a correlation, since it leads to the result that for a monatomic fluid the quantity, λ^*, defined by the equation

$$\lambda^* = 1.936 \times 10^7 \left[\frac{M}{RT} \right]^{1/2} \lambda V^{2/3} = F_\lambda(V_R) \tag{2}$$

is a function of the reduced molar volume $V_R = (V/V_0)$ only, where V is the molar volume and V_0 is a characteristic molar volume of the fluid which is but weakly temperature dependent. In the above relation, M represents the molecular mass and R the gas constant.

Earlier studies have shown that if Eq. (2) is carried over to polyatomic fluids, the function F_λ is universal among a large group of liquids including n-alkanes, alcohols, and glycols, although the function is not that predicted for the hard-sphere theory [13]. For the n-alkanes, the most recent form [13] for the function F_λ has been developed as a result of a successful attempt to obtain a simultaneous representation of the thermal conductivity, viscosity, and self-diffusion coefficients over the temperature range 100–400 K and pressures up to 600 MPa. In that study [13], it emerged that it is not the function λ^* which is universal, but a slightly modified version of it, namely,

$$\log \frac{\lambda^*}{R_\lambda} = 1.0655 - 3.538 \left[\frac{1}{V_R}\right] + 12.121 \left[\frac{1}{V_R}\right]^2$$
$$- 12.469 \left[\frac{1}{V_R}\right]^3 + 4.562 \left[\frac{1}{V_R}\right]^4 \tag{3}$$

and

$$R_\lambda = 0.1989C + 1.199 - 2.547C^{-1} + 6.404C^{-2} - 4.094C^{-3} \tag{4}$$

The factor R_λ, introduced to account for deviations from the behavior of smooth hard spheres, was correlated as a function of the number of carbon atoms, C, in the molecule.

The characteristic molar volume V_0 was consequently correlated as a function of the temperature and also the number of carbon atoms C. The universal equations obtained [13] for the n-alkanes were as follows.

CH_4–C_4H_{10}:
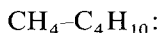
$$10^6 V_0 = -2.574\theta^{-4} + 0.4842C^2\theta^{-3} + 4.311C^{-1}\theta^{-2} + 3.607\theta^{-1} + 1.982C^{-2}$$
$$+ 14.656C - 0.03418C^3 - 0.03498C^2\theta^2 + 9.161 \times 10^{-4}C^4\theta^2 \tag{5}$$

C_5H_{12}–$C_{16}H_{34}$:
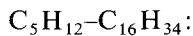
$$10^6 V_0 = 106.677 - 13.655\theta + 1.6266\theta^2$$
$$+ (C - 6)(18.028 - 1.2\theta)(0.944 + 0.0035C)$$

where

$$\theta = T/100$$

Thus, Eqs. (2)–(5) form a consistent set of equations that can be used for the prediction of the thermal conductivity of n-alkanes. Equivalent

equations were derived for the viscosity and self-diffusion coefficients, with
the exception of the relation for V_0, which, being characteristic only of the
fluid, is the same for all these properties. The equation for V_0 was based on
the correlation of measurements of the three properties that covered the
liquids from methane to n-hexadecane. In the case, however, of Eq. (4), for
R_λ, this was based [13] on data covering methane to n-tridecane and only
a few atmospheric pressure measurements of n-tetradecane. Thus, the
application of the above scheme to the prediction of the thermal conduc-
tivity of n-hexadecane produced deviations from the present measurements
of up to $\pm 8\%$ at the highest temperatures. It was thus preferred to correct
Eq. (4) so as to take into consideration the new measurements of n-hexa-
decane. The new equation for R_λ is

$$R_\lambda = 0.00225C^3 - 0.0774C^2 + 1.186C - 4.672 + 14.435C^{-1}$$
$$- 16.009C^{-2} + 6.296C^{-3} \tag{6}$$

This equation does not alter the results of the aforementioned scheme but
extends its application to n-alkanes higher than n-hexadecane. Equation (6)
together with Eqs. (2), (3), and (5) can now be used for the prediction of
the thermal conductivity of n-alkanes from methane up to n-hexadecane
with an uncertainty of $\pm 5\%$. Figure 3 shows the deviations of the present
measurements of n-hexadecane from the values of this scheme. The maxi-
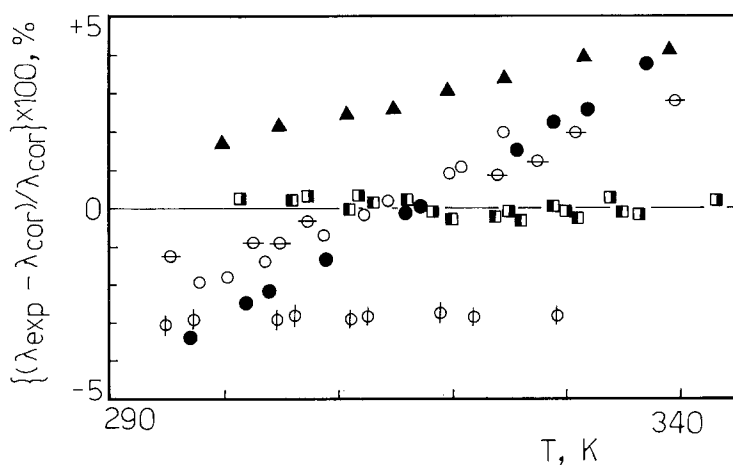

Fig. 3. Deviations of the experimental thermal conductivity values from the
correlated ones. n-Hexadecane (●); n-decane (▲); ethanol (■); butanol (▢).
n-Hexadecane + ethanol: (○) 92%. n-Decane + butanol: (◌) 30%; (⊖)
70%.

mum deviation is less than $\pm 3.5\%$. In this figure, the deviations of the experimental data of n-decane from the values predicted by this scheme are also shown. The maximum deviation is less than $\pm 5\%$, which is within the uncertainty of the scheme.

In the case of ethanol and butanol, the experimental data were used to calculate the equation for V_0 from Eqs. (2), (3), and (6). The values obtained were correlated as a function of temperature as follows:

$$\text{for ethanol,} \qquad V_0 = 27.35 \times 10^{-6} + 20 \times 10^{-9} T \tag{7}$$

$$\text{for butanol,} \qquad V_0 = 56.05 \times 10^{-6} + 12 \times 10^{-9} T \tag{8}$$

In Fig. 3, the deviations of the experimental data from the above scheme are shown. The maximum deviation is less than $\pm 0.3\%$.

4.2. The Mixtures

In order to correlate the thermal conductivity of the mixtures, the procedure adopted was one recently used successfully [15, 16] in the correlation of the thermal conductivity of mixtures of alcohols and glycols with water. According to this procedure, it was postulated that the mixture will be like an equivalent liquid with a mole fraction average molecular weight, a mass fraction average density, and a characteristic molar volume V_0^{MIX}, given by the following mixing rule,

$$V_0^{\text{MIX}} = X V_0^{\text{I}} + (1 - X) V_0^{\text{II}} - X(1 - X) D \tag{9}$$

where, V_0^{I} and V_0^{II} are the characteristic molar volumes of the pure components and X the mole fraction of component I. Thus, Eqs. (2), (3), (6), and (9) were used in this scheme for the calculation of the factor D. It should also be noted that a mole fraction average R_λ was used, while V_0 for the pure components was predicted as described in the previous section. The factor D was consequently found to be a constant characteristic of the pure components and independent of the temperature and composition. For the n-hexadecane + ethanol mixture the value of D was found equal to $15.5 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$, while for the n-decane + butanol mixture it was $2.0 \times 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$. In Fig. 3, the deviations of the experimental data for the mixtures from those predicted by this scheme are shown. The maximum deviation is less than $\pm 3\%$, which is within the accuracy of the scheme.

The advantage of this scheme is that only one accurate measurement at one composition and at one temperature is sufficient to calculate the factor D, while measurements of the thermal conductivity of the pure

components are not required. Having thus calculated the factor D, the scheme can be used to predict all mixture compositions at this range of temperatures and possibly at higher pressures [15, 16].

5. CONCLUSIONS

New absolute measurements of the thermal conductivity of n-hexadecane as well as of binary mixtures of n-hexadecane with ethanol and n-decane with butanol are reported in the temperature range 295×345 K at atmospheric pressure, with an estimated uncertainty of $\pm 0.5\%$. A recently developed correlative scheme for the thermal conductivity of mixtures was found to represent the thermal conductivity of the mixtures satisfactorily with an uncertainty of $\pm 3\%$.

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